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Ionic liquid salt bridge based on tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide for stable liquid junction potentials in highly diluted aqueous electrolyte solutions

Hideaki Sakaida, Yuki Kitazumi, Takashi Kakiuchi*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

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ABSTRACT

A moderately hydrophobic ionic liquid, tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide ($[\text{TBMOEP}^+][\text{C}_2\text{C}_2\text{N}^-]$), shows a very stable liquid junction potential upon contact with an aqueous solution whose ionic strength is as low as 1 μmol dm^{-3}. The stability with the maximum excursion of the potential within ±0.5 mV for 30 min is very promising for accurate determination of pH and other single ion activities potentiometrically.

1. Introduction

An ionic liquid (IL) having a moderate hydrophobicity works as a salt bridge, which is in many respects superior to traditional KCl-type salt bridges [1–3]. The virtue of ionic liquid salt bridge (ILSB) is due to the thermodynamic nature of the phase-boundary potential formed by the partition of the cations and anions constituting the IL into an aqueous sample solution (W). When the IL-constituting cation and anion have a similar hydrophobicity whose standard Gibbs energy of the transfer of ions from water to an IL, typically, 20 kJ mol^{-1}, is much smaller than those of other ions present in W, the phase-boundary potential between the IL and W is dominated by the partition of the IL-constituting ions. Any moderately hydrophobic ions can essentially be used for an ILSB. Actually, however, it is important to choose a cationic and an anionic species whose diffusion coefficients in W are comparable with each other. This is because, experimentally, the true distribution equilibrium is seldom established between the salt bridge and a sample solution.

In the dissolution process of the IL, the transport of the IL-constituting cations and anions contributes to the phase-boundary potential in two ways [4,5]. First, when the net current across the ILSB|W interface is zero, the sum of the ion transfer currents due to the transfer of the ILSB-constituting cation and anion should be null. The phase-boundary potential taking account of this nonthermodynamic contribution when the net current is zero is called the mixed potential [4–6]. Second, the diffusion of the IL-constituting cations and anions in W gives rise to the diffusion potential, which becomes significant when the ionic strength of W is lower than the solubility of the IL in W [7]. When these two contributions are minimized by choosing the IL-constituting cationic and anionic species whose diffusion coefficients are comparable, ILSBs are expected to exhibit a stable phase-boundary potential even when the ionic strength of a sample solution is in the submillimolar range or lower.

Because KCl-type salt bridges do not work satisfactorily in samples of low ionic strength on the order of 50 μmol dm^{-3} [8–14], well-tuned ILSBs would have distinct advantages over KCl-

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* Corresponding author.
E-mail address: kakiuchi@scl.kyoto-u.ac.jp (T. Kakiuchi).

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type salt bridges. Recently, we demonstrated the stability of the phase-boundary potential at the IL|W interface down to the ionic strength of 20 μmol dm^{-3} using *N*-alkyl-*N*-methylpyrrolidinium bis(pentafluoroethanesulfonyl)amide [15]. There are, however, samples whose ionic strengths are comparable to or lower than 20 μmol dm^{-3}, e.g., boiler feed water and rain water in unpolluted regions [16,17]. In the present paper, we will report that the ILSB that consists of tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide ([TBMOEP$^+$][C$_2$C$_2$N$^-$]) shows a stable phase-boundary potential when it is in contact with 1 μmol dm^{-3} aqueous LiI, NaI, and KI solutions. The advantage of tetraalkylphosphonium-based salts over tetraalkylammonium-based ones includes the faster reaction rate in preparing phosphonium ions and the lower melting points of ionic liquids [18,19], though the latter seems to depend on the type of anions combined [20,21]. For application of ILs to IL-W two-phase systems, the solubility of the ILs in W and the value of the phase-boundary potential are crucial [1,2,22]. Both properties are determined by the standard Gibbs energy of ion transfer [1]. Generally, a tetraalkylphosphonium ion is 3–4 kJ mol^{-1} more hydrophobic than the corresponding tetraalkylammonium [23]. The choice of [TBMOEP$^+$][C$_2$C$_2$N$^-$] in the present study is based on our study of moderately hydrophobic ILs based on tetraalkylphosphonium ions [24].

2. Experimental

2.1. Materials

Tributyl(2-methoxyethyl)phosphonium chloride and tributyl (2-methoxyethyl)phosphonium bromide (TBMOEPBr) were synthesized from tributylphosphine (Kanto Chemical Co.) and either 2-chloroethylmethylether (Tokyo Chem. Ind.) or 2-bromoethylmethylether (Tokyo Chem. Ind.). [TBMOEP$^+$][C$_2$C$_2$N$^-$] was prepared by mixing equimolar amounts of TBMOEPBr and hydrogen bis(pentafluoroethanesulfonyl)amide (Central Glass Co., Japan) in methanol. After removing methanol and other volatile impurities by drying the mixture with an evaporator and then with a vacuum pump, the viscous liquid obtained was washed 30 times with copious water. The IL was further purified with a column packed with activated charcoal and silica gel [25]. Other chemicals used were of reagent grade. Water was purified with a Milli-Q system (Millipore Co.).

2.2. Methods

Potentiometric measurements were made using the following cell:

I	II	III	IV	V	VI	VII
		10 mmol dm^{-3}		x μmol dm^{-3}		
Ag	AgBr	TBMOEPBr	[TBMOEP$^+$][C$_2$C$_2$N$^-$]	MI	AgI	Ag
		(W$_{\text{ref}}$)	(IL)	(W)		

(I)

where MI is either LiI, NaI, or KI. The phase-boundary potential between III and IV was kept constant by the distribution of TBMOEP$^+$ as the potential determining ion [1]. In phase V, x was changed between 1 and 1000. The Ag/AgI electrode was used for the right hand side electrode, because the dissolution of AgCl and AgBr in the sample solution is nonnegligible when the concentration of MCl or MBr is on the order of 1 μmol dm^{-3} [15]. In the case of AgI, the dissolution of AgI is totally negligible even when the feed concentration of MI is 1 μmol dm^{-3}. The cell (I) was constructed in a glass tube with 10 mm inner diameter equipped with a disk of glass frit in the middle, as described elsewhere [2]. The phase III was below the glass frit. The thickness of the [TBMOEP$^+$][C$_2$C$_2$N$^-$] layer (phase IV) above the glass frit was typically 6 mm. The aqueous solution (phase V) of about 1 cm^3 was layered above the IL layer. The temperature was maintained at 25.0 ± 0.5 °C by circulating water through the jacket of the glass cell. The cell was housed in a box for light shielding. The cell voltage, i.e., the potential of the right-hand-side terminal with respect to that of the left, E, was measured with an electrometer (ADCMT-8240, ADC, Japan), and was sent to a computer through a GP-IB interface. Ag/AgI and Ag/AgBr electrodes were prepared by anodization of silver wires of 0.5 mm diameter in an aqueous solution of ca. 80 mmol dm^{-3} KI or 80 mmol dm^{-3} KBr at 10 mA for 15 min. The silver wires were first polished with an emery paper and then treated by ultrasonic cleaning successively with Milli-Q water, 2% aqueous ammonia, 2% nitric acid, and Milli-Q water.

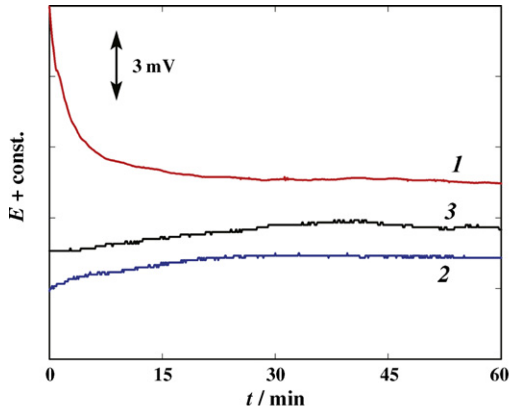

Fig. 1. Time courses of E in cell (I) when phase V is 0.1 mmol dm^{-3} KI under light shielding (Curve 1). Curves 2 and 3 exemplify similar time courses of E when the right-hand side electrode is Ag/AgBr and Ag/AgCl electrodes in the same concentrations of KBr and KCl, respectively.

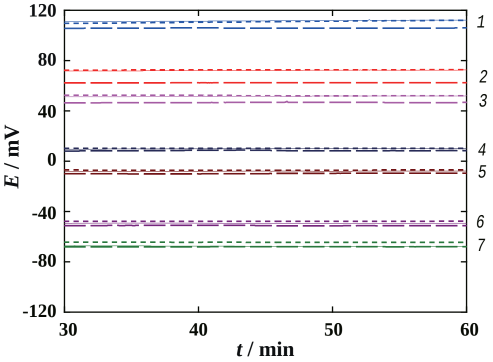

Fig. 2. Stability of E from 30 min after the setting of cell (I) for further 30 min when phase V was for LiI (solid lines), NaI (long dashed lines), and KI (dashed lines) at 1 (*1*), 5 (*2*), 10 (*3*), 50 (*4*), 100 (*5*), 500 (*6*), and 1000 (*7*) μmol dm^{-3}.

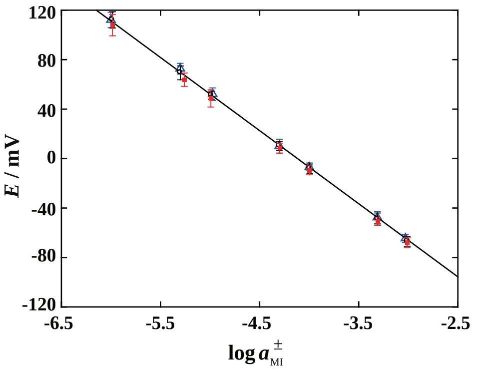

Fig. 3. Dependence of E on the common logarithm of the mean activity of LiI (○), NaI (□), and KI (△)) at 25 °C. The solid line has the slope of 59.16 mV per decade and is shown as the guide for eyes.

The solubility of $[TBMOEP^+][C_2C_2N^-]$ in W was determined by precipitation titration with an aqueous solution of sodium tetraphenylborate [26] to be 0.2 mmol dm^{-3}. Additional visual inspection experiments confirmed that the solubility is between 0.16 and 0.21 mmol dm^{-3}. The conductivity of aqueous solutions of TBMOEPBr, lithium bis(pentafluoroethanesulfonyl)amide, and hydrogen bis(pentafluoroethanesulfonyl)amide was measured with a bridge-type conductivity meter (HECS362D with HECS363D, Husou, Japan) and a dip-in-type cell (CT-5710B, DKK-TOA, Japan) at 25.0 °C. The estimated values of limiting molar ion conductivity were 25.5 (single measurement) and 26.1 ± 0.7 (triplicate measurements) S cm^2 mol^{-1} for TBMOEP$^+$ and $C_2C_2N^-$, respectively.

3. Results and discussion

3.1. Time courses of *E*

Curve 1 in Fig. 1 shows a typical time course of the cell voltage, E, in cell (I) when phase V in cell (I) contained 100 μmol dm^{-3} KI. In initial 15 min, E varied rapidly, but became stabilized after 30 min. For a comparison, the time courses of E are shown when phase V contained KBr (curve 2) or KCl (curve 3) and phase VI was the corresponding AgBr or AgCl electrodes. For all these cases, it took about 30 min before a stable reading of E was attained. Beyond 30 min, E was stable over 30 min. The initial drifts over 30 min in Fig. 1 are presumably ascribed to the slow response of the Ag/AgX electrodes [27], because the response of the phase-boundary potential across the IL|W interface is much faster, on the order of a few minutes, and the magnitude of the change in the potential is much smaller [2,7].

The time courses of E recorded 30 min after the commencement of E measurements are shown for 30 min in Fig. 2 for LiI (solid lines), NaI (long dashed lines), and KI (dashed lines) at x = 1 (*1*), 5 (*2*), 10 (*3*), 50 (*4*), 100 (*5*), 500 (*6*), and 1000 (*7*). In each line, the excursion of E was within ±0.5 mV, with two exceptions, 1 μmol dm^{-3} solutions of LiI (1.8 mV) and KI (2.5 mV). Except for these two cases, the maximum excursion in 30 min averaged over 19 curves in Fig. 2 was 0.53 ± 0.25 mV.

3.2. Constancy of *E* against the activity of MI in low ionic strength solutions

Fig. 3 shows the plots of E versus the common logarithm of the mean activity of LiI (○), NaI (□), and KI (△). The error bars show the standard deviations for triplicate measurements at each concentration of MI (MI = LiI, NaI, and KI). The solid line in Fig. 3 is not regression curves, but are to show the Nernst slope, 59.16 mV per decade change in the mean ionic activity at 25 °C. The mean activity coefficients of MI were calculated from the ionic strength of the solution in the molarity scale, I, using the Debye–Hückel's limiting law at 25 °C [28]

$$\log_{10}\gamma^{\pm} = -0.511\sqrt{I} \qquad (1)$$

assuming that the electrolyte present in phase V is only MI (MI = LiI, NaI, or KI). At the highest concentration, 1 mmol dm^{-3}, this would overestimate $\log_{10}\gamma_{\pm}$ by 4% in comparison with the value estimated by the Debye–Hückel theory [28,29]. In all cases of LiI, NaI, and KI solutions, experimental points are on the Nernst slope. This suggests that the Ag/AgI electrode responds reversibly to the activity of I$^-$ in phase V and the phase-boundary potential across the IL|W interface stays constant within experimental error over the change in the concentration of MI from x = 1 to 1000.

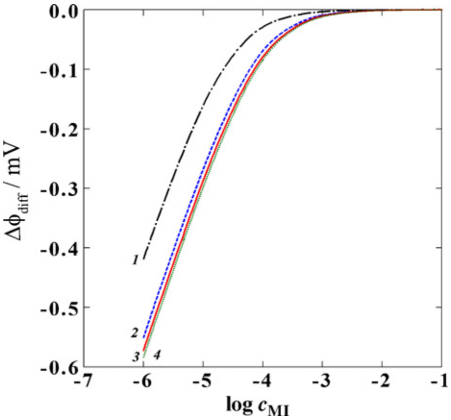

Fig. 4. Calculated ϕ^{W}_{diff} values using Eq. (2) as a function of the HI (curve 1), LiI (curve 4), NaI (curve 3), and KI (curve 2). See text for the parameters used.

3.3. Contribution of diffusion potential

The diffusion potential due to the dissolution of the IL becomes significant when the ionic strength of the sample solution is smaller than the solubility of the IL [7]. The lowest ionic strength examined in the present study, 1 μmol dm^{-3}, is a two hundredth of the solubility of $[TBMOEP^+][C_2C_2N^-]$. Assuming the absence of the concentration gradient of MI in W, the Henderson equation [30] for the diffusion potential has the form

$$\Delta\phi^{W}_{diff} = \left(\frac{u_{TBMOEP^+} - u_{C_2C_2N^-}}{u_{TBMOEP^+} + u_{C_2C_2N^-}}\right) \times \frac{RT}{F}\ln\frac{c^{W}_{[TBMOEP^+][C_2C_2N^-]}\left(u_{TBMOEP^+} + u_{C_2C_2N^-}\right) + c^{W}_{MI}\left(u_{M^+} + u_{I^-}\right)}{c^{W}_{MI}\left(u_{M^+} + u_{I^-}\right)} \qquad (2)$$

where $\Delta\phi^{W}_{diff}$ is the diffusion potential in W referred to the electrostatic potential in W at the interface between the ILSB and W against that of the bulk W phase, $c^{W}_{[TBMOEP^+][C_2C_2N^-]}$ is the solubility of $[TBMOEP^+][C_2C_2N^-]$, and u_i is the mobility of ion i (i = M$^+$, I$^-$, TBMOEP$^+$ or $C_2C_2N^-$) in W, which is related to the molar ionic conductivity through $u_i = \lambda_i/F$ for monovalent ions.

The values of ϕ^{W}_{diff} calculated using Eq. (2) are plotted in Fig. 4 as a function of the concentration of MI in W (MI stands for HI (curve 1), LiI (curve 4), NaI (curve 3), and KI (curve 2)). The values of limiting molar ion conductivity used in the calculation are 25.5 (TBMOEP$^+$), 26.1 ($C_2C_2N^-$), 349.8 (H$^+$), 38.68 (Li$^+$), 50.10 (Na$^+$), 73.53 (K$^+$), and 76.84 (I$^-$) S cm^2 mol^{-1}. The latter five values were taken from the literature [28] and $c^{W}_{[TBMOEP^+][C_2C_2N^-]}$ on the sample solution side of the IL|W interface was set to 0.2 mmol dm^{-3}. It is seen that $\Delta\phi^{W}_{diff}$ becomes appreciable when the concentration of MI is smaller than the solubility of the IL and grows exponentially with c_{MI}. When the concentration of MI is 1 μmol dm^{-3}, $\Delta\phi^{W}_{diff}$ reaches nearly 0.6 mV. Actually, this is too small to be discerned in the plots in Fig. 3, and within the experimental uncertainty the contribution of the diffusion potential was not detected.

Another factor that can give rise to the deviation from the Nernst slope is the dissolution of $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ in phase V. It can raise the ionic strength during the measurement of 1 h to the level close to its solubility, although the partition equilibrium of $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ may not have been attained during a potentiometric measurement. In fact, we found that the dissolution of $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ was slow; it took two days to dissolve 0.10 g $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$, with vigorously stirring of the solution, for preparing a 1 $\mathrm{dm^3}$ aqueous solution of 0.16 $\mathrm{mmol\,dm^{-3}}$. It is therefore not sure whether the phase V was saturated with $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ during a potentiometric measurement. If so, the ionic strength of W is elevated by 0.2 $\mathrm{mmol\,dm^{-3}}$. Then, from Fig. 4 one can see that the magnitude of the diffusion potential is small, about 0.2 mV. In addition, the mean activity of MI is affected to become smaller. Actually, this latter effect on the plots in Fig. 3 is negligibly small. For example, the mean activity of MI at $c_{\mathrm{MI}} = 1\ \mu\mathrm{mol\,dm^{-3}}$, 0.9988, is lowered to 0.9835 by the saturation of W with $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$. This causes the change in $\log a^{\pm}$ by 6.7×10^{-3}, which is invisible in the plots.

Although the plots in Fig. 3 are not sensitive enough to detect the contribution of the diffusion potential to E even at 1 $\mu\mathrm{mol\,dm^{-3}}$, the deviation of experimental points from the Nernst slope is definitely smaller than those found in the ILSBs made of 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide [7] at $I = 50\ \mu\mathrm{mol\,dm^{-3}}$ and *N*-alkyl-*N*-methylpyrrolidinium $\mathrm{C_2C_2N^-}$ [15] at 10 $\mu\mathrm{mol\,dm^{-3}}$, which fact suggests that pH of very dilute aqueous samples can be determined with the accuracy better than 0.5/59 = 0.008 by using $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$.

3.4. Difference in E for different iodide salts

If the liquid junction potential between the IL and the iodide solution (phase V) does not depend on the type of electrolyte in phase V, the difference in E obtained with two different iodide solutions at a given value of $a^{\pm}$ is

$$\Delta E = E(\mathrm{LiI}) - E(\mathrm{KI}) = -\frac{RT}{F}\ \ln\frac{a_{\mathrm{I^-}}^{\mathrm{V}}(\mathrm{LiI})}{a_{\mathrm{I^-}}^{\mathrm{V}}(\mathrm{KI})} \qquad (3)$$

where $a_{\mathrm{I^-}}^{\mathrm{V}}(\mathrm{LiI})$ and $a_{\mathrm{I^-}}^{\mathrm{V}}(\mathrm{KI})$ are the activities of $\mathrm{I^-}$ in phase V containing, Li and KI, respectively. The plots in Fig. 3 for LiI, NaI, and KI can be represented as the single line within experimental error, so that $\Delta E \simeq 0$ in the concentration range studied. This result is reasonable, because in the low concentration range between 1 $\mu\mathrm{mol\,dm^{-3}}$ and 1 $\mathrm{mmol\,dm^{-3}}$ the contribution of ion-specific interactions to the activity of $\mathrm{I^-}$ is negligible, and is consistent with our presumption that the $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ properly functions as a salt bridge in these dilute solutions. Further tuning of IL-constituent ions for the comparable mobility values is desired for more precise verification of the stability of the liquid junction potential between the IL and an aqueous solution of very low ionic strength.

4. Conclusions

The phase-boundary potential between the IL, $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$, and a dilute aqueous solution is stable down to a micromolar range of 1:1 electrolytes. This is important because in this concentration range the Debye–Hückel limiting law, Eq. (1), which does not require ion-specific adjustable parameters, is employed to reliably calculate the activity coefficients of single ions. The relatively low solubility of $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$, 0.2 $\mathrm{mmol\,dm^{-3}}$, is preferable for its use as a salt bridge because even when a sample solution is saturated with the IL the Debye–Hückel limiting law still applies at this ionic strength with 2% error in the common logarithm of the ion activity. In the determination of single ion activities and other potentiometric measurements of very dilute aqueous solutions, this merit of low solubility of the IL outweighs a possible drawback of the larger electrochemical polarizability at the IL|W interface [5], which can make the phase-boundary potential vulnerable to lipophilic interfering ions. In addition, the weakness of tetraalkylphosphonium ions, that is, the decomposition in alkaline solutions [31,32] is not a problem in use of $[\mathrm{TBMOEP^+}][\mathrm{C_2C_2N^-}]$ as the ILSB for very dilute aqueous solutions.

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