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Activity Coefficients of Hydrochloric Acid in Concentrated Electrolyte Solutions. 1. $HCl + NaCl + H_2O$, $HCl + LiCl + H_2O$, and $HCl + BaCl_2 + H_2O$ at 298.15 K

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Electromotive force (emf) measurements have been made using a Harned cell without a liquid junction of the type Pt, H_2(0.1013 25 MPa)|HCl(I_A), MeCl(I_B)|AgCl,Ag containing mixtures of (i) HCl and NaCl, (ii) HCl and LiCl, and (iii) HCl and $BaCl_2$, at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K. From these emf measurements, the mean activity coefficients of hydrochloric acid in ternary solutions of $HCl + NaCl + H_2O$, $HCl + LiCl + H_2O$, and $HCl + BaCl_2 + H_2O$ have been determined, using the Nernst equation. The Harned equation has been used to fit the mean activity coefficients of hydrochloric acid by a least squares method, and the values of the logarithm of the mean activity coefficient of pure hydrochloric acid, log $\gamma_A{}^0$, and the Harned interaction coefficients, α_{AB} and β_{AB}, together with their standard deviations are obtained. The results show that the measured mean activity coefficients of hydrochloric acid in the ternary solutions studied obey Harned's rule at constant total ionic strengths from (4 to 7) mol kg^{-1} and at a temperature of 298.15 K.

Introduction

In recent years there has been an increasing interest, both experimental and theoretical, in the thermodynamic properties of aqueous electrolyte solutions at high concentrations (Pitzer, 1979; Roy et al., 1983; Harvie et al., 1984; Pabalan and Pitzer, 1990). In particular, the mean activity coefficients of an individual strong electrolyte in aqueous solutions are required for understanding various ionic interactions and equilibria in aqueous mixtures. In view of the great importance of hydrochloric acid in hydrometallurgy, electrochemistry, biochemical systems, and other aqueous solutions of practical and theoretical interest, measurements of the mean activity coefficient of hydrochloric acid in aqueous electrolyte solutions at high concentrations are a matter of considerable importance.

Since Harned and Ehlers (1933) used the electromotive force cell without a liquid junction of the type

$$\mathrm{Pt,H_2(1\ atm)|HCl(m)|AgCl,Ag} \qquad \text{(A)}$$

which is usually referred to as a Harned cell, to accurately study the mean activity coefficients of pure hydrochloric acid at molalities from (0 to 4) mol kg^{-1}, and Åkerlöf and Teare (1937) made additional measurements for the same electrochemical cell as cell A at significantly higher molalities of hydrochloric acid from (3 to 16) mol kg^{-1}, there have been many references concerning the determination of the mean activity coefficients of hydrochloric acid in mixed aqueous electrolyte solutions, using the emf method (Harned and Owen, 1958; Robinson and Stokes, 1970; Pitzer, 1991). Recently, Pal et al. (1991) made emf measurements in a Harned cell without a liquid junction to determine the mean activity coefficients of hydrochloric acid in solutions of $HCl + MCl + H_2O$ ($M = CH_3NH_3$, $(CH_3)_2NH_2$, and $(CH_3)_3NH$), at constant total molalities from (0.1 to 3.0) mol kg^{-1} and at temperatures from (5 to 35) °C. The measured mean activity coefficients of hydrochloric acid in all the mixtures were found to obey Harned's rule; Roy et al. (1992) used a Harned cell without a liquid junction to study the mean activity coefficients of hydrochloric acid in $HCl + ThCl_4 + H_2O$ solutions at constant total ionic strengths from (0.006 to 3) mol kg^{-1} and at temperatures from (5 to 55) °C, and the results were used in determining the nature and extent of ion−ion interactions for $H^+ + Th^{4+} + Cl^- + H_2O$ system, using the Pitzer ion interaction model; Mikiya et al. (1992) estimated the activities of hydrochloric acid in aqueous solutions of $HCl + NaCl + H_2O$ and $HCl + NiCl_2 + H_2O$, using Pitzer's ion interaction model; Zhang et al. (1993) determined the activities of hydrochloric acid in a mixed solvent of methanol and water, using the electromotive force of cell B without a liquid junction:

$$\mathrm{pH{-}glass\ electrode|HCl(m),CH_3OH(1-\mathit{x}),H_2O(\mathit{x})|AgCl,Ag} \qquad \text{(B)}$$

However, a survey of the literature showed that the mean activity coefficients of hydrochloric acid in aqueous solutions of hydrochloric acid and metal chloride salts at constant total ionic strengths higher than 3 mol kg^{-1} have hardly been studied. In the present work a series of experiments are made to measure the electromotive force of cell C without a liquid junction:

$$\mathrm{Pt,H_2(0.101\ 325\ MPa)|HCl(\mathit{I}_A),MeCl(\mathit{I}_B)|AgCl,Ag} \qquad \text{(C)}$$

with Me = Na, Li, and Ba, respectively, at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K. I_A and I_B are ionic strengths of HCl and MeCl (Me =Na, Li, and Ba), respectively. The mean activity coefficients of hydrochloric acid in the ternary solutions of $HCl + NaCl + H_2O$, $HCl + LiCl + H_2O$, and $HCl + BaCl_2 + H_2O$ are then determined from the emf measurements by the Nernst equation. The results show that the mean activity coefficients of hydrochloric acid in all the solutions studied in this work follow Harned's rule at constant total ionic strengths from (4 to 7) mol kg^{-1} and at a temperature of 298.15 K.

Experimental Section

All the salts used in this study are reagent grade, purified by recrystallization three times from water, dried,

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Table 1. Experimental Cell Potential, *E*, and log γ_A of HCl (A) + NaCl (B) + H_2O at Each Constant Total Ionic Strength, *I*, and at 298.15 K

I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A
$I = 4.0$ mol kg^{-1}											
4.00	0.00	0.122 63	0.243 02	2.40	1.60	0.141 24	0.196 64	0.80	3.20	0.174 25	0.156 13
3.60	0.40	0.126 75	0.231 07	2.00	2.00	0.147 03	0.187 22	0.40	3.60	0.193 15	0.146 85
3.20	0.80	0.131 31	0.218 11	1.60	2.40	0.154 01	0.176 71				
2.80	1.20	0.135 90	0.208 29	1.20	2.80	0.162 70	0.165 68				
$I = 5.0$ mol kg^{-1}											
5.00	0.00	0.095 66	0.374 11	3.00	2.00	0.115 91	0.313 81	1.00	4.00	0.150 18	0.262 67
4.50	0.50	0.100 21	0.358 50	2.50	2.50	0.121 97	0.302 19	0.50	4.50	0.169 34	0.251 22
4.00	1.00	0.105 27	0.341 29	2.00	3.00	0.129 28	0.288 82				
3.50	1.50	0.110 16	0.328 99	1.50	3.50	0.138 36	0.274 53				
$I = 6.0$ mol kg^{-1}											
6.00	0.00	0.070 22	0.509 96	3.60	2.40	0.092 22	0.434 88	1.20	4.80	0.127 78	0.372 82
5.40	0.60	0.075 24	0.490 42	3.00	3.00	0.098 56	0.420 96	0.60	5.40	0.147 19	0.359 23
4.80	1.20	0.080 83	0.468 71	2.40	3.60	0.106 22	0.404 63				
4.20	1.80	0.086 03	0.453 77	1.80	4.20	0.115 69	0.387 02				
$I = 7.0$ mol kg^{-1}											
7.00	0.00	0.045 80	0.649 48	4.20	2.80	0.069 65	0.558 76	1.40	5.60	0.106 53	0.485 50
6.30	0.70	0.051 31	0.625 74	3.50	3.50	0.076 27	0.542 42	0.70	6.30	0.126 20	0.469 77
5.60	1.40	0.057 47	0.599 28	2.80	4.20	0.084 29	0.523 05				
4.90	2.10	0.063 00	0.581 53	2.10	4.90	0.094 16	0.502 04				

Table 2. Experimental Cell Potential, *E*, and log γ_A of HCl (A) + LiCl (B) + H_2O at Each Constant Total Ionic Strength, *I*, and at 298.15 K

I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A
$I = 4.0$ mol kg^{-1}											
4.00	0.00	0.122 63	0.243 02	2.40	1.60	0.135 94	0.241 37	0.80	3.20	0.164 18	0.241 18
3.60	0.40	0.125 37	0.242 73	2.00	2.00	0.140 46	0.242 78	0.40	3.60	0.181 96	0.241 37
3.20	0.80	0.128 60	0.240 99	1.60	2.40	0.146 23	0.242 49				
2.80	1.20	0.131 87	0.242 39	1.20	2.80	0.153 79	0.240 98				
$I = 5.0$ mol kg^{-1}											
5.00	0.00	0.095 66	0.374 11	3.00	2.00	0.108 76	0.374 24	1.00	4.00	0.136 70	0.376 62
4.50	0.50	0.098 34	0.374 33	2.50	2.50	0.113 11	0.377 10	0.50	4.50	0.154 39	0.377 59
4.00	1.00	0.101 60	0.372 31	2.00	3.00	0.118 81	0.377 32				
3.50	1.50	0.104 70	0.375 15	1.50	3.50	0.126 40	0.375 65				
$I = 6.0$ mol kg^{-1}											
6.00	0.00	0.070 22	0.509 96	3.60	2.40	0.082 99	0.512 94	1.20	4.80	0.110 49	0.518 98
5.40	0.60	0.072 81	0.510 97	3.00	3.00	0.087 13	0.517 55	0.60	5.40	0.128 05	0.521 01
4.80	1.20	0.076 08	0.508 90	2.40	3.60	0.092 74	0.518 55				
4.20	1.80	0.078 97	0.513 49	1.80	4.20	0.100 32	0.516 95				
$I = 7.0$ mol kg^{-1}											
7.00	0.00	0.045 80	0.649 48	4.20	2.80	0.058 10	0.656 37	1.40	5.60	0.085 04	0.667 16
6.30	0.70	0.048 26	0.651 54	3.50	3.50	0.062 00	0.663 04	0.70	6.30	0.102 45	0.670 53
5.60	1.40	0.051 51	0.649 67	2.80	4.20	0.067 49	0.665 09				
4.90	2.10	0.054 15	0.656 30	2.10	4.90	0.075 03	0.663 79				

and stored before use. Each stock solution of NaCl, LiCl, and $BaCl_2$ is prepared by dissolving a known mass of salt and diluting it to an appropriate molality with a known mass of double distilled and ion-exchanged water. Reagent-grade hydrochloric acid is distilled twice to the azeotropic concentration, keeping the middle fraction each time, and the final azeotropic mixture is diluted to give an appropriate stock solution of hydrochloric acid. Molalities of all the stock solutions of salts and hydrochloric acid are determined by gravimetric chloride analysis. The maximum uncertainty in the molalities is less than ±0.03%. Cell solutions are made by direct weighing of the stock solutions and water. Buoyancy corrections are applied to all the weighings. The uncertainties in the calculated molalities of the cell solutions introduced by weighing errors could not exceed 0.04%.

The silver−silver chloride electrodes are constructed according to the procedures given by Bates (1973). Bias potentials of the silver−silver chloride electrodes are always less than 0.03 mV. The platinum−hydrogen electrodes are prepared in a manner recommended by Hill and Ives (1980). Experimental details of the cell design and the purification of hydrogen gas have been described in previous studies (Bates, 1973). In all the experiments, the temperature is controlled to (298.15 ± 0.02) K.

Electromotive force measurements are made using a digital ion meter (PXSJ-216 model) with a precision to within ±0.1 mV and a stability of ±0.3 mV/2 h. Equilibrium is considered to be reached when the cell potentials vary by 0.05 mV or less over a 1/2 h period. The experimental precision of the emf measurements is estimated to be ±0.3 mV.

It is reasonable to carefully consider the effects of the increasing solubility of silver chloride with the hydrochloric acid concentration on the emf measurements. By assuming the formation of argento−trichloride complex, Zhao and Lei (1986) have shown that the error of potential produced by the solubility of silver chloride is less than 0.1 mV even at the high concentration of hydrochloric acid of 7 mol kg^{-1}. Therefore, the solubility of silver chloride is considered to have negligible influence on the emf of the Harned cell studied in this work.

Table 3. Experimental Cell Potential, *E*, and log γ_A of HCl (A) + $BaCl_2$ (B) + H_2O at Each Constant Total Ionic Strength, *I*, and at 298.15 K

I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A	I_A/(mol kg^{-1})	I_B/(mol kg^{-1})	*E*/V	log γ_A
I = 4.0 mol kg^{-1}											
4.00	0.00	0.122 63	0.243 02	2.40	1.60	0.133 24	0.136 61	0.80	3.20	0.164 95	0.027 22
3.60	0.40	0.123 75	0.216 83	2.00	2.00	0.138 33	0.110 34	0.40	3.60	0.184 17	−0.000 82
3.20	0.80	0.126 08	0.189 26	1.60	2.40	0.144 86	0.082 88				
2.80	1.20	0.129 08	0.163 92	1.20	2.80	0.153 32	0.054 93				
I = 5.0 mol kg^{-1}											
5.00	0.00	0.095 66	0.374 11	3.00	2.00	0.109 46	0.240 75	1.00	4.00	0.144 77	0.100 98
4.50	0.50	0.097 53	0.341 61	2.50	2.50	0.115 33	0.207 86	0.50	4.50	0.164 95	0.064 75
4.00	1.00	0.100 70	0.306 77	2.00	3.00	0.122 76	0.172 81				
3.50	1.50	0.104 42	0.275 44	1.50	3.50	0.132 19	0.136 60				
I = 6.0 mol kg^{-1}											
6.00	0.00	0.070 22	0.509 96	3.60	2.40	0.087 16	0.350 07	1.20	4.80	0.126 14	0.179 26
5.40	0.60	0.072 81	0.471 36	3.00	3.00	0.093 82	0.310 53	0.60	5.40	0.147 33	0.134 51
4.80	1.20	0.076 85	0.429 37	2.40	3.60	0.102 16	0.267 75				
4.20	1.80	0.081 25	0.392 15	1.80	4.20	0.112 60	0.223 05				
I = 7.0 mol kg^{-1}											
7.00	0.00	0.045 80	0.649 48	4.20	2.80	0.065 83	0.463 46	1.40	5.60	0.108 55	0.261 00
6.30	0.70	0.049 09	0.604 99	3.50	3.50	0.073 27	0.417 25	0.70	6.30	0.130 79	0.207 41
5.60	1.40	0.053 95	0.555 95	2.80	4.20	0.082 55	0.366 60				
4.90	2.10	0.059 04	0.512 95	2.10	4.90	0.094 02	0.313 20				

Table 4. Harned Coefficients of HCl (A) + NaCl (B) + H_2O at Each Constant Total Ionic Strength, *I*/(mol kg^{-1}), and at 298.15 K

I	log γ^0_{Aexp} [a]	log γ^0_{Aexp} [b]	log $\gamma_A{}^0$	α_{AB}	β_{AB}	$10^4\sigma$
4.0	0.246 01	0.243 02	0.24267 ± 0.0005	0.02997 ± 0.0007	−0.00093 ± 0.0002	6.52
5.0	0.376 58	0.374 11	0.37355 ± 0.0008	0.03135 ± 0.0008	−0.00093 ± 0.0002	10.35
6.0	0.507 86	0.509 96	0.50920 ± 0.0011	0.03273 ± 0.0010	−0.00092 ± 0.0002	14.32
7.0	0.640 48	0.649 48	0.64850 ± 0.0015	0.03413 ± 0.0011	−0.00091 ± 0.0002	18.39

[a] Robinson and Stokes (1970). [b] This study.

Table 5. Harned Coefficients of HCl (A) + $BaCl_2$ (B) + H_2O at Each Constant Total Ionic Strength, *I*/(mol kg^{-1}), and at 298.15 K

I	log γ^0_{Aexp} [a]	log γ^0_{Aexp} [b]	log $\gamma_A{}^0$	α_{AB}	β_{AB}	$10^4\sigma$
4.0	0.246 01	0.243 02	0.24272 ± 0.0004	0.06497 ± 0.0005	0.00074 ± 0.0001	4.89
5.0	0.376 58	0.374 11	0.37362 ± 0.0007	0.06423 ± 0.0007	0.00097 ± 0.0001	8.28
6.0	0.507 86	0.509 96	0.50927 ± 0.0009	0.06333 ± 0.0008	0.00112 ± 0.0001	11.86
7.0	0.640 48	0.649 48	0.64859 ± 0.0012	0.06234 ± 0.0009	0.00122 ± 0.0001	15.57

[a] Robinson and Stokes (1970). [b] This study.

Table 6. Harned Coefficients of HCl (A) + LiCl (B) + H_2O at Each Constant Total Ionic Strength, *I*/(mol kg^{-1}), and at 298.15 K

I	log γ^0_{Aexp} [a]	log γ^0_{Aexp} [b]	log $\gamma_A{}^0$	α_{AB}	β_{AB}	$10^4\sigma$
4.0	0.246 01	0.243 02	0.24263 ± 0.0006	0.00045 ± 0.0008	−0.00002 ± 0.0002	7.83
5.0	0.376 58	0.374 11	0.37350 ± 0.0010	−0.00080 ± 0.0010	−0.00002 ± 0.0002	12.14
6.0	0.507 86	0.509 96	0.50913 ± 0.0013	−0.00208 ± 0.0011	−0.00002 ± 0.0002	16.63
7.0	0.640 48	0.649 48	0.64842 ± 0.0017	−0.00388 ± 0.0012	−0.00002 ± 0.0002	21.27

[a] Robinson and Stokes (1970). [b] This study.

Results and Discussion

Tables 1−3 present the emf measurements of cell C, corrected to a hydrogen gas pressure of 0.101 325 MPa, at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K.

The reaction in cell C is

$$(1/2)\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag(s)} + \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \qquad (1)$$

The cell potential, *E*, is given by the Nernst equation

$$E = E^0 - \frac{RT}{F}\ln a_H a_{Cl} \qquad (2)$$

where *a* refers to activity. Values of *R* and *F* are 8.314 cm^3 MPa mol^{-1} K^{-1} and 96 487 C mol^{-1}, respectively. The value of E^0, the standard potential of the silver−silver chloride electrodes on a molality basis, is taken as 0.222 59 V in this study, as reported by Roy et al. (1980, 1992) and Simonson et al. (1987).

The logarithm of the mean activity coefficient of hydrochloric acid, log γ_A, is calculated from the cell potential, by rearranging the Nernst equation to give

$$\log \gamma_A = \frac{F(E^0 - E)}{2RT\ln 10} - \frac{1}{2}\log(II_A) \qquad (3)$$

for HCl + NaCl + H_2O and HCl + LiCl + H_2O, and

$$\log \gamma_A = \frac{F(E^0 - E)}{2RT\ln 10} - \frac{1}{2}\log[(I + 2I_B)I_A] \qquad (4)$$

for HCl + $BaCl_2$ + H_2O. Where, I refers to the constant total ionic strength of solution.

The values of log γ_A in solutions of $HCl + NaCl + H_2O$, $HCl + LiCl + H_2O$, and $HCl + BaCl_2 + H_2O$ at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K are presented in Tables 1−3.

Harned's rule (Harned and Owen, 1958; Harned and Robinson, 1968) has been useful to describe mixed electrolyte solutions at constant total ionic strength. It was demonstrated that, for many solutions, containing acid and the acid salt, the mean activity coefficient of the acid can be adequately expressed as a function of ionic strength:

$$\log \gamma_A = \log {\gamma_A}^0 - \alpha_{AB} I_B - \beta_{AB} {I_B}^2 \qquad (5)$$

where ${\gamma_A}^0$ is the mean activity coefficient of pure hydrochloric acid at an ionic strength equal to the constant total ionic strength of the mixed solution, and the terms α_{AB} and β_{AB} are the Harned interaction coefficients, which are functions of both the temperature and total ionic strength of the aqueous electrolyte solution.

Equation 5 is used in fitting log γ_A by a least squares method, and log ${\gamma_A}^0$ as well as the Harned interaction coefficients α_{AB} and β_{AB} are determined.

The values of log ${\gamma_A}^0$, α_{AB}, and β_{AB}, together with their standard deviations, and the overall root mean square deviation, σ, of the fit of log γ_A are given in Tables 4−6. Also, in Tables 4−6, the experimental log ${\gamma_A}^0$ values obtained in this study and in the literature (Robinson and Stokes, 1970) are presented. From the results in Tables 4−6, some conclusions can be made here. First the mean activity coefficients of hydrochloric acid in solutions of $HCl + NaCl + H_2O$, $HCl + LiCl + H_2O$, and $HCl + BaCl_2 + H_2O$ follow Harned's rule, at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K. The quadratic term $\beta_{AB} {I_B}^2$ in eq 5 is negligible; therefore, the logarithm of the mean activity coefficient of hydrochloric acid in all solutions studied in this work can be adequately expressed as

$$\log \gamma_A = \log {\gamma_A}^0 - \alpha_{AB} I_B \qquad (6)$$

Finally, at constant total ionic strengths up to 7 mol kg^{-1}, the experimental and correlated log ${\gamma_A}^0$ values, obtained in this study, agree well with the literature data.

In the following paper in this issue, the mean activity coefficients of hydrochloric acid in quaternary solutions of $HCl + BaCl_2 + KCl + H_2O$, $HCl + LiCl + KCl + H_2O$, and $HCl + NaCl + KCl + H_2O$ will be studied at constant total ionic strengths of (4, 5, 6, and 7) mol kg^{-1} and at a temperature of 298.15 K, using the electromotive force method.

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