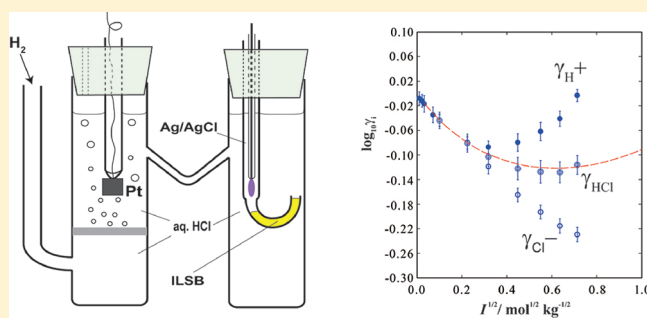


Determination of Single-Ion Activities of H^+ and Cl^- in Aqueous Hydrochloric Acid Solutions by Use of an Ionic Liquid Salt Bridge

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ABSTRACT: Single-ion activities of H^+ and Cl^- in aqueous hydrochloric acid solutions up to $500 \text{ mmol} \cdot \text{dm}^{-3}$ HCl have been determined, independently of each other, with reasonable accuracy, 95% confidence interval of $\log_{10}\gamma$ being ± 0.012 at 25°C , by use of an ionic liquid salt bridge inserted in a Harned cell. The geometric averages of those activities agree well with the literature values of the mean ionic activity of HCl determined with a Harned cell up to an ionic strength of $500 \text{ mmol} \cdot \text{dm}^{-3}$. The agreement supports the assumption used in estimating the single-ion activities, that is, the liquid junction potentials on both sides of the ionic liquid salt bridge stay constant, within the confidence interval of the cell voltage, $\pm 1 \text{ mV}$, over the concentration range of HCl between 10 and $500 \text{ mmol} \cdot \text{dm}^{-3}$. The single-ion activity coefficient values of H^+ and Cl^- over the concentration range studied show fairly good agreement with the recent theoretical predictions by the “smaller-ion-shell” model proposed by Fraenkel (Mol. Phys. 2010, 108, 1435; J. Phys. Chem. B 2011, 115, 557), which fact is significant and implicative in physical and analytical chemistry of electrolyte solutions.



1. INTRODUCTION

The single-ion activity of ionic species is a quantity that is not thermodynamically measurable, although measuring pH, which is conceptually defined in terms of the activity of hydrogen ion, is an everyday practice in laboratories as well as the field and at on-site monitoring posts all over the world. The immeasurability of single-ion activities is linked to the unmeasurability of the liquid junction potential between two electrolyte solutions: as Harned put it, “We are thus confronted with the interesting perplexity that it is not possible to compute liquid junction potentials without a knowledge of activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potentials”.¹ Once we have a reliable salt bridge that gives a stable and constant liquid junction potential upon contact with sample solutions of different compositions, it is possible to estimate the single-ion activities, for example, pH.² However, the performance of traditional salt bridges based on a concentrated KCl solution is far from ideal in proper functioning, particularly when they are in contact with a dilute aqueous solution,^{3–5} where the Debye–Hückel limiting law, which is the exact limiting law at low concentration,⁶ applies in calculating the activity coefficients of ions.

Many of the problems inherent to KCl-type salt bridges can be circumvented by use of a salt bridge made of a moderately hydrophobic ionic liquid, that is, an ionic liquid salt bridge (ILSB).^{2,7,8} A well-tuned ILSB for equitransference of the IL-constituting cation and anion shows a stable liquid junction potential even in low ionic strength (on the order of a few micromolar) 1:1 electrolyte solutions,^{9,10} and has been successfully

used for determining pH in dilute sulfuric acids to the accuracy of $0.01 \Delta\text{pH}$ for 95% confidence interval,¹¹ which was not possible with a combination of a glass electrode and a KCl-type reference electrode.⁵

We herein show the single-ion activities of H^+ and Cl^- , determined independently, up to $0.5 \text{ mol} \cdot \text{dm}^{-3}$ HCl at 25.0°C by inserting an ILSB that consists of tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide ($[\text{TBMOP}^+][\text{C}_2\text{F}_5\text{SO}_2\text{N}^-]$) inserted in the middle of a Harned cell. The geometric mean of the single-ion activities of H^+ and Cl^- agreed with thermodynamically reliable mean activity values of HCl determined with a Harned cell. The agreement supports the reliability of the single-ion activities of H^+ and Cl^- obtained by use of the ILSB. A comparison with the theory recently proposed by Fraenkel^{12,13} is illuminating for physical and analytical chemistry of electrolyte solutions.

2. EXPERIMENTAL SECTION

2.1. Materials. The methods of synthesis and purification of $[\text{TBMOP}^+][\text{C}_2\text{F}_5\text{SO}_2\text{N}^-]$ have been described elsewhere.⁹ Other chemicals used were of reagent grade. Water was purified with a Milli-Q system (Millipore Co.). Standardized HCl solutions (Kanto Chem., Japan) were used as received or diluted to prepare HCl solutions of different concentrations. The exact concentrations

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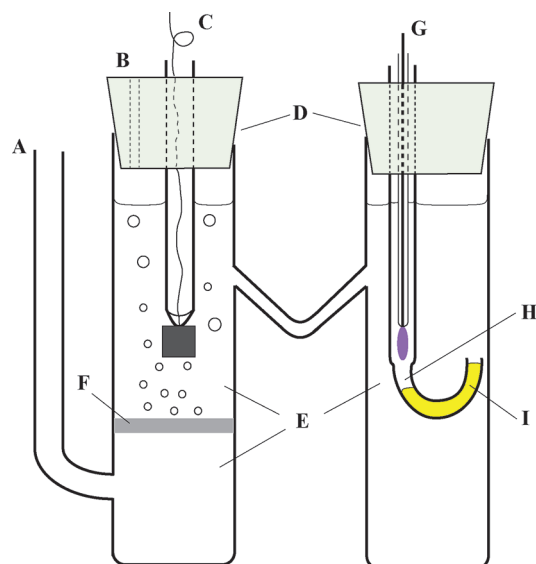


Figure 1. Illustration of cell configuration: (A) H_2 gas inlet; (B) H_2 gas outlet; (C) platinum wire connected to platinized platinum plate; (D) silicone rubber stoppers; (E) aqueous HCl solution; (F) coarse glass frit disk; (G) Ag/AgCl electrode; (H) aqueous HCl solution; (I) ionic liquid.

were calculated from the values of four-digit factors supplied by Kanto Chem. The concentration scale was converted from molarity to molality by use of the density data of aqueous HCl solutions.¹⁴

2.2. Methods. Potentiometric measurements were made with cell I:

I	II	III	IV	V	VI
Ag	AgCl	$x \text{ mmol dm}^{-3}$ HCl	$[\text{TBMOP}^+][\text{C}_2\text{C}_2\text{N}^-]$	$y \text{ mmol dm}^{-3}$ $\text{H}_2(\text{g}), \text{HCl}$	Pt
		(W1)	(ILSB)	(W2)	(I)

The shape of the cell is illustrated in Figure 1. The cell was kept in a water bath whose temperature was maintained at $25.00 \pm 0.02^\circ\text{C}$. For the platinum electrode, a platinum plate of 1 cm^2 was platinized in $3.5 \text{ mmol} \cdot \text{dm}^{-3}$ solution of platinum chloride containing 0.05% Pb^{2+} .¹⁵ Hydrogen gas of purity higher than 99.999% was supplied by a hydrogen generator (H2PEM-100, Parker) at a flow rate of $100 \text{ cm}^3 \cdot \text{min}^{-1}$. Before entering the cell, hydrogen gas was passed through two presaturators filled with solution of the same composition as that in W2 in cell I. The Ag/AgCl electrode was prepared according to the method described by Bates.¹⁵ The cell voltage (E), that is, the potential of the right-hand-side terminal of cell I with respect to the left, was measured with an electrometer (MT8252, ADC, Japan), which was calibrated with a voltage standard (6161, ADC).

3. RESULTS AND DISCUSSION

3.1. Stability of Cell Voltage and ILSB. We first measured E when the concentration of HCl was $10 \text{ mmol} \cdot \text{dm}^{-3}$ in phase W1 and 0.1 or $0.5 \text{ mmol} \cdot \text{dm}^{-3}$ in phase W2 ($x = 10$ and $y = 0.1$ or 0.5 in cell I) to check the stability of E and the effectiveness of the ILSB. Typical time courses of E for four independent runs are shown in Figure 2 when $x = 10$ and $y = 0.5$ after the measured E value became stable within $\pm 1 \text{ mV}$, 30 min after the start of the

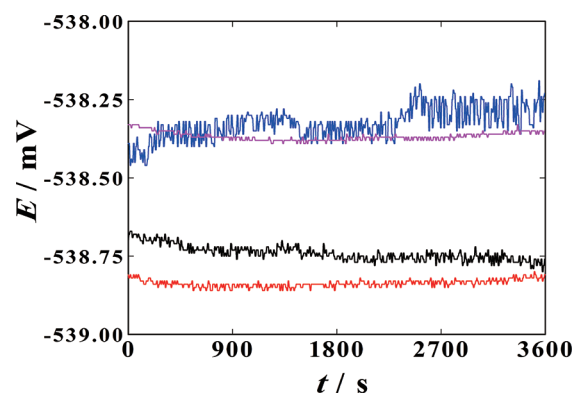


Figure 2. Example of time courses of E when $x = 10$ and $y = 0.5$, recorded on separate days.

measurement of E in most of the cases. After the stabilization, the maximum excursion of E in each run was within $\pm 0.25 \text{ mV}$. Each run in Figure 2 was measured on a different day. The cell was constructed every time anew and disassembled after each measurement.

The average values of four independent measurements were -0.5797 and -0.5386 V at $y = 0.1$ and 0.5 , respectively, and their 95% confidence intervals were $\pm 0.4 \text{ mV}$ in both cases. This variability of 0.4 mV includes four possible sources: potential of the Ag/AgCl electrode, liquid junction potentials on both sides of the ILSB, and potential of the hydrogen electrode.

If the liquid junction potential remains constant upon contact with these two solutions at $y = 0.1$ and 0.5 , the difference in E , $\Delta E = -0.5386 - (-0.5797) = 0.0411 \text{ V}$, is ascribed to the ratio of the activity coefficients of H^+ in the two solutions:²

$$\Delta E = \frac{RT}{F} \ln \frac{a_{\text{H}^+, 0.1}}{a_{\text{H}^+, 0.5}} \quad (1)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and $a_{\text{H}^+, 0.1}$ and $a_{\text{H}^+, 0.5}$ stand for the activities of H^+ at 0.1 and $0.5 \text{ mmol} \cdot \text{dm}^{-3}$ ionic strength values. The pH value at $y = 0.5$ was obtained to be 3.310 ± 0.010 , if it is assumed that the pH at $y = 0.1$ is given by the Debye–Hückel limiting law (DHL). This value agrees well with the calculated pH value, 3.309 , based on the DHL at $y = 0.5$.

3.2. Single-Ion Activities of H^+ and Cl^- . First, we measured ΔE for 11 different concentrations of HCl from $y = 0.1$ to 500 at $x = 0.5$. The activity coefficient of H^+ was calculated from ΔE by use of eq 1 and converted to the molality scale. The average values obtained from quadruple measurements are listed in the third column of Table 1. Figure 3 (●) shows the decadic logarithm values of the measured single-ion activity coefficient of H^+ , γ_{H^+} , at 10 different concentrations between $y = 0.5$ and 500 as a function of the square-root of the ionic strength in molality. The error bars indicate the 95% confidence intervals of quadruple measurements conducted on different days.

Similarly, the single-ion activity coefficient of Cl^- , γ_{Cl^-} , was estimated at $y = 1 \text{ mmol} \cdot \text{dm}^{-3}$ for seven different concentrations of HCl, $x = 10, 50, 100, 200, 300, 400$, and 500 , with the assumption that a relationship similar to eq 1 holds also for Cl^- in phase III. The values obtained from quadruple measurements obtained on different days are listed in the fourth column in Table 1. Figure 3 (○) shows the average values of γ_{Cl^-} for

Table 1. Values of Single-Ion Activity Coefficients of H^+ and Cl^- and Mean Activity Coefficients of HCl^a

c ($\text{mmol} \cdot \text{dm}^{-3}$)	m ($\text{mmol} \cdot \text{kg}^{-1}$)	$\log_{10} \gamma_{\text{H}^+}$	$\log_{10} \gamma_{\text{Cl}^-}$	$\log_{10} \gamma_{\text{HCl}}^b$	$\log_{10} \gamma_{\text{HCl}}^c$
0.5	0.5	-0.012 ± 0.010			
1.0	1.0	-0.017 ± 0.014			-0.0152
5.0	5.0	-0.035 ± 0.013			-0.032
10	10	-0.044 ± 0.010	-0.044 ± 0.010	-0.044 ± 0.010	-0.043
50	50	-0.082 ± 0.010	-0.080 ± 0.010	-0.081 ± 0.010	-0.080
100	100	-0.087 ± 0.010	-0.108 ± 0.012	-0.097 ± 0.012	-0.099
200	201	-0.080 ± 0.014	-0.164 ± 0.011	-0.123 ± 0.014	-0.122
300	303	-0.062 ± 0.015	-0.192 ± 0.011	-0.127 ± 0.015	-0.120
400	404	-0.041 ± 0.014	-0.213 ± 0.012	-0.127 ± 0.014	-0.121
500	506	-0.003 ± 0.010	-0.227 ± 0.012	-0.115 ± 0.012	-0.120

^a Values are given with 95% confidence intervals at 25.0 °C. ^b This work. ^c Hamer and Wu.¹⁶

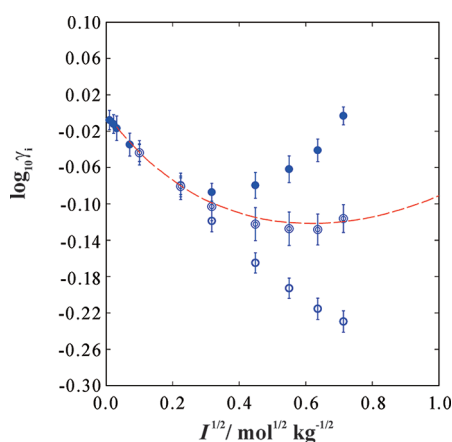


Figure 3. Decadic logarithm values of the single-ion activities of (\bullet) H^+ and (\circ) Cl^- and the mean activity coefficients (\odot) calculated from corresponding single-ion activity coefficients of H^+ and Cl^- at 25 °C. Error bars show 95% confidence intervals for quadruple measurements. (---) Literature values of the mean activity coefficients of HCl experimentally obtained.¹⁶

quadruple measurements at each concentration; error bars indicate 95% confidence intervals.

The geometric average values of the experimentally obtained single-ion activity coefficients γ_{H^+} and γ_{Cl^-} at seven concentrations of HCl are listed in the fifth column in Table 1 and shown as double circles in Figure 3. The mean activity coefficient of HCl in water, γ_{HCl} , is measurable with a Harned cell, that is, cell I without the ILSB, and is considered to be of thermodynamic value. The values of γ_{HCl} critically compiled by Hamer and Wu¹⁶ are displayed as the dashed line in Figure 3. The γ_{HCl} values calculated from the present experimental values of γ_{H^+} and γ_{Cl^-} well agree with the dashed line up to the highest concentration studied, $0.5 \text{ mol} \cdot \text{dm}^{-3}$ ($0.506 \text{ mol} \cdot \text{kg}^{-1}$). This agreement supports the assumption made in estimating γ_{H^+} and γ_{Cl^-} from E in cell I, that is, the constancy of the liquid junction potential between the ILSB and the aqueous HCl solution over the change in γ between 10 and 500 within experimental error.

3.3. Comparison with Other Values of γ_{H^+} and γ_{Cl^-} Deduced from Experimental Results. There have been several attempts to estimate the single-ion activities, in particular, those of H^+ at different ionic strengths. At the concentration of $0.1 \text{ mol} \cdot \text{kg}^{-1}$ HCl , the classical approach of extrapolating experimental values of

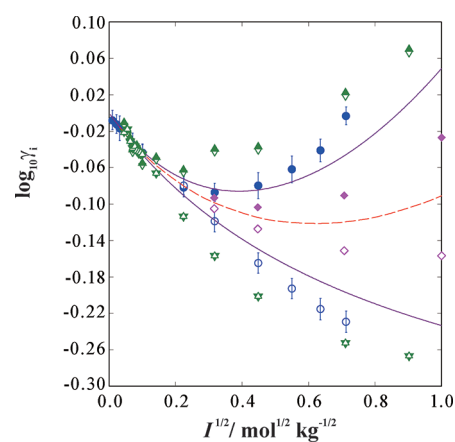


Figure 4. Comparison of single-ion activity coefficients of H^+ (\blacktriangle and ∇ , Schneider et al.;²¹ \bullet , Bates et al.;¹⁹ \odot , this work) and those of Cl^- (\triangle and ∇ , Schneider et al.;²¹ \diamond , Bates et al.;¹⁹ \circ , this work) with theoretical curves (—) predicted by the SiS model.¹³ (---) Same as described for Figure 3.

the cell voltage to zero ionic strength gave the values of $\log_{10} \gamma_{\text{H}^+}$ at 25 °C as -0.086 by Hitchcock and Taylor¹⁷ and -0.092 by Bates et al.¹⁸ These values fall within the experimental uncertainty in the present study, -0.0871 ± 0.01 at the same concentration.

It is more interesting to see γ_{H^+} and γ_{Cl^-} values at higher ionic strengths. Bates et al.¹⁹ estimated the single-ion activity coefficients of H^+ and Cl^- from the mean activity of HCl , on the basis of the hydration model.²⁰ Their data are plotted in Figure 4 (\blacklozenge , \diamond). Their values of $\log_{10} \gamma_{\text{H}^+}$ are smaller than the present values; that is, the activity of H^+ is smaller in the entire concentration range. Concomitantly, their Cl^- values calculated from the mean activity coefficient values are greater than the present values at all concentrations.

Figure 4 also shows the single-ion activities of H^+ (\blacktriangle and ∇) and Cl^- (\triangle and ∇) reported more recently by Schneider et al.²¹ Their data in Figure 4 were obtained by use of a glass electrode for H^+ and an ion-selective electrode for Cl^- . The liquid junction potential at the contact of a sample solution with a $\text{Ag}|\text{AgCl}$ electrode was corrected via the Henderson equation²² with two different assumptions (distinguished as solid and open symbols).²¹ The values for γ_{H^+} (\blacktriangle and ∇) are both above the corresponding points of the present work, and those for γ_{Cl^-} (\triangle and ∇) are both below the points obtained in the present

work. The discrepancy above $I = 0.05 \text{ mol} \cdot \text{kg}^{-1}$ is greater than the confidence intervals attached to the values obtained in the present study for both H^+ and Cl^- .

3.4. Comparison with Theoretical Predictions. Very recently, Fraenkel¹² proposed a model for the single-ion activities of electrolyte solutions by extending the Debye–Hückel theory in a sophisticated way. His smaller-ion shell (SiS) model distinguishes the activity of the cation from that of the anion of unequal size within the framework of the unrestricted primitive model. Theoretical curves calculated from his theory with parameters optimized for aqueous hydrochloric acid solutions¹³ are reproduced as two solid lines in Figure 4. The agreement with the present results is by and large surprisingly good for both γ_{H^+} and γ_{Cl^-} ; the discrepancy is generally greater for the two other data sets by Bates et al.¹⁹ and Schneider et al.²¹

The agreement between the SiS prediction and our results is not, however, perfect over the entire concentration range studied. The difference exceeds the error bars at higher concentrations above $I = 0.2 \text{ mol} \cdot \text{kg}^{-1}$; the experimental γ_{H^+} values are higher and those of γ_{Cl^-} are lower than theoretical predictions. The minimum in the experimental $\log_{10} \gamma_{\text{H}^+}$ versus \sqrt{I} plot is located at $I \approx 0.1 \text{ mol} \cdot \text{kg}^{-1}$, which is slightly smaller than $\approx 0.15 \text{ mol} \cdot \text{kg}^{-1}$ predicted by the SiS model. Changing the adjustable parameter in the SiS model, the closest distance between hydroxonium ion and chloride ion, 3.610 Å, by $\pm 3\%$ did not appreciably improve the fit. There seems to be room for further optimizing the fitting of the SiS model to experimental mean activity coefficients of HCl (Figure 1b in ref 13) in this concentration range.

Another possibility is systematic deviation of the liquid junction potential at the ILSB from a constant value with increasing concentration of HCl. At $0.5 \text{ mol} \cdot \text{kg}^{-1}$, the experimental $\log_{10} \gamma_{\text{H}^+}$ value is higher by 0.05, which corresponds to a 3 mV change in E in the positive direction. Deviation of the liquid junction potential in this direction can be caused by a shift in the liquid junction potential due to partition of H^+ ion into the ILSB or to protonation of bis(pentafluoroethanesulfonyl)amide, as is the case for interference of the phase-boundary potential in liquid-membrane-type ion-selective electrodes.^{23,24} The protonation of bis-(pentafluoroethanesulfonyl)amide is, however, unlikely, because of the high acidity of bis(perfluoroalkylsulfonyl)imides^{25,26} and the highly polar environment in the IL phase.^{27,28} Further studies are required to examine the possible deviation of the liquid junction potential values at higher concentrations from a constant value determined by the partitioning of the ILSB constituent ions.

4. CONCLUSIONS

The values of the single-ion activities of H^+ and Cl^- , once thought to be elusive²⁹ and the subject of disputes to date,^{30–38} can be estimated to the extent of the accuracy of the liquid junction potential, as Frank³⁹ pointed out and Bates⁴⁰ remarked in relation to the determination of pH. Filling a new liquid in a glass tube in the old-fashioned cell enables us to estimate those values much more reliably and readily than relying on a KCl-type salt bridge or an elaborate calculation of the liquid junction potential. An immediate consequence of the approach based on the ILSB is the accurate determination of pH for two types of solutions for which the pH measurements have been difficult; that is, low ionic strength solutions, such as rainwater and boiler feedwater, and high ionic strength solutions, such as marine water and blood. Reliable

experimental values of single-ion activities would serve as a reference for comparison with theoretical predictions.^{12,13,41–44}

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