

Stability of a Ag/AgCl Reference Electrode Equipped with an Ionic Liquid Salt Bridge Composed of 1-Methyl-3-octylimidazolium Bis(trifluoromethanesulfonyl)-amide in Potentiometry of pH Standard Buffers

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The stability of a Ag/AgCl reference electrode equipped with a gelled ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ($C_8mimC_1C_1N$), as a salt bridge, was examined in the potentiometry of pH standard solutions. The variation in the liquid junction potential (LJP) of the ionic liquid (IL)-type reference electrode, measured with respect to a double junction-type KCl reference electrode, was within 1 mV when one standard solution was replaced by another, except for the phthalate standard. The time course of the potential of the IL-type reference electrode showed a standard deviation of ± 0.3 mV in all buffer solutions. The reproducible deviation of the potential of the IL-type reference electrode in the phthalate pH standard amounted to 5 mV. The deviation is due to the partition of the hydrogen phthalate in the $C_8mimC_1C_1N$, influencing the phase boundary potential (PBP) across the interface between $C_8mimC_1C_1N$ and the phthalate standard. If a citrate standard is used instead of the phthalate buffer, the IL salt bridge works satisfactorily as a salt bridge for a reference electrode suitable for potentiometric pH measurements.

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Introduction

Recently, a new salt bridge using a hydrophobic ionic liquid has been proposed¹⁻³ as an alternative to the conventional KCl salt bridge (KCISB). The ionic liquid salt bridge (ILSB) is promising for solving most problems inherent to the conventional KCISB, such as the contamination of samples, the requirement of frequently renewing the KCl solution, clogging of the junction, and the dependence of the liquid junction potential (LJP) on the type of the junction.² The ILSB has distinct advantages over the KCISB in potentiometric measurements of pH, for which it has been known that problems associated with the conventional KCISB hamper accurate pH determinations.⁴⁻⁷ In potentiometric pH measurements using a glass electrode and a reference electrode, a pH cell should be calibrated using pH standards, such as phosphate, phthalate, and borax buffers before a measurement.^{8,9} A salt bridge that shows a stable LJP between a salt bridge and a pH standard over time is desirable when one standard is replaced by another. In the present work, we gelled an ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ($C_8mimC_1C_1N$), to form a disk and mounted it on a cylindrical plastic tube membrane holder for examining the stability of the potential with respect to a double junction-type reference electrode equipped with a KCISB. We will demonstrate that the ILSB shows a stable potential in pH standard buffers, and meets the requirements for

a reference electrode, except for the case of the phthalate buffer, where hydrogen phthalate ions interfere with the phase boundary potential (PBP) across the ILSB | phthalate buffer interface.

Experimental

Reagents

1-Methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)-amide ($C_8mimC_1C_1N$) was obtained from Nippon Synthetic Chemical Industry Co., Ltd. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, average M_w 40000) was obtained from Aldrich. A phthalate standard solution (0.05 mol kg^{-1} $KHC_8H_4O_4$, $pH = 4.01 \pm 0.05$ at 25°C), a phosphate standard solution ($0.025 \text{ mol kg}^{-1}$ $KH_2PO_4 + 0.025 \text{ mol kg}^{-1}$ Na_2HPO_4 , $pH = 6.86 \pm 0.05$ at 25°C), and a borax standard solution (0.01 mol kg^{-1} $Na_2B_4O_7 \cdot 10H_2O$, $pH = 9.18 \pm 0.05$ at 25°C) were obtained from Horiba, Ltd. (150-4, 150-7, and 150-9). The 0.05 mol kg^{-1} citrate buffer solution ($pH 3.78$ at 25°C)¹⁰ was prepared by dissolving 11.41 g of $KH_2C_6H_5O_7$ (Kanto Chemical Co., Inc., 98%) in pure water and diluting it to $1.000 \pm 0.0004 \text{ dm}^3$. A 3.33 mol dm^{-3} potassium chloride solution (Horiba, 300) was used. Other chemicals were of reagent grade.

$C_8mimC_1C_1N$ was gelled by dissolving 8 g of P(VdF-HFP) and 0.008 dm^3 $C_8mimC_1C_1N$ in 0.1 dm^3 acetone and evaporating acetone in the mixture for two weeks at room temperature to obtain a disk-shaped membrane.¹¹

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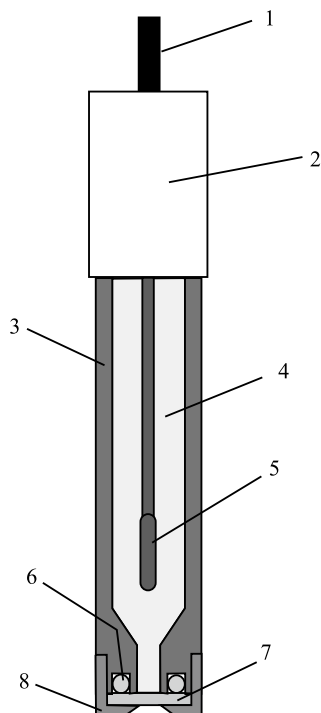


Fig. 1 Schematic view of the ionic liquid-type reference electrode. 1, Lead wire; 2, cap; 3, plastic tube; 4, 3.3 mol dm⁻³ KCl aqueous solution; 5, Ag/AgCl electrode; 6, O-ring; 7, gelled ionic liquid; 8, cylindrical cap.

Methods

Figure 1 illustrates the structure of an ionic liquid (IL)-type reference electrode equipped with gelled C₈mimC₁C₁N. In the IL-type reference electrode, a disk-shaped membrane of the gelled ionic liquid, whose diameter and thickness were 12 mm and 1 mm, respectively, was mounted with a silicone O-ring to the cylindrical body of a reference electrode. The inner cell was composed of an Ag/AgCl electrode in a 3.3 mol dm⁻³ KCl aqueous solution. The Ag/AgCl electrode was prepared by immersing a 0.8-mm diameter silver wire in molten AgCl at 480°C, and drying it at room temperature. The resistance of the gelled C₈mimC₁C₁N membrane obtained by measuring the resistance between the IL-type reference electrode and the Ag/AgCl electrode in a 3.3 mol dm⁻³ KCl aqueous solution with a resistance meter (ADC Corporation, 8340A) was about 5 × 10³ ohm. Schemes 1 and 2 show the electrochemical cells that we employed to evaluate the IL-type and KCl-type references, respectively.

The left-half cells (phases I, II and III) in the entire cells (A) and (B) were composed of double junction-type reference electrodes (Horiba, Ltd., 2565A); the right-half cells in cells (A) and (B) were composed of an IL-type (Fig. 1) and a ceramic junction-type (Horiba, Ltd., 2060A) reference electrode, respectively. The double-dashed vertical bar indicates a liquid-liquid junction between two electrolyte solutions of the same composition, and the single dashed vertical bar indicates a liquid-liquid junction between two electrolyte solutions of different compositions. The cell voltage, E , *i.e.*, the potential of the right-hand-side terminal referred to that of the left in cell (A), was measured with a pH meter (Horiba, Ltd., F55) at a sampling rate of 0.1 Hz. A beaker containing a sample solution was set in a water bath kept at 25.0 ± 0.1°C. The electrodes were first rinsed with MilliQ water, and then dipped into a

I	II	III	IV	V	VI	VII
Ag/AgCl	3.3 mol dm ⁻³ KCl	3.3 mol dm ⁻³ KCl	pH standard solutions	gelled IL	3.3 mol dm ⁻³ KCl	AgCl/Ag (A)

Scheme 1

I	II	III	IV	V	VI
Ag/AgCl	3.3 mol dm ⁻³ KCl	3.3 mol dm ⁻³ KCl	pH standard solutions	3.3 mol dm ⁻³ KCl	AgCl/Ag (B)

Scheme 2

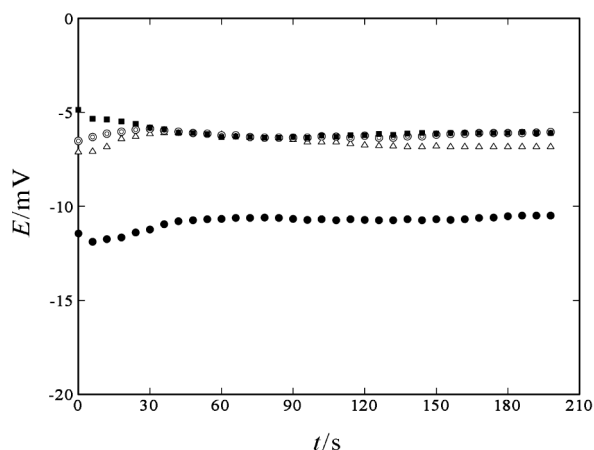


Fig. 2 Time dependence of E in cell (A) for 3 min in a phosphate standard, a phthalate standard, a borate standard, and a citrate standard. Double circle, a phosphate standard; filled circle, a phthalate standard; filled square, a borate standard; open triangle, a citrate standard.

beaker for a potentiometric measurement. The E of cell (A) was measured for 3 min in each measurement. Phase IV in cells (A) and (B) was changed in the following order: phosphate, phthalate, citrate, and borate. A series of measurements was repeated three times. The electrodes used for the measurements were washed for 10 s with MilliQ water after a measurement in each solution.

Results and Discussion

Figure 2 shows the time dependence of E for 3 min in four buffers. E reached a steady value after 3 min for all cases. The change in the values of E was within 0.3 mV in a few minutes after starting the measurements for the four buffers. The values of E after 3 min in a series of measurements are given in Fig. 3. The results of the same measurements using a ceramic junction-type reference electrode are also shown in Fig. 3.

The variation of E in Fig. 3 is ascribed to the variation of the LJP between the KCl solution (phase III) and each buffer (phase IV), and that of the PBP between the IL (phase V) and the buffer (phase IV). The variation of the LJP between the KCl

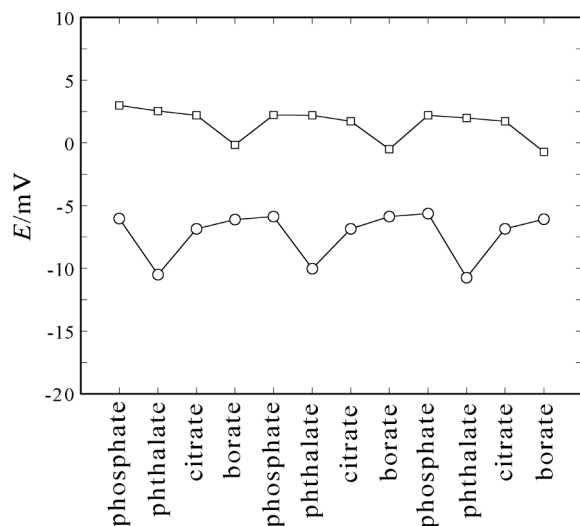


Fig. 3 E of IL-type and KCl-type electrodes after 3 min for measurements of pH standard solutions. Open circle, IL-type; open square, KCl-type.

solution and each buffer is known to be within 0.01 pH or 0.6 mV at 25°C.¹² The PBP between the IL (phase V) and the buffer (phase IV) is determined dominantly by the distribution potential by the partition of the cation and anion constituting the IL between the IL and an aqueous solution, when the ionic strength of the aqueous solution contacting with the IL is higher than 1 mmol dm⁻³.³ We therefore presume that the variation of E in cell (A) was caused by the distribution potential of the IL between the IL and a buffer solution. In Fig. 3, E in the phthalate buffer is lower than that in other buffer solutions by 4 mV. In contrast, the change in E was less than 1 mV in the citrate standard, whose pH was close to that of the phthalate standard. The small change in E in the citrate standard indicates that the specific change of E observed only in the phthalate buffer depends not on the pH, but on the composition of the solution.

The reproducible drop of E in the phthalate buffer suggests that the partition of the hydrogen phthalate (HPh⁻) in C₈mimC₁C₁N is non-negligible, and influences the PBP across the interface between C₈mimC₁C₁N and the phthalate standard. The PBP between an IL and water is constant, provided that the dissolution of the ions in W to the IL is negligible. The standard ion-transfer potential of the HPh⁻ in the nitrobenzene-water two phase system, $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{HPh}^-}^0$, is -195 mV,¹³ which is close to that of C₈mim⁺ ion, $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{C}_8\text{mim}^+}^0 = -220$ mV;¹⁴ that is, the hydrophobicity of the HPh⁻ is similar to that of C₈mim⁺. The dissolution of HPh⁻ into the ILSB in exchange for the transfer of C₁C₁N⁻, whose $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{C}_1\text{C}_1\text{N}^-}^0 = 114$ mV,¹⁵ from the ILSB to the phthalate buffer is therefore likely to take place, causing a change in the PBP. From a model of the mixed potential for the PBP across the two immiscible electrolyte solutions,^{16,17} it is expected that the PBP between the IL and the phthalate buffer, $\Delta\phi_{\text{IL}}^{\text{phtha}} = \phi_{\text{phtha}} - \phi_{\text{IL}}$, where ϕ_{phtha} and ϕ_{IL} are the inner potentials in the phthalate buffer and the IL, respectively, shifts to the positive direction, and hence E in cell (A) shifts to the negative. The expected direction of the shift of E is consistent with the results given in Fig. 3.

The variation in E of an IL-type reference electrode when one standard buffer solution was replaced by another was within 1 mV for the phosphate, borax, and citrate standards. The

standard deviation of E for triplicate measurements of the same solution was 0.4 mV. Figure 3 shows that the variation in the LJP of the ILSB is comparable to that of the KCISB, except for the case of the phthalate standard.

When a two-point calibration of a pH cell composed of a glass electrode and a reference electrode with buffers having pH values of pH_{S1} and pH_{S2} is made, the operative Nernst slope, k' , is represented by

$$k' = \frac{E_{S_2} - E_{S_1}}{\text{pH}_{S_2} - \text{pH}_{S_1}}, \quad (1)$$

where E_{S_2} and E_{S_1} are the pH cell voltage for buffers pH_{S2} and pH_{S1}, respectively, referred to the reference electrode. Practically, it may seem that the reproducible deviation of the PBP by 4 mV in the case of the phthalate buffer can be taken into account by the calibration procedure of the electrochemical cell. When the calibration is made at 25°C with the phthalate buffer (pH = 4.005) and the phosphate buffer (pH = 6.865), the theoretical difference in E is 169.20 mV. Assuming a 4-mV deviation of the PBP at the IL | buffer interface, we would read 173.2 mV for ΔE , and the calibration slope would be -60.56 mV/pH. If a sample solution whose pH value is 4.005, but with no partitioning of ions in the IL is measured with this cell, the reading of a pH meter using this cell would give a value of 4.069. Whether the error of 0.064 pH unit is permissible depends on the purpose of the pH measurements.

One serious problem concerning HPh⁻ interference in an ILSB made of C₈mimC₁C₁N is that HPh⁻ replaces C₁C₁N⁻ in the IL, and remains in the IL after contact of the ILSB with a HPh⁻ buffer. In this respect, the use of a citrate buffer, whose dissolution into the ILSB is negligible, is highly recommended when the two-point calibration of the pH cell is made before measuring an acid solution. It is expected that the HPh⁻ interference in the ILSB is reduced by positively shifting the standard transfer potentials of ions constituting the IL.

In Fig. 3, the ceramic plug-type KCISB showed an offset voltage of about 2 mV and a slight drift with the repetition of the measurements. Moreover, this KCISB showed a systematically lower value of E in the borate buffer. The reason for this behavior is not clear at this moment, but is likely to be ascribed to the ceramic plug.¹⁸

Conclusions

The variation of the liquid junction potential (LJP) of the ILSB when one standard buffer solution was replaced by another is within 1 mV for phosphate, borax, and citrate standards and comparable to that of the KCISB, except for the case of the phthalate standard. The time course of the potential of the IL-type is stable with a standard deviation of 0.4 mV in the buffer solutions. The specific deviation of the PBP between C₈mimC₁C₁N and the phthalate standard was observed. The partition of the hydrogen phthalate in C₈mimC₁C₁N shifts the PBP across the interface between C₈mimC₁C₁N and the phthalate standard. If a citrate standard is used instead of the phthalate, the ILSB works more satisfactorily as a salt bridge suitable to potentiometric pH measurements in an acidic pH range. The present test of the stability of the ILSB equipped reference electrodes is based on the assumption that the double junction-type KCISB reference electrode is stable within an error of ±0.1 mV in pH standard buffers, the assumption of which may be questioned for a more critical evaluation of the stability of ILSBs.

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