© 2010 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 83, No. 7, 777–781 (2010) 777

Liquid Junction Potential between Different Solvents: The Component due to Solvent–Solvent Interactions Is Dipole Potential in Nature

Kosuke Izutsu[†]

Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390-8621

Received February 25, 2010; E-mail: izutsu@almond.ocn.ne.jp

The liquid junction potential between different solvents contains three components, i.e., component (a) due to electrolyte concentrations and ionic mobilities, component (b) due to the solvation of ions, and component (c) due to solvent–solvent interactions. The values of component (b) are actually much smaller than the values calculated from theoretical equations, but other researchers considered the equation to be valid and came to the conclusion that component (c) depended on electrolytes. From electrolyte-independent characteristics and others, we report here that component (c) is not the diffusion potential but the dipole potential.

The liquid junction potential (abbreviated LJP) between different solvents contains three components, i.e., component (a) due to electrolyte concentrations and ionic mobilities, component (b) due to the solvation of ions, and component (c) due to solvent–solvent interactions. The problem of the LJP between different solvents has considerably been studied but it has not been clarified enough. Especially, there remain different opinions about the origin of component (c). In this report, we review the essential parts of our previous (somewhat scattered) results and results from other researchers, add new discussions, and propose definitely our opinion that this component is really not a diffusion potential but a dipole potential.

Our detailed experimental studies with emf cells showed that under appropriate conditions, the three components of the LJP could be measured separately from the others, and thus the characteristics of each of the three components could be known.

First, we review our results on the ionic parts of the LJP, i.e., components (a) and (b).[1–7] As with other researchers, we considered that the ionic parts of the LJP between solvents S_L and S_R (L and R show left and right) can be expressed theoretically by eq 1:

$$E_j(\mathrm{a+b}) = (-1/F)\int_{\mathrm{SL}}^{\mathrm{SR}} \sum_i (t_i/z_i)\mathrm{d}\mu_i$$
$$\mu_i = \mu_i^0 + RT\ln a_i \tag{1}$$

where t_i, z_i, and a_i are the transport number, charge, and activity of ionic species i, and μ_i and μ_i^0 are its chemical potential and standard chemical potential, respectively, and except for z_i, all parameters vary between S_L and S_R. The equation can be divided into two equations, i.e., eq 2 for component (a) and eq 3 for component (b).

$$E_j(\mathrm{a}) = (-RT/F)\int_{\mathrm{SL}}^{\mathrm{SR}} \sum_i (t_i/z_i)\mathrm{d}\ln a_i \tag{2}$$

$$E_j(\mathrm{b}) = (-1/F)\int_{\mathrm{SL}}^{\mathrm{SR}} \sum_i (t_i/z_i)\mathrm{d}\mu_i^0 \tag{3}$$

In the experimental studies of the characteristics of components (a) and (b), we used cells of the following type:

$$\begin{array}{l}\mathrm{Ag|5\ mM\ AgClO_4,\ 20\ mM\ Et_4NClO_4(S_1)}\text{¦¦}\\ \mathrm{20\ mM\ Et_4NClO_4(S_1)}\underset{j_1}{\text{¦}}c_1\ \mathrm{MX(S_1)}\underset{J}{\text{¦}}c_2\ \mathrm{MX(S_2)}\underset{j_2}{\text{¦}}\mathrm{20\ mM\ Et_4NClO_4(S_2)}\text{¦¦}\\ \mathrm{5\ mM\ AgClO_4,\ 20\ mM\ Et_4NClO_4(S_2)|Ag} \qquad \text{Cell 1}\end{array} \tag{4}$$

In the study of component (a), the emfs were measured, for fixed MX, by varying concentrations c_1 and c_2 in various ways.[1–3] The emfs were corrected for the LJPs at j_1 and j_2 by calculating them with the Henderson equation. On the other hand, in the study of component (b), for fixed concentrations of c_1 and c_2, the electrolyte MX was varied.[3–6] In this case, the emfs were corrected for component (a) at J as well as for the LJPs at j_1 and j_2.

In the case of component (a), equations for its calculation were obtained for 1:1[1,2] and z_M:z_X[3] electrolytes by integrating eq 2, assuming linear variations in a and t at the junction. See Ref. 7 for the junction with different electrolytes on the two sides. The equations always explained quantitatively the experimental (actual) variations in component (a), showing their applicability to the estimation of the component.

In the case of component (b), eq 5 was derived from eq 3 by assuming linear variations in t and μ^0 at the junction.

$$E_j(\mathrm{b}) = \left(-\frac{1}{2F}\right)[(t_{\mathrm{ML}} + t_{\mathrm{MR}})\Delta G_t^0(\mathrm{M}) - (t_{\mathrm{XL}} + t_{\mathrm{XR}})\Delta G_t^0(\mathrm{X})] \tag{5}$$

Here, $\Delta G_t{}^0(\mathrm{M})$ and $\Delta G_t{}^0(\mathrm{X})$ are the Gibbs energies of transfer of M^+ and X^-. This equation predicts that the component is independent of electrolyte concentrations and that cation M^+ makes the side on which the solvation is stronger more positive, while anion X^- makes more negative. These characteristics have experimentally been confirmed. However, the experimental results show that at miscible

---

[†] Present address: 4-31-6-208 Kichijoji-honcho, Musashino, Tokyo 180-0004

Published on the web June 18, 2010; doi:10.1246/bcsj.20100052

junctions, eq 5 is not quantitatively valid. Though the variation in the actual values of component (b) and the theoretical values obtained by eq 5 are nearly linearly related, the slopes of the near-linear relations are much smaller than unity. The average slopes are 0.46 ± 0.029 for water (H_2O)/S (S: organic solvents), 0.32 ± 0.031 for formamide (FA)/S, 0.33 ± 0.025 for ethylene glycol (EG)/S, and 0.26 ± 0.08 for methanol (MeOH)/S. Between two aprotic solvents, the slopes were even smaller, and for MX of sodium, lithium, and alkaline earth metal salts, the slopes were almost equal to zero, showing that the variation in μ^0-values did not contribute to component (b). From the comparison between the theoretical emfs and the experimental data, we found that the actual values of component (b) are really proportional to the values calculated by eq 5 ($E_j(b)_{calcd}$) and can be estimated by ($E_j(b)_{calcd} \times$ (slope)).

Due to the mutual diffusion of solvents, a transition layer of thickness 0.05–1 mm is formed at miscible junctions and the solvent composition there varies gradually from S_L to S_R.[6] The values of a, t, and μ^0 also vary through this transition layer from the values in S_L to those in S_R. The diffusion of ionic species occurs as the result of their random-walk movements in two modes, i.e., due to the concentration gradients which gives rise to component (a) and due to the gradients in μ^0-values which gives rise to component (b). No special force works on the ionic species in diffusion. The fact that the magnitudes of component (a) agreed well with the values estimated from theoretical equations shows that the diffusion by concentration gradient occurred as expected theoretically. On the other hand, the fact that component (b) was much smaller than estimated from eq 5 shows that the diffusion due to the gradients in μ^0-values did not occur as theoretically expected or it was slower than that. In order that the random-walk movement can result in the ionic diffusion expected from the theoretical gradient in μ^0, the ion solvation must match the theoretical μ^0-value anytime and anywhere. But, there are at least two factors that slow down the matching:[6] (1) The distance that the random-walking ions can jump at a time is of the order of radii of solvent molecules (0.3–0.7 nm) and it is too short for ion solvation to match strictly the theoretical μ^0-values. (2) For easily solvating cations (Na, Li, and alkaline earth metal ions), the average residence time of solvent molecules in the first solvating sphere is too long (10 ps–1 ns) to match the variation in theoretical μ^0-values, because the average jump-time of random-walking ions is very short (0.1–10 ps).

All researchers other than us considered the equation for component (b) to be valid, though details of the equation were slightly different from one group to another.[8–14] For example, Alfenaar, De Ligny, and Remijnse[8] carried out a study of the diffusion potential between different solvents. They expressed the diffusion potential E_j, similarly to that in Ref. 9, by

$$E_j = -\frac{1}{F}\int_{SL}^{SR}\sum_i t_i^r d\mu_i = -\frac{1}{F}\sum_{\text{ion}}\int_{SL}^{SR}\frac{t_i}{z_i}d\mu_i - \frac{1}{F}\sum_{\substack{\text{uncharged}\\ \text{particles}}}\int_{SL}^{SR} t_i^r d\mu_i \qquad (6)$$

where t_i^r is the reduced electrical transport number. The two terms on the right side show the ionic part and the solvent part, respectively, but they are mutually dependent. Here, they considered that the solvent contribution is also a diffusion potential. For cell Ag|AgX|MX(S_L)¦MX(S_R)|AgX|Ag with the same activities for MX in S_L and S_R, the term due to the differences in ionic concentrations disappears and:

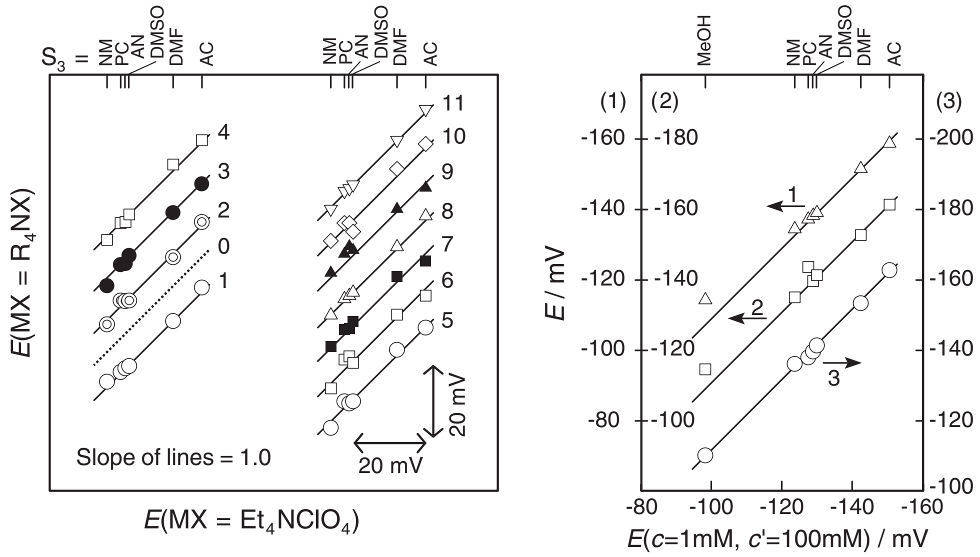
$$E_j = -(t_M/F)\Delta\mu^0(M) + (t_X/F)\Delta\mu^0(X) + E_{j,solv} \qquad (7)$$

where $\Delta\mu^0 = \Delta G_t^0$ (Gibbs energy of ionic transfer). From the emf measurements of this cell and the known values of ΔG_t^0, they obtained the solvent component, $E_{j,solv}$, using H_2O as S_L, H_2O–MeOH mixtures as S_R, and alkali metal halides as MX. They concluded that $E_{j,solv}$ is not only a function of the solvent composition but also of the kind of electrolyte that participates in the diffusion process of solvent molecules. Cox, Parker, and Waghorne[10] expressed the LJP between different solvent in the same way as the diffusion potential in Ref. 8. In the experimental study of the solvent contribution, they used a cell of the type Ag|0.01M $AgClO_4$(S_1 = acetonitrile (AN))¦0.1M Et_4NPic(S_3)¦0.01M $AgClO_4$(S_2)|Ag, and because $t(Et_4N^+) \approx t(Pic^-)$ and $\Delta\mu^0(Et_4N^+) \approx \Delta\mu^0(Pic^-)$, they considered that the variation in emf with the variation in S_3 should correspond to the variation in the solvent component ($E_{j,solv}$). They confirmed that the variation in $E_{j,solv}$ is in a linear relation with the variation in the mutual heats of solution of solvents. But they still believed that the transport of solvent molecules with ions is responsible for $E_{j,solv}$. Murray and Aikens[11] studied the LJP between different solvents by use of equations similar to those in Ref. 8 and by use of a cell as shown by N|NX(s)|MX(sat'd, S_1)¦MX(sat'd, S_2)|NX(s)|N. They felt that the emf of the cell corresponded to the solvent contribution of the LJP, because the solutions were saturated with MX. This means however that they believed in the validity of the equation for component (b). Senanayake and Muir[12] and Popovych and his co-workers[13] also carried out studies on the LJP between different solvents, and felt nearly the same way about the validity of the equation for component (b) and the role of electrolytes for component (c). Gaboriaud[14] position was somewhat unique, he considered components (a) and (b) in the same way as above but he denied the presence of component (c). All other than Gaboriaud believed that by taking the difference between the total LJP (estimated by using an extra-thermodynamic assumption) and the sum of the theoretical values of components (a) and (b), component (c) could be obtained. As described above, according to our experimental work, the actual values of component (b) at miscible junctions are much smaller than expected from eq 5. Thus, component (c) obtained by other researchers contained the overestimated part of component (b) and, because component (b) is often the largest among the three components,[15] the overestimated part occupied a considerable part of component (c) thus estimated, giving an impression that component (c) was dependent on ions.

In studying component (c), we used cells of the following types:[2,3,6,16–21]

Ag|5 mM $AgClO_4$, 25 mM Et_4NClO_4(S_1 = AN)¦¦
c MX(S_1 = AN)¦c' MX(S_3)¦c MX(S_2)¦¦
J_1 J_2
5 mM $AgClO_4$, 25 mM Et_4NClO_4(S_2)|Ag Cell 2 (8)

or



(a)
Cell 2, c=1 mM, c' =100 mM;
MX: 0 Et_4NClO_4, 1 Me_4NClO_4, 2 Pr_4NClO_4,
3 Bu_4NClO_4, 4 Hex_4NClO_4, 5 Et_4NCl,
6 Et_4NBr, 7 Et_4NI, 8 Et_4NNO_3, 9 Et_4NPic,
10 Et_4NBF_4, 11 Bu_4NBPh_4.

(b)
Cell 2, MX=Et_4NClO_4.
(1) c=100mM, c'=1mM;
(2) c=c'= 50mM;
(3) c=c'= 10mM.

Figure 1. The independence of component (c) from electrolyte species (a) and electrolyte concentrations (b). The use of cell 2.[16]

$$\begin{array}{l} \mathrm{Ag|5\ mM\ AgClO_4,\ 25\ mM\ Et_4NClO_4(S_1 = AN)}\,\Vert \\ c\ \mathrm{Et_4NClO_4(S_1 = AN)}\underset{J_1}{\vdots}c'\ \mathrm{MX(S_3)}\underset{J_2}{\vdots}c\ \mathrm{Et_4NClO_4(S_2)}\,\Vert \\ \mathrm{5\ mM\ AgClO_4,\ 25\ mM\ Et_4NClO_4(S_2)|Ag} \qquad \text{Cell 2}' \quad (9) \end{array}$$

Here, usually $c = 1\,\mathrm{mM}$ and $c' = 100\,\mathrm{mM}$. We compared for various MX the emf variation with solvents S_3. The detection of component (c) was possible because the sum of the values of component (c) at S_1/S_3 (J_1) and S_3/S_2 (J_2) was not equal to the value at S_1/S_2. In this cell, by using AN as S_1, the value of component (c) at S_1/S_3 was kept small for S_3 of aprotic solvents. When the emf variation with S_3 for various tetraalkylammonium salts as MX were plotted against that for MX = Et_4NClO_4, linear relations of unit slopes were obtained for all MX and for all S_2-solvents studied (regardless of their protic or aprotic nature). As an example, the case of S_2 = DMSO is shown in Figure 1. Here, $M^+ = Me_4N^+$, Et_4N^+, Pr_4N^+, Bu_4N^+, or Hex_4N^+ and $X^- = BPh_4^-$, BF_4^-, Pic^-, ClO_4^-, NO_3^-, I^-, Br^-, or Cl^-. When S_2 was a protic solvent (H_2O, FA, EG, or MeOH) and MX was either sodium, lithium, or alkaline earth metal salt and if corrections were not made for the values of components (a) and (b) at J_1 and J_2, the slopes were between 1.5–2.2 and much larger than 1.0. However, even in these cases, the slopes became very close to 1.0 if corrections were made for these values.[2,3,6] Thus, component (c) is always independent of electrolyte species. This component is also independent of electrolyte concentrations. Though small decreases occurred in the magnitudes of component (c) with the increase in electrolyte concentrations (Figure 2), it does not mean the participation of electrolytes in the generation of component (c) but it is merely an influence to the orientation of solvent molecules.[1,19] Here, it should be noted that even for MX = Bu_4NBPh_4 or Hex_4NClO_4, the magnitudes of component (c) were the same as for other electrolytes. Because Bu_4N^+, Hex_4N^+, and BPh_4^- are hardly solvated, the opinion that the transport of solvent molecules across the junction is accompanied by the transport of ions does not seem to be realistic. Other mechanisms which are electrolyte-independent must be considered.

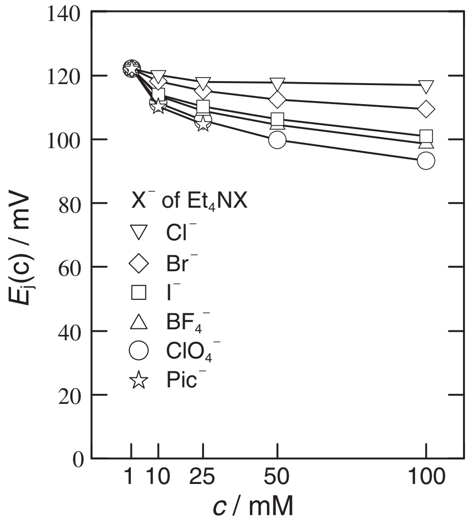


Figure 2. Effect of electrolyte concentrations on component (c) at the junction c $Et_4NX(H_2O)\vdots c$ $Et_4NX(DMSO)$.

In addition to the independence of electrolytes, the magnitude of component (c) increases with the increase in the strength of solvent–solvent interaction and its direction corresponds to that the solvent as a Lewis acid has more

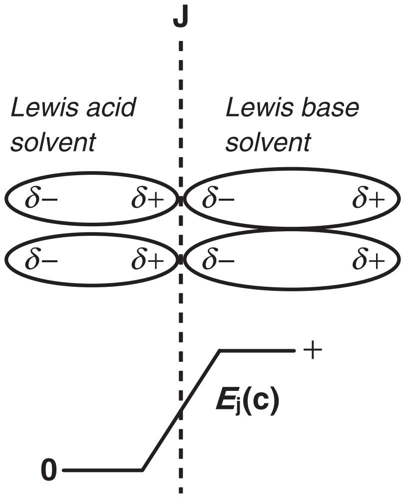


Figure 3. Schematic representation of the characteristics of component (c).

negative potential than the solvent as a Lewis base. In order to explain these characteristics, we proposed in 1983[16] a model as in Figure 3, in which the solvents on the two sides of the junction interact as a Lewis acid and a Lewis base and some of the solvent molecules are oriented perpendicularly to the junction giving a potential difference. Naturally we considered that component (c) might be a dipole potential, but at that time we did not explicitly reported this, because more information seemed necessary to conclude it.

The model was originally proposed only to explain the above characteristics of component (c). But after that it became apparent that this model can explain many other characteristics, including those that demand component (c) to be a dipole potential. Especially important is the phenomena at mixed solvent/pure solvent (and also at mixed solvent/mixed solvent) junctions; component (c) varies in many cases linearly or near-linearly against the volume fraction of the mixed solvents.[17,18,20] This phenomena can be explained by the model as follows: at a junction with a mixed solvent on one side (c_L MX($\mathrm{S_L} + \mathrm{S_{L'}}$)¦$c_\mathrm{R}$ MX($\mathrm{S_R}$)), the fractions of the areas occupied by $\mathrm{S_L}$ and $\mathrm{S_{L'}}$, respectively, on the ($\mathrm{S_L} + \mathrm{S_{L'}}$) side of the interphase will be equal, if specific adsorption of one solvent does not occur at the junction, to the volume fractions of $\mathrm{S_L}$ and $\mathrm{S_{L'}}$ in the bulk of the mixed solvent, i.e., ϕ_SL and $\phi_\mathrm{SL'}$. Here, if component (c) is a dipole potential, it should be proportional to the number of the oriented dipoles per unit area. If we express component (c) at pure $\mathrm{S_L}$¦$\mathrm{S_R}$ and $\mathrm{S_{L'}}$¦$\mathrm{S_R}$ junctions in terms of $E_\mathrm{j}(\mathrm{c})_\mathrm{SL}$ and $E_\mathrm{j}(\mathrm{c})_\mathrm{SL'}$, respectively, component (c) at the ($\mathrm{S_L} + \mathrm{S_{L'}}$)¦$\mathrm{S_R}$ junction will be $E_\mathrm{j}(\mathrm{c})_\mathrm{SL+SL'} = \phi_\mathrm{SL}E_\mathrm{j}(\mathrm{c})_\mathrm{SL} + \phi_\mathrm{SL'}E_\mathrm{j}(\mathrm{c})_\mathrm{SL'} = \phi_\mathrm{SL}(E_\mathrm{j}(\mathrm{c})_\mathrm{SL} - E_\mathrm{j}(\mathrm{c})_\mathrm{SL'}) + E_\mathrm{j}(\mathrm{c})_\mathrm{SL'} = \phi_\mathrm{SL'}(E_\mathrm{j}(\mathrm{c})_\mathrm{SL'} - E_\mathrm{j}(\mathrm{c})_\mathrm{SL}) + E_\mathrm{j}(\mathrm{c})_\mathrm{SL}$, showing that the magnitude of component (c) varies linearly with the volume fraction of the mixed solvent.

The model considers the direct interaction of the solvents on the two sides, but this direct-interaction model deviates from reality in that the actual junction has a transition layer (thickness: 0.05–1 mm) where the solvent composition gradually varies from $\mathrm{S_L}$ to $\mathrm{S_R}$. However recently, we showed this model to be applicable also in the presence of such transition layer.[21] If we consider the transition layer by dividing into many sliced thin parts and sum up the values of component (c) at each part, then it gives component (c) which is the same as that of the direct-interaction model.

As described above, other researchers believed in the validity of the equation for component (b) and found that component (c) is a function of both the solvent and the electrolyte. But the results of our experimental studies showed that component (b) is much smaller than expected from the theoretical equation and that component (c) is electrolyte-independent. The difference in opinion about component (b) seems to be the cause of the difference in the opinion about component (c). From many characteristics, we now conclude explicitly that component (c) is a dipole potential. The phenomenon as in Figure 3 is expected to occur as a result of the accumulation of phenomena in the transition layer at the junction. The magnitude of component (c) is equal to zero when no solvent–solvent interaction occurs and it increases with the increase in the strength of interactions, by causing orientation of solvent molecules (dipoles) and by making the solvent side as a Lewis acid more negative than that as a Lewis base. It is known that the orientation of dipoles gives dipole potentials at the interface between two phases,[22] thus it is not surprising that the dipole potential exists as a component of the LJP between different solvents. Contrarily, the opinion that component (c) is caused by the contribution of ionic species, i.e., it is a diffusion potential, is contradicted by the following two observations: (1) The electrolyte composed of ionic species that are nearly solvation-free gives component (c) which is similar in magnitude and direction to that for the electrolyte composed of strongly-solvated ions. (2) The values of the total LJP, estimated by the extra-thermodynamic assumption of $\mathrm{Ph_4AsBPh_4}$, agreed well with values estimated by our three component method, that evaluates each of the three components separately.[23] Then, how about the co-existence of the diffusion potential and the dipole potential in component (c)? Though the possibility is not perfectly eliminated, the contribution of the diffusion potential must be very small to the extent of being not experimentally detectable.

References

1 K. Izutsu, T. Nakamura, M. Muramatsu, Y. Aoki, *J. Electroanal. Chem.* **1991**, *297*, 49.

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

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

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

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

6 K. Izutsu, N. Kobayashi, *J. Electroanal. Chem.* **2005**, *574*, 197.

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

8 M. Alfenaar, C. L. De Ligny, A. G. Remijnse, *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 986.

9 A. J. Staverman, *Trans. Faraday Soc.* **1952**, *48*, 176.

10 B. G. Cox, A. J. Parker, W. E. Waghorne, *J. Am. Chem.*

Soc. **1973**, *95*, 1010.

11 R. C. Murray, Jr., D. A. Aikens, *Electrochim. Acta* **1976**, *21*, 1045.

12 G. Senanayake, D. M. Muir, *J. Electroanal. Chem.* **1987**, *237*, 149.

13 C. Kahanda, O. Popovych, *Aust. J. Chem.* **1994**, *47*, 921, and references therein.

14 R. Gaboriaud, *J. Chim. Phys.* **1975**, *72*, 347.

15 The variations of component (a) for the variations in c_1/c_2 from 100 mM/1 mM to 1 mM/100 mM are within ±40 mV. As to the actual values of component (b), the biggest difference in magnitudes reaches 370 mV for PC/H_2O, 250 mV for H_2O/AN, and 200 mV for H_2O/DMF. Contrarily, the value of component (c) was 122 mV for H_2O/DMF and H_2O/DMSO, 44 mV for H_2O/AN, and 30 mV for H_2O/PC (at 1 mM $Et_4NPic(H_2O)$¦1 mM $Et_4NPic(S)$ under the assumption that the values at H_2O/NB and at AN/aprotic solvents are equal to zero). See Ref. 23 for details.

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

17 a) K. Izutsu, T. Nakamura, N. Gozawa, *J. Electroanal. Chem.* **1984**, *178*, 165. b) K. Izutsu, T. Nakamura, N. Gozawa, *J. Electroanal. Chem.* **1984**, *178*, 171.

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

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

20 K. Izutsu, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 703.

21 K. Izutsu, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 39.

22 S. Trasatti, R. Parsons, *Pure Appl. Chem.* **1986**, *58*, 437.

23 K. Izutsu, *Pure Appl. Chem.* **1998**, *70*, 1873.