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Liquid Junction Potential between Electrolyte Solutions in Different Solvents Studied by Use of Mixed Solvent/Pure Solvent Junctions

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Of the three components of the liquid junction potential between electrolyte solutions in different solvents, the component due to the interaction between different solvents (component (c)) was studied using mixed solvent/pure solvent junctions. According to our model of component (c), the component at a mixed solvent/pure solvent junction should vary linearly with the volume fraction of the mixed solvent. We previously confirmed this experimentally. However, there are exceptional cases in which nonlinear (curved) relationships are observed. In the present work, I found that most of the curved relationships are obtained for mixtures between an amphiprotic solvent (water, formamide, or *N*-methylformamide) and an aprotic solvent of very low acceptor number (*N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, acetone, or hexamethylphosphoric triamide). In contrast, for an aprotic solvent of moderate acceptor number (nitromethane, dimethyl sulfoxide, acetonitrile, or propylene carbonate), linear or near-linear relationships are observed. The observed curved relationships were concluded to be due to that the structure-forming amphiprotic solvent is more likely to and the aprotic solvent less likely to settle at the interphasial region than in the bulk, because the dipolar molecules of the aprotic solvent of very low acceptor number have a vague positive charge-center.

The liquid junction potential (ljp) between electrolyte solutions in different solvents contains three components, i.e., component (a) due to the differences in electrolyte concentrations on the two sides of the junction and in cationic and anionic mobilities, component (b) due to the differences in ion solvation on the two sides of the junction, and component (c) due to the interactions between different solvents at the junction. Components (b) and (c) are specific to the ljp between different solvents. We ran detailed experimental studies on the ljp between different solvents, using emf-cells constructed with dual four-way stopcocks giving free diffusion junctions, and found that, at junctions with the same electrolyte on both sides, the ljp was reproducible within ±1 mV and very stable (drift within $1\,\mathrm{mV\,h^{-1}}$), even when the values of the ljp were over 200 mV and even though the mixing of the two solutions occurred continuously at the junction.[1] Moreover, we showed that, by using appropriate cell construction, the variation of each of the three components could be measured separately from the others;[2] thus we could study the characteristics of the three components.

Here, I summarize the reasons why the ljp was divided in the three components. In obtaining the theoretical equations for the part of the ljp which depend on ionic transfer (components (a) and (b)), like other investigators,[3] we considered that eq 1 holds at the junction c_L MX($\mathrm{S_L}$)¦c_R MX($\mathrm{S_R}$) (MX is the electrolyte, c its concentration, S the solvent, and subscripts L and R show the left and right sides of the junction).

$$E_\mathrm{j}(\mathrm{a+b}) = \left(-\frac{1}{F}\right)\int_\mathrm{SL}^\mathrm{SR}\sum\left(\frac{t_\mathrm{i}}{z_\mathrm{i}}\right)\mathrm{d}\mu_\mathrm{i}, \qquad \mu_\mathrm{i} = \mu^0{}_\mathrm{i} + RT\ln a_\mathrm{i} \tag{1}$$

$E_\mathrm{j}(\mathrm{a+b})$ shows the part of the ljp which depends on ionic transfer, z_i and t_i show the charge and the transport number of ionic species i, and μ_i and $\mu^0{}_\mathrm{i}$ show the chemical potential and the standard chemical potential of i. This equation looks the same as that for the ljp between the same solvent on the two sides, but, in this case, $\mu^0{}_\mathrm{i}$ changes from the value in $\mathrm{S_L}$ to that in $\mathrm{S_R}$. Equation 1 can conveniently be divided in the following two equations that correspond to components (a) and (b), respectively.

$$E_\mathrm{j}(\mathrm{a}) = \left(-\frac{RT}{F}\right)\int_\mathrm{SL}^\mathrm{SR}\sum\left(\frac{t_\mathrm{i}}{z_\mathrm{i}}\right)\mathrm{d}\log a_\mathrm{i}, \qquad E_\mathrm{j}(\mathrm{b}) = \left(-\frac{1}{F}\right)\int_\mathrm{SL}^\mathrm{SR}\sum\left(\frac{t_\mathrm{i}}{z_\mathrm{i}}\right)\mathrm{d}\mu^0{}_\mathrm{i} \tag{2}$$

By integrating these equations under the conditions that t_i, a_i, and $\mu^0{}_\mathrm{i}$ change linearly at the junction from the values in $\mathrm{S_L}$ to those in $\mathrm{S_R}$, we get eqs 3 and 4.

$$E_\mathrm{j}(\mathrm{a}) = \left(-\frac{RT}{F}\right)\left[(t_\mathrm{ML} - t_\mathrm{XL})\ln\frac{a_\mathrm{MXR}}{a_\mathrm{MXL}} + (t_\mathrm{MR} - t_\mathrm{ML} - t_\mathrm{XR} + t_\mathrm{XL})\left(1 - \frac{a_\mathrm{MXL}}{a_\mathrm{MXL} - a_\mathrm{MXR}}\ln\frac{a_\mathrm{MXR}}{a_\mathrm{MXL}}\right)\right] \tag{3}$$

$$E_\mathrm{j}(\mathrm{b}) = \left(-\frac{1}{2F}\right)[(t_\mathrm{ML} + t_\mathrm{MR})\Delta\mu^\circ(\mathrm{M}) - (t_\mathrm{XL} + t_\mathrm{XR})\Delta\mu^\circ(\mathrm{X})] \tag{4}$$

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Here, $\Delta\mu^0$ is the change in chemical potential between $\mathrm{S_L}$ and $\mathrm{S_R}$ and is equal to the Gibbs free energies of ionic transfer ($\Delta G_\mathrm{t}{}^0$) between $\mathrm{S_L}$ and $\mathrm{S_R}$. In calculating E_j(a) and E_j(b), we used the values of the limiting molar conductivities in Ref. 4 (in order to get the values of t) and the values of $\Delta G_\mathrm{t}{}^0$ in Ref. 5 which were obtained under extra-thermodynamic assumptions.

In the experimental studies of components (a) and (b), we used Cell 1 containing a single junction between different solvents (J), where $\mathrm{M} = \mathrm{mol\,dm^{-3}}$.

$$\begin{aligned}&\mathrm{Ag}|5\,\mathrm{mM\ AgClO_4},25\,\mathrm{mM\ [Et_4N]ClO_4(S_L)}\text{¦¦}\\&25\,\mathrm{mM\ [Et_4N]ClO_4(S_L)}\underset{\mathrm{j_1}}{\text{¦}}\,c_\mathrm{L}\ \mathrm{MX(S_L)}\underset{\mathrm{J}}{\text{¦}}\,c_\mathrm{R}\ \mathrm{MX(S_R)}\underset{\mathrm{j_2}}{\text{¦}}\\&25\,\mathrm{mM\ [Et_4N]ClO_4(S_R)}\text{¦¦}5\,\mathrm{mM\ AgClO_4},\\&25\,\mathrm{mM\ [Et_4N]ClO_4(S_R)}|\mathrm{Ag}\qquad\qquad\text{Cell 1}\quad(5)\end{aligned}$$

For component (a),[6–8] the emf-variation was measured by varying the ratio $c_\mathrm{L}/c_\mathrm{R}$ in five steps (100/1, 10/1, 1/1, 1/10, and 1/100) for each MX. In this case, the ljps at $\mathrm{j_1}$ and $\mathrm{j_2}$ also changed, but because these junctions were between the same solvent, the values of the ljps could be calculated using the Henderson equation and the emfs were corrected for them. Thus, the variation in corrected emfs corresponds to the variation in the ljp at J, and since components (b) and (c) should be constant, it corresponds to the actual variation in component (a) at J. The relationships between the experimental variations in component (a) with electrolyte concentrations and the theoretical values obtained by eq 3 were always linear with unit slopes, showing that this equation is valid and can be used in estimating component (a). Usually, component (a) was on the order of 30 mV or less.

For component (b),[8–11] the electrolyte MX was varied in various ways keeping $c_\mathrm{L} = c_\mathrm{R}$ and corrections were made for the ljps at $\mathrm{j_1}$ and $\mathrm{j_2}$. Thus, the corrected emf-variation of the cell corresponded to the actual variation in component (b) at J. Component (b) was independent of electrolyte concentrations. The relationships between the experimental variations of component (b) with electrolyte species and the theoretical values obtained by eq 4 were always linear or near-linear, but unit slopes could be obtained only at immiscible junctions (like nitrobenzene (NB)¦water (W)); at miscible junctions, the slopes were much smaller than unity (for example, 0.43 to 0.50 at W¦S, 0.28 to 0.33 at formamide (FA)¦S, 0.29 to 0.36 at ethylene glycol (EG)¦S, 0.17 to 0.26 at methanol (MeOH)¦S (S: miscible organic solvent), and near zero between two aprotic solvents). The reason for the slopes of less than unity at miscible junctions has been discussed in Ref. 11; the gradual change of μ^0 through the junction (0.05–1 mm in thickness, in contrast to $\approx$1 nm at immiscible junctions) and the specific nature of ionic transfer due to the gradient in μ^0 may be responsible for them. Though eq 4 holds only qualitatively, the approximate value of component (b) can be estimated by multiplying the slope by the value obtained by eq 4. Here, both the magnitude of component (b) and its variation with electrolyte species may become considerably large (over 200 and 300 mV, respectively, at W¦S junctions). See Ref. 12 for E_j(a) and E_j(b) at the junction with different electrolytes and different solvents on the two sides.

For the study of component (c),[11,13–17] we used Cell 2 containing two junctions between different solvents ($\mathrm{J_1}$ and $\mathrm{J_2}$).

$$\begin{aligned}&\mathrm{Ag}|5\,\mathrm{mM\ AgClO_4},5\,\mathrm{mM\ [Et_4N]ClO_4(S_1)}\text{¦}\\&10\,\mathrm{mM\ [Et_4N]ClO_4(S_1)}\text{¦}c\ \mathrm{MX(S_1)}\underset{\mathrm{J_1}}{\text{¦}}\,c_3\ \mathrm{MX(S_3)}\underset{\mathrm{J_2}}{|}\\&c\mathrm{MX(S_2)}|10\,\mathrm{mM\ [Et_4N]ClO_4(S_2)}\text{¦}5\,\mathrm{mM\ AgClO_4},\\&5\,\mathrm{mM\ [Et_4N]ClO_4(S_2)}|\mathrm{Ag}\qquad\qquad\text{Cell 2}\quad(6)\end{aligned}$$

Here, typically $\mathrm{MX} = \mathrm{[Et_4N]ClO_4}$, $c = c_3 = 10\,\mathrm{mM}$, and $\mathrm{S_1}$ = acetonitrile (AN). $\mathrm{S_2}$ was either W, MeOH, ethanol (EtOH), acetone (Ac), *N*,*N*-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO) and the solvent in middle compartment ($\mathrm{S_3}$) was varied in various ways. Here, for component (a), the sum at the two junctions ($\mathrm{J_1}$ and $\mathrm{J_2}$) is actually equal to the value at c $\mathrm{MX(S_1)}$¦c $\mathrm{MX(S_2)}$, irrespective of $\mathrm{S_3}$, and equals zero because the electrolyte concentrations on the two sides are the same. The actual situation for component (b) is more complicated but, with $\mathrm{MX} = \mathrm{[Et_4N]ClO_4}$, the sum at the two junctions is, irrespective of $\mathrm{S_3}$, nearly equal (within 4 mV) to the value at c $\mathrm{MX(S_1)}$¦c $\mathrm{MX(S_2)}$. Thus, as far as components (a) and (b) are concerned, the emf-variation due to the variation in $\mathrm{S_3}$ should be very small. Nevertheless, the emf of the cell actually varied considerably with the variation in $\mathrm{S_3}$, sometimes by about 100 mV, which is very large. The variation was closely related to the strength of the interaction between different solvents at the junction. Moreover, the variation was independent of electrolyte species and concentrations; this was confirmed in detail by using MX other than $\mathrm{[Et_4N]ClO_4}$, from $\mathrm{[Bu_4N][BPh_4]}$, the ions of which are almost unsolvated, to $\mathrm{LiClO_4}$ and $\mathrm{Mg(ClO_4)_2}$, the ions of which are fairly strongly solvated, and by using c and c_3 other than the typical values. Alfenaar et al.[3a] and Cox et al.[3b] detected a third component of the ljp, in addition to the two components, (a) and (b), and attributed it, as proposed by Staverman,[3c] to the solvent molecules carried through the junction with ionic transfer. But their experimental studies were insufficient. Gaboriaud,[3d] denying this idea, claimed that the third component does not exist. According to our detailed experimental studies, a third component really exists but, from the electrolyte-independent nature of the emf-variations, it cannot be due to the solvent molecules which are associated with the ionic transfer. A component arising solely from the interaction between different solvents must be considered. The magnitude and sign of this component are well understood if we assume, as in Figure 1, that the solvent molecules on the two sides interact with each other as a Lewis acid and a Lewis base and some of the molecules are oriented at the interphase to cause a potential difference.[13] This model is only for understanding the behavior of component (c). However, at the junction where interactions between different solvents occur, it seems reasonable to consider that orientations of solvent molecules give a potential difference, just like the surface or dipole potential at the boundary, and contributes to the ljp as the third component. It should be stressed that the detection of component (c) was possible because the sum of its values at $\mathrm{S_1}$¦$\mathrm{S_3}$ and $\mathrm{S_3}$¦$\mathrm{S_2}$ was different from its value at $\mathrm{S_1}$¦$\mathrm{S_2}$. If we assume that component (c) equals zero at W¦NB, where solvent–solvent interaction is very weak, component (c) between solvents that interact strongly, like W¦DMF or W¦DMSO, is estimated to be over 100 mV (with the W side more negative). At junctions between AN and other aprotic solvents, however, component (c) is always within ±10 mV because their interactions are weak.

Here, it is noted that, for many junctions between different solvents, the sum of the three components ((a), (b), and (c)) estimated directly by the respective proposed methods agreed well (within 6 or 7 mV) to the values estimated indirectly under the extra-thermodynamic assumption of tetraphenylarsonium tetraphenylborate ($[Ph_4As][BPh_4]$) as reference electrolyte.[18]

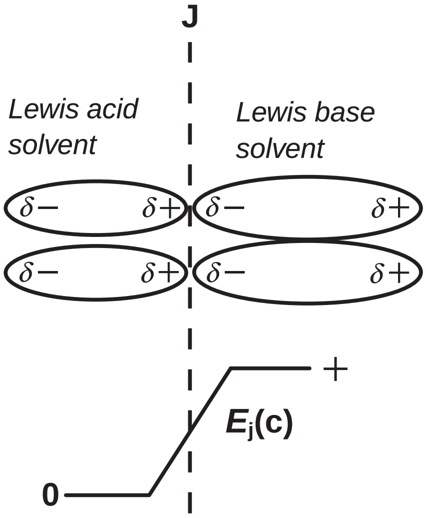

Figure 1. Schematic representation of the origin of component (c).

As a part of the study of component (c), we ran, more than 20 years ago, an experiment using a salt bridge containing a mixed solvent[15] (for cells with mixed solvent/mixed solvent salt bridges, see Ref. 16). The cell construction was as follows:

$$\begin{aligned}&Ag|5\,mM\ AgClO_4, 5\,mM\ [Et_4N]ClO_4(S_1)¦\\&1\,mM\ [Et_4N]ClO_4(S_1)¦100\,mM\ MX(S_3+S_3')¦\\&1\,mM\ [Et_4N]ClO_4(S_2)¦5\,mM\ AgClO_4,\\&5\,mM\ [Et_4N]ClO_4(S_2)|Ag \qquad \text{Cell 3} \qquad (7)\end{aligned}$$

where $S_1 = AN$, $MX = [Et_4N]ClO_4$ or $[Et_4N]BF_4$. For different combinations of solvents S_2 and $(S_3 + S_3')$, we measured the emf by changing the composition of $(S_3 + S_3')$ gradually from S_3 to S_3'. For the case with $S_1 = AN$ and $S_2 = DMSO$, examples of the emf-variation with the composition of the solvent mixtures, $(S_3 + S_3')$, are shown in Figure 2, plotted against their volume fraction as well as their mole fraction. Here, AN was used as S_1 to keep component (c) between AN and other aprotic solvents small, while $[Et_4N]ClO_4$ or $[Et_4N]BF_4$ was used as MX to keep the variation of components (a) and (b) with the composition of $(S_3 + S_3')$ very small. The volume fraction was calculated from the volumes of the pure solvents before mixing. With the exception of the three cases in the lower right (d, e, and f), the relationships are linear or near-linear with respect to the volume fraction rather than the mole fraction. Experiments were carried out for more than 110 different combinations of S_2 and $(S_3 + S_3')$, and, as summarized in Table 1, the emfs in many cases varied linearly or near-linearly with the volume fraction of the mixed solvent.

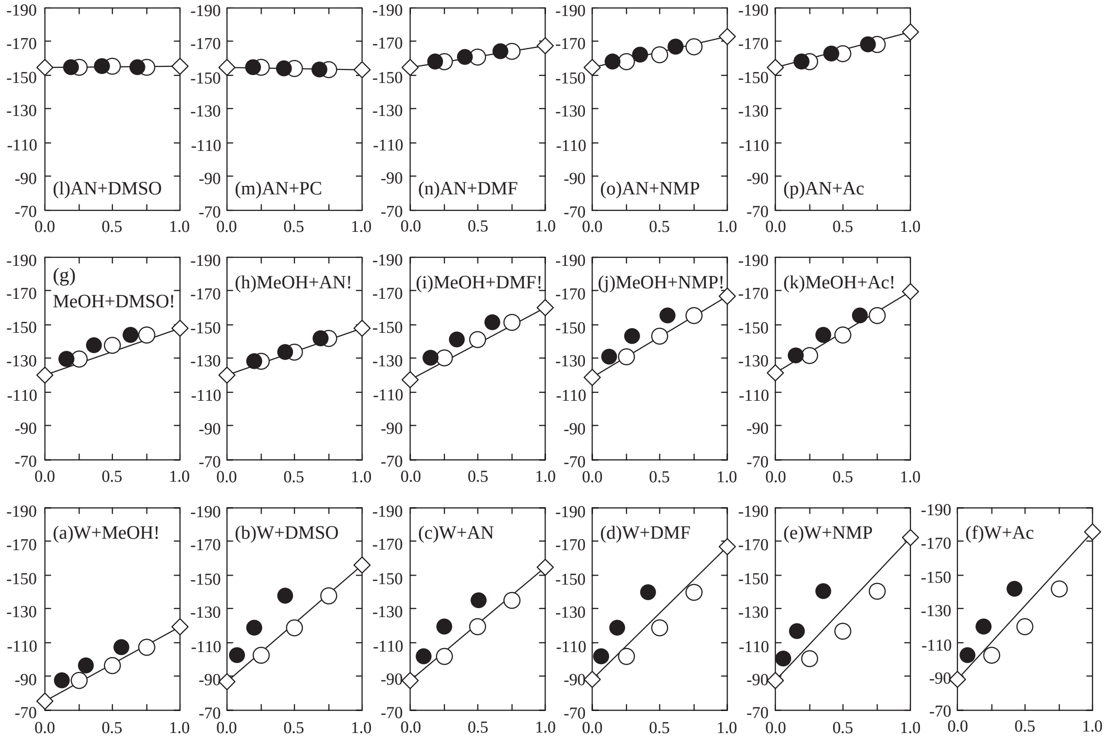

Figure 2. Variations of the emfs of Cell 3 (ordinate) with bridge solvent compositions (abscissa) for the case $S_2 = DMSO$. The emfs (in mV) are plotted against volume fraction (○) and mole fraction (●) of S_3'. $(S_3 + S_3')$ is shown on each figure, where the "!" shows that the electrolyte MX was $[Et_4N]BF_4$. Otherwise, $MX = [Et_4N]ClO_4$.

Table 1. Classification of the Emf-Variations of Cell 3 with Solvent Composition of ($S_3 + S_3'$) According to the Linearity with Volume Fraction and Mole Fraction a),b),c),d)

$S_3 + S_3'$	S_1 = AN, S_2 =					
	W	MeOH	EtOH	DMSO	DMF	Ac
AN + DMSO	L(C)	L(NL)	L(NL)	L(L)	L(NL)	L(NL)
AN + PC	L(L)	L(L)	L(L)	L(L)	L(L)	L(L)
AN + DMF	L(C)	L(NL)	L(L)	L(L)	L(L)	L(L)
AN + NMP	L(C)	L(NL)	L(NL)	NL(L)	L(L)	L(NL)
AN + Ac	NL(L)	L(L)	L(L)	NL(L)	L(L)	L(L)
PC + DMSO	C(C) e),f)	L(L)	L(L)	L(L)	L(L)	L(L)
PC + DMF	NL(C)	L(L)	L(L)	L(L)	L(L)	L(L)
PC + Ac	C(C) e),f)	L(L)	L(L)	NL(C)	NL(C)	L(L)
Ac + DMSO	L(L)	L(L)	L(L)	NL(NL)	NK(NL)	L(L)
Ac + DMF	C(C) e),f)	L(L)	L(L)	L(L)	L(L)	L(L)
DMSO + DMF	L(L)	L(L)	L(L)	L(L)	L(L)	L(L)
W + AN	L(L)	L(C)	NL(C)	NL(C)	NL(C)	NL(C)
W + DMSO	L(C)	NL(C)	NL(C)	L(C)	NL(C)	L(C)
W + DMF	C(C) f)	L(C)	NL(C)	C(C) f)	C(C) f)	C(C) f)
W + NMP	C(C) f)	L(C)	NL(C)	C(C) f)	C(C) f)	C(C) g)
W + Ac	C(NL)	L(C)	C(C) f)	C(C) f)	C(C) g)	C(C) g)
MeOH + W h)	L(NL)	L(NL)	—	L(C)	—	—
MeOH + DMSO h)	L(C)	NL(C)	—	NL(C)	—	—
MeOH + AN h)	C(C) e),f)	L(L)	—	L(NL)	—	—
MeOH + DMF h)	NL(C)	L(C)	—	NL(C)	—	—
MeOH + NMP h)	C(C) f)	L(C)	—	L(C)	—	—
MeOH + Ac h)	NL(L)	L(L)	—	NL(C)	—	—

a) Classification of the results: L, NL, and C show linear, near-linear, and curved relationships, respectively; the relationships without parentheses show "against volume fraction" and those in parentheses "against mole fraction." b) The two plots are curved in opposite directions. c) MX = $[Et_4N]ClO_4$. d) The abbreviations of solvents: Ac, acetone; AN, acetonitrile; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; HMPA, hexamethylphosphoric triamide; MeOH, methanol; NMP, *N*-methyl-2-pyrrolidone; PC, propylene carbonate; and W, water. e) Both plots are curved in the same direction. f) The deviation from the straight line is smaller for the volume fraction than for the mole fraction. g) The opposite relationship of f). h) The electrolyte MX = $[Et_4N]BF_4$.

Although Cell 3 has two junctions between different solvents, these results seem to show that component (c) at a mixed solvent/pure solvent junction varies linearly or near-linearly with the volume fraction of the mixed solvent. These results support the model of Figure 1. At a junction with a mixed solvent on one side (c_L MX($S_L + S_L'$)¦c_R MX(S_R)), the fractions of areas occupied by S_L and S_L', respectively, on the ($S_L + S_L'$) side of the interphase will be equal to the volume fractions of S_L and S_L' in the bulk of mixed solvent, i.e., ϕ_{SL} and $\phi_{SL'}$. Here, component (c) is like a dipole potential and is proportional to the number of dipoles per unit area. If we express component (c) at pure S_L¦S_R and pure S_L'¦S_R junctions in terms of $E_j(c)_{SL}$ and $E_j(c)_{SL'}$, respectively, component (c) at the ($S_L + S_L'$)¦S_R junction will be $E_j(c)_{SL+SL'} = \phi_{SL}E_j(c)_{SL} + \phi_{SL'}E_j(c)_{SL'} = \phi_{SL}(E_j(c)_{SL} - E_j(c)_{SL'}) + E_j(c)_{SL'} = \phi_{SL'}(E_j(c)_{SL'} - E_j(c)_{SL}) + E_j(c)_{SL}$. Thus, by gradually varying from S_L to S_L', the magnitude of component (c) will vary between $E_j(c)_{SL}$ and $E_j(c)_{SL'}$ linearly with volume fraction.

The majority of the results in Table 1 are linear or near-linear with volume fraction and support our model of component (c). However, there are cases where nonlinear (curved) relationships against volume fraction are obtained. In Table 1, the main group of nonlinearity against volume fraction is for ($S_3 + S_3'$)-mixtures between W and DMF, *N*-methyl-2-pyrrolidone (NMP) and Ac and S_2 of DMSO, DMF, Ac, and W. Because of the importance of component (c), it seemed necessary to study the cases of nonlinearity. Thus, in the present study, we ran more experimental work by using formamide (FA) and *N*-methylformamide (NMF) instead of W in ($S_3 + S_3'$). By combining the results of the present work with those of the previous work, we found that most of the curved relations are observed for the mixtures of an amphiprotic solvent (W, FA, or NMF) with an aprotic solvent of very low acceptor number (DMF, *N*,*N*-dimethylacetamide (DMA), NMP, Ac, or hexamethylphosphoric triamide (HMPA)), though on the contrary, linear or near-linear relations are obtained with an aprotic solvent of a little higher acceptor number (nitromethane (NM), AN, DMSO, or propylene carbonate (PC)).

Experimental

The cell used for emf measurements was prepared with dual four-way stopcocks for high performance liquid chromatography[13] and was designed as follows:

Ag|5 mM $AgClO_4$, 5 mM $[Et_4N]ClO_4$(AN)¦
20 mM $[Et_4N]ClO_4$(AN)¦*c* $[Et_4N]ClO_4$(AN)¦
c $[Et_4N]ClO_4$($S_3 + S_3'$)¦*c* $[Et_4N]ClO_4$(DMSO)¦
20 mM $[Et_4N]ClO_4$(DMSO)¦5 mM $AgClO_4$,
5 mM $[Et_4N]ClO_4$(DMSO)|Ag Cell 4 (8)

Table 2. Emfs of Cell 4 with the Variation of (S_3 + S_3') as a Function of Volume Fraction of S_3'

S_3[a)]	S_3'[a)]	Composition of S_3' in volume fraction[b)]				
		0	0.25	0.50	0.75	1
FA	NM	(0)75/89.5	(0.20)86.5/96	(0.43)98.5/104	(0.69)111/113.5	(1)125/124
	DMSO	(0)75/89.5	(0.16)86.5/97.5	(0.36)100.5/107.5	(0.63)115.5/119	(1)**130**/**130**
	AN	(0)75.5/89.5	(0.20)86.5/97.5	(0.43)100.5/106.5	(0.69)113.5/116.5	(1)129.5/129.5
	PC	(0)75.5/89.5	(0.13)88/97.5	(0.32)100.5/106	(0.58)113.5/116	(1)127.5/128.5
	DMF	(0)75.5/90	(0.15)88/98.5	(0.34)103/108	(0.61)122/123.5	(1)143/141
	DMA	(0)75.5/90	(0.13)87/97	(0.30)103.5/107	(0.56)122.5/123	(1)147.5/143
	NMP	(0)75.5/90	(0.12)87.5/97.5	(0.29)101.5/108	(0.55)120.5/123.5	(1)149/144
	Ac	(0)75.5/90	(0.15)86.5/98	(0.35)108/109	(0.62)120.5/124	(1)150.5/147
	HMPA	(0)75.5/90	(0.07)81.5/96.5	(0.19)96.5/106.5	(0.41)125.5/127	(1)169.5/162
NMF	NM	(0)94.5/102.5	(0.27)99.5/106.5	(0.52)106/111	(0.76)114/116.5	(1)124/121
	DMSO	(0)93/101	(0.22)101.5/108.5	(0.45)111/116	(0.71)121.5/123.5	(1)**130**/**130**
	AN	(0)94.5/103	(0.27)102.5/107	(0.53)109/112.5	(0.77)119.5/119.5	(1)130/129.5
	PC	(0)94.5/101.5	(0.19)101/107	(0.41)109/113.5	(0.67)117/120.5	(1)125.5/128.5
	DMF	(0)94.5/102	(0.20)104/110	(0.43)115/119	(0.69)128/129	(1)142.5/141
	DMA	(0)94/102	(0.17)103.5/110	(0.39)115/119	(0.66)129.5/131.5	(1)146.5/145
	NMP	(0)95/102.5	(0.17)103.5/109.5	(0.38)115.5/118.5	(0.65)130.5/130.5	(1)149/145.5
	Ac	(0)94/102.5	(0.21)102.5/110	(0.44)113.5/117.5	(0.70)127.5/128.5	(1)150.5/147.5
	HMPA	(0)94.5/102.5	(0.10)99.5/107	(0.25)111.5/128	(0.50)139/138	(1)171.5/159.5

a) The abbreviations of solvents: DMA, *N*,*N*-dimethylacetamide; FA, formamide; NM, nitromethane; and NMF, *N*-methylformamide. For others, see Table 1. b) The values in parentheses show the corresponding mole fraction and the emfs are shown in the order 20 mM/100 mM.

where c was 20 or 100 mM and S_3 was FA or NMF. The cell had free-diffusion junctions of 1 mmϕ paths and the results were reproducible within ± 1 mV and stable to within 1 mV h^{-1}. Here, in order to eliminate the influence of the potential changes of the Ag^+/Ag electrodes, the emf values in every series of measurements made reference to the emf of the cell with (S_3 + S_3') = DMSO, which was taken to be 130 mV for both $c = 20$ and 100 mM. Though Table 2 and Figure 3 were obtained with Cell 4, Table 1 and Figures 2, 4, and 5 were obtained with Cell 3, the junction of which was 1 mM [Et_4N]ClO_4(S_1 = AN)¦100 mM MX(S_3 + S_3')¦1 mM [Et_4N]ClO_4(S_2); the difference in electrolyte concentrations did not have a significant influence, except in that the magnitude of the emf variation with the variation of (S_3 + S_3') was somewhat different. FA and NMF were analytical grade Nacalai Tesque products. They were dried with molecular sieves and then used for distillation under a reduced nitrogen atmosphere. Other chemicals were the same as those used previously.[13] Measurements were carried out between 20 and 25 °C.

Results and Discussion

The experimental results obtained in the present study, where S_2 = DMSO, S_3 = FA or NMF, S_3' = aprotic solvents, c MX = 20 or 100 mM [Et_4N]ClO_4 in Cell 4, are shown in Table 2. In Figure 3, the relationships are only illustrated for 20 mM MX, because those for 100 mM MX are approximately the same, except that some influence of electrolyte concentration on the magnitude of emf-variations can be observed. For the mixtures of FA and NMF with NM, AN, DMSO, and PC, the relationships are linear or near-linear with volume fraction. However, for the mixtures of FA and NMF with DMF, DMA, NMP, Ac, and HMPA, the relationships deviate from linearity with the volume fraction and, for some, are nearer to linearity with the mole fraction. This situation is similar to that for the salt bridges of S_2 = DMSO, S_3 = W, and S_3' = aprotic solvents; as in Figures 2a–2f; the relationships are linear or near-linear against volume fraction for S_3' of methanol (MeOH), DMSO, and AN, but deviate from linearity for S_3' of DMF, NMP, and Ac.

As described above, from our model of component (c),[13] we expect that the emf-variation with the composition of mixed solvent is linear with volume fraction. This is satisfied for the mixtures of S_3 of W, FA, and NMF and S_3' of solvents like (MeOH,) NM, AN, DMSO, and PC (Figures 2a–2c, 3f–3i, and 3o–3r). However, curved relationships with volume fraction are obtained for mixtures of S_3 of W, FA, and NMF and S_3' of aprotic solvents like DMF, DMA, NMP, Ac, and HMPA (Figures 2d–2f, 3a–3e, and 3j–3n). It should be noted that DMF, DMA, NMP, Ac, and HMPA are solvents with very weak acidity (i.e., are very weak electron acceptors), with acceptor numbers of 16.0, 13.6, 13.3, 12.5, and 10.6, respectively, in contrast to 20.5 for NM, 19.3 for DMSO, 18.9 for AN, and 18.3 for PC. The deviation from linearity with volume fraction increases with the decrease in the acidity of S_3'. Sorting based on solvent acidity is the only way to sort DMF, DMA, NMP, Ac, and HMPA in one group and NM, AN, DMSO, and PC in the other.

In Figures 2a–2f, and in Figure 3, the variation in composition of (S_3 + S_3') from S_3 to S_3' causes emf-variation, which is due to the variations in component (c) for the junctions S_1(AN)¦$\mathbf{S_3}$(W, FA, or NMF), S_1(AN)¦$\mathbf{S_3'}$(aprotic solvents), $\mathbf{S_3}$(W, FA, or NMF)¦S_2(DMSO) and $\mathbf{S_3'}$(aprotic solvent)¦S_2(DMSO), where bold $\mathbf{S_3}$ and $\mathbf{S_3'}$ show that the volume fractions of S_3 and S_3' vary from 1 to 0 and from 0 to 1, respectively, with $(\phi_{S3} + \phi_{S3'}) = 1$. Judging from the strength of the solvent–solvent interaction, the emf-variation occurs mainly by variation in component (c) for $\mathbf{S_3}$(W, FA, or

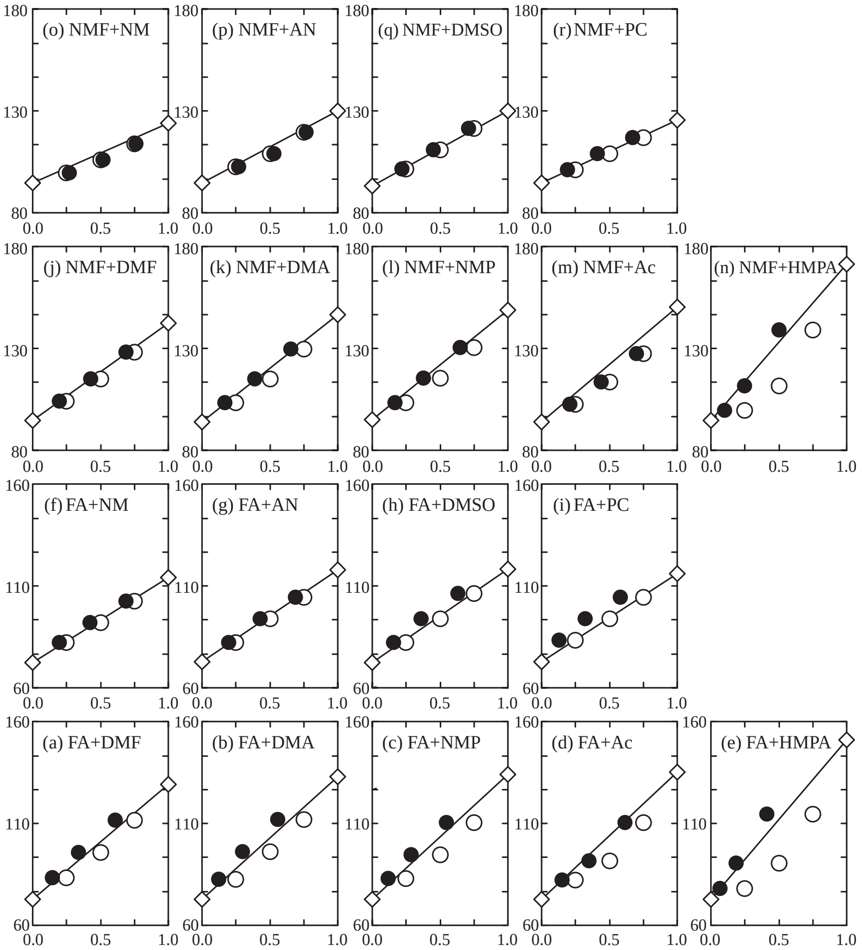

Figure 3. Variations of the emfs of Cell 4 ($c = 20$ mM) with bridge solvents, ($S_3 + S_3'$). The emfs (in mV) are plotted against volume fraction (○) and mole fraction (●) of S_3'. ($S_3 + S_3'$) is shown on each figure.

NMF)¦S_2(DMSO), next by that for S_1(AN)¦$\mathbf{S_3}$(W, FA, or NMF) which occurs in the opposite direction; the variations in component (c) for $\mathbf{S_3'}$(aprotic solvent)¦S_2(DMSO) and S_1(AN)¦$\mathbf{S_3'}$(aprotic solvents) are relatively small.

This kind of relationship can also be observed for cells with S_2 = W, Ac, or DMF, S_3 = W, and S_3' = aprotic solvents, as shown in Figures 4a–4o. In Figure 4a to 4e, S_2 is W and the emf-variation by the addition of S_3' to S_3 occurs by variations of component (c) mainly at $\mathbf{S_3'}$(aprotic solvent)¦S_2(W) and then at S_1(AN)¦$\mathbf{S_3}$(W) (oppositely directed); those at S_1(AN)¦$\mathbf{S_3'}$(aprotic solvent) and $\mathbf{S_3}$(W)¦S_2(W) are small or equal to zero. In Figure 4f to 4j, S_2 = Ac and the emf-variation occurs by variations of component (c), mainly at $\mathbf{S_3}$(W)¦S_2(Ac) and then at S_1(AN)¦$\mathbf{S_3}$(W) (oppositely directed); those at S_1(AN)¦$\mathbf{S_3'}$(aprotic solvent) and $\mathbf{S_3'}$(aprotic solvent)¦S_2(Ac) are small. In Figure 4k to 4o, S_2 = DMF and the emf-variation occurs mainly at $\mathbf{S_3}$(W)¦S_2(DMF) and partly at S_1(AN)¦$\mathbf{S_3}$(W) (oppositely directed); the variations for S_1(AN)¦$\mathbf{S_3'}$(aprotic solvent) and $\mathbf{S_3'}$(aprotic solvent)¦S_2(DMF) are small. In all these cases, the relationships are linear with volume fraction for S_3' of DMSO and AN but curved for S_3' of DMF, NMP, and Ac; the electron-accepting properties of solvents are important here too. It is noted, however, that in Figure 4p to 4t, where S_2 = MeOH and S_3 = W, the emf-variations look linear with volume fraction for all S_3'. It seems that the variations at $\mathbf{S_3}$(W)¦S_2(MeOH) and $\mathbf{S_3'}$(aprotic solvent)¦S_2(MeOH) occur in opposite directions and approximately cancel each other out. Similar near-linear relations are observed for S_2 = EtOH, probably for the same reasons.

The curved relationships against volume fraction seem to come from the phenomena on the side of mixed solvent, ($S_3 + S_3'$), because similar behaviors are observed for S_2 = W, Ac, DMF, and DMSO, which are quite different. All of the curved relationships hitherto mentioned were for mixtures of S_3 of amphiprotic solvents (W, FA, or NMF) and S_3' of aprotic solvents of weak acidity (DMF, DMA, NMP, Ac, or HMPA). The deviations from linearity occurred in the direction such that the fraction of the area occupied by the aprotic solvent at the interphasial region was less than the volume fraction in the bulk or that the fraction of the area occupied by the amphiprotic solvent at the interphasial region was larger than the volume fraction in the bulk. Dipolar molecules of very weakly acidic aprotic solvents have a very vague positive charge-center. On the other hand, the amphiprotic solvents have three- or two-dimensional structures: W molecules, having high hydrogen-bonding ability, are combined with one another to form three-dimensional networks; FA molecules, having chain and ring-dimer structures, are combined by hydrogen bond to form three-dimensional networks; in NMF, linear but short-chain structures predominate. We conclude that

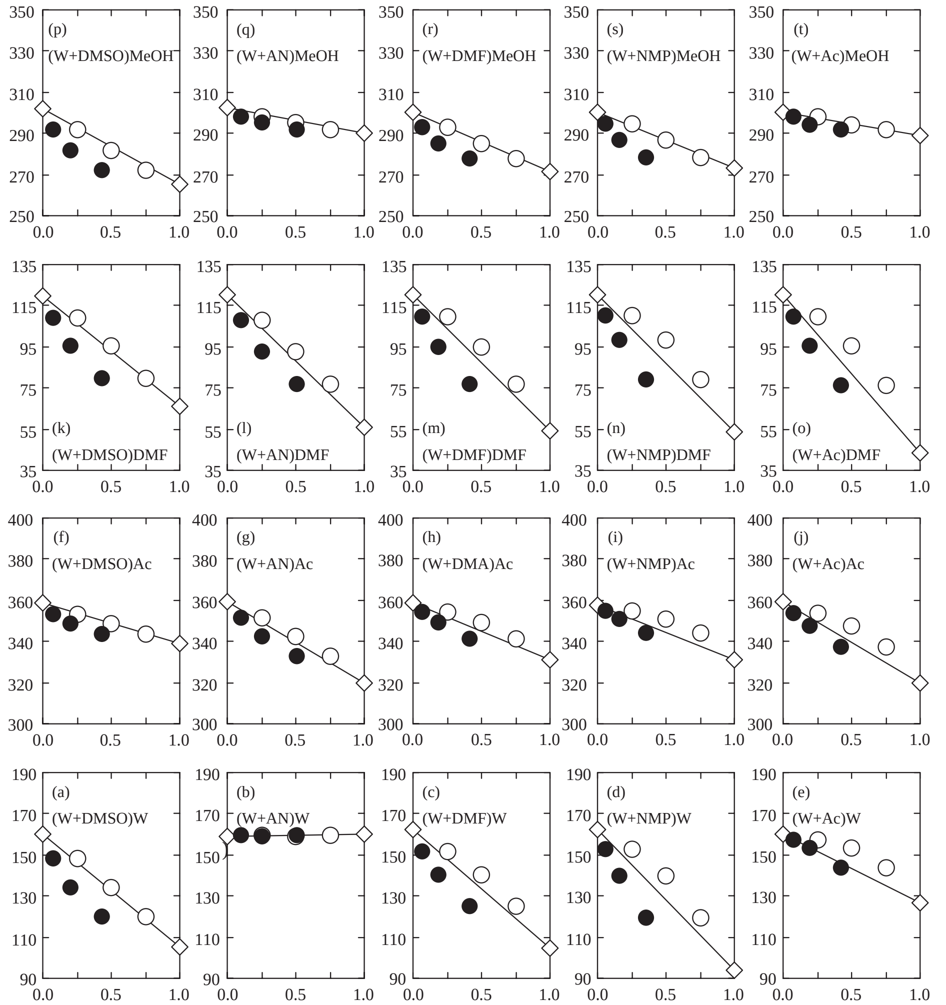

Figure 4. Variations of the emfs of Cell 3 with bridge solvents. The emfs (in mV) are plotted against volume fraction (○) and mole fraction (●) of S_3'. ($S_3 + S_3'$) and S_2 are shown on each figure.

because of the weak positive charge-center of the molecules of the aprotic solvent of weak acidity, the structure-forming amphiprotic solvent will be more likely to and the aprotic solvents less likely to settle at the interphasial region than in the bulk, justifying the curved relationships with volume fraction.

A considerable number of structural studies of mixtures involving (amphiprotic solvent + aprotic solvent) have been performed using computer simulation methods (Monte Carlo and molecular dynamics calculations), diffraction methods (X-ray and neutron diffraction measurements) and spectroscopic methods (nuclear magnetic resonance and various infrared vibration spectroscopies).[19] Among the reports about solvent mixtures relevant to the present work are, for example, Ref. 20 for W + DMSO, Ref. 21 for W + AN, Ref. 22 for W + DMF, Ref. 23 for W + DMA, Ref. 24 for W + NMP, Ref. 25 for W + Ac, Ref. 26 for W + HMPA, Ref. 27 for FA + DMSO, Ref. 28 for FA + DMF, and Ref. 29 for NMF + DMF. Unfortunately however, it is not clear from these reports why curved relationships are obtained for the mixtures of W, FA, and NMF with DMF, DMA, NMP, Ac, and HMPA.

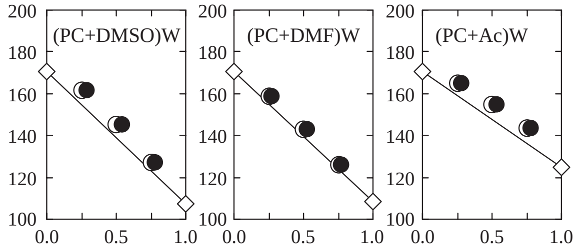

Figure 5. Variations of the emfs of Cell 3 with bridge solvents. The emfs (in mV) are plotted against volume fraction (○) and mole fraction (●) of S_3'. ($S_3 + S_3'$) and S_2 are shown on each figure. In the case of (PC + DMF)W, the relationship is classified as NL (near-linear) against volume fraction but C (curved) against mole fraction.

In addition to the mixtures between amphiprotic solvents and very weakly acidic aprotic solvents, there is another example of deviation from linearity with volume fraction, as is given in Figure 5, for cells with S_2 = W, S_3 = PC, and S_3' of aprotic solvents like DMSO, DMF, and Ac. Here, the variations in component (c) at $\mathbf{S_3}$(PC)¦S_2(W) and $\mathbf{S_3'}$(aprotic solvent)¦S_2(W) are the main parts of the emf-variation, the latter being larger than the former. Here, the volume fraction and mole fraction are very near to each other and the relations with both fractions are curved in the same direction, i.e., the fraction of the area occupied by $\mathbf{S_3}$(PC) at the interphasial region is larger than the volume fraction in the bulk. It should be noted that the curved relation is obtained even for $S_3' =$ DMSO. Since linear relations are obtained for S_2 other than W, the curved relations seem to be due to the "partial miscibility" of W as S_2 and PC as S_3.

Here, it should be mentioned that when $S_3 = S_1$ and $S_3' = S_2$, as in Figures 2l and 4b, the emf does not vary at all (within ±1 mV) with compositions of $(S_3 + S_3')$. This is the case, without exception, for all combinations of S_1 and S_2 and all kinds of MX, including electrolytes ranging from $[Et_4N]ClO_4$ and $[Et_4N]Br$ to $NaClO_4$, $LiClO_4$, and $Mg(ClO_4)_2$. This means that, for component (c) as well as for components (a) and (b), the sum of the values at $S_1 \vdots (S_1 + S_2)$ and $(S_1 + S_2) \vdots S_2$ is always equal to the value at $S_1 \vdots S_2$.

Conclusion

According to our model of component (c), the component at a mixed solvent/pure solvent junction should vary linearly with the volume fraction of the mixed solvent. Though this linearity with volume fraction really occurs in the majority of cases, there are exceptional cases where nonlinear (curved) relationships are observed. In the present experimental study, I found that most of the curved relationships are obtained for mixtures between an amphiprotic solvent (W, FA, or NMF) and an aprotic solvent of very low acceptor number (DMF, DMA, NMP, Ac, or HMPA). In contrast, if the aprotic solvent has a moderate acceptor number (NM, DMSO, AN, or PC), linear or near-linear relationships are obtained. The deviations from linearity always occur in the direction such that the fraction of the area occupied by the amphiprotic solvent at the interphasial region is larger or the fraction of the area occupied by the aprotic solvent at the interphasial region is less than the volume fractions in the bulk. I conclude that the "vague" positive charge-center of the dipolar molecules of a very weakly acidic aprotic solvent and the structure-forming property of an amphiprotic solvent together make the amphiprotic solvent more favored and aprotic solvents less favored to settle at the interphasial region than in the bulk.

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References

1 K. Izutsu, T. Nakamura, T. Yamashita, *J. Electroanal. Chem.* **1987**, *225*, 255.

2 K. Izutsu, T. Nakamura, T. Kitano, C. Hirasawa, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 783.

3 a) M. Alfenaar, C. L. DeLigny, A. G. Remijnse, *Recl. Trav. Chim. Pay-Bas* **1967**, *86*, 986. b) B. G. Cox, A. J. Parker, W. E. Waghorne, *J. Am. Chem. Soc.* **1973**, *95*, 1010. c) A. J. Staverman, *Trans. Faraday Soc.* **1952**, *48*, 176. d) R. Gaboriaud, *J. Chim. Phys.* **1975**, *72*, 347.

4 B. S. Krumgalz, *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 571, and others.

5 Y. Marcus, *Pure Appl. Chem.* **1983**, *55*, 977.

6 K. Izutsu, T. Nakamura, M. Muramatsu, Y. Aoki, *J. Electroanal. Chem.* **1991**, *297*, 41.

7 K. Izutsu, T. Nakamura, Y. Aoki, *J. Electroanal. Chem.* **1992**, *334*, 213.

8 K. Izutsu, T. Arai, T. Hayashijima, *J. Electroanal. Chem.* **1997**, *426*, 91.

9 K. Izutsu, T. Nakamura, T. Yamashita, *J. Electroanal. Chem.* **1988**, *256*, 43.

10 K. Izutsu, T. Nakamura, in *Ion-selective Electrodes*, ed. by E. Pungor, Pergamon Press, **1989**, Vol. 5, p. 425.

11 K. Izutsu, N. Kobayashi, *J. Electroanal. Chem.* **2005**, *574*, 197; K. Izutsu, *Rev. Polarogr.* **2005**, *51*, 73.

12 K. Izutsu, M. Muramatsu, Y. Aoki, *J. Electroanal. Chem.* **1992**, *338*, 125.

13 K. Izutsu, T. Nakamura, I. Takeuchi, N. Karasawa, *J. Electroanal. Chem.* **1983**, *144*, 391.

14 K. Izutsu, T. Nakamura, N. Gozawa, *J. Electroanal. Chem.* **1984**, *178*, 165.

15 K. Izutsu, T. Nakamura, N. Gozawa, *J. Electroanal. Chem.* **1984**, *178*, 171.

16 K. Izutsu, N. Gozawa, *J. Electroanal. Chem.* **1984**, *171*, 373.

17 K. Izutsu, T. Nakamura, M. Muramatsu, *J. Electroanal. Chem.* **1990**, *283*, 435.

18 K. Izutsu, T. Nakamura, M. Muramatsu, Y. Aoki, *Anal. Sci.* **1991**, *7*, Suppl. 1411; K. Izutsu, T. Nakamura, T. Arai, M. Ohmaki, *Electroanalysis* **1995**, *7*, 884.

19 Y. Marcus, *Solvent Mixtures, Properties and Selective Solvation*, Marcel Dekker, New York, **2002**, Chap. 3.

20 R. L. Mancera, M. Chalaris, K. Refson, J. Samios, *Phys. Chem. Chem. Phys.* **2004**, *6*, 94.

21 I. Bakó, Y. Megyes, T. Grósz, G. Pálinkás, J. Dore, *J. Mol. Liq.* **2006**, *125*, 174.

22 a) H. Ohtaki, Y. Niwa, K. Ozutsumi, M. Probst, B. Mroz, F. R. Perez, J. Alvarez, S. Bolado, *J. Mol. Liq.* **2006**, *129*, 49. b) Z. Xu, H. Li, C. Wang, H. Pan, S. Han, *J. Chem. Phys.* **2006**, *124*, 244502.

23 K. Tomikawa, H. Kanno, H. Kimoto, *Can. J. Chem.* **2004**, *82*, 1468.

24 A. M. Zaichikov, *Russ. J. Gen. Chem.* **2006**, *76*, 626.

25 D. S. Venables, C. A. Schmuttenmaer, *J. Chem. Phys.* **2000**, *113*, 11222.

26 Y. M. Kessler, A. N. Petrov, I. I. Vaisman, V. V. Goncharov, G. A. Al'per, *Russ. J. Phys. Chem.* **1990**, *64*, 247.

27 O. F. Nielsen, D. H. Christensen, E. Praestgaard, *J. Chem. Phys.* **1985**, *82*, 1183.

28 Yu. G. Bushuev, A. M. Zaichikov, *Russ. Chem. Bull.* **1998**, *47*, 2338.

29 K. Fujii, T. Kumai, T. Takamuku, Y. Umebayashi, S. Ishiguro, *J. Phys. Chem. A* **2006**, *110*, 1798.