



HOKKAIDO UNIVERSITY

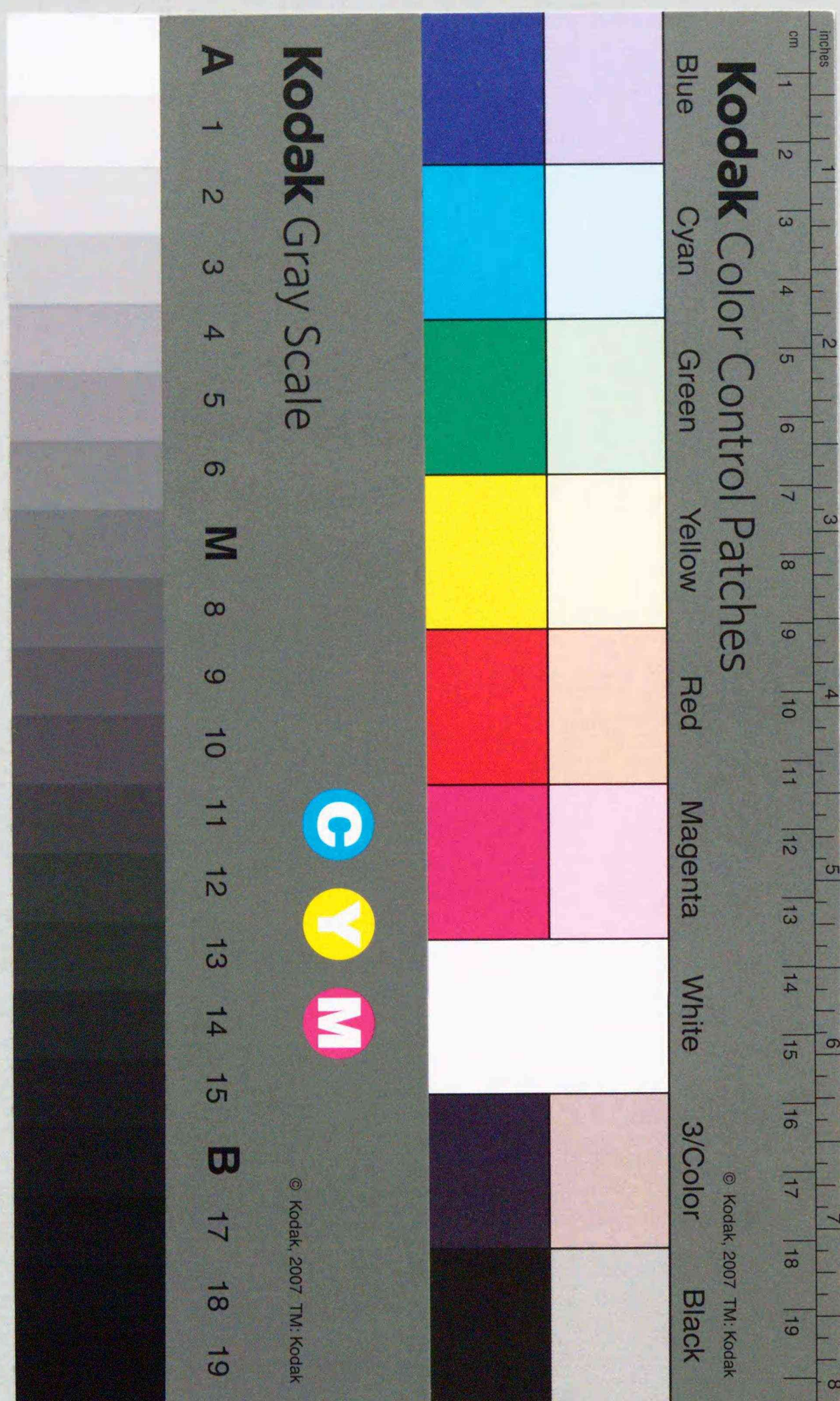
Title	A Study on Electron Transfer Reaction across Single Microdroplet/Water Interface
Author(s)	Chikama, Katsumi
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第4543号
Issue Date	1998-09-30
DOI	https://doi.org/10.11501/3145366
Doc URL	https://hdl.handle.net/2115/51562
Type	doctoral thesis
File Information	000000330558.pdf



*A Study on Electron Transfer Reaction across
Single Microdroplet / Water Interface*

Graduate School of Science, Hokkaido University

KATSUMI CHIKAMA



①

**A Study on Electron Transfer Reaction across
Single Microdroplet / Water Interface**

Graduate School of Science, Hokkaido University

Katsumi CHIKAMA

Contents

Chapter 1. Introduction

1.1	What Occurs in Microdroplet ?	1
1.2	Charge Transfer Reaction across a Liquid / Liquid Interface	5
	i) Ion Transfer Process	7
	ii) Electron Transfer Process	8
1.3	Purpose and Content of the Thesis	13
1.4	References	15

Chapter 2. Laser Trapping - Spectroscopy - Electrochemistry of Single Microdroplets in Water

2.1	The Principle of Laser Trapping	27
2.2	Laser Trapping, Spectroscopic, and Electrochemical Measurements of Single Microparticles in Solution	31
2.3	Experimental Check of the Performance of the Laser Trapping - Spectroscopy - Electrochemistry System	35
2.4	Summary	45
2.5	References	46

Chapter 3. Determination of Electron Transfer Rate across Microdroplet / Water Interface

3.1	Introduction	48
3.2	Experimental	49
3.2.1	Sample Preparation	50

3.2.2	Spectroscopic and Electrochemical Measurements	52
	i) Ensemble Measurements	52
	ii) Single Droplets Measurements	54
3.2.3	Optimization of the Experimental Conditions	56
	i) Distribution Coefficient	57
	ii) Electrolytic Condition	58
	iii) Liquid-Junction Potential	59
	iv) Optimization of Spectroscopic Conditions	60
3.3	A Droplet - Unresolved Study on Interfacial Electron Transfer	
	: Ensemble Measurements	65
3.3.1	Coulometric and Fluorometric Study on Interfacial Electron Transfer	
	Reaction	65
3.3.2	Rate Determining Step	70
	i) Diffusion Process in Water Phase	74
	ii) Diffusion Process in Droplet	75
	iii) Electron Transfer Process across Droplet / Water Interface	75
3.3.3	Determination of Interfacial Electron Transfer Rate	76
	i) Fluorometric Determination of the FeCp-H Concentration	76
	ii) Analysis of Electron Transfer Rate	79
3.4	Interfacial Electron Transfer across Single Droplet / Water Interface	81
3.4.1	Single Droplet Measurements	82
3.4.2	Analysis of Electron Transfer Rate	89
3.5	Conclusion	94
3.6	References	95

Chapter 4. Droplet Size and Liquid-Junction Potential Effects on Interfacial Electron Transfer Rate

4.1	Introduction	97
4.2	Experimental	98
4.2.1	Sample Preparation	98
4.2.2	Optimization of the Experimental Conditions	99
	i) Spectroscopic Condition	99
	ii) Fluorescence Lifetime	101
	iii) Redox Potential	104
4.3	Results and Discussion	105
4.3.1	Interfacial Electron Transfer in the FeCp-H / Fe(CN) ₆ ³⁻ System	106
	i) Surface Area / Volume Ratio Effects on Interfacial Electron Transfer Rate	106
	ii) Liquid-Junction Potential Dependence of Interfacial Electron Transfer Rate	111
	iii) Micrometer Size Dependence of Interfacial Electron Transfer Rate	113
4.3.2	Interfacial Electron Transfer in the FeCp-DM / Fe(CN) ₆ ³⁻ System	118
4.3.3	Interfacial Electron Transfer in the FeCp-DCM / Fe(CN) ₆ ³⁻ System	122
4.3.4	Surfactant Effect on Interfacial Electron Transfer Rate	127
4.4	Factors Governing Interfacial Electron Transfer Rate and Origin of the Micrometer Droplet Dependence	130
4.4.1	Liquid-Junction Potential Dependence of Interfacial Electron Transfer Rate	
	i) Liquid-Junction Potential Dependence	131

	ii) Comparison with Theory	132
4.4.2	Origin of the Droplet Size Effect on Electron Transfer Rate	139
	i) Rate Determining Step	140
	ii) Liquid-Junction Potential and Ion Transfer	143
	iii) Adsorption of Solutes	145
	iv) Photochemistry and Photophysics of Perylene	150
	v) Physical Properties of the Micrometer-Sized TBP Droplet	153
4.5	Conclusion	156
4.6	References	157

Chapter 5. Summary, Conclusions, and Future Perspective	159
--	-----

Acknowledgment	162
-----------------------	-----

Publication List	163
-------------------------	-----

Chapter 1

Introduction

1.1 What Occurs in Microdroplets ?

Chemistry at immiscible liquid / liquid interfaces, including that in oil-in-water and water-in-oil emulsions, has received broad interest in both basic and applied sciences. In chemistry, liquid / liquid interfaces play essential roles in separation science (*i.e.*, solvent extraction, chromatography, and so forth)¹⁻³⁾ as well as in organic synthesis (*i.e.*, phase transfer catalysis⁴⁾, emulsion polymerization, and so forth). Biological cells are also an example of liquid / liquid interfacial systems, in which two water phases are separated by a membrane wall. It is noteworthy that vectorial electron transfer (ET) and ion transfer (IT) in biological systems are based on such unique structures. Thus, ET and IT at liquid / liquid interfaces have been studied as a model of those in biological systems. In the field of applied sciences, furthermore, liquid / liquid interfacial systems have been widely employed: foods, photographs, paints, cosmetics, and so forth. Clearly, detailed understandings of chemistry *at* and *across* liquid / liquid interfaces afford wide benefit for further advances in various sciences.

So far, chemistry *at* and *across* flat macroscopic liquid / liquid interfaces has been studied on the basis of electrochemical and spectroscopic techniques⁵⁻²⁰⁾. Thermodynamic studies²¹⁻²³⁾ and molecular dynamic calculations²⁴⁻³⁴⁾ have been also explored to elucidate physical characteristics of the interface. These studies have succeeded in providing chemical and physical characteristics of flat liquid / liquid interfaces.

However, such an information may not be necessarily useful for discussion on chemistry in emulsion systems, since emulsion are consisted of microspherical liquid (*i.e.*, droplet) / liquid interfaces.

It is worth emphasizing that the factors governing chemical and physical processes at microdroplet / solution interfaces are expected to be different from those at macroscopic flat liquid / liquid interfaces, as shown schematically in Figure 1-1³⁵⁾. For instance, *mass transfer of a solute from the surrounding solution phase to a droplet is facilitated for smaller droplets, since the surface area (A) / volume (V) ratio of a droplet (A / V ratio) increases with decreasing the droplet radius (r)*. This is easily predicted from available diffusion theories. Namely, mass transfer of a solute to a droplet surface is governed by spherical diffusion, while that to a flat surface is based essentially on linear diffusion. Thus, water-to-droplet mass transfer becomes faster for smaller droplets.

Besides the mass transfer process, effects of a surface charge on chemical and physical processes are different between microdroplet / solution and macroscopic flat liquid / liquid interfaces. Commonly, the thickness of the electrical double layer at an interface is around several hundreds of nanometer. In a macroscopic system, such an electrical double layer influences the interfacial layer alone and, the bulk solution phase is not affected by the double layer. *In the case of a microdroplet, on the other hand, effects of the electrical double layer on the chemical and physical processes at the interface and in the droplet become important with decreasing r, since the thickness of the double layer approaches to r.*

Furthermore, recent theoretical studies indicate that thermal fluctuation at a liquid / liquid interface plays important roles in chemical and physical properties of the surface^{24-26,30,31,33)}. Thermal fluctuation at a liquid surface is characterized by the wavelength of a capillary wave (λ).

For a macroscopic flat liquid / liquid interface with the total length of the interface of l , capillary waves with various λ shorter than l are allowed, while λ produced at a droplet surface should be smaller than $2\pi r$ ³⁶⁾. In the case of a droplet, therefore, surface phenomena should depend on the droplet size. Besides these, a pressure (ΔP) or chemical potential difference ($\Delta\mu$) between a droplet and the surrounding solution phase increases with decreasing r as predicted by the Young - Laplace equation³⁵⁾; $\Delta P = 2\gamma/r$ and $\Delta\mu = \Delta V_m \Delta P$ where γ and ΔV_m are an interfacial tension and a mole volume of the surrounding phase, respectively. These discussions indicate clearly that *chemical and physical processes at droplet / solution interfaces are different from those at macroscopic flat liquid / liquid interfaces.*

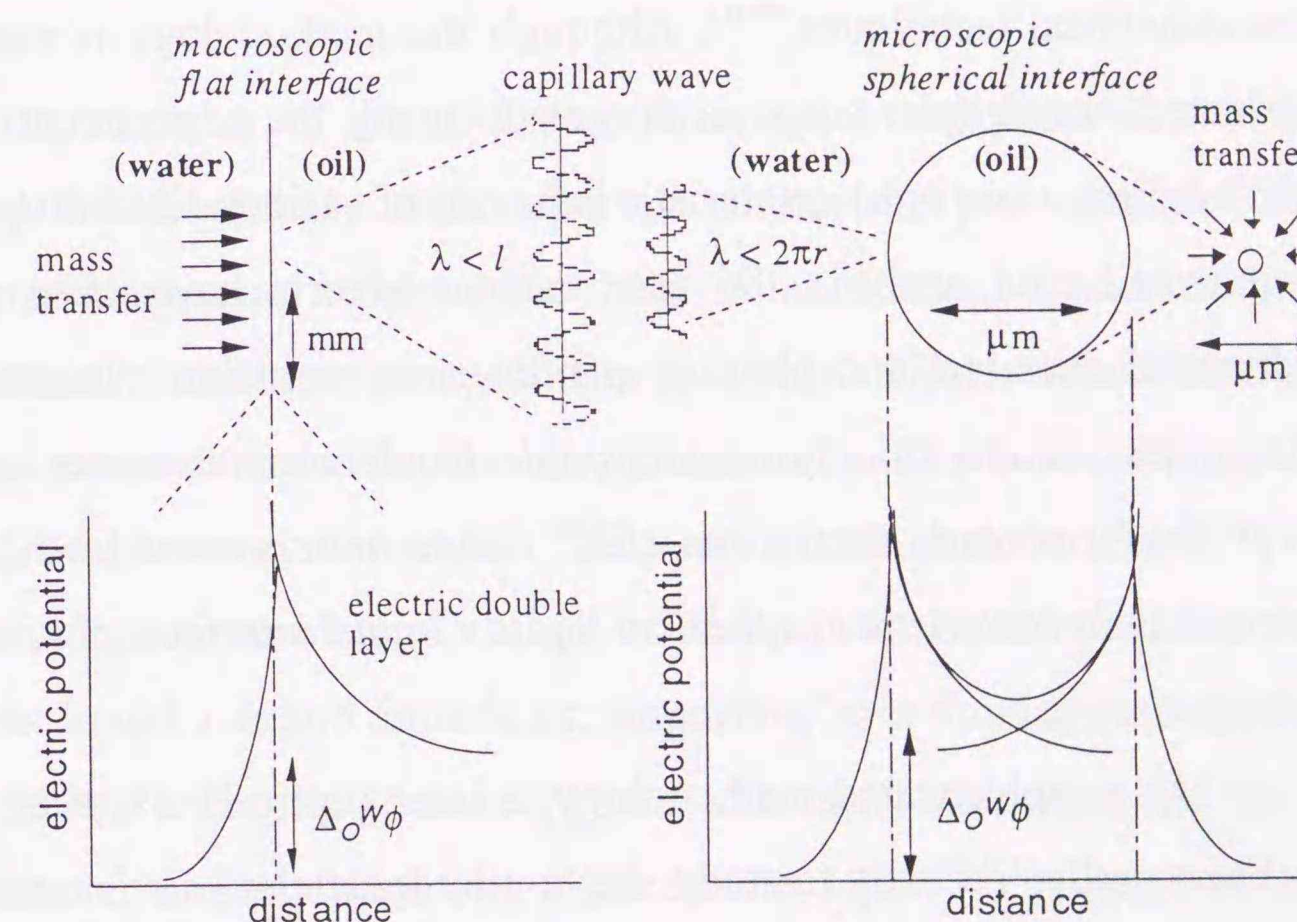


Figure 1-1. Schematic illustration of physical properties of flat macroscopic and spherical microscopic liquid / liquid interfaces.

*In order to elucidate characteristic features of the chemistry at or across droplet / solution interfaces, single droplet measurements are absolutely necessary since chemical and physical processes at the interface are dependent on the droplet radius as mentioned above. However, experimental studies on individual microdroplets are very difficult, since droplets undergo vigorous Brownian motion in solution and, the works along the line has been rarely explored. As a limited example, although photochemical dynamics in single droplets dispersed in a rigid matrix has been reported³⁷⁻³⁸), an application of the method to various systems is very difficult. As an another example, a hanging droplet method has been proposed³⁹), by which single droplets are produced at the end of a micropipet tip in solution, and the chemical and physical processes at millimeter-sized liquid / liquid interface have been studied by electrochemical techniques⁴⁰⁻⁴⁸). Although the methodology is easy to be conducted, the droplet shape is distorted during the experiments so that detailed discussions on characteristic behavior of various-sized droplet need complicated data analysis. So far, various efforts have been paid to understand chemical and physical processes in emulsion systems^{1,2,49-52}). Nonetheless, *detailed and systematic single droplet measurements have been never explored and, therefore, clear vision on chemical and physical processes, characteristic to spherical liquid / liquid interfaces, has not been given yet.**

As a sophisticated methodology, a laser (optical) trapping method has been applied recently to study single microparticles in solution⁵³⁻⁵⁷). It has been demonstrated that Brownian motion of single microparticles or droplets in solution can be frozen and manipulated simultaneously in a non-destructive and non-contact manner by a focused laser beam. Since various microparticles such as droplets, biological cells, and so forth can be

trapped and positioned in arbitrary space, the laser trapping method has wide applicabilities to study single microparticles⁵⁸⁻⁶⁵). Furthermore, the trapping method can be combined with spectroscopic and electrochemical techniques, so that chemical and physical processes *at* and *across* single microdroplet / solution interfaces can be followed directly by this particular method⁶⁶⁻⁶⁷). *On the basis of the laser trapping - spectroscopy - electrochemistry technique, chemical characteristics at a microdroplet / solution interface, different from that at macroscopic flat liquid / liquid interfaces, can be elucidated.*

1.2 Charge Transfer Reaction across a Liquid / Liquid Interface.

A number of the studies on chemistry at macroscopic flat liquid / liquid interfaces have been reported among the past decades⁶⁸⁻⁷⁷), and various important results have been demonstrated. Understandings of interfacial phenomena proceeding *at* or *across* a liquid / liquid interface are key to elucidate the molecular mechanisms of a distribution equilibrium of a solute between two phases⁷⁸⁻⁸³), ion-selective electrodes⁸⁴⁻⁸⁹), phase transfer processes of ions⁴). Kinetics of electron transfer and ion transfer across liquid / liquid interfaces, important as a fundamental process in solvent extraction, is governed by the interfacial structures and the radial profile of an interfacial electrical double layer⁹⁰⁻¹⁰¹). These interfacial phenomena are supposed to be dependent on nature of a liquid / liquid interface. At liquid / liquid interfaces, orientations of solvent molecules and solvation structures around an ion are different from those in the relevant homogeneous solution. In an electric double layer, spatial distributions of

ions are also different as compared to those in bulk systems owing to a potential difference across the interface.

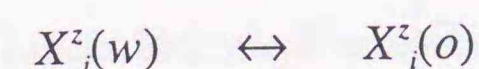
Chemical and physical phenomena at liquid / liquid interfaces have been studied by a variety of techniques such as surface specific spectroscopies: total internal reflection fluorescence spectroscopy⁵⁻¹⁰, non-linear optical spectroscopy (second harmonic generation and sum frequency generation technique)¹¹⁻²⁰, an elastic laser light scattering method¹⁰²⁻¹⁰⁴, fluorescence emission⁵, X-ray reflection¹⁰⁵⁻¹⁰⁶, neutron reflection¹⁰⁷⁻¹⁰⁹, ellipsometry¹¹⁰⁻¹¹¹, and so forth. As an example, a second harmonic generation (SHG) technique can provide valuable information about orientations of molecules at an interface. Also, total internal reflection (TIR) spectroscopy can sense both static and dynamic processes occurring in the interfacial layers. Combining the SHG method with an electrochemical techniques, Corn *et al.* reported molecular orientations of a dye at an electrically polarized 1,2-dichloroethane / water interface, and it has been shown that dye molecules near the water / hydrocarbon interface are ordered as compared with those in homogeneous solutions. Molecules at interfaces show specific properties different from those in bulk solutions.

So far, charge transfer reactions across liquid / liquid interfaces have been investigated by electrochemical and spectroscopic methods. Molecular dynamics-aided computer simulations of electron transfer (ET) or ion transfer (IT) at liquid / liquid interfaces have been also demonstrated²⁴⁻³⁴. These interfacial reactions are expected to be reflected by the interfacial structures and/or various characteristics such as an interfacial tension, an interfacial charge, a liquid-junction potential, and so forth.

The present thesis concerns about ET and IT across a microdroplet / water interface. As the background of the research, interfacial ET and IT processes are reviewed briefly in the following.

i) Ion Transfer Process.

Ion transfer (IT) across a liquid / liquid interface is expressed as,



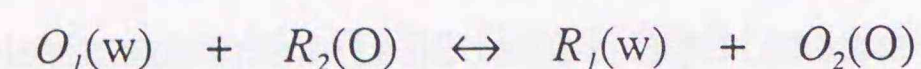
where X^z_i is an ion with the charge number z_i and, w or o denotes the ion in an aqueous or organic phase, respectively. Typically, two immiscible solvents such as nitrobenzene / water and 1,2-dichloroethane (DCE) / water systems are employed. IT across a liquid / liquid interface has been investigated kinetically by galvanostatic, potentiometric and voltammetric techniques such as chronopotentiometry, chronocoulometry, cyclic voltammetry, convolution potential sweep voltammetry, phase selective a.c. voltammetry and equilibrium impedance measurements with a four or two electrodes system^{68-77,112-115}. These techniques have been applied to study IT across macroscopic flat liquid / liquid interfaces.

As a characteristics of interfacial IT, IT across a liquid / liquid interface accompanies dramatic changes in solvation structures around an ion. Since an ion in water is strongly hydrated, IT of the ion from water to an oil phase needs a large dehydration energy, depending on the size of the ion and nature of an organic solvent. As an example, the free energy change of IT of Na^+ or Me_4N^+ from water to DCE is 52 or 26 kJmol^{-1} , respectively⁷³. Also, interfacial IT is characterized by a standard ion transfer potential, which is a parameter quantifies the relative affinity of an ion in the two phases. In the DCE / water system, the value for Me_4N^+ , Et_4N^+ , Pr_4N^+ , or Bu_4N^+ has been reported to be 0.182, 0.044, -0.091, or -0.225 mV, respectively⁷³. Besides quaternary ammonium ions^{73,116-118}, the values for metallic cations^{73,119-120} (Cs^+ , Na^+ , K^+ , *etc.*) and inorganic anions^{73,121-125}

(PF₆⁻, ClO₄⁻, BF₄⁻, *etc.*) in the nitrobenzene / water and DCE / water systems have been reported. Such studies are important as the fundamental basis for solvent extraction, including complexation reactions of anions or cations with crown ethers ¹²⁶⁻¹³⁰. Potential step chronoamperometry and chronoabsorptometry of pigments (Rose Bengal or Eosin-Y, *etc.*) at liquid / liquid interfaces have been also developed and shown to be highly potential to study dynamic aspect of the IT processes ¹³¹⁻¹³⁶. On the basis of electrochemical and spectroscopic methods, the kinetic parameter (standard rate constant; k^0 , charge transfer coefficient; α) of IT and the potential dependence of the ion transfer rate have been discussed in details ¹³⁷⁻¹⁴⁵. Also, electrical double layer effects on IT have been reported ¹⁴⁶⁻¹⁴⁸.

ii) Electron Transfer Process.

An ET reaction across a liquid / liquid interface takes place when a water-soluble oxidant (O_1 is an oxidized form and R_1 is a reduced form) is contacted with a reductant (R_2 is a reduced form and O_2 is an oxidized form) at the interface.



Analogous to ordinary electrochemical reactions, ET reactions across liquid / liquid interfaces can be discussed on the basis of the relevant standard rate constant (k^0) and charge transfer coefficient (α).

The mechanism of ET across a liquid / liquid interface is similar to

that of a homogeneous electron transfer. In both cases, the ET process accompanies the change in the oxidation states and their inner-sphere structures of the reactants / products including the bond breaking or formation. Polarization of solvent molecules necessary for ET must be also considered. Namely, electrostatic interactions of charged reactants with polar solvent molecules are very important, and the electron energy levels of the reactants in a polar medium are different from those in vacuum as well as in the products. However, the energy conservation law requires that the electron energy levels in the initial and final states must coincide within the uncertainly limit. In accordance with the Frank-Condon principle, ET occurs at a fixed configuration and its probability depends on the overlap of the electronic wave functions in the initial and final states, which decreases exponentially with increasing the distance between the reactants. Consequently, the reactants must first approach each other as closely as possible. Then, thermal fluctuations in orientational vibrations of solvent molecules and intramolecular vibrations of the reactants bring the system to an activated state, in which the radiationless ET can occur. Reorganization of solvent molecules and the intramolecular degrees of freedom play the main contribution to the Frank-Condon barrier of the ET process. The ET probability has been calculated on the basis of the Levich's quantum-mechanical model ¹⁴⁹. Recently, the problem has been addressed by Marcus, from point of view of the non-equilibrium thermodynamic theory ¹⁵¹⁻¹⁵³.

The theories demonstrate that an ET rate is determined by the activation free energy of the process. Marcus has pointed out that the reorganization energies of solvent molecules (λ_o) and reactants (λ_i) before and after an ET event are very important; λ_o and λ_i are so-called outer-sphere and inner-sphere reorganization energies, respectively. Marcus derived the relationship between the activation free energy and the

reorganization energy ($\lambda_o + \lambda_i$) of ET in 1956¹⁵⁰). It is well known that the theory is successful to predict various ET reactions in homogeneous systems. Recently, the Marcus theory has been extended to interfacial liquid / liquid ET reactions¹⁵¹⁻¹⁵³.

An ET reaction is the simplest chemical reaction and, so far, experimental studies on ET in homogeneous solutions have been explored extensively among the past decades¹⁵⁴. For liquid / liquid interfacial ET, however, the experimental work is rather difficult compared to that in homogeneous systems, since the solution resistance of an organic solvent is very high owing to the low dielectric constant and the narrow potential window. Nonetheless, efforts have been devoted to study liquid / liquid interfacial ET reactions on the basis of electrochemical methods such as cyclic voltammetry with a four-electrodes galvanic cell, an a.c. impedance method, current scan polarography, and scanning electrochemical microscopy. Spectroscopic measurements have been also employed to study an ET process across liquid / liquid interfaces. Furthermore, experimental results have been compared with those predicted by the Marcus theory. These studies revealed the important roles of the liquid-junction potential, the structure and thickness of the interface layer, and shape of the reactants in the interfacial ET event.

The first example of an ET reaction across a liquid / liquid interface was demonstrated for reduction of Cu^{2+} by $\text{V}(\text{CO})_6$ at a DCE / water interface, $\text{V}(\text{CO})_6 + 2\text{Cu}^{2+} \rightarrow \text{V}^{3+} + 6(\text{CO}) + 2\text{Cu}$, as observed by deposition of Cu at the interface¹⁵⁵. Later, Samec *et al.* reported a voltammetric study on ET across a liquid / liquid interface for the first time¹⁵⁶⁻¹⁶³: ET between ferrocene in nitrobenzene and $\text{Fe}(\text{CN})_6^{3-}$ in water. They demonstrated that the observed ET rate constant was almost independent of the liquid-junction potential owing to the double layer effect on the ET rate

or changes in the concentrations of the reactants at the interface. However, the ferrocenium cation in the nitrobenzene phase produced by the ET reaction distributes to the water phase, so that this ion transfer process makes the detailed discussion difficult. A reaction system must be thus chosen to avoid ion transfer of ET products. Otherwise, the contribution of the ion transfer process to the observed ET rate must be separated for the kinetic analysis.

Schiffrin *et al.* reported the ET reaction between metal biphtharocyanine complexes in DCE and $\text{Fe}(\text{CN})_6^{3-}$ in water^{4,164-165}. The metal biphtharocyanine cation produced by the ET reaction does not distribute to the water phase owing to its high hydrophobicity, so that the reaction system is advantageous for detailed analysis of the interfacial ET mechanism. Actually, the ET rate constant (cm s^{-1}) has been determined by a cyclic voltammetric study and it has been shown that the rate constant is smaller than that calculated from the relevant ET rates at an electrode / solution system. The results can be explained by the differences in the solvent reorganization energy and the ET distance between the two systems. The structures of the liquid / liquid interface is also an important factor determining the ET rate. As another examples, the ET reactions between metal porphyrines in an organic phase and $\text{Fe}(\text{CN})_6^{3-}$ in a water or between 7,7,8,8-tetracyanoquinodimethane (TCNQ) in an organic phase and $\text{Fe}(\text{CN})_6^{4-}$ in water have been studied by polarography methods¹⁶⁶⁻¹⁷⁶.

Generally, an interfacial ET reaction accompanies ion transfer (IT) of the redox product(s) across the two phases and the separation of these two processes is generally difficult as described above. As a possible approach, Schiffrin *et al.* reported an a.c. impedance study on ET between lutetium diphthalocyanine ($\text{Lu}(\text{pc})_2$), bis (pyridine) (meso-tetraphenylporphyrinato) ruthenium(II), or TCNQ in DCE and a $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$ redox couple

in water¹⁷⁷). This method is very advantageous since the IT process can be separated from the ET process. The ET rate constant ($\text{cmM}^{-1}\text{s}^{-1}$) was thus determined and compared with the theoretical value predicted by the Marcus theory. As a result, the observed value was in good agreement with the theoretical one. However, it is noteworthy that the effects of the electrical double layer, the molecular shape of the reactants, and the ion pair formation at the interface on the ET rate cannot be discussed by such a method. Therefore, strict comparisons of the observed data with those predicted by the Marcus theory are very difficult.

As another experimental approach, Bard *et al.* reported interfacial ET reactions by a scanning electrochemical microscope (SECM)¹⁷⁸⁻¹⁸³. SECM using a microelectrode can induce an interfacial ET in minute dimension with free from effects of solution resistance and uncompensated resistance during electrochemical measurements. IT coupled with ET can be also neglected. Thus, detailed discussions on the factor determining the interfacial ET rate are possible on the basis of SECM experiments. Actually, liquid-junction potential and distance dependencies of the ET rate constant have been demonstrated by Bard and his co-workers.

Liquid / liquid interfacial ET reactions are important as a model of vectorial ET in biological systems. Schiffrin *et al.* reported the ET reaction across a phospholipid monolayer constructed at a DCE / water interface by cyclic voltammetry¹⁸⁴⁻¹⁸⁵. Since the membrane possesses an ultimate thickness, the ET reaction does not proceed directly across the membrane, but takes place in the presence of an electron mediator in the membrane. The distance between two reactants separated by the interface is therefore a very important factor governing interfacial ET reactions.

Both experimental and theoretical studies on liquid / liquid

interfacial ET reactants have been accumulated among the past decades as described above. However, our knowledge about electron transfer reactions across liquid / liquid interfaces is still limited and superficial, compared to that on homogeneous ET reactions. Clearly, elucidations of the factors determining the interfacial ET rate and the relevant molecular mechanisms are absolutely necessary for further advances in the studies on liquid / liquid interfacial reactions.

1.3 Purpose and Content of the Thesis.

The studies on interfacial electron transfer reactions so far reported are limited to those across macroscopic flat liquid / liquid interfaces and, no report has been appeared on those across a microscopic curved liquid / liquid (*i.e.*, droplet / solution) interface. As discussed in the previous section, emulsion systems composed of droplets in solution play very important roles in various fields, so that the study on chemical processes across a droplet / solution interface is worth to be explored. In order to study emulsion systems, single droplet measurements are absolutely necessary, since interfacial processes depend on the size of a droplet. Thus, a laser trapping method was applied to single droplets measurements. The laser trapping method can be combined with electrochemical and spectroscopic techniques so that the method is very fruitful to study chemistry *in* or *across* a single droplet / solution interface. In this study, therefore, a new and novel methodology of a laser trapping - spectroscopy - electrochemistry technique was developed. On the basis of development of such a methodology, electron transfer reactions across a single microdroplet / solution interface were studied in detail.

The purpose of the thesis is to elucidate characteristic features of the electron transfer process across a single microdroplet / water interface, in special reference to the droplet size effects on the electron transfer rate in micrometer dimension. Since there has been no report on the electron transfer process across a spherical liquid / liquid interface, the present study is the first demonstration for the direct observation of the interfacial electron transfer process in micrometer dimension. The thesis consists of five chapters.

In Chapter 1, roles of emulsions in various sciences were overviewed and, characteristics of chemical and physical processes *at* or *across* liquid / liquid interfaces were described. Furthermore, general features of the electron transfer (ET) and ion transfer (IT) processes across liquid / liquid interfaces were discussed. The importance of the chemistry of single microdroplets in solution were also described.

In Chapter 2, the principle of laser trapping was explained and a laser trapping - microspectroscopy - electrochemistry system constructed in this study was outlined, together with its performance and characteristics of the system. This is the fundamental basis for evaluation of the accuracy and reliability of the experimental results on single microdroplets in water.

In Chapter 3, after explanation of the fluorometric and coulometric method for determining the interfacial ET rate, the results on the ET reaction between ferrocene in oil droplets and hexacyanoferrate(III) in water, observed as an ensemble average for various-sized droplets, were described. *It was shown that the interfacial ET rate constant could be determined directly through fluorescence quenching of 9,10-diphenylanthracene or perylene by ferrocene in oil droplets.* On the basis of several controlled experiments, the rate determining step was shown to be the interfacial ET process. Also, analytical equations employed in the

present experiments were derived and explained in detail.

The ET reaction across the laser-trapped individual tri-n-butyl phosphate droplets / water interface was studied. *The surface area / volume (A / V) ratio dependence of the ET rate constant ($M^{-1}s^{-1}$) was observed for the first time.* On the basis of the droplet size dependence of the ET rate, furthermore, the rate constant ($cmM^{-1}s^{-1}$) per unit droplet surface area was determined.

In Chapter 4, the liquid-junction potential dependence and the characteristic droplet size effects on the ET rate constant were described. The ET rate was shown to increase with decreasing in the liquid-junction potential and the results were discussed in terms of the Marcus theory. *The most important findings of the study is the observation of the characteristic droplet size effect on the ET rate at the droplet radius below $5\ \mu m$. This size effect was shown to be specific to the spherical micro-liquid / liquid interface* and discussed in terms of the chemical and physical properties of the tri-n-butylphosphate droplet / water interface.

In Chapter 5, the principal results of the study were summarized and future perspective of the research was discussed.

1.4 References.

- 1) S.P.Carter and H.Freiser, *Anal.Chem.*, **51**,1100 (1979).
- 2) H.Watarai and H.Freiser, *J.Am.Chem.Soc.*, **105**,189 (1983).
- 3) H.Freiser, *Bull.Chem.Soc.Jpn.*, **61**,39 (1988).
- 4) V.J.Cunnane, D.J.Schiffrin, C.Beltran, G.Geblewicz and T.Solomon, *J.Electroanal.Chem.*, **247**,203 (1988).
- 5) M.J.Wirth and I.D.Bubage, *J.Phys.Chem.*, **96**,9022 (1992).

- 6) J.M.Kovaleski and M.J.Wirth, *J.Phys.Chem.*, **99**,4091 (1995).
- 7) J.M.Kovaleski and M.J.Wirth, *J.Phys.Chem.*, **100**,10304 (1996).
- 8) K.Nakatani, S.Ishizaka and N.Kitamura, *Anal.Sci.*, **12**,701 (1996).
- 9) K.Bessho, T.Uchida, A.Yamauchi, T.Shioya and N.Teramae, *Chem.Phys.Lett.*, **264**,381 (1997).
- 10) R.A.W.Dryfe, Z.Ding, R.G.Wellington, P.F.Brevet, A.M.Kuznetsov and H.H.Girault, *J.Phys.Chem.A*, **101**,2519 (1997).
- 11) S.G.Grubb, M.W.Kim, T.Rasing and Y.R.Shen, *Langmuir*, **4**,452 (1988).
- 12) A.J.Bell, J.G.Frey and T.J.VanderNoot, *J.Chem.Soc.,Faraday Trans.*, **88**,2027 (1992).
- 13) D.A.Higgins, R.M.Corn, *J.Phys.Chem.*, **97**,489 (1993).
- 14) K.L.Kott, D.A.Higgins, D.G.Hanken and R.M.Corn, *J.Am.Chem.Soc.*, **115**,5342 (1993).
- 15) J.C.Conboy, J.L.Daschbach and G.L.Richmond, *J.Phys.Chem.*, **98**,9688 (1994).
- 16) R.P.Naujok, D.A.Higgins, D.G.Hanken and R.M.Corn, *J.Chem.Soc.,Faraday Trans.*, **91**,1411 (1995).
- 17) A.A.T.Luca, P.Hebert, P.F.Brevet and H.H.Girault, *J.Chem.Soc.,Faraday Trans.*, **91**,1763 (1995).
- 18) J.C.Conboy and G.L.Richmond, *Electrochim.Acta*, **40**,2881 (1995).
- 19) R.P.Naujok, H.J.Paul and R.M.Corn, *J.Phys.Chem.*, **100**,10497 (1996).
- 20) H.J.Paul and R.M.Corn, *J.Phys.Chem. B*, **101**,4494 (1997).
- 21) T.Kakiuchi and M.Senda, *Bull.Chem.Soc.Jpn.*, **56**,2912 (1983).
- 22) H.H.Girault and D.J.Schiffrin, *J.Electroanal.Chem.*, **170**,127 (1984).
- 23) T.Kakiuchi, M.Nakanishi and M.Senda, *Bull.Chem.Soc.Jpn.*, **61**,1845 (1988).
- 24) M.Meyer, M.Mareschal and M.Hayoun, *J.Chem.Phys.*, **89**,1067 (1988).

- 25) P.Linse, *J.Chem.Phys.*, **86**,4177 (1988).
- 26) I.L.Carpenter and W.J.Hehre, *J.Phys.Chem.*, **94**,531 (1990).
- 27) I.Benjamin, *J.Phys.Chem.*, **95**,6675 (1991).
- 28) I.Benjamin, *J.Chem.Phys.*, **96**,577 (1992).
- 29) I.Benjamin, *J.Chem.Phys.*, **97**,1432 (1992).
- 30) I.Benjamin, *Science*, **261**,1558 (1993).
- 31) A.R.Buuren, S.J.Marrink and H.J.C.Berendsen, *J.Phys.Chem.*, **97**,9206 (1993).
- 32) K.J.Scweighfor and I.Benjamin, *J.Phys.Chem.*, **99**,9974 (1995).
- 33) I.Benjamin, *Chem.Rev.*, **96**,1449 (1996).
- 34) M.Tarek and M.L.Klein, *J.Phys.Chem.*, **101**,8639 (1997).
- 35) A.W.Adamson, *Physical Chemistry of Surfaces*, John Wiley & Sons, New York, (1990).
- 36) V.G.Levich, *Physicochemical Hydrodynamics*, translated by Scripta Technica, Prentice-Hall, Englewood Cliffs, NJ. p.591, (1962)
- 37) K.K.Pandey and S.Hirayama, *J.Photochem.Photobio.A Chem.*, **99**,165 (1996).
- 38) K.Nakamura, T.Kowaki, A.D.Scully and S.Hirayama, *J.Photochem.Photobio.A Chem.*, **104**,141 (1997).
- 39) C.J.Slevin and P.R.Unwin, *Langmuir*, **13**,4799 (1997).
- 40) G.Taylor and H.H.Girault, *J.Electroanal.Chem.*, **208**,179 (1986).
- 41) J.A.Campbell and H.H.Girault, *J.Electroanal.Chem.*, **266**,465 (1989).
- 42) A.A.Stewart, G.Taylor and H.H.Girault, *J.Electroanal.Chem.*, **296**,491 (1990).
- 43) A.A.Stewart, Y.Shao, C.M.Pereira and H.H.Girault, *J.Electroanal.Chem.*, **305**,135 (1991).
- 44) M.C.Osborne, Y.Shao, C.M.Pereira and H.H.Girault, *J.Electroanal.Chem.*, **364**,155 (1994).

- 45) V.Marecek, A.Lhotsky and S.Racinski, *Electrochim.Acta*, **40**,2905 (1995).
- 46) V.J.Cunnane, D.J.Schiffrin and D.E.Williams, *Electrochim.Acta*, **40**,2943 (1995).
- 47) P.D.Beattie, A.Dalay and H.H.Girault, *Electrochim.Acta*, **40**,2961 (1995).
- 48) P.D.Beattie, A.Dalay and H.H.Girault, *J.Electroanal.Chem.*, **380**,167 (1995).
- 49) P.D.I.Fletcher, A.M.Howe and B.H.Robinson, *J.Chem.Soc.,Faraday Trans.1.*, **83**,985 (1987).
- 50) W.J.Albey, R.A.Choudhery, N.Z.Atay and B.H.Robinson, *J.Chem.Soc., Faraday Trans.1.*, **83**,2407 (1987).
- 51) D.J.McClements and S.R.Dungan, *J.Phys.Chem.*, **97**,7304 (1993).
- 52) L.K.Tong, In *The Theory of the Photographic Process*, T.H.James, ed., Macmillan, New York p.339 (1977).
- 53) A.Ashkin, *Phys.Rev.Lett.*, **24**,156 (1970).
- 54) A.Ashkin and J.M.Dziedzic, *Appl.Phys.Lett.*, **19**,283 (1971).
- 55) A.Ashkin, *Science*, **210**,1081 (1980).
- 56) A.Ashkin, J.M.Dziedzic, J.E.Bjorkholm and S.Chu, *Opt.Lett.*, **11**,288 (1986).
- 57) H.Misawa, M.Koshioka, K.Sasaki, N.Kitamura and H.Masuhara, *Chem.Lett.*, 469 (1991).
- 58) H.Misawa, N.Kitamura and H.Masuhara, *J.Am.Chem.Soc.*, **113**,7859 (1991).
- 59) M.Koshioka, H.Misawa, K.Sasaki, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **96**,2909 (1992).
- 60) K.Nakatani, H.Misawa, K.Sasaki, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **97**,1701 (1993).

- 61) K.Nakatani, T.Uchida, S.Funakura, A.Sekiguchi, H.Misawa, N.Kitamura and H.Masuhara, *Chem.Lett.*, 717 (1993).
- 62) K.Nakatani, T.Uchida, H.Misawa, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **97**,5197 (1993).
- 63) K.Nakatani, T.Uchida, N.Kitamura and H.Masuhara, *J.Electroanal.Chem.*, **375**,383 (1994).
- 64) K.Nakatani, T.Uchida, H.Misawa, N.Kitamura and H.Masuhara, *J.Electroanal.Chem.*, **367**,109 (1994).
- 65) H.Yao, Y.Inoue, H.Ikeda, K.Nakatani, H.-B.Kim and N.Kitamura, *J.Phys.Chem.*, **100**,1494 (1996).
- 66) K.Nakatani, M.Wakabayashi, K.Chikama and N.Kitamura, *J.Phys.Chem.*, **100**,6749 (1996).
- 67) K.Nakatani, T.Suto, M.Wakabayashi, H.-B Kim and N.Kitamura, *J.Phys.Chem.*, **99**,4745 (1995).
- 68) J.Koryta and P.V.Vanysek, In *Advances in Electrochemistry and Electrochemical Engineering*, Gerischer,H.; Tobias,C.W., Eds.; John Wiley & Sons, New York, vol 12 (1981).
- 69) V.E.Kazarinov, Ed.; *The Interface Structure and Electrochemical Processes at the Bounday Between Two Immiscible Liquids*, Springer-Verlag, Berlin (1987).
- 70) H.H.Girault and D.J.Schiffrin, In *Electroanalytical Chemistry*, Bard A.J.; Dekker M., Eds.; New York, vol 15 (1989).
- 71) H.H.Girault, In *Modern Aspects of Electrochemistry*, White R.E.; Conway B.E.; Brockris J.O., Eds.; New York, vol 25 (1993).
- 72) Z.Samec and T.Kakiuchi, In *Advances in Elecrochemistry and Electrochemical Science*, Gerischer H.; Tobias C.W., Eds.; VCH: Weinheim, vol 4 (1995).

- 73) A.G.Volkov and D.W.Deamer, Eds.; *Liquid-Liquid Interfaces*, CRC Press: Boca Raton (1996).
- 74) J.Koryta, *Electrochim.Acta*, **24**,293 (1979).
- 75) J.Koryta, *Electrochim.Acta*, **33**,189 (1988).
- 76) M.Senda, T.Kakiuchi and T.Osakai, *Electrochim.Acta*, **36**,253 (1991).
- 77) P.vanysek, *Electrochim.Acta*, **40**,2841 (1995).
- 78) J.Rais, M.Kyrs and M.Pivonkova, *J.Inorg.nucl.Chem.*, **30**,611 (1968).
- 79) J.Rais and M.Kyrs, *J.Inorg.Nucl.Chem.*, **31**,175 (1969).
- 80) M.Pivonkova and M.Kyrs, *J.Inorg.Nucl.Chem.*, **31**,175 (1969).
- 81) J.Rais, *Collect.Czech.Chem.Comm.*, **36**,3253 (1970).
- 82) J.Czapkiewicz and B.Czapkiewicz-Tutaj, *J.Chem.Soc.,Faraday Trans.*, **76**,1663 (1979).
- 83) L.Q.Hung, *J.Electroanal.Chem.*, **115**,159 (1980).
- 84) T.Kakiuchi and M.Senda, *Bull.Chem.Soc.Jpn.*, **57**,1801 (1984).
- 85) T.Kakiuchi, I.Obi and M.Senda, *Bull.Chem.Soc.Jpn.*, **58**,1636 (1985).
- 86) T.Kakiuchi and M.Senda, *Bull.Chem.Soc.Jpn.*, **60**,3099 (1987).
- 87) S.Kihara, K.Maeda, M.Suzuki, Y.Sohrin, O.Shirai and M.Matsui, *Anal.Sci.*, **7**,1415 (1991).
- 88) M.Senda, *Anal.Sci.*, **7**,585 (1991).
- 89) C.Wei, A.J.Bard, G.Nagy and K.Toth, *Anal.Chem.*, **67**,1346 (1995).
- 90) Z.Samec, V.Marecek and D.Homolka, *J.Electroanal.Chem.*, **126**,121 (1981).
- 91) J.D.Reid, O.R.Melroy and R.P.Buck, *J.Electroanal.Chem.*, **147**,71 (1983).
- 92) P.Hajkova, D.Homolka, V.Marecek and Z.Samec, *J.Electroanal.Chem.*, **151**,277 (1983).
- 93) Z.Samec, V.Marecek and D.Homolka, *J.Electroanal.Chem.*, **187**,31 (1985).

- 94) G.M.Torrie and J.P.Valleau, *J.Electroanal.Chem.*, **206**,69 (1986).
- 95) Z.Samec, V.Marecek, K.Holub, S.Racinsky and P.Hajkova, *J.Electroanal.Chem.*, **225**,65 (1987).
- 96) T.Kakiuchi, M.Kobayashi and M.Senda, *Bull.Chem.Soc.Jpn.*, **60**,3109 (1987).
- 97) T.Kakiuchi, J.Noguchi and M.Senda, *J.Electroanal.Chem.*, **336**,137 (1992).
- 98) C.M.Pereira, A.Martins, M.Rocha, C.J.Silva and F.Silva, *J.Chem.Soc.,Faraday Trans.*, **90**,143 (1994).
- 99) Q.Cui, G.Zhu and E.Wang, *J.Electroanal.Chem.*, **372**,15 (1994).
- 100) Q.Cui, G.Zhu and E.Wang, *J.Electroanal.Chem.*, **383**,7 (1995).
- 101) T.Wandlowski, K.Holub, V.Marecek and Z.Samec, *Electrochim.Acta*, **40**,2887 (1995).
- 102) I.A.Mclure and I.L.Pegg, *J.Mol.Struct.*, **80**,393 (1982).
- 103) H.Lofgren, R.D.Neuman, L.E.Scriven and H.T.Davis, *J.Colloid.Interface Sci.*, **98**,175 (1984).
- 104) Z.Zhang, I.Tsuyumoto, S.Takahashi, T.Kitamori and T.Sawada, *J.Phys.Chem.*, **101**,4163 (1997).
- 105) D.K.Schwartz, M.L.Schlossman, E.H.Kawamoto, G.J.Kellogg, P.S.Pershan and B.M.Ocko, *Phys.Rev. A*, **41**,5687 (1990).
- 106) B.M.Ocko, X.Z.Wu, E.B.Sirota, S.K.Sinha and M.Deutsch, *Phys.Rev.Lett.*, **72**,242 (1994).
- 107) J.Penfold and R.K.Thomas, *J.Phys.A.Condens.Matter*, **2**,1369 (1990).
- 108) L.T.Lee, D.Langevin and B.Farnoux, *Phys.Rev.Lett.*, **67**,2678 (1991).
- 109) L.T.Lee, D.Langevin, E.K.Mann and B.Farnuox, *Physica B*, **198**,83 (1994).
- 110) A.Schmidt, *Phys.Rev.A*, **38**,567 (1988).

- 111) S.Bosch, *Surf.Sci.*, **289**,411 (1993).
- 112) J.Koryta, P.Vanysek and M.Brezina, *J.Electroanal.Chem.*, **75**,211 (1977).
- 113) Z.Samec, V.Marecek, J.Weber and D.Homolka, *J.Electroanal.Chem.*, **99**,385 (1979).
- 114) T.Osakai, T.Kakiuchi and M.Senda, *Bull.Chem.Soc.Jpn.*, **57**,370 (1984).
- 115) S.Kihara, M.Suzuki, K.Maeda, K.Ogura, S.Umetani, M.Matsui and Z.Yoshida, *Anal.Chem.*, **58**,2954 (1986).
- 116) Z.Samec, V.Marecek, J.Koryta and M.W.Khalil, *J.Electroanal.Chem.*, **83**,393 (1977).
- 117) Z.Samec and V.Marecek, *J.Electroanal.Chem.*, **200**,17 (1986).
- 118) Z.Samec, A.R.Brown, L.J.Yellowlees and H.H.Girault, *J.Electroanal.Chem.*, **288**,245 (1990).
- 119) Z.Samec, V.Marecek and J.Weber, *J.Electroanal.Chem.*, **100**,841 (1979).
- 120) S.A.Dassie, L.M.Yudi and A.M.Baruzzi, *Electrochim.Acta*, **40**,2953 (1995).
- 121) S.Kihara, M.Suzuki, K.Maeda, K.Ogura, M.Matsui and Z.Yoshida, *J.Electroanal.Chem.*, **210**,147 (1986).
- 122) T.Kakiuchi, J.Noguchi and M.Senda, *J.Electroanal.Chem.*, **327**,63 (1992).
- 123) T.Osakai, S.Himeno and A.Saito, *J.Electroanal.Chem.*, **360**,299 (1993).
- 124) H.Wang, Z.Yu and E.Wang, *J.Electroanal.Chem.*, **380**,69 (1995).
- 125) H.Katano, T.Osakai, S.Himeno and A.Saito, *Electrochim.Acta*, **18**,2935 (1995).

- 126) T.Kakiuchi, Y.Nishiwaki, T.Osakai and M.Senda, *Bull.Chem.Soc.Jpn.*, **59**,781 (1986).
- 127) H.Matsuda, Y.Yamada, K.Kanamori, Y.Kudo and Y.Takeda, *Bull.Chem.Soc.Jpn.*, **64**,1497 (1991).
- 128) T.Kakiuchi and M.Senda, *J.Electroanal.Chem.*, **300**,432 (1991).
- 129) A.Sabela, V.Marecek, J.Koryta and Z.Samec, *Collect.Czech.Chem.Comm.*, **59**,1287 (1994).
- 130) P.D.Beattie, R.G.Wellington and H.H.Girault, *J.Electroanal.Chem.*, **396**,317 (1995).
- 131) T.Kakiuchi, Y.Takasu and M.Senda, *Anal.Chem.*, **64**,3096 (1992).
- 132) T.Kakiuchi and Y.Takasu, *Anal.Chem.*, **66**,1853 (1994).
- 133) T.Kakiuchi and Y.Takasu, *J.Electroanal.Chem.*, **365**,293 (1994).
- 134) T.Kakiuchi and Y.Takasu, *J.Electroanal.Chem.*, **381**,5 (1995).
- 135) T.Kakiuchi and Y.Takasu, *J.Phys.Chem.B*, **101**,5963 (1997).
- 136) Z.Ding, R.G.Wellington, P-F.Brevet and H.H.Girault, *J.Electroanal.Chem.*, **420**,35 (1997).
- 137) O.R.Melroy and R.P.Buck, *J.Electroanal.Chem.*, **136**,19 (1982).
- 138) H.H.Girault and D.J.Schiffrin, *J.Electroanal.Chem.*, **195**,213 (1985).
- 139) R.P.Buck and W.E.Bronner, *J.Electroanal.Chem.*, **197**,179 (1986).
- 140) H.H.Girault, *J.Electroanal.Chem.*, **257**,47 (1988).
- 141) T.Kakiuchi, *J.Electroanal.Chem.*, **322**,55 (1992).
- 142) Z.Samec and V.Marecek, *J.Electroanal.Chem.*, **333**,319 (1992).
- 143) H.Wang, Y.Yao and E.Wang, *J.Electroanal.Chem.*, **372**,21 (1994).
- 144) K.Kntturi, J.A.Manzanares and L.Murtomaki, *Electrochim.Acta*, **40**,2979 (1995).
- 145) A.V.Indenbon, *Electrochim.Acta*, **40**,2985 (1995).
- 146) T.Kakiuchi, J.Noguchi and M.Senda, *J.Electroanal.Chem.*, **336**,137 (1992).

- 147) M.Senda, *Anal.Sci.*, **10**,649 (1994).
- 148) Z.Samec, T.Kakiuchi and M.Senda, *Electrochim.Acta*, **40**,2971 (1995).
- 149) V.G.Levich, In *Advances in Electrochemistry and Electrochemical Engineering*, Gerischer H.; Tobias C.W., Eds.; John Wiley & Sons, New York, vol 12 (1981).
- 150) R.A.Marcus, *J.Chem.Phys.*, **24**,966 (1956).
- 151) R.A.Marcus, *J.Phys.Chem.*, **94**,4152 (1990).
- 152) R.A.Marcus, *J.Phys.Chem.*, **94**,1050 (1990).
- 153) R.A.Marcus, *J.Phys.Chem.*, **95**,2010 (1991).
- 154) R.D.Cannon, *Electron Transfer Reaction*, Butterworths, London (1980).
- 155) M.Guaninazzi, G.Silvestri and G.Serravalle, *J.Chem.Soc.Chem.Comm.*, 200 (1975).
- 156) Z.Samec, V.Marecek and J.Weber, *J.Electroanal.Chem.*, **96**,245 (1979).
- 157) Z.Samec, *J.Electroanal.Chem.*, **99**,197 (1979).
- 158) Z.Samec, *J.Electroanal.Chem.*, **103**,1 (1979).
- 159) Z.Samec, V.Marecek, and J.Weber, *J.Electroanal.Chem.*, **103**,11 (1979).
- 160) Z.Samec, *J.Electroanal.Chem.*, **111**,211 (1980).
- 161) Z.Samec, V.Marecek, J.Weber and D.Homolka, *J.Electroanal.Chem.*, **126**,105 (1981).
- 162) J.Hanzlik, J.Hovolka, Z.Samec and S.Toma, *Coll.Czech.Chem.Comm.*, **53**,903 (1987).
- 163) J.Hanzlik, Z.Samec and J.Hovolka, *J.Electroanal.Chem.*, **216**,303 (1987).
- 164) H.H.Girault and D.J.Schiffrin, *J.Electroanal.Chem.*, **244**,15 (1988).

- 165) G.Geblewicz and D.J.Schiffrin, *J.Electroanal.Chem.*, **244**,27 (1988).
- 166) T.Gennett, D.F.Milner and M.J.Weaver, *J.Phys.Chem.*, **89**,2787 (1985).
- 167) S.Kihara, M.Suzuki, K.Maeda, K.Ogura, M.Matsui and Z.Yoshida, *J.Electroanal.Chem.*, **271**,107 (1989).
- 168) A.A.Stewart, J.A.Campbell, H.H.Girault and M.Eddowes, *Ber.Bunsenges.Phys.Chem.*, **94**,83 (1990).
- 169) K.Maeda, S.Kihara, M.Suzuki and M.Matsui, *J.Electroanal.Chem.*, **303**,171 (1991).
- 170) Y.Cheng and D.J.Schiffrin, *J.Electroanal.Chem.*, **314**,153 (1991).
- 171) Q-Z.Chen, K.Iwamoto and M.Seno, *Electrochim.Acta*, **36**,291 (1991).
- 172) S.Kihara, K.Maeda, M.Suzuki, Y.Sohrin, O.Shirai and M.Matsui, *Anal.Sci.*, **7**,1415 (1991).
- 173) M.Senda, *Electrochim.Acta*, **40**,2993 (1995).
- 174) T.Kakiuchi, *Electrochim.Acta*, **40**,2999 (1995).
- 175) V.J.Cunnane, G.Geblewicz and D.J.Schiffrin, *Electrochim.Acta*, **40**,3005 (1995).
- 176) H.Katano, K.Maeda and M.Senda, *J.Electroanal.Chem.*, **396**,391 (1995).
- 177) Y.Cheng and D.J.Schiffrin, *J.Chem.Soc.,Faraday Trans.*, **89**,199 (1993).
- 178) D.O.Wipf and A.J.Bard, *J.Electroanal.Chem.*, **138**,469 (1991).
- 179) C.Wei, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **99**,16033 (1995).
- 180) T.Solomon and A.J.Bard, *Anal.Chem.*, **67**,2787 (1995).
- 181) T.Solomon and A.J.Bard, *J.Phys.Chem.*, **99**,17487 (1995).
- 182) M.Tsionsky, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **100**,17881 (1996).

- 183) M.Tsionsky, A.J.Bard and M.V.Mirkin, *J.Am.Chem.Soc.*, **119**,10785 (1997).
- 184) Y.Cheng, V.J.Cunnane, A-K.Kontturi, K.Kontturi and D.J.Schiffrin, *J.Phys.Chem.*, **100**,15470 (1996).
- 185) Y.Cheng and D.J.Schiffrin, *J.Chem.Soc.,Faraday Trans.*, **90**,2517 (1994).

Chapter 2

Laser Trapping - Spectroscopy - Electrochemistry of Single Microdroplets in Water

The principal aim of the study is to elucidate characteristic features of an electron transfer reaction across a microdroplet / water interface. In order to pursue the present study, simultaneous manipulation and characterization of individual microdroplets undergoing Brownian motion in water should be achieved. So far, experimental investigations on minute samples with the size in micrometer dimension have been conducted on the basis of a mechanical method using a micropipet and a micromanipulator. By using such a method, samples are more or less damaged owing to direct mechanical contact of a pipet with the sample. Although mechanically rigid samples such as glass beads and polymer beads could be manipulated by a pipet, soft materials such as microdroplets, biocells, capsules and so forth are very difficult to be manipulated by the mechanical method. Furthermore, contact-mode manipulation with the use of a micropipet disturbs analytical procedures of microsamples. Therefore, noncontact and nondestructive manipulation of single microdroplets in solution is absolutely necessary to conduct the present study.

The most probable candidate for noncontact and nondestructive manipulation of a single microparticle is an application of laser trapping, by which single microparticles in solution can be manipulated arbitrary in space by a focused laser beam¹⁻⁵⁾. If one can combine the laser trapping method with an appropriate analytical method, single microdroplet measurements are realized^{6-24,26)}. In the present study, a laser trapping - spectroscopy - electrochemistry system was constructed and employed

throughout the present study on single micro-oil droplets in water. Before describing the experimental results on electron transfer processes across a single microdroplet / water interface, therefore, the principle of laser trapping and performance of the constructed system are described.

2.1 The Principle of Laser Trapping.

Laser trapping of a microparticle is essentially based on light refraction by a particle. Figure 2-1 illustrates the simplest model of the principle of laser trapping, in which a light beam (*i.e.*, photon) is reflected by a mirror.

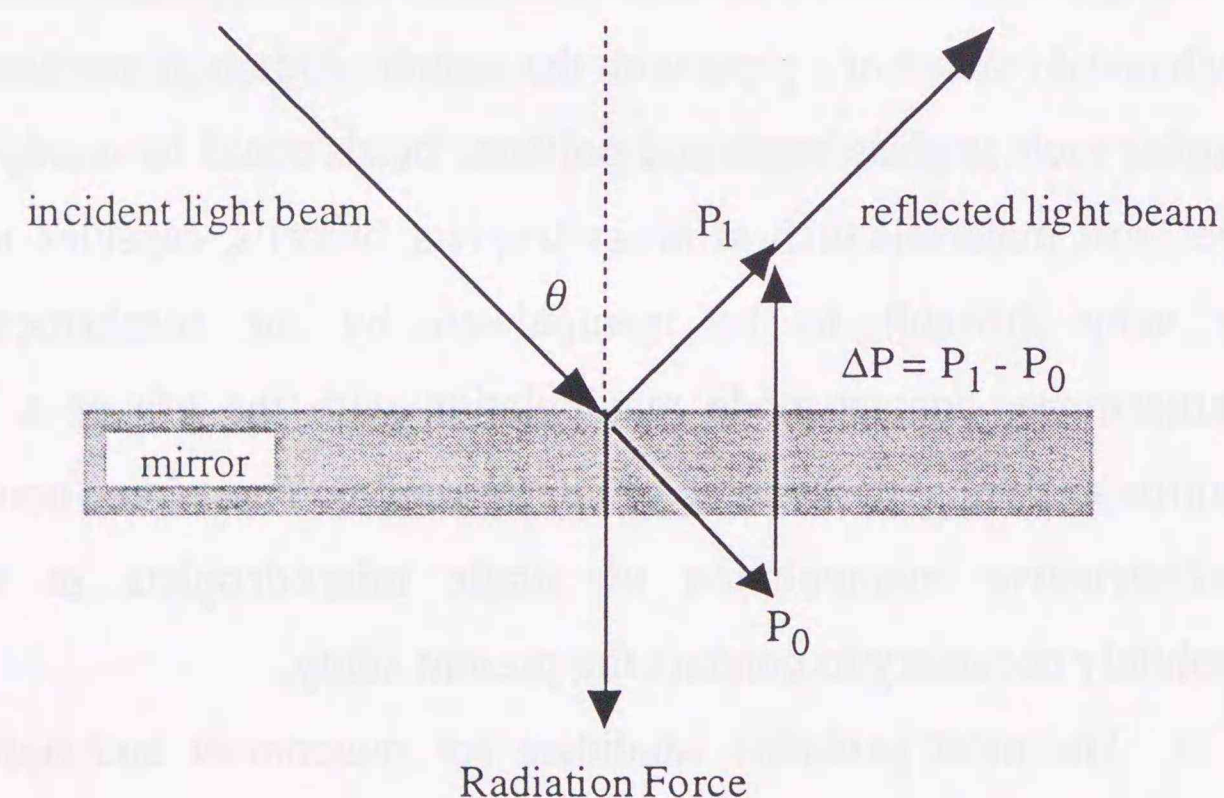


Figure 2-1. Generation of radiation force.

When a light beam is irradiated to a mirror at an incidence angle of θ , the beam is reflected to the direction opposite to the incident beam with the same angle. Upon light reflection, light momentum (P_0) changes to P_1 . The change in light momentum, $\Delta P = P_1 - P_0$, should be conserved, so that the same amount of ΔP is exerted to the mirror with a direction opposite to that of ΔP (*i.e.*, $-\Delta P$). The force exerted to the mirror is called the radiation force or radiation pressure (F) and is expressed by,

$$F = 2P \cos \theta / c$$

where P and c are laser power and the light velocity, respectively. For example, F is calculated to be 7×10^{-9} N when a light beam with power of 1 W is irradiated to a mirror perpendicularly ($\theta = 0$). Although the radiation force is very weak to "move" the mirror, the force is sufficiently enough for manipulation of a microparticle.

Let's assume that a dielectric microparticle is irradiated by a focused laser beam as illustrated schematically in Figure 2-2. When the size of a microparticle is larger than the wavelength of the incident laser beam, light scattering by the particle is explained in terms of "Mie scattering".

Refraction of a light ray, *a*, by a spherical particle leads to a light momentum change, $\Delta P = P_1 - P_0$, as in the case of the explanation for light reflection in Figure 2-1, where P_0 and P_1 are light momentum before and after refraction, respectively. The amount of ΔP should be thus exerted on the particle with a direction opposite to that of ΔP (*i.e.*, $-\Delta P$) owing to conservation law. The same is true for a light ray, *b*, except for the direction of $-\Delta P$. The sum of $-\Delta P$ generated at each point of the particle irradiated by the laser beam is the radiation force (F) exerted on the particle. When the refractive index of a particle (n_1) is larger than that of the

surrounding medium ($n_2 < n_1$), the force is directed to the focal point of the laser beam.

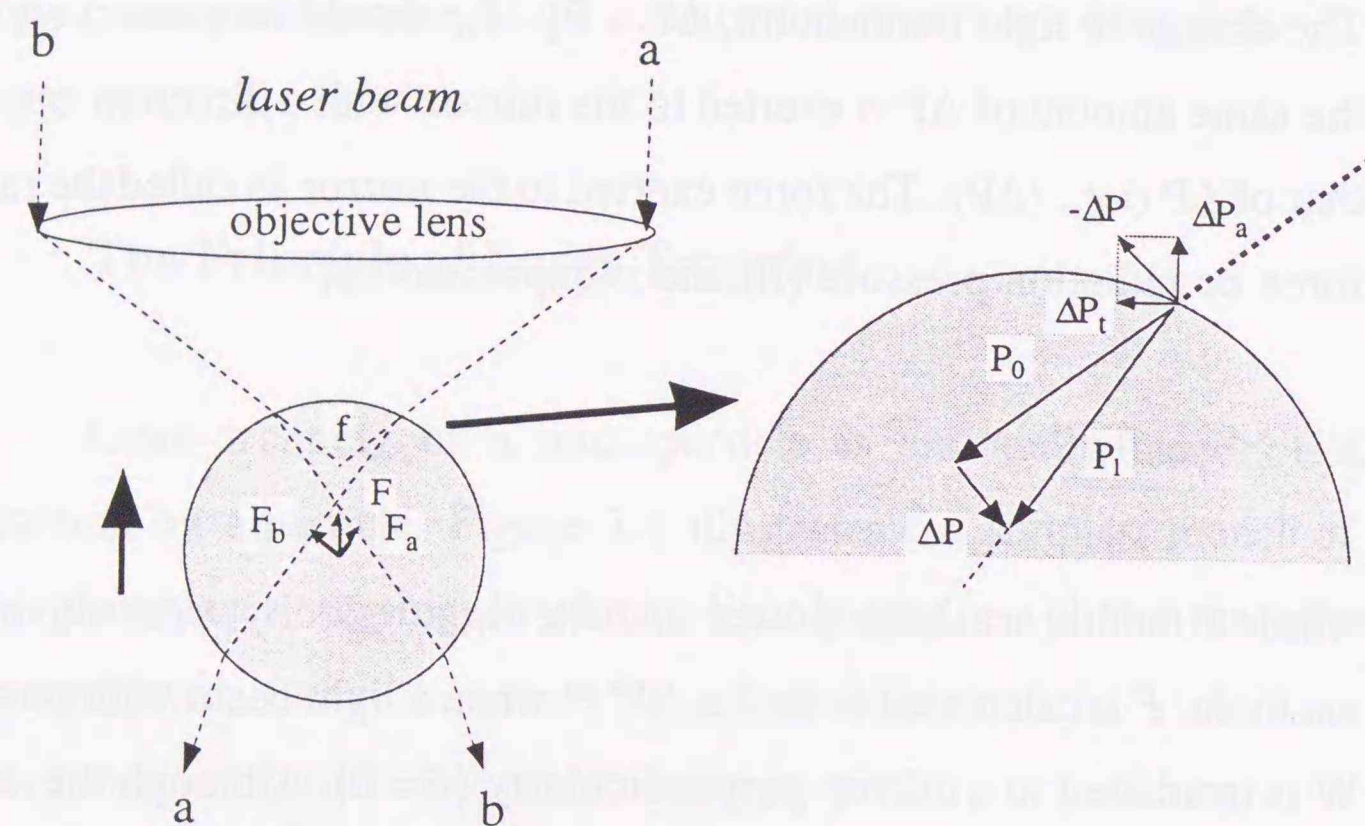


Figure 2-2. Principle of laser trapping of a spherical microparticle.

It is noteworthy that $-\Delta P$ possesses both axial (ΔP_a) and transaxial (ΔP_t) components, and F directs to the high-intensity region of the laser beam depending on the contributions of ΔP_a and ΔP_t to $-\Delta P$. When the particle is irradiated by a laser beam with a large cone angle as shown in Figure 2-2, the contribution of ΔP_a to $-\Delta P$ and, therefore, to F becomes dominant compared to that of ΔP_t , so that the particle is lifted-up along the laser beam axis (Z axis) and manipulated along the Z axis. Contrarily, if the particle is irradiated with a small cone angle through an objective lens, the

contribution of ΔP_t to $-\Delta P$ becomes more important as compared with that of ΔP_a . In such a case, the particle is trapped in the X Y plane depicted by the focal point of the laser beam. Under ordinary conditions at room temperature, the radiation force is strong enough to suppress Brownian motion of a microparticle in solution. When the laser beam focus is scanned in space, the microparticle follows the laser beam. Thus, noncontact and nondestructive manipulation of single microparticles is realized by laser trapping. Actually, three dimensional laser manipulation of various individual microparticles ($n_1 > n_2$) such as polymer beads, oil droplets, glass beads, capsules, biocells, and so forth has been reported^{5-25,27)}.

2.2 Laser Trapping, Spectroscopic, and Electrochemical Measurements of Single Microparticles in Solution.

The laser trapping technique is certainly potential enough to suppress the Brownian motion and manipulate single microparticles in solution. A combination of the method with analytical techniques engages single microparticle measurements. A laser trapping - spectroscopy - electrochemistry system, capable of simultaneous manipulation and spectroscopic / electrochemical analysis of single microdroplets in solution, has been thus constructed. A block diagram of the system used in this study is illustrated in Figure 2-3.

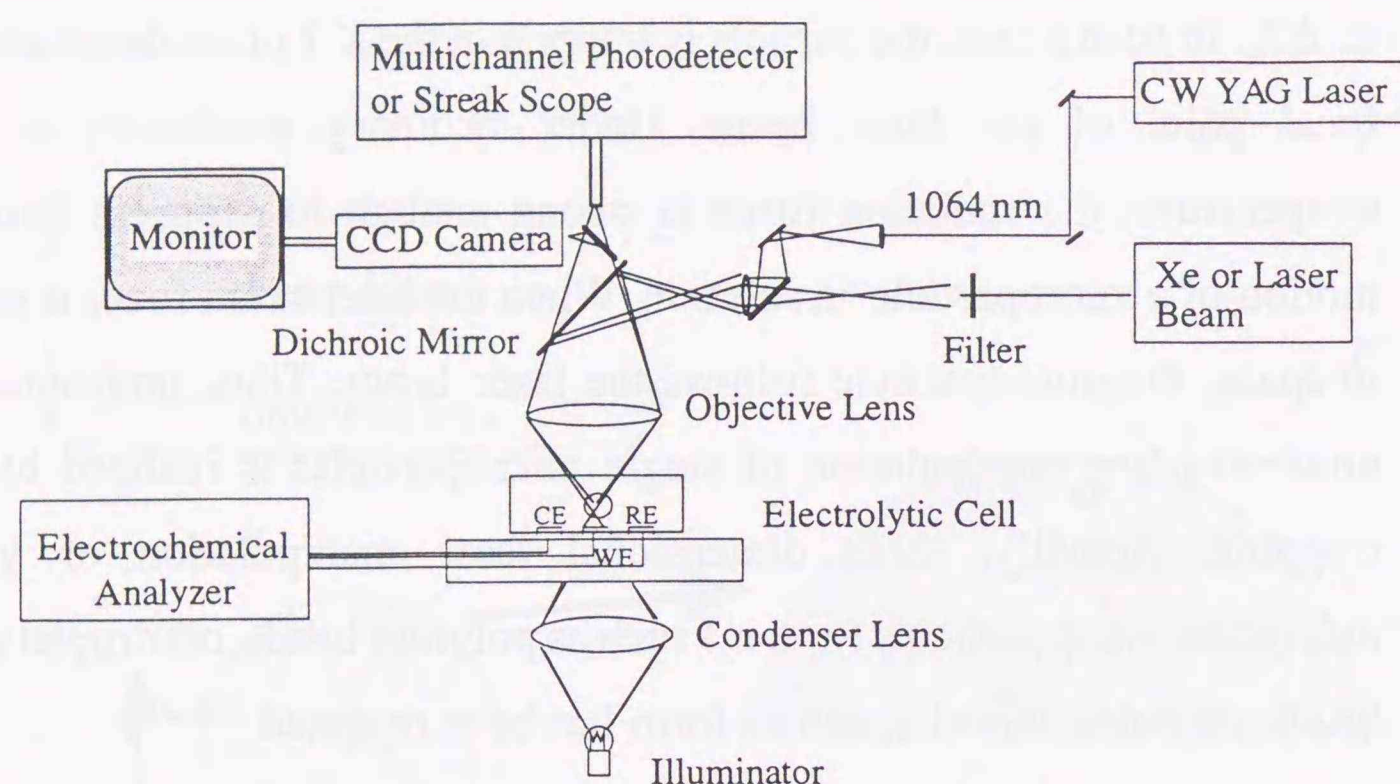


Figure 2-3. A block diagram of a Laser Trapping - Spectroscopy - Electrochemistry system.

In the actual experiments, following apparatus were used:

- Continuous wave Nd^{3+} : YAG laser (SL902T, Spectron Laser Systems)
- Xe lamp (C4264, Hamamatsu Photonics Co.)
- Optical microscope (Optiphot II, Nikon Co.)
- Multichannel photodetector (PMA-10, Hamamatsu Photonics Co., ICCD-576E/G, Princeton Instruments Inc., or Instaspec V, Oriel Co.)
- Polychromator (Multispec 257, Oriel Co.)
- Objective lens (x 40 or x 100, numerical aperture = 1.30, Nikon Co.)
- Electrochemical analyzer (BAS100B / W, Bioanalytical Systems Inc.)
- CCD camera (CCD-IRIS, Sony Co.)
- Video (SLV-F11, Sony Co.)

Monitor (M5, Sanyo Electric Co., Ltd.)

ND filter (25 %, 50 %, or 70 %, Toshiba Co.)

Filter (U340 or U360, Hoya Co., Ltd.)

Filter (UV-D33S, Toshiba Co.)

Filter (GG420, Hoya Co., Ltd.)

Bandpass filter (400FS10-25 AM-22609, Andover Co.)

For laser trapping of a microdroplet, absorption of an incident light beam should be avoided since trapping is based on light refraction by a particle as described above. Also, a light beam must be focused to its wavelength size. In the experiments, therefore, a 1064 nm laser beam from a continuous wave Nd^{3+} : YAG laser (~500 mW) was used as a trapping light source. The laser beam was introduced to an optical microscope, reflected by a dichroic mirror, and then focused onto a single microdroplet through an objective lens (x 100, NA = 1.30 or x 40, NA = 1.30). In order to trap single particles, the laser beam was focused to a ~1 μm spot size with the beam being passed through the objective lens as wide as the numerical aperture. Appropriate optics outside the microscope was used to fulfill such conditions.

All the sample materials used in this study are transparent at 1064 nm except for H_2O , so that heat generation of the sample solution by laser irradiation is neglected. H_2O absorbs a 1064 nm light beam through the overtone band of the O-H stretching mode. In practice, it has been reported that temperature increases ca. 4 $^{\circ}\text{C}$ when a focused 1064 nm laser beam with 1.0 W is irradiated to water (volume = 1.0 μm^3)²⁶. In the present experiments, laser power is ~500 mW and the laser beam is not focused to a water phase. Therefore, temperature elevation of the sample due to

absorption of the incident light beam by water is concluded to be very low, and does not affect single microdroplet measurements.

For single microdroplet measurements, monitoring both trapping behavior and the size of a droplet to be studied are very important. Thus, trapping behavior was monitored by a CCD camera attached to the microscope and, the images were recorded on a video if necessary.

For fluorescence measurements, a Xe light beam, passed through an appropriate glass filter(s) to select an excitation wavelength, was led to the microscope coaxially with the 1064 nm beam and irradiated to a laser-trapped droplet (spot size $\sim 10 \mu\text{m}$). Fluorescence from the droplet was collected by the same objective lens and analyzed by a polychromator - multichannel photodetector set through an optical fiber. To improve the instrumental sensitivity, a cut-off filter for excitation light was set to the microscope before leading the fluorescence to the detector.

Picosecond fluorescence spectroscopy was also done by using a picosecond laser light source (N_2 -laser pumped dye laser, 10 Hz, ~ 500 ps, styrene 420, 420 nm, Laser Photonics) and a streak scope (C4334, Hamamatsu Photonics Co.).

Besides fluorescence spectroscopy of a laser-trapped microdroplet in water, the system enables one to conduct absorption spectroscopy, though this analytical mode has not been used in the present study. Briefly, a Xe light beam, the same with that used for fluorescence spectroscopy, is employed as a monitoring beam and the beam (beam size $\sim 1.0 \mu\text{m}$) is irradiated to the center of a laser-trapped droplet. The light intensity passed through the droplet is reflected by a half mirror set under the microscope stage and led to the polychromator-multichannel photodetector set through an optical fiber. Absorption spectroscopy of single microdroplets or microparticles (polymer beads, microcapsules and so forth) as small as the

diameter of $8 \mu\text{m}$ has been made possible with the detection limit of 0.05 in absorbance unit. The other details have been reported elsewhere¹⁸⁾.

Electrochemical measurements of single microdroplets were performed by setting a home-made electrochemical cell on the stage of the microscope. The electrode potential and/or current were controlled and monitored by an electrochemical analyzer. In the present experiments, single microdroplets were laser trapped in the electrolytic cell and the droplet was positioned above a working electrode to induce interfacial electron transfer between a solute in the droplet and an oxidant in the surrounding water phase. Using the laser trapping method, a single droplet can be contacted on or positioned in the vicinity of a microelectrode. Thus, various electrochemical measurements on single microdroplets can be done on the basis of the present experimental setup^{13-16,25)}.

2.3 Experimental Check of the Performance of the Laser Trapping - Spectroscopy - Electrochemistry System.

Laser trapping - spectroscopy - electrochemistry experiments on single microdroplets in solution have been never explored except for the works reported from our research group, so that experimental checks of the system performance are essential to discuss the experimental observations described in the following chapters. In this section, therefore, the performance of the system is briefly described.

Laser Trapping.

On the basis of the experimental setup in Figure 2-3, various microparticles have been shown to be manipulated. Typical examples confirmed experimentally in this research group are as follows:

- tri-n-butylphosphate droplet ($n_1 = 1.42$) in water ($n_2 = 1.33$) : this work
- nitrobenzene droplet ($n_1 = 1.55$) in water: ^{13,14,25)}
- *o*-dibutylphthalate droplet ($n_1 = 1.49$) in water: ^{15,16)}
- polymer beads ($n_1 = \sim 1.6$) in water: ¹⁷⁻¹⁹⁾
- microcapsule (n_1 (toluene) = 1.49) in water: ^{20,21)}
- vesicle in water: ²²⁾
- biocell in water: ²⁴⁾

Besides these, laser trapping of glass beads, semiconductor particles, silica gels and so forth has been reported by Masuhara *et al.* ²⁷⁾. The minimum size of a particle to be manipulated is around 0.3 μm , which is determined simply by the resolution limit of an optical microscope. Particles larger than 40 μm (diameter) do not show vigorous Brownian motion, so that laser trapping is not necessary for single particle measurements. However, as described later, laser trapping is preferable for reproducible and reliable spectroscopic measurements even for non-Brownian particles.

Laser Trapping - Spectroscopy.

Figure 2-4 shows fluorescence spectra of perylene (Pe, 1.0×10^{-6} M) in tri-n-butylphosphate (TBP) determined by the system shown in Figure 2-3 (a; using a transparent thin-layer cell with the optical path length of $\sim 100 \mu\text{m}$) and by a conventional spectrofluorometer (b; S-4500, Hitachi Ltd., using a quartz cuvette with the optical path length of 10 mm). The absorbance of each sample solution was adjusted below 0.05 at the excitation wavelength (400 $\sim$ 420 nm).

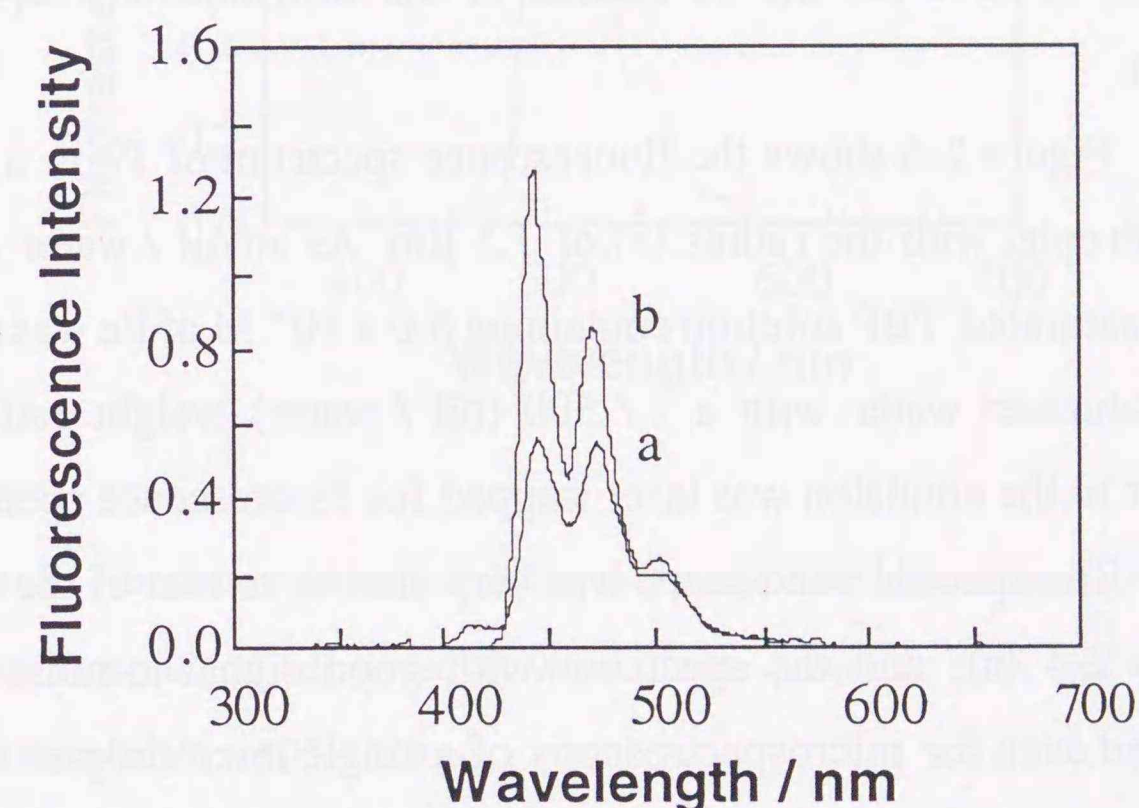


Figure 2-4. Fluorescence spectra of Pe in TBP. a) recorded by the system in Figure 2-3 with a thin-layer cell (optical path length = $\sim 100 \mu\text{m}$, excitation wavelength = 400 $\sim$ 420 nm). b) recorded by a spectrofluorometer with a quartz cuvette (optical path length = 10 mm, excitation wavelength = 400 nm).

Both spectra exhibited peaking wavelengths at around 440 and 470 nm with a shoulder around 500 nm. Although the peaking wavelengths agree very well with each other, the ratio of the fluorescence band intensity, I_{440} / I_{470} , is much smaller for the spectrum (a) compared with that determined by a spectrofluorometer (b). This is because transmittance of the microscope optics, including the objective, decreases with shifting to the shorter wavelength, in particular at $\lambda < 450$ nm. At the present stage, this inner filter effect on the fluorescence spectrum has not been corrected, since a correction is not necessarily for the present purpose of the study. However, the correction coefficient at each wavelength can be easily obtained by comparing the fluorescence intensities of the two spectra, and this can be used for the correction of the instrumental response of the system.

Figure 2-5 shows the fluorescence spectrum of Pe in a single TBP microdroplet with the radius (r) of 1.5 μm . As an oil / water emulsion, a water-saturated TBP solution containing 5.0×10^{-4} M of Pe was dispersed in TBP-saturated water with a 1 / 500 (oil / water) weight ratio. A single droplet in the emulsion was laser trapped for fluorescence spectroscopy.

The spectral band shape was very similar to that of the spectrum in Figure 2-4 (a), and the spectrum with good signal-to-noise ratios was obtained even for microspectroscopy of a single microdroplet with $r = 1.5$ μm . However, the fluorescence spectrum of Pe is somewhat distorted at $\lambda < 450$ nm. This is explained by concentration quenching of the Pe fluorescence, since the concentration of Pe is very high (5.0×10^{-4} M). Under optimized conditions, a reliable and reproducible fluorescence spectrum can be obtained for a droplet as small as $r = 1.0$ μm . Besides the spectrum measurements, fluorescence decays of Pe in the absence and presence of ferrocene (FeCp-H) as a quencher in single TBP droplets ($r =$

8.0 μm) dispersed in water can be also measured, as a typical example is shown in Figure 2-6. In both cases, the fluorescence exhibited a single exponential decay, which demonstrated that time-resolved fluorescence spectroscopy could be done even for single microdroplets.

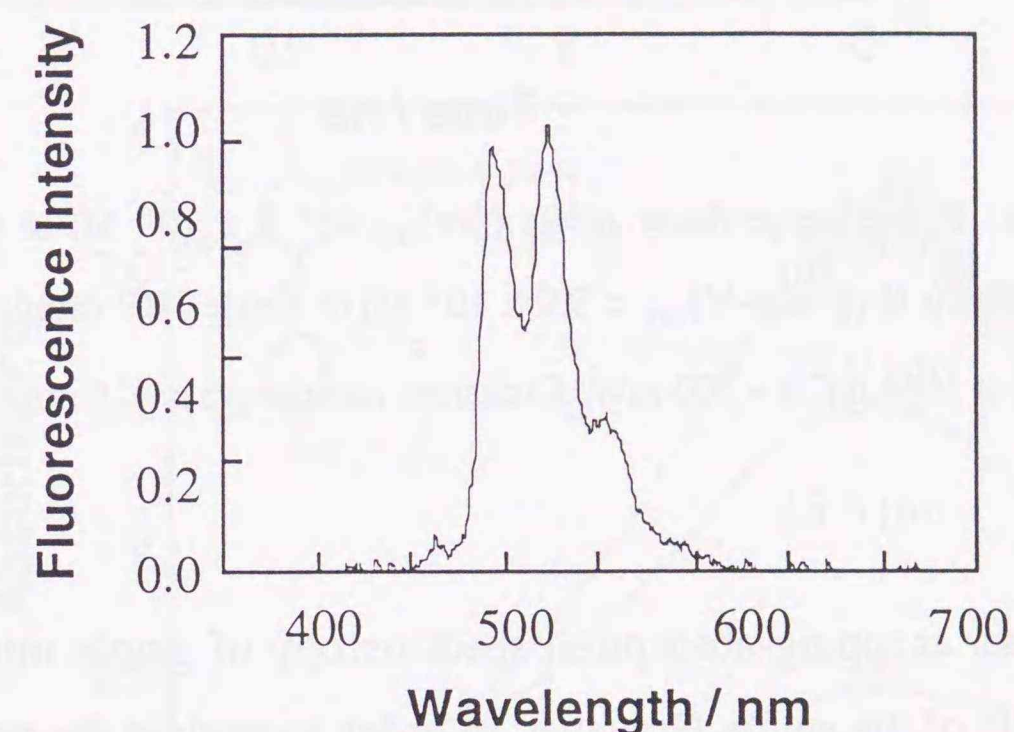


Figure 2-5. Fluorescence spectrum of Pe in a single TBP microdroplet ($r = 1.5$ μm , $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4}$ M) dispersed in water. Laser power at 1064 nm = 500 mW. Excitation wavelength = 400 ~ 420 nm.

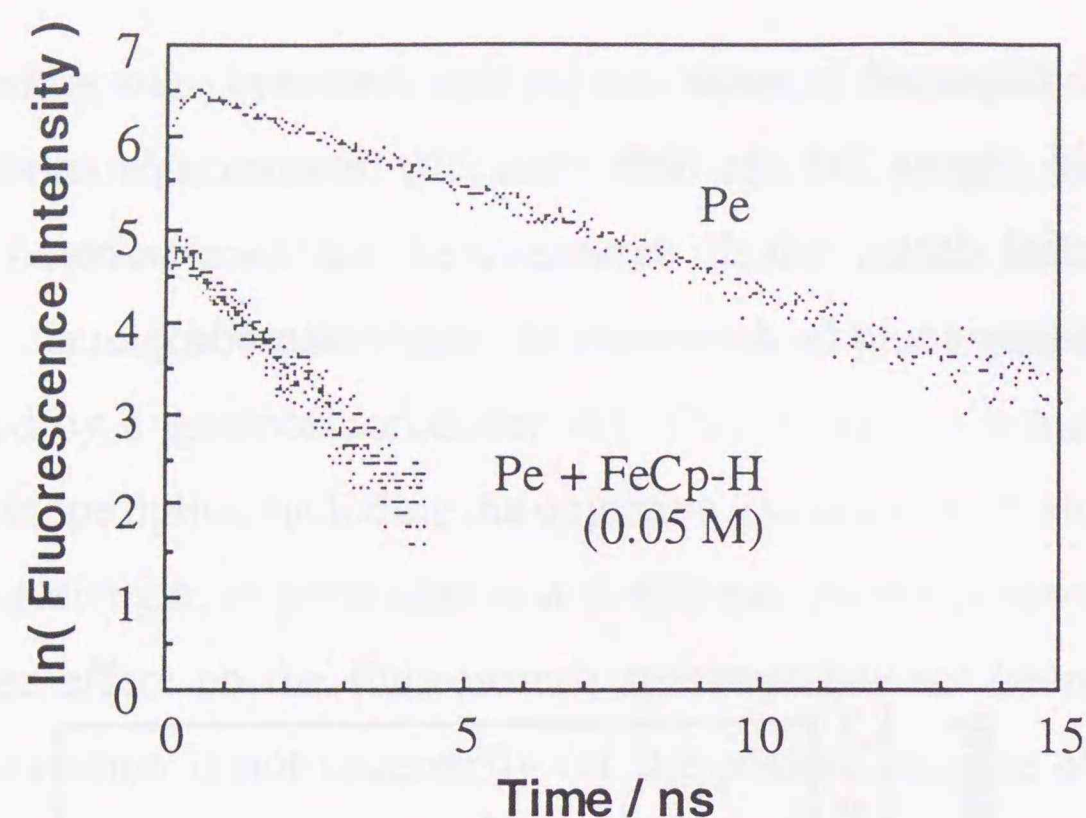


Figure 2-6. Fluorescence decay of Pe ($[Pe]_{TBP} = 5.0 \times 10^{-4}$ M) in the absence and presence of FeCp-H ($[FeCp-H]_{TBP} = 5.0 \times 10^{-2}$ M) in single TBP droplets ($r = 8.0$ μm). Laser power at 1064 nm is ~ 500 mW. Excitation wavelength = 416 nm.

Laser trapping-absorption spectroscopy of single microdroplets is not the issue of the study. However, in order to explain the performance of the experimental setup, some results on absorption spectroscopy on microdroplets reported from this laboratory are described briefly.

Figure 2-7 shows absorption spectra of a cyan dye (C-Dye) in single *o*-dibutyl phthalate (DBP) droplets in water. The spectral band shape agrees very well with that in a dilute C-Dye / DBP solution (5.0×10^{-5} M). The lowest detection limit of absorbance (A) was 0.05, and the linear response of absorbance was obtained upto $A \sim 1.5$. This has been confirmed by a droplet radius dependence of A of C-Dye (670 nm). As shown in Figure 2-8, the absorbance of C-Dye was proportional linearly to r as predicted from the Lambert-Beer's law, with the optical path length being corresponded to $2r$. In the experiments, the probe beam was introduced coaxially with the

trapping laser beam, so that the probe beam was always irradiated to the center of a laser-trapped droplet. Thus, laser trapping is the indispensable basis for absorption microspectroscopy of single microdroplets in solution. A reliable and reproducible absorption spectrum can be obtained for the droplets with $r > 4.0$ μm under the present experimental setup.

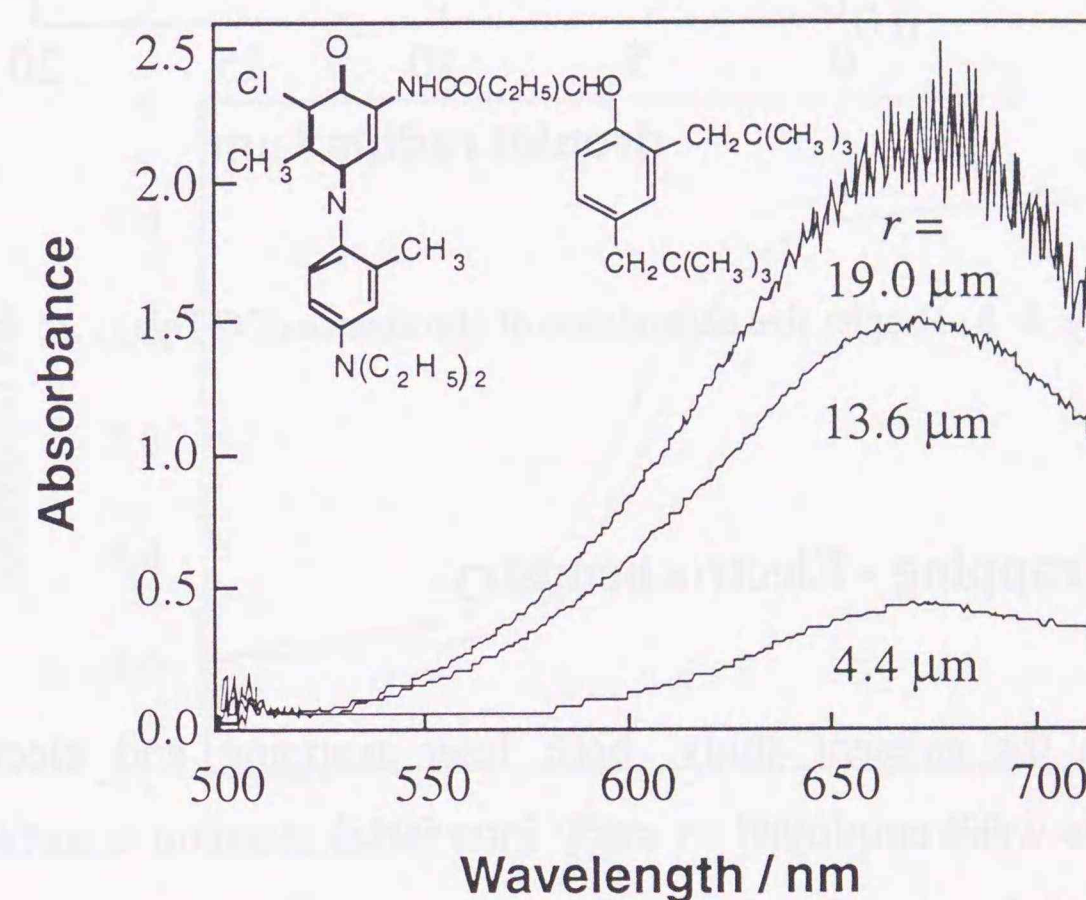


Figure 2-7. Absorption spectra of C-Dye (1.85×10^{-2} M) in single DBP microdroplets ($r = 4.4, 13.6,$ and 19.0 μm) dispersed in water. Laser power at 1064 nm is ~ 500 mW.

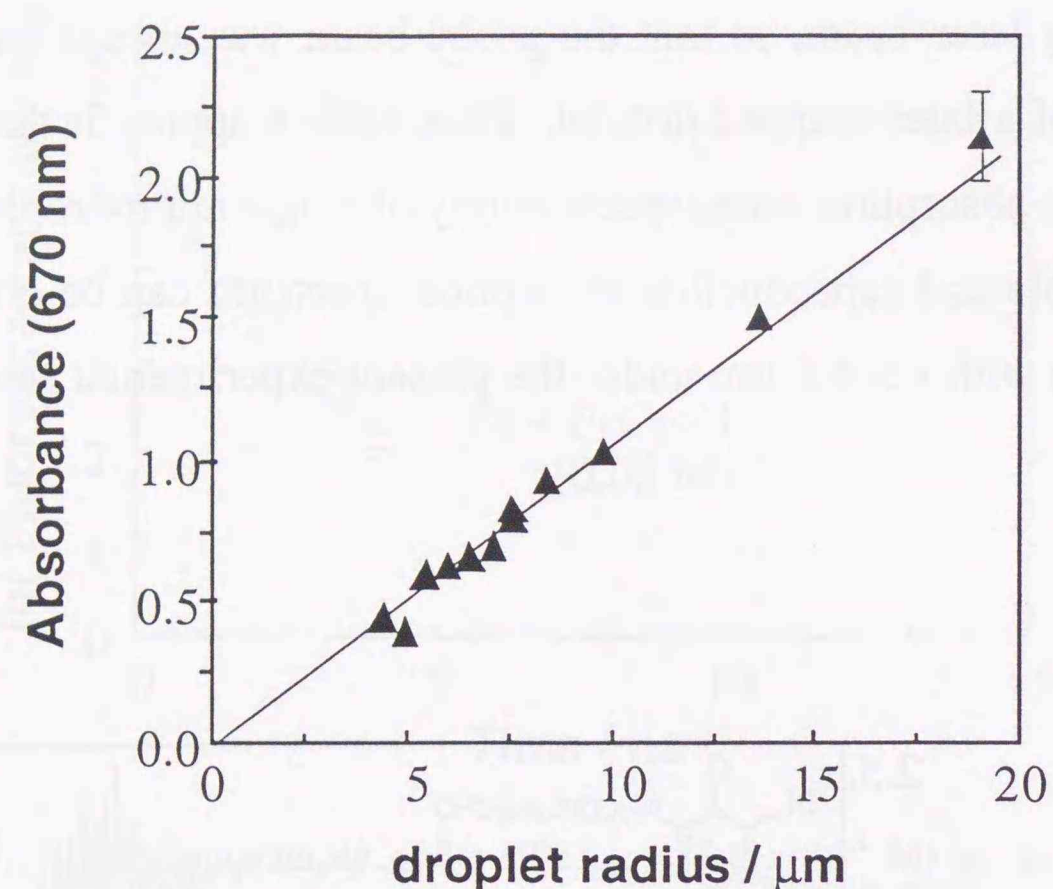


Figure 2-8. Droplet size dependence of absorbance of C-Dye (1.85×10^{-2} M).

Laser Trapping - Electrochemistry.

In the present study, both laser trapping and electrochemical techniques were employed to study interfacial electron transfer processes across a single microdroplet / water interface. Unique performance of the laser trapping - electrochemical technique using a microelectrode are overviewed.

Figure 2-9 shows a cyclic voltammogram (CV) of hexacyanoferrate (III) (Fe(III)) in water observed at a gold microelectrode ($8.6 \mu\text{m}$ wide x $59.4 \mu\text{m}$ long x $0.2 \mu\text{m}$ thick). A cathodic current at around ~ 200 mV corresponds to reduction of Fe(III) to Fe(II). At a micrometer-sized electrode, mass transfer of a solute to the electrode surface proceeds very efficiently owing to hemispherical diffusion of the solute. This is proved by

a characteristic sigmoidal current-potential curve in the CV, which is different from a peak current observed at a mm-sized electrode (linear diffusion). Using microelectrodes, new and novel electrochemical measurements can be performed in micrometer dimension as their examples are described later. Under the present experimental conditions, the detection limit of the electrochemical response was ~ 10 pA.

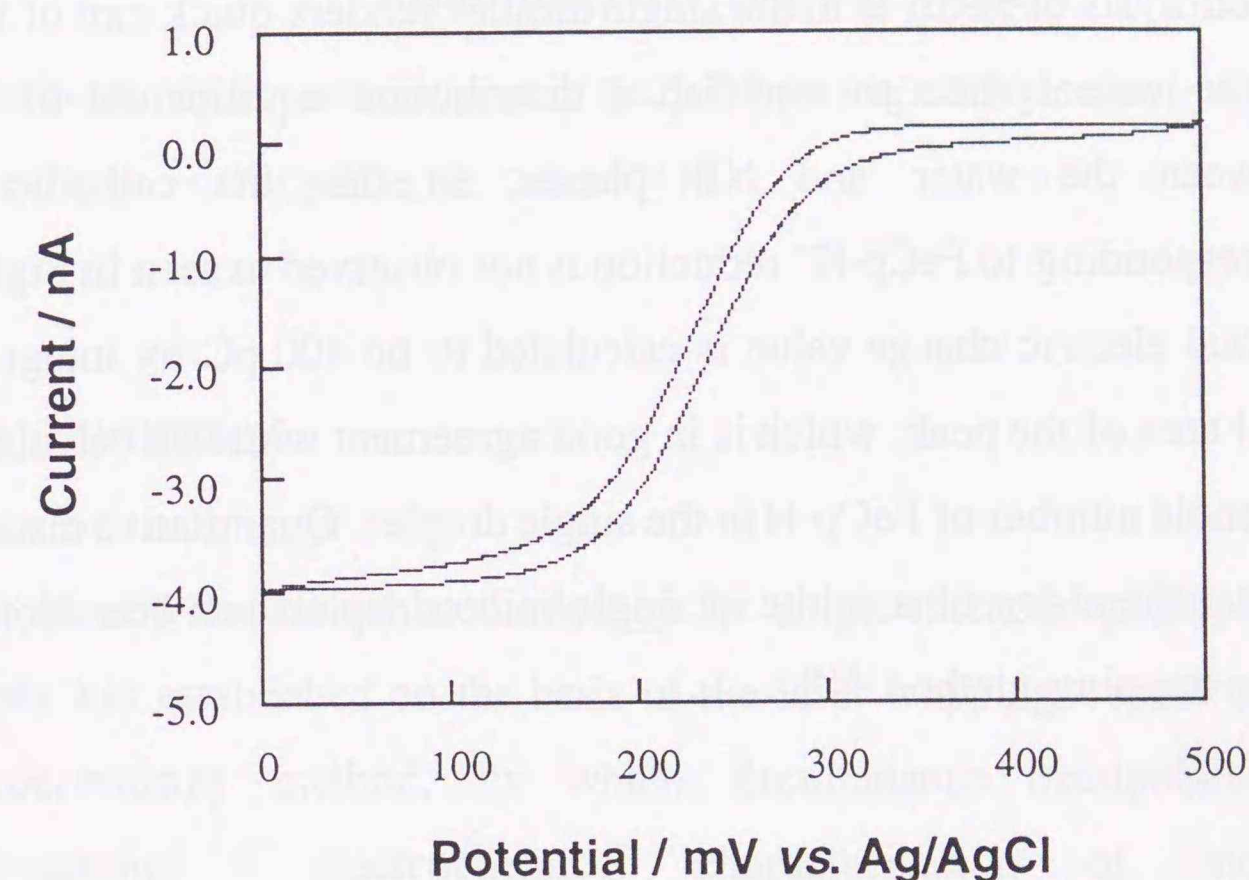


Figure 2-9. Cyclic voltammogram (potential sweep rate of 10 mV/s) of hexacyanoferrate(III) (1.0×10^{-3} M) in an aqueous MgSO_4 (0.1 M) solution observed at a gold microelectrode.

A combination of the microelectrochemical technique with laser trapping of a single droplet is very fruitful. A typical example is as follows. A single nitrobenzene (NB) droplet containing FeCp-H is contacted with a microelectrode by laser trapping in an aqueous solution and, FeCp-H in the droplet is oxidized at an appropriate potential. Figure 2-10 shows a CV of FeCp-H in a single droplet ($r = 4.0 \mu\text{m}$). The peak current around a potential of $\sim 400 \text{ mV}$ (vs. Ag/AgCl) corresponds to oxidation of FeCp-H to a ferrocenium cation (FeCp-H^+) in the droplet. FeCp-H in the droplet is oxidized completely to FeCp-H^+ within $\sim 1 \text{ s}$ at the forward potential sweep. Electrolysis of FeCp-H in the single droplet renders quick exit of the cation to the water phase to establish a distribution equilibrium of FeCp-H^+ between the water and NB phases, so that the cathodic current corresponding to FeCp-H^+ reduction is not observed as seen in Figure 2-10. A total electric charge value is calculated to be 400 pC by integrating the total area of the peak, which is in good agreement with that calculated from the mole number of FeCp-H in the single droplet. Quantitative discussion on electrochemistry of a solute in single microdroplets can be done by the laser trapping method^{13,14}.

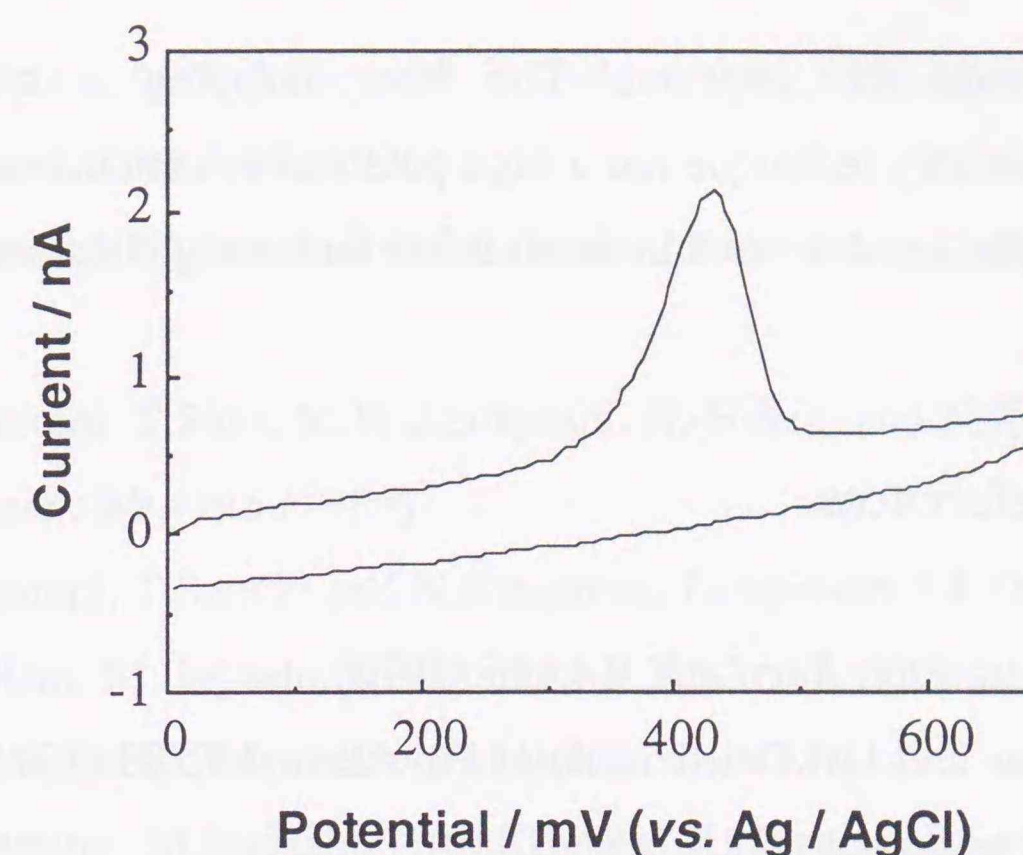


Figure 2-10. Cyclic voltammogram of FeCp-H in a single NB droplet ($r = 4.0 \mu\text{m}$) dispersed in water. FeCp-H in NB: $2.0 \times 10^{-2} \text{ M}$.

2.4 Summary.

A new and novel methodology for single microdroplet (particles) analysis was established on the basis of the laser trapping - spectroscopy - electrochemistry method, by which simultaneous manipulation and spectroscopic / electrochemical characterization of individual microdroplets in solution were made possible. Besides manipulation of a particle, laser trapping is absolutely necessary to conduct accurate and reproducible spectroscopic / electrochemical measurements. So far, chemistry in emulsion systems has been studied by droplet-unresolved methods owing to a lack of a manipulation method of a single droplet and, the results obtained by these studies are regarded as an ensemble average of those for various droplets with different sizes and properties. Clearly, for elucidation of the chemistry in emulsion systems, single droplet

measurements are required. The laser trapping - spectroscopy - electrochemistry technique has a high potential to conduct such studies, as the examples are described in detail in the following chapters.

2.5 References.

- 1) A.Ashkin, *Phys.Rev.Lett.*, **24**,156 (1970).
- 2) A.Ashkin and J.M.Dziedzic, *Appl.Phys.Lett.*, **19**,283 (1971).
- 3) A.Ashkin, *Science*, **210**,1081 (1980).
- 4) A.Ashkin, J.M.Dziedzic, J.E.Bjorkholm and S.Chu, *Opt.Lett.*, **11**,288 (1986).
- 5) H.Misawa, M.Koshioka, K.Sasaki, N.Kitamura and H.Masuhara, *Chem.Lett.*, 469 (1991).
- 6) H.Misawa, N.Kitamura and H.Masuhara, *J.Am.Chem.Soc.*, **113**,7859 (1991).
- 7) M.Koshioka, H.Misawa, K.Sasaki, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **96**,2909 (1992).
- 8) K.Nakatani, H.Misawa, K.Sasaki, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **97**,1701 (1993).
- 9) K.Nakatani, T.Uchida, S.Funakura, A.Sekiguchi, H.Misawa, N.Kitamura and H.Masuhara, *Chem.Lett.*, 717 (1993).
- 10) K.Nakatani, T.Uchida, H.Misawa, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **97**,5197 (1993).
- 11) K.Nakatani, T.Uchida, N.Kitamura and H.Masuhara, *J.Electroanal.Chem.*, **375**,383 (1994).
- 12) K.Nakatani, T.Uchida, H.Misawa, N.Kitamura and H.Masuhara, *J.Electroanal.Chem.*, **367**,109 (1994).
- 13) K.Nakatani, M.Wakabayashi, K.Chikama and N.Kitamura, *J.Phys.Chem.*, **100**,6749 (1996).
- 14) K.Nakatani, M.Sudo and N.Kitamura, *J.Phys.Chem.B*, **102**,2908 (1998).
- 15) K.Nakatani, T.Suto, M.Wakabayashi, H.-B Kim and N.Kitamura, *J.Phys.Chem.*, **99**,4745 (1995).
- 16) K.Nakatani, T.Suzuki and N.Kitamura, *Langmuir*, **14**,2286 (1998).
- 17) H.-B Kim, M.Hayashi, K.Nakatani, N.Kitamura, K.Sasaki, J.Hotta and H.Masuhara, *Anal.Chem.*, **68**,409 (1996).
- 18) N.Kitamura, M.Hayashi, H.-B Kim and K.Nakatani, *Anal.Sci.*, **12**,49 (1996).
- 19) H.-B Kim, S.Habuchi, M.Hayashi and N.Kitamura, *Anal.Chem.*, **70**,105 (1998).
- 20) H.-B Kim, S.Yoshida, A.Miura and N.Kitamura, *Chem.Lett.*, 923 (1996).
- 21) H.-B Kim, S.Yoshida and N.Kitamura, *Anal.Chem.*, **70**,51 (1998).
- 22) N.Kitamura, N.Sekiguchi and H.-B Kim, *J.Am.Chem.Soc.*, **120**,1942 (1998).
- 23) H.Yao, Y.Inoue, H.Ikeda, K.Nakatani, H.-B.Kim and N.Kitamura, *J.Phys.Chem.*, **100**,1494 (1996).
- 24) H.-B Kim, O.Kogi and N.Kitamura, unpublished results.
- 25) K.Nakatani, N.Terui, K.Hasebe and N.Kitamura, *Chem.Lett.*, 457 (1996).
- 26) M.Ishikawa, H.Misawa, N.Kitamura, R.Fujisawa and H.Masuhara, *Bull.Chem.Soc.Jpn.*, **69**,59 (1996).
- 27) H.Masuhara, F.C.De Schryver, N.Kitamura and N.Tamai, *Microchemistry - Spectroscopy and Chemistry in Small Domain*, North-Holland, Amsterdam (1994).

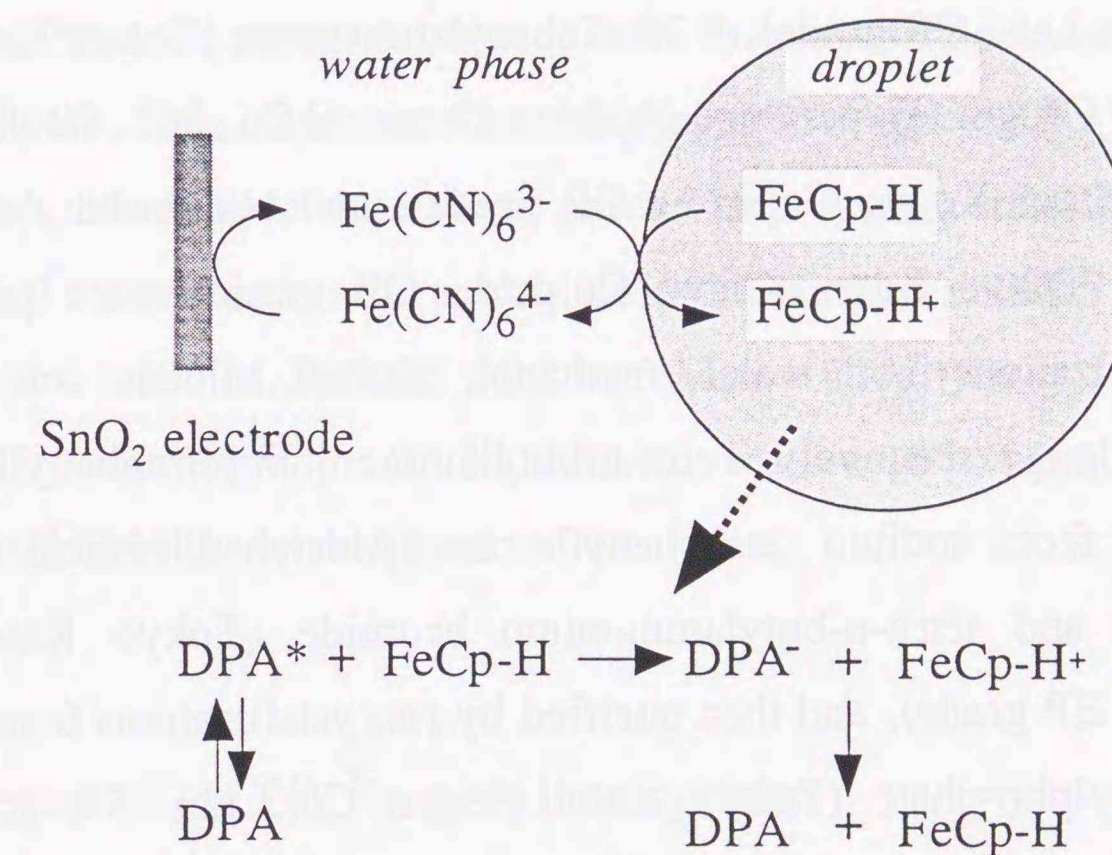
Determination of Electron Transfer Rate across Microdroplet / Water Interface

3.1 Introduction.

Electron transfer (ET) reactions at liquid / liquid interfaces have been studied by electrochemical (*i.e.*, cyclic voltammometry or scanning electrochemical microscopy) and spectroscopic methods¹⁻¹¹). These studies revealed factors governing the interfacial ET rate, including the relevant free energy change and liquid-junction potential (Galvani potential) dependencies. It is noteworthy, however, that these studies have been conducted for flat macroscopic liquid / liquid interfaces. In contrast to such flat interfaces, a spherical microscopic liquid (*i.e.*, droplet) / liquid interface is very unique and interfacial ET reactions are expected to be dependent strongly on the droplet size. However, the work along the line has not been reported until now. On the basis of the potential application of the laser trapping - spectroscopy - electrochemistry method, the ET reaction across a droplet / solution interfaces was discussed as a function of the droplet size.

In this chapter, the interfacial ET reaction between ferrocene in single oil droplets and $\text{Fe}(\text{CN})_6^{3-}$ in the surrounding water phase is described. The experimental approach to study the interfacial ET process is as follows (Scheme 3-1). A single oil droplet containing ferrocene (FeCp-H) and 9,10-diphenylanthracene (DPA) is trapped by 1064 nm laser beam above a working electrode without direct contact. Then, the interfacial ET reaction

between FeCp-H and $\text{Fe}(\text{CN})_6^{3-}$ is induced by bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in the water phase in a transparent thin-layer electrode cell. For determination of the interfacial ET rate, a time course of the FeCp-H concentration in the droplet during the electrolysis must be known. For this purpose, fluorescence quenching of DPA by FeCp-H in microdroplets is applied, as discussed later in detail. Since arbitrary-sized, single droplets can be selected and manipulated, the interfacial ET rate can be discussed as a function of the droplet size.



Scheme 3-1. Electron transfer reaction between ferrocene (FeCp-H) in a single microdroplet and $\text{Fe}(\text{CN})_6^{3-}$ in the water phase. 9,10-diphenylanthracene (DPA) is a fluorescence probe.

3.2 Experimental.

3.2.1 Sample Preparation.

ferrocene - $\text{Fe}(\text{CN})_6^{3-}$ - 9,10-diphenylanthracene system:

Water was used after deionization and distillation (GSR-200, Advantec Toyo Co., Ltd.). Potassium hexacyanoferrate (II) and (III) (Wako Pure Chemical Industries Ltd., GR grade), ferrocene (Wako Pure Chemical Industries Ltd., GR grade), 9,10-diphenylanthracene (Tokyo Kasei Kogyo Co., Ltd., GR grade), perylene (Aldrich Chemical Co., Inc., 99+%), MgSO_4 (Tokyo Kasei Kogyo Co., Ltd., GR grade), and tetra-n-butylammonium chloride (Tokyo Kasei Kogyo Co., Ltd., GR grade) were purified by recrystallizations from water, methanol, ethanol, toluene, and acetone / diethyl ether, respectively. Tetra-n-butylammonium tetraphenylborate was prepared from sodium tetraphenylborate (Aldrich Chemical Co., Inc., 99.5 %) and tetra-n-butylammonium bromide (Tokyo Kasei Kogyo Co., Ltd., EP grade), and then purified by recrystallizations from acetone. Tri-n-butylphosphate (Tokyo Kasei Kogyo Co., Ltd., GR grade) was purified by washing with 0.1 M KNO_3 and 0.1 M NaOH three times for each and then distilled under vacuum. Sodium dodecylsulfate (Wako Pure Chemical Industries Ltd., GR grade) and Triton-X100 (Kodak Co., scintillation grade) were used without further purification.

All glass apparatuses used for sample preparations were treated in a cleaning solution (sulfuric acid and potassium permanganate). After this treatment, the glasswares were rinsed in an aqueous 3 % hydrogen peroxide solution, washed with water and then dried at 500 °C in an oven. These treatments were needed to remove impurities and to prepare stable

emulsions.

A sample emulsion was prepared as follows. As an oil phase, ferrocene (FeCp-H ; 0 or 0.10 M), 9,10-diphenylanthracene (DPA; 1.0×10^{-2} M), and tetra-n-butylammonium tetraphenylborate (TBA^+TPB^- ; 1.0×10^{-2} M) were dissolved in water-saturated tri-n-butylphosphate (TBP), while $\text{K}_4\text{Fe}(\text{CN})_6$ (4.0×10^{-4} M), MgSO_4 (0.10 M), tetra-n-butylammonium chloride (TBA^+Cl^- ; 1.0×10^{-2} M) were dissolved in TBP-saturated water as a water phase. Then, the TBP (0.10 g) and aqueous (9.80 g) solutions, prepared separately as mention above, were mixed vigorously together with a TBP-saturated aqueous solution (3 wt%) of sodium dodecylsulfate (SDS as a stabilizer). This emulsion was redispersed in water (10.0 g) as a sample emulsion. These procedures were needed to prepare a stabilized emulsion. The final concentration of each solute in the sample emulsion is as follows: DPA = 1.0×10^{-2} M, FeCp-H = 0.1 or 0 M and TBA^+TPB^- = 1.0×10^{-2} M in the TBP phase, MgSO_4 = 0.1 M, TBA^+Cl^- = 1.0×10^{-2} M and $\text{K}_4\text{Fe}(\text{CN})_6$ = 2.0×10^{-4} M in the water phase.

ferrocene - $\text{Fe}(\text{CN})_6^{3-}$ - perylene system:

Almost the same procedures with those for the preparation of the FeCp-H - $\text{Fe}(\text{CN})_6^{3-}$ - DPA emulsion were employed to prepare this sample emulsion. FeCp-H (5.0×10^{-2} M), perylene (Pe; 5.0×10^{-4} M) and TBA^+TPB^- (1.0×10^{-2} M) were dissolved in water-saturated TBP, while $\text{K}_4\text{Fe}(\text{CN})_6$ (4.0×10^{-4} M), MgSO_4 (0.10 M) and TBA^+Cl^- (1.0×10^{-2} M) were dissolved in TBP-saturated water. As a stabilizing agent, an anionic surfactant of SDS (2 wt%) or nonionic surfactant of Triton-X100 (2 wt%) was dissolved in TBP-saturated water. As an oil / water emulsion, the TBP

(0.05 g) solution was dispersed in the mixture of the aqueous solution (12.350g) and the surfactant solution (0.10 g). This emulsion was redispersed in water (12.5 g) with or without $K_4Fe(CN)_6$. As described later, the use of Pe as a fluorescence probe is more favorable to analyze interfacial ET reaction kinetics.

In these emulsions, the size of a TBP droplet was ranged between 0.1 and 40 μm , and the average droplet diameter was about 4.0 μm as long as the observation was made under an optical microscope. Although the emulsion involves a surfactant as a stabilizer, the droplet size distribution changes with a time and the mixing condition. In the case of ensemble measurements, preparation of the emulsion was performed under the same conditions as long as possible. It is noteworthy that single droplet measurements are free from such problems.

3.2.2 Spectroscopic and Electrochemical Measurements.

Spectroscopic and electrochemical studies on the interfacial ET reaction were conducted on the basis of both droplet-unresolved (ensemble) and droplet-resolved (single droplet) measurements. Experimental conditions of each method are follows.

i) Ensemble Measurements

An electrolytic cell used in this study is shown in Figure 3-1.

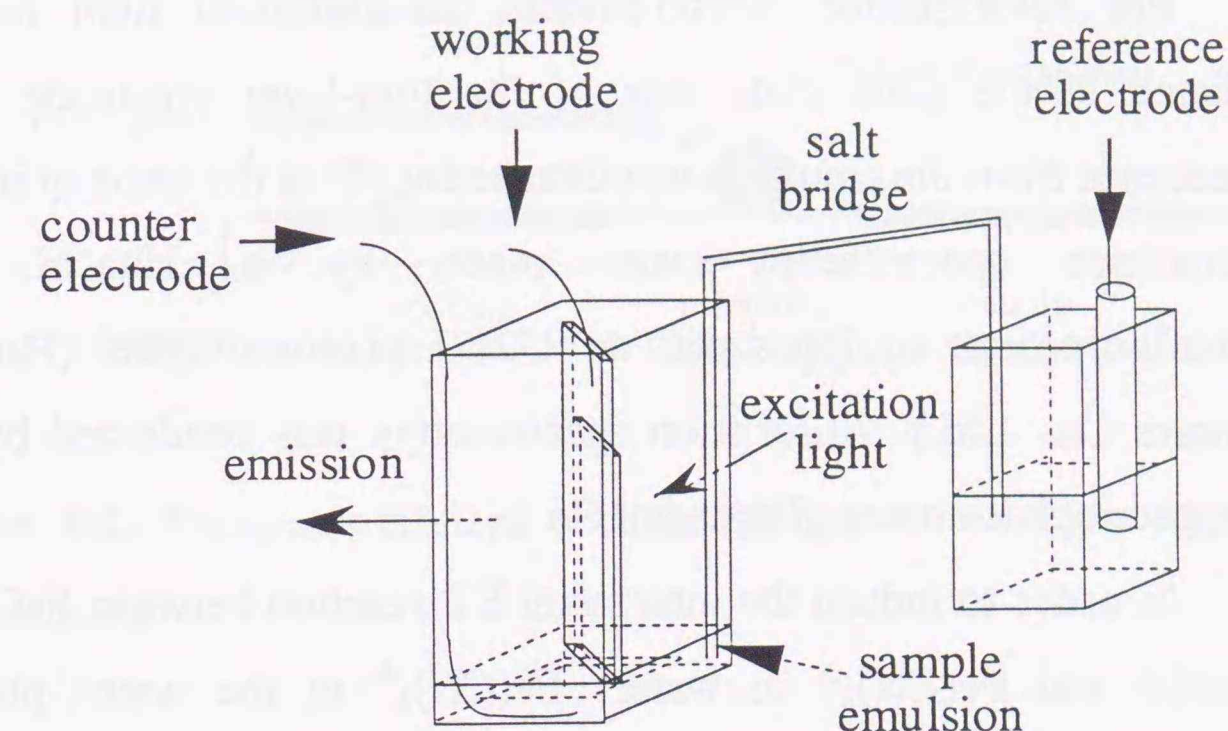


Figure 3-1. Electrolytic cell system.

As an optically transparent thin-layer electrode cell, an SnO_2 electrode (effective electrode area; 8 mm wide x 26 mm long) was covered by a glass plate with a Teflon film (= 50 μm thickness) being placed in between as a spacer. The cell was set in a quartz cuvette (optical path length = 10 mm) as illustrated in Figure 3-1. A sample emulsion ($FeCp-H - Fe(CN)_6^{3-} - DPA$ emulsion) was then filled in the thin-layer electrode by capillarity. A lead wire was attached to the SnO_2 electrode with an indium and/or silver paste as a grew. Pt wire and $Ag/AgCl$ electrodes were used as counter and reference electrodes, respectively. The reference electrode was set in a supporting electrolyte solution and the two solutions were connected by a salt bridge (Teflon tube; diameter = 1 mm) containing an aqueous solution of $MgSO_4$ (0.70 M), gelatin (3.0 wt%), and agar (3.0 wt%). A Teflon sheet was set between the counter and working electrodes to prevent direct contact of the two electrode.

For fluorescence measurements, an excitation light beam was irradiated to the glass plate side of the thin-layer electrode cell and fluorescence from the emulsion was detected at 90° to the angle of incidence. Fluorescence spectroscopy was made by a Hitachi MPF-4 spectrofluorometer equipped with an R928-F photomultiplier (Hamamatsu Photonics Co., Ltd.). Absorption spectroscopy was conducted by a UV-200S spectrophotometer (Shimadzu Co.).

In order to induce the interfacial ET reaction between FeCp-H in a droplet(s) and $\text{Fe}(\text{CN})_6^{3-}$ in water, $\text{Fe}(\text{CN})_6^{4-}$ in the water phase was electrolyzed by a potential step method (800 mV vs. Ag/AgCl)¹²⁾. The time dependencies of the current at the SnO_2 electrode and the fluorescence intensity of DPA in the TBP droplets were measured simultaneously. The fluorescence spectra of DPA in the droplets were also measured before and after bulk electrolysis. Electrochemical measurements were conducted by a potentiostat (HA-301, Hokuto Denko Co.) and a function generator (HB-104, Hokuto Denko Co.) under aerated conditions at room temperature (~297 K).

ii) Single Droplets Measurements.

The electrolytic cell structure used in this study is shown in Figure 3-2.

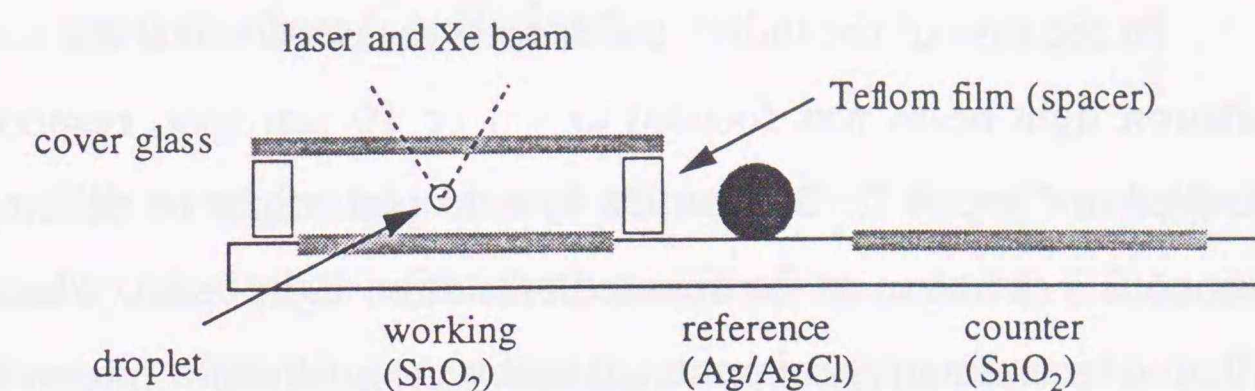


Figure 3-2. Transparent thin-layer electrode cell (gap ~ 70 μm) for single droplets measurements.

An optically transparent SnO_2 electrode connected with a lead wire by an Ag paste was covered by a glass plate with a Teflon film (= 50 μm thickness) being placed in between as a spacer. As a counter electrode, other SnO_2 electrode was used and a reference electrode was an Ag/AgCl wire (diameter = 50 μm). For fabrication of the Ag/AgCl electrode, an Ag wire was oxidized in an aqueous 0.1 M HCl solution for about 30 min by a current step method (current density = $4.0 \times 10^{-4} \text{ Acm}^{-2}$) after washing the wire in an aqueous 3 M HNO_3 solution.

The laser - trapping - microspectroscopy - electrochemistry system described in Chapter 2 (Figure 2-3) was used for the measurements. A sample emulsion ($\text{FeCp-H} - \text{Fe}(\text{CN})_6^{4-} - \text{DPA}$ or $\text{FeCp-H} - \text{Fe}(\text{CN})_6^{4-} - \text{Pe}$ emulsion) was placed in between the thin-layer electrode cell and, then, the cell was set on the stage of the optical microscope. A single droplet was trapped by a 1064 nm laser beam and $\text{Fe}(\text{CN})_6^{4-}$ in the surrounding water phase was oxidized by a potential step method at 800 mV (vs. Ag/AgCl). During the electrolysis, fluorescence spectra of DPA or Pe in the trapped droplet were measured sequentially.

In the case of the individual droplet measurements, the trapping or excitation light beam was focused to ~ 1 or $10\ \mu\text{m}$ spot, respectively, as described in Chapter 2. DPA or Pe in a droplet might be decomposed by continuous irradiation of the focused excitation light beam. Therefore, an excitation beam intensity was attenuated by glass filters to minimize sample decomposition. In the ensemble measurements, the contribution of fluorescence quenching of DPA by dissolved oxygen in the emulsion to the spectrum measurements was small. However, in the individual droplet measurements, the mole number of DPA or Pe in single droplets is very low, so that photodecomposition (*i.e.*, photooxidation) of the compound by O_2 becomes serious and, this influences reproducibility of the experiments. To avoid photodecomposition, therefore, the sample emulsion was deaerated by purging an N_2 gas stream for about 15 min. Under such conditions, decomposition of DPA or Pe could be minimized.

During the experiments, a focused 1064 nm laser beam is irradiated continuously to the sample emulsion and this might lead to generation of heat or convection of the sample solution. In order to minimize such effects, laser power was set 500 mW as described in Chapter 2 and the laser beam was not focused on the SnO_2 electrode. In practice, heat generation was not confirmed under the present experimental conditions.

3.2.3 Optimization of the Experimental Conditions.

In Scheme 3-1, the overall interfacial ET processes are described. In order to determine the interfacial ET rate constant, several experimental conditions should be optimized. Following points are checked to determine actual experimental conditions.

i) Distribution Coefficient.

The concentration of each solute in the TBP or water phase is not necessarily the same with that described in section 3.2.1, owing to distribution of the solute between the two phases in the emulsion. Thus, the concentrations of FeCp-H in the TBP ($[\text{FeCp-H}]_{\text{TBP}}$) and water phases ($[\text{FeCp-H}]_{\text{w}}$) were measured, and the distribution coefficient of FeCp-H between TBP and water was determined.

The sample emulsion described in section 3.2.1 was left standing until a phase separation took place completely and, the water phase was separated. $[\text{FeCp-H}]_{\text{w}}$ was then determined by atomic absorption spectroscopy (170-5, Hitachi Ltd.). $[\text{FeCp-H}]_{\text{TBP}} = 6.8 \times 10^{-2}\ \text{M}$ and $[\text{FeCp-H}]_{\text{w}} = 1.6 \times 10^{-4}\ \text{M}$ indicate the distribution coefficient to be $K = [\text{FeCp-H}]_{\text{TBP}} / [\text{FeCp-H}]_{\text{w}} = 4.0 \times 10^2$. $[\text{FeCp-H}]_{\text{TBP}}$ is lower than that at the emulsion preparation, since FeCp-H in TBP distributes to the water phase. In the absence of SDS, on the other hand, the distribution coefficient was 3.0×10^3 ¹³⁾. Distribution of FeCp-H to water is facilitated by the presence of SDS.

The K value of DPA was determined as follows. The sample emulsion was left standing until a phase separation took place completely and, DPA in the oil phase was extracted with ethyl acetate. On the basis of visible absorption measurements of DPA in ethyl acetate, $[\text{DPA}]_{\text{TBP}}$ was determined to be $9.98 \times 10^{-2}\ \text{M}$. The distribution coefficient was thus determined to be $K = [\text{DPA}]_{\text{TBP}} / [\text{DPA}]_{\text{w}} = 1.0 \times 10^5$. DPA is almost insoluble in water. Similarly, Pe was insoluble in water, as confirmed by the fact that fluorescence of Pe was not observed from the water phase. $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ did not distribute to the TBP phase, owing to a high negative charge of the compound¹⁴⁾.

ii) Electrolytic Condition.

Figure 3-3 shows a cyclic voltammogram of the sample emulsion: FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA - SDS emulsion. In the cyclic voltammogram, the anodic and cathodic peaks were observed at 160 and 60 mV, respectively. These peaks correspond to the redox reaction of a $\text{Fe}(\text{CN})_6^{4-} / \text{Fe}(\text{CN})_6^{3-}$ couple in the water phase and, no other peak can be observed in the potential range of 0 ~ 800 mV (vs. Ag/AgCl). Thus, it is concluded that FeCp-H in the TBP droplets or water phase is not electrolyzed in this applied potential range. Similarly, the supporting electrolytes are not oxidized in this potential range. These results indicate that, even when a TBP droplet(s) is contacted with the electrode surface, electroactive species solubilized in the droplet is not oxidized at the electrode. This will be explained by the fact that the droplet surface stabilized by the surfactant inhibits direct contact of the electroactive species with the electrode. FeCp-H (1.6×10^{-4} M) distributed to the water phase is supposed to be solubilized in micelles or microemulsion and, the actual concentration oxidized at the electrode will be very low. Therefore, an oxidation peak of FeCp-H in the water phase is not observed. On the basis of these experimental observations, a bulk electrolysis potential was set 800 mV (vs. Ag/AgCl).

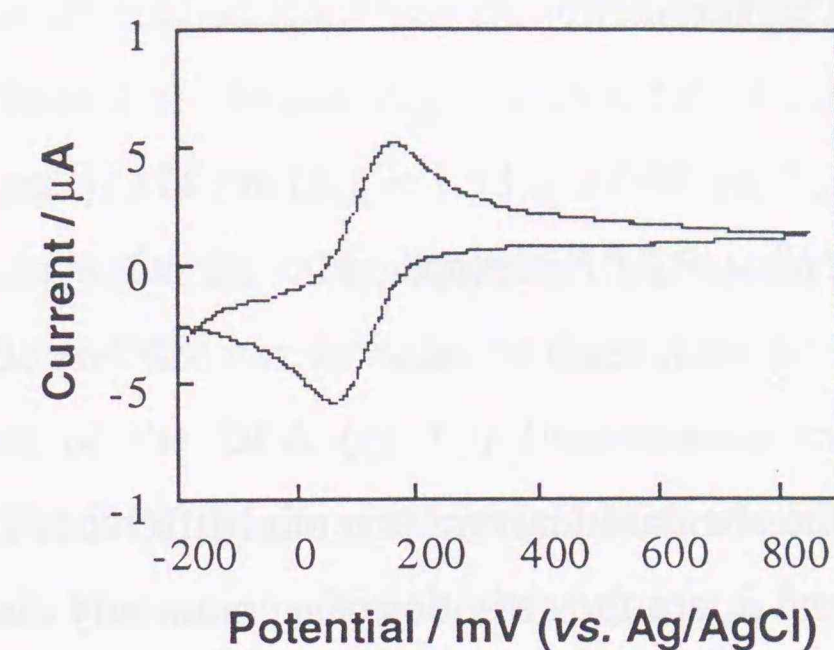


Figure 3-3. Cyclic voltammogram of the FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA - SDS emulsion. Sweep rate was 10 mV/s.

iii) Liquid-Junction Potential.

A redox reaction between solutes across a liquid / liquid interface is depended on the liquid-junction potential (Galvani potential) difference. At given temperature and pressure, a thermodynamic equilibrium of the potential is determined by the equality of the chemical potential for an electrolyte component commonly distributed to the both phases. The potential difference across a liquid / liquid interface is determined by the inhomogeneous distribution of ionic components between the two phases in the vicinity of the interface, which leads to this particular type of the phase boundary potential, being called the distribution potential. The distribution potential is established, when ionic species are partitioned in equilibrium between the water and organic phases.

By taking account the concentration dependence of the chemical potential of an ion, a liquid-junction potential difference ($\Delta_o^w \phi$) is given as a

Nernst-Donnan equation¹⁵⁻²⁰,

$$\Delta_o^w\phi = \Delta_o^w\phi^0 + (RT/F) \ln(a_o/a_w) \quad 3-1$$

where $\Delta_o^w\phi^0$ is the standard Galvani potential difference for a liquid / liquid system and, a_o and a_w are the activities of a commonly distributed ion in oil and water phases, respectively. R , T and F are the gas constant, the absolute temperature, and the Faraday constant, respectively. Eq. 3-1 indicates that the $\Delta_o^w\phi$ value can be controlled through an a_o/a_w ratio. Assuming the activity coefficient to be unity, an a_o/a_w ratio is equal to a c_o/c_w ratio, where c_o and c_w are the concentration of the ion in the oil or water phase, respectively. In the present emulsion, TBA^+TPB^- (1.0×10^{-2} M) and TBA^+Cl^- (1.0×10^{-2} M) are dissolved in the TBP and water phases, respectively. Therefore, an TBA^+ ion is commonly dissolved in both phases. The counter ion of TBA^+ (TPB^- in the TBP phase and Cl^- in the water phase) does not distribute to other phase. MgSO_4 (0.10 M) is dissolved in the water phase, but not in TBP. Therefore, the $\Delta_o^w\phi$ value is determined by the concentration of TBA^+ in each phase and kept at a constant value under the present condition. Consequently, the contribution of $\Delta_o^w\phi$ to the ET process at the liquid / liquid interface is kept constant at given $[\text{TBA}^+]_{\text{TBP}}$ and $[\text{TBA}^+]_w$.

iv) Optimization of Spectroscopic Conditions.

A absorption and fluorescence spectra of DPA in TBP are shown in

Figure 3-4. The absorption spectrum exhibited four peaks: 338 nm (molar extinction coefficient at 338 nm; $\epsilon_{338} = 3.75 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), 354 nm ($\epsilon_{354} = 8.17 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), 374 nm ($\epsilon_{374} = 1.33 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and 394 nm ($\epsilon_{394} = 1.25 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). On the other hand, the fluorescence spectrum showed two peaks at 408 and 428 nm. In order to determine the interfacial ET rate, the time course of the DPA (or Pe) fluorescence intensity during the electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in the emulsion must be measured in good signal-to-noise ratios. For this purpose, selection of both excitation and fluorescence monitoring wavelengths is very important. Although excitation of DPA at 394 nm, showing the maximum absorbance at a given concentration, is preferable, scattering (Rayleigh and/or Raman) of excitation light disturbs fluorescence measurements owing to the small Stokes shift of DPA. Irradiation at 338 or 354 nm results in a very low excitation efficiency. Therefore, the excitation and fluorescence monitoring wavelengths were set 374 and 428 nm, respectively.

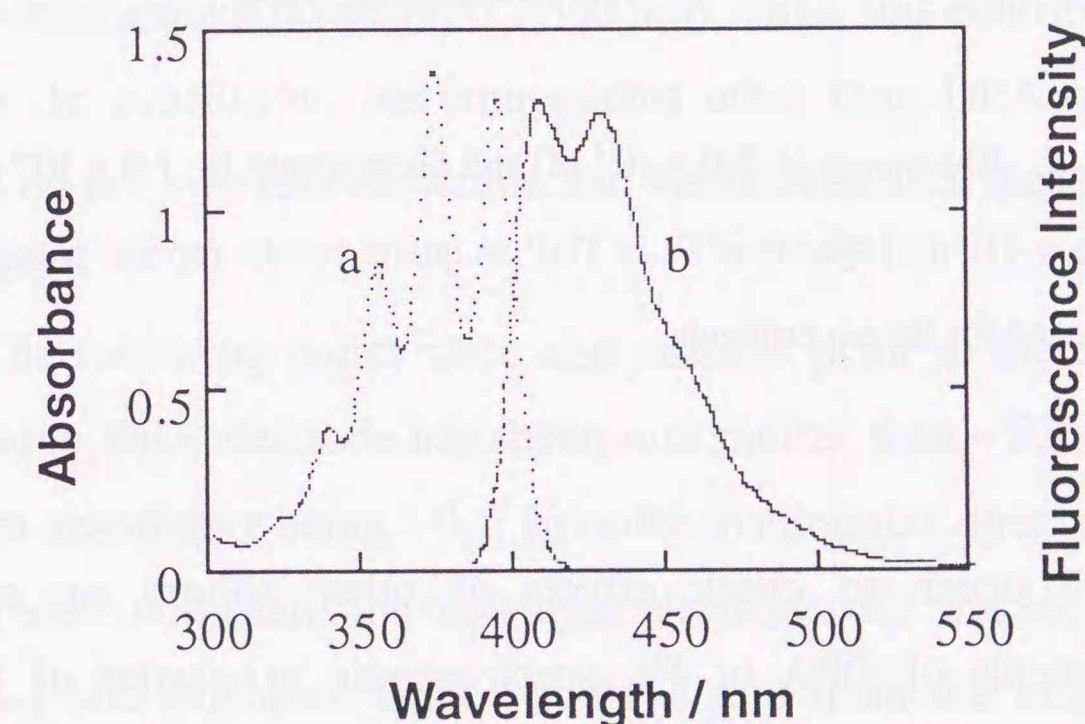


Figure 3-4. Absorption (a; 1.0×10^{-4} M) and fluorescence (b; 5.0×10^{-6} M, excitation wavelength = 374 nm) spectra of DPA in TBP. A quartz cuvette (optical path length = 10 mm) was used for the experiments.

The absorption and fluorescence spectra of Pe in TBP are shown in Figure 3-5. The absorption peak wavelengths of Pe were 388 ($\epsilon_{388} = 1.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 410 ($\epsilon_{410} = 2.89 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and 437 nm ($\epsilon_{437} = 3.88 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Similar to the discussion on the absorption and fluorescence spectra of DPA, the excitation and fluorescence monitoring wavelengths were set 410 and 470 nm, respectively.

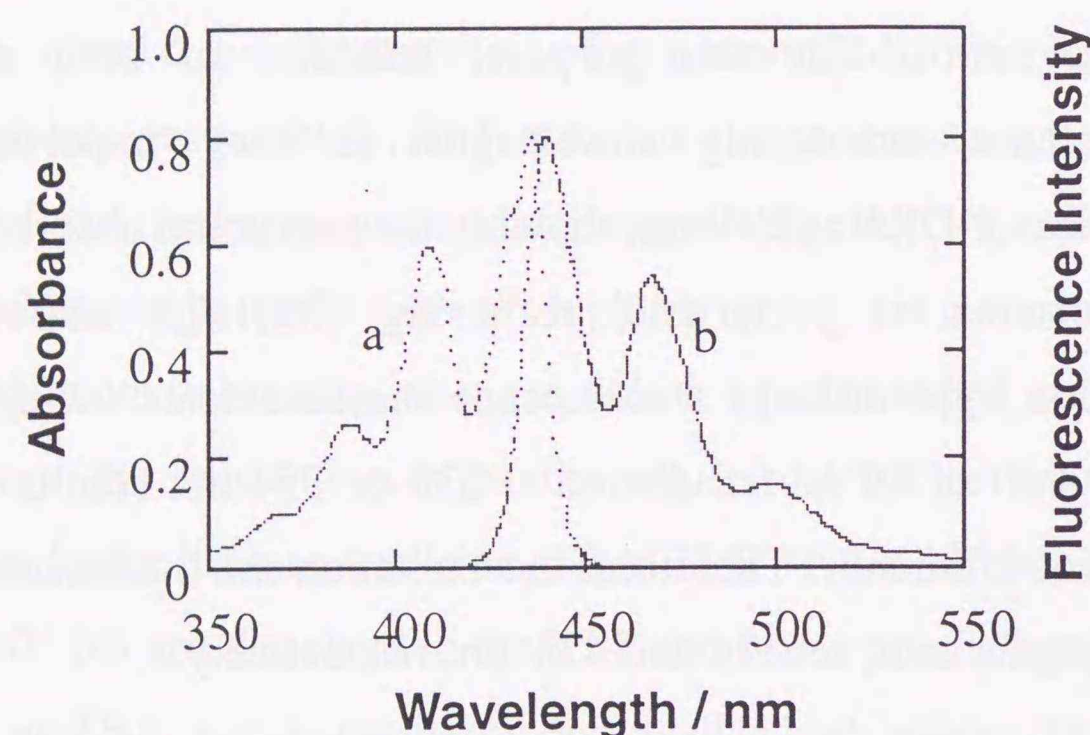


Figure 3-5. Absorption (a; $2.0 \times 10^{-5} \text{ M}$) and fluorescence (b; $2.0 \times 10^{-6} \text{ M}$, excitation wavelength = 410 nm) spectra of Pe in TBP. A quartz cuvette (optical path length = 10 mm) was used for the experiments.

In order to check effects of other solutes on spectroscopic measurements of DPA or Pe, spectroscopic properties of $\text{K}_4\text{Fe}(\text{CN})_6$ / $\text{K}_3\text{Fe}(\text{CN})_6$ and FeCp-H / FeCp-H^+ were studied as the data were summarized in Figures 3-6 and 3-7, respectively. It is noteworthy that these compounds are essentially non-emissive, so that only the absorption spectrum of each species is shown here. Absorption of $\text{K}_4\text{Fe}(\text{CN})_6$ was not

observed in the visible region, while $\text{K}_3\text{Fe}(\text{CN})_6$ exhibited an absorption peak around 420 nm ($\epsilon_{420} = 1.0 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). This might interfere spectroscopic measurements of DPA or Pe. In the thin-layer electrode cell with the optical path length of $\sim 70 \mu\text{m}$, however, absorbance of $\text{Fe}(\text{CN})_6^{3-}$ at 420 nm is very small as calculated by the Lambert - Beer law ($\epsilon cl = (1.0 \times 10^3) \times (2.0 \times 10^{-4}) \times (70 \times 10^{-4}) = 1.4 \times 10^{-3}$). Therefore, it is concluded that this does not interfere the fluorescence measurements of DPA or Pe.

FeCp-H exhibited absorption peaks at 326 ($\epsilon_{326} = 53 \text{ M}^{-1}\text{cm}^{-1}$) and 430 nm ($\epsilon_{430} = 95 \text{ M}^{-1}\text{cm}^{-1}$). Clearly, the molar absorptivities are very small and FeCp-H is confined in TBP droplets. The absorbance of FeCp-H in a single TBP droplet with the diameter of $1 \sim 40 \mu\text{m}$ is calculated to be below 0.05 at 420 nm, so that absorption of FeCp-H does not disturb the spectroscopic measurements of DPA or Pe. On the other hand, the absorption spectrum of FeCp-H^+ possesses a peak around 620 nm ($\epsilon_{620} \sim 400 \text{ M}^{-1}\text{cm}^{-1}$). The molar absorptivity is small and the absorption peak is outside of the wavelength interested (400 ~ 500 nm). Thus, this contribution is also neglected. In conclusion, the components other than DPA or Pe in the emulsion do not interfere excitation and the fluorescence measurements of DPA or Pe.

The following points were also checked prior to the experiments. The working SnO_2 electrode has absorption shorter than $\sim 500 \text{ nm}$ with the maximum absorbance being ~ 0.1 . In order to minimize direct excitation of the SnO_2 electrode itself, the thin-layer electrode cell was set as shown in Figure 3-1 and excitation light was irradiated from the non-fluorescent cover glass side. Under such a configuration, a photocurrent was not observed at the SnO_2 electrode.

Complex formation between TBA^+TPB^- and FeCp-H , DPA, or Pe was not observed, as confirmed by the fact that the shape of the absorption

spectrum containing each solute was identical to that of the emulsion.

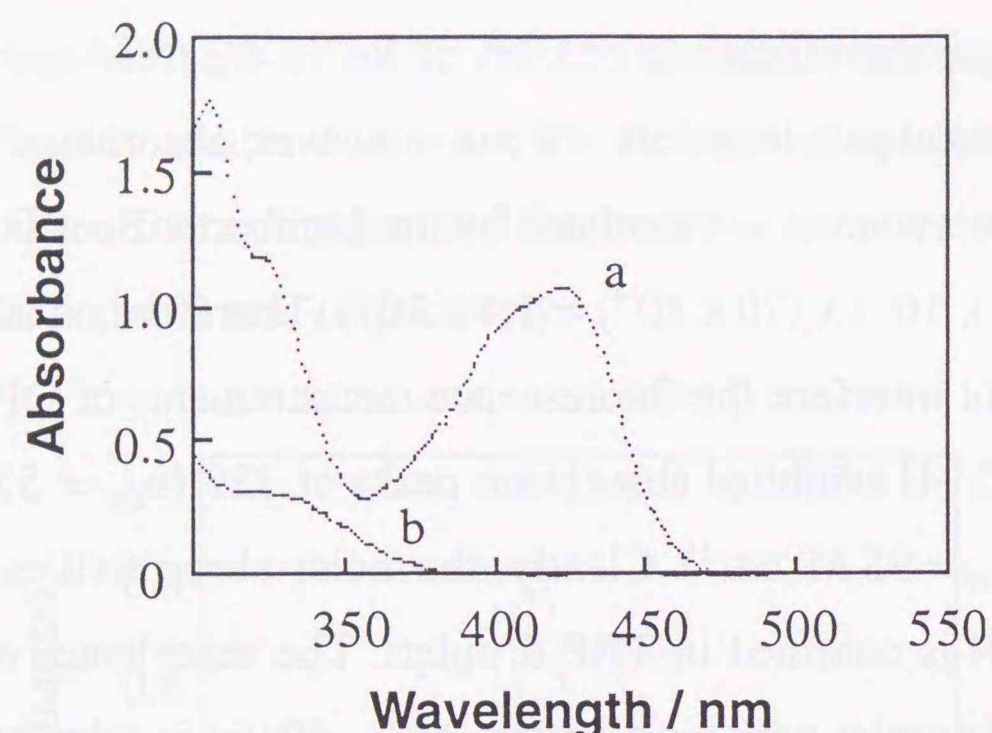


Figure 3-6. Absorption spectra of $\text{K}_3\text{Fe}(\text{CN})_6$ (a) and $\text{K}_4\text{Fe}(\text{CN})_6$ (b) ($1.0 \times 10^{-3} \text{ M}$) in water. A quartz cuvette (optical path length = 10 mm) was used for the experiments.

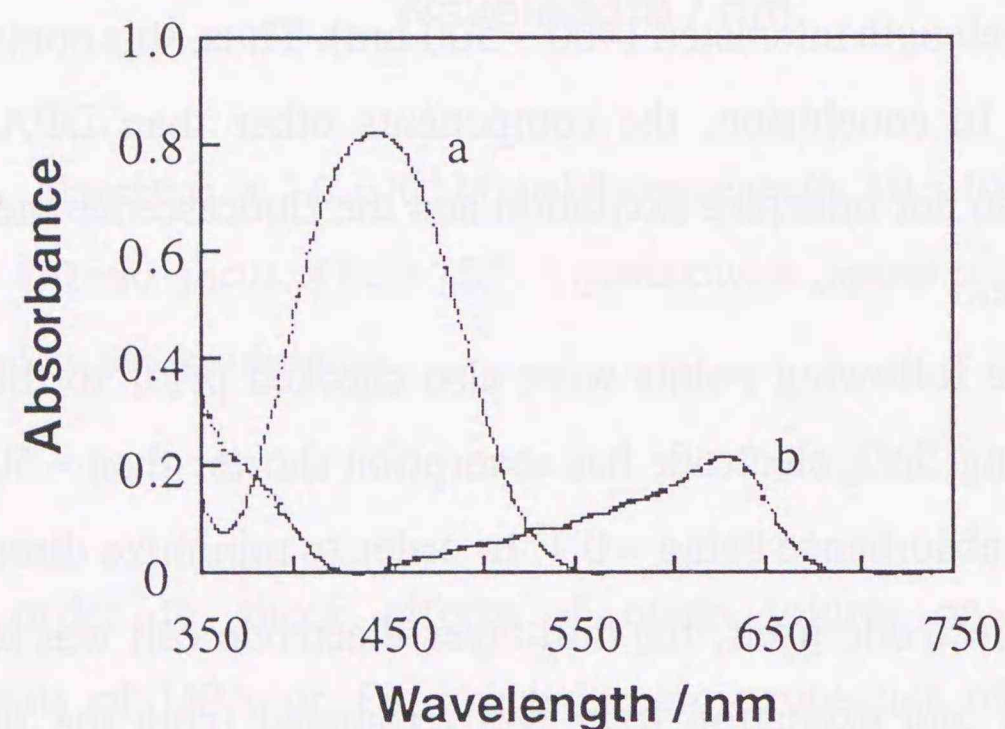


Figure 3-7. Absorption spectra of FeCp-H (a; $1.0 \times 10^{-2} \text{ M}$, recorded by using a quartz 10 mm cuvette) and FeCp-H^+ (b: $5.0 \times 10^{-2} \text{ M}$, recorded by using a cell with the optically path length of $\sim 150 \mu\text{m}$) in TBP.

3.3 A Droplet-Unresolved Study on Interfacial Electron Transfer: Ensemble Measurements.

Before describing the interfacial electron transfer reaction at a *single* TBP droplet / water interface, the results determined for a large number of TBP droplets (ensemble measurements) are explained. It is noteworthy that such a study is the fundamental basis for conducting single droplet measurements and is very important to know whether the overall reaction scheme (Scheme 3-1) is valid or not. Also, one must decide the rate determining step of the reactions in Scheme 3-1 to analyze the interfacial electron transfer process. In the following, experimental results and the kinetics analysis are described.

3.3.1 Coulometric and Fluorometric Study on Interfacial Electron Transfer Reaction.

A sample studied was a $\text{FeCp-H} - \text{Fe}(\text{CN})_6^{4-} - \text{DPA}$ emulsion. $\text{Fe}(\text{CN})_6^{4-}$ ($2.0 \times 10^{-4} \text{ M}$) in the water phase was oxidized by a potential step method at 800 mV (vs. Ag/AgCl) in the presence ($[\text{FeCp-H}]_{\text{TBP}} = 0.10 \text{ M}$) or absence of FeCp-H . The time dependence of the current observed at the SnO_2 electrode is shown in Figure 3-8, where (a) and (b) represent the data in the presence and absence of FeCp-H , respectively. In the absence of FeCp-H in the oil phase (*i.e.*, droplets), the electrode current relevant to oxidation of $\text{Fe}(\text{CN})_6^{4-}$ in the water phase decreased very rapidly with the electrolytic time (t) and, the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ was almost completed at $t \sim 10 \text{ s}$. In the presence of FeCp-H , on the other hand, the time course of the current was slow compared to that without FeCp-H and the oxidation of

$\text{Fe}(\text{CN})_6^{4-}$ continued upto $t \sim 100$ s.

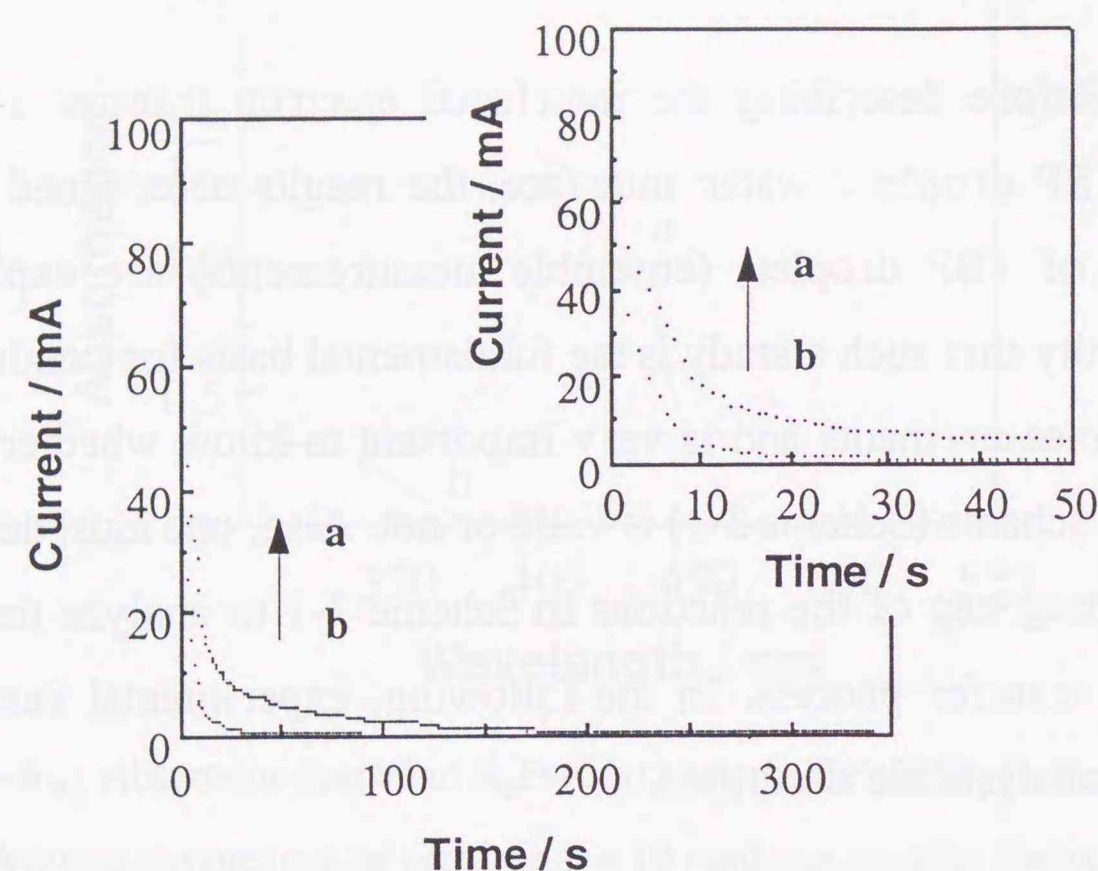


Figure 3-8. Time dependence of the current at the SnO_2 electrode during bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ ($[\text{FeCp-H}]_{\text{TBP}} = 0.10$ M (a) or $[\text{FeCp-H}]_{\text{TBP}} = 0$ M (b)).

The time dependence of the fluorescence intensity of DPA at 428 nm was measured simultaneously during the bulk electrolysis. The data in the presence of FeCp-H is shown in Figure 3-9. It is clearly seen in the figure that the fluorescence intensity increases with the electrolytic time and almost leveled-off at $t \sim 100$ s. It is noteworthy that the spectral band shape of the DPA fluorescence is the same before and after electrolysis as demonstrated in Figure 3-10. The results in Figure 3-8 and 3-9 prove that the interfacial electron transfer between $\text{Fe}(\text{CN})_6^{3-}$ in the water phase and FeCp-H in the TBP droplets takes place as expected from Scheme 3-1.

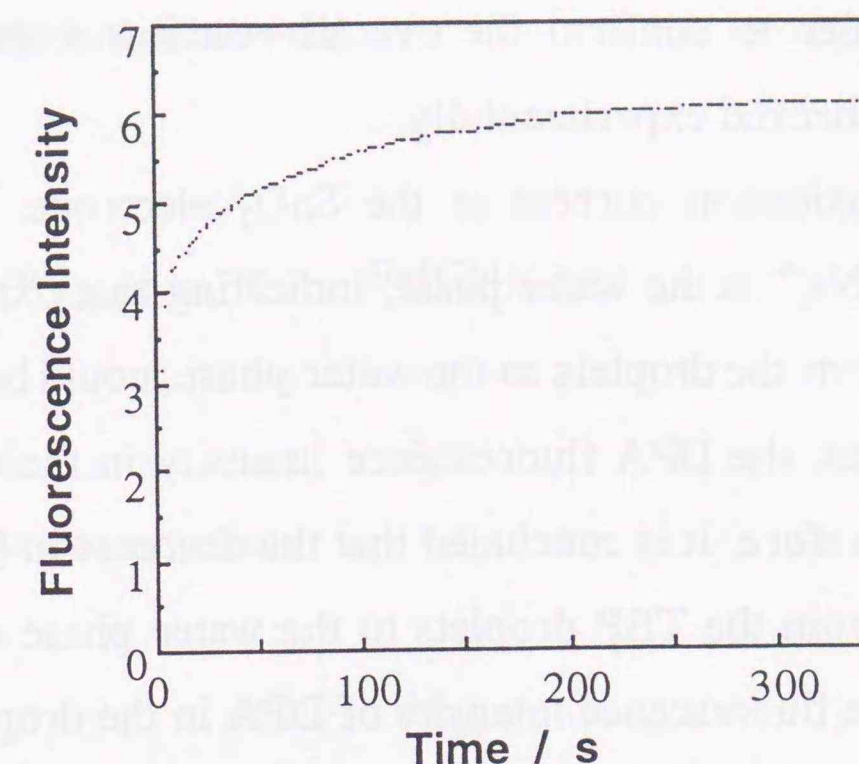


Figure 3-9. Time dependence of the fluorescence intensity of DPA at 428 nm in TBP droplets during the bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in water (excitation wavelength = 374 nm).

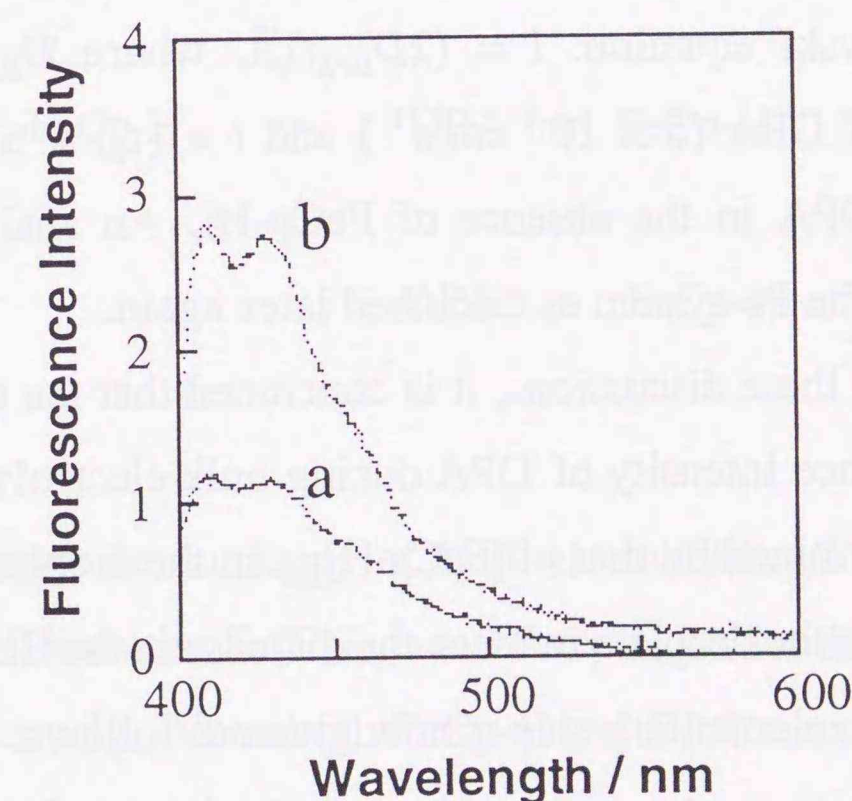


Figure 3-10. The fluorescence spectra of DPA before and after bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in water (excitation wavelength = 374 nm).

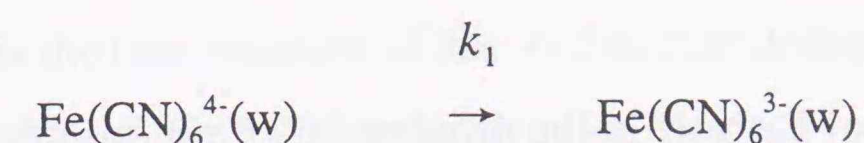
In order to confirm the overall reaction scheme, the following points were checked experimentally.

The oxidation current at the SnO_2 electrode was not observed without $\text{Fe}(\text{CN})_6^{4-}$ in the water phase, indicating that oxidation of FeCp-H , distributed from the droplets to the water phase, could be neglected. Under such conditions, the DPA fluorescence intensity in the droplets remained constant. Therefore, it is concluded that the decrease in $[\text{FeCp-H}]_{\text{TBP}}$ due to distribution from the TBP droplets to the water phase does not cause the increase of the fluorescence intensity of DPA in the droplets.

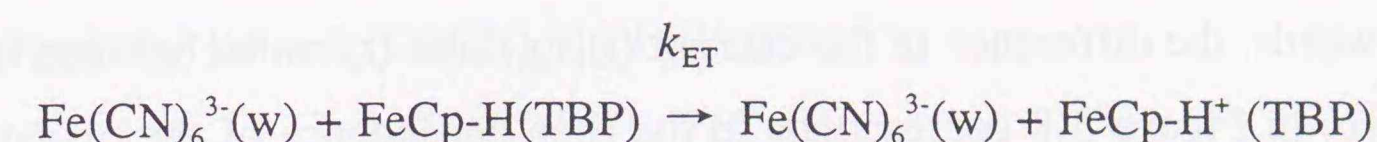
Fluorescence quenching of DPA by $\text{Fe}(\text{CN})_6^{4-}$ or $\text{Fe}(\text{CN})_6^{3-}$ at the droplet / water interface can be neglected, since the diffusion distance (l) of DPA within the fluorescence lifetime (τ_0) of the molecule is much shorter than the droplet size (μm order). Actually, the diffusion distance of the excited state of DPA (l) is estimated to be 3 nm on the basis of the Einstein - Smoluchowski equation: $l = (2D_{\text{DPA}}t)^{1/2}$, where D_{DPA} is the diffusion coefficient of DPA ($5 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$) and $t = (\tau_0) = 6.7 \text{ ns}$ (fluorescence lifetime of DPA in the absence of FeCp-H). An analogous argument is possible for the Pe system as discussed later again.

From these discussions, it is concluded that the time dependence of the fluorescence intensity of DPA during bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in water is determined by that of $[\text{FeCp-H}]_{\text{TBP}}$ in the droplets, and the decrease in $[\text{FeCp-H}]$ in the droplets renders the increase in the fluorescence intensity of DPA. Each elementary step is now given as follows.

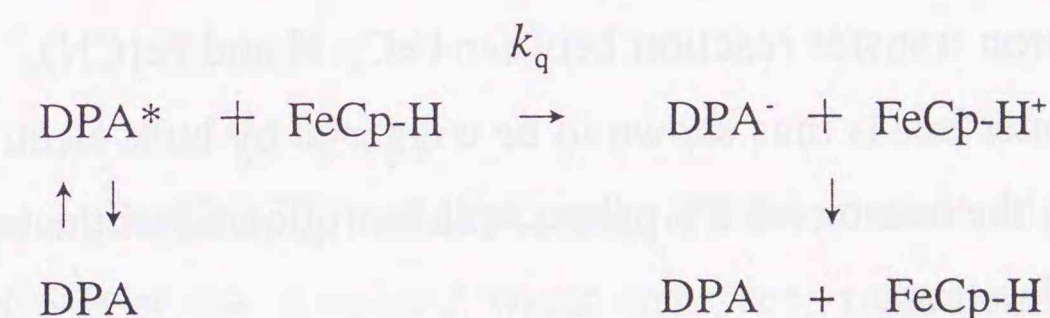
1. in water phase (at electrode)



2. at droplet / water interface



3. in droplet



k_1 and k_{ET} are the rate constants of bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ at the electrode and ET between $\text{Fe}(\text{CN})_6^{3-}$ and FeCp-H across the droplet / water interface, respectively. When both FeCp-H and DPA coexist in the droplet as in the case for the droplet before electrolysis, the excited singlet state of DPA (DPA^*) is quenched efficiently by FeCp-H (rate constant; k_q). Upon electrolysis, FeCp-H is oxidized by $\text{Fe}(\text{CN})_6^{3-}$ at the droplet / water interface. This leads to an enhancement of the fluorescence intensity of DPA owing to a decrease in $[\text{FeCp-H}]_{\text{TBP}}$ in the droplets. It is noteworthy that the

fluorescence of DPA is not quenched by FeCp-H⁺. Therefore, the fluorescence intensity from the droplet increases with the electrolytic time as demonstrated in Figure 3-9.

The total amount of FeCp-H in the droplets is 2.5 times higher than that of Fe(CN)₆³⁻ in the water phase. Thus, Fe(CN)₆⁴⁻ produced by the ET reaction with FeCp-H at the droplet / water interface should be oxidized again to Fe(CN)₆³⁻ at the electrode (*i.e.*, redox cycle) to fulfill complete oxidation of FeCp-H in the droplets during the bulk electrolysis. In other words, the difference in the current (*i*) vs. time (*t*) curve between (a) and (b) in Figure 3-8 corresponds to the time dependence of the oxidation of FeCp-H in the droplets. The total electric charge calculated by integrating the *i*-*t* curve in Figure 3-8 at *t* < 150 s was ~ 7 x 10⁻⁴ C, which was in good agreement with that estimated from the total amount of FeCp-H in the droplets (7 x 10⁻⁴ C).

The electron transfer reaction between FeCp-H and Fe(CN)₆³⁻ at the droplet / water interface is thus shown to be triggered by bulk electrolysis of Fe(CN)₆⁴⁻ and, the interfacial ET process can be followed on the basis of the fluorometric method.

3.3.2 Rate Determining Step.

The overall reaction involves several elementary steps such as an interfacial ET across the droplet / water boundary and diffusion of the reactant in each phase. For kinetic analysis of the interfacial ET, firstly, the rate determining step should be elucidated. In the following, each elementary step proceeding in the emulsion system is discussed in detail.

Diffusion of Fe(CN)₆³⁻ from the water phase to a droplet proceeds in

a spherical manner, so that the steady state concentration of Fe(CN)₆³⁻ in the vicinity of the droplet surface becomes constant very rapidly. Now, *k*₁ or *k*₂ is the rate constant of the oxidation reaction of Fe(CN)₆⁴⁻ at the electrode or that of FeCp-H in the droplet, respectively, and *k*₋₁ or *k*₋₂ is the rate constant of the relevant reverse reaction. In such a case, the differential equation for the concentration of Fe(CN)₆³⁻ or FeCp-H is given as in,

$$\begin{aligned} d[n\text{Fe(CN)}_6^{3-}]/dt = & k_1[\text{Fe(CN)}_6^{3-}] - k_{-1}[\text{Fe(CN)}_6^{3-}]_{\text{int}} \\ & - k_{\text{ET}}[\text{Fe(CN)}_6^{3-}]_{\text{int}}[\text{FeCp-H}]_{\text{int}} \end{aligned} \quad 3-2$$

$$d[n\text{FeCp-H}]/dt = k_2[\text{FeCp-H}] - k_{-2}[\text{FeCp-H}]_{\text{int}} - k_{\text{ET}}[\text{Fe(CN)}_6^{3-}]_{\text{int}}[\text{FeCp-H}]_{\text{int}} \quad 3-3$$

where [Fe(CN)₆³⁻]_{int} and [FeCp-H]_{int} are the concentrations of Fe(CN)₆³⁻ and FeCp-H at the droplet / water interface, respectively. [nFe(CN)₆³⁻] and [nFeCp-H] are the amounts of Fe(CN)₆³⁻ and FeCp-H per unit surface area at the droplet / water interface, respectively. *k*_{ET} represents the interfacial ET rate constant per unit surfacial area of a droplet. All of the FeCp-H molecules in a droplet are oxidized, since the droplet size is in micrometer. This is very different from the situations at a macroscopic flat liquid / liquid interface. Therefore, the amount of FeCp-H reacted with Fe(CN)₆³⁻ per droplet surface area is considered here. This is given as in eq.3-4,

$$(4/3)\pi r^3 d[\text{FeCp-H}]/dt = 4\pi r^2 \{k_{-2}[\text{FeCp-H}]_{\text{int}} - k_2[\text{FeCp-H}]\} \quad 3-4$$

where r is the droplet radius. Under the steady state condition, $d[\text{Fe}(\text{CN})_6^{3-}]/dt = d[\text{FeCp-H}]/dt = 0$, so that eq.3-2 and eq.3-3 are rewritten as follows.

$$(k_{-1} + k_{\text{ET}}[\text{FeCp-H}]_{\text{int}}) [\text{Fe}(\text{CN})_6^{3-}]_{\text{int}} = k_1[\text{Fe}(\text{CN})_6^{3-}] \quad 3-5$$

$$k_2[\text{FeCp-H}] - k_{-2}[\text{FeCp-H}]_{\text{int}} = k_{\text{ET}}[\text{Fe}(\text{CN})_6^{3-}]_{\text{int}}[\text{FeCp-H}]_{\text{int}} \quad 3-6$$

In the case of $k_{-1} \ll k_{\text{ET}}[\text{FeCp-H}]_{\text{int}}$, eq.3-5 gives eq.3-7.

$$k_{\text{ET}}[\text{FeCp-H}]_{\text{int}} [\text{Fe}(\text{CN})_6^{3-}]_{\text{int}} = k_1[\text{Fe}(\text{CN})_6^{3-}] \quad 3-7$$

Furthermore, eq.3-8 is derived from eqs.3-4, 3-6, and 3-7,

$$[\text{FeCp-H}] = [\text{FeCp-H}]^0 - (3/r) k_1[\text{Fe}(\text{CN})_6^{3-}]t \quad 3-8$$

where $[\text{FeCp-H}]^0$ represents the initial concentration of FeCp-H in the droplet. When the diffusion process of $\text{Fe}(\text{CN})_6^{3-}$ in the water phase is the rate determining step, the overall reaction rate is given by eq.3-8.

In the case of $k_{-1} \gg k_{\text{ET}}[\text{FeCp-H}]_{\text{int}}$, on the other hand, eq.3-9 is derived from eq.3-5.

$$k_{-1}[\text{Fe}(\text{CN})_6^{3-}]_{\text{int}} = k_1[\text{Fe}(\text{CN})_6^{3-}] \quad 3-9$$

Equations 3-4, 3-6, and 3-9 give eq.3-10.

$$d[\text{FeCp-H}]/dt = -3(k_2/r) k_{\text{ET}}[\text{Fe}(\text{CN})_6^{3-}][\text{FeCp-H}] / (k_{-2} + k_{\text{ET}}k_1/k_{-1} [\text{Fe}(\text{CN})_6^{3-}]) \quad 3-10$$

When $k_{-2} \ll k_{\text{ET}}[\text{Fe}(\text{CN})_6^{3-}]$, eq.3-11 is derived from eqs.3-4, 3-6, and 3-10,

$$[\text{FeCp-H}] = [\text{FeCp-H}]^0 \exp\{-3(k_2/r)t\} \quad 3-11$$

Equation 3-11 is the rate equation when diffusion of FeCp-H in the droplets is the rate determining step.

In the case of $k_{-2} \gg k_{\text{ET}}[\text{Fe}(\text{CN})_6^{3-}]$, eq.3-12 is derived from eqs.3-4, 3-6, and 3-10.

$$[\text{FeCp-H}] = [\text{FeCp-H}]^0 \exp\{-3(k_{\text{ET}}/r)[\text{Fe}(\text{CN})_6^{3-}]t\} \quad 3-12$$

If the ET process across a droplet / water interface is the rate determining step, the rate is given by eq.3-12.

In the next section, the rate determining step of the interfacial ET is discussed on the basis of these equations and the experimental observations.

i) Diffusion Process in Water Phase.

When diffusion of $\text{Fe}(\text{CN})_6^{3-}$ in the water phase is the rate determining step, the time dependence of $[\text{FeCp-H}]_{\text{TBP}}$ should exhibit a linear relation against the electrolytic time. However, it is clear from Figure 3-8 that $[\text{FeCp-H}]_{\text{TBP}}$ does not decrease linearly with the electrolytic time. Therefore, diffusion of $\text{Fe}(\text{CN})_6^{3-}$ in the water phase is not the rate determining step.

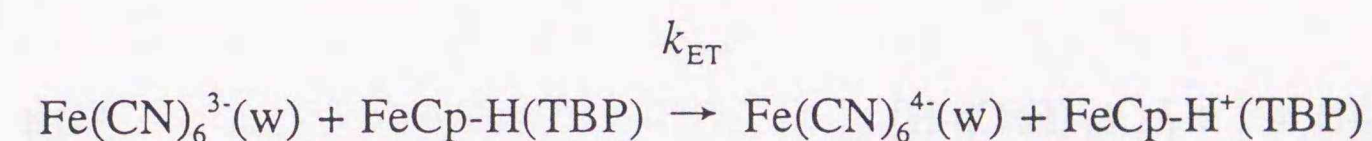
The diffusion time (t) of $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$ in the thin-layer electrode cell can be calculated by the equation: $l = (2D_{\text{Fe(III)}}t)^{1/2}$ where $D_{\text{Fe(III)}}$ is the diffusion constant of $\text{Fe}(\text{CN})_6^{3-}$ in water ($= 6.0 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$) and l is the thickness ($l = 70 \mu\text{m}$) of the cell. The diffusion time is thus estimated to be several seconds. The value is very short compared with the observed time response of the current (Figure 3-8) or fluorescence intensity (Figure 3-9) upon bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$. This supports the conclusion that the diffusion process in water is not the rate determining step.

ii) Diffusion Process in Droplet.

When diffusion of FeCp-H in the droplet is the rate determining step, the ET rate is expressed as in eq.3-11. This indicates that the time course of $[\text{FeCp-H}]_{\text{TBP}}$ should be independent of $[\text{Fe}(\text{CN})_6^{3-}]_w$. However, the time course of $[\text{FeCp-H}]_{\text{TBP}}$ was depended on $[\text{Fe}(\text{CN})_6^{3-}]_w$ as described later in Chapter 4. Therefore, diffusion of FeCp-H in the droplets is not the rate determining step. The diffusion time of FeCp-H in the droplet calculated by the equation of $l = (2D_{\text{FeCp-H}}t)^{1/2}$ ($D_{\text{FeCp-H}} = 3.7 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$) was very short ($< 1 \text{ s}$) compared with the time course of the electrode current or fluorescence intensity. Thus, it is concluded that the diffusion of FeCp-H in the droplets is not the rate determining step.

iii) Electron Transfer Process across Droplet / Water Interface.

From above discussions, the rate determining step is suggested to be the ET process across the droplet / water interface,



When this is the case, the rate equation is given by eq.3-12 as described before and the equation is rewritten as in eq.3-13,

$$\ln([FeCp-H]_{TBP} / [FeCp-H]_{TBP}^0) = -k_{obs} [Fe(CN)_6^{3-}]_w t \quad 3-13$$

where $k_{obs} (= (3/r)k_{ET})$ is the apparent ET rate constant per unit concentration ($M^{-1}s^{-1}$). The equation predicts that $\ln([FeCp-H]_{TBP})$ decreases linearly with the electrolytic time (t). In the next section, this prediction is compared with the experimental observations.

3.3.3 Determination of Interfacial Electron Transfer Rate.

i) Fluorometric Determination of the FeCp-H Concentration.

The fluorescence intensity of DPA in the droplets increases upon bulk electrolysis of $Fe(CN)_6^{4-}$ in the water phase and, this is ascribed to the interfacial ET across the droplet / water boundary as described before. In order to estimate $[FeCp-H]_{TBP}$ from the observed fluorescence intensity (I_F), the following Stern - Volmer relation was applied²¹⁾,

$$I_F^0 / I_F(t) = 1 + k_q \tau_0 [FeCp-H]_{TBP} \quad 3-14$$

where I_F^0 is the fluorescence intensity of DPA (I_F) at $[FeCp-H]_{TBP} = 0$ and assumed to be equal to I_F at a constant value upon bulk electrolysis: $t \sim 300$ s. $I_F(t)$ is I_F at each electrolytic time. τ_0 is the fluorescence lifetime of DPA in the absence of FeCp-H in the droplet and k_q is the rate constant of the

fluorescence quenching reaction. If τ_0 and k_q are known, therefore, $[FeCp-H]_{TBP}$ at each electrolytic time is determined on the basis of $I_F(t)$ and the Stern-Volmer equation.

The fluorescence lifetimes of DPA in the presence and absence of FeCp-H in the droplet were measured by a single photon counting method. Sample emulsions were prepared by the same procedures with those for bulk electrolysis. The results are shown in Figure 3-11. The observed decay curve was analyzed by a double exponential function and its average fluorescence lifetime was determined to be 6.7, 3.7, or 2.8 ns at $[FeCp-H]_{TBP} = 0, 0.06$, or 0.10 M, respectively. Since FeCp-H in the droplets distributes slightly to the water phase, the actual $[FeCp-H]_{TBP}$ was corrected by the distribution coefficient of the compound between the two phases. The fluorescence lifetime ratio (τ / τ_0) was plotted against $[FeCp-H]_{TBP}$ as shown in Figure 3-12. The plot exhibited a linear relationship between τ_0 / τ and $[FeCp-H]_{TBP}$ and the slope gave k_q to be $3.1 \times 10^9 M^{-1}s^{-1}$. On the basis of these results, the interfacial ET reaction can be now analyzed.

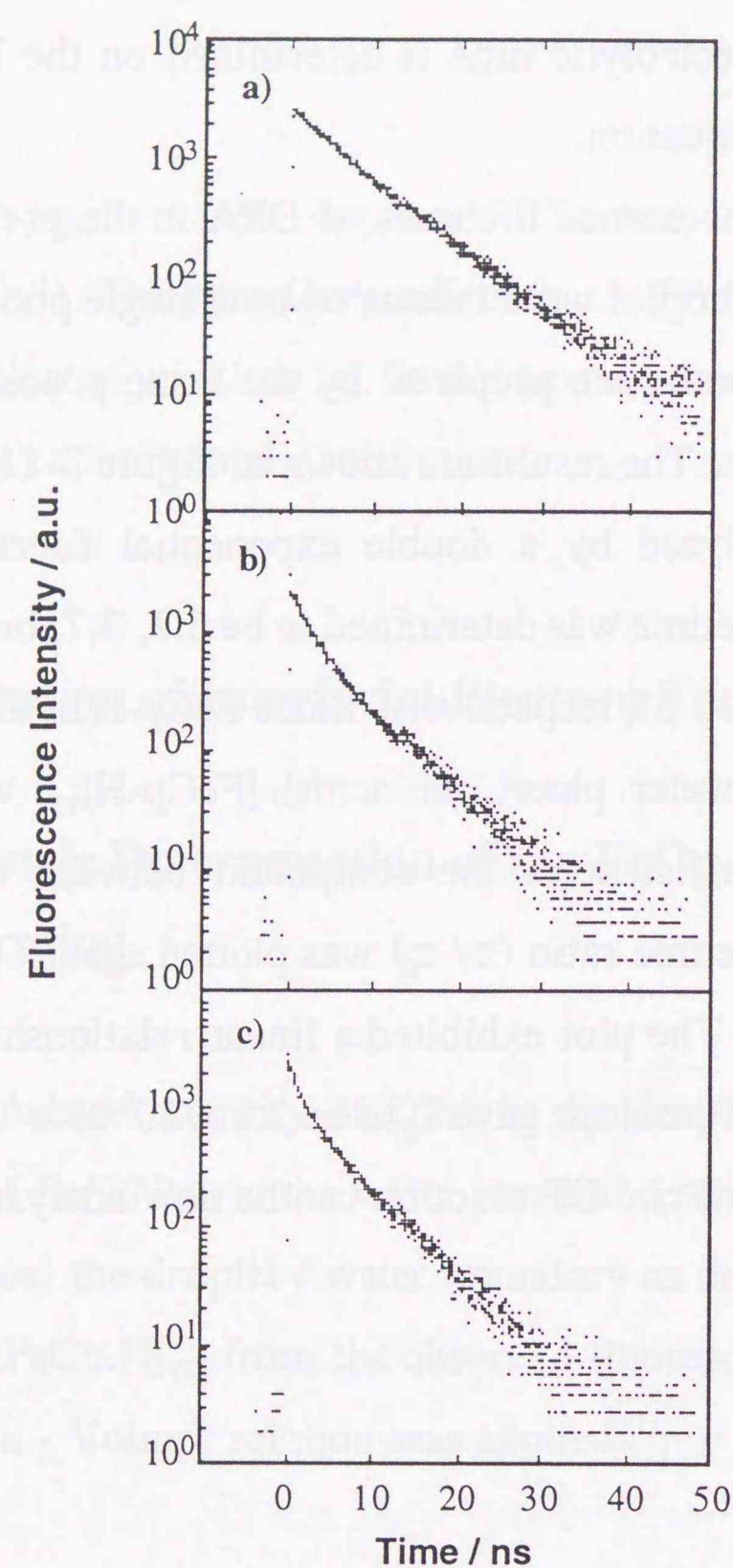


Figure 3-11. Fluorescence decay curves of DPA ($[DPA]_{TBP} = 1.0 \times 10^{-2}$ M, a; $[FeCp-H]_{TBP} = 0$ M, b; $[FeCp-H]_{TBP} = 0.06$ M, c; $[FeCp-H]_{TBP} = 0.1$ M, excitation wavelength = 420 nm, monitoring wavelength = 428 nm).

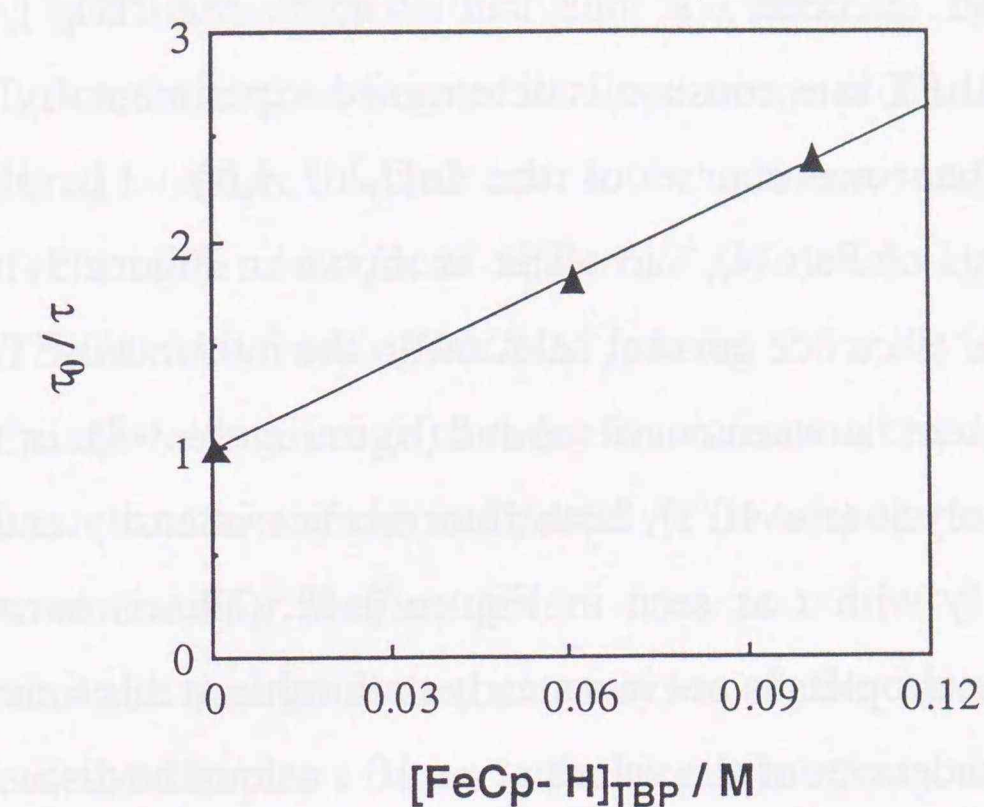


Figure 3-12. Stern-Volmer plot for fluorescence quenching of DPA by FeCp-H.

ii) Analysis of Electron Transfer Rate.

Combining eq.3-13 with eq.3-14, the analytical equation can be derived as follows,

$$\ln \{ I_F^0 / I_F(t) - 1 \} = -k_{\text{obs}} [\text{Fe}(\text{CN})_6^{3-}]_w t + \ln (k_q \tau_0 [\text{FeCp-H}]_{TBP}) \quad 3-15$$

Since $I_F(t)$ is the fluorescence intensity of DPA during the bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in the water phase, the ET rate constant ($k_{\text{obs}} / \text{M}^{-1}\text{s}^{-1}$) is determined on the basis of eq.3-15 and the time dependence of $I_F(t)$ in

Figure 3-8. In this equation, τ_0 and k_q are constant for given fluorescence probe and quencher. If one can estimate $[\text{Fe}(\text{CN})_6^{3-}]_w$, therefore, the interfacial ET rate constant is determined experimentally.

The time course of the $\ln\{I_F^0 / I_F(t) - 1\}$ value during bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in water is shown in Figure 3-13, together with that of the electrode current relevant to the interfacial ET (i.e., difference in the current between curve (a) and (b) in Figure 3-8). In the early stage of the electrolysis ($t < 10$ s), both fluorescence intensity and current change nonlinearly with t as seen in Figure 3-13. This is because $[\text{Fe}(\text{CN})_6^{3-}]_w$ around the droplets is not in a steady state value at this time domain, and the time dependencies of the values at $t < 10$ s cannot be discussed here. On the other hand, $\ln\{I_F^0 / I_F(t) - 1\}$ and $\ln(\text{current})$ decreased linearly with t at $t > 10$ s, indicating that the concentration of $\text{Fe}(\text{CN})_6^{3-}$ in the water phase becomes a steady state value: 2.0×10^{-4} M. Also, the results indicate that the rate determining step of the present reaction is the ET process across the droplet / water interface as predicted from eq.3-15.

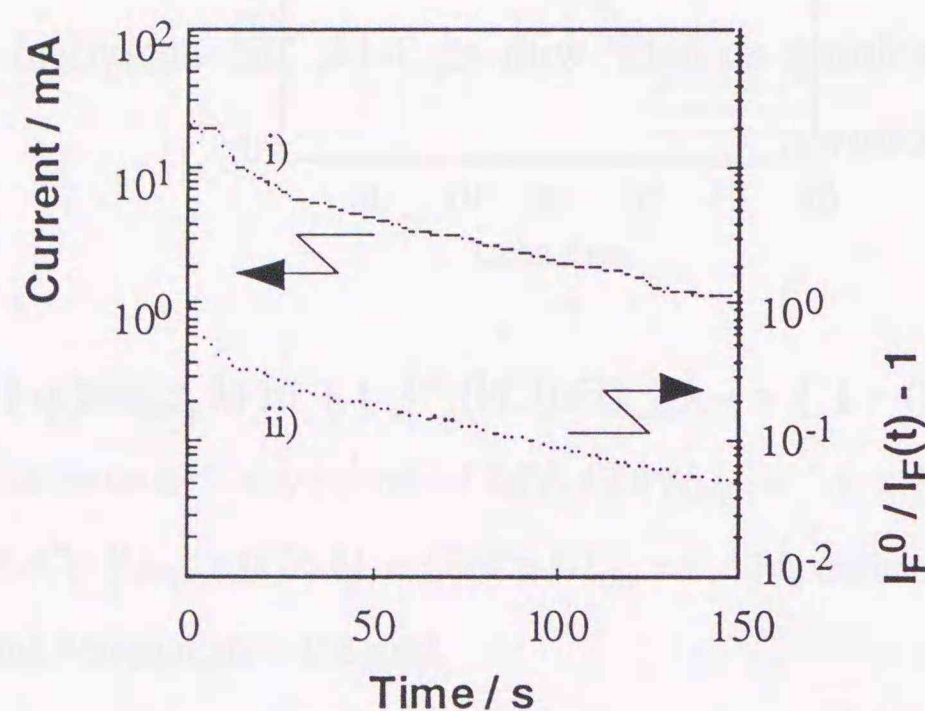


Figure 3-13. Time dependencies of the electrode current (i) (difference between the curves (a) and (b) shown in Figure 3-8) and $\ln\{I_F^0 / I_F(t) - 1\}$ (ii) (I_F^0 is I_F at a $t = \sim 300$ s).

It is noteworthy that the time dependence of the fluorescence intensity is in good agreement with that of the current. Therefore, the interfacial ET rate, corresponding to the slope of the plot in Figure 3-13, can be determined by either the time course of the fluorescence intensity or electrode current. The interfacial ET rate constant, k_{obs} , was thus determined to be $80 \text{ M}^{-1}\text{s}^{-1}$ with $[\text{Fe}(\text{CN})_6^{3-}]_w$ being 2.0×10^{-4} M. Although this value is the ensemble average of those for various-sized droplets in the emulsion, the rate constant of the interfacial ET reaction proceeding in the emulsion is determined for the first time.

Fluorometric and coulometric analyses of the electron transfer reaction across the droplet / water interface were very successful. In particular, the fluorescence intensity change of a probe (DPA) during the electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ can be used as a direct measure of the interfacial ET rate. The methodology can be used for single droplet measurements as described in the following sections.

3.4 Interfacial Electron Transfer across Single Droplet / Water Interface.

The bimolecular rate constant of the interfacial ET reaction in the $\text{FeCp-H} - \text{Fe}(\text{CN})_6^{4-} - \text{DPA}$ emulsion system has been determined directly on the basis of the fluorometric and coulometric measurements as described above. However, the result obtained is the average of those for various droplets with different sizes, so that the value of $k_{obs} = 80 \text{ M}^{-1}\text{s}^{-1}$ does not represent the true value for the interfacial ET. Clearly, k_{obs} is strongly dependent on the size of the droplet, so that a clear picture of the ET reaction across the droplet / water interface is obtained through single

droplet measurements alone. Thus, single microdroplet measurements were conducted on the basis a laser trapping - spectroscopy - electrochemistry method.

3.4.1 Single Droplet Measurements.

An FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA emulsion prepared by the procedures mentioned before (section 3.2.1) was poured onto the transparent thin-layer electrode cell (Figure 3-2) and one droplet was positioned above the working SnO_2 electrode without direct contact by the laser trapping method. Analogous to the experiments described in section 3.3, $\text{Fe}(\text{CN})_6^{4-}$ in the water phase was electrolyzed by a potential step method (800 mV vs. Ag/AgCl) and subsequent fluorescence intensity change of DPA in the laser-trapped droplet was monitored by microspectroscopy.

A typical example of the time dependence of the fluorescence intensity of DPA during bulk electrolysis, determined for individual droplets (droplet radius; $r = 7.0$ or $17.0 \mu\text{m}$), is shown in Figure 3-14. As clearly seen in the figure, the fluorescence intensity of DPA in a single microdroplet increased with the electrolytic time (t) and was saturated at a certain time similar to the results on droplet-unsolved measurements (Figure 3-9). It is worth noting that the fluorescence spectral band shape of DPA does not vary with t except for its absolute intensity (Figure 3-15). Thus, no side reaction takes place in the emulsion system and photodecomposition of DPA can be neglected even for single droplet measurements. On the other hand, the sample emulsion involves a number of TBP droplet and the interfacial ET is induced by bulk electrolysis, so that the electrode current relevant to ET for a single droplet cannot be measured.

However, the electrode current at SnO_2 increased with t in a time constant similar to that in Figure 3-14 and almost leveled-off at $t > 200$ s as the data were shown in Figure 3-16. Phenomenologically, the results shown in Figures 3-14, 3-15, and 3-16 are very similar to those obtained for a large number of droplets (Figures 3-8, 3-9, and 3-10). Therefore, analogous discussion and kinetic analyses made for the results on the ensemble measurements can be applied to the present results, and the ET rate constant across the single droplet / water interface can be determined directly on the basis of the time dependence of the fluorescence intensity of DPA in individual droplets.

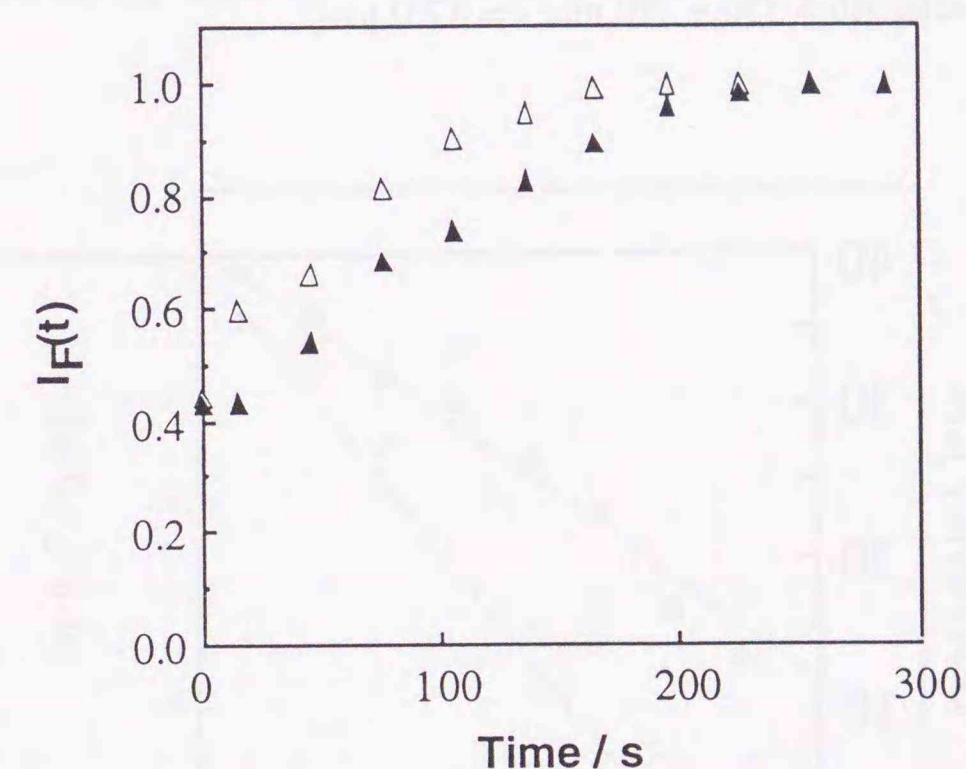


Figure 3-14. Time dependence of the fluorescence peak (at 428 nm) intensity of DPA (excitation wavelength = 350 ~370 nm) in single droplets (Δ ; $r = 7.0 \mu\text{m}$, $\blacktriangle$; $r = 17.0 \mu\text{m}$). The emulsion contains $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$ and $[\text{SDS}] = 1.2 \times 10^{-4} \text{ M}$. Other reactant concentrations are described in Section 3.2.1.

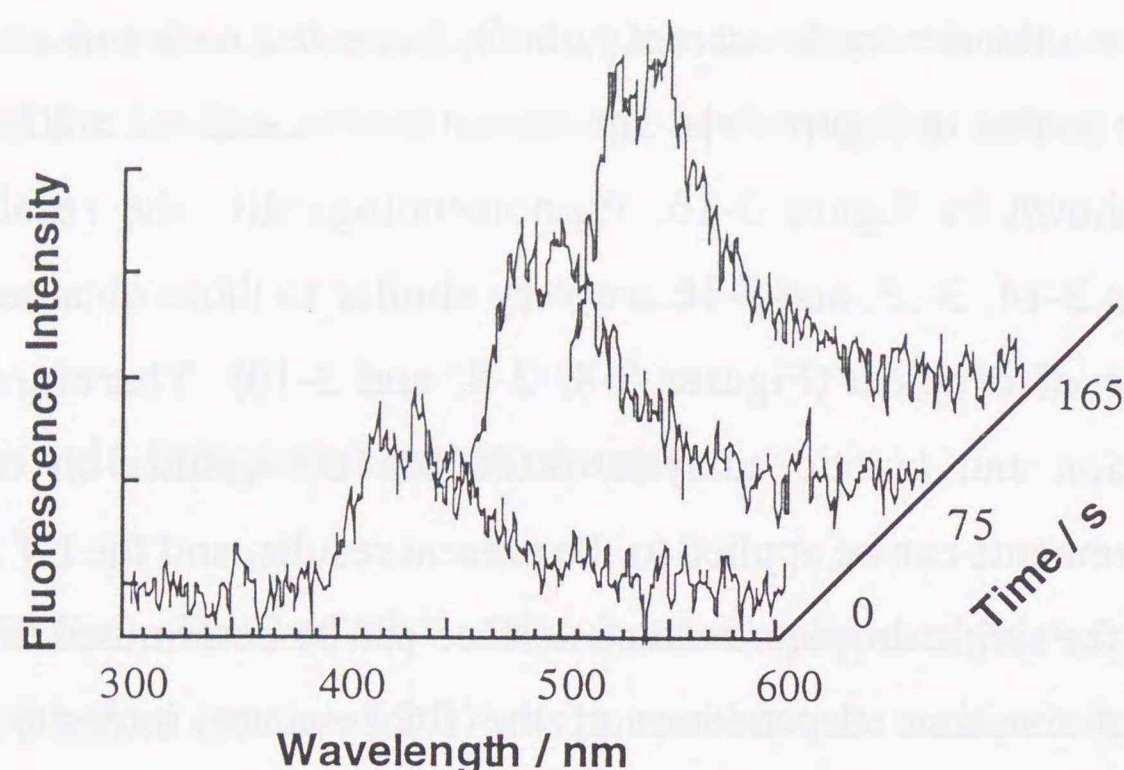


Figure 3-15. Time dependence of the fluorescence spectrum of DPA in a single droplet (excitation wavelength = 350 ~ 370 nm, $r = 17.0 \mu\text{m}$).

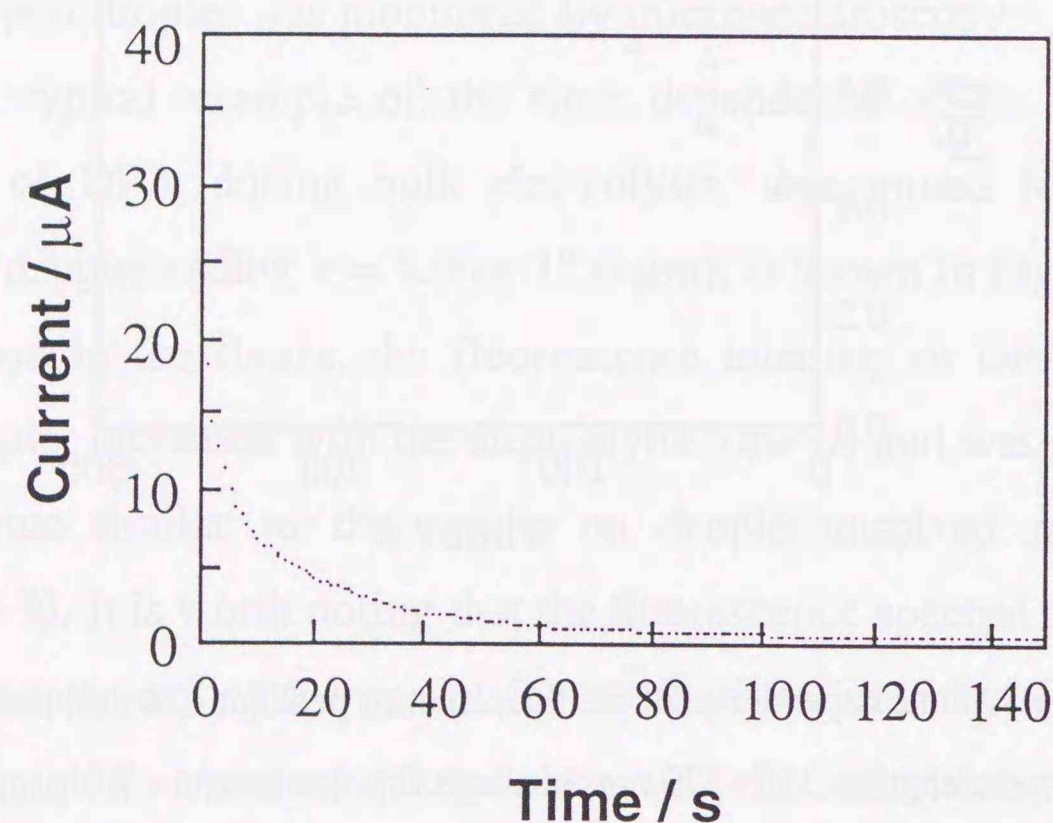


Figure 3-16. Time dependence of the electrode current at SnO_2 .

The time dependence of the $\ln\{I_F^0 / I_F(t) - 1\}$ value relevant to the data in Figure 3-14 is shown in Figure 3-17. At $t < 10$ s, $[\text{Fe}(\text{CN})_6^{3-}]_w$ does not reach a steady state value, so that the relevant data cannot be used for kinetic analysis as mentioned in section 3.3. At $t > 10$ s, however, $\ln\{I_F^0 / I_F(t) - 1\}$ decreased linearly with the electrolytic time, demonstrating that the rate determining step was the ET process across the droplet / water interface and the slope of the plot gave the ET rate constant. *The results prove that the fluorometric and coulometric methods can be applied for determining the ET rate across the individual microdroplet / water interface.* Furthermore, it is worth pointing out that the slope of the plot in Figure 3-17 is larger for the smaller droplet. *The droplet size dependence of the interfacial ET rate was demonstrated for the first time.*

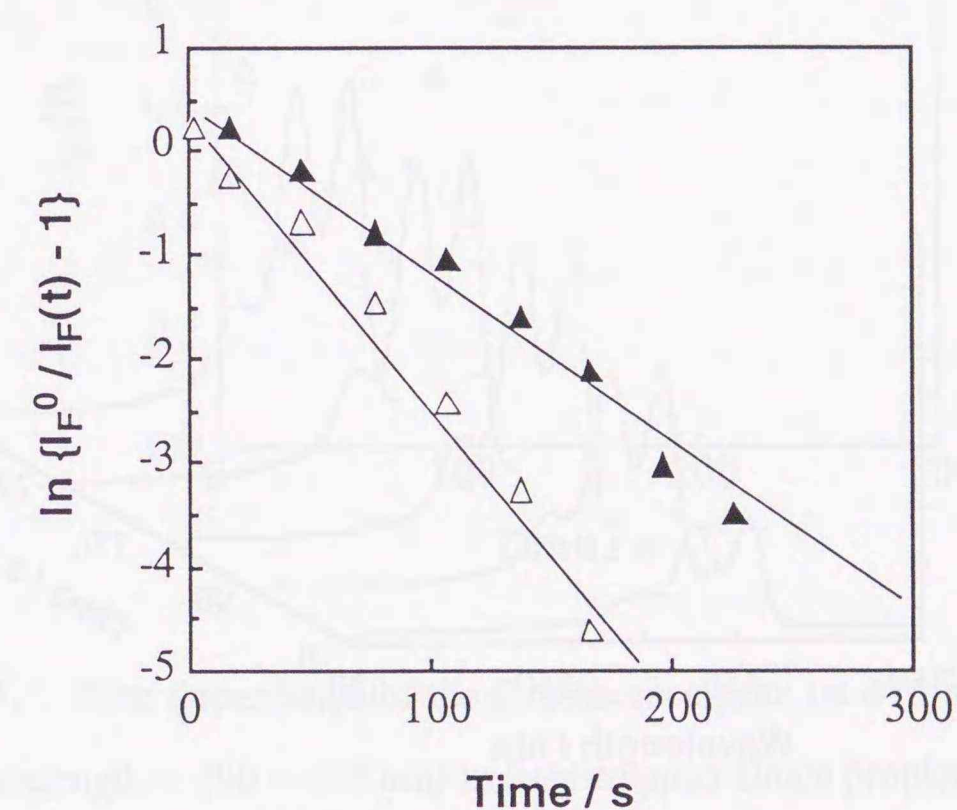


Figure 3-17. Time dependence of the fluorescence intensity in single droplets (Δ ; $r = 7.0 \mu\text{m}$, $\blacktriangle$; $r = 17.0 \mu\text{m}$). The data correspond to those in Figure 3-14.

Analogous single droplet measurements were conducted for the FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion, stabilized by an anionic (SDS) or nonionic surfactant (Triton- X100). The use of Pe as a fluorescence probe instead of using DPA was advantageous for measurements of the droplets smaller than $r = 5 \mu\text{m}$. Although the fluorescence quantum yield of DPA or Pe is ~ 1.0 , absorbance at the excitation wavelength (350 ~ 370 nm and 400 ~ 420 nm for DPA and Pe, respectively) is larger for Pe as compared with that for DPA. Therefore, Pe is excited more efficiently as compared to DPA, leading to more intense fluorescence intensity. Actually, the fluorescence spectra of Pe during electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ were obtained in good signal-to-noise ratios, as demonstrated in Figure 3-18.

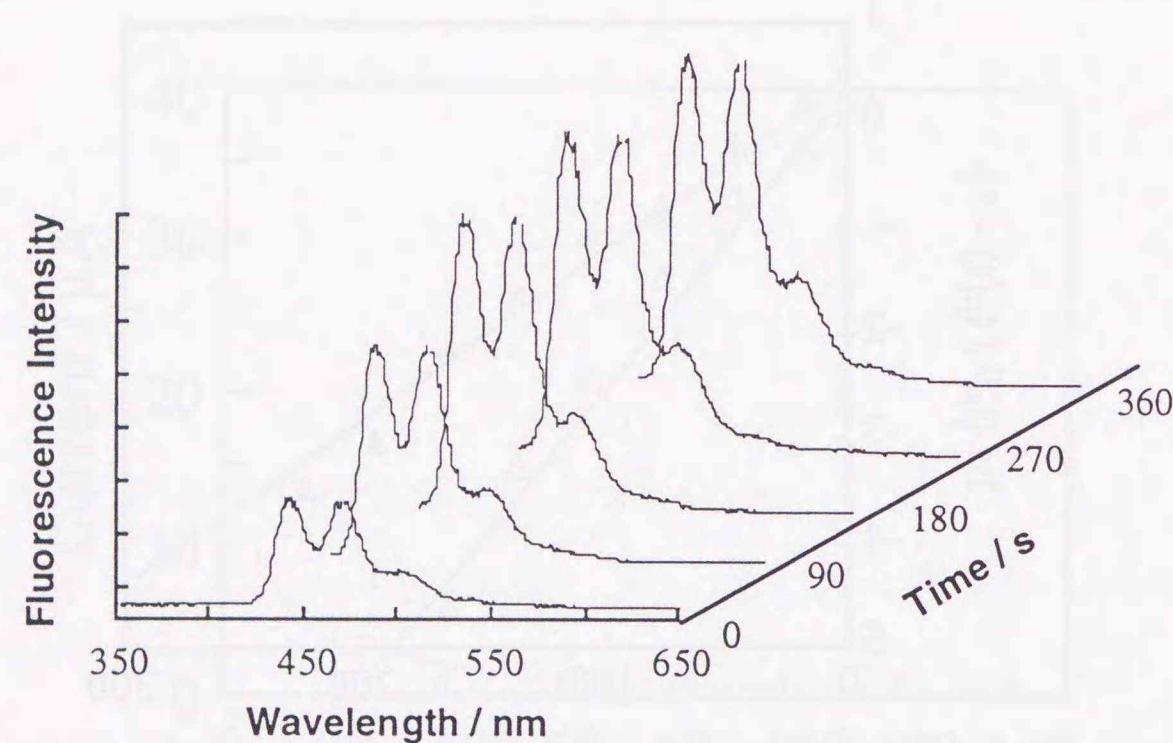


Figure 3-18. Time dependence of the fluorescence spectrum of Pe (excitation wavelength; 400 ~ 420 nm) in a laser trapped single droplet ($r = 9.5 \mu\text{m}$).

As a typical example, the time dependence of the fluorescence intensity in single droplets ($r = 1.2$ and $9.5 \mu\text{m}$) in the presence of SDS is shown in Figure 3-19. Figures 3-18 and 3-19 demonstrate that the fluorescence intensity of Pe in the droplet increases upon electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ without any change in the spectral band shape analogous to the results with using DPA. Thus, the $\ln\{I_F^0 / I_F(t) - 1\}$ value was plotted against the electrolytic time as shown in Figure 3-20.

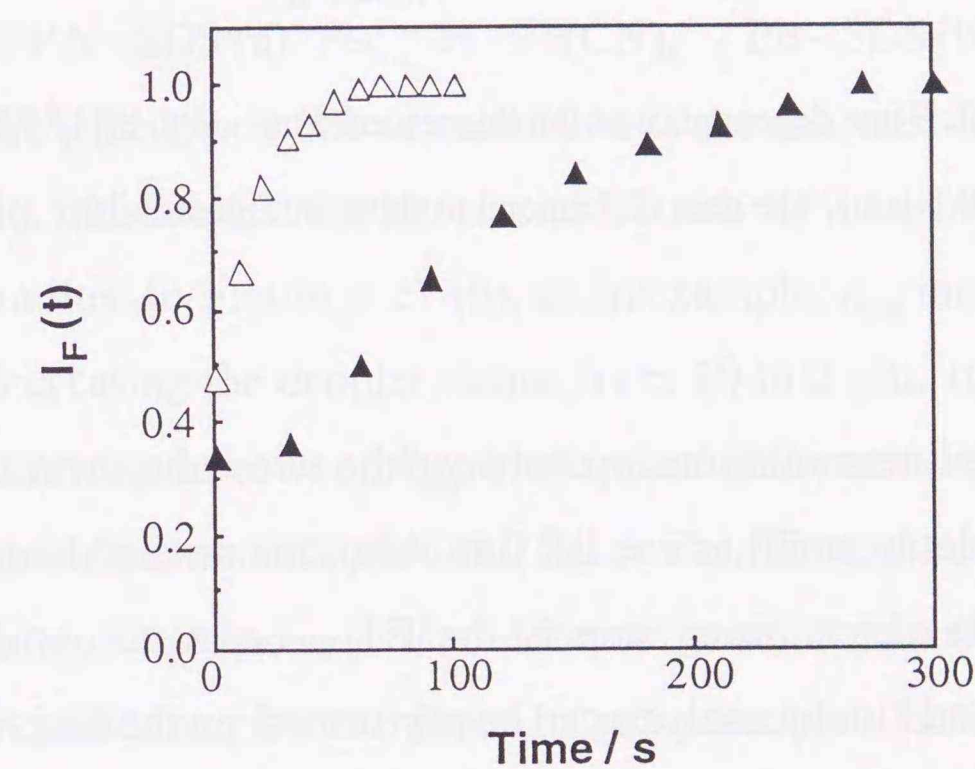


Figure 3-19. Time dependence of the fluorescence peak (at 470 nm) intensity of Pe (excitation wavelength = 400 ~ 420 nm) in laser-trapped single droplets (Δ ; $r = 1.2 \mu\text{m}$, $\blacktriangle$; $r = 9.5 \mu\text{m}$). The emulsion contains $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$ and $[\text{SDS}] = 1.2 \times 10^{-4} \text{ M}$. Other reactant concentrations are described in Section 3.2.1.

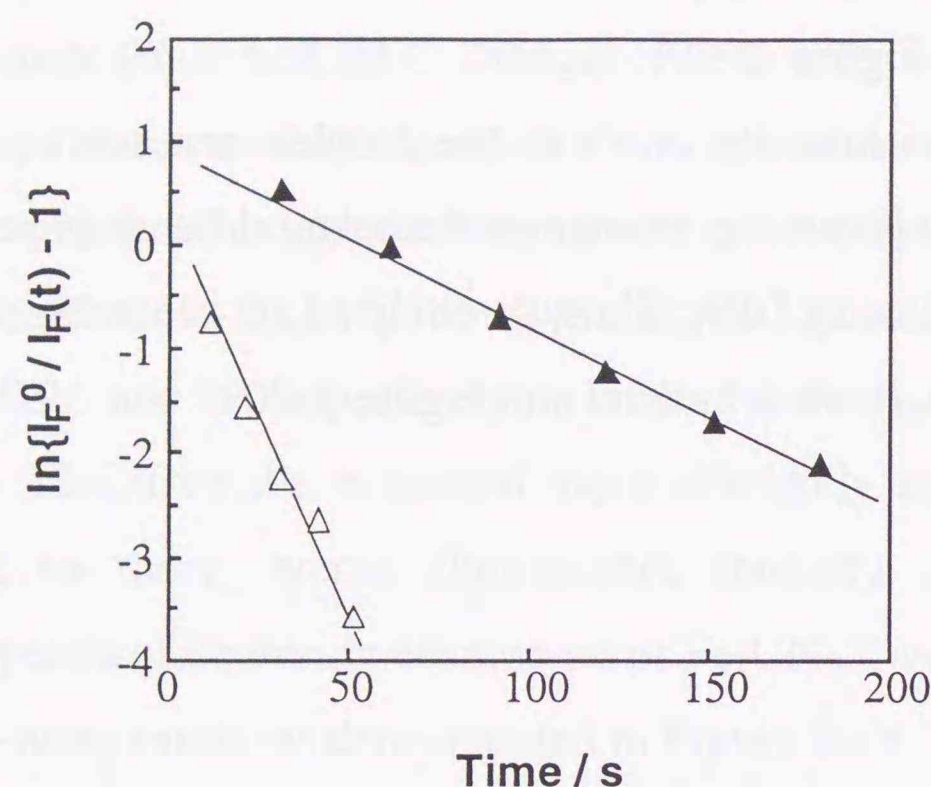


Figure 3-20. Time dependence of the fluorescence intensity: $\ln\{I_F^0 / I_F(t) - 1\}$ (Δ ; $r = 1.2 \mu\text{m}$, $\blacktriangle$; $r = 9.5 \mu\text{m}$). The data correspond to those in Figure 3-19.

The linear relationship between the two values was obtained for the single droplet as small as $r = 1.2 \mu\text{m}$. Also, the results demonstrate clearly that the rate determining step is the ET process across droplet / water interface, and kinetic analysis can be performed on the basis of the results in Figure 3-20 and eq.3-15. Furthermore, the droplet size effect on the interfacial ET rate was also observed, analogous to the DPA system. For the emulsion stabilized with a nonionic surfactant (Triton-X100), analogous results were obtained though the data are not shown here.

3.4.2 Analysis of Electron Transfer Rate.

It has been shown that the $\ln\{I_F^0 / I_F(t) - 1\}$ value is correlated linearly with the electrolytic time as typical examples have been shown in the preceding section. The slope of the $\ln\{I_F^0 / I_F(t) - 1\}$ vs. t plot represents the interfacial ET rate. The ET reaction can be thus discussed as a quasi-first order reaction, since $[\text{Fe}(\text{CN})_6^{3-}]_w$ is regarded as a constant value at $2.0 \times 10^{-4} \text{ M}$. Analogous experiments with those described in section 3.3 have been conducted for various-sized droplets under several conditions and the relevant rate constant (k_{obs}) was determined.

The droplet size dependence of k_{obs} determined for the FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA - SDS (a), FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe - SDS (b), or FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe - Triton-X 100 (c) emulsion is summarized in Figure 3-21. All the results indicate that the interfacial ET rate increases with decreasing the droplet radius. In Figure 3-21 (b), as an example, k_{obs} increases by a ~ 5 -fold with decreasing the droplet radius from 10 to $2 \mu\text{m}$. It is noteworthy that such a size dependence of k_{obs} is observed irrespective of nature of a surfactant and a fluorescence probe (DPA or Pe). Thus, the size dependence of k_{obs} is intrinsic nature of the electron transfer reaction across the spherical droplet / water interface. In macroscopic flat liquid / liquid interfacial systems, mass transfer of a solute to the interface proceeds in a linear fashion (linear diffusion), while the mass transfer process is governed by spherical diffusion in a droplet / water system. In the present system, therefore, mass transfer of $\text{Fe}(\text{CN})_6^{3-}$ from the water phase to the droplet surface becomes more efficient with decreasing the droplet radius, since the surface area (A) / volume (V) ratio of a droplet increases with decreasing r . In such a case, k_{obs} can be written as in eq.3-16,

$$k_{\text{obs}} = (A / V) k_{\text{ET}} \quad 3-16$$

where k_{ET} is the ET rate constant per unit surface area of a droplet ($k_{\text{ET}} / \text{cmM}^{-1}\text{s}^{-1}$). A and V are given by $4\pi r^2$ and $4\pi r^3/3$, respectively, so that eq.3-16 is rewritten as follows,

$$k_{\text{obs}} = (3 / r) k_{\text{ET}} \quad 3-17$$

This equation implies that k_{obs} should be proportional inversely to the droplet radius, when the A / V ratio governs the size dependence of k_{obs} .

The observed k_{obs} in Figure 3-21 (a), (b), or (c) was thus plotted against the relevant r^{-1} value, as shown in Figure 3-22.

As clearly seen in Figure 3-22, k_{obs} was a linear function of r^{-1} ($r > \sim 1 \mu\text{m}$). Thus, it is concluded that *the droplet size dependence of k_{obs} can be explained by the change in the A / V ratio with r .* Assuming $[\text{Fe}(\text{CN})_6^{3-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$, k_{ET} can be calculated by the slope of the k_{obs} vs. r^{-1} plot and the results are summarized in Figure 3-23. In the FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion, k_{ET} was determined to be $\sim 0.02 \text{ cmM}^{-1}\text{s}^{-1}$. This is the first demonstration for determination of the interfacial ET rate constant per surface area of a droplet.

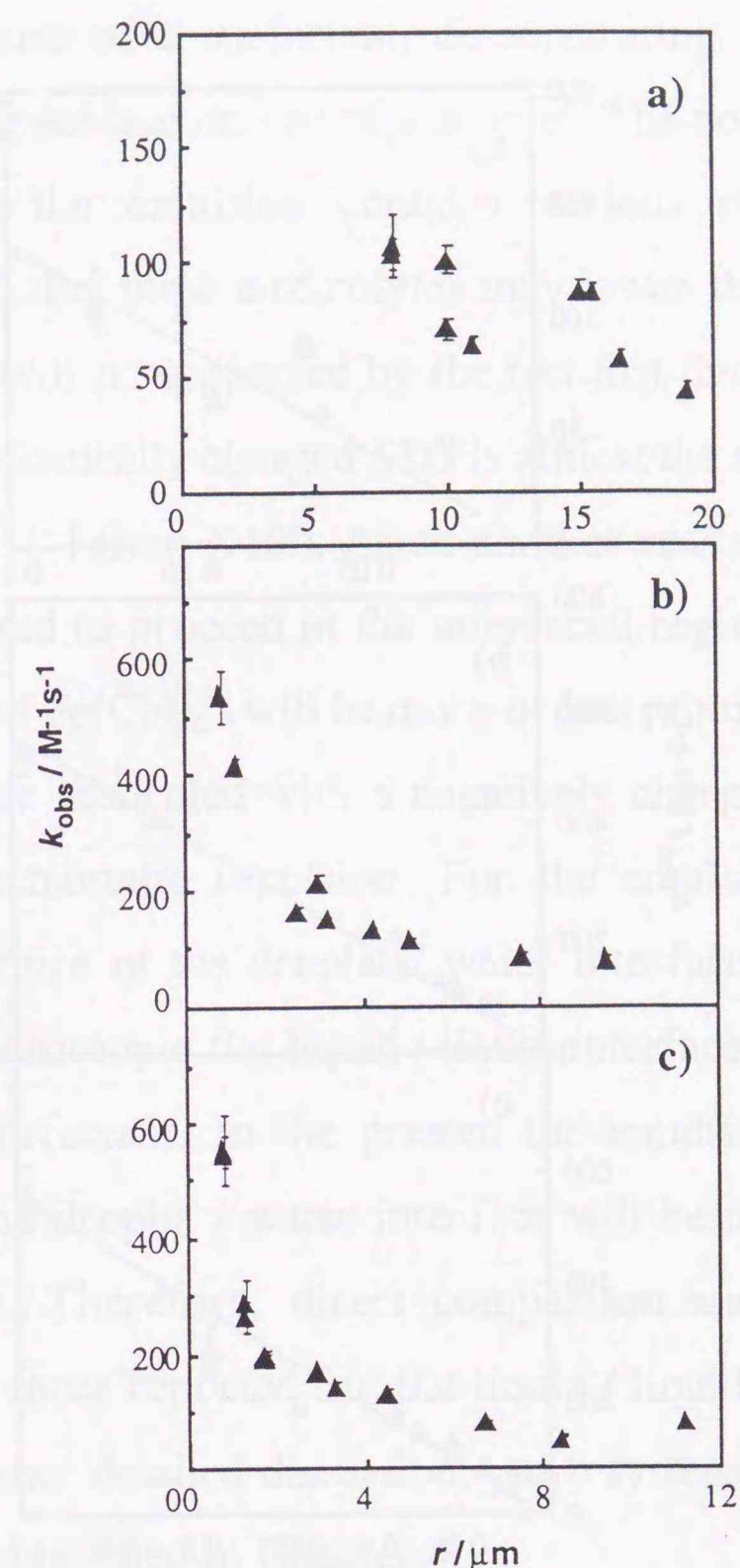


Figure 3-21. The droplet size dependence of k_{obs} (a; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA emulsion in the presence of SDS ($1.0 \times 10^{-3} \text{ M}$), b; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion in the presence of SDS ($1.2 \times 10^{-4} \text{ M}$), c; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion in the presence of Triton-X100 ($1.2 \times 10^{-4} \text{ M}$)).

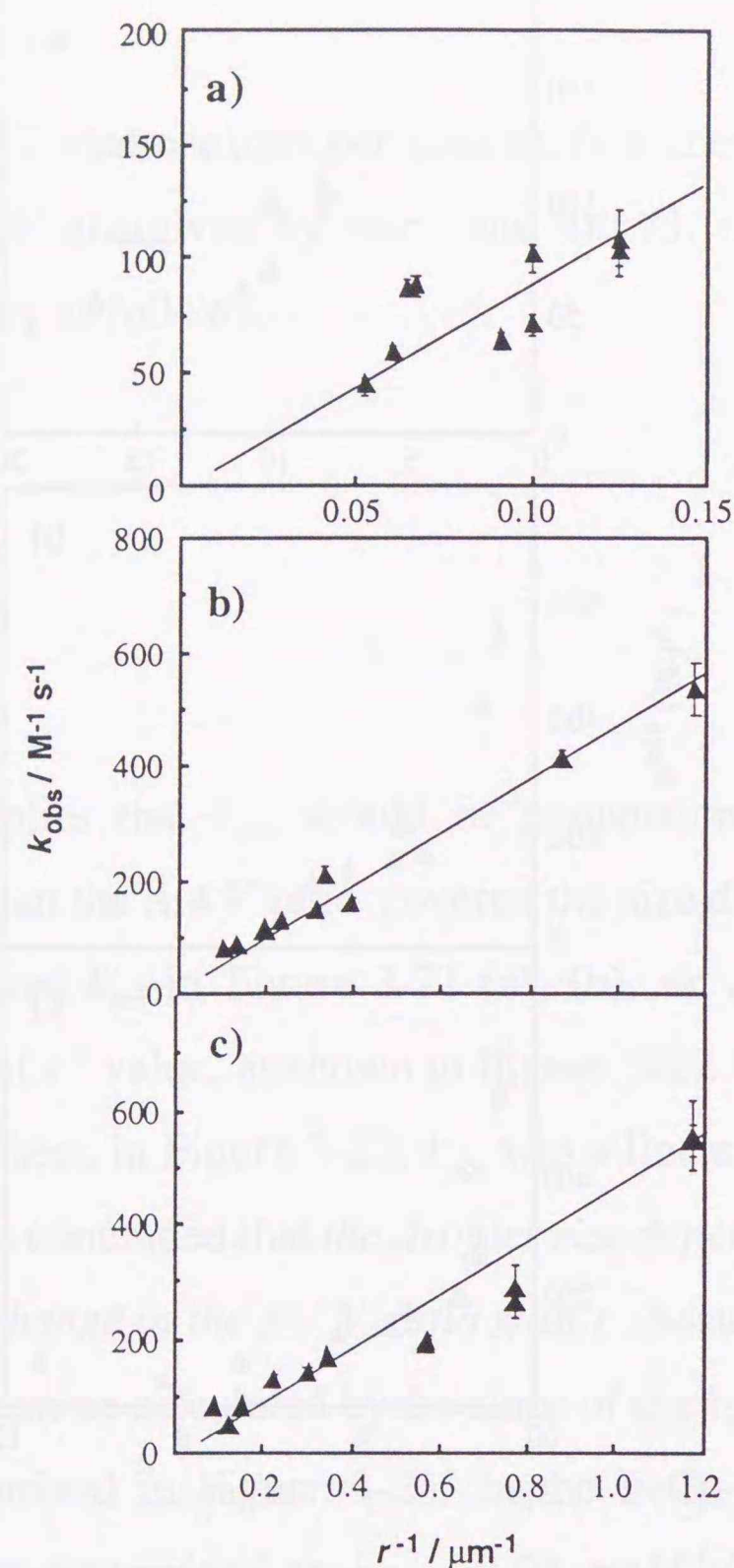


Figure 3-22. The surface area / volume ratio dependence of k_{obs} (a; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - DPA emulsion in the presence of SDS, b; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion in the presence of SDS, c; FeCp-H - $\text{Fe}(\text{CN})_6^{4-}$ - Pe emulsion in the presence of Triton-X100. These data correspond to those in Figure 3-21 a), b), and c), respectively).

It is worth pointing out that k_{ET} is almost constant at $\sim 0.02 \text{ cmM}^{-1}\text{s}^{-1}$, regardless of nature of a surfactant, demonstrating that the ET rate is independent of the surface charge of a droplet. The possible reasons are as follows. Firstly, the emulsion contains various electrolytes at high concentrations, so that these electrolytes may lower the surface charge of the droplet. This will be supported by the fact that the ET rate constant in the presence of anionically charged SDS is almost the same with that in the presence of neutral Triton-X100. As another reason, secondly, the ET reaction is supposed to proceed in the interfacial region of a droplet. The negatively charged $\text{Fe}(\text{CN})_6^{3-}$ will be more or less prohibited to approach to the droplet surface adsorbed with a negatively charged surfactant (SDS) owing to the electrostatic repulsion. For the emulsions studied in this chapter, the structure of the droplet / water interface might be different from that at a macroscopic flat liquid / liquid interface, since the droplet is stabilized by a surfactant. In the present emulsion systems, the ET reaction across the droplet / water interface will be influenced by such a surface structure. Therefore, direct comparison and discussion of the present data with those reported for flat liquid / liquid interfaces might be difficult. For further detailed discussion, more systematic experiments are needed, which is described in Chapter 4.

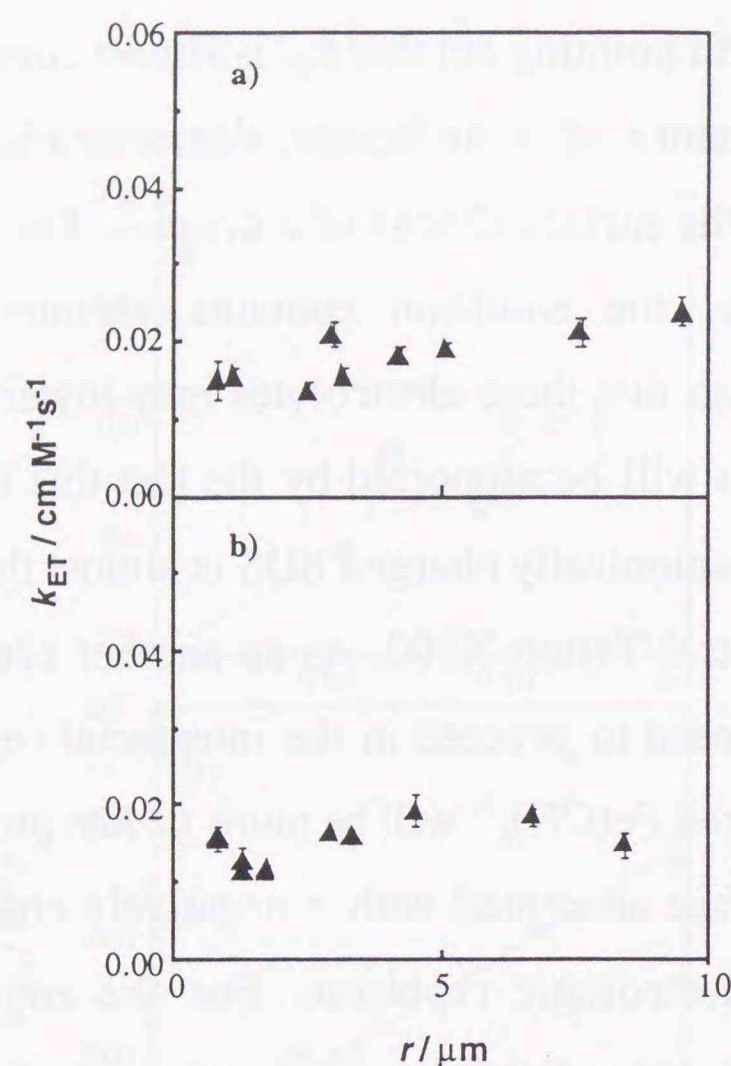


Figure 3-23. The droplet size dependence of k_{ET} . (a; FeCp-H - $Fe(CN)_6^{4-}$ - Pe emulsion in the presence of SDS, b; FeCp-H - $Fe(CN)_6^{4-}$ - Pe emulsion in the presence of Triton-X100, these data correspond to those in Figure 3-22 a) and b), respectively).

3.5 Conclusion.

The rate determining step and the ET rate across the droplet / water interface in the oil-in-water emulsion were determined by the coulometric and fluorometric measurements. Also, the methodology was successfully applied to determining the interfacial ET rate for individual microdroplets with $r \sim 1 \mu m$. Clearly, such experiments are made possible only by the laser trapping - spectroscopy - electrochemistry method. As the most important results, it was shown that the interfacial ET rate constant (k_{obs}) was dependent on the droplet size and increased with decreasing r . This was

explained satisfactorily in terms of the change in the droplet surface area / volume ratio of a droplet. The size dependence of k_{obs} was demonstrated experimentally for the first time. On the basis of the analysis of the size dependence of k_{obs} , the ET rate constant per unit area (k_{ET}) was determined experimentally.

The present study indicated that interfacial ET reactions in an oil-in-water or water-in-oil emulsion system must be discussed on the basis for individual droplet measurements. Thus, the laser trapping - spectroscopy - electrochemistry method is the indispensable basis for studying the chemistry in emulsion systems.

3.6 References.

- 1) Z.Samec and V.Marecek, *J.Electroanal.Chem.*, **103**,11 (1979).
- 2) J.Hanzlik, J.Hovolka, Z.Samec and S.Toma, *Coll.Czech.Chem.Comm.*, **53**,903 (1987).
- 3) G.Geblewicz and D.J.Schiffrin, *J.Electroanal.Chem.*, **244**,27 (1988).
- 4) V.J.Cunnane, D.J.Schiffrin, C.Beltran, G.Geblewicz and T.Solomon, *J.Electroanal.Chem.*, **247**,203 (1988).
- 5) Y.Cheng and D.J.Schiffrin, *J.Electroanal.Chem.*, **314**,153 (1991).
- 6) S.Kihara, M.Suzuki, K.Maeda, K.Ogura, M.Matsui and Z.Yoshida, *J.Electroanal.Chem.*, **271**,107 (1989).
- 7) Y.Cheng and D.J.Schiffrin, *J.Chem.Soc.Faraday Trans.*, **89**,199 (1993).
- 8) V.J.Cunnane, G.Geblewicz and D.J.Schiffrin, *Electrochim.Acta*, **40**,3005 (1995).
- 9) C.Wei, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **99**,16033 (1995).

- 10) M.Tsionski, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **100**,17881 (1996).
- 11) M.Tsionski, A.J.Bard and M.V.Mirkin, *J.Am.Chem.Soc.*, **119**,10785 (1997).
- 12) A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York (1980).
- 13) K.Nakatani, T.Uchida, H.Misawa, N.Kitamura and H.Masuhara, *J.Phys.Chem.*, **97**,5197 (1993).
- 14) S.A.Myers, R.A.Mackay and A.B.Toth, *Anal.Chem.*, **65**,3447,(1993).
- 15) J.Koryta and P.Vanysek, In *Advances in Electrochemistry and Electrochemical Engineering* , ed by H.Gerischer and C.W.Tobias, John Wiley & Sons, New York, vol. 12, p. 113 (1981).
- 16) V.E.Kazarinov, *The Interface Structure and Electrochemical Processes at the Boundary Between Two Immiscible Liquids* , Springer-Verlag, Berlin (1987).
- 17) H.H.Girault and D. J. Schiffrin, In *Electroanalytical Chemistry* ed by A.J.Bard and Marcel Dekker, New York, vol. 15, Chap. 1 (1989).
- 18) H.H.Girault, In *Modern Aspects of Electrochemistry*, ed by R.E.White, B.E.Conway and J.O.Bockris, New York, vol. 25, p. 1 (1993).
- 19) Z.Samec and T.Kakiuchi, In *Advances in Electrochemistry and Electrochemical Science*, ed by H.Gerischer and C.W.Tobias, VCH, Weinheim, vol. 4 (1995).
- 20) A.G.Volkov and D.W.Deamer, *Liquid-Liquid Interfaces*, CRC Press, Boca Raton (1996).
- 21) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York (1970).

Chapter 4

Droplet Size and Liquid-Junction Potential Effects on Interfacial Electron Transfer Rate

4.1 Introduction.

In Chapter 3, it was shown that the ET reaction rate across the single microdroplet / water interface could be determined by the coulometric and fluorometric methods. Also, it was found that the interfacial ET rate was governed by the surface area / volume (A / V) ratio of the droplet. Besides the A / V ratio, the ET rate is expected to be governed by other factors. For the liquid / liquid interfacial ET, it has been reported that the rate is dependent on the liquid-junction potential^{1,2}. Therefore, this should be discussed in detail for the present system. Nonetheless, the emulsions studied in Chapter 3 involve a surfactant, so that detailed discussions on the liquid-junction potential dependence of the ET rate were difficult. Thus, analogous studies on emulsions without a surfactant are required to reveal the interfacial ET. Furthermore, although the droplet size studied in Chapter 3 was limited to $r > 5 \mu\text{m}$, another characteristic droplet size effect on the ET rate might be observed for smaller droplets with $r < 5 \mu\text{m}$, since the structures and properties of the droplet / water interface are expected to be varied with r . In addition to these problems, it is known that FeCp-H^+ produced upon the interfacial ET in an oil phase takes place ion transfer to the surrounding water phase. Thus, this might also influence the observed interfacial ET rate value. Clearly, these points must be clarified experimentally.

In this chapter, the liquid-junction potential and droplet size effects on the ET rate across the single microdroplet / water interface are discussed in detail. Also, several ferrocene derivatives (FeCp-X) having a different ion transfer potential were used instead of FeCp-H to elucidate the ion transfer effect on the ET rate.

4.2 Experimental.

4.2.1 Sample Preparation.

Dimethylferrocene (FeCp-DM; Aldrich Chemical Co., Inc., GR grade), Decamethylferrocene (FeCp-DCM; Aldrich Chemical Co., Inc., 99+%), and LiCl (Wako Pure Chemical Industries Ltd., GR grade) were recrystallized from methanol. Purifications of other reagents were described in Chapter 3.

As an oil phase, FeCp-H (5.0×10^{-2} M) and a fluorescence probe (DPA, 1.0×10^{-2} M or Pe, 5.0×10^{-4} M) were dissolved in water-saturated TBP together with TBA⁺TPB⁻ (1.0×10^{-2} M). As described in Chapter 3, absorbance of Pe at the excitation wavelength (400 ~ 420 nm) is larger than that of DPA (350 ~ 370 nm) under the present conditions, so that more intense fluorescence spectra can be obtained for Pe. Thus, the use of Pe as a fluorescence probe is very favorable for studying small droplets with $r < 5$ μm . Besides FeCp-H, furthermore, FeCp-DM (4.0×10^{-2} M) and FeCp-DCM (2.0×10^{-2} M) were used as an electron donor in the oil phase. As a water phase, K₄Fe(CN)₆ (2.0×10^{-4} M), MgSO₄ (1.0×10^{-1} M), and TBA⁺Cl⁻ (1.0×10^{-1} , 1.0×10^{-2} , or 1.0×10^{-3} M) were dissolved in TBP-saturated water. The TBP solution was dispersed in the aqueous solution at the weight

ratio of TBP / water = 1 / 500. In the emulsion, the droplet size was distributed in the range of 0.1 ~ 40 μm in diameter as long as observation was made under an optical microscope. The sample emulsion was deaerated by purging a N₂ gas stream prior to the measurements to prevent oxidation of Fe(CN)₆⁴⁻ and photodecomposition of DPA or Pe.

4.2.2 Optimization of the Experimental Conditions.

The experimental conditions employed in the present study are the same with those described in Chapter 3. However, variations of FeCp-X, an electrolyte concentration, and so forth might influence experimental conditions. Thus, spectroscopic and electrochemical conditions were checked prior to the experiments, as described below.

i) Spectroscopic Condition.

The spectroscopic conditions for measuring the fluorescence spectrum of DPA or Pe were described in Chapter 3. Also, it was shown that absorption of an excitation light beam by Fe(CN)₆⁴⁻ or Fe(CN)₆³⁻ was negligible in the thin-layer electrode cell (gap ~ 70 μm). In order to check absorption effects by FeCp-X, furthermore, the absorption spectra of FeCp-DM and FeCp-DCM in TBP were measured as the results were shown in Figures 4-1 and 4-2, respectively.

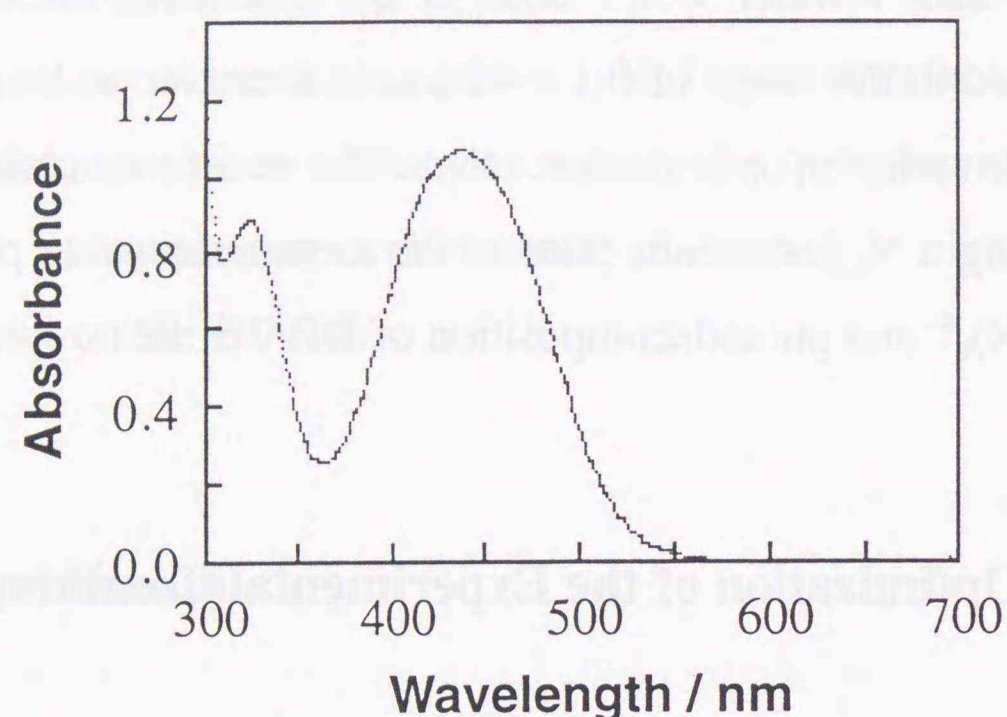


Figure 4-1. The absorption spectrum of FeCp-DM (1.0×10^{-2} M) in TBP determined in a quartz cuvette (optical path length = 10 mm).

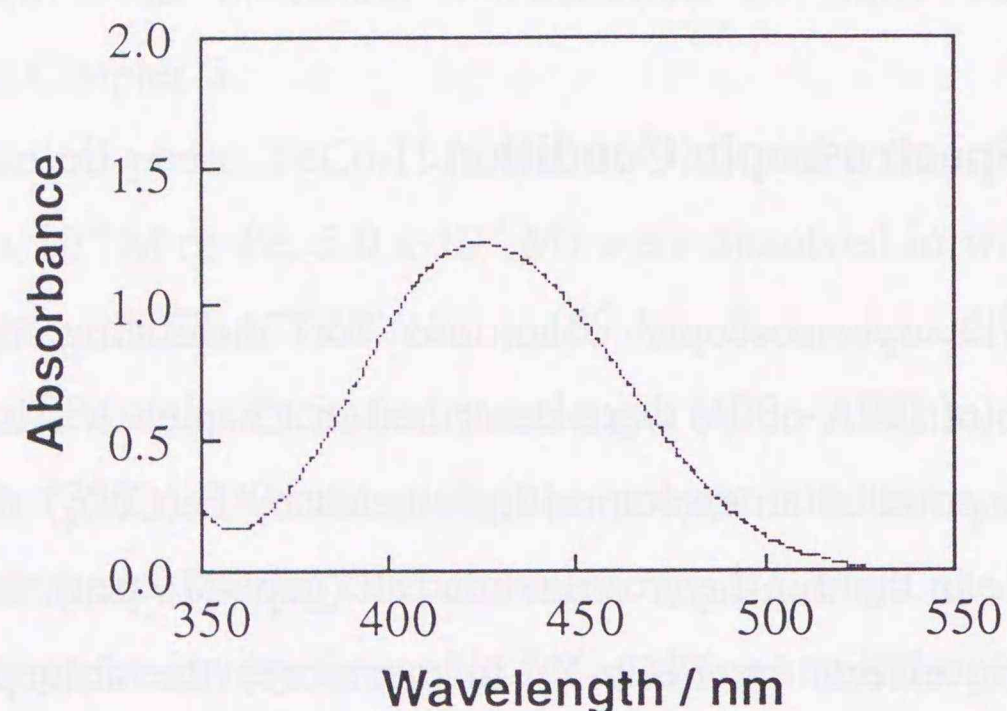


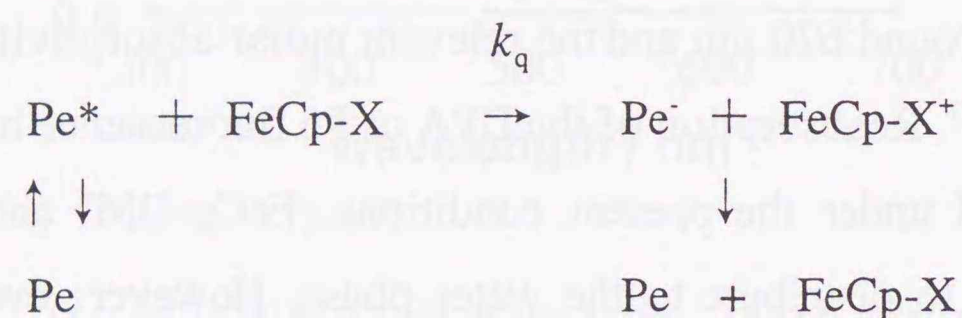
Figure 4-2. The absorption spectrum of FeCp-DCM (1.0×10^{-2} M) in TBP determined in a quartz cuvette (optical path length = 10 mm).

FeCp-DM exhibited the absorption peaks at 324 ($\epsilon_{324} = 88 \text{ M}^{-1}\text{cm}^{-1}$) and 436 nm ($\epsilon_{436} = 105 \text{ M}^{-1}\text{cm}^{-1}$), while FeCp-DCM showed the peak at 425 nm ($\epsilon_{425} = 122 \text{ M}^{-1}\text{cm}^{-1}$). Since absorbance of FeCp-X at the excitation wavelength in a micrometer sized droplet is very small (absorbance < 0.05), absorption of an excitation light beam by FeCp-X does not influence the fluorescence measurements. Although the data are not presented here, the absorption peak wavelength of FeCp-DM⁺ or FeCp-DCM⁺ in a TBP droplet was at around 620 nm and the relevant molar absorptivity was below $\sim 400 \text{ M}^{-1}\text{cm}^{-1}$ ⁴⁾. Reabsorption of the DPA or Pe fluorescence by FeCp-X⁺ was not observed under the present conditions. FeCp-DM⁺ and FeCp-DCM⁺ are unlikely to distribute to the water phase. However, even if these species distribute to the water phase, absorption of the fluorescence of DPA or Pe by FeCp-X⁺ in the water phase does not disturb the experiments, since the absorption wavelength of the ion is above 600 nm and the molar absorptivity is very small ($\sim 400 \text{ M}^{-1}\text{cm}^{-1}$) in the thin-layer electrode cell. Furthermore, complex formation between TBA⁺TPB⁻ and FeCp-X, DPA or Pe does not take place in the present system as confirmed by the fact that the shape of the absorption spectrum of FeCp-X, DPA or Pe was identical to that in the presence of TBA⁺TPB⁻.

ii) Fluorescence Lifetime.

Fluorescence quenching of Pe by FeCp-X in a droplet takes place via the following reaction scheme. In order to evaluate the interfacial ET rate, one must know the fluorescence quenching rate constant (k_q) of Pe by FeCp-X. Thus, fluorescence lifetime measurements of Pe in the presence and absence of FeCp-X were conducted on the basis of a single photon

counting method. The concentration of Pe in TBP was set 2.0×10^{-5} M, while the quencher concentration was set 5.0×10^{-2} (FeCp-H), 4.0×10^{-2} (FeCp-DM), or 2.0×10^{-2} M (FeCp-DCM). The experiments were conducted using a thin-layer cell (optical path length = ~ 100 μ m). Under the condition, reabsorption of the Pe fluorescence by Pe itself or FeCp-X was not observed.



The observed fluorescence decay curves were shown in Figure 4-3. The decay curve of Pe in the presence of FeCp-H or FeCp-DM was analyzed by a double exponential function and its averaged fluorescence lifetime at each $[\text{FeCp-X}]_{\text{TBP}}$ was determined, while that in the presence of FeCp-DCM was analyzed by a single exponential function. TBP is a highly viscous solvent and the concentration of FeCp-H or FeCp-DM is high. These will be a possible reason for a non-single exponential decay of Pe in the FeCp-H and FeCp-DM systems.

The fluorescence lifetime of Pe without FeCp-X was determined to be 4.72 ns ($= \tau_0$), while that in the presence of FeCp-H, FeCp-DM, or FeCp-DCM was 1.27, 1.55, or 2.79 ns, respectively. These values gave the fluorescence quenching rate constant (k_q) to be 1.15×10^{10} (with FeCp-H), 1.08×10^{10} (with FeCp-DM), or $7.33 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (with FeCp-DCM).

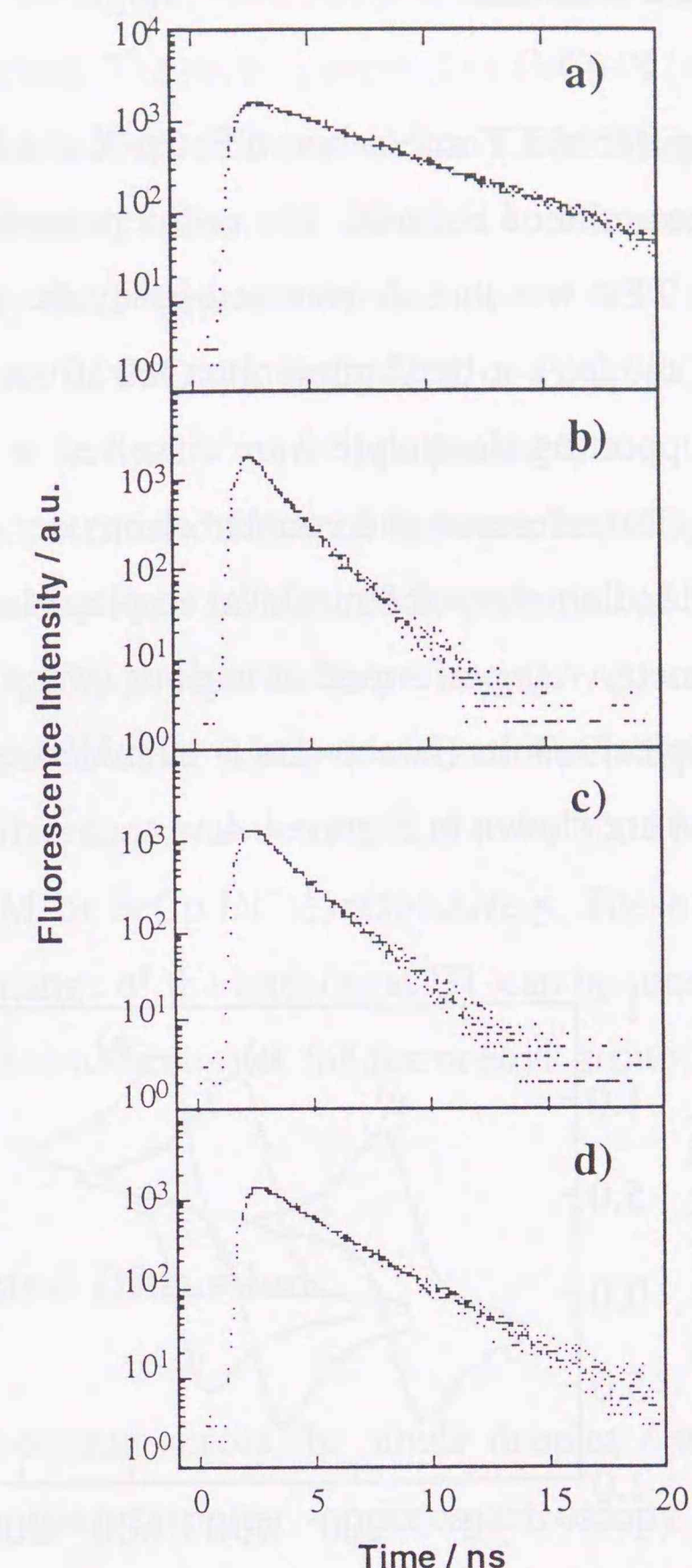


Figure 4-3. Fluorescence decay curves of Pe ($[\text{Pe}]_{\text{TBP}} = 2.0 \times 10^{-5}$ M, a; in the absence of FeCp-X, b; $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2}$ M, c; $[\text{FeCp-DM}]_{\text{TBP}} = 4.0 \times 10^{-2}$ M, d; $[\text{FeCp-DCM}]_{\text{TBP}} = 2.0 \times 10^{-2}$ M, excitation wavelength = 420 nm, monitoring wavelength = 470 nm).

iii) Redox Potential.

The interfacial ET rate between FeCp-X and $\text{Fe}(\text{CN})_6^{3-}$ is dependent on the redox potential of FeCp-X. The redox potential of FeCp-X (X = H, DM, DCM) in TBP was thus determined by cyclic voltammetry. FeCp-X (1.0×10^{-3} M) and tetra-n-butylammonium tetrafluoroborate (TBA^+TFB^- ; 0.10 M) as a supporting electrolyte were dissolved in TBP. Ag and Pt wires were used as quasi-reference and counter electrodes, respectively, while a Pt disk electrode (diameter = 0.8 mm) was employed as a working electrode. Cyclic voltammetry was performed at various sweep rates (90, 40, 10, and 5 mV/s) and typical results (sweep rate = 10 mV/s) on FeCp-H, FeCp-DM, and FeCp-DCM are shown in Figure 4-4.

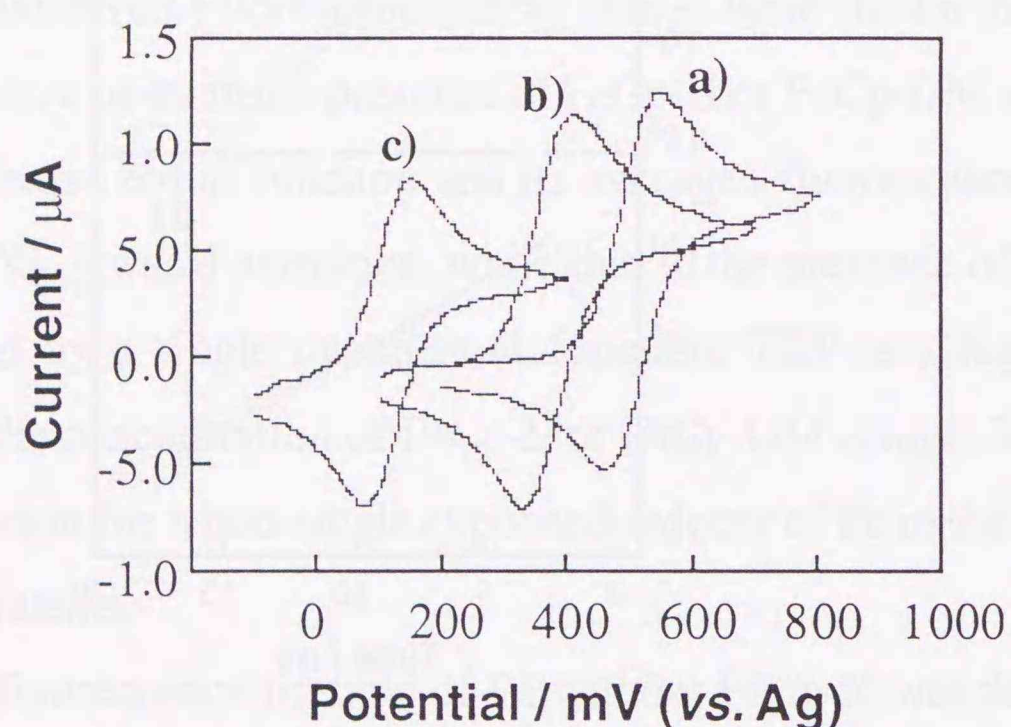


Figure 4-4. Cyclic voltammograms of FeCp-X (1.0×10^{-3} M) in TBP (a; FeCp-H, b; FeCp-DM, c; FeCp-DCM) at sweep rate = 10 mV/s.

As seen in the figure, each FeCp-X derivative exhibited a reversible cyclic voltammogram. The redox potential of FeCp-X (vs. Ag) in TBP was thus determined to be 506, 370, or 113 mV for FeCp-H, FeCp-DM, or FeCp-DCM, respectively. Also, the diffusion coefficient of FeCp-X in TBP was determined by the sweep rate dependence of the voltammogram. The diffusion coefficient of FeCp-H, FeCp-DM, or FeCp-DCM in TBP was 3.7×10^{-6} , 3.5×10^{-6} , or $1.9 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$, respectively.

The redox potential difference between $\text{Fe}(\text{CN})_6^{3-}$ and FeCp-X was then calculated on the basis of the redox potential of $\text{Fe}(\text{CN})_6^{3-}$ in water (determined vs. Ag by a separate experiment). As a reference, a water soluble ferrocene derivative (FeCp-MeOH or FeCp-EtOH) was used. The redox potential difference was determined to be 30, 166, and 423 mV for FeCp-H, FeCp-DM, or FeCp-DCM, respectively. These results indicate that the free energy change of the interfacial ET can be tuned by ~ 400 mV by the choice of the substituent(s) of the ferrocenyl group.

4.3 Results and Discussion.

The ET reaction across the single droplet / water interface was measured by the laser trapping - microspectroscopy - electrochemistry technique. As described in Chapter 3, the bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in the water phase induces the interfacial ET reaction, and the time course of the ET reaction can be followed by that of the fluorescence intensity of DPA or Pe in the droplet. In this section, the experimental results on several reaction systems (variation of FeCp-X, fluorescence probe, or electrolyte concentration) are described.

4.3.1 Interfacial Electron Transfer in the FeCp-H / Fe(CN)₆³⁻ System.

i) Surface Area / Volume Ratio Effects on Interfacial Electron Transfer Rate.

Single TBP droplets containing FeCp-H were laser trapped and positioned above a working SnO₂ electrode without direct contact. All of the Fe(CN)₆⁴⁻ molecules in the water phase was oxidized during the first 10 s by a potential step method (at 800 mV vs. Ag/AgCl) to induce the interfacial ET reaction between FeCp-H in the droplet and Fe(CN)₆³⁻ in the water phase.

The amount of Fe(CN)₆³⁻ produced by bulk electrolysis is two times larger than that of FeCp-H in the droplets, so that the reaction proceeds via a pseudo-first order kinetics. As described in Chapter 3, DPA or Pe acts as a fluorescence probe for the ET reaction. The fluorescence is quenched by FeCp-H in the droplet, but not by FeCp-H⁺ produced by the ET reaction. Therefore, the time dependence of the concentration of FeCp-H can be followed by that of the fluorescence intensity of DPA during the electrolysis.

A typical example of the time dependence of the fluorescence spectrum of DPA in a single TBP droplet ($r = 14.5 \mu\text{m}$) is shown in Figure 4-5. As clearly seen in the figure, the fluorescence intensity of DPA increased with an electrolytic time (t) without any change in the spectral band shape. The time dependence of the fluorescence intensity at the peak position (428 nm) observed for a single droplet with r of 7.5 or 14.5 μm is shown in Figure 4-6. The fluorescence intensity increased with the electrolytic time and reached a constant value at $t \sim 100$ s. As in the case of

data analysis described in Chapter 3, $\ln\{I_F^0 / I_F(t) - 1\}$ was then plotted against t as shown in Figure 4-7. The $\ln\{I_F^0 / I_F(t) - 1\}$ value showed a linear relation with t , demonstrating that the rate determining step was the ET process across the droplet / water interface.

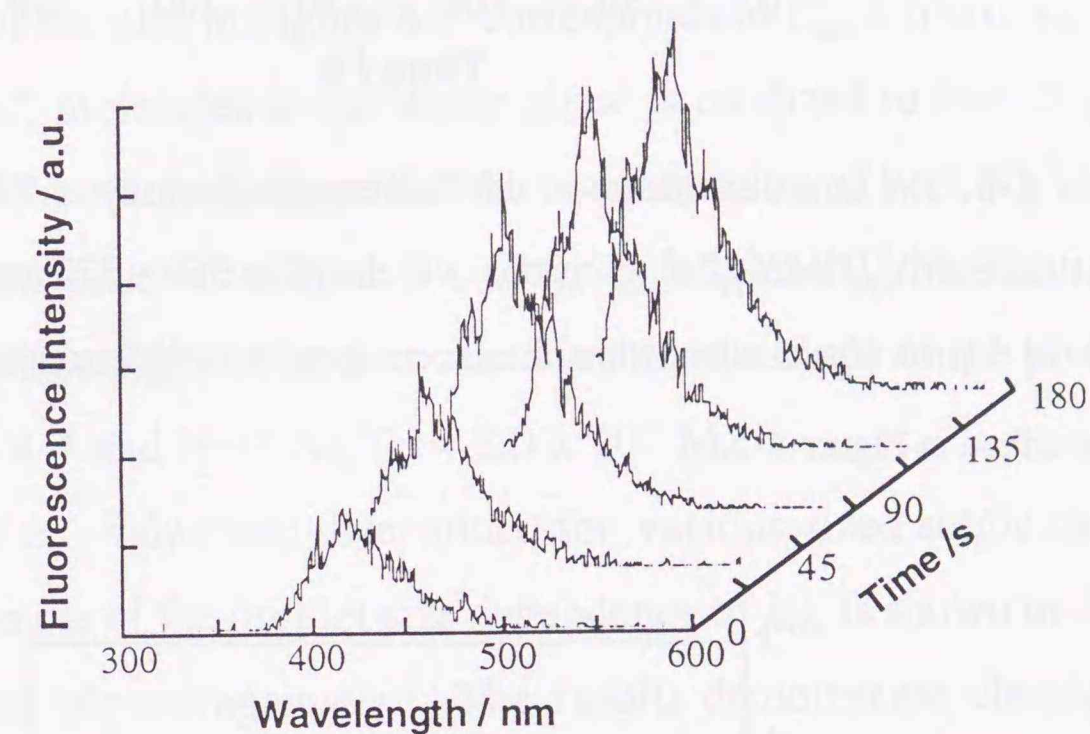


Figure 4-5. The time dependence of the DPA fluorescence spectrum in a single TBP droplet ($r = 14.5 \mu\text{m}$, excitation wavelength = 350 ~ 370 nm, $[\text{DPA}]_{\text{TBP}} = 1.0 \times 10^{-2}$ M, $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2}$ M, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2}$ M, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-2}$ M ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0$), $[\text{MgSO}_4]_{\text{w}} = 0.1$ M and $[\text{Fe(CN)}_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4}$ M) in the absence of a surfactant.

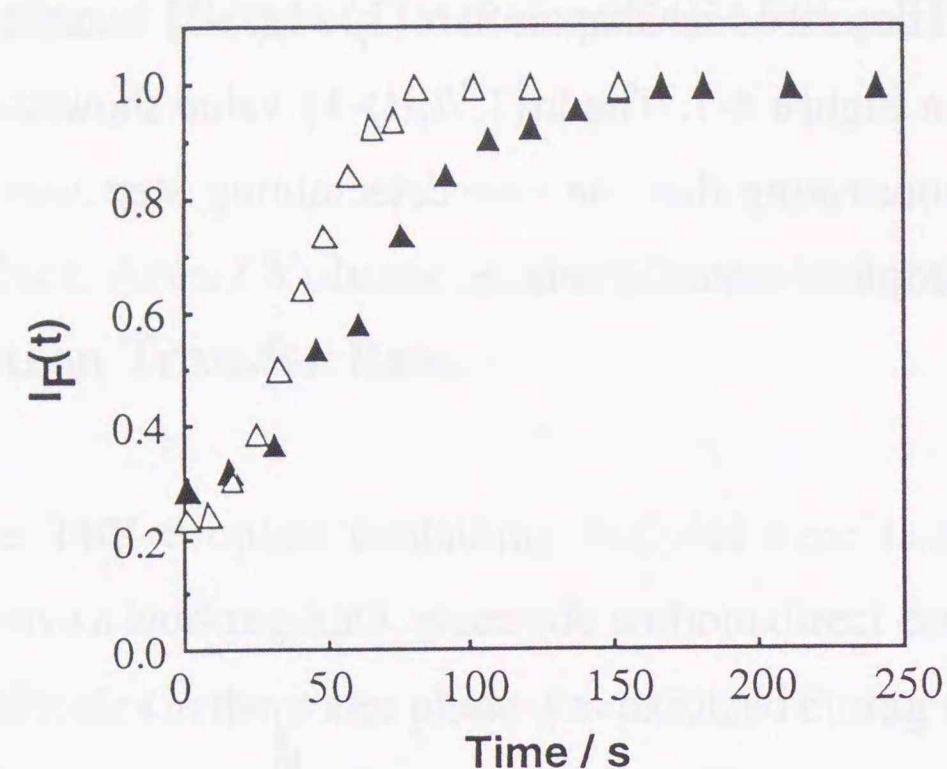


Figure 4-6. The time dependence of the fluorescence intensity of DPA (at 428 nm) in single droplets ($\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$, excitation wavelength = 350 ~ 370 nm, $\triangle$; $r = 7.5 \mu\text{m}$, $\blacktriangle$; $r = 14.5 \mu\text{m}$). The concentration of each component in the emulsion is the same with that described in Figure 4-5.

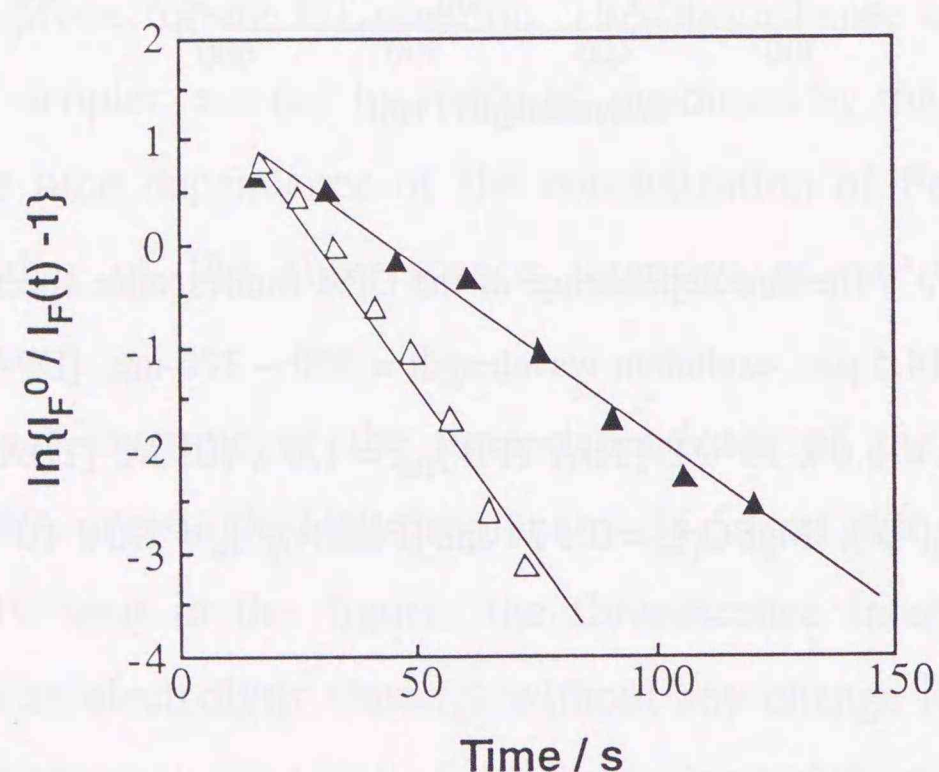


Figure 4-7. The time dependence of $\ln\{I_F^0 / I_F(t) - 1\}$ ($\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$, $\triangle$; $r = 7.5 \mu\text{m}$, $\blacktriangle$; $r = 14.5 \mu\text{m}$). The data correspond to those in Figure 4-6.

The kinetic equation shown below was thus used for data analysis,

$$\ln\{I_F^0 / I_F(t) - 1\} = -k_{\text{obs}} [\text{Fe}(\text{CN})_6^{3-}]_w t + \ln(k_q \tau_0 [\text{FeCp-X}]_{\text{TBP}}^0)$$

where τ_0 is the fluorescence lifetime of DPA ($= 9 \text{ ns}$) and k_q is the fluorescence quenching rate constant of DPA by FeCp-H ($= 9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The slope of the plot in Figure 4-7 corresponds to $k_{\text{obs}} \times [\text{Fe}(\text{CN})_6^{3-}]_w$. All of the $\text{Fe}(\text{CN})_6^{4-}$ molecules in the water phase is oxidized to $\text{Fe}(\text{CN})_6^{3-}$ during first 10 s of the electrolysis, so that the concentration of $\text{Fe}(\text{CN})_6^{3-}$ reaches in a steady state value at $t > 10 \text{ s}$: $[\text{Fe}(\text{CN})_6^{3-}]_w = 2.0 \times 10^{-4} \text{ M}$. The interfacial ET rate constant k_{obs} can be thus calculated by the slope of the plot at $t > 10 \text{ s}$ in Figure 4-7 and $[\text{Fe}(\text{CN})_6^{3-}]_w = 2.0 \times 10^{-4} \text{ M}$.

The k_{obs} value was determined for various-sized single droplets. A typical example of the droplet size dependence of k_{obs} is shown in Figure 4-8 where k_{obs} is plotted against r^{-1} . The results demonstrate clearly that the interfacial ET rate increases with decreasing the droplet radius. Furthermore, k_{obs} was a linear function of r^{-1} , indicating that the interfacial ET process is governed essentially by the surface area (A) / volume (V) ratio of a droplet. This is one of the micrometer size dependencies of the interfacial ET rate (discussed later in detail).

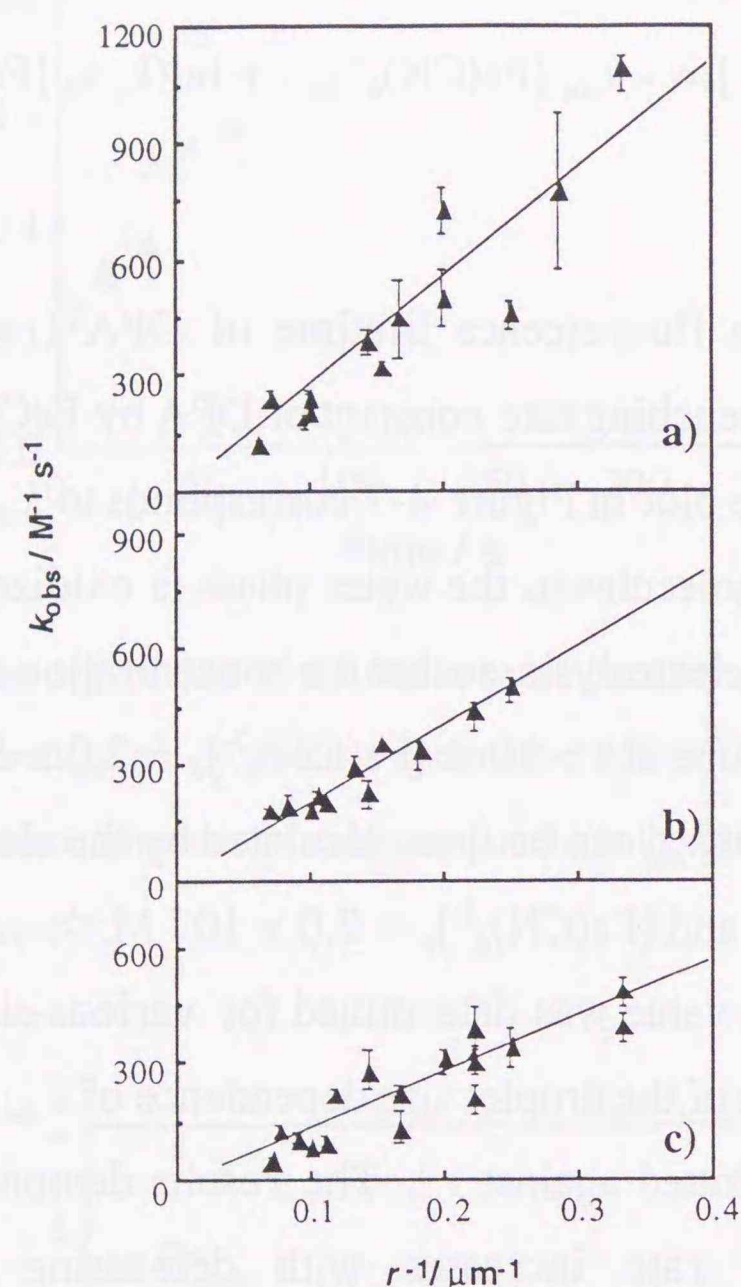


Figure 4-8. The surface area / volume ratio (r^{-1}) dependence of k_{obs} , ($[\text{DPA}]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$ and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$, a; $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-3} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}\phi} = \Delta_{\text{TBP}}^{\text{w}\phi^0} + 59 \text{ mV}$), b; $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-2} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}\phi} = \Delta_{\text{TBP}}^{\text{w}\phi^0}$), c; $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-1} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}\phi} = \Delta_{\text{TBP}}^{\text{w}\phi^0} - 59 \text{ mV}$)).

ii) Liquid-Junction Potential Dependence of Interfacial Electron Transfer Rate.

Besides the droplet size, the interfacial ET rate is predicted to be governed by the liquid-junction potential ($\Delta_{\text{TBP}}^{\text{w}\phi}$) between the TBP and water phases. Thus, liquid-junction potential dependence of the ET rate was studied in detail.

In the present system, the liquid-junction potential ($\Delta_{\text{TBP}}^{\text{w}\phi}$) is determined by distribution of TBA^+ between the TBP and water phases. Thus, electric neutrality between the two phases is achieved by ion transfer of TBA^+ . Namely, since $\Delta_{\text{TBP}}^{\text{w}\phi}$ is determined by TBA^+ , the liquid-junction potential difference is kept constant during the bulk electrolysis.

$\Delta_{\text{TBP}}^{\text{w}\phi}$ is given by the Nernst - Donnan equation as described in Chapter 3 (eq.3-1). In this system, TBA^+ is dissolved in both TBP and water phases, so that $\Delta_{\text{TBP}}^{\text{w}\phi}$ is determined by the activity ratio of TBA^+ in both phases. If the activity coefficient is equal to unity in both phases, $\Delta_{\text{TBP}}^{\text{w}\phi}$ is determined by the concentration of TBA^+ in both phases. In the present experiments, the concentration of TBA^+TPB^- in the TBP droplet ($[\text{TBA}^+\text{TPB}^-]_{\text{TBP}}$) was fixed $1.0 \times 10^{-2} \text{ M}$, since the dissolution limit of TBA^+TPB^- in TBP is $\sim 1.0 \times 10^{-2} \text{ M}$. $\Delta_{\text{TBP}}^{\text{w}\phi}$ was thus controlled by varying the concentration of TBA^+Cl^- in water ($[\text{TBA}^+\text{Cl}^-]_{\text{w}}$) from 1.0×10^{-3} ($\Delta_{\text{TBP}}^{\text{w}\phi} = \Delta_{\text{TBP}}^{\text{w}\phi^0} + 59 \text{ mV}$) to $1.0 \times 10^{-1} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}\phi} = \Delta_{\text{TBP}}^{\text{w}\phi^0} - 59 \text{ mV}$).

It is noteworthy that the redox potential and the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$ in water might be influenced by a variation of $[\text{TBA}^+]_{\text{w}}$. Therefore, before studying the liquid-junction potential dependence of k_{obs} , redox behavior of $\text{Fe}(\text{CN})_6^{3-}$ at several $[\text{TBA}^+]_{\text{w}}$ was examined by cyclic voltammetry. An Ag/AgCl wire, a Pt wire, and a Pt disk electrode ($r = 0.6 \text{ mm}$) were used as reference, counter and working

electrodes, respectively. An aqueous solution containing $\text{K}_3\text{Fe}(\text{CN})_6$ (1.0×10^{-3} M) and MgSO_4 (1.0×10^{-1} M) was used as a sample and deoxygenated by purging an N_2 gas stream prior to experiments. The redox potential of $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$ determined at $[\text{TBA}^+]_w$ of 1.0×10^{-2} or 1.0×10^{-3} M agreed very well with each other, while that shifted to a positive direction by 20 mV at $[\text{TBA}^+]_w = 1.0 \times 10^{-1}$ M. On the other hand, the diffusion coefficient of the compound was essentially independent of $[\text{TBA}^+]_w$, indicating that the viscosity of water was not influenced appreciably by the variation of $[\text{TBA}^+]_w$. From these results, it was concluded that the redox behavior of $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$ was independent of $[\text{TBA}^+]_w$.

The liquid-junction potential dependence of the interfacial ET rate was thus studied. The droplet size dependence of k_{obs} at various $[\text{TBA}^+]_w$ ($= 1.0 \times 10^{-1} \sim 1.0 \times 10^{-3}$ M) are included in Figure 4-8. As seen in the figure, a good linear relationship between k_{obs} and r^{-1} was obtained at each $[\text{TBA}^+]_w$, demonstrating that k_{obs} was governed by the interfacial A / V ratio of the droplet, irrespective of the $\Delta_{\text{TBP}}^w \phi$ value. It is worth pointing out, furthermore, that the slope of the plot decreases with decreasing in $[\text{TBA}^+]_w$. The results indicates that the ET rate decreases with the negative shift of $\Delta_{\text{TBP}}^w \phi$. Since the slope of the plot corresponds to the ET rate constant per unit droplet surface area ($k_{\text{ET}} / \text{cmM}^{-1}\text{s}^{-1}$), it is concluded that k_{ET} is dependent strongly on $\Delta_{\text{TBP}}^w \phi$. Actually, k_{ET} varied by a factor of ~ 2 with the change in $\Delta_{\text{TBP}}^w \phi$: $k_{\text{ET}} = 4.5 \times 10^{-2}$, 6.7×10^{-2} , and $9.4 \times 10^{-2} \text{ cmM}^{-1}\text{s}^{-1}$ at $[\text{TBA}^+]_w = 1.0 \times 10^{-1}$, 1.0×10^{-2} , and 1.0×10^{-3} M, respectively. The observed ET rate constant (k_{ET}) for the $\text{FeCp-H} / \text{Fe}(\text{CN})_6^{3-}$ system agreed well with the reported value ($\sim 10^{-2} \text{ cmM}^{-1}\text{s}^{-1}$)^{5,6}.

Although this liquid-junction potential dependence of k_{ET} is discussed later in detail, the present results are worth comparing with the results described in Chapter 3. Namely, the k_{ET} value determined in the

absence of a surfactant is larger than that in the presence of SDS or Triton-X 100 ($k_{\text{ET}} \sim 2.0 \times 10^{-2} \text{ cmM}^{-1}\text{s}^{-1}$). This will be explained by assuming that the adsorption layer of the surfactant acts as a blocking layer of the ET reaction, where the ET process is interrupted by the adsorption layer at the droplet / water interface. In the presence of a surfactant, $[\text{TBA}^+]_w$ effects on the ET rate cannot be studied. A surfactant adsorbs on the droplet interface, so that the potential difference at the interface is influenced by the surfactant charge, leading to the change in the local potential at the interface and, thus, that in the free energy of the ET reaction. Therefore, the liquid-junction potential dependence of k_{ET} in the presence and absence of a surfactant cannot be discussed in detail.

iii) Micrometer Size Dependence of Interfacial Electron Transfer Rate.

Analogous experiments with those described above have been also conducted by using Pe as a fluorescence probe. The use of Pe is advantageous to conduct fluorescence measurements for smaller droplets, since the probe molecule in the droplet can be excited efficiently as compared to DPA. Actually, droplets smaller than $r = 6 \sim 7 \mu\text{m}$ cannot be measured by using DPA, while those as small as $r \sim 1 \mu\text{m}$ have been measured with good signal-to-noise ratios.

Figure 4-9 shows the time dependence of the fluorescence spectrum of Pe in a single droplet ($r = 4.0 \mu\text{m}$) during bulk electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in the water phase. The time dependence of the fluorescence intensity at 470 nm in a single droplet ($r = 1.9$, or $6.5 \mu\text{m}$) is shown in Figure 4-10. As in the case of the experiments with DPA, the fluorescence intensity of Pe in the

single droplet increased with an electrolytic time without any change in the spectral band shape and leveled-off at a certain value (Figure 4-10), indicating that the interfacial ET between $\text{Fe}(\text{CN})_6^{3-}$ and FeCp-H could be followed by the time course of the fluorescence intensity of Pe. It is noteworthy that the interfacial ET for the droplet as small as $r \sim 2 \mu\text{m}$ can be measured directly by using Pe as a fluorescence probe. Plotting the $\ln\{I_F^0 / I_F(t) - 1\}$ values against t , one can obtain a good linear relationship between the two values as shown in Figure 4-11.

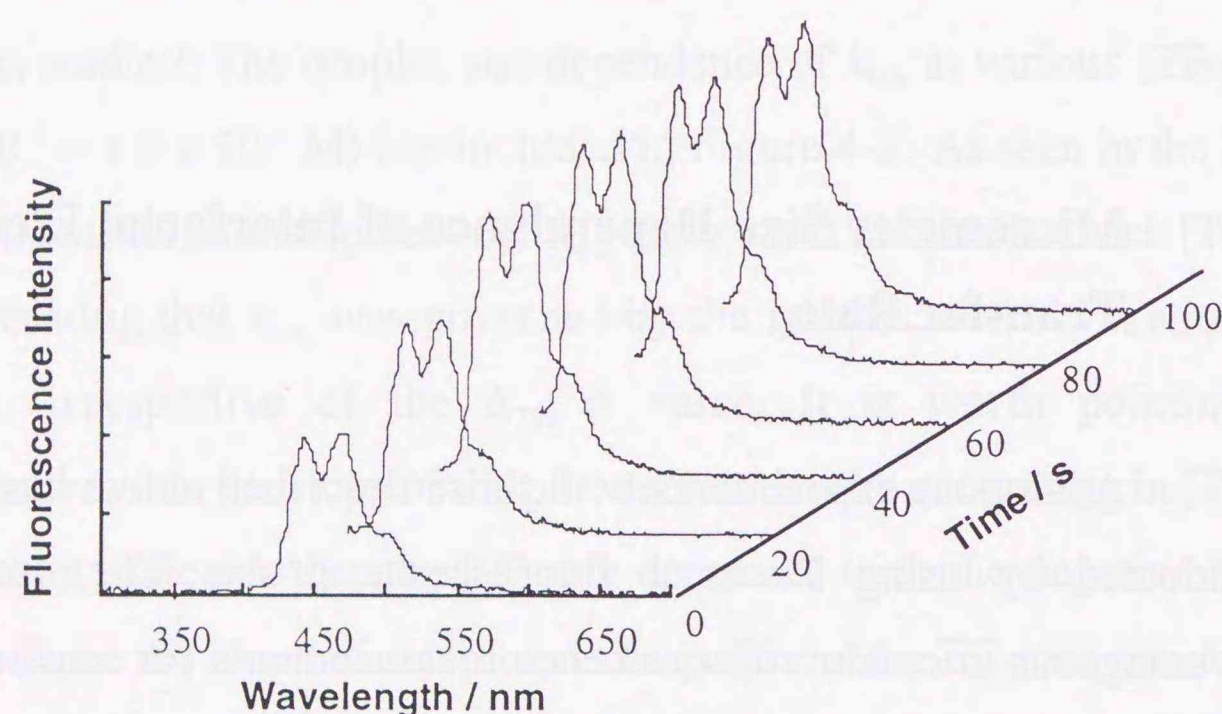


Figure 4-9. Time dependence of the fluorescence spectrum of Pe in a single TBP droplet ($r = 4.0 \mu\text{m}$) during bulk electrolysis. Excitation wavelength = $400 \sim 420 \text{ nm}$, $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$, $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-1} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$) and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$.

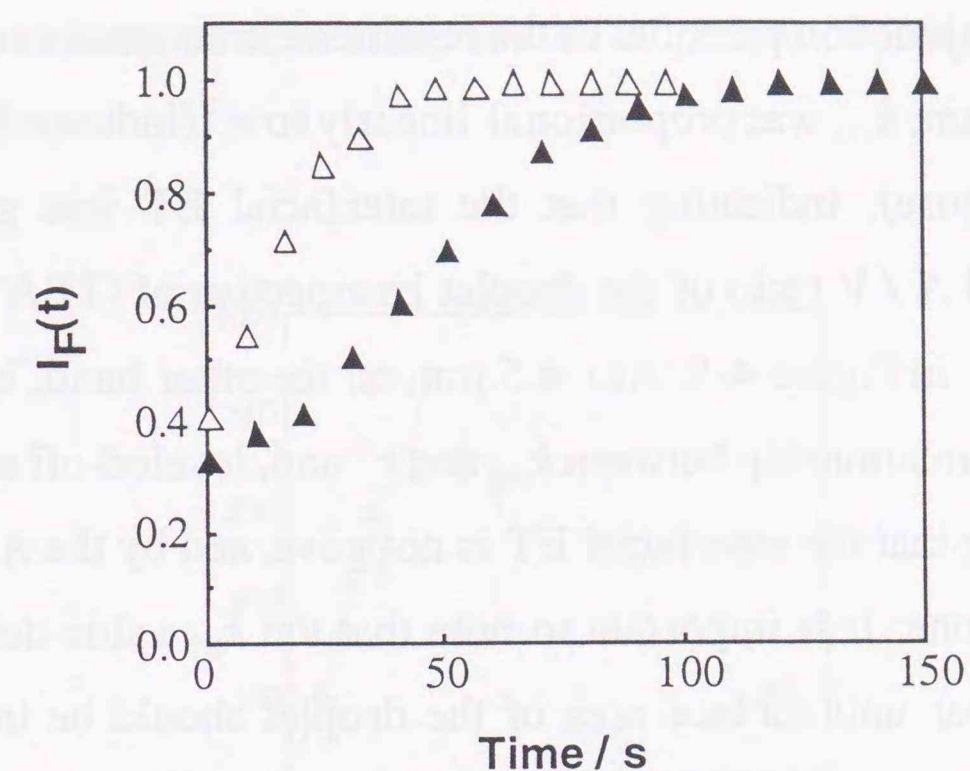


Figure 4-10. Time dependence of the fluorescence intensity (at 470 nm) of Pe in a single droplet ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$, $\triangle$; $r = 1.9 \mu\text{m}$, $\blacktriangle$; $r = 6.5 \mu\text{m}$). The concentration of each component in the emulsion was the same with that described in Figure 4-9.

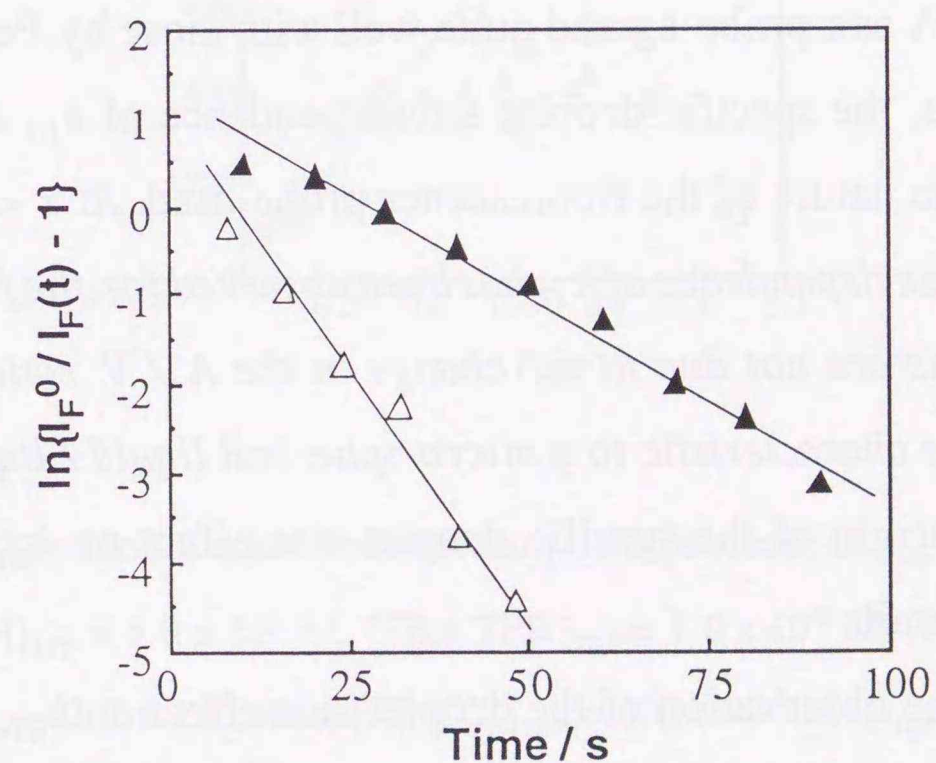


Figure 4-11. Time dependence of $\ln\{I_F^0 / I_F(t) - 1\}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$, $\triangle$; $r = 1.9 \mu\text{m}$, $\blacktriangle$; $r = 6.5 \mu\text{m}$). The data correspond to those in Figure 4-10.

The droplet size dependence of k_{obs} was thus studied as a function of the liquid-junction potential as the results were summarized in Figure 4-12. At $r > 5 \mu\text{m}$, k_{obs} was proportional linearly to r^{-1} (indicated by the solid line in the figure), indicating that the interfacial ET was governed by the interfacial A/V ratio of the droplet irrespective of $[\text{TBA}^+]_{\text{w}}$, analogous to the results in Figure 4-8. At $r < 5 \mu\text{m}$, on the other hand, k_{obs} deviates from the linear relationship between k_{obs} and r^{-1} and, leveled-off at a certain value, suggesting that the interfacial ET is not governed by the A/V ratio of the droplet alone. It is important to note that the k_{ET} value defined as the rate constant per unit surface area of the droplet should be independent of r , when the A/V ratio governs exclusively k_{obs} . As shown in Figure 4-13, although k_{ET} was almost constant at $r > 5 \mu\text{m}$, that decreased sharply at $r < 5 \mu\text{m}$. It is concluded that, at $r < 5 \mu\text{m}$, the interfacial ET rate is determined by the factor other than the A/V ratio at the droplet. Although the absolute k_{ET} values was dependent on $\Delta_{\text{TBP}}^{\text{w}}\phi$, such a size effect on k_{ET} was confirmed irrespective of $\Delta_{\text{TBP}}^{\text{w}}\phi$. It is noteworthy that, at $r > 5 \mu\text{m}$, k_{ET} determined by using DPA as a probe agreed quite well with those by Pe, for given $\Delta_{\text{TBP}}^{\text{w}}\phi$. Therefore, the specific droplet size dependence of k_{ET} at $r < 5 \mu\text{m}$ is not ascribed to nature of the fluorescence probe used. At $r < 5 \mu\text{m}$, the specific droplet size dependence of k_{ET} has been observed for the first time. Since the size effects are not due to the change in the A/V ratio of a droplet, the results are characteristic to a micro-spherical liquid/liquid interface. The possible origin of the specific droplet size effect on k_{ET} will be discussed later in detail.

The observation of the droplet size effect on k_{ET} is one of the most important results of the study and is very striking. In the present system, however, FeCp-H^+ produced upon the ET reaction is likely to distribute to the water phase and this disturbs clear analysis of the observed data in

Figure 4-13. Therefore, in order to discuss the droplet size effect clearer, the reaction systems other than the use of FeCp-H are worth to be studied in detail.

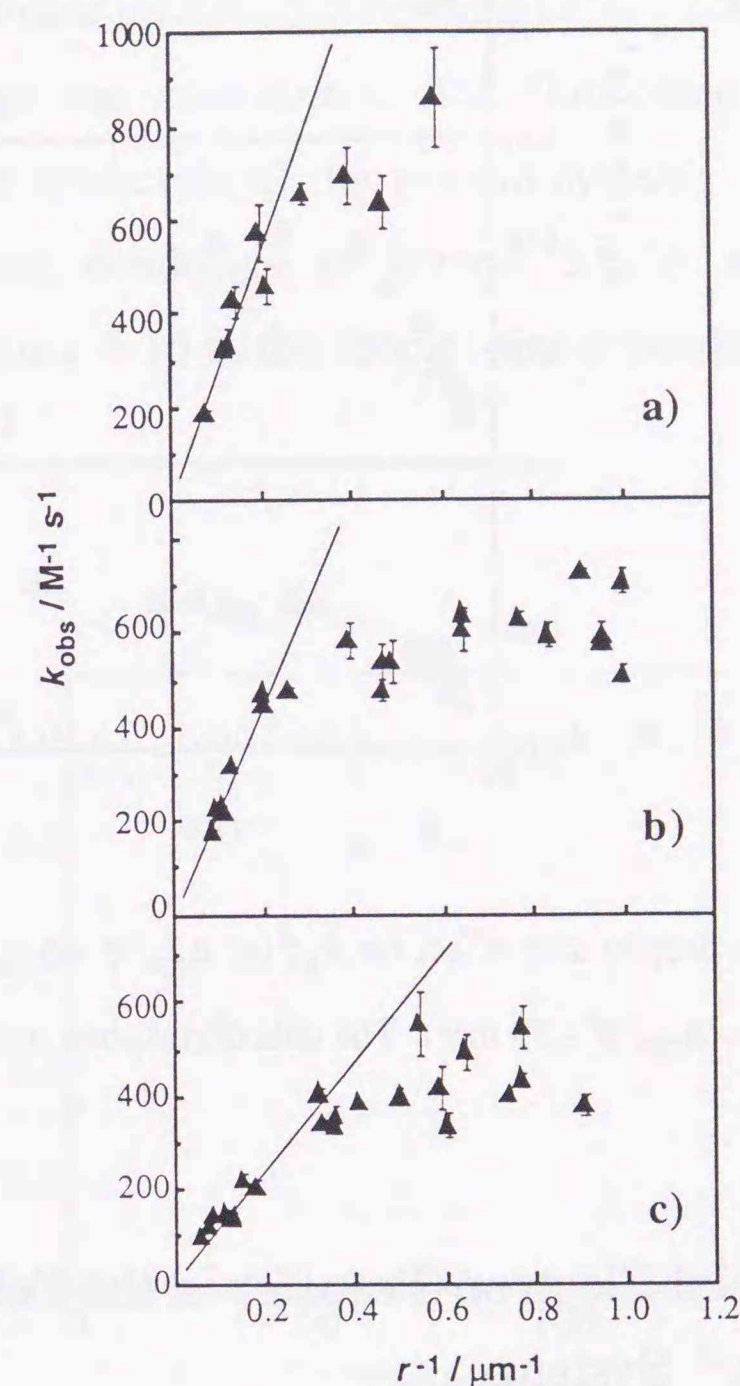


Figure 4-12. The surface area / volume ratio (r^{-1}) dependence of k_{obs} ($[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$, $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$ and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$, a; $[\text{TBA}^+\text{Cl}^-]_{\text{TBP}} = 1.0 \times 10^{-3} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 + 59 \text{ mV}$), b; $[\text{TBA}^+\text{Cl}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0$), c; $[\text{TBA}^+\text{Cl}^-]_{\text{TBP}} = 1.0 \times 10^{-1} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$)).

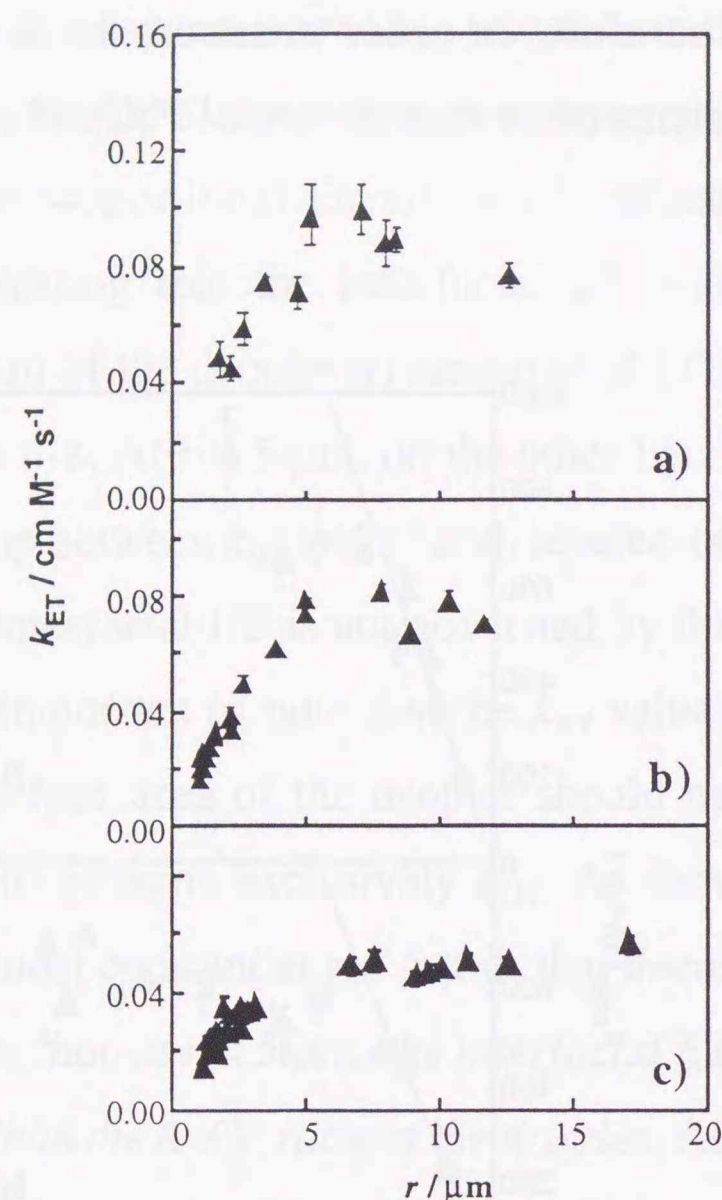


Figure 4-13. The droplet size effect on k_{ET} (a; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0 + 59$ mV, b; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0$, c; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0 - 59$ mV). The data correspond to those in Figure 4-12.

4.3.2 Interfacial Electron Transfer in the FeCp-DM / $\text{Fe}(\text{CN})_6^{3-}$ System.

In order to test whether the droplet size effect at $r < 5$ μm has a generality or not, the interfacial ET reaction of FeCp-DM was studied. FeCp-DM is a bulky molecule having two methyl groups on the ferrocenyl moiety and is expected to be less likely to distributed to the water phase as compared with FeCp-H.

The interfacial ET reaction between FeCp-DM in a TBP droplet and

$\text{Fe}(\text{CN})_6^{3-}$ in the surrounding water phase took place as confirmed by the increase in the fluorescence intensity of Pe from a single droplet ($r = 1.3$ or 10.6 μm) upon electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ in water. A typical example is shown in Figure 4-14 and the relevant $\ln\{I_F^0 / I_F(t) - 1\}$ vs. t plot is shown in Figure 4-15. The linear relationship between $\ln\{I_F^0 / I_F(t) - 1\}$ and t in Figure 4-15 indicates that the coulometric and fluorometric analyses of the interfacial ET are applicable to the present system. Thus, single droplet measurements were conducted at several $\Delta_{TBP}^w\phi$ and the results are summarized in Figure 4-16 as the droplet size dependence of k_{obs} .

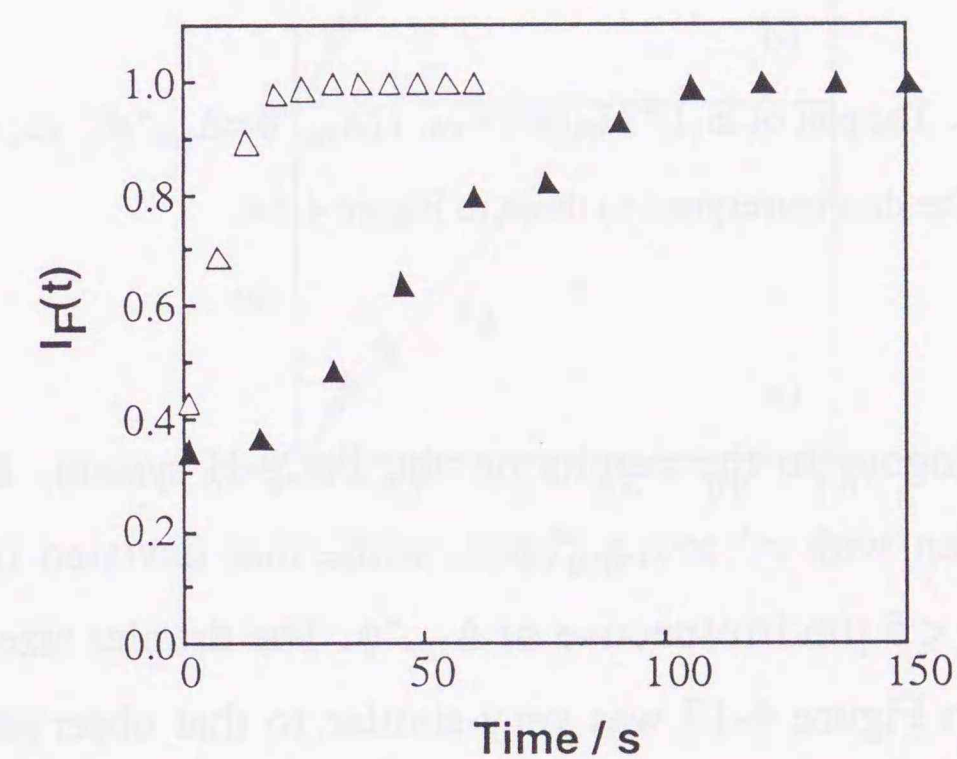


Figure 4-14. The time dependence of the fluorescence intensity (at 470 nm) of Pe in single droplets (excitation wavelength = 400 ~ 420 nm, Δ ; $r = 1.3$ μm , $\blacktriangle$; $r = 10.6$ μm , $[\text{Pe}]_{TBP} = 5.0 \times 10^{-4}$ M, $[\text{FeCp-DM}]_{TBP} = 4.0 \times 10^{-2}$ M, $[\text{TBA}^+\text{TPB}^-]_{TBP} = 1.0 \times 10^{-2}$ M, $[\text{MgSO}_4]_w = 0.1$ M, $[\text{TBA}^+\text{Cl}^-]_w = 1.0 \times 10^{-2}$ M ($\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0$) and $[\text{Fe}(\text{CN})_6^{4-}]_w = 2.0 \times 10^{-4}$ M).

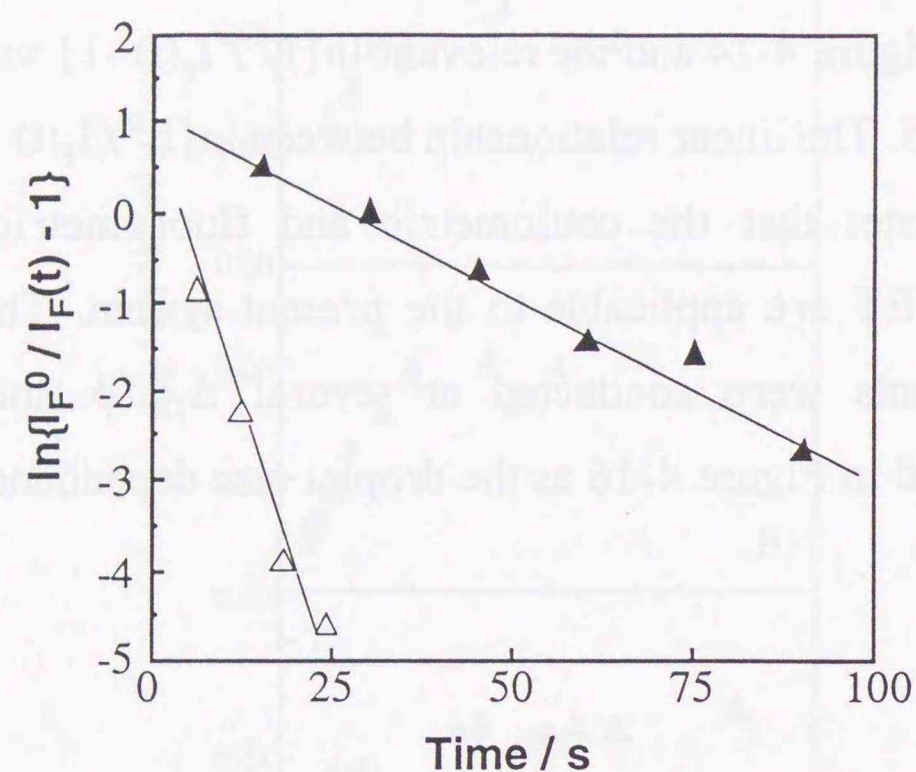


Figure 4-15. The plot of $\ln\{I_F^0 / I_F(t) - 1\}$ vs. t ($\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$, $\triangle$; $r = 1.3 \mu\text{m}$, $\blacktriangle$; $r = 10.6 \mu\text{m}$). The data correspond to those in Figure 4-14.

Analogous to the results on the FeCp-H system, k_{obs} exhibited a linear relation with r^{-1} at $r > 5 \mu\text{m}$, while that deviated from the linear relation at $r < 5 \mu\text{m}$ irrespective of $\Delta_{TBP}^w \phi$. The droplet size dependence of k_{ET} shown in Figure 4-17 was very similar to that observed for FeCp-H. Thus, the droplet size dependence of k_{obs} or k_{ET} at $r < 5 \mu\text{m}$ is not fortuitous, but is worth to be discussed in detail.

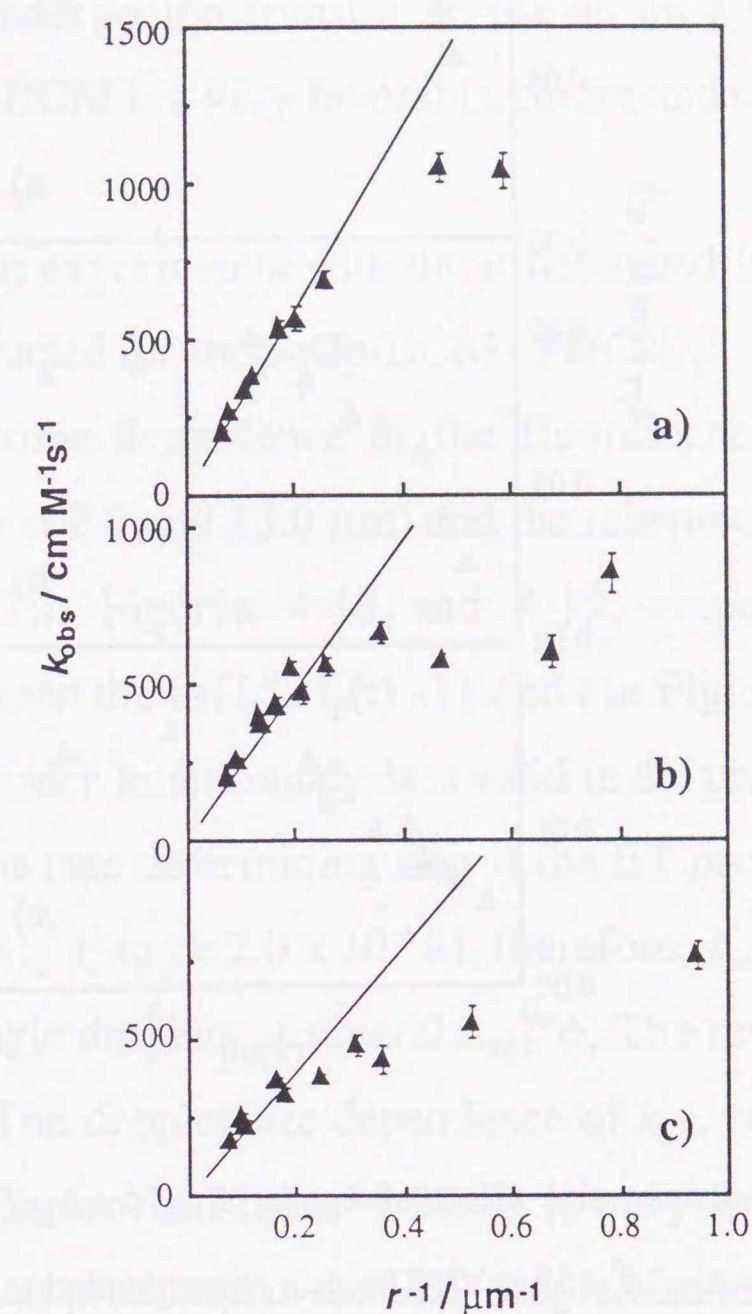


Figure 4-16. The surface area / volume ratio (r^{-1}) dependence of k_{obs} (a; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0 + 59 \text{ mV}$, b; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$, c; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0 - 59 \text{ mV}$). The concentration of each component in the emulsion was the same with that described in Figure 4-14.

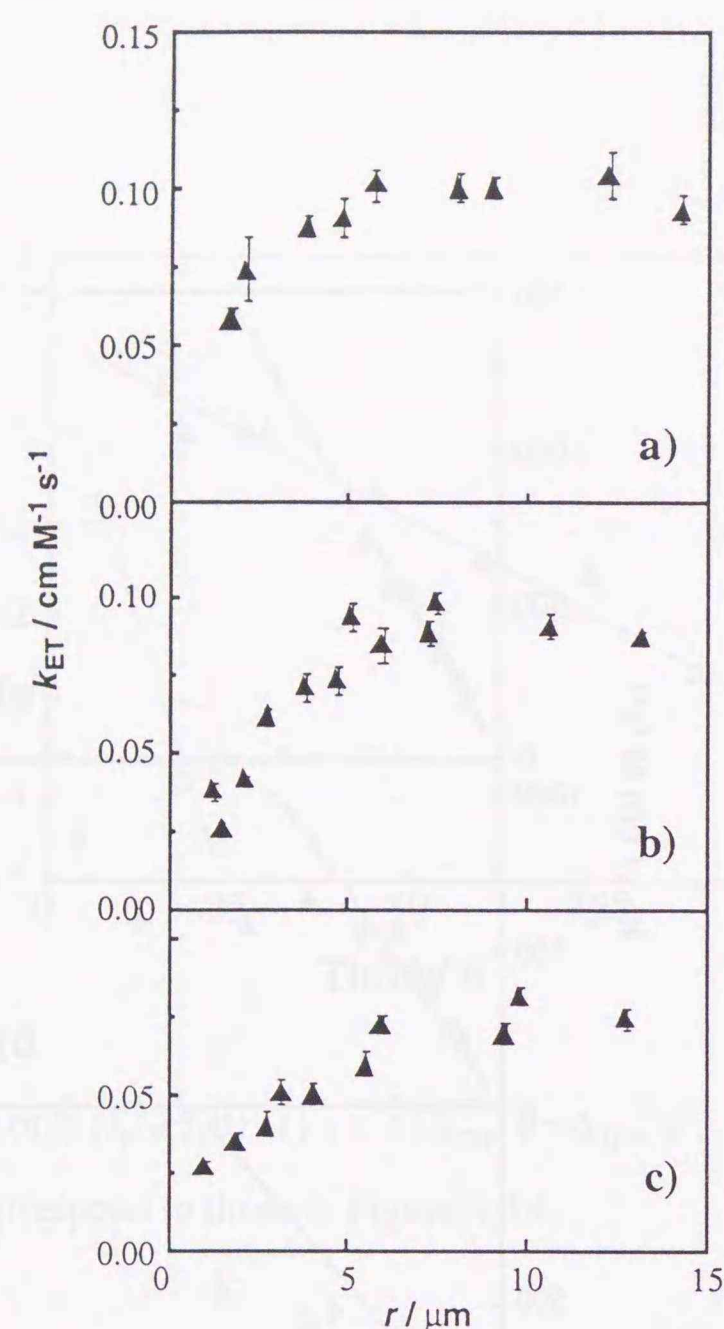


Figure 4-17. The droplet size effect of k_{ET} (a; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0 + 59$ mV, b; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$, c; $\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0 - 59$ mV). The data corresponded to those in Figure 4-16.

4.3.3 Interfacial Electron Transfer in the FeCp-DCM / $\text{Fe}(\text{CN})_6^{3-}$ System.

The characteristic droplet size dependence of k_{ET} at $r < 5 \mu\text{m}$ has been observed for both FeCp-H and FeCp-DM, so that the size effect at $r < 5 \mu\text{m}$ will be a general feature. However, both FeCp-H^+ and FeCp-DM^+ produced upon the interfacial ET undergo ion transfer to the surrounding

water phase, so that more explicit data are needed to discuss the droplet size effect on k_{ET} . FeCp-DCM possesses ten methyl groups on the ferrocenyl moiety and is hydrophobic. Also, it has been reported that FeCp-DCM cations do not undergo ion transfer across an oil / water interface and, therefore, FeCp-DCM is a very favorable compound to study a droplet size dependence of k_{ET} .

Analogous experiments with those described in sections 4.3.1. and 4.3.2. were conducted for the FeCp-DCM - $\text{Fe}(\text{CN})_6^{3-}$ - Pe system. A typical example of the time dependence of the fluorescence intensity of Pe in single droplets ($r = 2.5$ and $13.0 \mu\text{m}$) and the relevant $\ln\{I_F^0 / I_F(t) - 1\}$ vs. t plot are shown in Figures 4-18 and 4-19, respectively. The linear relationship between the $\ln\{I_F^0 / I_F(t) - 1\}$ and t in Figure 4-19 indicates that the pseudo-first order kinetic analysis is valid in the present system, and it is concluded that the rate determining step is the ET process at the interface. Knowing $[\text{Fe}(\text{CN})_6^{3-}]_w$ to be 2.0×10^{-4} M, therefore, k_{obs} was determined for various-sized single droplets at several $\Delta_{TBP}^w \phi$. The results are summarized in Figure 4-20. The droplet size dependence of k_{ET} , relevant to the data in Figure 4-20, is shown in Figure 4-21. It is very important to note that FeCp-DCM cations produced in the TBP droplet are not likely to transfer to the water phase. Nonetheless, the characteristic droplet size effect on k_{ET} at $r < 5 \mu\text{m}$ was observed. Thus, it is concluded that the size effect on k_{ET} at $r < 5 \mu\text{m}$ is not ascribed to ion transfer of the ferrocenium cation and is due to the intrinsic nature of the microscopic spherical liquid / liquid interface.

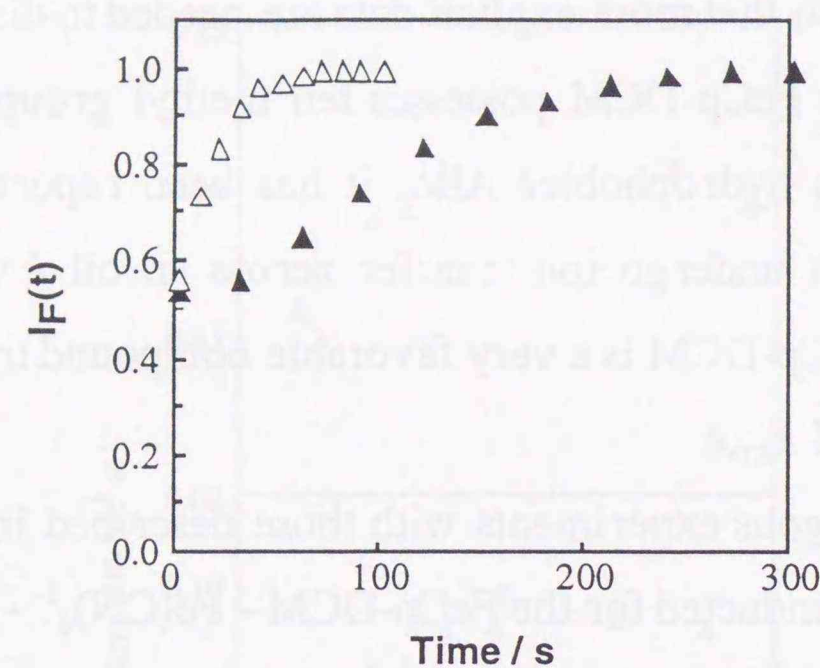


Figure 4-18. Time dependence of the fluorescence intensity (at 470 nm) of Pe in single droplets (excitation wavelength = 400 ~ 420 nm, $\triangle$; $r = 2.5 \mu\text{m}$, $\blacktriangle$; $r = 13.0 \mu\text{m}$, $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$, $[\text{FeCp-DCM}]_{\text{TBP}} = 2.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-3} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 + 59 \text{ mV}$) and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$).

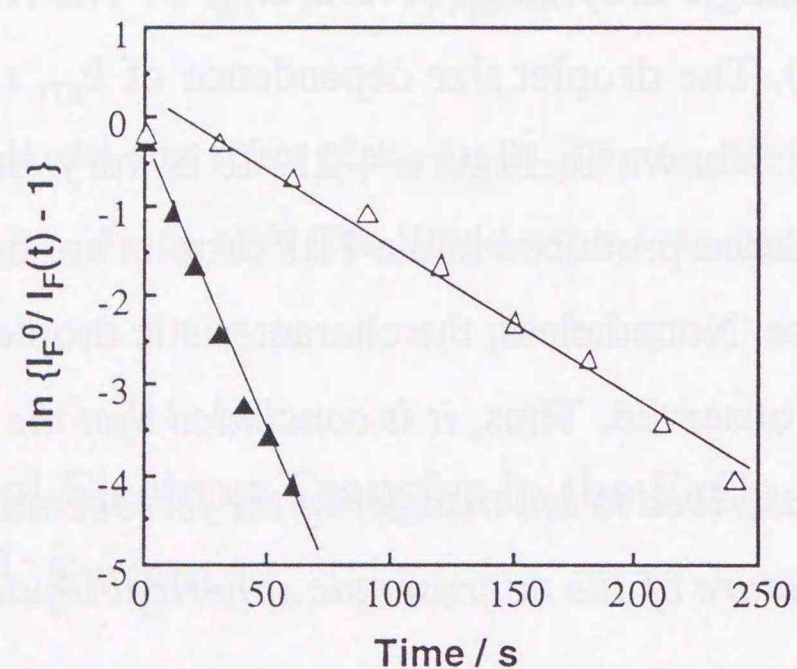


Figure 4-19. The plot of $\ln \{I_F^0 / I_F(t) - 1\}$ vs. t ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 + 59 \text{ mV}$, $\triangle$; $r = 2.5 \mu\text{m}$, $\blacktriangle$; $r = 13.0 \mu\text{m}$). The concentration of each component in the emulsion was the same with that described in Figure 4-18.

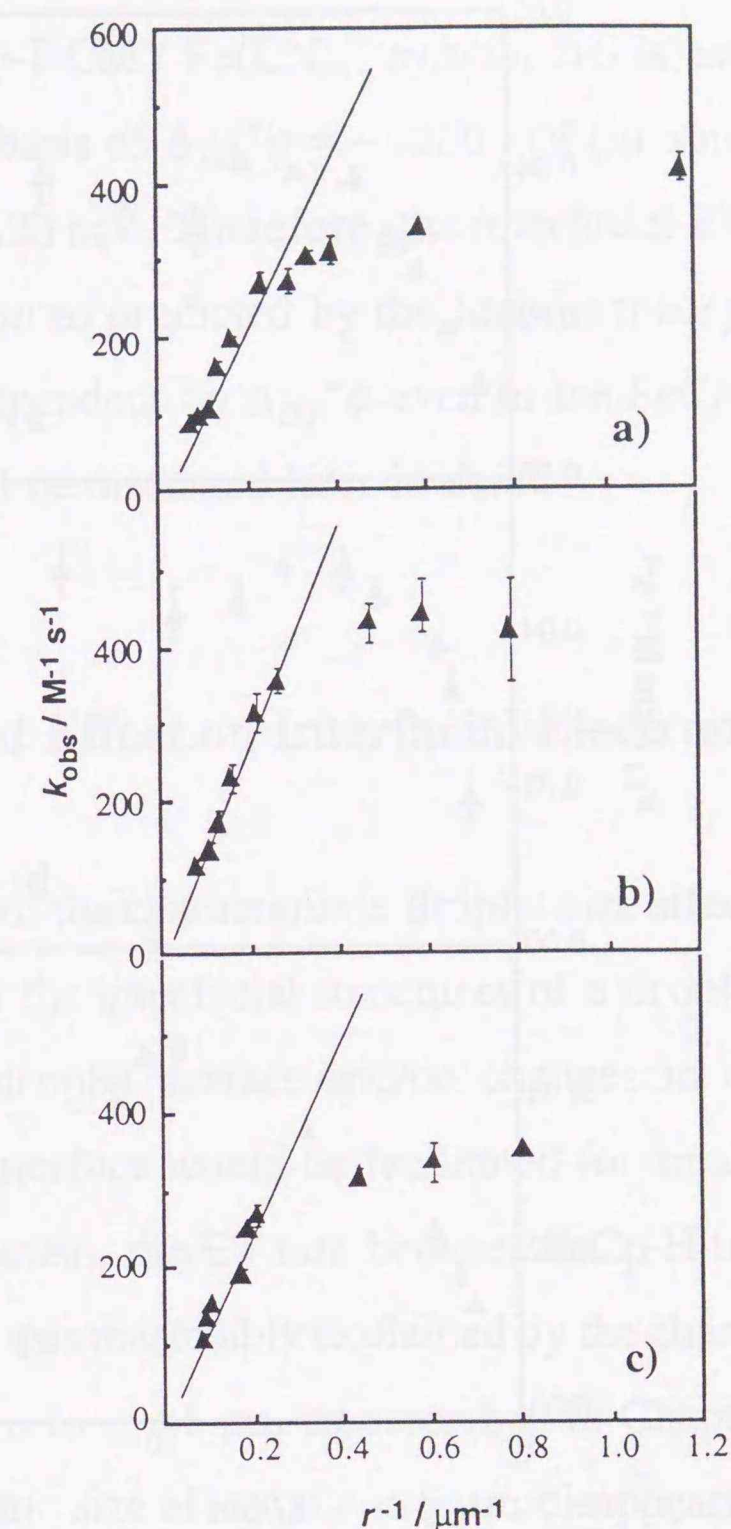


Figure 4-20. The surface area / volume ratio (r^{-1}) dependence of k_{obs} (a; $\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 + 59 \text{ mV}$, b; $\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0$, c; $\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$). The concentration of each component in the emulsion was the same with that described in Figure 4-18.

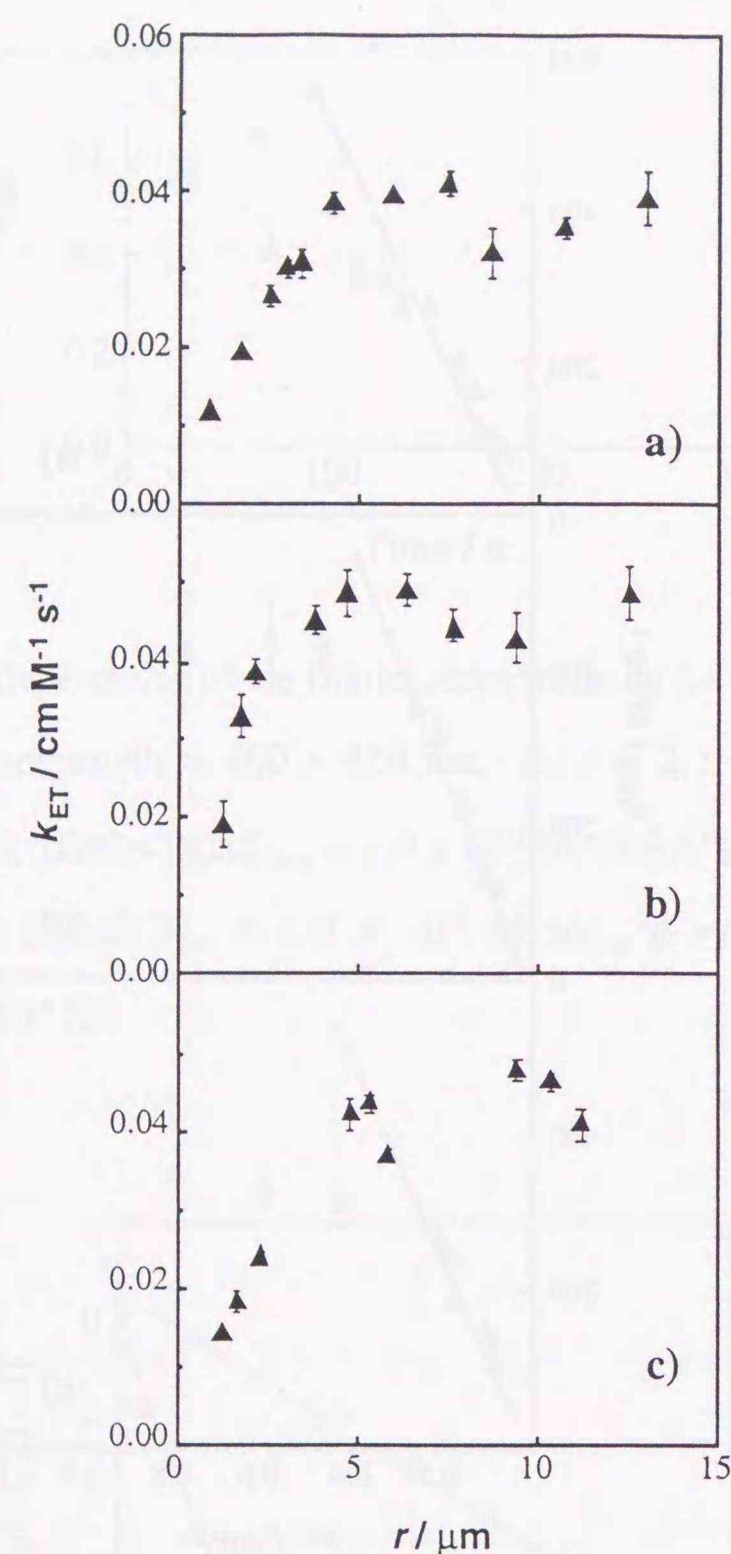


Figure 4-21. The droplet size effect of k_{ET} (a; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0 + 59$ mV, b; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0$, c; $\Delta_{TBP}^w\phi = \Delta_{TBP}^w\phi^0 - 59$ mV). The data correspond to those in Figure 4-20.

Besides the observation of the droplet size dependence of k_{ET} at $r < 5$ μm , it should be noted that k_{ET} is independent of $\Delta_{TBP}^w\phi$ and almost constant at $\sim 4.0 \times 10^{-2} \text{ cm M}^{-1} \text{ s}^{-1}$ irrespective of $\Delta_{TBP}^w\phi$. This is in marked contrast to

the results obtained for FeCp-H and FeCp-DM, where the large $\Delta_{TBP}^w\phi$ dependence of k_{ET} has been observed as described in the preceding section. In the present FeCp-DCM / $\text{Fe}(\text{CN})_6^{3-}$ system, ΔG is estimated to be $-10 \sim -20 \text{ kJ mol}^{-1}$ on the basis of $\Delta_{TBP}^w\phi = \sim -250$ mV (in a nitrobenzene / water system) and $\Delta E = 423$ mV. Therefore, the interfacial ET reaction proceeds in the normal region as predicted by the Marcus theory and, thus, the ET reaction must be dependent on $\Delta_{TBP}^w\phi$ even in the FeCp-DCM system. The possible reason will be discussed later in detail.

4.3.4 Surfactant Effect on Interfacial Electron Transfer Rate.

The origin of the characteristic droplet size effect on k_{ET} at $r < 5$ μm might be related to the interfacial structures of a droplet, since adsorption of a solute on a droplet surface and/or changes in chemical / physical properties of the interface would be facilitated for smaller droplets. In the presence of a surfactant, the ET rate between FeCp-H in a TBP droplet and $\text{Fe}(\text{CN})_6^{3-}$ in water was reasonably explained by the change in the A/V ratio of the droplet down to $r \sim 1$ μm as described in Chapter 3. This indicates that the characteristic size effect at $r < 5$ μm disappears by adsorption of a surfactant on the droplet surface. Disappearance of the size effect was observed for both anionic (SDS) and neutral (Triton-X 100) surfactants. Such results are the key to elucidate the origin of the droplet size effect on k_{ET} at $r < 5$ μm . In order to obtain clearer information, therefore, experiments were done for the FeCp-DM and FeCp-DCM systems in the presence of SDS.

SDS-stabilized emulsions were prepared as described in Chapter 3 ([SDS] = 2 wt%). The concentration of FeCp-DM or FeCp-DCM in TBP

was set 4.0×10^{-2} or 2.0×10^{-2} M, respectively, and those of other solutes were the same with those described for the FeCp-H system. As a water phase, MgSO_4 (1.0×10^{-1} M), TBA^+Cl^- (1.0×10^{-1} M), and $\text{K}_4\text{Fe}(\text{CN})_6$ (2.0×10^{-4} M) were dissolved in TBP-saturated water.

The droplet size dependence of k_{obs} in the presence of SDS thus obtained for the FeCp-DM or FeCp-DCM systems is shown in Figure 4-22. It is clear from the figure, k_{obs} is in proportion to r^{-1} down to $r \sim 1 \mu\text{m}$ for both systems in marked contrast to the results in the absence of a surfactant, demonstrating that the ET rate (k_{obs}) is essentially governed by the A/V ratio of a droplet alone. The relationships between k_{ET} and the droplet radius relevant to the data in Figure 4-22 are shown in Figure 4-23. The results demonstrated that k_{ET} for the FeCp-DM or FeCp-DCM system was almost constant at 7.5×10^{-2} or $1.9 \times 10^{-2} \text{ cmM}^{-1}\text{s}^{-1}$, respectively.

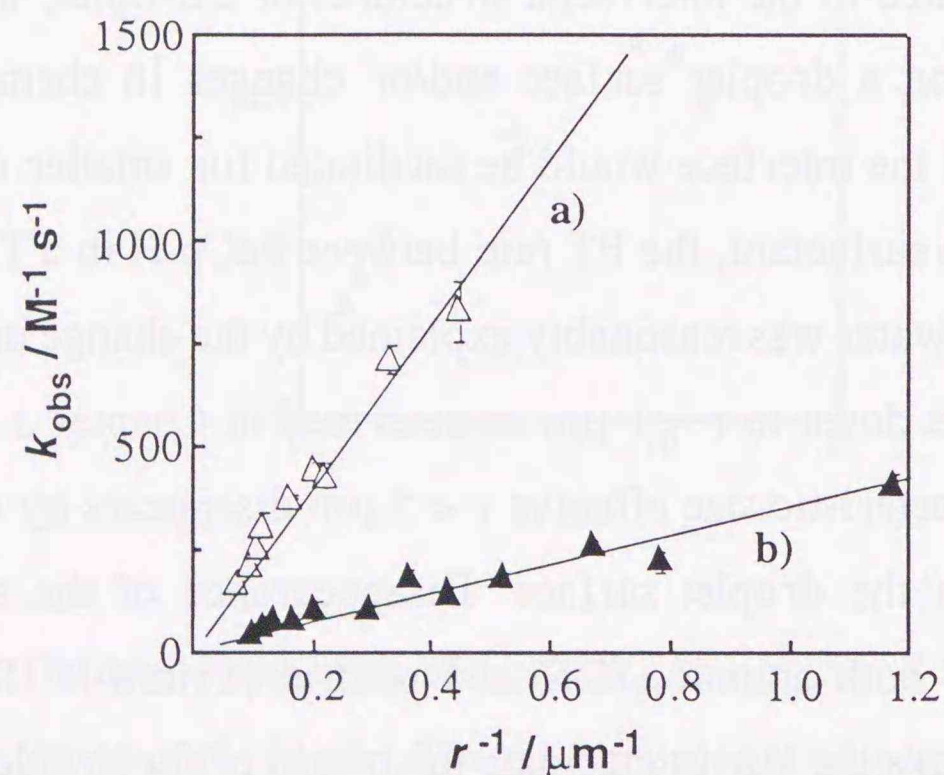


Figure 4-22. The surface area / volume ratio (r^{-1}) dependence of k_{obs} (TBP / SDS / W system, $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4}$ M, $[\text{TBA}^+\text{TPB}]_{\text{TBP}} = 1.0 \times 10^{-2}$ M, $[\text{MgSO}_4]_{\text{w}} = 0.1$ M, $[\text{TBA}^+\text{Cl}]_{\text{TBP}} = 1.0 \times 10^{-1}$ M and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4}$ M, a; $[\text{FeCp-DM}]_{\text{TBP}} = 4.0 \times 10^{-2}$ M, b; $[\text{FeCp-DCM}]_{\text{TBP}} = 2.0 \times 10^{-2}$ M).

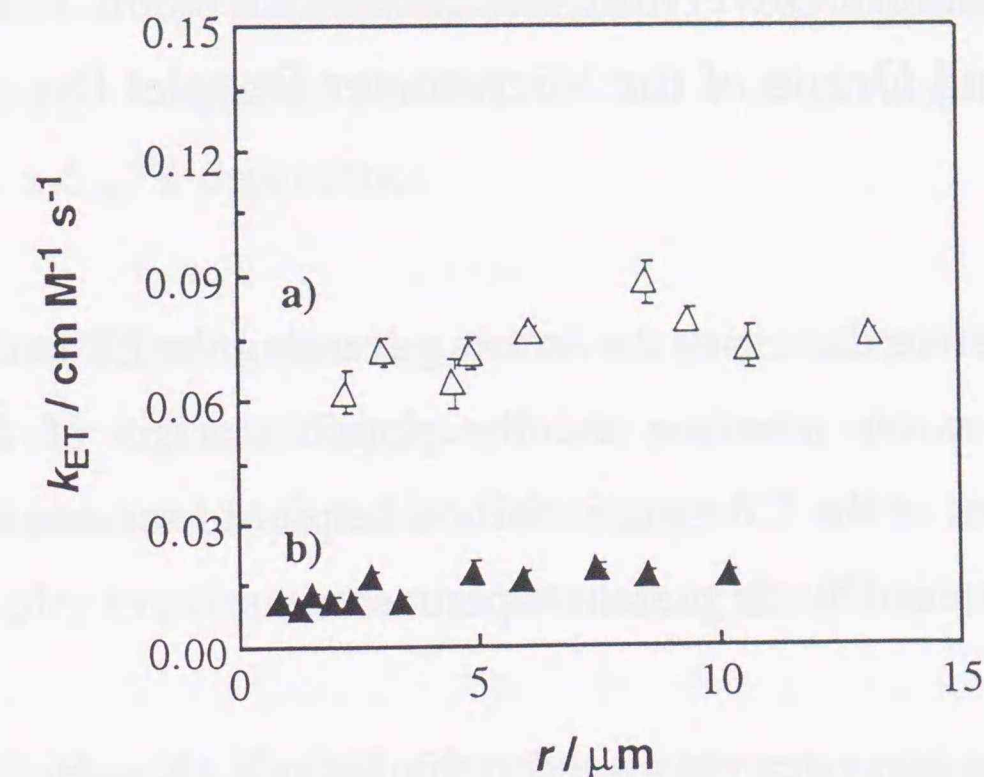


Figure 4-23. The droplet size effect of k_{ET} (TBP / SDS / W system, a; FeCp-DM, b; FeCp-DCM). The data correspond to those in Figure 4-22.

SDS is supposed to be solubilized in the vicinity of the droplet / water interface with the polar head group and the alkyl chain being directed to the water phase and the droplet interior, respectively. This adsorption layer on the droplet surface influences strongly on the ET process. Firstly, k_{ET} is smaller than that without SDS. This will be because the absorption layer of SDS acts as a blocking layer for the ET event as discussed in Chapter 3. It is very important to note, secondly, that the adsorption layer vanishes the droplet size effect on k_{ET} by either the adsorption layer itself or change in the surface structure of the droplet. Since a nonionic surfactant (Triton-X 100) also showed analogous effects, the electric charge of a surfactant is not an important factor, but the adsorption layer plays an essential role for the interfacial ET. Based on these findings, the size effect on k_{ET} is discussed in the following section.

4.4 Factors Governing Interfacial Electron Transfer Rate and Origin of the Micrometer Droplet Dependence.

Before discussing the factors governing the ET rate across the TBP droplet / water interface and the plausible origin of the droplet size dependence of the ET rate, it will be helpful to summarize the principal results obtained by the present experiments.

i) The reaction rates obtained for the FeCp-X (X = H, DM, or DCM) / $\text{Fe}(\text{CN})_6^{4-}$ / fluorophore (Pe or DPA) systems obeyed a pseudo-first order reaction kinetics. Thus, it can be concluded that *the rate determining step is the interfacial ET process, irrespective of the system studied.*

ii) All the FeCp-X / $\text{Fe}(\text{CN})_6^{4-}$ / fluorophore systems exhibited the interfacial A / V ratio effect on k_{obs} at $r > 5 \mu\text{m}$, where k_{obs} increased with decreasing the droplet size. However, the relevant rate constant per unit surface area, k_{ET} , was essentially independent of r . At $r > 5 \mu\text{m}$, therefore, *the interfacial ET rate is governed by the A / V ratio of a droplet.*

iii) *The droplets smaller than $r \sim 5 \mu\text{m}$ showed characteristic droplet size dependence of k_{obs} . Namely, k_{ET} defined as the rate constant per unit surface area of the droplet was dependent on r and decreased sharply with decreasing r . Clearly, this cannot be explained by the A / V ratio effects. The characteristic droplet size dependence of k_{ET} was confirmed irrespective of $\Delta_{\text{TBP}}^w \phi$ and the nature of FeCp-X.*

iv) In the case of the FeCp-H / $\text{Fe}(\text{CN})_6^{4-}$ / fluorophore and FeCp-DM /

$\text{Fe}(\text{CN})_6^{4-}$ / fluorophore systems, the observed k_{ET} was dependent on $\Delta_{\text{TBP}}^w \phi$. Nevertheless, k_{ET} determined for FeCp-DCM under analogous conditions did not show a $\Delta_{\text{TBP}}^w \phi$ dependence.

v) It is very important to note that *the characteristic droplet size effect on k_{ET} observed at $r < 5 \mu\text{m}$ disappears in the presence of a surfactant.* The physical and chemical structures at the droplet / water interface were suggested to play important roles in determining the ET rate.

As addressed in ii), one of the factors governing the interfacial ET rate is the surface area / volume (A / V) ratio of a droplet. The smaller is the droplet, the more efficient is mass transfer of $\text{Fe}(\text{CN})_6^{3-}$ to the droplet surface, owing to spherical diffusion. This has been observed for the droplets with $r > 5 \mu\text{m}$. Besides the A / V effects, other factors also determine the ET rate. In the followings, discussion is focused on the liquid-junction potential and droplet size ($r < 5 \mu\text{m}$) dependencies of the interfacial ET rate.

4.4.1 Liquid-Junction Potential Dependence of Interfacial Electron Transfer Rate.

i) Liquid-Junction Potential Dependence.

k_{ET} was shown to be depended on $\Delta_{\text{TBP}}^w \phi$ for the FeCp-H and FeCp-DM systems (Figures 4-13 and 4-17). A Gibbs free energy change (ΔG) of the ET reaction is give by,

$$\Delta G = -F(\Delta_{TBP}^w \phi + \Delta E) \quad 4-1$$

$$\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0 + (RT/F) \ln([TBA^+]_{TBP} / [TBA^+]_w) \quad 4-2$$

where ΔE is the redox potential difference between the redox species (FeCp-X and Fe(CN)_6^{3-}) and $\Delta_{TBP}^w \phi$ is the liquid-junction potential at the TBP / water interface as calculated by eq.4-2. Since ΔG is a function of $\Delta_{TBP}^w \phi$, the ET rate should depend on $\Delta_{TBP}^w \phi$. Equations 4-1 and 4-2 predict that a decrease in $[TBA^+]_w$ from 1.0×10^{-1} to 1.0×10^{-3} M leads to an increase in $\Delta_{TBP}^w \phi$ and, therefore, to a more negative shift of ΔG . This agrees well with the experimental observations, where k_{ET} increases with decreasing in $[TBA^+]_w$. For the $\text{FeCp-DCM} / \text{Fe(CN)}_6^{3-}$ system, however, the ET rate was not dependent on $\Delta_{TBP}^w \phi$. More detailed and quantitative discussions are necessary to explain the present results. Thus, the results were discussed in terms of the available ET theory.

ii) Comparison with Theory.

The observed ET rate constants ($k_{ET} / \text{cmM}^{-1}\text{s}^{-1}$) were compared with those predicted from the Marcus theory⁷⁻⁹.

In the Marcus theory, a medium is treated as a dielectric continuum and electron transfer is assumed to take place in a transition state. The main issue of the theory is to predict the activation Gibbs free energy (ΔG^*) of an electron transfer step. Since an electron jump is much faster than the atomic motions, both inner-sphere (bond length, angle, and so forth) and outer-

sphere (solvation structures) structures of an electron transfer product are the same with those of the reactant in the transition state. The theory addressed the important roles of these reorganization energies in determining ΔG^* . Thus, the theoretical prediction of the reorganization energies and their contribution to ΔG^* is the main concern of the theory. The theoretical formalisms for the heterogeneous liquid / liquid ET are as follows.

It is assumed that a liquid / liquid interface is flat and very sharp (very thin interface and solvent composition in each phase is uniform) and two redox reactants are thought to be spherical. When the reactants are in contact at the liquid / liquid interface, an electron transfer takes place. In such a case, a general kinetic equation for the heterogeneous ET reaction (k_{ET}) is given as,

$$k_{ET} = 2\pi (a_1 + a_2) (\Delta R)^3 \kappa \nu \exp(-\Delta G^* / RT) \quad 4-3$$

where a_1 and a_2 are the radii of a reactant 1 in one phase (Fe(CN)_6^{3-} in water in the present case) and a reactant 2 in other phase (FeCp-X in a TBP phase in the present case), respectively. ΔR is a parameter relating to an electron transfer distance and typically taken to be 0.1 nm. κ is the transmission coefficient of the electron transfer and is taken as unity for an adiabatic reaction, and ν is the relevant frequency for the molecular motions. According to the Marcus theory, ΔG^* is given by,

$$\Delta G^* = w^r + (\lambda + \Delta G + w^p - w^r)^2 / 4\lambda \quad 4-4$$

where w^r and w^p are the coulombic works necessary to bring the reactants together to the electron transfer distance and to separate the products, respectively. λ is the reorganization energy, which consists of outer- (λ_o) and inner-sphere (λ_i) Gibbs energy contributions from the two redox couples. ΔG is the Gibbs free energy change for the ET reaction. The outer-sphere reorganization energy (λ_o) relates to polarization of solvent molecules around the redox species, while the inner-sphere reorganization energy (λ_i) concerns about the change in the molecular structures of the redox species before and after electron transfer. λ_o is given as,

$$\begin{aligned} \lambda_o = & (\Delta e)^2 (1 / \epsilon_{op,1} - 1 / \epsilon_{s,1}) / 2a_1 + (\Delta e)^2 (1 / \epsilon_{op,2} - 1 / \epsilon_{s,2}) / 2a_2 \\ & - (\Delta e)^2 \{ (\epsilon_{op,2} - \epsilon_{op,1}) / \epsilon_{op,1} (\epsilon_{op,2} + \epsilon_{op,1}) - (\epsilon_{s,2} - \epsilon_{s,1}) / \epsilon_{s,1} (\epsilon_{s,2} + \epsilon_{s,1}) \} / 4d_1 \\ & - (\Delta e)^2 \{ (\epsilon_{op,1} - \epsilon_{op,2}) / \epsilon_{op,2} (\epsilon_{op,1} + \epsilon_{op,2}) - (\epsilon_{s,1} - \epsilon_{s,2}) / \epsilon_{s,2} (\epsilon_{s,1} + \epsilon_{s,2}) \} / 4d_2 \\ & - 2(\Delta e)^2 \{ 1 / (\epsilon_{op,1} + \epsilon_{op,2}) - 1 / (\epsilon_{s,1} + \epsilon_{s,2}) \} / (a_1 + a_2) \end{aligned} \quad 4-5$$

where $\epsilon_{op,1}$ and $\epsilon_{s,1}$ are the optical and static dielectric constants of a medium 1, respectively, and $\epsilon_{op,2}$ and $\epsilon_{s,2}$ are those of a medium 2. d_1 and d_2 are the distances from the reactants 1 and 2 to the interface, respectively. Δe is an electric charge. The coulombic work term is expressed as,

$$\begin{aligned} w = & -\{ (e_1)^2 / 4d_1\epsilon_{s,1} - (e_2)^2 / 4d_2\epsilon_{s,2} \} \{ (\epsilon_{s,2} - \epsilon_{s,1}) / (\epsilon_{s,2} + \epsilon_{s,1}) \} \\ & + 2 e_1 e_2 / R (\epsilon_{s,1} + \epsilon_{s,2}) \end{aligned} \quad 4-6$$

where e_1 and e_2 are the charges of the reactants 1 and 2, respectively, and R

is the distance between the two reactants (w^r). The same equation is applied to the products 1 and 2 as well (w^p). The electrical double layer at the interface and electrostatic interactions between reactants or products contribute to w^r .

In the present case, λ_i for the $\text{Fe}(\text{CN})_6^{4-} / \text{Fe}(\text{CN})_6^{3-}$ and $\text{FeCp-H} / \text{FeCp-H}^+$ redox couples have been reported to be 39.7¹⁰⁾ and 0.6 kJmol^{-1 11)}, respectively. The inner-sphere reorganization energies for FeCp-DM and FeCp-DCM are not known. However, λ_i of FeCp-H indicates that the value is fairly small for a large conjugated ring (*i.e.*, cyclopentadienyl ring) owing to large electronic delocalization in the macrocyclic ring, and the contribution of the substituents on the cyclopentadienyl ring to λ_i seems to be very small. Therefore, λ_i for FeCp-X ($X = \text{DM}$ or DCM) is assumed to be the same with that for FeCp-H : 0.6 kJmol⁻¹.

The coulombic work terms for formation of the precursor and successor complexes were calculated to be $w^r = 7.2$ kJmol⁻¹ and $w^p = 6.5$ kJmol⁻¹, respectively. λ_o was also calculated to be $\lambda_o = 65.7$ kJmol⁻¹ ($\epsilon_{s,1} = 78.5$, $\epsilon_{op,1} = 1.80$, $\epsilon_{s,2} = 7.96$, $\epsilon_{op,2} = 2.03$, $a_1 = d_1 = 0.45$ nm, $a_2 = d_2 = 0.55$ nm, $R = 1.0$ nm, and $\kappa v = 10^{12}$ s⁻¹ were used for the calculations^{9,10)}). For the calculations of the standard Gibbs free energy (ΔG), the liquid-junction potential difference, $\Delta_{TBP}^w \phi^0$, at a TBP / water interface must be known. However, the $\Delta_{TBP}^w \phi^0$ value has not been reported. Therefore, $\Delta_{TBP}^w \phi$ was assumed to be the same with that of a nitrobenzene / water interface (= -0.248 V). Knowing ΔE (energy gap for ET) for the $\text{FeCp-H} / \text{Fe}(\text{CN})_6^{3-}$, $\text{FeCp-DM} / \text{Fe}(\text{CN})_6^{3-}$, and $\text{FeCp-DCM} / \text{Fe}(\text{CN})_6^{3-}$ systems to be 30, 166, and 423 mV, respectively, ΔG for each reaction system was calculated based on eq.4-2. Since ΔG^* is expressed by eq.4-4, the k_{ET} value for a given system was calculated by eq.4-3. The calculated (theoretical) and observed k_{ET} values are summarized in Table together with the relevant ΔG value.

$\Delta_{TBP}^w \phi$ / mV	FeCp-H				FeCp-DM				FeCp-DCM			
	ΔG / kJmol ⁻¹	k_{ET} / cm M ⁻¹ s ⁻¹		ΔG / kJmol ⁻¹	k_{ET} / cm M ⁻¹ s ⁻¹		ΔG / kJmol ⁻¹	k_{ET} / cm M ⁻¹ s ⁻¹		ΔG / kJmol ⁻¹	k_{ET} / cm M ⁻¹ s ⁻¹	
		observed	calculated		observed	calculated		observed	calculated		observed	calculated
-190	15.5	9.1×10^{-2}	3.5×10^{-4}	2.4	1.0×10^{-1}	4.3×10^{-3}	-22.3	4.1×10^{-2}	2.1×10^{-1}	-16.7	4.3×10^{-2}	9.4×10^{-2}
-250	21.2	6.8×10^{-2}	1.1×10^{-4}	8.1	9.1×10^{-2}	1.5×10^{-3}	-12.9	4.2×10^{-2}	5.4×10^{-2}			
-310	26.9	4.5×10^{-2}	3.0×10^{-5}	11.9	7.5×10^{-2}	7.3×10^{-4}						

Table. The $\Delta_{TBP}^w \phi$ dependence of k_{ET} .

The interfacial ET reactions studied here are in so called "normal region", in which the reactions are endothermic or moderately exothermic. Therefore, k_{ET} is predicted to increase with decreasing in ΔG and, thus, with shifting $\Delta_{TBP}^w \phi$ to a more positive value. In the case of FeCp-H and FeCp-DM, the observed k_{ET} increased with shifting $\Delta_{TBP}^w \phi$ from -310 to -190 mV and this tendency agreed well with the theoretical prediction. However, the observed k_{ET} was larger than the relevant calculated value. For the FeCp-DCM system, furthermore, the observed k_{ET} was independent of $\Delta_{TBP}^w \phi$ in contrast to the theoretical prediction.

It is well known that the Marcus theory has succeeded in explaining various homogeneous ET reactions. However, the theory for liquid / liquid interfacial ET has developed very recently and has been rarely compared with experiments. Therefore, the theory may not be necessary satisfactory. Furthermore, liquid / liquid interfacial ET is very much complicated compared to homogenous ET, so that the assumptions described above may not be appropriate. For example, although a liquid / liquid interface is assumed to be flat and sharp, this is not warranted. Molecular dynamics simulations and thermodynamic studies demonstrated that nitrobenzene / water and 1,2-dichloroethane / water interfaces were very thin with the thickness of the layer of ~ 1.0 nm¹³⁻¹⁷). In the TBP / water system, however, miscibility of TBP with water is 4.67 %¹²), so that the interface will be much thicker than 1.0 nm and might not be sharp. Furthermore, it has been reported that thermal capillary waves propagate at a liquid / liquid interface, so that this also leads to a non-flat liquid / liquid interface. Owing to these reasons, close contact of two reactants at the TBP / water interface is not warranted. Although the optical and static dielectric constants of pure TBP and water were used for the calculation of λ_0 , the values will be varied if two solvents are mixed in the interfacial layer. All these are uncertainty

factors in calculating k_{ET} . In the present case, furthermore, the true $\Delta_{TBP}^w \phi$ value cannot be determined experimentally owing to high electric resistance of TBP, so that ΔG calculated are approximate values. Taking these problems into account, it will be concluded that agreement between the experiments and the theory is fair, and the liquid-junction potential dependence of the ET reaction rate can be discussed within the framework of the Marcus theory. However, for more strict discussions of the liquid-junction potential dependence of the ET rate, the various experimental conditions such as a solvent, an ionic strength and so forth should be optimized, which is the future problem to be studied.

In the case of FeCp-DCM, on the other hand, it is worth noting that k_{ET} does not show a liquid-junction potential dependence and is almost constant in the $\Delta_{TBP}^w \phi$ range between -190 and -310 mV. This will be due to ion transfer of the solute(s) across the liquid / liquid interface. The standard ion transfer potential of FeCp-H⁺, FeCp-DM⁺, or FeCp-DCM⁺ at the DCE / water interface has been reported to be -0.021, -0.090, or -0.257 V, respectively, while the standard distribution potential difference is -0.248 or -0.354 V at a nitrobenzene / water or DCE / water interface, respectively. From these data, it is predicted that ion transfer of FeCp-H⁺ takes place more readily than that of TBA⁺, so that electric neutrality is kept by ion transfer of FeCp-H⁺ from TBP to the water phase. Before electrolysis (*i.e.*, interfacial electron transfer), the liquid-junction potential is determined by the $[TBA^+]_{TBP} / [TBA^+]_w$ ratio. However, the standard ion transfer potential of FeCp-DCM⁺ is comparable to that of TBA⁺ so that both FeCp-DCM⁺ and TBA⁺ distribute to the water phase upon interfacial ET to keep electrical neutrality between the two phases. The change in distribution of TBA⁺ between the two phases brings about that in the liquid-junction potential. Also, the concentration of TBA⁺ in a droplet is lower than that of FeCp-

DCM, so that all TBA⁺ molecules in the droplet will distribute to water phase during the ET reaction. As a result, the liquid-junction potential is not determined by TBA⁺. This will be the possible reason for the absence of the potential dependence of the ET rate in the FeCp-DCM system.

FeCp-DM exhibited the potential dependence of the ET rate similar to FeCp-H. The standard ion transfer potential of FeCp-DM⁺ is more positive than that of TBA⁺, so that FeCp-DM⁺ is distributed to the water phase faster than TBA⁺. Therefore, electric neutrality between the two phases is achieved by ion transfer of FeCp-DM⁺ upon interfacial ET. As a result, the potential dependence of ET rate can be observed analogous to the FeCp-H system, since the liquid-junction potential is kept by the $[TBA^+]_{TBP} / [TBA^+]_w$ ratio.

4.4.2 Origin of the Droplet Size Effect on Electron Transfer Rate

The interfacial ET reaction between FeCp-X in a single TBP droplet and Fe(CN)₆³⁻ in the water phase accompanies ion transfer of FeCp-X⁺ and TBA⁺, so that this makes the overall phenomena complicated and clear discussion on the results is rather difficult. However, the main issue of this dissertation is to elucidate characteristic behavior of the ET process at a spherical micro-liquid / liquid interface, different from that across flat liquid / liquid interfaces. In this respect, the observation of the characteristic droplet size effect on k_{ET} at $r < 5 \mu m$ is very important and, its possible origin and the factors governing the effects are worth discussing in detail. In the following, possible reasons for the droplet size effects are discussed.

i) Rate Determining Step.

In the present experiments, the interfacial ET reaction was monitored by fluorometry and the ET rate was determined by the slope of an $\ln\{I_F^0 / I_F(t) - 1\}$ vs. t plot. This analysis is valid only when the rate determining step is the interfacial ET step. The rate determining step may change with decreasing the droplet size. FeCp-H distributes slightly to the water phase, so that oxidation of FeCp-H in water will not be neglected. However, although FeCp-DM and FeCp-DCM dissolve scarcely in water, analogous droplet size effect on k_{obs} has been observed, so that the oxidation of FeCp-X in water is not the reason of the size effect.

If the rate determining step is diffusion of $Fe(CN)_6^{3-}$ in water, on the other hand, the relevant rate (v_{diff}) is given as¹⁷⁾,

$$v_{diff} = D_{Fe(III)} [Fe(CN)_6^{3-}]_w \{ (\pi D_{Fe(III)} t)^{1/2} + r^{-1} \}$$

where $D_{Fe(III)}$ is the diffusion coefficient of $Fe(CN)_6^{3-}$ in water ($\sim 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ determined by cyclic voltammetry). Since $(\pi D_{Fe(III)} t)^{1/2}$ is negligibly small compared to r^{-1} at $r < \sim 10 \text{ } \mu\text{m}$ and $t > 10 \text{ s}$, the diffusion limited rate constant ($k_{diff} = D_{Fe(III)} / r$) is calculated to be 5×10^{-2} , 1×10^{-2} , or $5 \times 10^{-3} \text{ cms}^{-1}$ at $r = 1, 5$, or $10 \text{ } \mu\text{m}$, respectively. The observed rate is faster than these values, so that diffusion of $Fe(CN)_6^{3-}$ in water is not a rate determining step of the present system.

Diffusion of FeCp-X in a TBP droplet is also considered here. $k_{ET} \times [FeCp-DCM(t)]_{TBP}$ at $t \sim 0 \text{ s}$ is determined to be $8 \times 10^{-4} \text{ cms}^{-1}$, which is 6 times smaller than k_{diff} at $r = 10 \text{ } \mu\text{m}$. The $k_{ET} [FeCp-X(t)]_{TBP}$ value decreases

with t . Furthermore, leveling-off of k_{obs} is observed at $r < 5 \text{ } \mu\text{m}$, independent of the concentration and substituent of FeCp-X ($X = H: 5.0 \times 10^{-2} \text{ M}$, DM: $4.0 \times 10^{-2} \text{ M}$, DCM: $2.0 \times 10^{-2} \text{ M}$). If diffusion of FeCp-X in a droplet influences the rate determining step, furthermore, the ET rate constant should depend on $[Fe(CN)_6^{3-}]_w$. In order to test this possibility, the ET reaction in an emulsion containing a higher concentration of $Fe(CN)_6^{3-}$ in water ($4.0 \times 10^{-2} \text{ M}$, two-fold) was studied; a TBP solution containing FeCp-H ($5.0 \times 10^{-2} \text{ M}$) or FeCp-DCM (2.0×10^{-2}), Pe ($5.0 \times 10^{-4} \text{ M}$) and TBA^+TPB^- (1.0×10^{-2}) was dispersed in water containing $Fe(CN)_6^{3-}$ ($= 4.0 \times 10^{-4}$), $MgSO_4$ (1.0×10^{-1}), and TBA^+Cl^- ($1.0 \times 10^{-1} \text{ M}$ at FeCp-H system, $1.0 \times 10^{-2} \text{ M}$ at FeCp-DCM system) with the weight ratio of 1/500 ($= \text{TBP} / \text{water}$). The results for FeCp-H and FeCp-DCM are shown in Figure 4-24.

The slope of the plot at $r > 5 \text{ } \mu\text{m}$ corresponds to $k_{obs} [Fe(CN)_6^{4-}]_w$. The slope value agreed very well with that at $[Fe(CN)_6^{4-}]_w = 2.0 \times 10^{-4} \text{ M}$. Thus, the diffusion process of FeCp-X in a droplet is not the rate determining step. k_{ET} calculated from the data in Figure 4-24 are shown in Figure 4-25. These plots agreed with the results shown in Figures 4-13 and 4-21. Therefore, it is concluded that the droplet size effect at $r < 5 \text{ } \mu\text{m}$ is not ascribed to the diffusion process in the droplet or water phase.

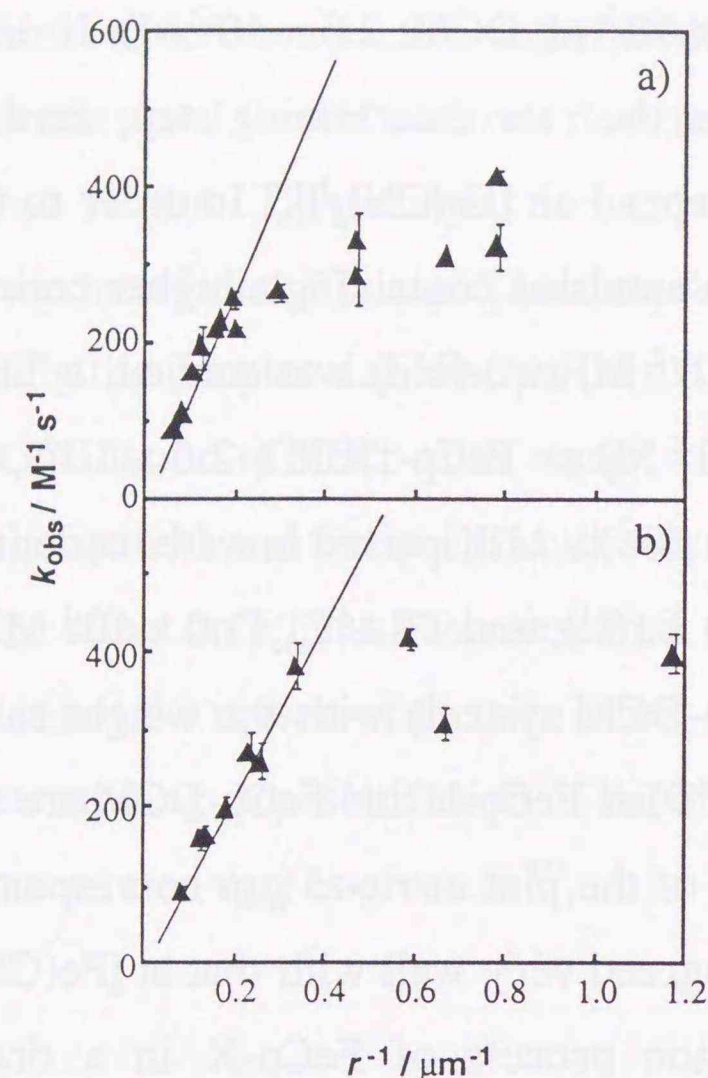


Figure 4-24. The surface area / volume ratio (r^{-1}) dependence of k_{obs} ($[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$, $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 4.0 \times 10^{-4} \text{ M}$, a; $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-1} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$), b; $[\text{FeCp-DCM}]_{\text{TBP}} = 2.0 \times 10^{-2} \text{ M}$, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 1.0 \times 10^{-2} \text{ M}$ ($\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0$)).

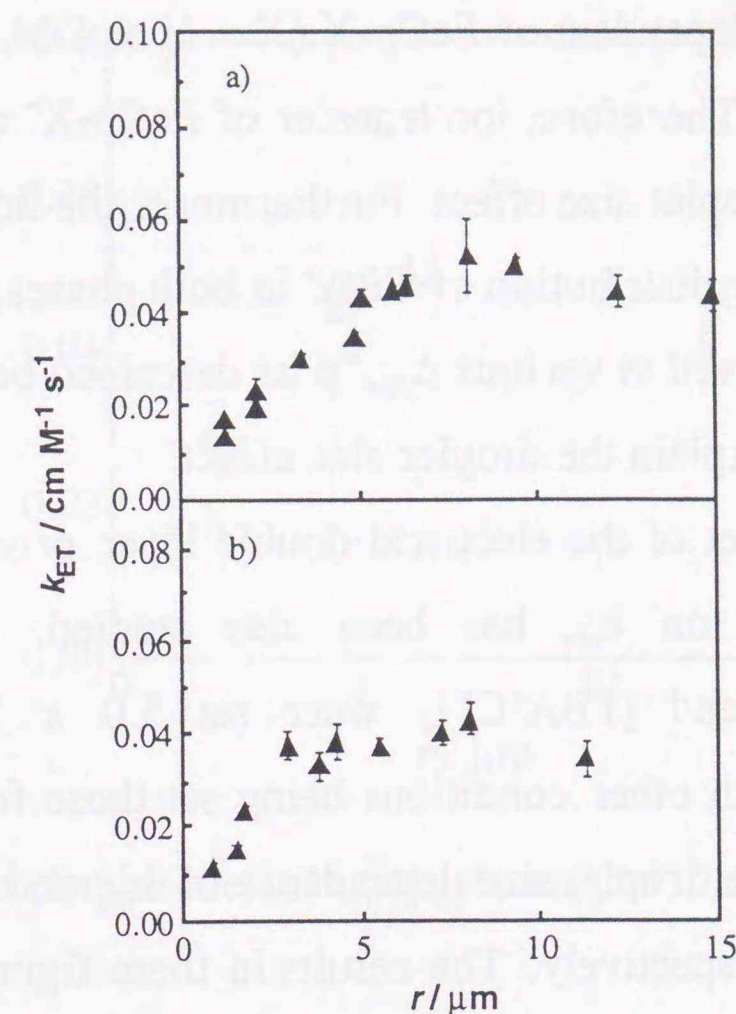


Figure 4-25. The droplet size effect of k_{ET} (a; FeCp-H system, $\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0 - 59 \text{ mV}$, b; FeCp-DCM system, $\Delta_{\text{TBP}}^{\text{w}}\phi = \Delta_{\text{TBP}}^{\text{w}}\phi^0$). The data correspond to those in Figure 4-24.

ii) Liquid-Junction Potential and Ion Transfer.

Electrical neutrality between the droplet and water phases during the interfacial ET reaction is expected to be kept by ion transfer of FeCp- X^+ and/or TBA^+ as described before. Thus, ion transfer of TBA^+ or FeCp- X^+ might directly govern the droplet size effect. If this is the case, however, the critical droplet radius, below which k_{obs} is levelled-off, should depend on the TBA^+ concentrations in both phases and nature of FeCp-X (*i.e.*, difference in the ion transfer potential). However, the critical droplet radius

was $\sim 5 \mu\text{m}$, independent of FeCp-X ($X = \text{H}$ or DM, DCM) and the TBA^+ concentrations. Therefore, ion transfer of FeCp-X^+ and/or TBA^+ is not an origin of the droplet size effect. Furthermore, the liquid-junction potential is determined by distribution of TBA^+ in both phases. Since the droplet size effect was observed at various $\Delta_{\text{TBP}}^w \phi$ as described before, the variation of $\Delta_{\text{TBP}}^w \phi$ cannot explain the droplet size effect.

The effect of the electrical double layer produced at the droplet / water interface on k_{obs} has been also studied. In the experiments, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}}$ and $[\text{TBA}^+\text{Cl}^-]_{\text{w}}$ were set 5.0×10^{-3} , 5.0×10^{-2} M, respectively, with other conditions being set those for the experiments in Figure 4-12. The droplet size dependence of k_{obs} or k_{ET} is shown in Figure 4-26 or 4-27, respectively. The results in these figures are essentially the same with those in Figures 4-12 and 4-13, proving that the electrical double layer at the droplet / water interface is not a factor governing the droplet size effect.

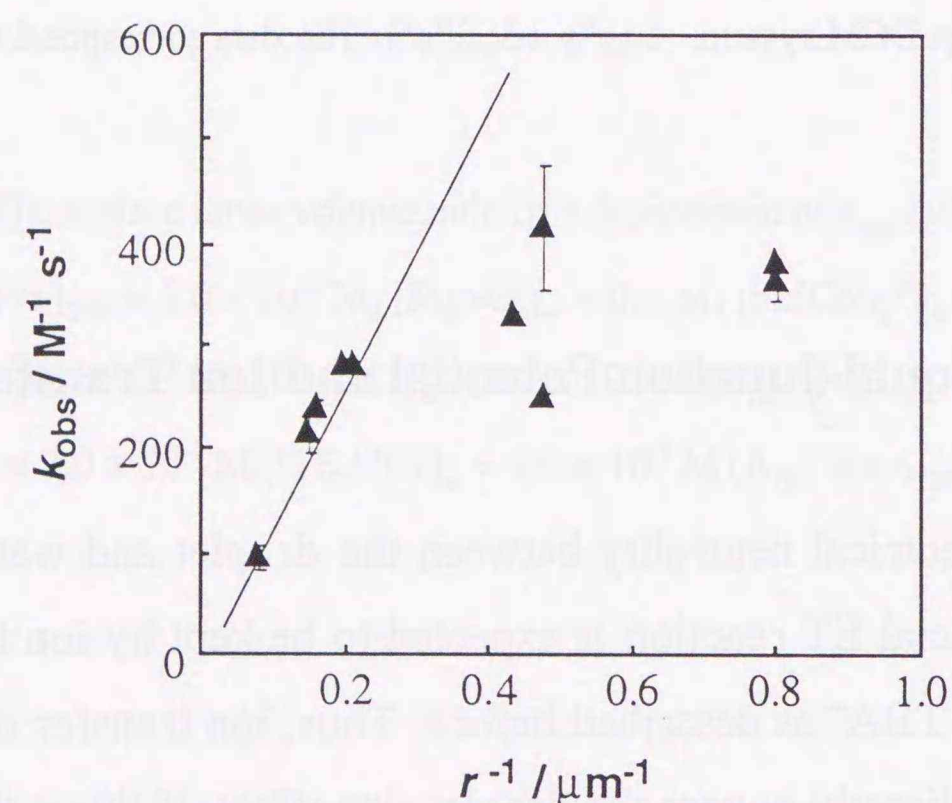


Figure 4-26. The surface area / volume ratio (r^{-1}) dependence of k_{obs} ($[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4}$ M, $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2}$ M, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 5.0 \times 10^{-3}$ M, $[\text{MgSO}_4]_{\text{w}} = 0.1$ M, $[\text{TBA}^+\text{Cl}^-]_{\text{w}} = 5.0 \times 10^{-2}$ M ($\Delta_{\text{TBP}}^w \phi = \Delta_{\text{TBP}}^w \phi^0 + 59$ mV and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4}$ M).

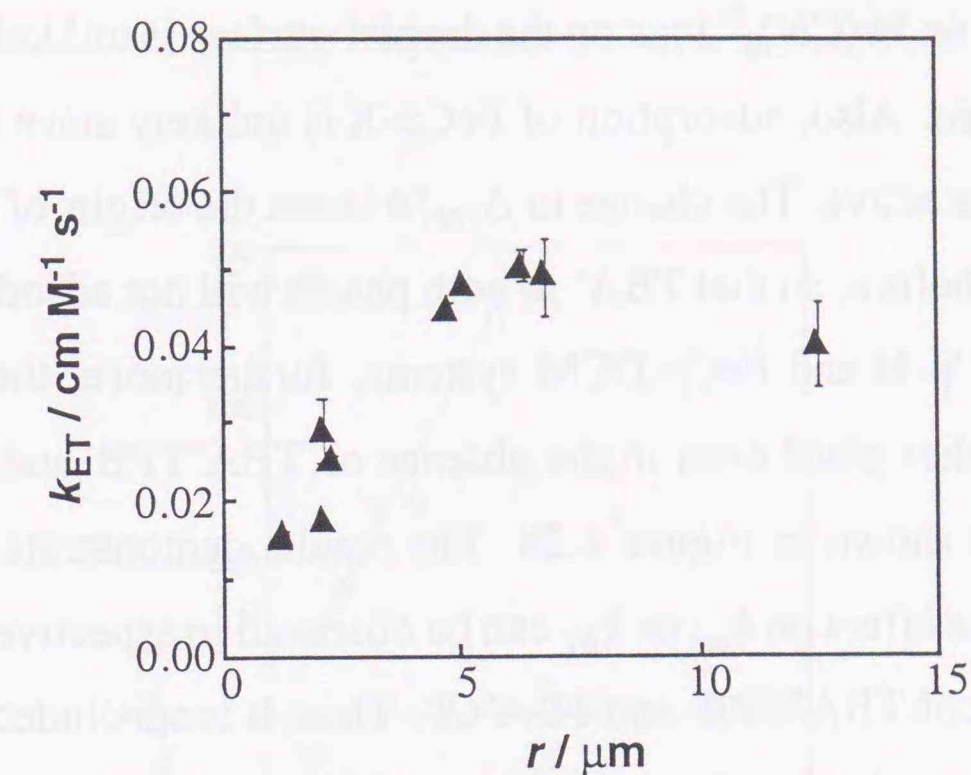


Figure 4-27. The droplet size effect of k_{ET} ($\Delta_{\text{TBP}}^w \phi = \Delta_{\text{TBP}}^w \phi^0$). The data correspond to those in Figure 4-26.

As another possibility, the change in the droplet size might lead to that in $\Delta_{\text{TBP}}^w \phi$, since it is expected that distribution of TBA^+ between the two phases is dependent on the TBP / water weight ratio¹⁵⁾. However, the TBP / water ratio was kept constant ($= 1 / 500$), so that $\Delta_{\text{TBP}}^w \phi$ should be constant. Thus, this possibility is also neglected.

iii) Adsorption of Solutes.

It has been reported that adsorption of a solute on a droplet / water interface is facilitated in micrometer dimension¹⁹⁾. Therefore, adsorption of the solute(s) may be a possible origin of the droplet size effect. The solutes involved in the present system are TBA^+TPB^- , TBA^+Cl^- , MgSO_4 , $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, K^+ , and FeCp-X. Adsorption of Mg^{2+} , SO_4^{2-} , K^+ ,

$\text{Fe}(\text{CN})_6^{4-}$ or $\text{Fe}(\text{CN})_6^{3-}$ ions on the droplet surface is unlikely owing to their ionic nature. Also, adsorption of FeCp-X is unlikely since the compound is not surface active. The change in $\Delta_{\text{TBP}}^w \phi$ is not the origin of the size effect as discussed before, so that TBA^+ in both phases will not adsorb on the surface. In the FeCp-H and FeCp-DCM systems, furthermore, the interfacial ET reaction takes place even in the absence of TBA^+TPB^- and TBA^+Cl^- as the results are shown in Figure 4-28. The results demonstrate clearly that the droplet size effect on k_{obs} or k_{ET} can be observed irrespective of the presence or absence of TBA^+TPB^- and TBA^+Cl^- . Thus, it is concluded that adsorption of a solute on the droplet surface, even if it takes place, is not an origin of the droplet size effect on k_{ET} . In these systems, the ET rate constants (k_{ET}) at $r > 5 \mu\text{m}$ were determined to be 3.5×10^{-2} and $3.0 \times 10^{-2} \text{ cm M}^{-1}\text{s}^{-1}$ for FeCp-H and FeCp-DCM , respectively.

The ionic strength effect on k_{obs} or k_{ET} has been also checked with LiCl being used as an additive in the water phase. TBP containing FeCp-H ($5.0 \times 10^{-2} \text{ M}$), TBA^+TPB^- ($1.0 \times 10^{-2} \text{ M}$), and Pe ($5.0 \times 10^{-4} \text{ M}$) was dispersed in an aqueous solution containing $\text{Fe}(\text{CN})_6^{4-}$ ($2.0 \times 10^{-4} \text{ M}$), MgSO_4 ($1.0 \times 10^{-1} \text{ M}$), TBA^+Cl^- ($1.0 \times 10^{-2} \text{ M}$), and LiCl ($9.0 \times 10^{-2} \text{ M}$) with a weight ratio of TBP / water = 1 / 500. In this emulsion, the total concentration of Cl^- in the water phase was adjusted to 0.1 M. The droplet size dependencies of k_{obs} and k_{ET} are summarized in Figures 4-30 and 4-31, respectively.

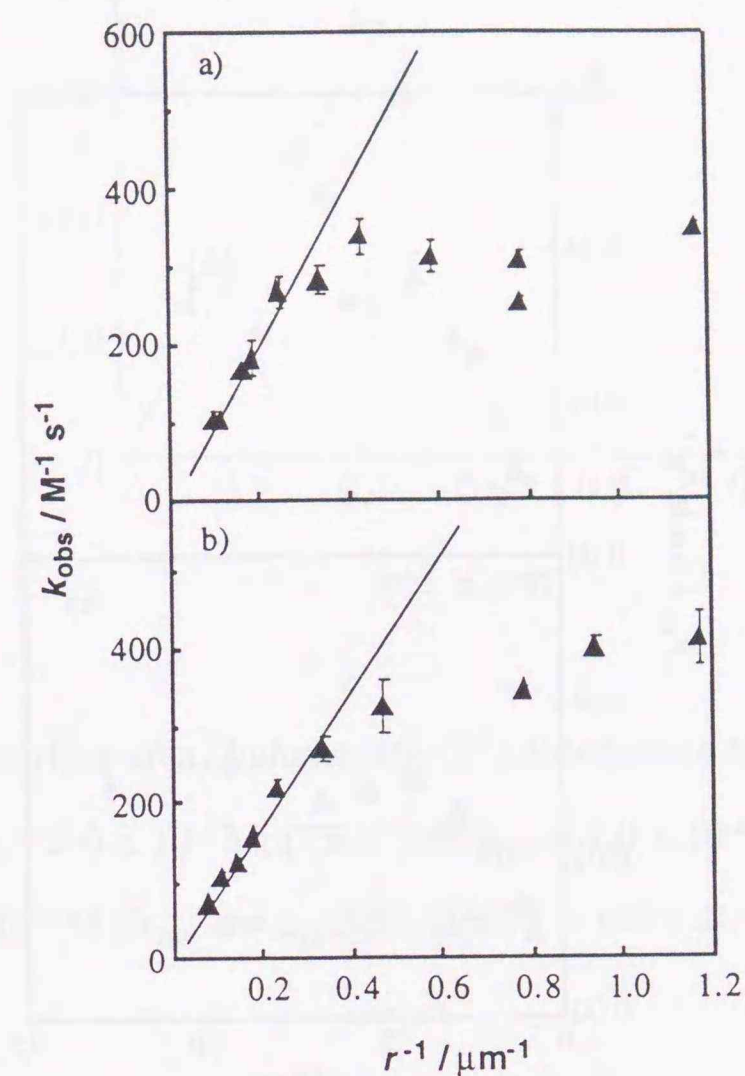


Figure 4-28. The surface area / volume ratio (r^{-1}) dependence of k_{obs} ($[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-4} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$ and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$, a; $[\text{FeCp-H}]_{\text{TBP}} = 5.0 \times 10^{-2} \text{ M}$, b; $[\text{FeCp-DCM}]_{\text{TBP}} = 2.0 \times 10^{-2} \text{ M}$).

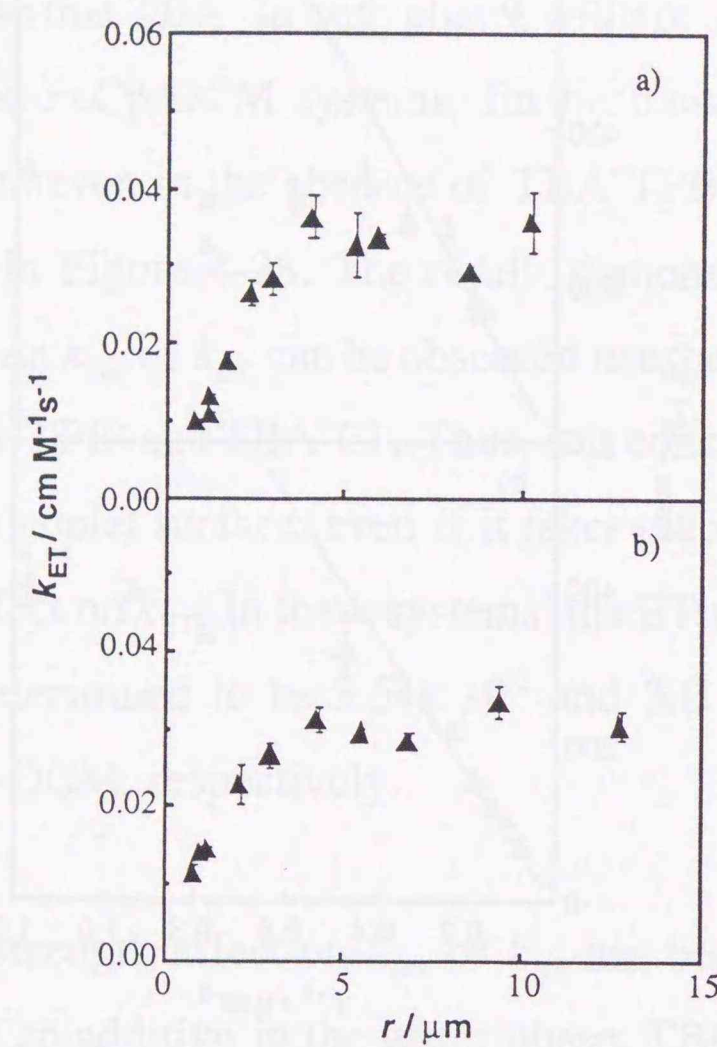


Figure 4-29. The droplet size effect of k_{ET} (a; FeCp-H system, b; FeCp-DCM system). The data correspond to those in Figure 4-28.

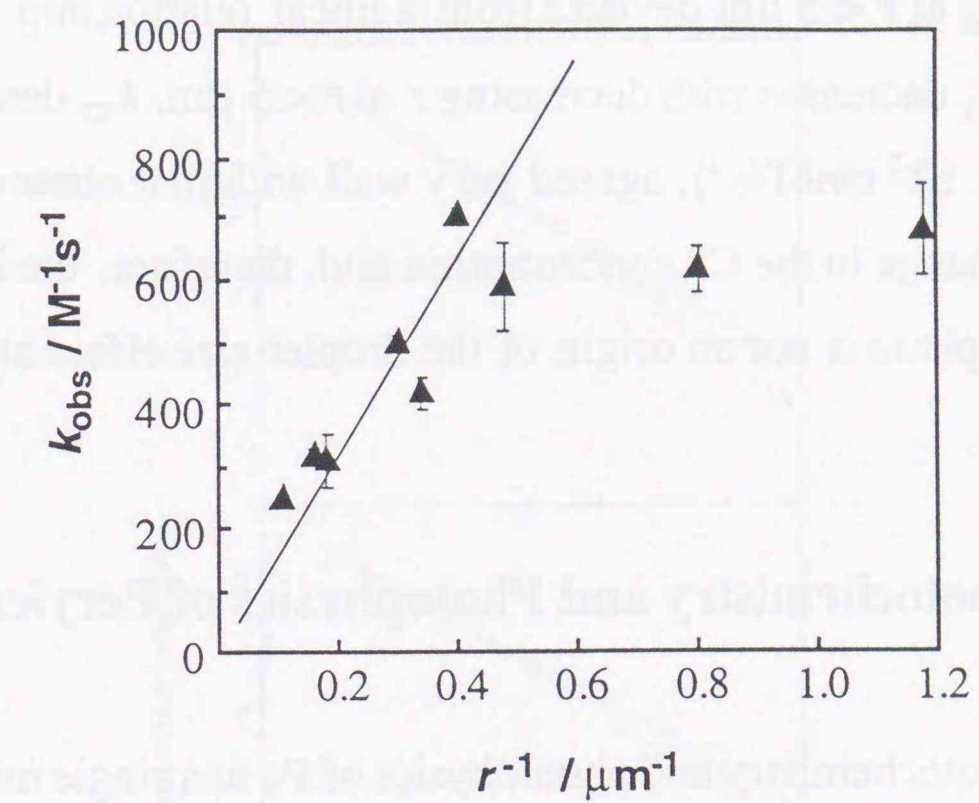


Figure 4-30. The surface area / volume ratio (r^{-1}) dependence of k_{obs} ($[Pe]_{TBP} = 5.0 \times 10^{-4}$ M, $[FeCp-H]_{TBP} = 5.0 \times 10^{-2}$ M, $[TBA^+TPB^-]_{TBP} = 1.0 \times 10^{-2}$ M, $[MgSO_4]_w = 0.1$ M, $[TBA^+Cl^-]_w = 1.0 \times 10^{-2}$ M ($\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$), $[LiCl]_w = 9.0 \times 10^{-2}$ M and $[Fe(CN)_6^{4-}]_w = 2.0 \times 10^{-4}$ M).

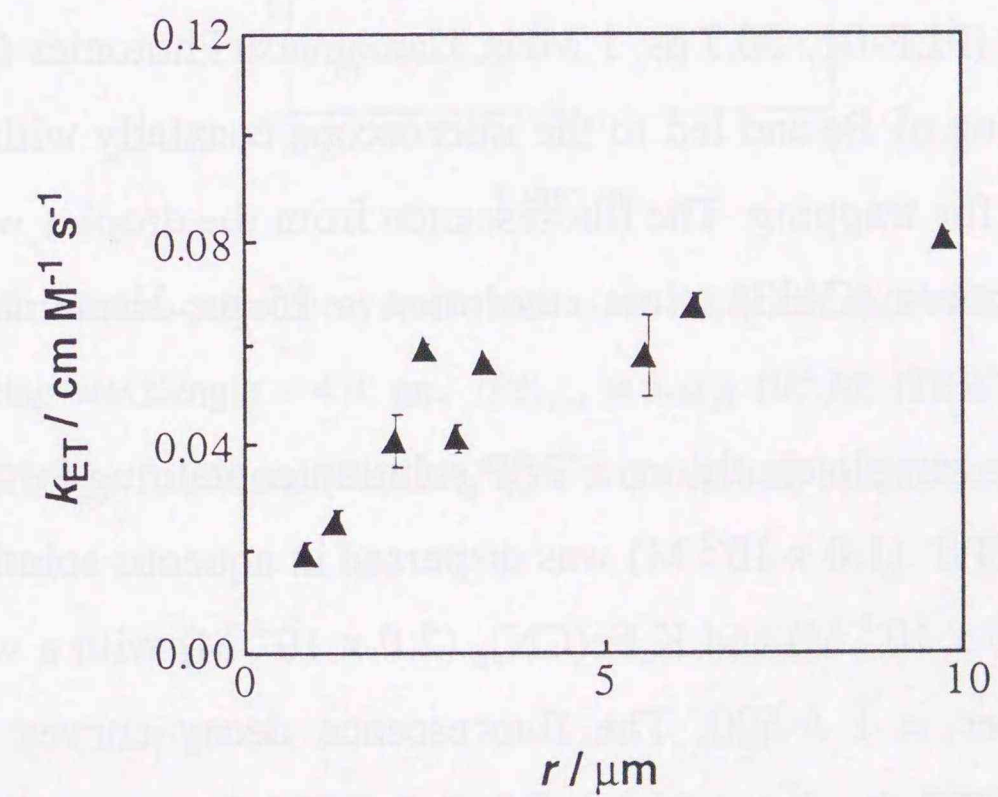


Figure 4-31. The droplet size effect of k_{ET} ($\Delta_{TBP}^w \phi = \Delta_{TBP}^w \phi^0$). The data correspond to those in Figure 4-30.

k_{obs} at $r < 5 \mu\text{m}$ deviates from a linear relationship between k_{obs} and r^{-1} , and k_{ET} decreases with decreasing r at $r < 5 \mu\text{m}$. k_{ET} determined at $r > 5 \mu\text{m}$ ($7.0 \times 10^{-2} \text{ cmM}^{-1}\text{s}^{-1}$), agreed very well with that observed in Figure 4-13. The change in the Cl^- concentration and, therefore, the ionic strength in the water phase is not an origin of the droplet size effect at $r < 5 \mu\text{m}$.

iv) Photochemistry and Photophysics of Perylene.

Photochemistry and photophysics of Pe in a single micrometer-sized droplet may be dependent on the droplet size. If this is the case, the fluorescence intensity of Pe before electrolysis of $\text{Fe}(\text{CN})_6^{4-}$ should be dependent on r through an r effect on k_q and τ_0 . The fluorescence lifetime of Pe was thus measured for various-sized single droplets by a single photon counting method. The block diagram of the optical system used for the present study was shown in Figure 2-3. 417 nm pulses from a picosecond diode laser (PLP-01, 26.7 ps, 1 MHz, Hamamatsu Photonics Co.) were used for excitation of Pe and led to the microscope coaxially with the 1064 nm laser beam for trapping. The fluorescence from the droplet was detected by a streak camera (C4334, time resolution ~ 15 ps, Hamamatsu Photonics Co.).

As a sample emulsion, a TBP solution containing Pe ($5.0 \times 10^{-3} \text{ M}$) and TBA^+TPB^- ($1.0 \times 10^{-2} \text{ M}$) was dispersed in aqueous solution containing MgSO_4 ($1.0 \times 10^{-1} \text{ M}$) and $\text{K}_4\text{Fe}(\text{CN})_6$ ($2.0 \times 10^{-4} \text{ M}$) with a weight ratio of TBP / water = 1 / 500. The fluorescence decay curves observed for individual TBP droplets with $r = 8.0, 4.5$, and $1.3 \mu\text{m}$ are shown in Figure 4-32.

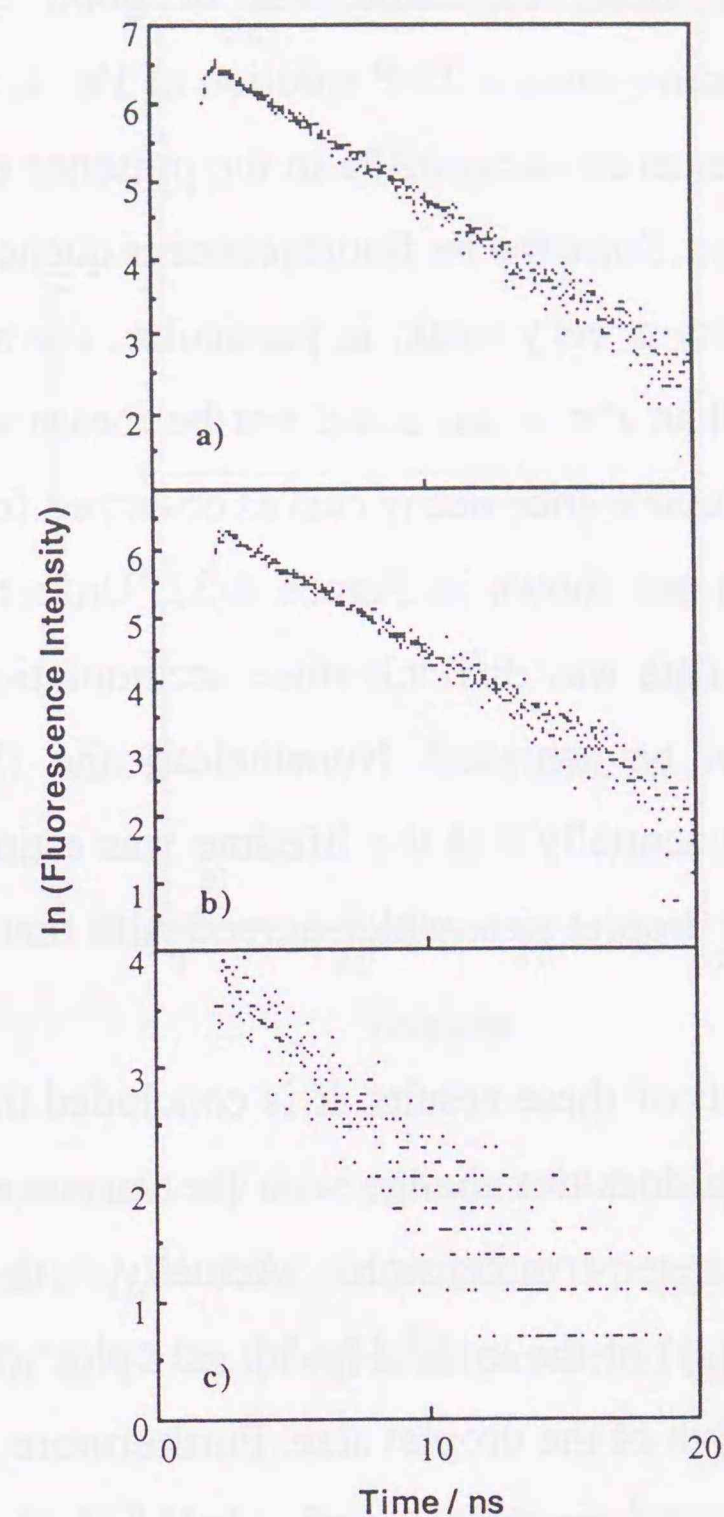


Figure 4-32. Fluorescence decay curve of Pe (a; $r = 8.0 \mu\text{m}$, b; $r = 4.5 \mu\text{m}$, c; $r = 1.3 \mu\text{m}$, monitoring wavelength = 470 nm, $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-3} \text{ M}$, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2} \text{ M}$, $[\text{MgSO}_4]_{\text{w}} = 0.1 \text{ M}$ and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4} \text{ M}$) in the absence of FeCp-H in the droplet.

Although the signal-to-noise ratios of the data for the droplet with $r = 1.3 \mu\text{m}$ were not necessarily good, the fluorescence exhibited a single exponential decay and its time constant was independent of the droplet size.

Furthermore, the observed value was in good agreement with that determined in a homogeneous TBP solution of Pe ($\tau_0 = \sim 4.3$ ns).

The fluorescence decay of Pe in the presence of FeCp-H (5.0×10^{-2} M) was also studied. Since the Pe fluorescence is quenched by FeCp-H in the droplet, its intensity is very weak, in particular, for small droplets. Thus, droplets smaller than $r < 5 \mu\text{m}$ could not be measured under the present conditions. The fluorescence decay curves observed for the droplets with $r = 8.0$ and $5.5 \mu\text{m}$ are shown in Figure 4-33. Unfortunately, quantitative discussion on the data was difficult since accumulation of enough photon number could not be achieved. Nonetheless, the fluorescence decayed almost single-exponentially and the lifetime was estimated to be ~ 1.5 ns irrespective of the droplet size, which agreed with that observed in the bulk system (~ 1.5 ns).

On the basis of these results, it is concluded that photocemistry or photophysics of Pe does not change with the variation of the droplet size even in micrometer dimension. Actually, the intercept value ($\ln\{k_q\tau_0[\text{FeCp-X}]_{\text{TBP}}\}$) of the $\ln\{I_F^0/I_F(t) - 1\}$ vs. t plot was almost constant at $0.6 \sim 0.8$ irrespective of the droplet size. Furthermore, since the interfacial ET rate is determined from the slope of an $\ln\{I_F^0/I_F(t) - 1\}$ vs. t plot, the k_{obs} value is not influenced by variations of k_q and τ_0 . Also, the $I_F^0/I_F(t)$ value calculated from the fluorescence lifetimes determined for the bulk solutions agreed with the observed value. Therefore, photophysics or photochemistry of Pe in single micrometer-sized droplets cannot explain the characteristic droplet size effect on k_{obs} at $r < 5 \mu\text{m}$.

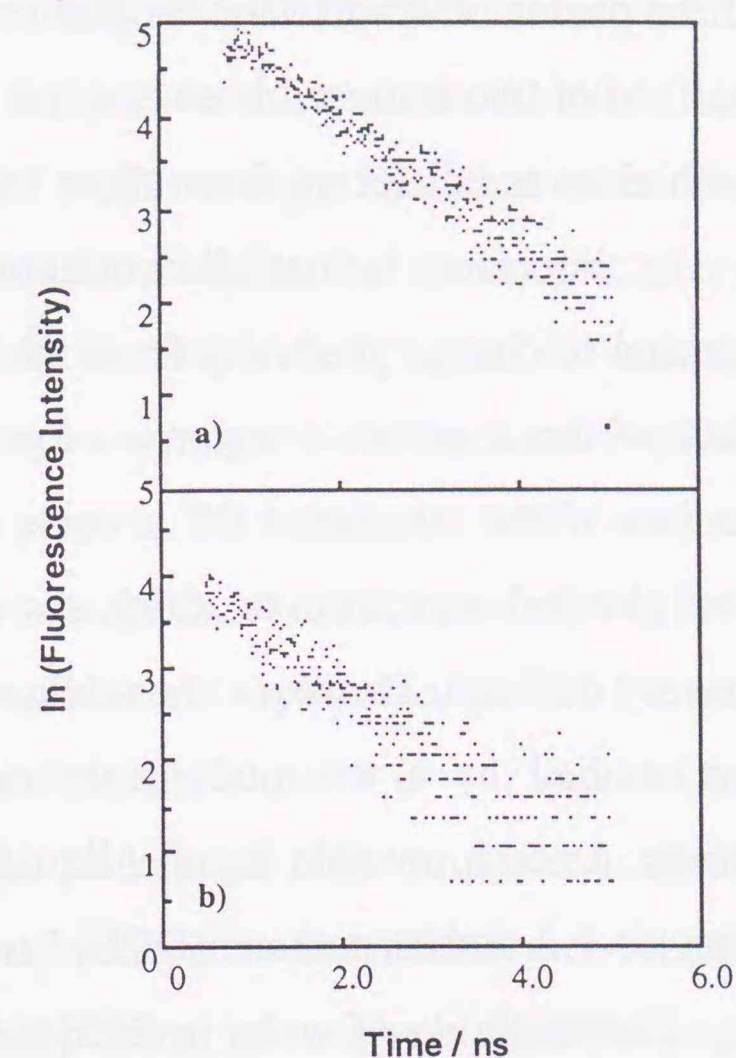


Figure 4-33. Fluorescence decay curve of Pe (a; $r = 8.0 \mu\text{m}$, b; $r = 5.5 \mu\text{m}$, monitoring wavelength = 470 nm, $[\text{Pe}]_{\text{TBP}} = 5.0 \times 10^{-3}$ M, $[\text{TBA}^+\text{TPB}^-]_{\text{TBP}} = 1.0 \times 10^{-2}$ M, $[\text{MgSO}_4]_{\text{w}} = 0.1$ M and $[\text{Fe}(\text{CN})_6^{4-}]_{\text{w}} = 2.0 \times 10^{-4}$ M) in the presence of FeCp-H in the droplet (5.0×10^{-2} M).

v) Physical Properties of the Micrometer-Sized TBP Droplet.

It is noteworthy that the critical droplet radius showing leveling-off of k_{obs} with r is independent of $\Delta_{\text{TBP}}^w\phi$ and the nature of FeCp-X ($X = \text{H}$, DM or DCM), while the size effect on k_{obs} disappears in the presence of a surfactant. Furthermore, the ET reaction proceeds efficiently even in the absence of an electrolyte in the TBP droplet. These results suggest the

possible origin of the present characteristic droplet-size effect at $r < 5 \mu\text{m}$.

At the interface of two immiscible electrolyte solutions, the solvent constitutions in both sides are different from those in the bulk phase. At a molecular level, the interface is not discontinuous, and the solvent constitution is expected to change gradually from the interface to the bulk phase. The thickness of this interfacial region is of primary importance to discuss the mechanism of the interfacial ET process. In general, a direct observation of the physical structure or thickness of a liquid / liquid interface region is very difficult. However, the thickness of a liquid / liquid interface has been studied by a thermodynamic method or molecular dynamics calculations. As an immiscible liquid / liquid system, typically, a nitrobenzene / water or 1,2-dichloroethane (DCE) / water system has been studied extensively. The solubility of water in DCE is 0.15 wt% and that of water in nitrobenzene is 0.24 wt%¹²⁾. Thermodynamic studies indicate that the thickness of the nitrobenzene (0.1 M TBA⁺TPB⁻) / water (0.1 M LiCl) interface is very thin ($\sim 1 \text{ nm}$)¹⁵⁻¹⁷⁾. Such an interfacial region will be composed of solvent molecules alone and, electrolyte ions, even if it presents, do not participate to the interface region. Molecular dynamics calculations also demonstrate that the thickness of a DCE / water interface is as thin as $\sim 1 \text{ nm}$ ¹⁴⁾. At the interface, furthermore, the structures and properties of the solvent are different from those in the bulk phase. For instance, hydrogen bonding of water is stronger at an organic solvent / water interface compared to that in bulk water. A second harmonic generation method also indicates that aromatic hydrocarbon molecules sit at the hydrocarbon / water interface in a more ordered fashion as compared with those in the bulk system²⁰⁾.

In the case of the nitrobenzene / water and DCE / water systems, the interfacial layer is very thin owing to mutual immisibilities of the two

solvents. Thus, an ideal liquid / liquid interface seems to be produced in such systems. In the present system, on the other hand, the solubility of water in TBP (4.67 wt%) is larger than that of the nitrobenzene / water or DCE / water system. This implies that the interfacial layer between TBP and water is expected to be thicker than 1 nm. If the interfacial layer is thick compared to the molecular size of FeCp-X or Fe(CN)₆³⁻ ($\gg 1 \text{ nm}$), the ET reaction will take place in the interfacial TBP / water mixed solvent layer. In relatively large droplets, the thickness of the interfacial layer is thin enough compared with the droplet size, so that the interfacial ET rate will be determined by the A / V ratio ($r > 5 \mu\text{m}$). On the other hand, the contribution of the interfacial layer to the overall reaction rate becomes important along with a decrease in r . Below a certain droplet radius, namely, the rate will be independent of r , where the ET reaction proceeding in the interfacial layer governs the overall reaction rate. Qualitatively, this is what is observed in the present experiments. Such the model is not unrealistic, since analogous droplet size effects have been reported (not single droplets measurements) for a dye formation reaction between a quinonediimine derivative in water and a naphthol derivative in oil droplets: the rate is dependent on r at $r > \sim 0.1 \mu\text{m}$, but is not at $r < \sim 0.1 \mu\text{m}$ ²¹⁾.

As an advantage of this model, the absence of the $\Delta_o^w\phi$ and additive effects on the critical droplet radius can be explained, assuming the relatively thick interfacial layer. Furthermore, although it has been reported that the ET reaction between FeCp-DCM and Fe(CN)₆³⁻ does not take place at a DCE / water interface⁴⁾, the reaction proceeds at the TBP / water interface even in the absence of TBA⁺TPB⁻ and TBA⁺Cl⁻ (Figures 4-28 and 4-29). This is also explained by assuming the thick interfacial mixed layer. When a surfactant is added to the TBP / water system, the thickness of the interfacial layer decreases since adsorption of the surfactant

on the droplet interface will bring about a decrease in the solubility of water in TBP. Indeed, k_{obs} was proportional to r^{-1} in the presence of SDS or Triton-X100 in the $\text{FeCp-H} / \text{Fe}(\text{CN})_6^{3-}$ system (Figure 3-22), indicating that the ET rate is determined by the A / V ratio alone. The observation of the A / V ratio effect on k_{obs} down to $r \sim 1 \mu\text{m}$ in the presence of SDS or Triton-X100 will support the important role of the thickness and properties of the interfacial layer in determining the ET rate. Assuming the relatively thick interfacial layer, the present results on the characteristic droplet size effect on k_{ET} are explained by a single context.

4.5 Conclusion.

The ET reaction rate between FeCp-X and $\text{Fe}(\text{CN})_6^{3-}$ across the TBP / water interface was determined for individual microdroplets and, *found two classes of the droplet size effect on the ET rate: the A / V ratio effect ($r > 5 \mu\text{m}$) and the intrinsic droplet size dependence ($r < 5 \mu\text{m}$).* So far, chemical reactions in emulsion systems have been studied for a large number of droplets and, single droplet measurements have been scarcely explored. Therefore, the droplet size dependence of a chemical reaction has not been discussed. In this regard, the present study is very important for further advances in chemistry in emulsion systems.

As a characteristics of the chemistry at a droplet / water interface, diffusion of an ion to the droplet surface proceeds in a spherical manner. This is in contrast to mass transfer at a flat liquid / liquid interface (linear diffusion). Thus, *the mass transfer process toward the droplet surface is facilitated for smaller droplets. This is the origin of the A / V ratio effect on k_{obs} observed at $r > 5 \mu\text{m}$.* This is easily expected from available diffusion

theories and analogous A / V effects on a reaction rate will be expected for various emulsion systems. On the other hand, *the droplet size dependence of k_{obs} or k_{ET} at $r < 5 \mu\text{m}$ is certainly characteristic to a micrometer-sized spherical liquid / liquid interface. The size dependence was explained reasonably in terms of the change in the interfacial structures of the droplet with r .* At the present stage, an experimental verification of the surface structure of a droplet is very difficult. However, *the present findings are very important, since characteristic features of a spherical micro-liquid / liquid interface, different from those at a flat liquid / liquid interface, were observed experimentally for the first time.* Further detailed and systematic studies reveal a new insight on microdroplet chemistry. It is worth to be pointed out that a study on a droplet-size dependence of a reaction rate is indispensable to elucidate detailed mechanisms of reactions in emulsion systems.

4.6 References.

- 1) C.Wei, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **99**,16033 (1995).
- 2) M.Tsionsky, A.J.Bard and M.V.Mirkin, *J.Phys.Chem.*, **100**,17881 (1996).
- 3) M.Tsionsky, A.J.Bard and M.V.Mirkin, *J.Am.Chem.Soc.*, **119**,10785 (1997).
- 4) V.J.Cunnane, G.Geblewicz and D.J.Schiffrin, *Electrochim.Acta*, **40**,3005 (1995).
- 5) Z.Samec, *J.Electroanal.Chem.*, **111**,211 (1980).
- 6) J.Hanzlik, J.Hovorka, Z.Samec and S.Toma, *Coll.Czech.Chem.Comm.*, **53**,903 (1987).

- 7) R.A.Marcus, *J.Phys.Chem.*, **94**,1050 (1990).
- 8) R.A.Marcus, *J.Phys.Chem.*, **94**,4152 (1990).
- 9) R.A.Marcus, *J.Phys.Chem.*, **95**,2010 (1991).
- 10) J.O'M.Bockris, S.U.M.Khan and D.B.Matthews, *J.Res.Inst.Catal.,Hokkaido Univ.*, **22**,1 (1974).
- 11) T.Gennett, D.F.Milner and M.J.Weaver, *J.Phys.Chem.*, **89**,2787 (1985).
- 12) J.A.Riddick and W.B.Bunger, *Techniques of Chemistry:Organic Solvents*, ed by A.Weissberger, Wiley-Interscience, New York (1970).
- 13) Y.Cheng and D.J.Schiffrin, *J.Chem.Soc.,Faraday Trans.*,**89**,199 (1993).
- 14) I.Benjamin, *Chem.Rev.*, **96**,1449 (1996).
- 15) H.H.Girault and D.J.Schiffrin, *J.Electroanal.Chem.*,**150**,43 (1983).
- 16) T.Kakiuchi, J.Noguchi and M.Senda, *J.Electroanal.Chem.*, **327**,63 (1992).
- 17) A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York (1980).
- 18) T.Kakiuchi, *Anal.Chem.*, **68**,3658 (1996).
- 19) K.Nakatani, M.Sudo and N.Kitamura, *J.Phys.Chem.B*, **102**,2908 (1998).
- 20) J.C.Conboy, J.L.Daschbach and G.L.Richmond. *J.Phys.Chem.*, **98**,9688 (1994).
- 21) L. K. J. Tong, In *The Theory of the Photographic Process*, ed by T. H. James, Macmillan, New York, p. 339 (1977).

Chapter 5

Summary, Conclusions, and Future Perspective

The electron transfer (ET) reaction between a ferrocene derivative (FeCp-X) and $\text{Fe}(\text{CN})_6^{3-}$ across a single microdroplets / water interface was studied and two classes of the droplet size effects on the ET rate were demonstrated experimentally.

So far, ET reactions across macroscopic flat liquid / liquid interfaces have been studied extensively among the past decades. However, there has been no report on ET across a single droplet / solution interface. Thus, a new and novel experimental methodology for single microdroplet measurements was developed. A laser trapping - spectroscopy - electrochemistry system, capable of simultaneous manipulation and spectroscopic / electrochemical measurements of individual micro-oil droplets in water, was constructed. Also, in order to determine the interfacial ET rate for individual droplets, the coulometric and fluorometric methods were developed, by which the time course of the FeCp-X concentration was followed by fluorescence quenching of a probe by FeCp-X in a droplet. On the basis of these methodological developments, it was shown that the interfacial ET rate constant could be determined for single microdroplets as small as the radius (r) of 1 μm (Chapter 3).

As the most important results of the study, *the droplet size dependence of the ET rate was demonstrated for the first time*. Since such a study can be done by a droplet - resolved method alone, the laser trapping - spectroscopy - electrochemistry technique has a high potential to study various chemical reaction / processes in emulsion systems. *At $r > 5 \mu\text{m}$, the interfacial ET rate was governed essentially by the surface area / volume (A*

A/V ratio of the droplet, by which the rate increased linearly with the increase in the inverse of r owing to spherical diffusion of the solute to the droplet surface. Such a feature is well known and solvent extraction is one example. Namely, distribution of a solute between two liquid/liquid phases reaches faster when the solution is shaken vigorously. Since mass transfer of a solute to the droplet surface proceeds in a spherical manner, a distribution equilibrium of the solute attains faster for smaller droplets owing to a large A/V ratio of droplets. Chemists know this empirically or theoretically. Nonetheless, this has been rarely shown experimentally owing to a lack of a manipulation method of single droplets in solution. *The present study proved explicitly the A/V ratio effect on the interfacial reaction rate (Chapters 3 and 4).*

The more striking result of the study is *the observation of the droplet size dependence of the ET rate at $r < 5 \mu\text{m}$, which cannot be explained by the variation of the A/V ratio of the droplet.* This is quite interesting, since analogous effects cannot be expected at flat liquid/liquid interfaces. Thus, *the size effect on the ET rate at $r < 5 \mu\text{m}$ is the intrinsic properties of the spherical micro-sized liquid/liquid interface.* Besides this, the ET rate was also shown to be dependent on the liquid-junction potential and an additive such as a surfactant, demonstrating the importance of chemical and physical properties of the droplet/water interface (Chapter 4).

The characteristic droplet size effect on the ET rate at $r < 5 \mu\text{m}$ was explained in terms of the interfacial structures of the droplet: relatively thick oil/water mixed interfacial layer. However, the experimental verification of the model is very difficult at the present stage, since there is no method to observe the interfacial layer of single microdroplets. Besides, the mixed interfacial layer model, the capillary waves propagating at the

droplet/water interface might be another possible reason for the size effect. Actually, the droplet size dependence of the water-to-nitrobenzene droplet mass transfer rate of a ferrocene derivative has been explained by the variation of the wavelength of the capillary wave with r ($2\pi r$). Nevertheless, experimental proof is difficult even for this system.

The thesis tried to elucidate characteristic features of the ET reaction across a single droplet/water interface. In this regard, the study was successful to show such an example. However, there exists still unresolved problems as mentioned above, and these will be clarified by complementary studies using more surface specific spectroscopies such as total internal reflection spectroscopy, second harmonic generation, or sum frequency generation spectroscopy.

Finally, it should be mentioned that, in micrometer dimension, various chemical and physical processes across droplet/solution interfaces are expected to be depend on the droplet size. In near future, various examples of the droplet size effects, similar to the present findings, will be revealed, whose knowledge will advance further researches in the chemistry of emulsion systems.

Acknowledgments

I would like to express my science gratitude to Professor Noboru Kitamura for his continuing guidance and stimulating criticism through out the works of this thesis.

I am much grateful and indebted to Dr. Kiyoharu Nakatani for his valuable discussions and advices.

I am much grateful to Associate Professor Haeng-Boo Kim, Dr. Hiroshi Yao for their helpful suggestions and discussions.

I am much grateful to Professor Kohei Uosaki, Professor Youichi Sasaki and Professor Masatsugu Shimomura for the examinations of this thesis.

I wish to thank all the members of the Analytical Chemistry Laboratory (Kitamura Laboratory), Division of Chemistry, Graduate School of Science, Hokkaido University for their friendships.

Sapporo, Hokkaido

Katsumi CHIKAMA

Katsumi Chikama

Publication Lists

1) Kiyoharu Nakatani, Katsumi Chikama, Haeng-Boo Kim and Noboru Kitamura

Fluorometric and Coulometric Analysis of Electron Transfer across Microdroplet / Water Interface
Chem.Lett., 793 (1994).

2) Yukinori Tani, Yoshio Umezawa, Katsumi Chikama, Akihide Hemmi and Mitsuyuki Soma

Non-stoichiometric Dissolution of Lanthanum Fluoride (LaF_3) and its Relevance to a Process of Ion-Selective Charge Separation at the Solid / Solution Interface
J.Electroanal.Chem., **378**, 205 (1994).

3) Kiyoharu Nakatani, Katsumi Chikama, Haeng-Boo Kim and Noboru Kitamura

Droplet - Size Dependence of Electron Transfer Rate across Single-Microdroplet / Water Interface
Chem. Phys. Lett., **237**, 133 (1995).

4) Kiyoharu Nakatani, Mari Wakabayashi, Katsumi Chikama and Noboru Kitamura

Electrochemical Studies on Mass Transfer of Ferrocene Derivatives across a Single-Nitrobenzene-Microdroplet / Water Interface
J.Phys.Chem., **100**, 6749 (1996).

5) Chikama Katsumi, Kiyoharu Nakatani and Noboru Kitamura

Liquid-Junction Potential Dependence of the Electron Transfer Rate across a Single-Microdroplet / Water Interface
Chem.Lett., 665 (1996).

6) Chikama Katsumi, Kiyoharu Nakatani and Noboru Kitamura
Characteristic Behavior of the Electron Transfer Reaction across a Tri-n-
butyl Phosphate Droplet / Water Interface : Micrometer Droplet - Size
Effect
Bull.Chem.Soc.Jpn., **71**, 1065 (1998).

7) Kiyoharu Nakatani, Katsumi Chikama and Noboru Kitamura
Laser Trapping, Spectroscopy - Electrochemistry of Individual
Microdroplets in Solution
Advances in Photochemistry, Wiley-Interscience, New York, vol.24, in
press.

