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ABSOLUTE ELECTROMOTIVE FORCES OF SINGLE ELECTRODES

By

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Abstract

The standard molal real free energies of solvation of single atomic ions α^{0}'s and the absolute electromotive forces φ^{0}'s of the electrodes associated with the oxidation and reduction of these ions have been estimated in non-aqueous media by an empirical method proposed previously. Using these absolute electromotive forces the absolute values of polarographic half-wave reduction potentials of aromatic hydrocarbons have been estimated. It has been found that these half-wave reduction potentials are linearly correlated with the $h\nu$-values of the π-π^* transition from the highest occupied to the lowest unoccupied molecular orbital of these molecules with a gradient 1/2, indicating an tendency to approach the work function of graphite with the decrease of $h\nu$.

Introduction

It is a long-standing problem in electrochemistry to determine the electrode potential referred to the energy level of the electron in vacuum. An empirical method has recently been developed in our laboratory to determine the standard molal real free energies of solvation $\alpha^{0\prime}$s of single atomic ions in non-aqueous media, CH_3OH, C_2H_5OH, HCOOH, CH_3CN, $HCONH_2$, NH_3, N_2H_4, DMSO, quinoline and also in fused salts, on which basis the absolute electromotive forces $\varphi^{0\prime}$s associated with the oxidation or reduction of these ions in non-aqueous media which are referred to the energy level of the gaseous electron in the standard state have been estimated for 70 elements[1,2,3]. Although the electromotive force determined in this way may differ in principle from the true absolute electrode potential by $\bar{\mu}^{0}_{e(g)}/F$, where $\bar{\mu}^{0}_{e(g)}$ is the electrochemical potential of the gaseous electron in the standard state and F is the Faraday, it will be called in the present work the absolute electromotive force or the absolute electrode potential for the convenience sake.

In the present work the values of α^{0}'s and φ^{0}'s will be estimated for

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single atomic ions in dimethylformamide (DMF), nitromethane (NM), N-methylformamide (N-MF), propylene carbonate (PC) and pyridine (P_y) by the empirical method proposed previously[1], and using these absolute potentials the polarographic absolute half-wave reduction potentials of aromatic hydrocarbons in some non-aqueous media will be estimated, and from the comparison of these absolute potentials with the frequencies of the electronic absorption spectra of the $\pi-\pi^*$ transition of these molecules it will be shown that the half-wave reduction potentials in the absolute scale may be regarded as the energy levels of the lowest unoccupied molecular orbitals of these molecules in condensed media.

Determination of α^0 and φ^0 in non-aqueous media

The empirical method proposed previously will briefly be surveyed here[1].

Let us consider the standard potential E°_{ij} of a redox system at a given temperature composed of a single atomic ion i of valency z_i and its pure element which is measured against a reference electrode composed of a single atomic ion j and its pure element. E°_{ij} is given by the absolute potential of each electrode in non-aqueous solution as

$$E^{\circ}_{ij}=\varphi^{\circ}_{i}-\varphi^{\circ}_{j} \tag{1}$$

and in aqueous solution with suffix aq as

$$E^{\circ}_{ij,aq}=\varphi^{\circ}_{i,aq}-\varphi^{\circ}_{j,aq} \tag{2}$$

On the other hand, the molal standard free energy of formation ΔF°_{i} of the gaseous ion i from its pure element may be correlated with the free energy of solvation of the ion i and the absolute potential in aqueous or non-aqueous solution by Eq. (3) or (4),

$$\Delta F^{\circ}_{i}=-\alpha^{\circ}_{i}+z_iF\varphi^{\circ}_{i}=-\alpha^{\circ}_{i,aq}+z_iF\varphi^{\circ}_{i,aq}\,, \tag{3}$$

where $-\alpha^{\circ}_{i}$ is the standard molal real free energy of solvation of the ion i in non-aqueous solution and $-\alpha^{\circ}_{i,aq}$ is that in aqueous solution, and for the ion j

$$\Delta F^{\circ}_{j}=-\alpha^{\circ}_{j}+z_jF\varphi^{\circ}_{j}=-\alpha^{\circ}_{j,aq}+z_jF\varphi^{\circ}_{j,aq}\,. \tag{4}$$

The relative free energy of solvation A_{ij} of the ion i in non-aqueous solution referred to that of the ion j

$$A_{ij}\equiv-\frac{1}{z_i}\alpha^{\circ}_{i}+\frac{1}{z_j}\alpha^{\circ}_{j}\,, \tag{5}$$

is obtained from Eqs. (1)-(4) as

$$A_{ij} = -\frac{1}{z_i}\,\alpha^{\circ}_{i,aq} + \frac{1}{z_j}\,\alpha^{\circ}_{j,aq} - (E^{\circ}_{ij} - E^{\circ}_{ij,aq})\,. \tag{6}$$

Each term of the right hand side of Eq. (6) is known or an experimentally measurable quantity. Therefore the relative solvation free energy A_{ij} can be estimated numerically. Then the value of $-\frac{1}{z_i}\alpha^{\circ}_i$ can be estimated when the value of $\frac{1}{z_j}\alpha^{\circ}_j$ is given.

If we assume here an ideal ion which should exhibit no interaction with any solvent, *i. e.*, the free energy of solvation should become equal to zero in aqueous and non-aqueous media, for such an ideal ion the value of A_{ij} becomes equal to $\frac{1}{z_j}\alpha^{\circ}_j$ as seen from Eq. (5). To find such an ideal ion the values of A_{ij} have been plotted previously against $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$ for a series of single atomic ions in non-aqueous media[1,2]. It has been found that A_{ij} indicates an excellent linear correlation with $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$, on which basis $\frac{1}{z_j}\alpha^{\circ}_j$ has been estimated as the value of A_{ij} at $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}=0$ in this correlation line.

In the present work the solvation free energies α°'s will be determined from the correlation between A_{ij} and $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$ for a series of single atomic ions in some non-aqueous media, NM, DMF, N-MF, PC and P_y and the absolute potentials φ^{0}'s of the associated redox systems will be estimated on the basis of Eq. (3) or (1).

Figs. 1~5 show the correlation lines between A_{ij} and $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$ in these non-aqueous solutions at 25°C. As seen from these Figures, the relation between A_{ij} and $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$ indicates an excellent linearlity in every case.

When the intersection point of the correlation line with the A_{ij}-axis is takan as the new origin in these diagrams, the value of A_{ij} read from this new origin indicates the value of $-\frac{1}{z_i}\alpha^{\circ}_i$ of the ion *i* in non-aqueous media. In this way we obtain a good proportionality relation between $-\frac{1}{z_i}\alpha^{\circ}_i$ and $x = -\frac{1}{z_i}\alpha^{\circ}_{i,aq}$,

$$-\frac{1}{z_i}\alpha^{\circ}_i = \beta x\,, \tag{7}$$

where β is the proportionality constant characteristic to the solvent.

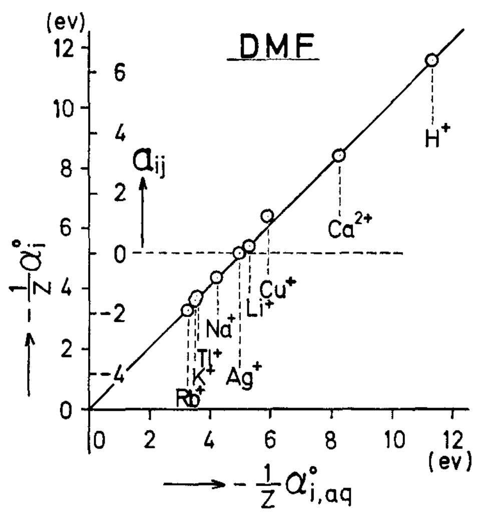


Fig. 1. The relative and absolute free energies of solvation $\boldsymbol{A}_{ij}$ and $-\frac{1}{z_i}\alpha_i^o$ in dimethylformamide plotted against $-\frac{1}{z_i}\alpha_{i,aq}^o$; the reference ion Ag$^+$. The Ref. for Ag$^+$, Li$^+$, Na$^+$, K$^+$, Rb$^+$, Tl$^+$ and Ca^{++} is 10), for H$^+$ 11, 12) and for Cu$^+$ 13).

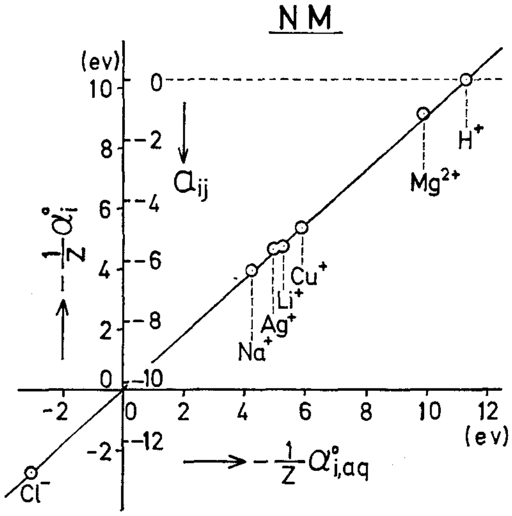


Fig. 2. The relative and absolute free energies of solvation $\boldsymbol{A}_{ij}$ and $-\frac{1}{z_i}\alpha_i^o$ in nitromethane plotted against $-\frac{1}{z_i}\alpha_{i,aq}^o$; the reference ion H$^+$. The Ref. for H$^+$ and Cl$^-$ is 14), and for Li$^+$, Na$^+$, Cu$^+$, and Mg^{++} 15).

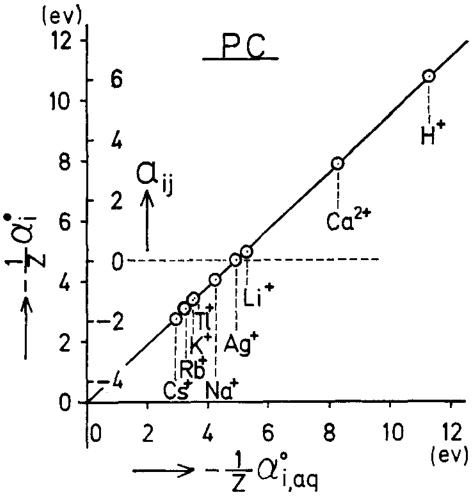


Fig. 3. The relative and absolute free energies of solvation $\boldsymbol{A}_{ij}$ and $-\frac{1}{z_i}\alpha_i^o$ in propylene carbonate plotted against $-\frac{1}{z_i}\alpha_{i,aq}^o$; the reference ion Ag$^+$. The ref. for Ag$^+$ and Tl$^+$ is 16), and for Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Tl$^+$ and Ca^{++} 17).

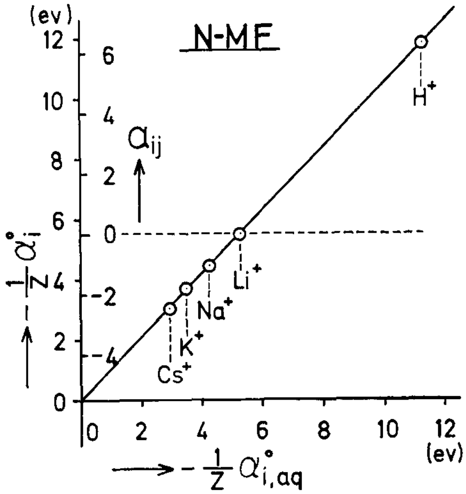


Fig. 4. The relative and absolute free energies of solvation $\boldsymbol{A}_{ij}$ and $-\frac{1}{z_i}\alpha_i^o$ in normal methylformamide plotted against $-\frac{1}{z_i}\alpha_{i,aq}^o$; the reference ion Li$^+$ 18).

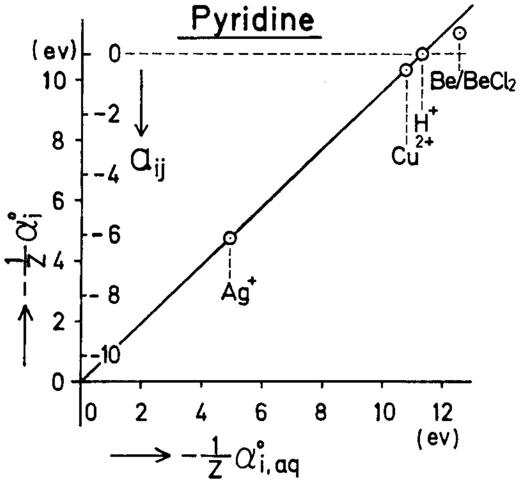


Fig. 5. The relative and absolute free energies of solvation $\boldsymbol{A}_{ij}$ and $-\frac{1}{z_i}\alpha_i^\circ$ in pyridine plotted against $-\frac{1}{z_i}\alpha_{i,aq}^\circ$; the reference ion H^+. The ref. for Cu^{++} is 19), for Ag 20) and for Be^{++} 21).

TABLE 1. The standard moral real free energy of solvation of proton, the absolute potential of the standard hydrogen electrode in non-aqueous solvents, and the prportionality constant β between $-\frac{1}{z_i}\alpha_i^\circ$ and $-\frac{1}{z_i}\alpha_{i,aq}^\circ$

Solvent		$-\alpha_{H^+}^\circ$ (ev)	ϕ_{H^+/H_2}° (v)	β
Water	(H_2O)	11.30	4.42	1.000
Dimethylformamide	(C_3H_7NO)	11.53	4.19	1.020
N-Methylformamide	(C_2H_5NO)	11.80	3.92	1.044
Nitromethane	(CH_3NO_2)	10.27	5.45	0.909
Propylene Carbonate	($C_4H_6O_3$)	10.75	4.97	0.952
Pyridine	(C_5H_5N)	10.85	4.87	0.960
Methanol	(CH_3OH)	11.22	4.50	0.994
Ethanol	(C_2H_5OH)	11.30	4.42	1.001
Formic acid	(HCOOH)	10.60	5.12	0.957
Acetonitrile	(CH_3CN)	11.04	4.68	0.974
Formamide	($HCONH_2$)	11.39	4.33	1.011
Hydrazine	(N_2H_4)	12.63	3.09	1.108
Ammonia	(NH_3)	12.64	3.08	1.115
Dimethyl Sulfoxide	(C_2H_6SO)	11.00	4.72	0.975
Quinoline	(C_9H_7N)	12.08	3.64	1.066

Using the value of $-\frac{1}{z_i}\alpha_i^\circ$ the absolute potential φ_i° can be estimated by Eq. (3) or (4), or directly by Eq. (1). In Table I the values of β, $-\alpha_{H^+}^\circ$ and φ_{H^+/H_2}° determined in this way are listed for the non-aqueous solvents together with those in the previous work[1].

It is found from Table I that the value of β is quite close to unity, but the absolute potential of the standard hydrogen electrode falls in the range from 3.08 V in NH_3 to 5.45 V in NM and the solvation free energy of proton falls in the range from 12.64 eV in NH_3 to 10.27 eV in NM. The values of φ_{H^+/H_2}° and $-\alpha_{H^+}^\circ$ in a series of non-aqueous solvents are shown in Figs. 6 and 7. The values of $\frac{1}{z_i}\alpha_i^\circ$ for other ions can be calculated by Eq. (7).

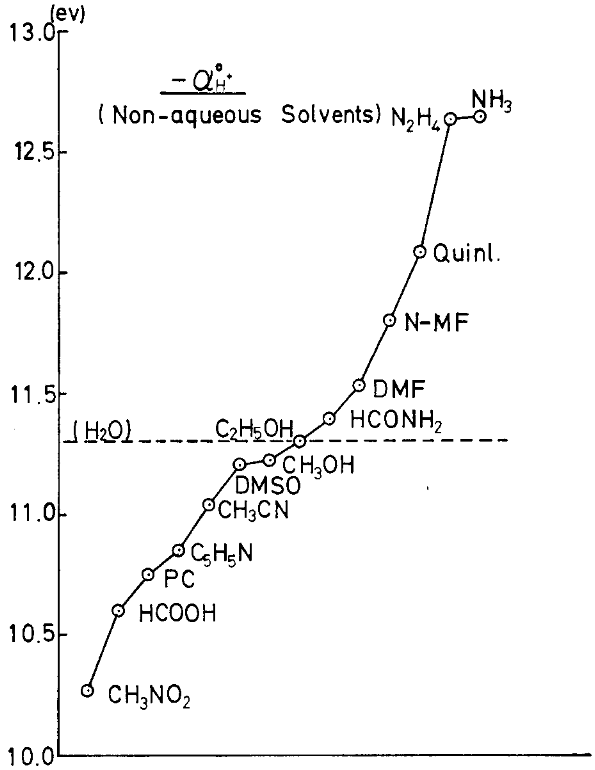


Fig. 6. The standard molal real free energy of solvation of proton in non-aqueous solvents; the dotted line shows that in water.

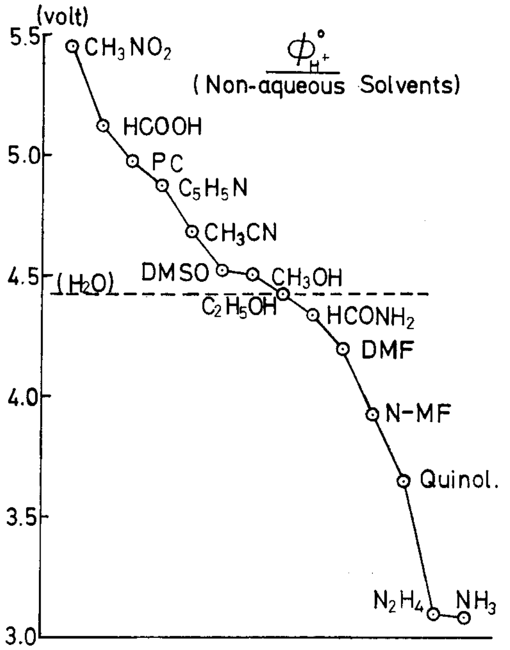


Fig. 7. The absolute potential of the standard hydrogen electrode in non-aqueous solutions; the dotted line shows that in water solution.

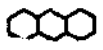
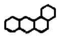
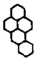
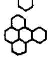
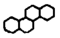
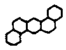
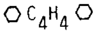
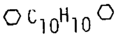
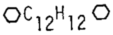
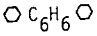
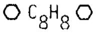
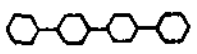
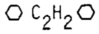
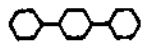
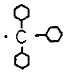
Absolute values of polarographic half-wave reduction potentials of aromatic hydrocarbons

The polarographic half-wave reduction potentials of aromatic hydrocarbons in non-aqueous media have often been measured against the aqueous saturated calomel electrode (SCE). It may be possible to estimate the half-wave potentials in the absolute scale using the absolute potential of the aqueous SCE. The electrode potential of SCE referred to the standard hydrogen electrode (SHE) in aqueous solution is given by Dobos[4] as 0.244 V and the absolute potential of the SHE in aqueous solution is given as 4.42 V as seen from Table I. Therefore the absolute potential of the aqueous SCE is estimated to be 4.66 V.

The absolute values of the half-wave reduction potentials $\varphi^\circ_{\mathrm{red}}$ estimated in this way from the experimental values referred to SCE in dioxane[5], in DMF[6] and in CH_3CN[7] are shown in Table II.

The $h\nu$-values of the p-bands of aromatic hydrocarbons classified by Clar[8] associated with the $\pi-\pi^*$ transition from the highest occupied to the

TABLE 2. The absolute half-wave reduction potentials in Dioxane[5], DMF[6] and CH_3CN[7] and the *hν*-values of the p-bands of aromatic hydrocarbons

No.		Compounds	*hν*, ev	φ^0_{red}, v		
				Dioxan	DMF	CH_3CN
1		Anthracene	3.31	2.70	2.71	2.69
2		1, 2-Benzanthracene	3.45	2.66		2.64
3		1, 12-Benzperylene	3.20			2.75
4		1, 2-Benzpyrene	3.22	2.81		2.82
5		4, 5-Benzpyrene	3.74	2.66		
6		Biphenyl	4.93	1.96	2.08	
7	$CH_2{:}CH{\cdot}CH{:}CH_2$	Butadiene	5.71	2.03		
8		Chrysene	3.88	2.36		2.39
9		Coronene	3.63	2.62	2.59	
10		1, 2·5, 6-Dibenzanthracene	3.53	2.63		
11	 C_4H_4	1, 4-Diphenylbutadiene	3.52	2.66		
12	 $C_{10}H_{10}$	1, 10-Diphenyldecapentaene	2.92	3.12		
13	 $C_{12}H_{12}$	1, 12-Diphenyldodecahexaene	2.79	3.21		
14	 C_6H_6	1, 6-Diphenylhexatriene	3.29	2.90		
15	 C_8H_8	1, 8-Diphenyloctatetraene	3.07	3.04		
16		Fluoranthene	3.46	2.89		
17		Naphthalene	4.35	2.16	2.13	2.17
18		Perylene	2.85	2.99	2.99	3.00
19		Phenanthrene	4.24	2.20	2.22	2.17
20		Pyrene	3.72	2.55		2.62
21		p-Quaterphenyl	4.25	2.46		
22	 C_2H_2	Stilbene	3.89	2.50	2.50	
23		p-Terphenyl	4.49	2.33		
24		Tetracene	2.63	3.08	3.08	
25		Triphenylene	4.36	2.17		2.18
26		Triphenylmethyl	2.50	3.61		

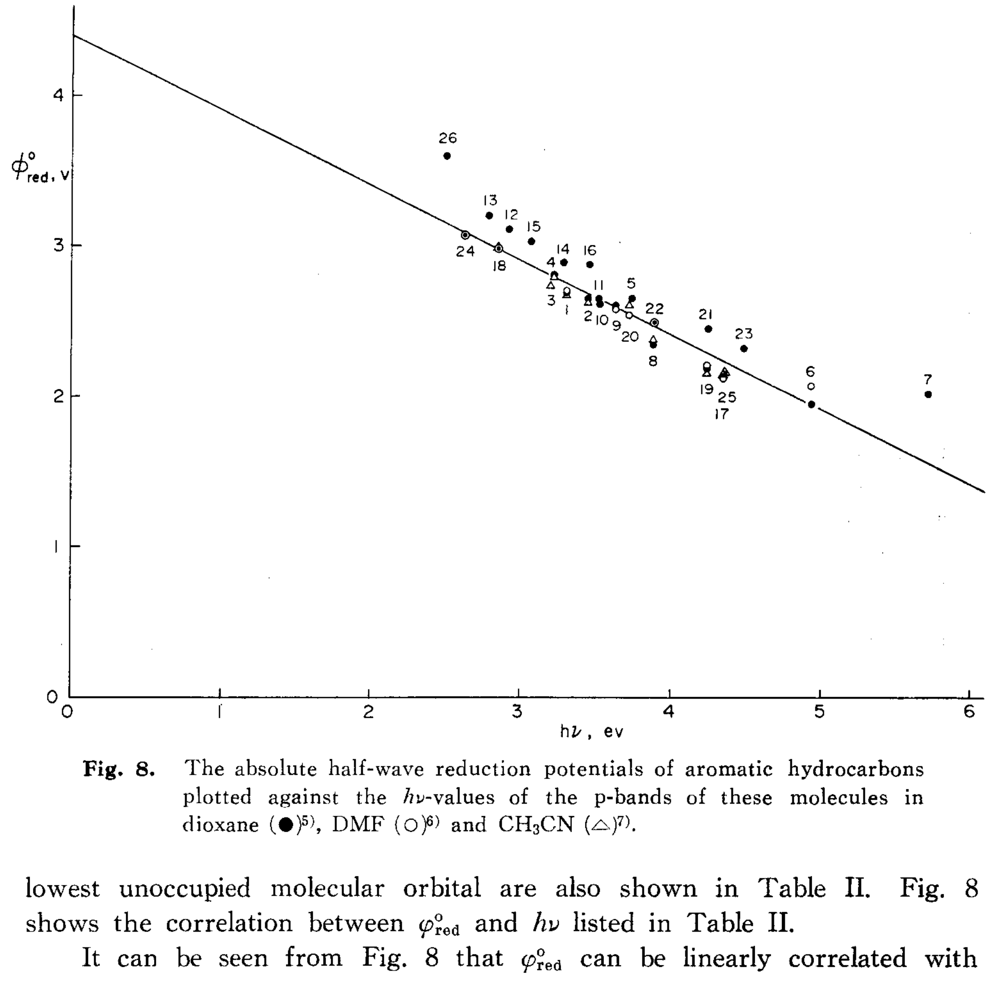


Fig. 8. The absolute half-wave reduction potentials of aromatic hydrocarbons plotted against the *hν*-values of the p-bands of these molecules in dioxane (●)[5], DMF (○)[6] and CH_3CN (△)[7].

lowest unoccupied molecular orbital are also shown in Table II. Fig. 8 shows the correlation between φ°_{red} and $h\nu$ listed in Table II.

It can be seen from Fig. 8 that φ°_{red} can be linearly correlated with $h\nu$, although rather scattering, with a gradient equal to 1/2, indicating a tendency to approach the work function of graphite $\Phi_{gr} = 4.39$ ev with $h\nu \rightarrow 0$, as pointed out by Matsen[9]. However, Matsen used $\varphi^\circ_{red} = 5.07$ v calculated from the zero-charge potential of the mercury electrode and the work function of mercury. As a result he obtained a somewhat higher limiting value for φ°_{red} at $h\nu = 0$ than that of Φ_{gr}.

It should be emphasized that the relation between φ°_{red} and $h\nu$ can be expressed by the equation independent of solvents,

$$F\varphi^\circ_{red} = \Phi_{gr} - \frac{1}{2} h\nu, \text{ ev} . \qquad (8)$$

It may be concluded from this fact that the free energy of solvation of a radical anion of aromatic hydrocarbon molecule is approximately constant independent of the solvent, since it may be given by the difference between the electron affinity of the molecule in the gas phase and the absolute half-wave potential.

Eq. (8) may well be explained by assuming that the energy levels of the highest occupied and lowest unoccupied molecular orbitals of the aromatic hydrocarbon molecule are disposed symmetrically about the work function of graphite, and the value of $\varphi^{\circ}_{\mathrm{red}}$ indicates the energy level of the lowest unoccupied molecular orbital of the molecule in the condensed media.

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