Medium Effects for Single Ions in Dimethyl Sulfoxide, *N,N'*-Dimethylformamide, and Propylene Carbonate

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The solubility products of thallium halides were measured in dimethyl sulfoxide, *N,N'*-Dimethylformamide, and propylene carbonate for the purpose of obtaining the values of the medium effect for these electrolytes on transfer from water to these solvents. The medium effects for cations were estimated from the standard potentials of metal/ion couples obtained by the method of the corrected rubidium scale. The medium effects for halide ions were calculated from the medium effects for thallium halides and the thallium ion. A comparison of extrathermodynamic assumptions was made for the values of the medium effect for the silver ion as estimated by various methods; the method of the corrected rubidium scale was found to give a reasonable result.

The significance of the medium effect in non-aqueous solution chemistry and the current status of the extrathermodynamic assumptions needed to estimate the medium effect for single ion have been reviewed in several recent, stimulating works.[1-8]

The medium effect, log $_{\mathrm{m}}\gamma$, is defined as a measure of the difference between the free energy of a solute, i, in its aqueous ($_{\mathrm{w}}G_{\mathrm{i}}^{\circ}$) and non-aqueous ($_{\mathrm{s}}G_{\mathrm{i}}^{\circ}$) standard states:

$$_{\mathrm{s}}G_{\mathrm{i}}^{\circ} - {}_{\mathrm{w}}G_{\mathrm{i}}^{\circ} = RT \ln {}_{\mathrm{m}}\gamma_{\mathrm{i}} \qquad (1)$$

For the 1 : 1 electrolyte:

$$\ln {}_{\mathrm{m}}\gamma_{\mathrm{i}} = \ln {}_{\mathrm{m}}\gamma_{\pm}^{2} = \ln {}_{\mathrm{m}}\gamma_{+} + \ln {}_{\mathrm{m}}\gamma_{-} \qquad (2)$$

where $_{\mathrm{m}}\gamma_{+}$, $_{\mathrm{m}}\gamma_{-}$, and $_{\mathrm{m}}\gamma_{\mathrm{i}}$ are the medium effects for the cation, the ainon, and the electrolyte respectively. Therefore, the solubility products of the AB salt in the solvent, S, $K_{\mathrm{s}}^{\mathrm{s}}$, are related to the solubility product in water, $K_{\mathrm{s}}^{\mathrm{w}}$, through:

$$K_{\mathrm{s}}^{\mathrm{w}} = K_{\mathrm{s}}^{\mathrm{s}}({}_{\mathrm{m}}\gamma_{+})({}_{\mathrm{m}}\gamma_{-}) \qquad (3)$$

Expressions like Eq. (3) relate the constants for a variety of equilibria in a solvent, S, to the equilibrium constants in water. A knowledge of the medium effect for any one ion would render accessible such knowledge for all other ions in the same solvent on the basis of the thermodynamic data for the complete electrolytes. The knowledge of the medium effects for single ions enables us to express any ionic activity and electromotive force series on a single scale, referred to the aqueous standard state.

The medium effects for single ions can not be determined exactly by rigorous thermodynamic methods. In spite of the limitations imposed by extract thermodynamics, though, many investigators have estimated at least approximate values for the medium effect for single ions with the aid of extrathermodynamic assumptions. One of the methods used is based on the "normalized potential scale" method originated by Pleskov.[9] In this method, the standard potential of the rubidium electrode is assumed to be a solvent-independent reference point for a universal series of standard electrode potentials(Rubidium Scale). Pleskov's method of the rubidium scale has been proved by estimating the change in the solvation energy of the rubidium ion with the solvent by the application of a modified Born equation(Corrected Rubidium Scale).[6,10,11] Other than the rubidium-rubidium ion, ferrocene-ferricinium[12] and iron(II-III) complexes of *o*-phenanthlorine[13] have been proposed as reference redox couples. Another way of estimating the medium effect is the "reference electrolyte" method.[1-5] This method is based on the assumption that the medium effect for an ideal reference electrolyte—composed of very large symmetrical ions as similar in size and structure as possible—can be divided equally between the anion and the cation. The number of proposed extrathermodynamic solutions has multiplied, and some discrepancies have been observed among the results obtained by various methods.

The objective of the present paper is, first, to estimate the medium effects for alkali metal, thallium, silver, halide, and perchlorate ions in dimethyl sulfoxide (DMSO), *N,N'*-Dimethylformamide(DMF), and propylene carbonate(PC) on the basis of the normalized potential scale which was previously determined on the assumption of the corrected rubidium scale method.[11] Then, the medium effects for the silver ion obtained in this work were compared with those estimated by other various extrathermodynamic methods in order to verify the applicability of the method of the corrected rubidium scale.

Experimental

Solvents and Electrolytes. The purification of solvents, the preparation and purification of tetraethylammonium iodide(TEAI) and thallium perchlorate, and the preparation of the thallium amalgam electrode have been described elsewhere.[11,14] The tetraethylammonium chloride(TEACl) and tetraethylammonium bromide(TEABr) were obtained commercially and were purified by recrystallization from an ethyl alcohol–ethyl acetate mixture. The electrolytes were dried in a vacuum oven for several tens of hours at 60—70 °C.

Procedure. The solubilities of thallium halides in DMF and PC were determined by potentiometric titration. A 0.002 M solution of thallium perchlorate was titrated with a 0.01 M solution of tetraethylammonium halide(TEAX). The indicator electrode was the thallium amalgam electrode, and the reference electrode was an aqueous saturated calomel electrode(SCE) equipped with a non-aqueous salt bridge.[11] Nitrogen gas was bubbled through the solution before and during the run of the titration. The potential of the cell was measured by means of Yokogawa Hewlett-Paccard Model 2727 potentiometer. The temperature was kept at 25±0.05 °C.

Table 1. Solubility products K_S (mol^2 l^{-2}) of thallium halides at 25 °C[a)]

	DMSO			DMF			PC		
	solubility $\times 10^3$	$f_{\pm}$	K_S $\times 10^6$	solubility $\times 10^5$	$f_{\pm}$	K_S $\times 10^9$	solubility $\times 10^6$	$f_{\pm}$	K_S $\times 10^{12}$
TlCl	1.99	0.89	3.16	5.25	0.97	2.62	2.24	1.00	5.01
TlBr	2.74	0.88	5.78	8.91	0.97	7.37	3.31	1.00	11.0
TlI	5.32	0.84	19.8	31.6	0.93	87.1	12.0	1.00	144.0

a) Solubilities are in mol l^{-1}. $f_{\pm}$ is salt activity coefficient. The values of solubility in DMF and PC were determined by potentiometric titration and those values in DMSO by polarographic amperometry.

The solubility of thallium halides in DMSO were rather high, and they could not be determined accurately by potentiometric titration. They were, however, determined by polarographic amperometry. The thallium halides were shaken with DMSO for twenty hours at 30 °C and then for ten hours at 25 °C. Pure DMSO and 0.1 M of tetraethylammonium perchlorate were added to the DMSO solution saturated with thallium halide, and then the polarogram was recorded. The concentration of thallium halide was determined from the magnitude of the diffusion current by using a predetermined calibration curve. The solubilities of thallium halides in DMF were also determined by polarographic amperometry in order to obtain auxiliary data.

Results and Discussion

The Determination of the Solubility Products of Thallium Halides. The potentiometric measurements for thallium salt were made with the following cell:

$$\text{aqueous SCE}\;\Big|\;\begin{matrix}\text{salt}\\ \text{bridge}\end{matrix}\;\Big|\;\text{TlClO}_4\quad 0.002\,\text{M}\;\Big|\;\text{Tl(Hg)}\qquad (A)$$

For the thallium amalgam electrode, it was found that the Nernst equation was nearly obeyed in all the solvents containing thallium perchlorate in the concentration range from 1×10^{-4} to 2×10^{-3} M as is shown in Fig. 1.

The titrations of thallium perchlorate with tetraethylammonium halides were carried out in the right-hand-half cell of Cell A. The titration curve shown in Fig. 2 is typical of the curves when 0.002 M $TlClO_4$ was titrated with 0.01 M TEAX in PC and DMF at 25 °C. In all the titration curves, we found one well-defined end point of titration corresponding to this rection:

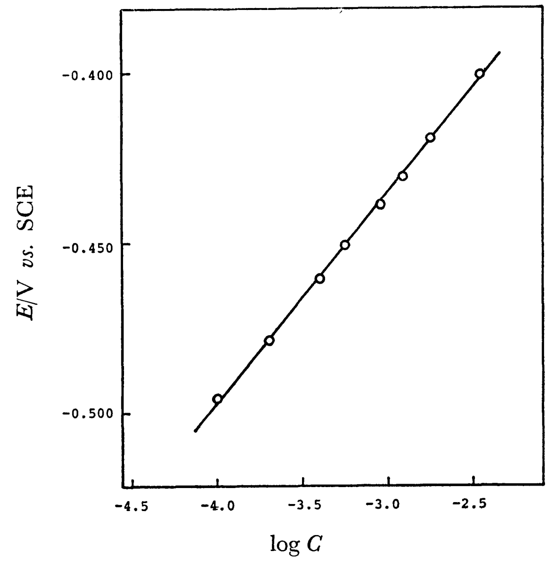

Fig. 1. Relation between the potential of the thallium amalgam electrode and the concentration of thallium perchlorate in PC at 25 °C.

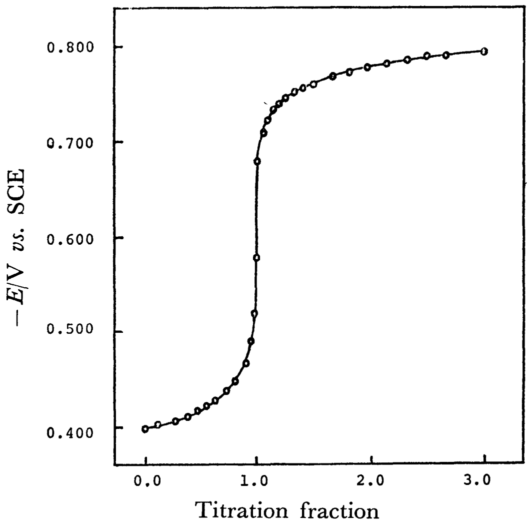

Fig. 2. The titration curve of 0.002 M $TlClO_4$ with 0.01 M TEACl in PC at 25 °C.

$$\text{Tl}^+ + \text{X}^- = \text{TlX}\downarrow \qquad (4)$$

The precipitation of TlX appeared soon after the titration started. The solubilities of TlX were calculated from the titration curves by using the Nernst equation; the results are given in Table 1. No further complex formation of the thallium ion with the halide ion was observed in these solvents, even in the presence of an excess concentration of the halide ion. In the presence of an excess concentration of the halide ion, the potential of the thallium amalgam electrode was found to be very stable. This electrode would be useful as a reference electrode of the second kind for electromotive force measurements in these solvents.

For the calculation of the solubility products of thallium halides, the complete dissociation of the salts was assumed, since the association between the perchlorate anion and metal ions has been found to be negligibly small in these solvents at the concentrations below 10^{-2} M.[15)] The salt activity coefficient, f, was calculated by means of the Debye-Hückel equation:

$$\log f_{\pm} = -\frac{A\sqrt{\mu}}{1+Ba\sqrt{\mu}} \qquad (5)$$

where A and B are constants and were calculated to

TABLE 2. SOLUBILITY PRODUCTS pK_s (molality) AND MEDIUM EFFECTS FOR ELECTROLYTES

	DMSO		DMF		PC		Water
	pK_s	ΔpK_s[a]	pK_s	ΔpK_s[a]	pK_s	ΔpK_s[a]	pK_s
TlCl	5.58	1.82	8.53	4.77	11.45	7.69	3.76[b]
TlBr	5.32	−0.15	8.08	2.61	11.11	5.64	3.62[b]
TlI	4.78	−2.41	7.01	−0.18	9.99	2.80	7.19[b]
$KClO_4$	−0.72[c]	−2.38	0.05[d]	−1.61	e)		1.7[d]

a) $\Delta pK_s = pK_s^s - pK_s^w$. b) Ref. 6. c) R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 3703 (1967). Correction for solvent molality was made. d) Ref. 4. Correction for solvent molality was made. e) not determined.

be respectively, 1.18 and 0.435 for DMSO, 1.73 and 0.493 for DMF, and 0.717 and 0.368 for PC by using the dielectric constants of these solvents. The ion-size parameter, *a*, has been determined to be 3.6 for DMSO, 5.0 for DMF, and 0.0 for PC.[14] The activity coefficients and solubility products of thallium halides are given in Table 1.

The solubility products of TlX in DMF as determined by polarographic amperometry were different by 10 per cent from the solubility products as determined by potentiometric titration. Accordingly, the values given in Table 1 must involve an uncertainty of this order.

In Table 2, the solubility products of thallium halides, pK_s, are listed in the molality scale, along with those of potassium perchlorate available in the literature. To convert from molar to molal pK_s, the solvent density of these solvents was used.

The medium effects for thallium halides, $\log {}_m\gamma_{TlX}$ were calculated by means of the following equation:

$$\log {}_m\gamma_{TlX} = \Delta pK_s = pK_s^s - pK_s^w \qquad (6)$$

The results are listed in Table 2. Equation (6) is strictly valid only when no crystal solvates are formed. We assumed an absence of solvates in all these solvent-solute combinations.

Estimation of the Medium Effects for Single Ions. The medium effects for alkali metal, thallium, and silver ions were calculated from the difference between the standard potentials of the metal electrode in an aqueous solution, E_w°, and in a non-aqueous solution, E_s°, estimated on the basis of the corrected rubidium scale:[14]

$$\log {}_m\gamma_{M^+} = (E_s^\circ - E_w^\circ)/0.05916 \qquad (7)$$

The medium effects for halide ions were calculated from:

$$\log {}_m\gamma_{X^-} = \log {}_m\gamma_{TlX} - \log {}_m\gamma_{Tl^+} \qquad (8)$$

where, X=Cl, Br, I. The medium effect for perchlorate was calculated from $\log {}_m\gamma_{KClO_4}$ and $\log {}_m\gamma_{K^+}$ in the same manner. The medium effects for individual ions thus estimated are summarized in Table 3. A positive value of a medium effect means a lower solvation energy (tighter solvation) in water than in other solvents. This is the case for most small anions. The solvation of halide ions depends on strong hydrogen bonding, which is available in water but not in DMSO, DMF, and PC. The tighter solvation of cations in DMSO and DMF is characterized by the solvent structure, especially by the strong Lewis basicity of these solvents. PC is a weaker Lewis base; accordingly, the cationic solvation of PC is weaker than that of water.

TABLE 3. MEDIUM EFFECTS FOR SINGLE IONS (Molality scale). Reference solvent is water

	DMSO	DMF	PC
Li^+	−1.49	−0.24	+5.53
Na^+	−1.10	+0.05	+3.82
K^+	−1.20	−0.37	+2.15
Rb^+	−0.58	+0.08	+2.52
Cs^+	−0.61	−0.08	+2.42
Tl^+	−3.16	−1.74	+2.53
Ag^+	−5.11	−2.30	+3.77
Cl^-	+4.98	+6.51	+5.36
Br^-	+3.01	+4.35	+3.31
I^-	+0.75	+1.56	+0.47
ClO_4^-	−1.18	−1.24	a)

a) not determined.

A Comparison of Extrathermodynamic Assumptions. It will now be interesting to compare the values of the medium effect for the single ions estimated in this work with those values estimated on the basis of other extrathermodynamic assumptions. For this purpose, the medium effect for the silver ion was examined, since, among the ions studied in this work, the silver ion has been studied most extensively by various methods.

In Fig. 3 we have plotted the medium effects for the silver ion in DMSO, DMF, PC, and acetonitrile (ACN). The classification of Assumptions 1–5 and the values of the medium effect estimated by these assumptions were taken from Ref. 3. The values from the rubidium scale method are denoted by R, and those from the corrected rubidium scale method, by B.

Each individual assumption has its own inherent limitations.[1] Assumption 1, which equates the medium effect for the tetraphenylarsonium cation with that for the tetraphenylboride anion, $\log {}_m\gamma_{Ph_4As^+} = \log {}_m\gamma_{Ph_4B^-}$, involves difficulty in dividing the medium effect for the reference electrolyte equally among the component cation and anion; moreover, the accuracy of the determined solubility products of the reference electrolyte is not sufficient. In Assumptions 2 and 3, the electrostatic interaction of solvent with very large anions, which were formed in the transition states for the S_N2 or S_NAr reaction, is assumed to be unchanged, $\log {}_m\gamma_{ArF} = \log {}_m\gamma_{ArN_3F^{-\ddagger}}$ or $\log {}_m\gamma_{CH_3I} = \log$

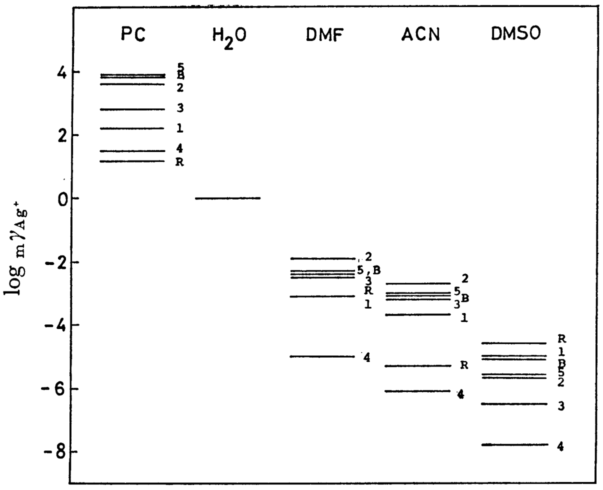

Fig. 3. A comparison of extrathermodynamic assumptions, leading to the medium effect for silver ion for transfer from water to other solvents at 25 °C. The assumptions are (1) $\log {}_m\gamma_{Ph_4As^+} = \log {}_m\gamma_{Ph_4B^-}$; (2) $\log {}_m\gamma_{ArF} = \log {}_m\gamma_{ArN_3F^{-\neq}}$; (3) $\log {}_m\gamma_{CH_3I} = \log {}_m\gamma_{NCSCH_3I^{-\neq}}$; (4) $\log {}_m\gamma_{Fe(C_5H_5)_2} = \log {}_m\gamma_{Fe(C_5H_5)_2^+}$; (5) Negligible liquid junction potential; (B) Corrected rubidium scale; (R) Rubidium scale.

${}_m\gamma_{NCSCH_3I^{-\neq}}$, but the large anions have a large polarizability and the electrostatic interaction of these anions with solvents must be affected by the solvent polarity. Assumption 4 equates the medium effect for ferrocene with that for the ferricinium cation, $\log {}_m\gamma_{Fe(C_5H_5)_2} = \log {}_m\gamma_{Fe(C_5H_5)_2^+}$. This assumption must be criticized in view of the large increase in the solubility of ferrocene on transfer from water to organic solvents, which would result in a serious change in the medium effect for ferrocene. Moreover, the electrostatic interaction of the ferricinium ion with solvent must be affected by the solvent polarity. Assumption 5 neglects the liquid junction potential in a cell composed of silver wire in a silver perchlorate solution connected by a proper non-aqueous salt bridge of tetraethylammonium picrate: the liquid junction potential of the aqueous and non-aqueous interface would not be completely eliminated. Assumption R neglects the change in the electrostatic interaction of the rubidium ion with solvents of different dielectric properties. Assumption B simplifies too much the change in the solvation energy of the rubidium ion with solvents mainly electrostatic in nature.

At this time we have no reason to defend any one assumption with confidence. However, it seems reasonable to support assumptions which give focusing values for the medium effect.

As is shown in Fig. 3, the internal coherency of the values of the medium effect as estimated by individual assumptions for different solvents is excellent except for the method of the rubidium scale; the magnitudes of the medium effect for the silver ion estimated by individual assumptions lie in this order; PC>H_2O> DMF>ACN>DMSO; only the values of the medium effect estimated by the method of the rubidium scale for DMSO and ACN are in an inverse order. Accordingly, the method of the rubidium scale is considered to be unfavourable as a universally-applicable method for these solvents. In this connection, the limitation of the assumption of rubidium scale must be overcome by the method of the corrected rubidium scale. Most values of the medium effect for the silver ion lie in ranges between 3 and 4 in PC, −2 and −3 in DMF, −3 and −4 in ACN, −5 and −6 in DMSO. The values of the medium effect for the silver ion, as estimated by the method of the corrected rubidium scale, lie in these ranges for all the solvents. Accordingly, it would be reasonable to say that the method of the corrected rubidium scale is one of the most reliable methods of estimating the medium effect for single ions.

It is quite interesting that the assumption of the negligible liquid junction potential seems reasonable, since the values of the medium effect estimated by this assumption lie in the focusing ranges. The method of the negligible liquid junction potential determines directly, unlike the other extrathermodynamic assumptions, the medium effect for the ion from the electrode potential measured against a silver-silver perchlorate electrode in the reference solvent. The practical procedure is very easy to comprehend.[3] Therefore, this method would throw light on the urgent problem in the non-aqueous electrochemistry of normalizing the potential of a given redox system directly to the water scale by measuring the cell potential.

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References

1) O. Popovych, *Crit. Rev. Anal. Chem.*, **1**, 73 (1970).
2) D. H. Bern and O. Popovych, *Anal. Chem.*, **44**, 817 (1972).
3) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1148 (1972).
4) A. J. Parker and R. Alexander, *ibid.*, **90**, 3313 (1968).
5) E. Grundwald, G. Baugham, and G. Kohnstam, *ibid.*, **82**, 5801 (1960).
6) J. F. Coetzee and J. J. Champion, *ibid.*, **89**, 2513, 2517 (1967).
7) R. G. Bates, "The Chemistry of Non-Aqueous Solvents," ed. by J. J. Lagowski, Academic Press, New York and London (1966), Chap. 3.
8) H. Strehlow, *ibid.*, Chap. 4.
9) V. A. Pleskov, *Usp. Khim.*, **16**, 254 (1947).
10) J. F. Coetzee, J. M. Simon, and R. J. Bertozzi, *Anal. Chem.*, **41**, 766 (1969).
11) N. Matsuura, K. Umemoto, M. Waki, Z. Takeuchi, and M. Omoto, This Bulletin, **47**, 806 (1974).
12) H. M. Koepp, H. Wendt, and H. Strehlow, *Z. Elektrochem.*, **64**, 483 (1960).
13) I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem.*, **69**, 3049 (1965).
14) N. Matsuura, K. Umemoto, and Z. Takeuchi, This Bulletin, **47**, 813 (1974).
15) N. Matsuura, K. Umemoto, and Y. Takeda, to be published.