



Title	STANDARD MOLAL REAL FREE ENERGIES OF SOLVATION OF INDIVIDUAL IONS AND ELECTROMOTIVE FORCES OF SINGLE ELECTRODES IN NON-AQUEOUS SOLUTIONS
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# STANDARD MOLAL REAL FREE ENERGIES OF SOLVATION OF INDIVIDUAL IONS AND ELECTROMOTIVE FORCES OF SINGLE ELECTRODES IN NON-AQUEOUS SOLUTIONS

By

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## Abstract

An empirical method has been proposed to estimate the standard molal real free energies of solvation  $\alpha^{\circ}$ 's of individual monoatomic ions in non-aqueous solvents on the basis of the standard electrode potentials. It has been found that the  $\alpha^{\circ}$ -values in non-aqueous solvents are proportional to those in water with the proportionality constant close to unity.

The standard electromotive forces of single electrodes in non-aqueous solutions which are referred to the standard state of electrons in gaseous state have been estimated using the values of  $\alpha^{\circ}$  for a series of ionic species.

## 1. Introduction

The standard molal real free energy  $\alpha_i^{\circ}$  of an individual ion  $M_i^{z+}$  in an aqueous or non-aqueous solution which is analogous to the work function of an electron in a metal may be defined as the electrochemical potential  $\bar{\mu}_i^{\circ}$  of the ion in its standard state in the solution referred to that  $\bar{\mu}_{i,g}^{\circ}$  in gaseous state

$$\alpha_i^{\circ} = \bar{\mu}_i^{\circ} - \bar{\mu}_{i,g}^{\circ}, \quad (1)$$

where the subscript g denotes the gaseous state and the superscript o means the standard state of the ion.

If we define the standard electromotive force of a single electrode  $\phi_i^{\circ}$  at a given temperature for a reaction<sup>\*\*)</sup>



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<sup>\*\*</sup>) For the reaction of anions, the sign of valency  $z$  should be taken negative.

A. MATSUDA

in terms of the electrochemical potential of an electron in the electrode  $\bar{\mu}_{e,m}^{\circ}$  referred to that of an electron  $\bar{\mu}_{e,g}^{\circ}$  in its standard state in gaseous state at the given temperature<sup>\*</sup>)

$$F\phi_1^{\circ} = \bar{\mu}_{e,g}^{\circ} - \bar{\mu}_{e,m}^{\circ}, \quad (2)$$

in which  $F$  is the Faraday, then  $\phi_1^{\circ}$  may be estimated using the value of  $\alpha_1^{\circ}$  as follows.

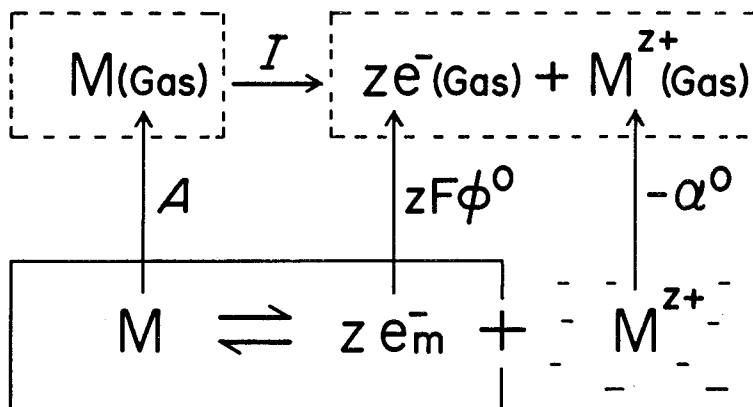
The molar free energy of the formation of the ion  $M_{i,g}^{z+}$  and electron in gaseous state with each in its standard state from the element  $M_i$  may be defined as

$$\Delta F_1^{\circ} = \bar{\mu}_{i,g}^{\circ} + z\bar{\mu}_{e,g}^{\circ} - \mu_{M_i}^{\circ}, \quad (3)$$

and can be written

$$\Delta F_1^{\circ} = \bar{\mu}_{i,g}^{\circ} + z\bar{\mu}_{e,g}^{\circ} - \bar{\mu}_i^{\circ} - z\bar{\mu}_{e,m}^{\circ}, \quad (4)$$

using the equilibrium relation of the reaction (I). Putting Eqs. (1) and (2) into Eq. (4) we obtain



**Fig. 1.** The thermodynamical cycle; the electromotive force of a single electrode, the standard molal real free energy of solvation of an ion and the free energy of formation of an element are all referred respectively to the standard states of the electron and the ion in gaseous state.

<sup>\*</sup>) If the standard electromotive force of a single electrode is expressed in terms of the absolute scale  $\phi_1^{\circ}$  (abs), which may be defined as  $\bar{\mu}_{e,m}^{\circ}$  referred to the state of an electron at rest at infinity, then a correction term for the reference state of the electron should be added to Eq. (2) as

$$F\phi_1^{\circ}(\text{abs}) = F\phi_1^{\circ} + \bar{\mu}_{e,g}^{\circ}(T=0) - \bar{\mu}_{e,g}^{\circ}(T)$$

*Free Energies of Solvation of Ions and EMF of Single Electrodes*

$$\Delta F_i^{\circ} = -\alpha_i^{\circ} + zF\phi_i^{\circ}, \quad (5)$$

On the other hand, as seen from the thermodynamical cycle in Fig. 1,  $\Delta F_i^{\circ}$  may be given by the free energy of atomization of the element  $M_i$

$$A_i = \mu_{M_i, g}^{\circ} - \mu_{M_i}^{\circ}, \quad (6 a)$$

and the free energy of ionization of the atom  $M_{i, g}$  to form the ion  $M_{i, g}^{z+}$  and electrons in gaseous states

$$I_i = \bar{\mu}_{i, g}^{\circ} + z\bar{\mu}_{e, g}^{\circ} - \mu_{M_i, g}^{\circ}, \quad (6 b)$$

as

$$\Delta F_i^{\circ} = A_i + I_i. \quad (7)$$

Therefore  $\phi_i^{\circ}$  may be estimated from  $\alpha_i^{\circ}$  and the thermochemical data for  $\Delta F_i^{\circ}$  on the basis of Eqs. (5) and (7).

It should be noted that  $\Delta F_i^{\circ}$  is independent of the solvent and therefore there exists a compensation effect between  $\alpha_i^{\circ}$  and  $\phi_i^{\circ}$  in different solvents, *e. g.*, between water and non-aqueous solvent, we obtain from Eq. (5)

$$z(\phi_i^{\circ} - \phi_{i, aq}^{\circ}) = \alpha_i^{\circ} - \alpha_{i, aq}^{\circ}, \quad (8)$$

as pointed out by Krishtalik<sup>1)</sup> in the case of the hydrogen electrode.

If we can find an ideal ion which has the same free energy of solvation in every solvent, then we can expect the same electromotive force for such an ion in every solvent as resulted from Eq. (8). Pleskov<sup>2)</sup> assumed that  $Rb^+$  ion would be the closest approach to such an ideal ion and the electrode potential series in different solvents would be connected with the  $Rb^+/Rb$  electrode as the common reference electrode. The electrode potential series connected in this way, however, is only a qualitative one, since in real systems we have no such an ideal ion.

The estimation of  $\alpha_{i, aq}^{\circ}$  was reported by Klein and Lange<sup>3)</sup> and by Randles<sup>4)</sup> for a series of ionic species based on the measurements of the contact potential difference between the electrode and solution. Frumkin and Damaskin<sup>5)</sup> estimated the electromotive force of the standard hydrogen electrode as 4.44 V on the basis of Eqs. (5) and (7) using the value of  $\alpha_{H^+, aq}^{\circ}$ . Case and Parsons<sup>6)</sup> estimated  $\alpha_i^{\circ}$  in some non-aqueous solvents using the values of  $\alpha_{i, aq}^{\circ}$  reported by Randles and the contact potential difference between aqueous and non-aqueous solutions.

Another series of  $\alpha_i^{\circ}$ -values in aqueous and non-aqueous solutions were determined by Izmailov<sup>7)</sup> on the basis of a reasonable physical model for the

bonding of the ion to the solvent.

Recently we have found an empirical method to estimate  $\alpha_i^\circ$  of monoatomic ions in non-aqueous solutions on the basis of the values of  $\alpha_{i,\text{aq}}^\circ$  and the standard electrode potentials of the ions in aqueous and non-aqueous solutions. In the present work  $\alpha_i^\circ$  and  $\phi_i^\circ$  estimated by the empirical method will be presented for a series of ionic species in some non-aqueous solvents and the validity of this method will be discussed.

## 2. Relation between $\alpha_i^\circ$ and $E_i^\circ$

The standard electrode potential of the reaction (I),  $E_i^\circ$ , referred to the standard hydrogen electrode is given by Eq. (2)

$$E_i^\circ = \phi_i^\circ - \phi_{\text{H}^+}^\circ, \quad (9)$$

and in aqueous and non-aqueous solutions by Eq. (5).

$$FE_{i,\text{aq}}^\circ = \left( \frac{1}{z} \Delta F_i^\circ - \Delta F_{\text{H}^+}^\circ \right) + \left( \frac{1}{z} \alpha_{i,\text{aq}}^\circ - \alpha_{\text{H}^+,\text{aq}}^\circ \right), \quad (10 \text{ a})$$

$$FE_i^\circ = \left( \frac{1}{z} \Delta F_i^\circ - \Delta F_{\text{H}^+}^\circ \right) + \left( \frac{1}{z} \alpha_i^\circ - \alpha_{\text{H}^+}^\circ \right), \quad (10 \text{ b})$$

The first term of the right side of these equations is constant at a constant temperature independent of the solvent. From these two equations we have an expression for  $\alpha_i^\circ$

$$-\frac{1}{z} \alpha_i^\circ = \mathbf{a}_i - \alpha_{\text{H}^+}^\circ, \quad (11)$$

where

$$\mathbf{a}_i \equiv \alpha_{\text{H}^+,\text{aq}}^\circ - \frac{1}{z} \alpha_{i,\text{aq}}^\circ - F \Delta E_i^\circ, \quad (12)$$

and

$$\Delta E_i^\circ \equiv E_i^\circ - E_{i,\text{aq}}^\circ. \quad (13)$$

It can be seen from Eqs. (11) and (12) that  $\mathbf{a}_i$  reveals the relative value of  $-\frac{1}{z} \alpha_i^\circ$  referred to  $-\alpha_{\text{H}^+}^\circ$  in the non-aqueous solution and is a function of the standard potentials in aqueous and non-aqueous solutions and the free energy of hydration which are measurable quantities. Therefore it may be possible to estimate  $\alpha_i^\circ$  according to Eq. (11) when the value of  $\alpha_{\text{H}^+}^\circ$  is known.

If we assume here an ideal ion which should exhibit no special interac-

## Free Energies of Solvation of Ions and EMF of Single Electrodes

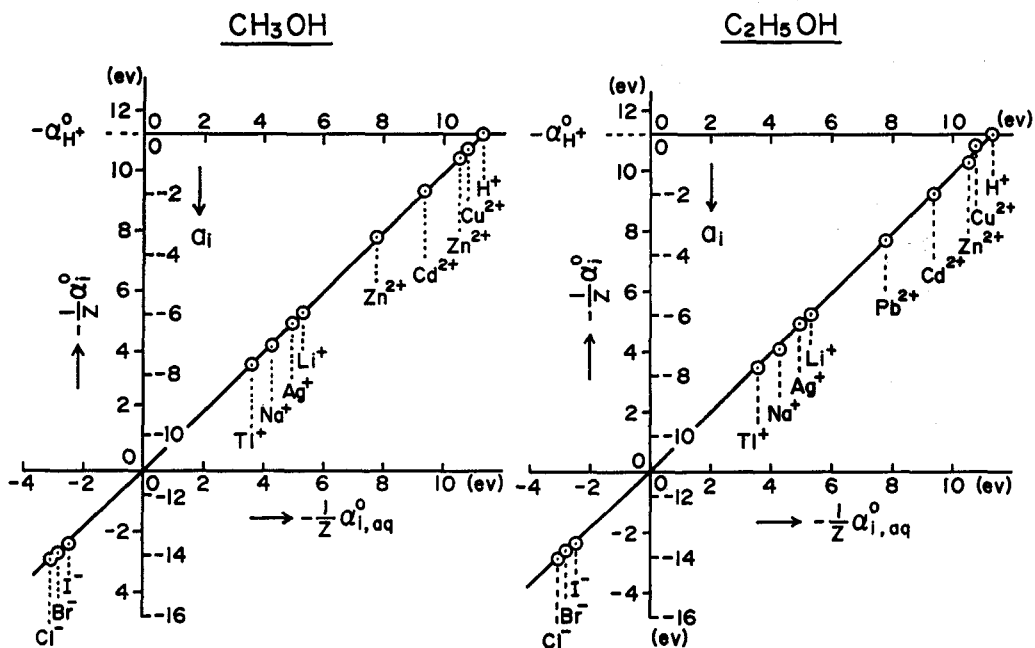


Fig. 2.  $\alpha_l$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  and  $-\frac{1}{z}\alpha_l^0$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  in CH<sub>3</sub>OH at 25°C.<sup>9)</sup>

Fig. 3.  $\alpha_l$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  and  $-\frac{1}{z}\alpha_l^0$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  in C<sub>2</sub>H<sub>5</sub>OH at 25°C.<sup>9)</sup>

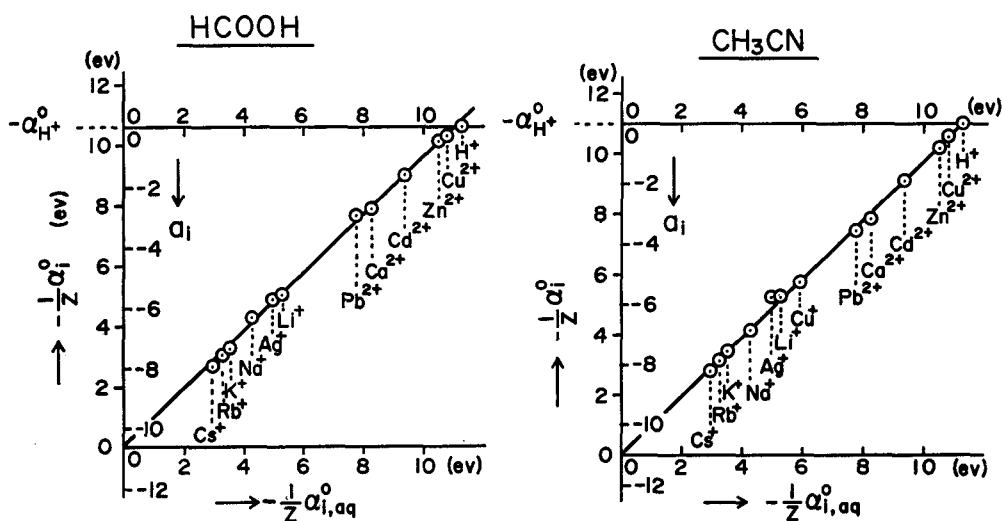


Fig. 4.  $\alpha_l$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  and  $-\frac{1}{z}\alpha_l^0$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  in HCOOH at 25°C.<sup>9)</sup>

Fig. 5.  $\alpha_l$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  and  $-\frac{1}{z}\alpha_l^0$  vs.  $-\frac{1}{z}\alpha_{l,aq}^0$  in CH<sub>3</sub>CN at 25°C.<sup>9)</sup>

A. MATSUDA

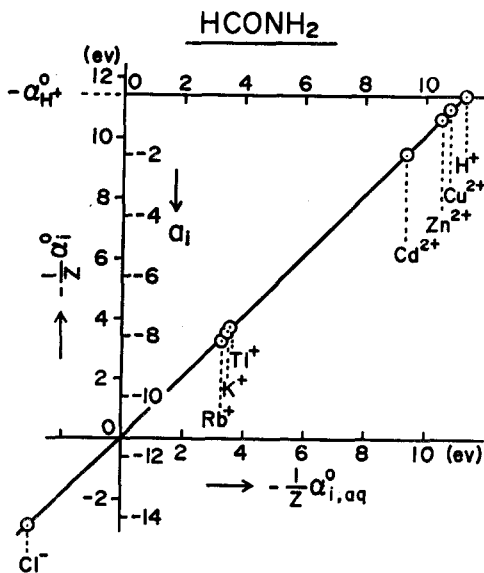


Fig. 6.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in HCONH<sub>2</sub> at 25°C.<sup>11,13)</sup>

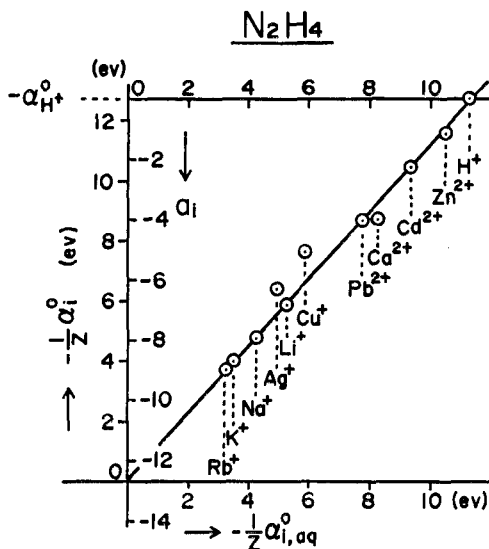


Fig. 7.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in N<sub>2</sub>H<sub>4</sub> at 25°C.<sup>8,9,14)</sup>

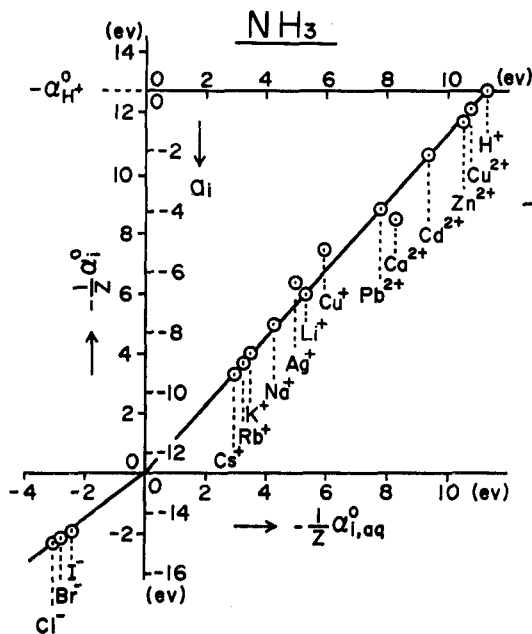


Fig. 8.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in NH<sub>3</sub>. The standard potentials in NH<sub>3</sub> were measured at -35°C.<sup>8,9,15)</sup> and the values of  $\alpha_{i,aq}^0$  at 25°C are used in this diagram.

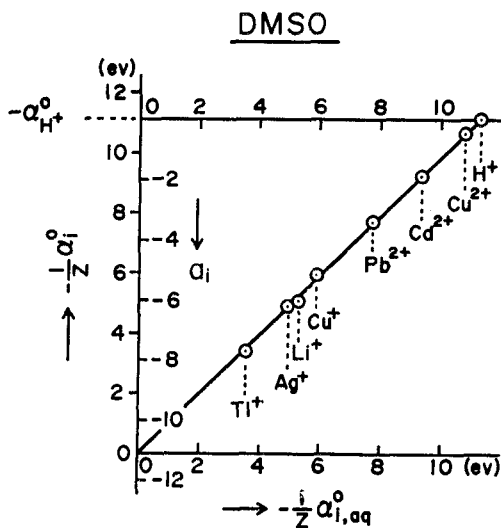


Fig. 9.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in DMSO at 25°C.<sup>12)</sup>

*Free Energies of Solvation of Ions and EMF of Single Electrodes*

tion with any solvent, *i. e.*, zero free energy of solvation in any solvent, then  $\alpha_i$  for such an ideal ion becomes equal to  $\alpha_{H^+}^0$  according to Eq. (11). It is suggested that such an ideal ion, if any, should exist as a limiting approach of the ions in real systems.

To answer this purpose for the estimation of  $\alpha_{H^+}^0$  in non-aqueous solvents the values of  $\alpha_i$  for a series of ionic species in some non-aqueous solvents are plotted against  $-\frac{1}{z}\alpha_{i,aq}^0$  in Figs. (2)-(11). In these Figures the position of  $-\alpha_{H^+}^0$  is chosen arbitrarily on the  $\alpha_i$ -axis and  $\alpha_i$  for an ion is measured from this position.

### 3. Graphic presentation of

$$-\frac{1}{z}\alpha_i^0 \text{ vs. } -\frac{1}{z}\alpha_{i,aq}^0$$

At present the standard electrode potentials are known only in a limited number of solvents. The available solvents in the present work are  $CH_3OH$ ,  $C_2H_5OH$ ,  $HCOOH$ ,  $CH_3CN$ ,  $HCONH_2$ ,  $N_2H_4$ ,  $NH_3$ , DMSO, Quinoline saturated with water and some fused salt which are quoted in some review articles.<sup>8,13</sup> The most of numerical values of  $E_i^0$  and  $E_{i,aq}^0$  in molal scale used for the calculation of  $\alpha_i$  are those in Electrochemical Data by Dobos<sup>9</sup> or those quoted by Strehlow,<sup>8</sup>

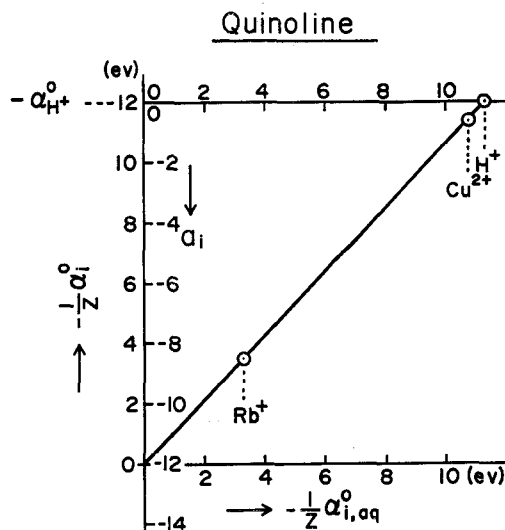


Fig. 10.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in Quinoline saturated with water at 25°C.<sup>8)</sup>

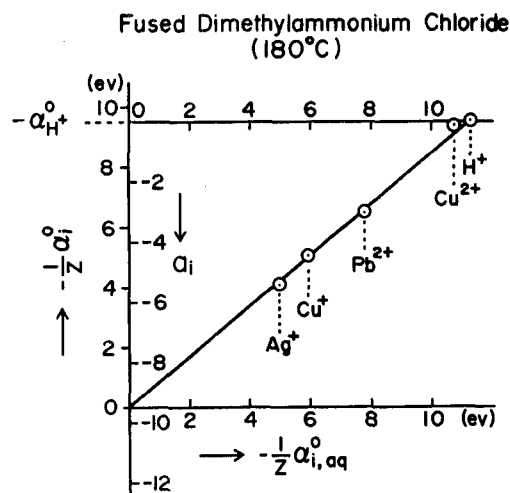


Fig. 11.  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  and  $-\frac{1}{z}\alpha_i^0$  vs.  $-\frac{1}{z}\alpha_{i,aq}^0$  in fused dimethylammonium chloride. The standard potential in the fused salt were measured at 180°C,<sup>13</sup> and the values of  $\alpha_{i,aq}^0$  at 25°C are used in this diagram.



and the values of  $-\alpha_{i,\text{aq}}^{\circ}$  are those in Randles' paper<sup>4)</sup> which are used in the work of Case and Parsons.<sup>6)</sup>

#### 4. Estimation of $\alpha_1^{\circ}$ and $\phi_1^{\circ}$

(i) Estimation of  $-\alpha_{\text{H}^+}^{\circ}$

It is surprising that there exists a good linear relation between  $\alpha_1$  and  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$  in every solvent, as seen from these Figures. It is suggested on the basis of this linear relation that the position  $\alpha_{i,\text{aq}}^{\circ}=0$  on this line may be assigned to an ideal ion which has no specific interaction with any

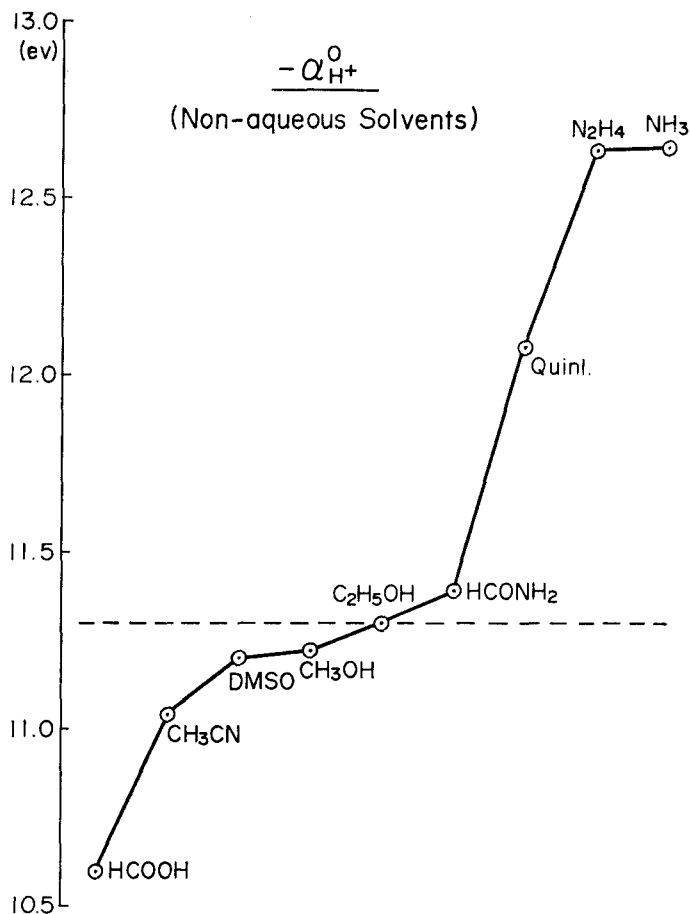


Fig. 12. The values of  $-\alpha_{\text{H}^+}^{\circ}$  in non-aqueous solvents; the dotted line shows the value in water.

*Free Energies of Solvation of Ions and EMF of Single Electrodes*

solvent molecule as well as water molecule. Then the value of  $\alpha_{\text{H}^+}^{\circ}$  in every solvent can be estimated according to Eq. (11) as the value of  $\mathbf{a}_1$  for the ideal ion. The values of  $-\alpha_{\text{H}^+}^{\circ}$  obtained in this way are listed in Tables I and illustrated in Fig. 12.

(ii) Estimation of  $-\alpha_i^{\circ}$

The value of  $-\frac{1}{z}\alpha_i^{\circ}$  for an ion is given by Eq. (11) as that of  $\mathbf{a}_1 - \alpha_{\text{H}^+}^{\circ}$  which can be read from the position of the ideal ion on the  $\mathbf{a}_1$ -axis in the diagrams. In this way we have the following proportionality relation between  $-\frac{1}{z}\alpha_i^{\circ}$  and  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$ , the position of the ideal ion being taken as the new origin,

$$-\frac{1}{z}\alpha_i^{\circ} = \beta x, \quad (14)$$

where  $x$  denotes  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$  and  $\beta$  is a constant characteristic to the solvent.

The available data of  $E_i^{\circ}$  for anions are limited to halogen ions in some solvents, but it is found that they are also located on the extension of the linear relation for cations, as seen from Figs. (2), (3) and (6), except in  $\text{NH}_3$  in Fig. (8).

The values of  $-\alpha_{\text{H}^+}^{\circ}$  and  $\beta$  in a series of non-aqueous solvents are listed

TABLE I. The Proportionality constant  $\beta$  between  $-\frac{1}{z}\alpha_i^{\circ}$  and  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$  and the standard molal real free energies of solvation of proton in non-aqueous solvents

Solvent	$\beta$	$-\alpha_{\text{H}^+}^{\circ}$ (ev)	$\pm\sigma$ (ev)	$\epsilon$
$\text{CH}_3\text{OH}$	0.994	11.22	0.03	32
$\text{C}_2\text{H}_5\text{OH}$	1.001	11.30	0.07	24
$\text{HCOOH}$	0.957	10.60	0.13	59
$\text{CH}_3\text{CN}$	0.974	11.04	0.04	36
$\text{HCONH}_2$	1.011	11.39	0.03	114
$\text{N}_2\text{H}_4$	1.108	12.63	0.05*	58
$\text{NH}_3$	1.115	12.64	0.04*	22
DMSO	0.995	11.20	0.07	49
Quinoline	1.066	12.08	0.03	26

\*)  $\text{Ag}^+$ ,  $\text{Cu}^+$  and  $\text{Ca}^{++}$  are omitted in the estimation of  $\pm\sigma$ , since these ions are likely to show some systematic deviation, as seen from Figs. 7 and 8.

## A. MATSUDA

in Table I. The standard deviation  $\pm\sigma$  of each point from Eq. (14) is also listed in this Table, which is approximately within a few centivolts. It is found that  $\beta$  is quite close to unity in every solvent independent of the dielectric constant  $\epsilon$  of the solvent.

(iii) Estimation of  $\phi_{H^+}^0$ 

The standard electromotive force  $\phi_{H^+,aq}^0$  of the hydrogen electrode in aqueous solution is evaluated as 4.42 V according to Eq. (5)\* using  $-\alpha_{H^+}^0 = 11.30$  eV reported by Randles and  $\Delta F_{H^+}^0 = 15.72$  eV obtained from the ther-

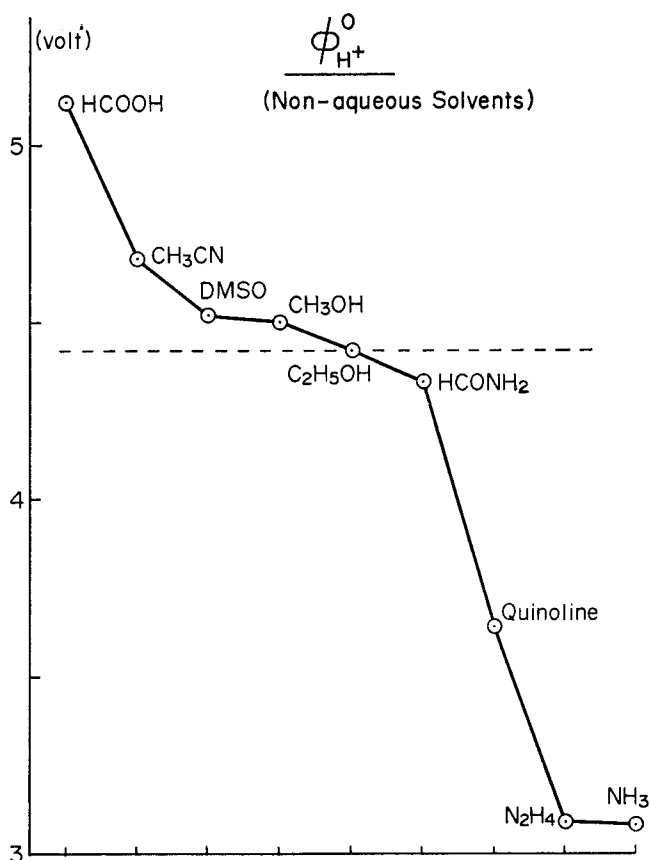


Fig. 13. The values of  $\phi_{H^+}^0$  in non-aqueous solutions; the dotted line is that in aqueous solution.

\*) A small drift of  $\phi_{H^+,aq}^0$ , 4.42 v in the present work and 4.44 v obtained by Frumkin and Damaskin, is due to a slight difference of the values of  $-\alpha_{H^+}^0$ ,<sub>aq</sub> used, 11.30 v in the former and 11.28 v in the latter.

TABLE II. Standard molal real free energies of solvation of individual ions and standard electromotive forces of single electrodes in non-aqueous solutions at 25°C

	H <sub>2</sub> O		CH <sub>3</sub> OH		C <sub>2</sub> H <sub>5</sub> OH		HCOOH		CH <sub>3</sub> CN		HCONH <sub>2</sub>		N <sub>2</sub> H <sub>4</sub>		NH <sub>3</sub>		DMSO		Quinoline		$\Delta F^0/z$	
	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	$-\alpha^0/z$	$\phi^0$	El. Chem.	Th.*** Chem.
1. H <sup>+</sup> /H <sub>2</sub>	11.30	4.42	11.22	4.50	11.30	4.42	10.60	5.12	11.04	4.68	11.39	4.33	12.63	3.09	12.64	3.08	11.20	4.52	12.08	3.64	15.72	15.72
2. Li <sup>+</sup> /Li	5.30	1.40	5.28	1.41	5.31	1.38	5.05	1.64	5.24	1.45	5.36	1.31	5.80	0.89	5.85	0.84	5.15	1.53	5.65	1.02	6.69	6.67
3. Na <sup>+</sup> /Na	4.26	1.71	4.19	1.78	4.20	1.76	4.27	1.70	4.16	1.81	4.31	1.66	4.70	1.27	4.90	1.07	4.24	1.73	4.54	1.43	5.97	5.97
4. K <sup>+</sup> /K	3.50	1.50	3.48	1.51	3.50	1.49	3.24	1.76	3.48	1.52	3.54	1.46	3.93	1.07	3.90	1.10	3.48	1.51	3.73	1.26	5.00	4.99
5. Rb <sup>+</sup> /Rb	3.27	1.43	3.25	1.52	3.27	1.50	3.03	1.67	3.19	1.51	3.22	1.47	3.62	1.08	3.56	1.15	3.25	1.52	3.49	1.21	4.70	4.77
6. Cs <sup>+</sup> /Cs	2.94	1.40	2.92	1.52	2.94	1.50	2.66	1.68	2.82	1.52	2.97	1.47	3.26	1.18	3.21	1.13	2.92	1.52	3.13	1.31	4.34	4.44
7. Tl <sup>+</sup> /Tl	3.56	4.08	3.52	4.12	3.57	4.08	3.41	4.23	3.47	4.17	3.66	3.99	3.94	3.70	3.97	3.67	3.48	4.17	3.79	3.85	7.64	7.64
8. Ag <sup>+</sup> /Ag	4.96	5.22	4.95	5.26	5.01	5.17	4.89	5.29	5.27	4.91	5.02	5.17	6.32	3.86	6.27	3.91	4.98	5.20	5.29	4.90	10.18	10.19
9. Cu <sup>+</sup> /Cu	5.91	4.94	5.87	4.98	5.91	4.94	5.66	5.19	5.79	5.06	5.98	4.87	7.54	3.31	7.36	3.49	6.01	4.85	6.30	4.55	10.85	10.85
10. Pb <sup>2+</sup> /Pb	7.76	4.29	7.75	4.30	7.78	4.27	7.65	4.40	7.49	4.56	7.85	4.22	8.61	3.44	8.65	3.40	7.77	4.28	8.27	3.80	12.05	12.07
11. Ca <sup>2+</sup> /Ca	8.26	1.55	8.21	1.62	8.26	1.57	7.89	1.92	7.88	1.93	8.35	1.48	8.63	1.18	8.37	1.44	8.22	1.61	8.81	1.02	9.81	9.83
12. Cd <sup>2+</sup> /Cd	9.33	4.02	9.28	4.07	9.31	4.04	8.98	4.37	9.14	4.21	9.43	3.92	10.36	2.99	10.47	2.88	9.29	4.06	9.95	3.42	13.36	13.37
13. Zn <sup>2+</sup> /Zn	10.51	3.66	10.40	3.76	10.38	3.78	10.09	4.07	10.22	3.94	10.59	3.57	11.48	2.68	11.61	2.55	10.45	3.73	11.20	2.98	14.17	14.18
14. Cu <sup>2+</sup> /Cu	10.78	4.77	10.71	4.84	10.92	4.63	10.29	5.26	10.59	4.96	10.94	4.61	11.94	3.64	12.04	3.51	10.70	4.84	11.45	4.10	15.55	15.58
15. Cl <sup>-</sup> /Cl <sub>2</sub>	-3.07	5.78	-2.91	5.62	-2.76	5.47	-3.32	5.97	-2.55	5.26	-2.95	5.60			-2.40	5.11					2.71	2.65
16. Br <sup>-</sup> /Br <sub>2</sub>	-2.81	5.49	-2.71	5.39	-2.52	5.20			-2.47	5.15					-2.24	4.91					2.68	2.66
16. I <sup>-</sup> /I <sub>2</sub>	-2.48	4.95	-2.38	4.86	-2.25	4.73			-2.27	4.75					-2.03	4.50					2.48	2.51

Free Energies of Solvation of Ions and EMF of Single Electrodes

\*)  $\alpha_1^0$  is calculated by Eq. (14) and  $\phi_1^0$  is estimated by Eq. (5).

\*\*)  $\alpha_{Cl^-}^0$  is estimated from the standard electrode potential of Ag/AgCl and  $\phi_{Cl^-}^0$  for  $Cl^-/\frac{1}{2}Cl_2$  is calculated by Eq. (5) using  $\Delta F_{Cl^-}^0$  obtained from the thermochemical data.

\*\*\*) The entropy term of the electronic states of a monoatomic ion is neglected in the thermochemical estimation of  $\Delta F^0$ .

mochemical data of the National Bureau of Standards.<sup>10)</sup> The values of  $\phi_{\text{H}^+}^{\circ}$  in non-aqueous solvents can be estimated according to Eq. (5) using  $\Delta F_{\text{H}^+}^{\circ} = 15.72$  eV and the value of  $\alpha_{\text{H}^+}^{\circ}$  in non-aqueous solutions listed in Table I. The values of  $\phi_{\text{H}^+}^{\circ}$  in non-aqueous solutions estimated in this way are illustrated in Fig. 13.

(iv) Estimation of  $\phi_i^{\circ}$

The standard electromotive force  $\phi_i^{\circ}$  in non-aqueous solvents can be estimated from  $E_i^{\circ}$  and  $\phi_{\text{H}^+}^{\circ}$  according to Eq. (9). In the case of ions in non-aqueous solvents for which we have no experimental data of  $E_i^{\circ}$ , it may be possible to estimate  $\alpha_i^{\circ}$  by the empirical relation Eq. (14) using  $\alpha_{i,\text{aq}}^{\circ}$ . Then  $\phi_i^{\circ}$  can be estimated according to Eq. (5) using the value of  $\alpha_i^{\circ}$  obtained in this way and the thermochemical data of  $\Delta F_i^{\circ}$ .

The results of  $-\frac{1}{z}\alpha_i^{\circ}$  and  $\phi_i^{\circ}$  obtained in this way and those of  $\Delta F_i^{\circ}$  calculated by Eq. (5) using  $\alpha_i^{\circ}$  and  $\phi_i^{\circ}$  are summarized in Table II for a series of ionic species. For comparison the values of  $\Delta F_i^{\circ}$  obtained from the thermochemical data in the list of N. B. S. are also listed in the Table. The comparison of the values of  $\Delta F_i^{\circ}$  obtained in the two different ways will serve as a criterion for the validity of the empirical method for the estimation of  $\alpha_i^{\circ}$  and  $\phi_i^{\circ}$  proposed in the present work.

## 5. Discussion

As illustrated in the Figures,  $\alpha_i$  changes linearly with  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$  and the gradient  $\beta$  is close to unity. The free energy of formation of an ion  $\frac{1}{z}\Delta F_i^{\circ} = -\frac{1}{z}\alpha_i^{\circ} + F\phi_i^{\circ}$  estimated on the basis of the proportionality relation of the free energies of solvation between water and non-aqueous solvent is numerically consistent with that obtained from the thermochemical data  $A_i + I_i$  and has a constant value for the given ion in different solvents, as seen from Table II and Fig. 14. These facts may prove the validity of the empirical method proposed for the estimation of  $\alpha_i^{\circ}$  and  $\phi_i^{\circ}$  in the present work.

The halogen ions are located approximately on the extension of the straight line for cations in most of non-aqueous solvents, as illustrated in the  $\alpha_i$  vs.  $-\frac{1}{z}\alpha_{i,\text{aq}}^{\circ}$  diagrams. Therefore it is suggested that the formation of the solvation bonding of ions to solvent molecules should be explained by some similar mechanism in water and non-aqueous solvents, although we have no theoretical explanation for this mechanism at present based on

## Free Energies of Solvation of Ions and EMF of Single Electrodes

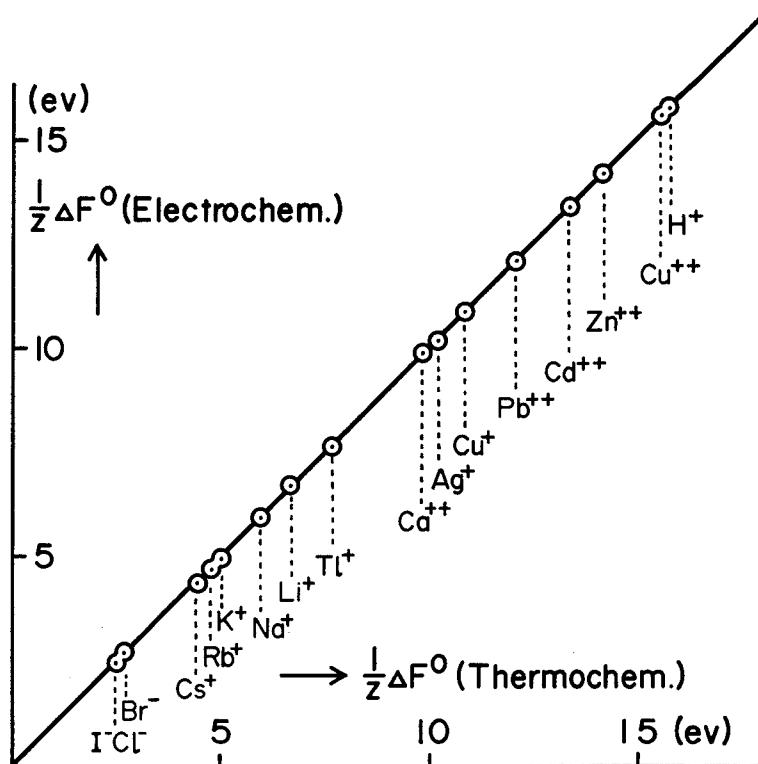


Fig. 14. The comparison of the free energies of formation of ions obtained electrochemically as the sum  $-\frac{1}{z}\alpha_i^0 + F\phi_i^0$  and thermodynamically as that  $A_i + I_i$ .

Table III. Linear relations between  $-\frac{1}{z}\alpha_i^0$  and  $-\frac{1}{z}\alpha_{i,aq}^0$  obtained from the data of Case and Parsons<sup>6)</sup> in non-aqueous solvents and original and corrected values of  $-\alpha_{H^+}^0$

Solvent	$A + \beta x$	$-\alpha_{H^+}^0$ (orig.)	$-\alpha_{H^+}^0$ (corr.)
CH <sub>3</sub> OH	0.29 + 0.996x	11.55	11.26
CH <sub>2</sub> OH <sub>2</sub>	0.23 + 1.000x	11.53	11.31
n-BuOH	0.01 + 1.018x	11.47	11.46
HCONH <sub>2</sub>	0.11 + 1.007x	11.45	11.34
HCOOH	0.32 + 0.964x	11.01	10.68
CH <sub>3</sub> CN	0.25 + 0.977x	11.18	10.93

any physical model for the bonding of ions to solvent molecules.

Case and Parsons<sup>6)</sup> estimated  $\alpha_i^0$  in several non-aqueous solvents on the basis of the free energy of transfer of  $\text{Cl}^-$  ion from aqueous to non-aqueous solvent  $\alpha_{\text{Cl}^-}^0 - \alpha_{\text{Cl}^-}^0, \text{aq}$ , using  $\alpha_{i, \text{aq}}^0$  reported by Randles. For comparison the relation between  $-\frac{1}{z}\alpha_i^0$  and  $-\frac{1}{z}\alpha_{i, \text{aq}}^0$  obtained using their data is shown in Fig. 15 in the case of  $\text{CH}_3\text{OH}$ . As seen from this Figure, there exists also a good linear relation between the free energies of solvation in water and methanol, but the straight line shows a small deviation upwards from the origin. The linearity relation obtained from their data can be expressed by the equations  $-\frac{1}{z}\alpha_i^0 = \Delta + \beta x$  listed in Table III.

In this Table  $\Delta$  denotes the drift of the straight line from the origin,  $-\alpha_{\text{H}^+}^0(\text{orig.})$  is the value obtained by Case and Parsons and  $-\alpha_{\text{H}^+}^0(\text{corr.})$  is that obtained by subtracting  $\Delta$  from  $-\alpha_{\text{H}^+}^0(\text{orig.})$ . It can be seen that

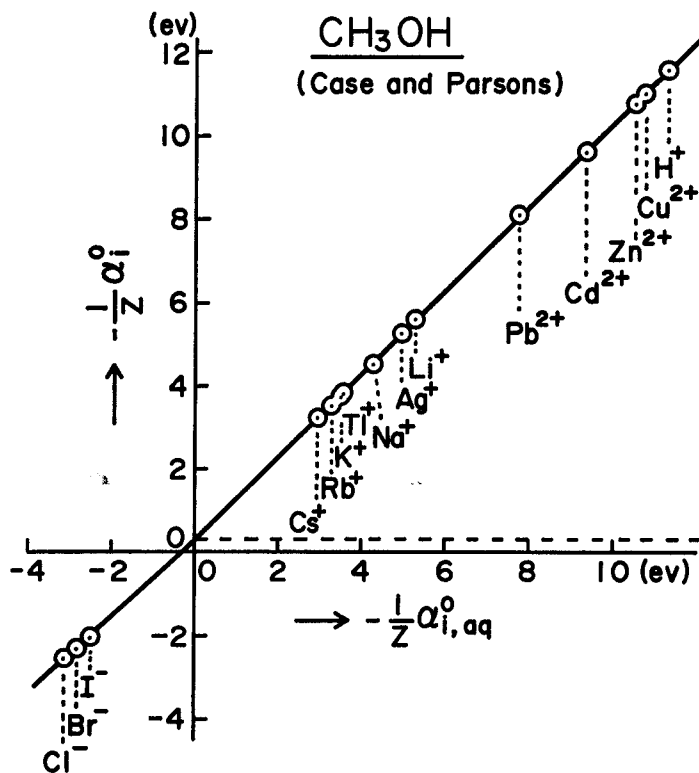


Fig. 15. The relation between  $-\frac{1}{z}\alpha_i^0$  and  $-\frac{1}{z}\alpha_{i, \text{aq}}^0$  obtained from the data of Case and Parsons<sup>6)</sup> in the case of  $\text{CH}_3\text{OH}$ .

*Free Energies of Solvation of Ions and EMF of Single Electrodes*

the values of  $-\alpha_{\text{H}^+}^{\circ}$  (corr.) are quite close to those estimated in the present work.

On the other hand, Izmailov<sup>7)</sup> estimated  $\alpha_i^{\circ}$  on the basis of the donor-acceptor concept in the frame of the molecular orbital theory of the bonding of the ion to the solvent molecules. The relation between  $-\frac{1}{z}\alpha_{\text{H}^+}^{\circ}$  obtained from the data of Izmailov is exemplified in Fig. 16 in the case of  $\text{CH}_3\text{COCH}_3$ . It is found that there exists also a good linear relation between the two quantities, but the straight line deviates downward from the origin in most cases of his results, and the corrected values of  $-\alpha_{\text{H}^+}^{\circ}$  are little smaller than those in the present work, as shown in Table IV.

The reason of the deviation  $\Delta$  in the cases of Case and Parsons and of Izmailov is not clear, but it should be emphasized that there exists a good

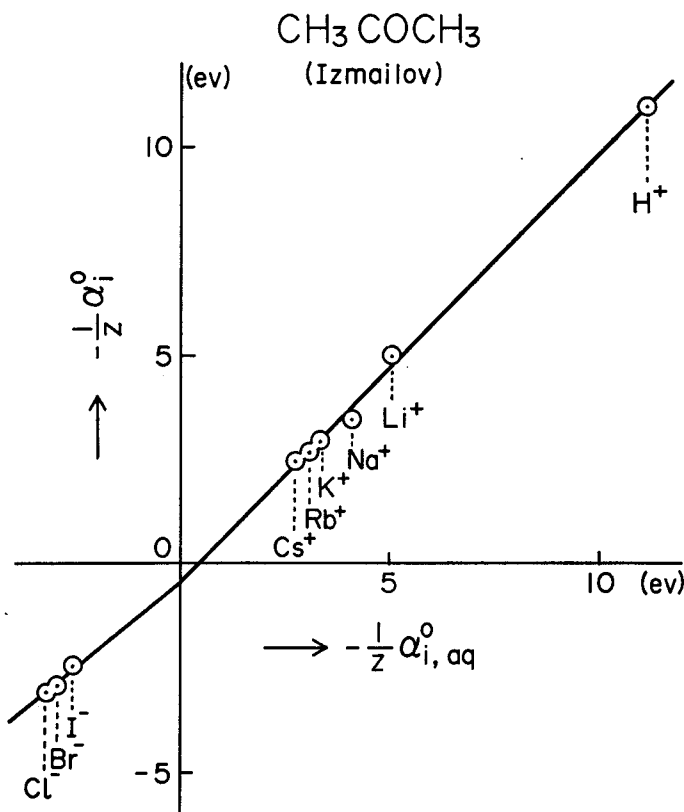


Fig. 16. The relation between  $-\frac{1}{z}\alpha_i^{\circ}$  and  $-\frac{1}{z}\alpha_{i, \text{aq}}^{\circ}$  obtained from the data of Izmailov<sup>7)</sup> in the case of  $\text{CH}_3\text{COCH}_3$ .



## A. MATSUDA

TABLE IV. Linear relations between  $-\frac{1}{z}\alpha_1^0$  and  $-\frac{1}{z}\alpha_{1,\text{aq}}^0$  obtained from the data of Izmailov<sup>7)</sup> and original and corrected values of  $-\alpha_{\text{H}^+}^0$

Solvent	$A + \beta x$	$-\alpha_{\text{H}^+}^0$ (orig.)	$-\alpha_{\text{H}^+}^0$ (corr.)
CH <sub>3</sub> OH	$-0.07 + 0.984x$	10.95	11.02
C <sub>2</sub> H <sub>5</sub> OH	$-0.16 + 0.985x$	10.91	11.07
C <sub>4</sub> H <sub>9</sub> OH	$-0.28 + 1.001x$	10.91	11.19
C <sub>5</sub> H <sub>11</sub> OH	$-0.33 + 1.016x$	10.93	11.26
CH <sub>3</sub> COCH <sub>3</sub>	$-0.46 + 1.026x$	10.93	11.39
CH <sub>3</sub> CN	$0.08 + 0.967x$	10.80	10.72
HCOOH	$0.10 + 0.947x$	10.54	10.44
NH <sub>3</sub>	$-0.52 + 1.133x$	12.05	12.57
N <sub>2</sub> H <sub>4</sub>	$-0.26 + 1.067x$	11.90	12.16

linear relation between  $-\frac{1}{z}\alpha_1^0$  and  $-\frac{1}{z}\alpha_{1,\text{aq}}^0$  in every solvent and the gradient  $\beta$  is quite close to unity.

The standard potentials used for the estimation of the  $\alpha_1$ -values in the present work are those measured at a temperature fixed at 25°C except in NH<sub>3</sub> in which they were measured at -33°C, and in fused dimethylammonium chloride in which they were measured at 180°C. However, the values of  $\alpha_1$  calculated by Eq. 12 using  $E_1^0$  at different temperatures are also found to be in good linear relation with those of  $-\alpha_{1,\text{aq}}^0$  at 25°C. It should be noted, however, that  $\alpha_1$  should include a term  $\left(\frac{1}{z}\Delta F_1^0 - \Delta F_{\text{H}^+}^0\right)$  which is dependent on the temperature, as seen from Eqs. (10 a) and (10 b). In the case of ammonia this term is so small that it can be neglected within an accuracy of a few centivolts, but in the case of fused dimethylammonium chloride this term is too large to be neglected. The free energies of solvation and the single electrode potentials in fused salts at high temperatures will be discussed in a later paper in the frame of the empirical method proposed in the present work.

It can be seen from Figs. (7) and (8) that the free energies of solvation in ammonia and hydrazin are quite close to each other, but Ca<sup>++</sup>, Cu<sup>+</sup> and Ag<sup>+</sup> ions are likely to show a systematic deviation from the linearity relation. This systematic deviation may suggest that there exist specific interactions between these ions and solvents, insofar as the experimental values of  $E_1^0$  for these ions are reliable in these solvents.<sup>14,15)</sup>

*Free Energies of Solvation of Ions and EMF of Single Electrodes*

Electrochemists recognize the significance to express the rates of electrode processes as the function of the absolute electrode potentials and the free energies of solvation of individual ions, but it has not yet been realized. The empirical method proposed in the present work on the basis of the standard electrode potentials will enable us to obtain these two quantities. It is also suggested that the proportionality of the free energies of solvation between water and non-aqueous solvents may provide a key word for the theoretical approach to the elucidation of the solvation bonding.

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