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A New Salt Bridge Based on the Hydrophobic Room-Temperature Molten Salt

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A conceptually new salt bridge based on a hydrophobic room-temperature molten salt (ionic liquid) has been demonstrated to be a promising alternative to traditional salt bridges based on a concentrated aqueous KCl phase. 1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ($C_8mimC_1C_1N$), which is immiscible with water and forms a liquid–liquid two-phase system, exhibits a stable phase-boundary potential when sandwiched by two aqueous electrolyte solutions. The phase-boundary potential between the interface is determined by the partition of C_8mim^+ and $C_1C_1N^-$ ions in the aqueous phase (W) and is little affected by the type of electrolytes and their concentrations in W, provided that ions dissolved in W are hydrophilic enough. The gelation of the molten salt phase does not affect the phase-boundary potential. The new salt bridge is free from most of the problems inherent to KCl-based salt bridges.

Over one hundred years since Bjerrum demonstrated that the insertion of a concentrated KCl aqueous solution between two dilute aqueous electrolyte solutions can effectively eliminate the liquid junction potential (ljp),[1] there has virtually been no choice but a concentrated aqueous potassium chloride solution to minimize the ljp between two aqueous electrolyte solutions of different compositions. The working principle of the salt bridge of this type is based on the similar mobility of K^+ and Cl^- ions and its high concentration in comparison with other electrolytes in the adjacent solution; the diffusion potential caused by the flow of a concentrated KCl solution out of the bridge overwhelms the ljp, irrespective of the type and the concentration of other electrolytes in a sample solution.[2] In fact, the elimination of the ljp using the KCl salt bridge is achieved only approximately and even a salt bridge comprised of a solution saturated with KCl cannot reduce the ljp below a few mV when a sample solution is fairly acidic or alkaline.[3] The performance of such extent is intrinsic to this type of salt bridges.[4]

Moreover, there are several inescapable problems in KCl-based salt bridges. First, the dissolution of KCl out of the bridge contaminates the sample solution, which necessitates in some cases the avoidance of KCl. Second, the flowing out of KCl causes the deterioration of the bridge. The decrease in the KCl concentration results in a less stable ljp and also affects the electrode potential of the reference electrode. This concentration change poses maintenance problems of renewing the internal solution frequently. Maintenance of the KCl solution is particularly troublesome in long-term pH measurements, such as those in industrial processes and environmental monitoring. Third, the contact of the concentrated KCl solution with a solution of low ionic strength, such as rain water, causes clogging of the junction, which leads to error in the determination of pH.[5–7] Usually, to suppress the dissolution of AgCl from the reference Ag/AgCl electrode into the concentrated KCl solution, the KCl solution used as the internal solution is saturated with AgCl, and hence contains complex ions, primarily $AgCl_2^-$ and $AgCl_3^{2-}$.[8,9] Upon contact with a dilute aqueous solution at the junction, these species precipitate as AgCl and the junction may be clogged with these precipitates. Fourth, due to the kinetic nature of the diffusion potential formed at the liquid junction, the ljp depends on the details of the mass transport at the junction.[10,11] Several different types of junction have been proposed and one type over others has been recommended depending on specific purposes. However, there seems to be no general rule in choice and none are ideal.

Recently, we reported that the phase-boundary potential between a hydrophobic room-temperature molten salt (RTMS, also called room-temperature ionic liquid) and an aqueous electrolyte solution is determined by the partition of the ions constituting the RTMS, as long as other ions in the aqueous phase are hydrophilic enough.[12] The phase-boundary potential in this case is of thermodynamic nature and does not depend on time and also on the shape of the interface. Based on these properties, we suggested that RTMSs immiscible with water, having moderate hydrophobicity, can be used as a new type of salt bridge.[12] The working principle of the salt bridge in this case is not the diffusion of ions, but on the equilibrium partition of ions constituting the bridge. In this paper, we will show that this conceptually new salt bridge can solve most of the problems inherent to century-old conventional salt bridges, while there do exist other factors to be taken into account in the use of RTMS-based salt bridges.

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I	II	III	IV	V	
	10 mmol dm^{-3}		a mmol dm^{-3}		
Ag/AgCl	C_8mimCl	C_8mimC_1C_1N		AgCl/Ag	**(A)**
	(W_{ref})	(RTMS)	(W)		

Scheme 1.

Experimental

Reagents. 1-Octyl-3-methylimidazolium chloride (C_8mimCl) was synthesized from 1-methylimidazole (Wako Pure Chem., 98+%) and 1-chlorooctane (Aldrich 99%).[13] 1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide (C_8mimC_1C_1N) was prepared by mixing equimolar amounts of methanol solutions of C_8mimCl and bis(trifluoromethylsulfonyl)imide acid (HC_1C_1N) solutions. HC_1C_1N was obtained from Central Glass Co., Ltd. (Japan). Poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VdF-HFP), average MW 400000) was purchased from Aldrich. Other chemicals were of reagent grade.

The gelation of C_8mimC_1C_1N was accomplished by adding P(VdF-HFP) in acetone.[14] Acetone was allowed to evaporate overnight to obtain a disk-shaped membrane. The gellation of C_8mimC_1C_1N was successful when the weight percent of C_8mimC_1C_1N to the sum of C_8mimC_1C_1N and P(VdF-HFP) was less than 80.

Methods. The electrochemical cell we employed for potentiometry is similar to the one we previously reported (Scheme 1).[12] C_8mim$^+$ in W_{ref} is the potential-determining ion that assures the stable phase-boundary potential between the RTMS and the W_{ref} phases. The phase-boundary potential across the RTMS|W interface may vary with the composition of the W phase. The cell voltage, i.e., the potential of the right-hand-side terminal referred to that of the left in the cell (**A**), E, was measured with an electrometer with a GPIB interface, as described elsewhere.[12] When the RTMS phase was not gelled, the structure of the glass cell for potentiometric measurements was the same as that reported previously.[12] The thickness of the RTMS phase was about 5 mm. The temperature of the cell was maintained at 25 ± 0.2 °C by circulating water through the outer jacket of the cell. Figure 1 illustrates the structure of the cell used for potentiometry of gelled C_8mimC_1C_1N. The lower aqueous phase is W_{ref} and the upper is the W in cell (**A**). The thickness of the gelled RTMS membrane was about 0.5 mm. The RTMS membrane was sandwiched by the upper and lower parts of the cylindrical cell containing aqueous solutions and Ag/AgCl electrodes with a clamp. Measurements in this case were made at room temperature, 25 ± 1 °C.

Each potentiometric measurement was usually started within one minute after filling of the aqueous solution in the upper compartment of the cell (phase **IV**). Before the filling, the solution was kept in a water bath that was used also for circulating water through the jacket of the glass cell, so that the temperature difference between the filling solution and the RTMS phase was minimized. Aqueous solutions of HCl, LiCl, NaCl, and KCl were saturated with C_8mimC_1C_1N prior to potentiometry measurements.

The solubility of C_8mimC_1C_1N was measured spectrophotometrically using a molar absorption coefficient of 4.18×10^3 mol dm^{-3} cm^{-1} at $\lambda_{max} = 212$ nm in W.[15] Samples for measuring the mutual solubility were prepared by equilibrating the RTMS with water in a sample tube immersed in a water bath at 25 ± 0.2 °C for 24 h. The solubility of C_8mimC_1C_1N in W was found to be 1.8 mmol dm^{-3} at 25 °C, which is slightly higher than the 1.4 mmol dm^{-3} we reported previously.[12]

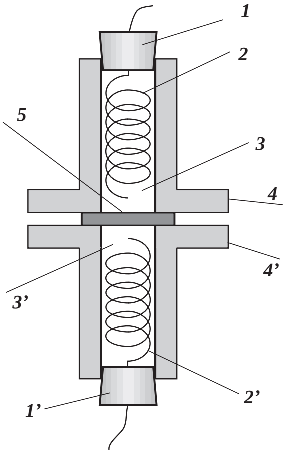

Fig. 1. Schematic view of the cell used for the potentiometric measurements with a gelled RTMS membrane. Thickness of the membrane was typically 0.5 mm. *1*, *1′*: rubber stoppers; *2*, *2′*: Ag/AgCl electrodes; *3*, *3′*: aqueous phases **IV** and **III** in cell (**A**), respectively; *4*, *4′*: glass tubes; *5*: RTMS membrane.

The factor of HCl solutions was determined to be 0.950 by the titration using sodium carbonate. Hereafter, we will use a nominal concentration for HCl, but this factor was taken into account in calculating the mean ionic activities. For measurements of E at different pH values, the KCl solutions were prepared with a phthalate buffer (pH = 4.0, $I = 0.16$ mol dm^{-3}), a phosphate buffer (pH = 7.0, $I = 0.22$ mol dm^{-3}), and borate buffers (pH = 10.0, 11.5, and 12.0, $I = 0.056$ mol dm^{-3}), where I is the ionic strength.

Results and Discussion

Response Time and Stability of Cell Voltage. We first examined the effect of the type and concentrations of MCl (M = H, Li, Na, and K) on the phase-boundary potential using cell (**A**). The cell voltage, E, was remarkably stable from the beginning of the measurement. Such a stable time dependence of E is exemplified for the first 30 min at different concentrations of HCl in both nongelled (Fig. 2a) and gelled (Fig. 2b) RTMS phases. Figures 3a and 3b show magnified views of Figs. 2a and 2b, respectively, for the initial 3 min at 0.1, 0.2, and 0.5 mol dm^{-3} HCl. One can see that E reaches a steady value within 1 min for all cases.

For nongelled RTMS, the standard deviation of E at a given concentration of HCl for 30 min was 0.2 mV on average for eleven concentrations between 1×10^{-3} to 2 mol dm^{-3}. For one sample of 10 mmol dm^{-3} HCl, the measurement was extended to 2 h and the standard deviation remained the same. This stability without significant long-term drift in E was seen for all electrolytes examined, i.e., KCl, NaCl, LiCl, and HCl, in the entire range of their concentrations between 1 mmol dm^{-3} and 2 mol dm^{-3}. The standard deviation for three sets of measurements for a given concentration of MCl (M = H, Li, Na, or K) was typically twice as large as the standard deviation within a single run. This suggests that the variation of E between different runs is related not to the variation of the phase-boundary potential at the RTMS|W interface but to other factors such as the change in the properties of Ag/AgCl electrodes, which

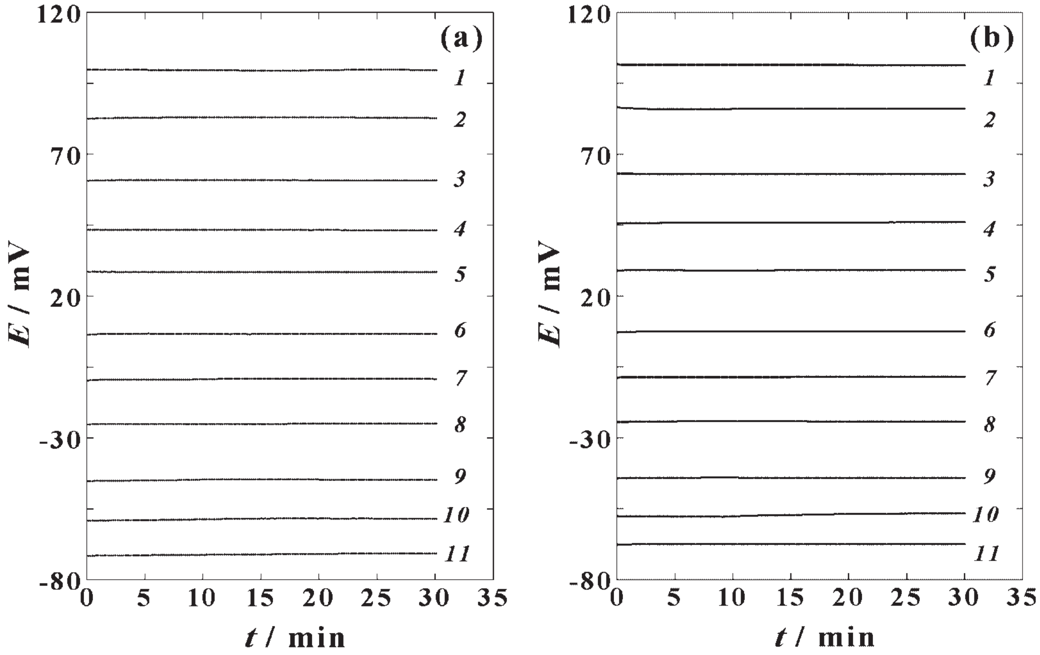

Fig. 2. Time dependence of the cell voltage for ungelled (**a**) and gelled (**b**) RTMS phases at different concentrations of HCl. Each point represents a value obtained from measurements for a single run. Concentrations of HCl: 1×10^{-3} (*1*), 2×10^{-3} (*2*), 5×10^{-3} (*3*), 1×10^{-2} (*4*), 2×10^{-2} (*5*), 5×10^{-2} (*6*), 1×10^{-1} (*7*), 2×10^{-1} (*8*), 5×10^{-1} (*9*), 1 (*10*), and 2 (*11*) mol dm^{-3}. Sampling interval: 10 s (**a**) and 5 s (**b**).

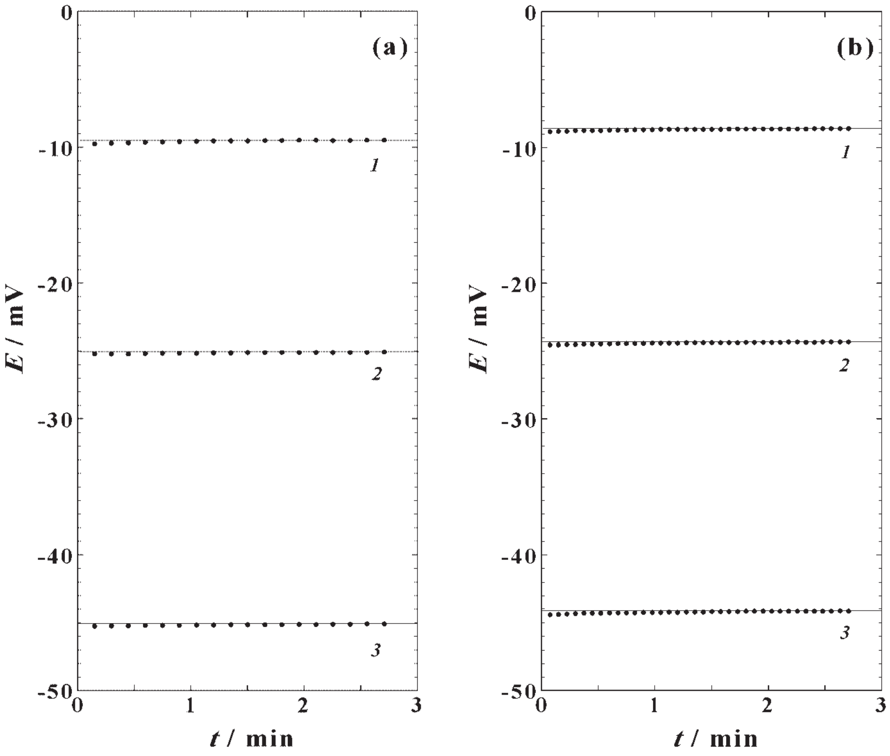

Fig. 3. Magnified view of Fig. 2 for ungelled (**a**) and gelled (**b**) RTMS phases in the first 3 min at three concentrations of HCl, 0.1 (*1*), 0.2 (*2*), and 0.5 (*3*) mol dm^{-3} HCl. Horizontal lines are to guide the eye.

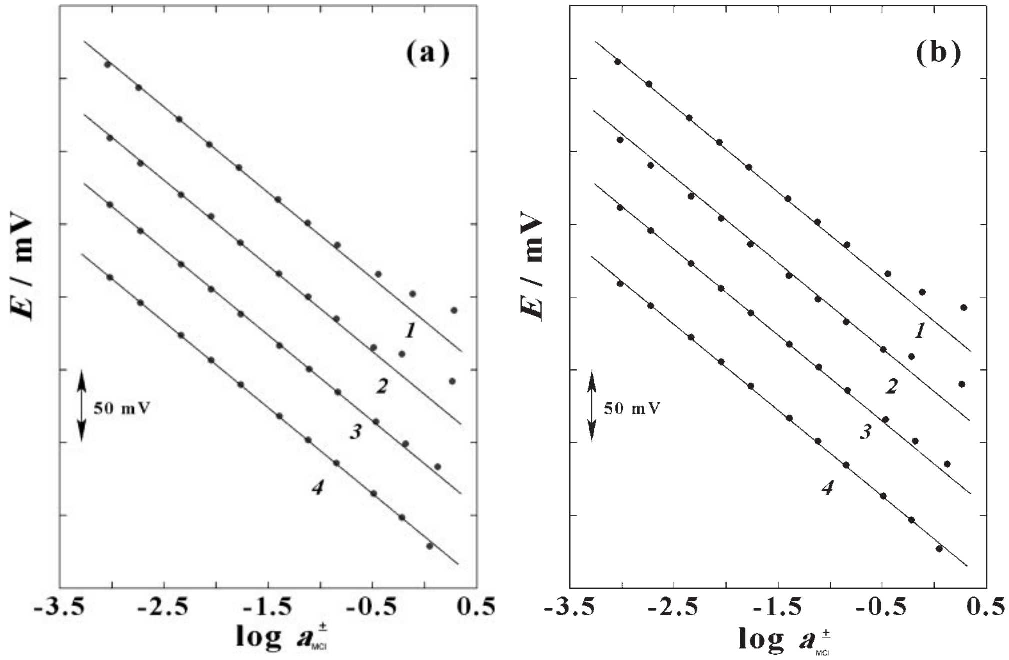

Fig. 4. Dependence of the cell voltage on the logarithm of the activity of the electrolytes, HCl (*1*), LiCl (*2*), NaCl (*3*), and KCl (*4*) for ungelled (**a**) and gelled (**b**) RTMS phases. Each point represents the average value of triplicate measurements over 30 min. Solid lines have a slope of 59.2 mV per decade, which is expected when Ag/AgCl ideally responds to the activity of Cl^- and $\Delta_{\mathrm{M}}^{\mathrm{W}}\phi$ remains constant.

often show variability of this magnitude in the potential in repeated washing and drying to prepare a new cell.

Effect of the Type and Concentration of MCl on the Phase-Boundary Potential at RTMS|W Interface. The variation of E with the logarithm of the mean ionic activity of MCl, $\log a^{\pm}_{\mathrm{MCl}}$ (M = K, Na, Li, or H), is shown in Figs. 4a and 4b for nongelled and gelled RTMS phases. The mean activity coefficients were taken from the literature for the concentrations higher than 0.1 mol dm^{-3} [16] or calculated otherwise using the extended Debye–Hückel theory.[17] The solid lines indicate the Nernstian slope at 25 °C, $\ln(10) \times RT/F = 59.2$ mV per decade. It can be seen in Figs. 4a and 4b that for all 1:1 electrolytes examined, E shows the Nernstian response over a wide concentration range. This linear variation is ascribed to the Nernstian response of the Ag/AgCl electrode (**V** in cell (**A**)) to the change in the activity of Cl^- ions in **IV**, and hence, is direct evidence that the phase-boundary potential between phases **III** and **IV**, $\Delta_{\mathbf{III}}^{\mathbf{IV}}\phi = \phi^{\mathbf{IV}} - \phi^{\mathbf{III}}$, remains constant when the composition of phase **IV** is varied, where $\phi^{\mathbf{III}}$ and $\phi^{\mathbf{IV}}$ are the inner potentials of phases **III** and **IV**. The stable value of $\Delta_{\mathbf{III}}^{\mathbf{IV}}\phi$ is established by equilibrium partition of $\mathrm{C_8mim^+}$ and $\mathrm{C_1C_1N^-}$ ions in W.[12]

The RTMS composed of $\mathrm{C_8mimC_1C_1N}$ thus works as a novel salt bridge whose working principle is the partition of the potential-determining ions, $\mathrm{C_8mim^+}$ and $\mathrm{C_1C_1N^-}$ ions, and hence, is of time-independent, thermodynamic character. The fact that $\Delta_{\mathbf{III}}^{\mathbf{IV}}\phi$ is governed by the partitioning of $\mathrm{C_8mim^+}$ and $\mathrm{C_1C_1N^-}$ ions into W irrespective of the type of MCl over the wide concentration range assures that both nongelled and gelled RTMSs work perfectly as ideal salt bridges. The RTMS bridge does not eliminate the phase-boundary potential between the RTMS|W interface, but it eliminates the ljp between the two aqueous solutions by maintaining the two phase-boundary potentials at constant values over the change in the composition of the electrolyte solutions.

Distribution Potential Determined by the Partition of $\mathbf{C_8mimC_1C_1N}$. When a hydrophobic RTMS composed of a single monovalent cationic species C^+ and a single monovalent anionic species A^- is in contact with water and there are no electrolytes other than C^+ and A^- in the two-phase system, the distribution potential is determined by the partition of C^+ and A^- between the two phases and is given by the equation:[12]

$$\begin{aligned}\Delta_{\mathrm{M}}^{\mathrm{W}}\phi = \phi^{\mathrm{W}} - \phi^{\mathrm{M}} &= -\frac{\Delta G_{\mathrm{C^+}}^{\mathrm{M}\to\mathrm{W},0} - \Delta G_{\mathrm{A^-}}^{\mathrm{M}\to\mathrm{W},0}}{2F} \\ &= \frac{\Delta_{\mathrm{M}}^{\mathrm{W}}\phi_{\mathrm{C^+}}^{0} + \Delta_{\mathrm{M}}^{\mathrm{W}}\phi_{\mathrm{A^-}}^{0}}{2}, \end{aligned} \tag{1}$$

where super- and subscripts, M and W, designate the RTMS and W phases, respectively, $\Delta G_{\mathrm{i}}^{\mathrm{M}\to\mathrm{W},0}$ is the standard Gibbs energy of transfer of i from M to the aqueous phase W, and $\Delta_{\mathrm{M}}^{\mathrm{W}}\phi_{\mathrm{i}}^{0}$ ($\mathrm{i} = \mathrm{C}^+$ or A^-) is the standard ion-transfer potential between M and W, respectively.[12] This equation has the same form as that of the distribution potential of a single 1:1 salt between two-immiscible solutions.[18] Strictly speaking, the change in the activities of $\mathrm{C_8mim^+}$ and $\mathrm{C_1C_1N^-}$ in W due to the change in the concentration of the electrolyte in W can affect $\Delta_{\mathrm{M}}^{\mathrm{W}}\phi$. The activity coefficients term neglected in Eq. 1 is

$$\frac{RT}{2F}\ln\frac{\gamma_{\mathrm{C^+}}^{\mathrm{M}}}{\gamma_{\mathrm{A^-}}^{\mathrm{M}}}\frac{\gamma_{\mathrm{C^+}}^{\mathrm{W}}}{\gamma_{\mathrm{A^-}}^{\mathrm{W}}} \simeq \frac{RT}{2F}\ln\frac{\gamma_{\mathrm{C^+}}^{\mathrm{W}}}{\gamma_{\mathrm{A^-}}^{\mathrm{W}}}, \tag{2}$$

where γ_i^α is the activity coefficient of ion i in the phase α ($i = C^+$ or A^- and $\alpha = R$ or W). The effect of the change in γ_i^W for C^+ and A^- in W on $\Delta G_i^{M\to W,0}$, however, would be small, because they are likely to change in parallel with each other with the change in the ionic strength. This explains the Nernstian slope between 0.002 to 0.5 mol dm^{-3} for all the electrolytes studied and up to 2 mol dm^{-3} in the case of KCl (Figs. 4a and 4b). The observed constancy of $\Delta_M^W\phi$ indicates that Eq. 1 applies well to the present system and implies that the distribution of M^+ and Cl^- in the RTMS phase is negligible.

It is important and interesting to know the value of $\Delta_{III}^{IV}\phi$ to understand the degree of interference by the partition of other ionic species. Unfortunately, no data are available for $\Delta G_i^{M\to W,0}$ and $\Delta_M^W\phi_i^0$ for relevant ionic species. In RTMS–W two-phase systems, these values depend on the particular RTMS employed because each RTMS has its own solvation environment. Because of this reason, it is not possible to have a unique scale for $\Delta G_i^{M\to W,0}$ and $\Delta_M^W\phi_i^0$ that is valid for different RTMSs. Nevertheless, it is convenient to have a ballpark measure of $\Delta G_i^{M\to W,0}$ and $\Delta_M^W\phi_i^0$. One convenient measure of this type that has been used for estimating the hydrophobicity of ionic species is the Gibbs energy of ion transfer and the standard ion-transfer potential in 1,2-dichloroethane (DCE)–water two-phase systems.[19,20] In fact, we found recently that these values are proportional to the half-wave potentials of ion transfer at the tetrahexylammonium C_1C_1N|W and octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate|W two-phase systems.[21,22] The apparent value of $\Delta_{DCE}^W\phi_{C1C1N}^0$ is 0.093 V. The solubility product of $C_8mimC_1C_1N$, K_s^W, is related to the difference in the standard ion-transfer potentials:[12]

$$K_s^W = \exp\left[\frac{F}{RT}\left(\Delta_M^W\phi_{C^+}^0 - \Delta_M^W\phi_{A^-}^0\right)\right]. \tag{3}$$

From the solubility of $C_8mimC_1C_1N$, 1.8 mmol dm^{-3}, $\Delta_{DCE}^W\phi_{C8mim}^0$ is evaluated to be −0.23 V. Then, from Eq. 1, $\Delta_{III}^{IV}\phi$ is estimated to be −0.07 V. Because of the similar magnitude of hydrophobicity of these ions, the value of $\Delta_{III}^{IV}\phi$ is therefore small. Indirect evidence for the balancing of the hydrophobicity of C_8mim^+ and $C_1C_1N^-$ has been obtained in the electrocapillarity of the $C_8mimC_1C_1N$|W interface.[23] On the other hand, the values of $\Delta_{DCE}^W\phi_i^0$ for H^+, Li^+, Na^+, and K^+ are 0.549, 0.591, 0.591, and 0.508 V, respectively. They are about 0.6 V away from the $\Delta_{III}^{IV}\phi$ value, which explains the absence of the interference of these ions.

Polarizability of the RTMS|W Interface. In this type of salt bridge, the polarizability of the liquid junction is an important factor to be examined for practical use of RTMS-based bridges. It has been shown that the charge-transfer resistance at zero current, $R_{I=0}$, is related to the solubility of the RTMS:[24]

$$R_{I=0} \propto \exp\left[\frac{F}{2RT}\left(\Delta_M^W\phi_{A^-}^0 - \Delta_M^W\phi_{C^+}^0\right)\right] = 1/\sqrt{K_s^W}. \tag{4}$$

The polarizability is, thus, inversely proportional to the squareroot of K_s^W or to the solubility of the RTMS.

The lower the solubility, the lesser the extent of sample contamination with the RTMS is. However, Eq. 4 shows that lowering the solubility inevitably leads to an increase in the polarization resistance; therefore, there must be a compromise between the solubility and the polarizability in selecting ions for a RTMS. A similar RTMS composed of C_8mim^+ and bis(pentafluoroethylsulfonyl)imide (C_2C_2N), having a lower solubility of 1.1 mmol dm^{-3} in W, also satisfactorily functions as a RTMS bridge, as reported preliminarily.[12] On the other hand, voltammetry measurements show that both $C_8mimC_1C_1N$ and $C_8mimC_2C_2N$ behave as electrochemically nonpolarized interfaces,[24,25] which makes these RTMSs appropriate as salt bridges.

Deviation of *E* from Nernstian Behavior. Figures 4a and 4b show that *E* deviates from the straight lines at higher concentrations of NaCl, LiCl, and HCl, and the degree of the deviation becomes more discernible in this order; the concentration where the deviation becomes greater than 2 mV is lower in the order NaCl (1 mol dm^{-3}), LiCl (0.5 mol dm^{-3}), and HCl (0.2 mol dm^{-3}). At 2 mol dm^{-3} LiCl and HCl, the deviation is about 20 mV. This is comparable to a calculated value of the ljp between a saturated aqueous KCl and 1 mol HCl, 16 mV.[3] It is also comparable with a calculated value, 17.1 mV, as the difference in ljp between 2 mol and 0.1 dm dm^{-3} HCl in contact with the aqueous saturated KCl phase.[26]

According to the concept of mixed potentials in ion-selective electrodes, the deviation in this direction is caused by the interference by cations in the aqueous phase or by anions in the RTMS phase.[27,28] The hydrophilicity of H^+, Li^+, and Na^+ are comparable and K^+ is less hydrophilic in the DCE–W two-phase systems, as described above.[29] We might expect a greater interference from K^+; however, the trends in Figs. 4a and 4b was opposite. We believe that the affinity of Li^+ and H^+ ions to $C_1C_1N^-$ is higher than Na^+ and K^+. The complex formation of Li^+ with $C_1C_1N^-$ has been confirmed recently by Raman spectroscopy.[30] This type of specific interaction between ions in the aqueous phase and those in the RTMS is presumed to be responsible for the anti-Hofmeister trend in the deviation from the Nernstian slopes. Another conceivable reason for the deviation from the Nernstian slope is the effect of dissolved oxygen on the potential of Ag/AgCl electrodes. The direction of the deviation agrees with this possible oxygen effect.[31] However, the magnitude of the deviation is on the order of sub mV, which is much smaller than the deviation in Figs. 4a and 4b.

Effect of the Gellation of RTMS on Stability of *E*. It can be clearly seen from a comparison of the results of nongelled and gelled RTMSs compared in Figs. 2, 3, and 4 that the gellation does not appreciably affect the stability of *E*. Although the gelled membrane was not saturated with water prior to the measurements, no appreciable drift in *E* was observed. The standard deviation within a single run, 0.068 mV, was comparable to or even better than that in non-gelled RTMS. The inertness of P(VdF-HFP) gel to the potentiometric response was seen in the all electrolytes examined and throughout the concentration range studied between 1×10^{-3} to 2 mol dm^{-3} (Figs. 4a and 4b). This is of particular importance in the practical use of the new salt bridge in a variety of occasions where gellation is required. P(VdF-HFP) seems to be satisfactory in this respect.

Another important conclusion deduced from the comparison is that the difference in the physical structure of the contact

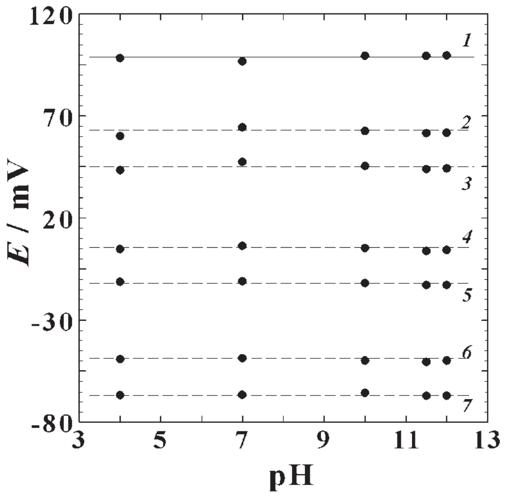

Fig. 5. Effect of pH on E at different concentrations of KCl in phase (**IV**) for an ungelled RTMS. The concentration of KCl: 1, 5, 10, 50, 100, 500, and 1000 mmol dm^{-3}.

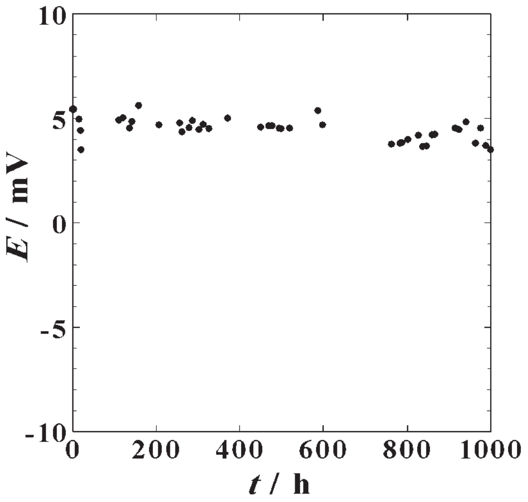

Fig. 6. Long-term stability of E of cell (**A**) from single-run measurements when 50 mmol dm^{-3} KCl was in phase (**IV**). Phase **III** was $C_8mimC_1C_1N$ without gellation.

between the RTMS and a sample solution does not appear to influence the values of E and its time dependence. This highlights the advantage of the liquid junction of the distribution-potential type over that of the diffusion-potential type for a salt bridge.

Effect of pH on $\Delta_{\mathrm{M}}^{\mathrm{W}}\phi$. Figure 5 shows the effect of pH on E at different concentrations of KCl in buffer solutions at pH = 4, 7, 10, 11.5, and 12. A phthalate buffer and a phosphate buffer were used for the former two, and borate buffers were used for the latter three. The Nernstian response was observed against the mean ionic activity of KCl at all pH values examined. The slopes at pH = 4, 7, 10, 11.5, and 12 were, 59.0, 59.3, 59.7, 59.1, and 59.8 mV/decade, respectively. $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$ is thus stable within the pH range examined. Ions used for preparing buffers were all hydrophilic and had no appreciable effect on $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$ for the same reason as the absence of interference of alkaline ions.

Contribution of Diffusion Potential to $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$. When a sample solution is not saturated with the RTMS, the RTMS starts to partition into the solution. This dissolution should give rise to a certain diffusion potential unless the mobility of the cation and the anion constituting the RTMS is the same. This diffusion potential can contribute to $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$.[32,33] In the diffusion of C_8mim^+ and $C_1C_1N^-$ ions in **IV**, the concentration of C_8mim^+ and $C_1C_1N^-$ at the interface between the phases **III** and **IV** is kept constant at 1.8 mmol dm^{-3} by the solubility product of $C_8mimC_1C_1N$, aside from the difference in the concentration of C_8mim^+ and $C_1C_1N^-$ at the interface due to the double-layer effect. There should be no concentration gradient of MCl in **IV**. The Henderson equation is in this case given by[4]

$$\Delta_{\mathrm{IV}}^{\mathrm{III}}\phi_{\mathrm{diff}} = \frac{u_{\mathrm{C8mim^+}}c^{\sigma}_{\mathrm{C8mim^+}} - u_{\mathrm{C1C1N^-}}c^{\sigma}_{\mathrm{C1C1N^-}}}{u_{\mathrm{C8mim^+}}c^{\sigma}_{\mathrm{C8mim^+}} + u_{\mathrm{C1C1N^-}}c^{\sigma}_{\mathrm{C1C1N^-}}} \times \frac{RT}{F}\ln\frac{u_{\mathrm{C8mim^+}}c^{\sigma}_{\mathrm{C8mim^+}} + u_{\mathrm{C1C1N^-}}c^{\sigma}_{\mathrm{C1C1N^-}} + u_{\mathrm{M^+}}c^{\sigma}_{\mathrm{M^+}} + u_{\mathrm{Cl^-}}c^{\sigma}_{\mathrm{Cl^-}}}{u_{\mathrm{M^+}}c^{\mathrm{IV}}_{\mathrm{M^+}} + u_{\mathrm{Cl^-}}c^{\mathrm{IV}}_{\mathrm{Cl^-}}}, \qquad (5)$$

where u_i is the mobility of ion i in W and c_i is the concentration of i. The superscript σ and **IV** designate the surface of the RTMS and the phase **IV**, respectively.

When the concentration of electrolytes in **IV**, $c_{\mathrm{MCl}}^{\mathrm{IV}}$, is much higher than $c^{\sigma}_{\mathrm{C8mim^+}}$ and $c^{\sigma}_{\mathrm{C1C1N^-}}$, Eq. 5 tells us that the ljp is negligible no matter how big the difference in the mobility of C_8mim^+ and $C_1C_1N^-$ in W is. This is because there is no concentration gradient in MCl in W and $c^{\mathrm{W}}_{\mathrm{C_8mim^+}} \simeq c^{\mathrm{W}}_{\mathrm{C_1C_1N^-}} \ll c^{\mathrm{W}}_{\mathrm{MCl}}$ everywhere in W.

When the electrolyte concentration of a sample solution is comparable to or lower than the solubility of $C_8mimC_1C_1N$, the diffusion potential may not be negligible. Our preliminary data of voltammetry of ion transfer (data not shown) suggest that there is no significant difference in the mobility of C_8mim^+ and $C_1C_1N^-$ in W. therefore, it seems that the diffusion potential on the aqueous side of the $C_8mimC_1C_1N$|W interface would be small even at lower ionic strengths.

Long-Term Stability. We monitored E over 40 days for the nongelled case as shown in Fig. 6. The aqueous phase (**IV**) was 0.05 mol dm^{-3} KCl saturated with $C_8mimC_1C_1N$. The initial value, about 4.8 mV, decreased to 4.2 mV after 40 days. There are four phase boundaries in cell (**A**), **I**|**II**, **II**|**III**, **III**|**IV**, and **IV**|**V**. The sum of fluctuations and drifts can contribute to E. It is unlikely that the observed drift is solely attributable to the variation of $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$, whose stability we are concerned with. We plan to do similar experiments with a better design of the cell for monitoring the long-term stability of $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$. We note at this moment that the stability of this magnitude may suffice for certain purposes, for example, monitoring of pH in wastewaters, even when the variation is ascribed to $\Delta_{\mathrm{III}}^{\mathrm{IV}}\phi$.

Safety and Other Points of Concern. While KCl is safe and chemically fairly inert, the risk potential of ionic liquids are currently under scrutiny.[34–36] In the present study, $C_8mimC_1C_1N$ was chosen as a representative of RTMSs that form a nonpolarized interface with an aqueous phase. Moderately hydrophobic ions, in particular anions, are potentially uncouplers in biological systems and must be handled with care. C_8mim^+ is one cationic surfactant whose toxicity and behavior in the environment have been revealed.[37–39] In this respect, the optimization of the type of ions constituting RTMS bridges should be made taking into account their possible environmental impacts.

Unlike KCl-bridges, the phase-boundary potential in the RTMS bridge is interfered with by hydrophobic ions whose standard ion-transfer potentials are close to the distribution potential of the RTMS, when the concentration of interfering ions is comparable or higher than the solubility of the RTMS in W. This type of interference is similar to that seen at the liquid-membrane-type ion-selective electrodes.[28,40]

Ions constituting the RTMS are soluble more or less in sample solutions. The dissolved ions may specifically interact with the electrode inserted in the sample solution, for example, a glass electrode for potentiometry or a platinum electrode for voltammetry, and may influence the response of these indicator electrodes. This point should be given thought before the use of RTMS bridges for particular applications. In pH measurements with a glass electrode, it seems unlikely that the interaction of C_8mim^+ or $C_1C_1N^-$ with the glass surface is strong to the extent that the potentiometric response of the glass to pH will be affected. The interaction of the constituent ions may become serious in the case of liquid-membrane electrodes and surface-sensitive studies in electrochemistry, e.g., electrosorption on the electrode surface.

Conclusion

After one hundred years of using KCl-type salt bridges, we now have an alternative that can solve many of the problems unavoidable in conventional salt bridges based on the diffusion potential. The RTMS bridge does not eliminate the phase-boundary potential between the RTMS|W interface, but it eliminates the ljp between the two aqueous solutions by maintaining the two phase-boundary potentials at constant values over the change in the composition of the electrolyte solutions. Further optimization is possible and necessary for specific purposes. Since many hydrophobic RTMSs do not mix with nonpolar organic solvents and also some alcohols, the RTMS bridge is promising also in bridging aqueous and nonaqueous media. RTMS bridges, after careful designing, can make a difference in electrochemical measurements, in particular potentiometry.

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