Liquid Junction Potential between Electrolyte Solutions in Different Solvents: Some Consideration on the Component Due to Solvent–Solvent Interactions

Kosuke Izutsu

Faculty of Science, Shinshu University,
Matsumoto 390-8621

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E-mail: izutsu@almond.ocn.ne.jp

The liquid junction potential between different solvents contains three components, i.e., (a) related to ionic concentrations and mobilities, (b) related to ion solvations, and (c) related to solvent–solvent interactions at the junction. In order to understand the characteristics of component (c), we formerly introduced a model that the two solvents at the junction directly interact each other as a Lewis acid and a Lewis base and some parts of the solvent molecules are oriented perpendicularly to the boundary. However, this direct-interaction model deviates from reality in that the actual junction has a transition layer; its solvent composition gradually varies from that on one side to that on the other and its thickness expands with time, usually between 0.05 and 1 mm. In this report, we show that this direct-interaction model is applicable also in the presence of such transition layer. For this, we divide the transition layer in steps and get the total component (c) by summing up component (c) at each step. Here, the value at each step is obtained from the experimental results for component (c) at mixed solvent/mixed solvent junctions. The extent of the solvent orientation at the boundary was also roughly estimated.

The liquid junction potential 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 ionic solvation on the two sides of the junction, and component (c) due to the solvent–solvent interactions at the junction.

We ran experimental studies on the characteristics of the three components.[1–7] In studying about component (c), we used Cell 1 or Cell 2 below:

$$\begin{gathered}\mathrm{Ag|5\ mM\ AgClO_4,\ 5\ mM\ Et_4NClO_4(S_1 = AN)}\vdots\\ c\ \mathrm{Et_4NClO_4(S_1 = AN)}\underset{\mathrm{J_1}}{\vdots}c_3\ \mathrm{MX(S_3)}\underset{\mathrm{J_2}}{\vdots}c\ \mathrm{Et_4NClO_4(S_2)}\vdots\\ \mathrm{5\ mM\ AgClO_4,\ 5\ mM\ Et_4NClO_4(S_2)|Ag} \qquad \text{Cell 1}\end{gathered}$$

$$\begin{gathered}\mathrm{Ag|5\ mM\ AgClO_4,\ 5\ mM\ Et_4NClO_4(S_1 = AN)}\vdots\\ \mathrm{10\ mM\ Et_4NClO_4(S_1 = AN)}\vdots c\ \mathrm{MX(S_1 = AN)}\underset{\mathrm{J_1}}{\vdots}c_3\ \mathrm{MX(S_3)}\underset{\mathrm{J_2}}{\vdots}\\ c\ \mathrm{MX(S_2)}\vdots\mathrm{10\ mM\ Et_4NClO_4(S_2)}\vdots\mathrm{5\ mM\ AgClO_4,}\\ \mathrm{5\ mM\ Et_4NClO_4(S_2)|Ag} \qquad \text{Cell 2} \qquad (1)\end{gathered}$$

The cell was constructed using dual four-way stopcocks for high-performance liquid chromatograph and the junctions between different solvents were formed in a tube of ca. 1 mm in diameter. The emf of these cells was measured, for a variety of combinations of c, c_3, MX, S_1, and S_2, by changing S_3 in various ways. Here, J_1 and J_2 are the junctions between different solvents and the emf-change of the cell with S_3 corresponded to the sum of the changes of component (c) at J_1 and J_2, as far as M^+ and X^- were not strongly solvated. Acetonitrile (AN) was used as S_1 in order to keep the magnitudes of component (c) between S_1 (=AN) and other aprotic solvents small.

Though there are some exceptions, the followings are the main characteristics of component (c) obtained from these studies.

(1) Component (c) is almost independent of the species and concentrations of the electrolytes at the junction. Contrarily, it depends on the interactions between different solvents at the junction: the direction and the magnitude of this component can be understood if we assume that the molecules of the two solvents at the junction interact each other as a Lewis acid and a Lewis base and some parts of them are oriented perpendicularly to the boundary as shown in Figure 1. The magnitude of component (c) increases with the increase in the strength of the interaction. Moreover, the component makes the solvent that works as a Lewis acid more negative than the solvent that works as a Lewis base.[3]

(2) At mixed solvent/pure solvent junctions, component (c) changes in many cases linearly or near-linearly against the volume fraction of the mixed solvent.[5] Similarly, at mixed solvent/mixed solvent junctions, it changes linearly or near-linearly against the volume fraction of each of the mixed solvents.[6]

Figure 1 was introduced to qualitatively interpret the characteristics of component (c). In the figure, direct interaction

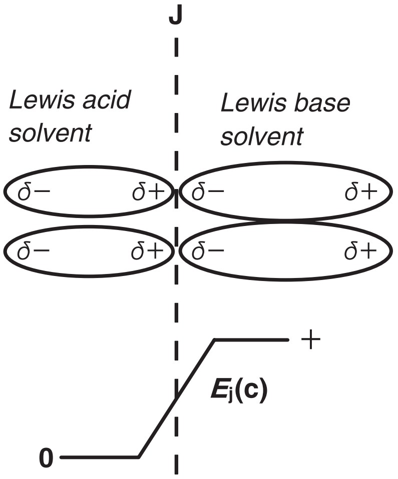

Figure 1. Schematic representation of the characteristics of component (c).

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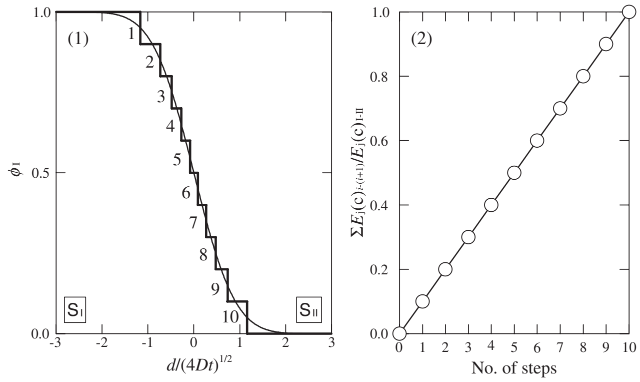

Figure 2. (1) Transition layer at the junction between solvents I and II; consideration by dividing in 10 steps. The case when component (c) for the mixtures of S_I and S_{II} is linear against the volume fraction (ϕ_I). d is the distance from the original junction, t time after the beginning of the junction, and D the diffusion coefficient of solvent molecules. (2) Summing up of component (c) at each step. $\Sigma E_j(c)_{i-i+1}$ shows the sum of component (c) from 1st step to i-th step.

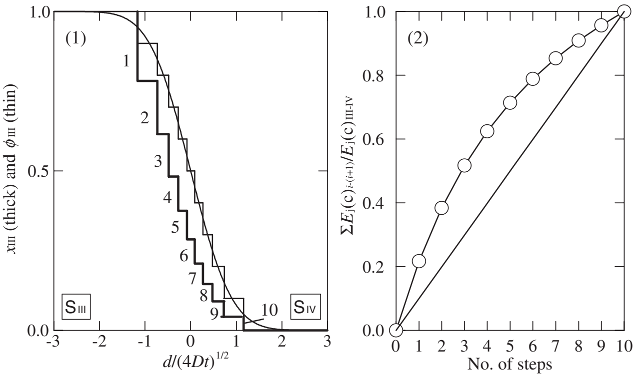

Figure 3. (1) Transition layer at the junction between solvents III and IV; consideration by dividing in 10 steps. The case when component (c) for the mixtures of S_{III} and S_{IV} is linear against the mole fraction (x_{III}). The thick line is for mole fraction (x_{III}) and the thin line for volume fraction (ϕ_{III}). (2) Summing up of component (c) at each step. $\Sigma E_j(c)_{i-i+1}$ shows the sum of component (c) from 1st step to i-th step.

was assumed at the boundary between solvent molecules on the two sides. In reality, however, such a direct interaction does not occur. The solvent molecules on the two sides diffuse each other after the formation of a junction and there exists a transition layer, in which solvent composition gradually varies from that on the one side to that on the other. The width of the transition layer increases with time, usually between 0.05 and 1 mm. However, the magnitude of component (c) does not vary with time.

In this paper, we report that Figure 1 is applicable even when there exists the transition layer. The simplest is, as observed in the majority of cases, when component (c) at the mixed solvent/mixed solvent junctions changes linearly (or near-linearly) against the volume fraction of each mixed solvent. This is true even when the mixed solvents on the two sides are composed of the same solvents (e.g., S_I and S_{II}). According to the model of Figure 1, component (c) should be proportional to the number of solvent molecules oriented at the boundary by interaction and the result of linearity to the volume fraction shows that the fractions of solvent molecules at the boundary are the same as those in the bulk. If we assume, instead of the smooth variation of solvent composition in the transition layer, a variation in n-steps ($i = 0$ to n) as in Figure 2(1), component (c) between S_I and S_{II} ($E_j(c)_{I-II}$) is the sum of the value at each step. Between the i-th and ($i + 1$)-th steps, ϕ_i of S_I and $(1 - \phi_{i+1})$ of S_{II} and $(1 - \phi_i)$ of S_{II} and ϕ_{i+1} of S_I interact in the opposite direction and give component (c) as the difference between the two, i.e., $\{\phi_i \times (1 - \phi_{i+1}) - (1 - \phi_i) \times \phi_{i+1}\} \times E_j(c)_{I-II} = (\phi_i - \phi_{i+1}) \times E_j(c)_{I-II} = (1/n) \times E_j(c)_{I-II}$. Thus, the magnitude of component (c) at each step is equal to $(1/n)$ of the magnitude of component (c) due to the direct interaction between S_I and S_{II}. This does not depend on the number of the steps (n) and the time after the formation of the junction. Thus, composition (c) in real transition layer may be considered to be the same as that of direct interaction between S_I and S_{II} and the model in Figure 1 may be used to qualitatively describe the real behavior of component (c).

As a somewhat exceptional case, when a mixed solvent composed of a protic solvent (S_{III}), such as water, formamide, and N-methylformamide, and an aprotic solvent of very low acidity (S_{IV}), such as DMF, DMA, acetone, and HMPA, forms a junction with a pure or mixed solvent, a more or less curved relation against volume fraction is observed for component (c).[1,5,6] When such solvents (S_{III} and S_{IV}) form a junction with S_{III} on the left and S_{IV} on the right, the transition layer is composed of the mixed solvent, ($S_{III} + S_{IV}$), which gives a curved relation against the volume fraction. In this case, the composition of the mixed solvent at the real boundary differs from the composition expected from the mutual diffusion, the fraction of the protic solvent being higher at the real boundary. Experimentally, in the case of largest deviation from linearity against volume fraction, a near-linear relation against mole fraction is obtained, though the deviation is usually smaller. Thus, we consider, as an extreme, the case of linear relation against mole fraction. As in the above, we divide the transition layer in n-steps. The mole fraction (x_i) corresponding to volume fraction ϕ_i of S_{III} is expressed by $x_i = A_{IV}\phi_i/\{(A_{IV} - A_{III})\phi_i + A_{III}\}$, where $A = M/d$ (M: molecular weight and d: density). Here, we consider that the value of component (c) between i- and ($i + 1$)-th steps is proportional to $\{x_i(1 - x_{i+1}) - (1 - x_i)x_{i+1}\}$. If we assume $n = 10$, $A_{III} = 50$, and $A_{IV} = 20$, component (c) vary as in Figure 3. The sum for n-steps is equal to the direct interaction at S_{III}/S_{IV} ($E_j(c)_{III-IV}$). Because this does not depend on the number of the steps (n) and the time after the formation of the junction, composition (c) in real transition layer may be considered to be the same as that of direct interaction between S_{III} and S_{IV}. Thus, here too, Figure 1 may be used as a model to qualitatively describe the real characteristics of component (c).

The magnitudes of component (c) between organic solvents and water have been estimated under the assumption that the component is zero at the nitrobenzene/water (W) junction and at the junctions between acetonitrile (AN) and other aprotic solvents.[8] For DMSO/W, DMF/W, and AN/W at c

$Et_4NPic(S)/c$ $Et_4NPic(W)$, they are 122, 122, and 44 mV for $c = 1$ mM and 104, 102, and 37 mV for $c = 25$ mM, with water side more negative. Though some influences of ionic atmosphere exist, component (c) at DMSO/W and DMF/W are over 100 mV. Figure 1 is not for quantitative estimation of component (c). But it seems worthwhile to know what parts of molecules should be oriented if, as in Figure 1, the solvent molecules on the two sides are oriented perpendicularly to the boundary and gives component (c). Here, we think of an organic solvent/water junction and assume that, for organic solvent, all the molecules at the monolayer of the boundary are oriented and, for water, the molecules at the monolayer of the boundary are oriented in the same number and in the same direction as the oriented organic solvent molecules. The dipole potential, g_{dipole}, for the oriented monolayer of solvent molecules can be expressed by $g_{\mathrm{dipole}} = N\vec{\mu}/\varepsilon\varepsilon_0$, where N is the number of oriented dipoles per unit area, $\vec{\mu}$ the dipole moment in C m, ε the relative permittivity, and ε_0 the permittivity of free space ($8.854 \times 10^{-12}\,\mathrm{C\,V^{-1}\,m^{-1}}$). We use the values of $\vec{\mu}$, ε, and the solvent density in the bulk of the solvents. Then, the g_{dipole}-value for organic solvent, that for water, and their sum (in mV and with water side more negative) are 136, 37, and 173 for DMSO/W; 131, 35, and 166 for DMF/W; and 188, 45, and 233, for AN/W. Thus, we can conclude that considerable parts of solvents (ca. 70%) must be oriented for DMSO/W and DMF/W junctions, i.e., junctions between strongly basic solvents and water (fairly strongly acidic solvent).

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