Studies on the electrochemical approach to ion solvation

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Abstract: Two problems are discussed concerning the electrochemical studies on ion solvation: one is the problem of electrochemical sensors for ion solvation and the other is the problem of comparing the electrode potentials in different solvents. On the former, the applications of ion-selective electrodes and pH-ISFETs are mainly considered. On the latter, the three components of the liquid junction potential (LJP) between different solvents are discussed and then a new method of estimating the LJP is presented, being compared with the conventional methods.

INTRODUCTION

The reactivities of chemical species in solutions are markedly influenced by how strongly they are solvated. If we can know the differences in solvation energies between two solvents (i.e., the Gibbs energies of transfer) for all chemical species participating in a reaction or in an equilibrium, we can quantitatively predict how the reaction or the equilibrium is different in the two solvents. Therefore, it is of prime importance in the chemistry of nonaqueous solutions to compile the data of the Gibbs energy of transfer for as many chemical species as possible.

Electrochemistry can provide useful techniques to get such data for ionic species. Some electrodes can work as sensors for ion solvation, responding thermodynamically to the solvation energies of the ions determining the electrode potentials. Metal ion/metal and metal ion/metal amalgam electrodes are examples of such electrodes. But, in the electrochemical study of ion solvation, we have to compare the electrode potentials in different solvents. Because it is thermodynamically impossible, a method based on some extra-thermodynamic assumption must be employed to make the comparison possible (ref. 1). The reliability of the data on ion solvation is influenced significantly by the reliability of the assumption.

In this review, two problems are discussed concerning the electrochemical studies of ion solvation. One is the problem of electrochemical sensors for ion solvation and the other is the problem of comparing the electrode potentials in different solvents. In the former, special emphasis is put on the application of ion-selective electrodes and pH-ISFETs. In the latter, the results of our study on the liquid junction potential between different solvents are discussed in some detail.

ELECTROCHEMICAL SENSORS FOR ION SOLVATION

Metal Ion/Metal and Metal Ion/Metal Amalgam Electrodes

These electrodes have widely been used for the study of ion solvation, because their responses are guaranteed to be thermodynamic (Nernstian). The Ag^+/Ag electrode is a typical example of the metal ion/metal electrode and potentiometry is employed in its use. For most metal ions, however, polarographic half-wave potentials for the process $M^{n+} + ne \rightleftharpoons M(Hg)$ are usually measured against some solvent-independent reference potential system (e.g., bis(biphenyl)chromium(+1/0) (ref. 2)). In the polarographic studies, we do not handle amalgam electrodes. Metal amalgams are formed *in situ* at the dropping mercury electrode. But, for the half-wave potentials to be the measure of metal ion solvation, we have to get reversible polarographic waves. The supporting electrolyte may give undesirable influences on the reversibility. For example, in basic aprotic solvents, the reduction waves of alkali and alkaline earth metal ions often become less reversible or even disappear by the influence of Et_4N^- as the cation of the supporting electrolyte (ref. 3).

Ion-Selective Electrodes (ISEs) and Ion-Selective Field-Effect Transistors (ISFETs)

The number of ISEs applicable in nonaqueous solutions are rather limited, mainly due to the dissolution and swelling of the electrodes. However, some ISEs and ISFETs work satisfactorily in nonaqueous solutions (ref. 4), and are applicable even as sensors for ion solvation, though their appropriate response must be confirmed before use.

A Univalent Cation-Sensitive Glass Electrode We applied a univalent-cation sensitive glass electrode to study the successive complexation of univalent cations (M^+: Li^+, Na^-, K^+, Rb^+, Cs^-, NH_4^+) in acetonitrile (AN) with donor solvent molecules (D: water, formamide (FA), *N*-methylformamide, pyridine, *N,N*-dimethylformamide (DMF), *N,N*-dimethyl-acetamide (DMA), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone, hexamethylphosphoric triamide (HMPA)) (ref. 5). Solvent D was added stepwise to the AN solution of cation M^+ and, from the variation in the glass electrode potential, the formation constants (β_1, β_2, etc.) for the complexing $M^+ + D \rightleftharpoons M_D^+$, $M^+ + 2D \rightleftharpoons M_{2D}^+$, etc. were obtained. The glass electrode was confirmed to respond to the solvation of alkali metal ions in almost the same way as the respective amalgam electrodes. The glass electrode was very easy to handle, gave reliable results, and was applicable to non-metallic cations like NH_4^+. From the temperature effect on β_1, the 1 : 1 complexing of Li^+ with donor solvent D was proved to be the replacement of one solvated AN molecule by one molecule of D: $Li(AN)_x^+ + D \square Li(AN)_{x-1} D^- + AN$ (ref. 6).

Cox et al. (ref. 7) obtained in propylene carbonate (PC) the complex formation constants of Li^+ and Na^+ with DMSO and used them to calculate the Gibbs energies of transfer from PC to PC-DMSO mixtures and to DMSO with Eqs. (1) and (2), respectively.

$$\Delta G_t^\circ(M^+, R \rightarrow R + D) = -nRT \ln \phi_R - RT \ln\left[1 + \sum_{i=1}^{n} \beta_i' \left(\phi_D / \phi_R\right)^i\right] \quad (1) \qquad \Delta G_t^\circ(M^+, R \rightarrow D) = -RT \ln \beta_n' \quad (2)$$

Here R shows the reference solvent (PC in this case), ϕ_D and ϕ_R the volume fraction of D and R in the mixed solvent, and $\beta_i' = \beta_i (1000\rho_D/M_D)^i$ (ρ_D and M_D: the density and relative molecular mass of D). The calculated ΔG_t° values agreed well with the values directly obtained by EMF measurements. As in this example, the ionic Gibbs energy of transfer from R to R-D mixtures and to D can often be obtained from the complex formation constants of the ion in R with D. However, Eqs. (1) and (2) are not sufficient when the relative permittivities of R and D are drastically different. For example, in the mixtures of PC ($\varepsilon_r \sim 64$) and monoglyme (DME, $\varepsilon_r \sim 7$), the Li^+ activity first decreased with the increase in the DME content, and, after passing a minimum at around 60(v/v)% DME, it increased again (ref. 8). In this case, the DME added to the PC solution of Li^+ ion decreased the Li^+ activity by complexation, but, at the same time, it gradually decreased the solvent permittivity and weakened the electrostatic solvation of Li^+ (increase in Li^+ activity). In the more DME-rich region, the association of Li^+ and ClO_4^- decreased the Li^+ activity again. In the mixtures of PC with dimethyl, diethyl and ethyl methyl carbonates ($\varepsilon_r \sim 7$), the complexing to Li^+ was not observed and only the influence of solvent permittivities determined the variation in the Li^+ activity (ref. 8).

Other ISEs and pH-ISFETs Some crystalline membrane ISEs have been used in nonaqueous solutions, sometimes to study ion solvation (ref. 9). For a long time, liquid membrane and coated wire ISEs were considered not applicable in nonaqueous solutions, because they are destroyed by solvents. However, Nakamura et al. found that a polyacrylamide (PAA) membrane coated onto a platinum disk electrode was durable in aprotic solvents and, by coupling it with appropriate functional compounds, prepared several ISEs for use in nonaqueous solvents (ref. 10). The membranes coupled to acyclic (ref. 11-a) and cyclic (ref. 11-b) ionophores responded in Nernstian ways to alkaline earth metal ions in aprotic solvents. They were used to study the stepwise complexing of Mg^{2+} and Ba^{2+} in AN and PC with DMF, DMSO and HMPA and to get the Gibbs energies of transfer of Ba^{2+} from PC to DMA and PC-DMA mixtures. The membrane coupled to cobalt-phthalocyanine responded to F^- and CN^- in aprotic solvents. It was used to determine the solubility product constants of alkali metal fluorides and cyanides in AN and PC (ref. 12).

Recently the pH measurements in nonaqueous solutions are becoming important. Although a pH glass electrode is the most popular pH-sensor in nonaqueous solutions, its response is often very slow, sometimes taking over an hour to reach a steady potential. We used some new pH-sensors, including pH-ISFETs (Si_3N_4- and Ta_2O_5-types), and compared their responses with that of the glass electrode (ref. 13). As shown in Fig. 1, the new pH-sensors responded much faster than the glass electrode, the Si_3N_4-ISFET being the fastest. Moreover, they responded in Nernstian or near-Nernstian ways to the pH and the transfer activity coefficient of H^+. We used the pH-ISFETs to
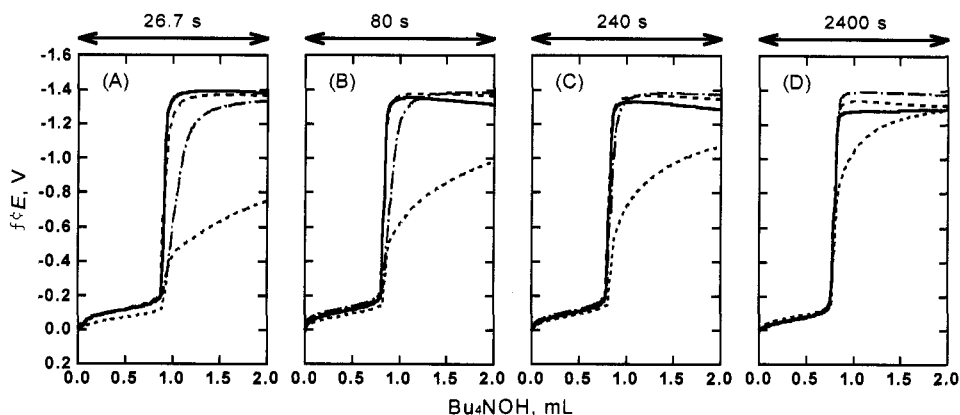
Titration of 5 mM picric acid in AN with 1 M Bu₄NOH. Titration speed: (A) 4.5, (B) 1.5, (C) 0.5,
(D) 0.05 mL/min□ pH-Sensor: a) —·—·—· IrO₂-sensor, b) ······· Ta₂O₅-ISFET,
c)————— Si₃N₄-ISFET, d) ·········· glass electrode.

Fig. 1 Comparison of the response speeds of four-types pH-sensors.

determine the transfer activity coefficient of H^+ (ref. 14), the acid dissociation constants (ref. 15), and the solubility product constants of metal hydroxides. Due to the rapid response of the Si_3N_4-ISFET, we can use it in rapid pH titrations (within 1 min), that are impossible with a pH glass electrode. In connection with the pH measurements in nonaqueous solutions, we recently found that 0.05 mol kg^{-1} potassium hydrogen phthalate in the solvent under study, recommended by the Commission on Electroanalytical Chemistry of IUPAC as the reference value pH-standard in aqueous-organic solvent mixtures, loses its buffer action in water-poor mixtures with aprotic solvents (ref. 16).

COMPARISON OF ELECTRODE POTENTIALS IN DIFFERENT SOLVENTS

–The Problem of the Liquid Junction Potential (LJP) between Different Solvents–

It is impossible to compare the electrode potentials in different solvents in purely thermodynamic ways. We have to apply some extra-thermodynamic assumption. Three assumptions are often employed (ref. 1). One is to assume a redox system with a solvent-independent potential. Ferrocene(+1/0), bis(biphenyl)chromium(+1/0) and cobaltcene(+1/0, 0/-1, +1/-1) are examples of such redox systems. The second is to assume a negligible LJP for an appropriate junction between different solvents. The third is to use the reference electrolyte (Ph_4AsBPh_4) assumption in getting the potentials of the Ag^+/Ag electrode in a common scale. In all cases, the reliability of the results depends on the reliability of the extra-thermodynamic assumption employed. Unfortunately, we cannot accurately know the reliability of the extra-thermodynamic assumptions.

If we can estimate the LJP between different solvents with some accuracy, we can make the electrochemical study of ion solvation more reliable. Therefore, to study the problem of the LJP between different solvents is of practical importance. Considerable number of reports have been published on this problem (ref. 17), but our knowledge about the LJP is still quite limited or fragmental due to its complicated nature.

We studied this problem in detail, intending to know how the LJPs are influenced by the electrolytes and solvents at the junction and, if possible, to develop an appropriate method to estimate the LJPs (ref. 18).
The LJP between different solvents contains three components: component a) caused by the difference in electrolyte concentrations (or activities) on the two sides of the junction and the difference between the cationic and anionic mobilities, component b) caused by the differences in ion solvations on the two sides of the junction, and component c) caused by the solvent-solvent interactions at the junction. Fortunately, we found that, under appropriate conditions, the variation in each of the three components could be measured separately from the others (Fig. 2). Thus, we could study the characteristics of the three components.

Characteristics of the Three Components of the LJP between Different Solvents

| Ag | 5mM AgClO₄ 25mM Et₄NClO₄ (S₁) | 25mM Et₄NClO₄ (S₁) | c₁ MX (S₁) | c₂ MX (S₂) | 25mM Et₄NClO₄ (S₂) | 5mM AgClO₄ 25mM Et₄NClO₄ (S₂) | Ag | (I) |

$$j_1 \qquad\qquad J \qquad\qquad j_2$$

| Ag | 5mM AgClO₄ 25mM Et₄NClO₄ (S₁) | 1mM Et₄NClO₄ (S₁) | 100mM MX (S₃) | 1mM Et₄NClO₄ (S₂) | 5mM AgClO₄ 25mM Et₄NClO₄ (S₂) | Ag | (II) |

$$J_1 \qquad\qquad J_2$$

Component a): The EMF of Cell (I) is measured varying c_1 and c_2, and corrections are made for the LJPs at j_1 and j_2.

Component b): The EMF of Cell (I) is measured varying MX, and corrections are made for the LJPs at j_1 and j_2 and component a) at J.

Component c): The EMF of Cell (II) is measured varying S_3. Corrections are made for the influence of components a) and b), if needed.

Fig. 2 Methods to get the actual variations of the three components

Junction with the same electrolyte on the two sides: $c_1 MX(S_1)$ $\mid c_2 MX(S_2)$

The characteristics of the three components are schematically shown in Fig. 3.

Component a) (ref. 18-j,l,n) The origin of component a) is somewhat similar to that of the LJP between solutions in the same solvent ($S_1 = S_2$). In deriving the equations for components a) and b), we assumed that the difference in ionic chemical potentials ($\mu(i) = \mu^\circ(i) + RT\ln a(i)$) between the two sides was the driving force for the transfer of ions across the junction. We got Eq. (3) for component a), by integrating $\int RT\Sigma(t_i/z_i)d\ln a(i)$ from S_1 to S_2 for linear variations of a (electrolyte activity) and t (ionic transport number) at the interphase region (z_M, z_X: charges of M and X including signs).

$$E_j(a) = \left(-\frac{RT}{z_M z_X F}\right)\left\{(z_X t_{M1} + z_M t_{X1})\ln\left(\frac{a_{MX2}}{a_{MX1}}\right) + [z_X(t_{M2} - t_{M1}) + z_M(t_{X2} - t_{X1})] \times \left[1 - \frac{a_{MX1}}{a_{MX2} - a_{MX1}}\ln\frac{a_{MX2}}{a_{MX1}}\right]\right\} \quad (3)$$

$E_j(a)$ is equal to zero when $a_{MX1} = a_{MX2}$. The validity of Eq. (3) was confirmed by the method as shown in Fig. 2. Some typical results are shown in Fig. 4, where the abscissa is for the $E_j(a)$ calculated by Eq. (3) and the ordinate for the actual variation in component (a). In most cases, linear relations of unit slopes are obtained. In some cases, fairly large deviations from typical behavior are observed (see the case of Et₄NClO₄ and W/DMSO in Fig. 4), but they are attributable to the influence of electrolyte concentrations to component c). As is apparent from Fig. 4, component a) is usually within ±40 mV. Especially for MX=Et₄NPic, component a) is often within ±5 mV, because the mobilities of Et₄N⁺ and Pic⁻ are near each other.

Component b) (ref. 18-g,h,l) We got Eq. (4) for component b), by integrating $\int \Sigma(t_i/z_i)d\mu^\circ(i)$ from S_1 to S_2 assuming linear variations of μ° and t at the interphase region.

$$E_j(b) = \left(-\frac{1}{2F}\right)\left[(t_{M1} + t_{M2})\Delta\mu^\circ(M) - (t_{X1} + t_{X2})\Delta\mu^\circ(X)\right] \quad (4)$$

Here $\Delta\mu^\circ(i) = \Delta G_t^\circ(i, S_1 \to S_2)$. Equation (4) shows that, by component b), cation M⁺ tends to make the potential of the solution in which the solvation is stronger more positive, while anion X⁻ tends to make it less positive (see Fig. 3b). We tested the validity of Eq. (4) by the method described in Fig. 2. The results for H₂O/organic solvent junctions are shown in Fig. 5, in which the abscissa is for the calculated $E_j(b)$ values and the ordinate for the actual variations in component b). When the solvents on the two sides are immiscible (H₂O/NB and H₂O/DCE), nearly linear relations of unit slopes are observed (Note a). However, when the solvents are completely or partially miscible, the near-linear relations have slopes of ~0.5, irrespective of the strength of solvent-solvent interactions.

Note a: We calculated the LJPs between immiscible solvents by another method which took electrolyte-distributions at the interface into account. The values obtained were in fair agreement with those by Eq. (4) (ref. 18-h).
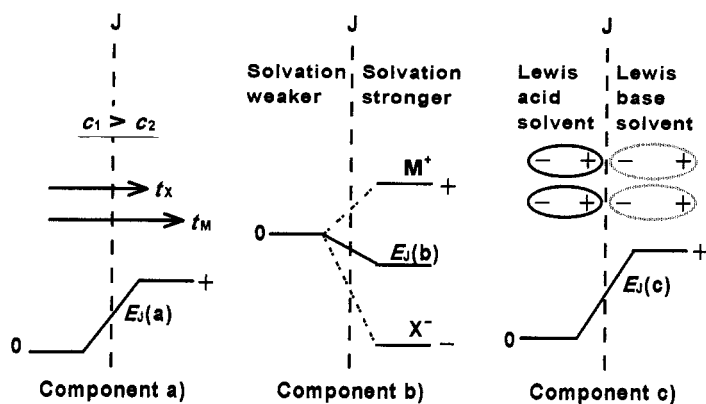
Fig. 3 Characteristics of the three components of the LJP between different solvents.
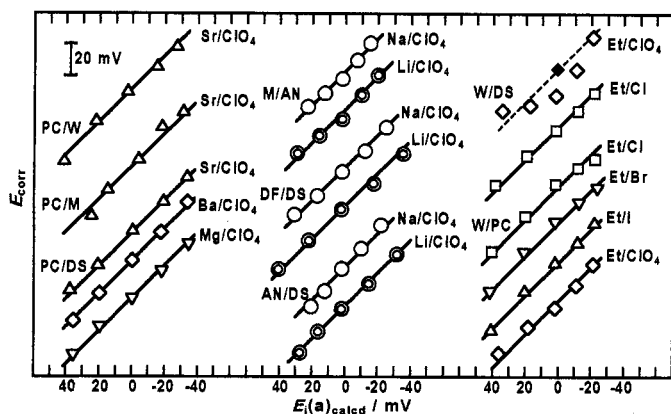

Fig. 4 Test of the validity of Eq. (3). (c_1,c_2)/mM=(100,1), (10,1), (1,1), (1,10), (1,100);◆ (25,25). (Et=Et$_4$N, DS=DMSO).
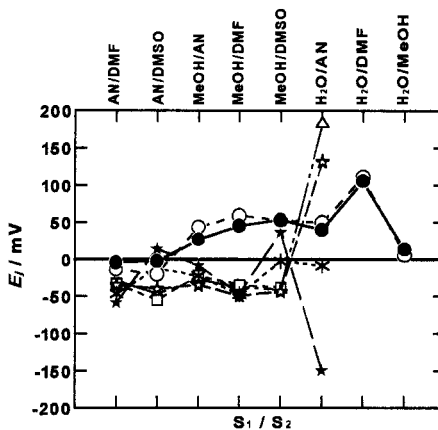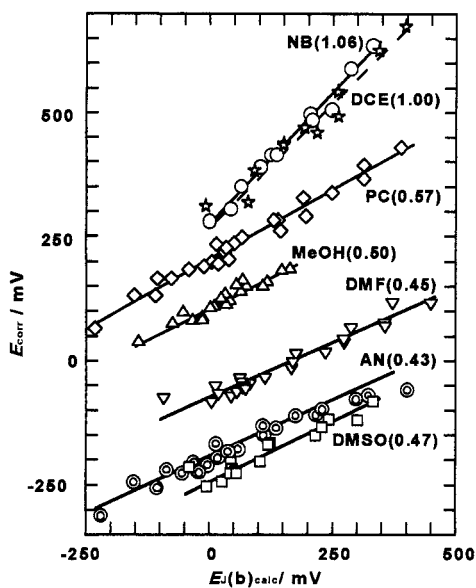

Fig. 5 Test of Eq. (4) at H$_2$O/organic solvent junctions.

Fig. 6 Comparison of the LJPs estimated by various methods. 25 mM Et$_4$NPic(S$_1$)/25 mM Et$_4$NPic(S$_2$). △ Fc(+1/0);
□ BCr(+1/0); ☆ Cc(+1/0); ★ Cc(0/-1); ✳ Cc(+1/-1); ○ Ag$^+$/Ag (Ph$_4$AsBPh$_4$); ● new method.

In Fig. 5, component b) sometimes varied by more than 200 mV with the electrolyte species. But, the experiments with different (c_1, c_2) showed that, as expected for component b), the variations were almost independent of electrolyte concentrations. For the miscible junctions of MeOH/, FA/ and aprotic solvent/aprotic solvents, the slopes of the near-linear relations were even smaller (0~0.4). Because of the complicated phenomena occurring at the junction, it is not easy to know the mechanism determining the slopes. Probably, at miscible junctions, the mixing of the solvents makes the ionic transfer (distribution) at the interphase region less effective than expected by $\Delta G_t^\circ(i, S_1 \to S_2)$. Though this problem must be elucidated by further studies, we can use the near-linear relations to estimate component b) by $E_j(b)_{calc} \times (slope)$.

Component c) (ref. 18-b,c,d,e,i) The method to study the characteristics of component c) is shown in Fig. 2. AN was usually used as S_1, because AN interacts only weakly with other aprotic solvents (ref. 17-c). If S_3 is aprotic, we can expect small values for component c) at J_1. If we briefly summarize the characteristics of component c), (1) it is, in principle, electrolyte independent, (2) its magnitude is closely related to the strength of solvent-solvent interactions (e.g. heats of mixing), (3) at the mixed-solvent/pure-solvent (and mixed-solvent/mixed-solvent) junctions its magnitude varies near-linearly with the mixed-solvent composition expressed in volume fraction. All these characteristics can be explained if we consider a model that the solvents at the junction interact as a Lewis acid and a Lewis base and some orientations of solvent molecules occur causing component c) (Fig. 6c). Thus, component c) is large between two strongly-interacting solvents, with the solvent side as a Lewis base more positive. Traditionally, the component due to the solvent-solvent interaction was considered to occur due to that the solvent molecules, released from the ions transferred across the junction to the opposite side, interact with the solvent on that side (ref.. 17-b). But the model cannot explain the experimental observations.

In order to estimate component c) experimentally, we have to make some assumptions. We got the values in Table 1, assuming component c) at H_2O/NB and AN/aprotic solvent junctions equal to zero. The former is because small potential differences have been reported for the compact double layer at H_2O/NB (ref. 19). The latter is because of the very weak interactions between AN and other aprotic solvents. In Table 1, the values partially decreased with the increase in the Et_4NPic concentration (~20% between 1 and 25 mM). It is probably due to the influence of electrolyte on the orientation mechanism in Fig. 3c. At H_2O/DMF and DMSO, component c) was estimated to be ≥ 100 mV. Between two aprotic solvents, however, component c) is expected to be much smaller (usually within ± 20 mV).

Table 1 Estimated values of component c) in mV*

$c/$	c $Et_4Npic(H_2O) \square c$ Et_4NPic (S) ; S =$\square$						
mM	NB	NM	PC	AN	Ac	DMF	DMSO
1	(0)	6	30	44	87	122	122
10	(0)	8	25	40	77	109	112
25	(0)	8	23	37	71	102	104

* The values at H_2O/NB and AN/aprotic solvents were assumed to be zero.

Junction with different electrolytes on the two sides: c_1 $MX(S_1)$ | c_2 $NY(S_2)$

In practical measurements, we often encounter junctions with different electrolytes on the two sides (c_1 $MX(S_1)\square c_2$ $NY(S_2)$). At those junctions, component b) is not independent of electrolyte concentrations, because t is a function of c_1 and c_2. We got the calculated values for components a) and b), numerically integrating Eqs. (5) and (6) under the conditions of linear variations in t, a and μ° at the interphase region (ref. 18-m).

$$E_j(a) = \left(\frac{-RT}{F} \right) \int_{S1}^{S2} \left[(t_M - t_X) d \ln a_{MX} + (t_N - t_Y) d \ln_{NY} \right] \qquad (5)$$

$$E_j(b) = \left(\frac{-1}{F} \right) \int_{S1}^{S2} \left[t_M d\mu^\circ(M) - t_X d\mu^\circ(X) + t_N d\mu^\circ(N) - t_Y d\mu^\circ(Y) \right] \qquad (6)$$

If we vary c_1 and c_2, components a) and b) vary simultaneously. However, if we estimate the magnitude of component b) by $E_j(b)_{calc} \times (slope)$, where $E_j(b)_{calc}$ is the value estimated by Eq. (6) and (slope) the one at the junction of $MX(S_1)/ MX(S_2)$ (see above), we can get a near-linear relation of unit slope between the actual variation of component a) and the values calculated by Eq. (5). Thus, we can treat components a) and b) somewhat quantitatively even when the electrolytes on the two sides are different. Here again, component c) is nearly electrolyte-independent.

A New Method for Estimating the LJP between Different Solvents

Table 2 LJPs estimated by the new and the conventional methods (mV)*

S_1/S_2	MX	New method				Conven.	Difference
		(a)	(b)	(c)	$E_j(1)$	$E_j(2)$	$E_j(1)-E_j(2)$
H_2O/AN	Et_4NPic	0	8	37	45	39	6
	Et_4NClO_4	-2	18	37	53	55	-2
	Et_4NI	-2	60	37	95	105	-10
	Et_4NCl	-2	131	37	166	169	-3
H_2O/DMF	Et_4NPic	0	2	103	105	111	-6
	Et_4NClO_4	-2	30	103	131	131	0
	Et_4NI	-2	73	103	174	177	-3
	Et_4NCl	-2	157	103	258	252	6
$H_2O/MeOH$	Et_4NPic	1	-18	30	13	6	7
	Et_4NClO_4	-2	18	30	46	40	6
	Et_4NI	-2	22	30	50	49	1
	Et_4NCl	-1	40	30	69	81	-12

Junction: 25 mM $MX(S_1)$/25mM $MX(S_2)$. $E_j(2)$: based on the Ph_4AsBPh_4 assumption.

In the above, we discussed the methods for estimating each of the three components of the LJP. If we sum the values of the three components, we get the total LJP. Previously we proposed the procedure as a new method for estimating the LJP between different solvents (ref. 18-k). Recently, we compared the values of LJP estimated by the new method with those obtained by several conventional methods based on extra-thermodynamic assumptions. In the conventional methods, the potentials of such reference redox systems as ferrocene(+1/0), bis(biphenyl)chromium(+1/0), cobaltcene(+1/0, 0/-1 and +1/-1) were assumed to be solvent-independent. The potentials of the Ag^+/Ag electrode obtained by the reference electrolyte (Ph_4AsBPh_4) assumption were also employed. Some examples of the results are shown in Fig. 6 and Table 2 (refs. 14,18-k). The results by the new method best agreed with the results based on the Ph_4AsBPh_4 assumption (within ±20 mV). For the methods based on reference redox systems, the results for the junctions with H_2O or MeOH on one side were either unavailable due to the solubility problem or in big deviation from the resu8lts by the new method. Among the extra-thermodynamic assumptions now available, the reference electrolyte (Ph_4AsBPh_4) assumption is usually considered most reliable. Thus, we can conclude that the new method is applicable to estimate the LJP between different solvents. *The advantage of our method is that we can predict how the LJPs are influenced by the solvents and the electrolytes at the junction.*

As in Table 2, the value of the LJP between different solvents sometimes exceeds 200 mV. It is interesting that, even in such cases, the LJP shows good reproducibility and stability (ref. 18-f).

Appropriateness of the Assumption of Negligible Liquid Junction Potential

In the study of ion solvation, Parker et al. employed the assumption of negligible LJP, considering that the LJP across Cell III was within ±20 mV (ref. 20).

$Ag|10mM\ AgNO_3(AN) \Vert 100mM\ Et_4NPic(AN) \Vert 10mM\ AgNO_3(S)|Ag$ (III)

The assumption was made because Et_4N^+ and Pic^- have mobilities near each other and their $\Delta G_t^{\circ}(i, AN{\rightarrow}S)$ values are small and because AN interacts only weakly with other aprotic solvents. If we apply the new method of estimation, we get for the junction at AN/S in (III), the value within ±10 mV if S is aprotic, but ~-30 mV if S=MeOH, and ~-50 mV if S= H_2O. Thus, the assumption is appropriate if S is aprotic, but not appropriate enough if S is MeOH or H_2O. When the assumption is not applicable, it is recommended to estimate the LJP by the new method and to correct for it.

CONCLUSIONS

1) The use of ISEs and ISFETs as sensors for ion solvation can increase the variety of target ionic species.
2) The knowledge concerning the LJP between different solvents and the new method to estimate it will help to increase the reliability of the electrochemical study of ion solvation.
3) It is desirable to use, if possible, the electrochemical method and the solubility method jointly.

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