Feature Article

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Potentiometric Determination of pH Values of Low Conductivity Solutions with the Glass Combination Electrode Equipped with Ionic Liquid Salt Bridge

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It is difficult to measure accurately and quickly pH of low conductivity solutions by use of pH glass combination electrodes based on a KCl salt bridge (KClSB). The reasons are the variation of the liquid junction potential (LJP) between a KClSB and a sample solution, and the change of pH in the sample solution due to the leakage of the concentrated KCl from the liquid junction. In order to solve the intrinsic problems, a new reference electrode, where an ionic liquid was used as the material of liquid junction, has proposed. The pH glass combination electrode equipped with an ionic liquid salt bridge (PUREIL electrode) enables us to measure accurately and quickly pH of less than 10 mS m^{-1} sample solutions such as pure water and boiler water. In this paper, we show the pH measurement of 10 mS m^{-1} sulfuric acid solution by use of PUREIL electrode.

Introduction

Accurate determination of pH is of fundamental importance in not only science and technology but also many facets of our life and environments. Potentiometry by use of an electrochemical cell that consists of a glass electrode and a reference electrode equipped with a salt bridge[*1] based on a concentrated KCl solution (abbreviated as KClSB) has been used as a reliable and convenient method of pH measurements[1,2]. However, the potentiometry with KClSB is not accurate enough for solutions of low conductivity. The reasons are the liquid junction potential (LJP) between a KClSB and a dilute solution and the change of ionic strength in sample solution due to the leakage of a concentrated KCl solution. Although the problem was pointed out in many studies[3-16] conducted in 1970s-1990s, it remains unsolved. A new salt bridge made of an ionic liquid[*2] (abbreviated as ILSB) was proposed as an alternative to the KClSB[17-20]. For the working principle of salt bridge, you can refer to p. 59 in this paper. In this paper, we report that the pH glass combination electrode equipped with ILSB (HORIBA, Ltd. PUREIL, 9600-10D) enable us to measure accurately pH of dilute solutions.

Figure 1 The picture of PUREIL electrode

Experimental

Reagents

The ionic liquid, tributyl (2-methoxyethyl) phosphonium bis(pentafluoroethanesulfonyl)amide (TBMOEPC_2C_2N) was obtained from Kanto Chemical Co., Inc. and used without further purification. 20 μmol dm^{-3} (10 mS m^{-1}) H_2SO_4 was prepared by diluting with MilliQ water a standardized sulfuric acid solution, which was certified to be $(5.00 \pm 0.01)\times 10^{-2}$ mol dm^{-3} by coulometric titration with NaOH solution (Nacalai Tesque, Inc., Japan). A phosphate standard solution (0.025 mol kg^{-1} KH_2PO_4+ 0.025 mol kg^{-1} Na_2HPO_4, pH

*1: Salt bridge: The third solution inserted between different two solutions in order to eliminate the liquid junction potential between the two solutions.

*2: Ionic liquid: the molten salt at the room tempreture

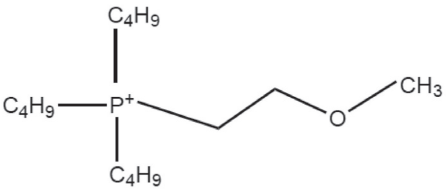
= 6.865 ± 0.005 at 25 °C) were obtained from Kanto Chemical Co., Inc. A 0.05 mol kg^{-1} citrate buffer solution (pH = 3.776 at 25 °C) was prepared by dissolving 11.41 g of $KH_2C_6H_5O_7$ (Kanto Chemical Co., Inc. 99 %) in pure water and diluting it to 1.0000 ± 0.0004 dm^3.

ILSB-Type Combination Electrode (PUREIL Electrode)

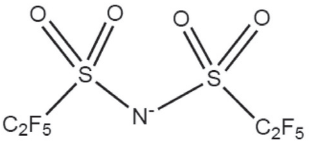
Figure 1 illustrates the structure of a combination electrode which consists of a glass electrode and a reference electrode equipped with a ring of gelled ILSB. $TBMOEPC_2C_2N$ was used as the ILSB. The structures of the cation and anion constituting $TBMOEPC_2C_2N$ are given in Figure 2. $TBMOEPC_2C_2N$ was gelled by dissolving 8 g of P (VdF-HFP) and 0.008 dm^3 $TBMOEPC_2C_2N$ in 0.1 dm^3 acetone. The mixture was dried to remove acetone for one week at room temperature to obtain a membrane of 2.5 mm thickness. The ring-shaped membrane was cut out from the membrane. The ring-shaped membrane of the gelled IL was mounted with a silicone O-ring to the cylindrical body of the combination electrode[21]. In the ILSB-type reference electrode, the inner cell was composed of a Ag/AgCl electrode in a 0.1 mol dm^{-3} KCl saturated with a $TBMOEPC_2C_2N$ and AgCl. In the glass electrode, the inner cell was composed of a Ag/AgCl electrode in a 0.1 mol dm^{-3} KCl saturated with a AgCl and 0.04 mol dm^{-3} KH_2PO_4 + 0.16 mol dm^{-3} Na_2HPO_4. The composition of the glass was the same as that of the glass electrode (HORIBA, Ltd. 9618).

pH measurement method

The electrochemical cell employed for the pH determination with the glass electrode and the ILSB-type reference electrode is represented as



Tributyl(2-methoxyethyl)phosphonium ($TBMOEP^+$)



Bis(pentafluoroethanesulfonyl)amide ($C_2C_2N^-$)

Figure 2 Structure of $TBMOEPC_2C_2N$

I	II	III	IV	V	VI	VII	VIII	VIV
Ag	AgCl	0.1 mol dm^{-3} KCl saturated with TBMOEP C_2C_2N and AgCl	gelled TBMOEP C_2C_2N	pH standards or x μmol dm^{-3} H_2SO_4	glass	0.1 mol dm^{-3} KCl saturated with AgCl 0.04 mol dm^{-3} KH_2PO_4 0.16 mol dm^{-3} Na_2HPO_4	AgCl	Ag (A)

The single vertical bar indicates the phase boundary, and the single dashed vertical bar indicates the 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., F53, resolution: 0.1 mV) at a sampling rate of 0.3 Hz. The polypropylene container containing 20 dm^3 sample solution (V in cell A) was set in a water bath kept at 25.0 ± 0.1 °C. Cell A was calibrated with two pH standard buffers before the measurement of H_2SO_4.

Calculation of pH Values from Cell Voltage

When cell A is calibrated with a standard buffer, pH_S, an unknown pH value of H_2SO_4 solutions, pH_x, in V in cell A is written

$$pH_x = pH_s - \frac{[E_{ex} - E_s - (E_{j(x)} - E_{j(s)})]F}{RT \ln 10} \quad \cdots\cdots\cdots\cdots (1)$$

where E_{ex} and E_S are the readings of the pH electrode for the H_2SO_4 solution and the standard buffer whose pH values are pH_x and pH_S, respectively, $E_{j(x)}$ and $E_{j(S)}$ are the liquid junction potentials (LJPs) at ILSB | x μmol dm^{-3} H_2SO_4 and ILSB | the standard buffer solution interfaces, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. Glass electrodes may exhibit the pH response smaller than the theoretical value, $RT\ln10 / F$ volts per pH unit. The common procedure is to use the operative Nernst slope, k', which is obtained from the two-point calibration of the electrode,

$$k' = \frac{E_{S1} - E_{S2}}{pH_{S2} - pH_{S1}}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where E_{S1} and E_{S2} are the pH cell voltages for the buffers pH_{S1} and pH_{S2}, respectively. When k' is used, eq(1) is represented by

$$pH_x = pH_s - \frac{E_{ex} - E_s - (E_{j(x)} - E_{j(s)})}{k'} \quad \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

If the ILSB works ideally, $E_{j(x)}$ is equal to $E_{j(S)}$ and eq(3) reduces to

$$\mathrm{pH_x}=\mathrm{pH_s}-\frac{E_{\mathrm{ex}}-E_{\mathrm{s}}}{k'} \quad \cdots\cdots (4)$$

The pH values of the sample solution were obtained from the measured E values with eq(4).

In order to make a comparison between the PUREIL electrode and the KCl type electrode, the pH of H_2SO_4 was measured by use of the KCl-type combination electrode (HORIBA, Ltd, 9681) according to the same procedure.

Result

Figure 3 shows the time courses of pH for 15 min at 10 mS m^{-1} H_2SO_4 solution. In Figure 3, ● and ■ are the pH values measured by use of PUREIL and KCl-type electrodes, respectively, and red line is the calculated pH value[20] of 10 mS m^{-1} H_2SO_4 solution.

The response time of PUREIL electrode is shorter than that of KCl-type. In the case of PUREIL electrode, the difference between experimental and calculated pH values is within 0.03 pH unit. On the other hand, the pH value measured by use of KCl-type is higher by 0.1 pH unit than the calculated pH value. Two reasons are considered. First, in the case of KCl-type, the pH in sample solution changes with time due to the leakage of a concentrated KCl from liquid junction. Second, the LJP between a KClSB and the low conductivity solution is unstable. Thus, we can measure accurately and quickly pH of the low conductivity solutions with a PUREIL electrode since the contamination of a sample solution is less and the LJP between the ILSB and sample is stable.

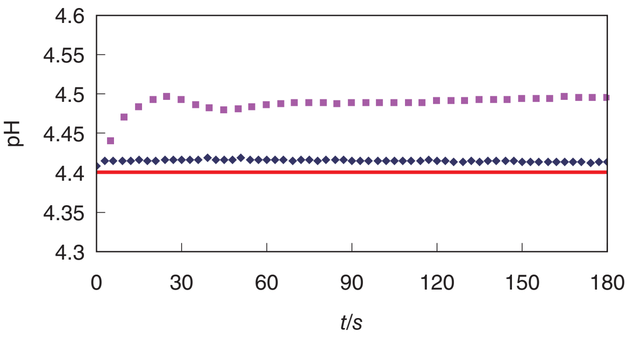


Figure 3 The time course of pH at 10 mS m^{-1} (20 μmol dm^{-3}) sulfuric acid solution. ●: PUREIL electrode, ■: KCl-type electrode, red line: the calculated pH value

Conclusions

PUREIL electrodes enable us to accurately and quickly determine the pH values of the low conductivity solution whose pH values can not be accurately measured by use of a KCl-type electrode used over 100 years. In this paper, although we measured the dilute H_2SO_4 solution, the accurate and high stable pH measurements of sample solutions such as rain water, river water, boiler water, and pure water are possible by use of PUREIL electrode. It is anticipated that the PUREIL electrode is certified as the standard electrode for the pH measurement of low conductivity solutions. Although we omitted details of the results due to space limitation, you can refer to our paper in preparation for these details[22].

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