894 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 894—898 (1976) [Vol. 49, No. 4

Activity Coefficients of Hydrochloric Acid in Hydrogen Chloride-Metal Perchlorate-Water Systems

Kiichi TERUYA, Kikuo SHIRAOGAWA, and Issei NAKAMORI
Department of Chemical Engineering, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812

(Received September 30, 1975)

In the $HCl-LiClO_4-H_2O$, $HCl-NaClO_4-H_2O$, $HCl-Mg(ClO_4)_2-H_2O$, $HCl-Ba(ClO_4)_2-H_2O$, $HCl-LiClO_4-NaClO_4-H_2O$, $HCl-NaClO_4-Ba(ClO_4)_2-H_2O$, and $HCl-LiClO_4-NaClO_4-Ba(ClO_4)_2-H_2O$ systems, the mean activity coefficients of hydrochloric acid, $\gamma_{\pm HCl}$, have been obtained at 25 °C by emf measuremts of the cell:

$$H_2(Pt)/HCl,\ MClO_4,\ M'(ClO_4)_2,\cdots/AgCl,\ Ag \quad (M=Li,\ Na;\ M'=Mg,\ Ba)$$

Moreover, the following relation has been examined with the experimental results:

$$\log \gamma_{\pm HCl} = \log \gamma^{\circ}_{\pm HCl} + \sum_i a_{i(HCl)} m_i \qquad (i \neq H, Cl)$$

where $\gamma^{\circ}_{\pm HCl}$ is the mean activity coefficient of hydrochloric acid in a solution containing only hydrochloric acid at the same ionic strength as the mixture; m_i is the molality of the i ion, and $a_{i(HCl)}$ is the parameter assigned to the three-ion system of hydrogen, chloride, and i ions, but is independent of the ionic strength. The results of the examination with $a_{M(HCl)}$ determined in our previous paper showed that $a_{ClO_4(HCl)}$ may be about zero regardless of the kind of metal ion coexisting in the solution. The activity coefficients calculated by the above relationship with the determined parameters agree, with deviation of only about 5%, with the experimental results for all the systems.

While a considerable amount of information is available about the activity coefficients in single electrolyte solutions,[1,2] experimental data on the activity coefficients in multicomponent electrolyte solutions are difficult to obtain and relatively few direct measurements have been reported. The activity coefficients in multicomponent electrolyte solutions are, however, important as fundamental data for the treatment of chemical processes, since most electrolyte solutions commonly encountered in chemical industry are multicomponent electrolyte solutions. Most of the direct measurements in the past have been limited to the hydrogen chloride–metal chloride–water systems.[3] Data on hydrogen chloride–metal perchlorate–water systems have been reported only by Bates and Urmston,[4] Prue and Read,[5] Stokes and Stokes,[6] and Weeks,[7] and most of these data are within the limits of low concentrations of hydrochloric acid.

Although many theoretical treatments of the properties of multicomponent electrolyte solutions have been proposed by various authors,[3,8–10] the principal object in these treatments has been the consideration of the interionic forces. As a result, the expressions for the activity and osmotic coefficients in multicomponent electrolyte solutions are complicated in form and contain a number of parameters which are functions of the ionic strength and so are cumbersome for engineering calculations.

In their previous papers, therefore, the present authors proposed a simple and convenient method of estimating the activity coefficients in multicomponent electrolyte solutions for use in engineering calculations[11] and showed that satisfactory results could be obtained when the method was applied to examinations of the activity coefficients of hydrochloric acid in hydrogen chloride–metal chloride–water systems.[12] The object here is to obtain the mean activity coefficients of hydrochloric acid at 25 °C by emf measurements in aqueous solutions containing one or more perchlorates of metal (lithium, sodium, magnesium, or barium) over a wide range of concentrations of hydrochloric acid and to a high total ionic strength, and to examine the method of estimation in these systems containing perchlorate ions on the basis of the experimental results.

Theoretical

The total excess Gibbs energy of an electrolyte solution may be dominated by the effect of the long-range electrostatic forces of the Debye-Hückel type, and the contributions due to the short-range forces resulting from ion–ion and ion–solvent interactions may be added to it with the increase in the concentrations of the solute species. In a previous paper,[11] by assuming that the short-range forces may be independent of the ionic strength, the following method was obtained for the estimation of the activity coefficients of a strong electrolyte 12, $\gamma_{\pm 12}$, in a solution containing 1, 2, $\cdots$, i (odd : cation, even : anion) ions:

$$\log \gamma_{\pm 12} = \log \gamma^{\circ}_{\pm 12} + \sum_i a_{i(12)} m_i \qquad (i \neq 1, 2) \tag{1}$$

where $\gamma^{\circ}_{\pm 12}$ is the mean activity coefficient of the electrolyte 12 in a solution containing only 12 at the same ionic strength as the mixture; m_i is the molality of the i ion and $a_{i(12)}$ is the parameter assigned to the three-ion system of the 1, 2, and i ions. As a result of the assumption used in the derivation of Eq. (1), this parameter may be independent of the ionic strength and the ions coexisting in the solution other than 1, 2 and i. In this treatment, molality scales are used for the concentrations of the ion and the electrolyte and the activity coefficients of the electrolyte.

In the hydrogen chloride (HCl)–metal perchlorate ($M(ClO_4)_n$)–water systems, the activity coefficients of hydrochloric acid, $\gamma_{\pm HCl}$, are given by Eq. (1) as 1=H, 2=Cl, 3=M, and 4=ClO_4 as follows:

$$\log \gamma_{\pm HCl} = \log \gamma^{\circ}_{\pm HCl} + a_{M(HCl)} m_{M^{n+}} + a_{ClO_4(HCl)} m_{ClO_4^-} \tag{2}$$

or:

$$\log (\gamma_{\pm HCl}/\gamma^{\circ}_{\pm HCl}) = [a_{M(HCl)} + n a_{ClO_4(HCl)}] m_{M(ClO_4)_n} \tag{3}$$

A considerable amount of information is available about the activity coefficients of hydrochloric acid in the solutions containing only hydrochloric acid, $\gamma^{\circ}_{\pm HCl}$, required in this treatment.[1,2] If this treatment is appropriate, $\log (\gamma_{\pm\mathrm{HCl}}/\gamma^{\circ}_{\pm\mathrm{HCl}})$ may be expected to vary linearly with $m_{\mathrm{M(ClO_4)}_n}$.

On the other hand, $a_{\mathrm{M(HCl)}}$ has been determined for various metal ions in investigations of the hydrogen chloride–metal chloride–water systems at 25 °C. The values are shown in Table 1.[12] It is, therefore, convenient to rewrite Eq. (2) as follows:

$$[\log (\gamma_{\pm\mathrm{HCl}}/\gamma^{\circ}_{\pm\mathrm{HCl}}) - a_{\mathrm{M(HCl)}} m_{\mathrm{M}^{n+}}] = a_{\mathrm{ClO_4(HCl)}} m_{\mathrm{ClO_4^-}} \qquad (4)$$

Thus, if the parameter for the perchlorate ion, $a_{\mathrm{ClO_4(HCl)}}$, may be independent of the ionic strength and the coexisting metal ion, M^{n+}, a straight line may be obtained by the plots of the left-hand side of Eq. (4) against $m_{\mathrm{ClO_4^-}}$ and $a_{\mathrm{ClO_4(HCl)}}$ can be determined from the slope of the resultant straight line. Therefore, the activity coefficients of hydrochloric acid in aqueous solutions containing more than one metal perchlorate may be evaluated by means of Eq. (1) using the $a_{\mathrm{M(HCl)}}$ and $a_{\mathrm{ClO_4(HCl)}}$ values determined in this work and the previous one.[12]

Experimental

The activity coefficients of hydrochloric acid in the hydrogen chloride–metal perchlorate–water systems were obtained by means of emf measurements of the following cell:

$$\mathrm{Pt(H_2)/HCl}(m_1),\ \mathrm{MClO_4}(m_2),\ \mathrm{M'(ClO_4)_2}(m_3),\cdots\mathrm{/AgCl,\ Ag}$$
$$(\mathrm{M{=}Li,\ Na;\ M'{=}Mg,\ Ba})$$

The techniques and equipment used for the emf measurements were the same as has been described in detail previously.[13] The emf measurements were made at 25.00± 0.05 °C. The emf values were reproducible to within about ±0.05 mV. The following systems were investigated: $\mathrm{HCl–LiClO_4–H_2O}$, $\mathrm{HCl–NaClO_4–H_2O}$, $\mathrm{HCl–Mg(ClO_4)_2–H_2O}$, $\mathrm{HCl–Ba(ClO_4)_2–H_2O}$, $\mathrm{HCl–LiClO_4–NaClO_4–H_2O}$, $\mathrm{HCl–NaClO_4–Ba(ClO_4)_2–H_2O}$, and $\mathrm{HCl–LiClO_4–NaClO_4–Ba(ClO_4)_2–H_2O}$. The reagents used in this work were special-grade and were used without further purification.

In the above-mentioned cell, the emf values corrected to 1.00 atm of hydrogen pressure, E, are expressed by the Nernst equation as follows:

$$E = E^{\circ} - (2RT/F) \ln (m_1 \gamma_{\pm\mathrm{HCl}}) \qquad (5)$$

where E° is the standard potential of the Ag–AgCl electrode and where m_1 is the molality of hydrochloric acid, while T is the absolute temperature; R, the gas constant and F, the Faraday. 0.22234 (V) has been given as the value of E° by Bates and Bower;[14] this value was used in this work. The emf values shown as the results are corrected to a hydrogen pressure of 1.00 atm. Using Eq. (5), the activity coefficients of hydrochloric acid, $\gamma_{\pm\mathrm{HCl}}$ (exp), were obtained.

Results and Discussion

The outlines of experimental conditions in the past[4–7] and in this work on the hydrogen chloride–metal perchlorate–water systems at 25 °C are summarized in Table 2. While the data in the past were obtained at low concentrations of hydrochloric acid from 0.01 to 0.1 mol kg^{-1}, these data were used also for the examinations of Eq. (3) or (4).

The experimental data and the calculated results in the three-component systems, $\mathrm{HCl–LiClO_4–H_2O}$, $\mathrm{HCl–NaClO_4–H_2O}$, $\mathrm{HCl–Mg(ClO_4)_2–H_2O}$, and $\mathrm{HCl–Ba(ClO_4)_2–H_2O}$, are shown in Table 3. The data in these systems are plotted in Figs. 1 and 2 on the basis of Eq. (3). The literature values are also plotted in these figures. Figures 1 and 2 show that a straight line is obtained by these plots for each system and that the parameters, $a_{\mathrm{M(HCl)}}$ and $a_{\mathrm{ClO_4(HCl)}}$, may be regarded as approximately independent of the ionic strength; therefore, the treatments on the basis of Eq. (1) may be approximately appropriate.

Plots drawn on the basis of Eq. (4) are shown in Fig. 3. All the data are scattered on the zero axis. It shows that $a_{\mathrm{ClO_4(HCl)}}$ seems to be about zero, regardless of the kind of metal ion coexisting in the solution.

The values calculated by Eq. (2) with $a_{\mathrm{M(HCl)}}$ in Table 1 and the $a_{\mathrm{ClO_4(HCl)}}$ determined above, and the percentage deviations between the experimental and the

Table 1. Parameters, $a_{\mathrm{M(HCl)}}$, assigned to the three-ion systems at 25 °C[12]

Metal ion, M	$\mathrm{Li^+}$	$\mathrm{Na^+}$	$\mathrm{K^+}$	$\mathrm{Rb^+}$	$\mathrm{Cs^+}$	$\mathrm{Mg^{2+}}$	$\mathrm{Ca^{2+}}$	$\mathrm{Sr^{2+}}$	$\mathrm{Ba^{2+}}$	$\mathrm{Al^{3+}}$	$\mathrm{La^{3+}}$	$\mathrm{Ce^{3+}}$
$-a_{\mathrm{M(HCl)}}$/mol^{-1} kg	0.003	0.030	0.061	0.090	0.100	0.126	0.157	0.170	0.200	0.374	0.499	0.559

Table 2. Systems investigated for the correlation (25 °C)

No.	System	Number of Data	m_{HCl} / mol kg^{-1}	$m_{\mathrm{M(ClO_4)}_n}$ / mol kg^{-1}	I_{T}[a] / mol kg^{-1}	Reference
1	$\mathrm{HCl–LiClO_4–H_2O}$	5	0.4454—0.9162	0.4612—2.3845	0.9492—3.2284	This work
2	$\mathrm{HCl–NaClO_4–H_2O}$	16	0.0481—1.9553	0.0504—5.0697	0.0989—5.5789	This work
		12	0.05—0.25	0.05—0.95	0.10—1.00	Bates, *el al.*[4]
		16	0.0041—0.2124	2.4621—2.8545	2.8543—3.0543	Prue, *et al.*[5]
3	$\mathrm{HCl–KClO_4–H_2O}$	5	0.0994	0.0132—0.1219	0.1126—0.2213	Bates, *et al.*[4]
4	$\mathrm{HCl–Mg(ClO_4)_2–H_2O}$	11	0.4543—0.9596	0.0850—1.7331	0.7381—6.0923	This work
5	$\mathrm{HCl–Ca(ClO_4)_2–H_2O}$	7	0.0108	0.0369—1.1063	0.1215—3.3297	Stokes, *et al.*[6]
6	$\mathrm{HCl–Sr(ClO_4)_2–H_2O}$	8	0.0101	0.0237—1.145	0.0812—3.4451	Weeks[7]
7	$\mathrm{HCl–Ba(ClO_4)_2–H_2O}$	11	0.4793—1.4630	0.2096—3.0325	1.9383—10.108	This work
		12	0.0101	0.0138—1.3169	0.0515—3.9608	Weeks[7]

a) Total ionic strength.

TABLE 3. ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN THE THREE-COMPONENT SYSTEMS AT 25 °C

$\frac{m_1}{\text{mol kg}^{-1}}$	$\frac{m_2}{\text{mol kg}^{-1}}$	$\frac{I_T{}^{a)}}{\text{mol kg}^{-1}}$	$\frac{E}{\text{mV}}$	$\gamma_{\pm\text{HCl}}$ (exptl)	$\gamma^0_{\pm\text{HCl}}$	$\gamma_{\pm\text{HCl}}$ (calcd)	$\frac{\text{Dev.}}{\%}$
(A) HCl(1)-LiClO$_4$(2)-H$_2$O System							
0.4880	0.4612	0.9492	271.15	0.792	0.802	0.799	0.9
0.4617	1.4312	1.8929	263.18	0.978	0.983	0.973	−0.5
0.4454	2.0309	2.4763	257.00	1.144	1.140	1.124	−1.7
0.9162	1.0093	1.9255	226.71	1.002	0.991	0.984	−1.8
0.8439	2.3845	3.2284	212.21	1.443	1.408	1.385	−4.0
(B) HCl(1)-NaClO$_4$(2)-H$_2$O System							
0.0485	0.0504	0.0989	389.42	0.799	0.797	0.794	−0.6
0.0485	0.4778	0.5263	392.88	0.747	0.759	0.734	−1.7
0.0485	0.9832	1.0317	391.18	0.772	0.814	0.760	−1.6
0.0485	2.0970	2.1455	381.63	0.929	1.049	0.908	−2.3
0.0481	3.4488	3.4969	368.62	1.206	1.517	1.195	−0.9
0.0481	4.9907	5.0388	351.26	1.691	2.410	1.707	0.9
0.5092	0.5117	1.0209	268.90	0.793	0.812	0.784	−1.1
0.5092	1.0127	1.5219	264.27	0.868	0.900	0.840	−3.2
0.5092	2.5993	3.1085	249.20	1.134	1.360	1.136	−0.2
0.5092	3.8091	4.3183	236.47	1.491	1.939	1.490	−0.1
0.5092	5.0697	5.5789	221.23	2.006	2.841	2.002	−0.2
0.9300	3.5785	4.5085	200.81	1.634	2.093	1.635	0.1
0.9300	3.6673	4.5973	199.44	1.679	2.102	1.632	−2.8
1.9553	1.0342	2.9895	176.00	1.261	1.313	1.222	−3.1
1.9553	2.2952	4.2505	161.17	1.682	1.901	1.623	−3.5
1.9553	3.6216	5.5769	145.75	2.271	2.839	2.211	−2.6
(C) HCl(1)-Mg(ClO$_4$)$_2$-H$_2$O System							
0.4545	1.4158	4.7017	243.33	1.463	2.177	1.444	−1.3
0.4646	0.9124	3.2018	258.42	1.067	1.398	1.073	0.6
0.4739	0.4348	1.7783	269.32	0.846	0.955	0.842	−0.5
0.4831	0.0850	0.7381	274.16	0.755	0.776	0.757	−0.3
0.8779	1.1836	4.4287	212.66	1.375	2.006	1.423	3.5
0.8930	1.7331	6.0923	190.28	2.090	3.312	2.003	−4.2
0.9012	0.6601	2.8815	225.44	1.045	1.274	1.052	0.7
0.9128	0.3915	2.0873	230.48	0.935	1.032	0.921	−1.5
0.9179	1.2168	4.5683	205.91	1.500	2.096	1.473	−1.8
0.9355	0.7302	3.1262	220.05	1.118	1.367	1.060	−1.1
0.9596	0.2623	1.7465	230.75	0.885	0.948	0.879	−0.7
(D) HCl(1)-Ba(ClO$_4$)$_2$-H$_2$O System							
0.4793	0.7701	2.7896	266.62	0.875	1.245	0.873	−0.2
0.4793	1.7334	5.6795	247.86	1.269	2.920	1.314	3.5
1.0101	0.3094	1.9383	228.81	0.873	0.994	0.862	−1.3
1.0101	0.8047	3.4242	220.40	1.028	1.487	1.027	−0.1
1.0101	1.3142	4.9527	210.91	1.237	2.348	1.287	3.6
1.0101	1.8327	6.5082	197.79	1.597	3.804	1.636	2.4
1.0101	2.5450	8.6451	181.65	2.186	7.216	2.235	2.2
1.0101	3.0325	10.108	174.41	2.517	10.70	2.648	5.2
1.4630	0.2096	2.0918	205.02	0.958	1.034	0.939	−2.0
1.4630	1.1614	4.9472	186.05	1.386	2.344	1.373	−0.9
1.4630	1.8091	6.8903	172.40	1.807	4.230	1.839	1.8

a) Total ionic steength.

calculated values are shown in Table 3 as $\gamma_{\pm\text{HCl}}$(calcd) and Dev. %(=100[$\gamma_{\pm\text{HCl}}$(calcd)−$\gamma_{\pm\text{HCl}}$(exptl)]/$\gamma_{\pm\text{HCl}}$(exptl)). The Dev.% in these systems are within about 5% over a wide range of ionic strengths, similar results were obtained for the data in the past.[4–7]

The experimental data and calculated results in the four-component systems, HCl–LiClO$_4$–NaClO$_4$–H$_2$O, and HCl–NaClO$_4$–Ba(ClO$_4$)$_2$–H$_2$O, are shown in Table 4, while the results in the five-component system, HCl–LiClO$_4$–NaClO$_4$–Ba(ClO$_4$)$_2$–H$_2$O, are given in Table 5. In the four- and five-component systems, the values calculated by means of Eq. (1)

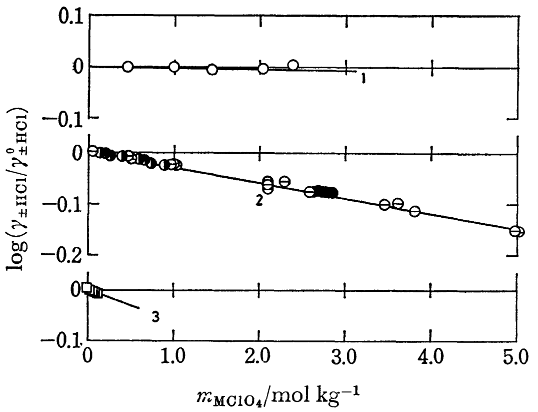

Fig. 1. Activity coefficients of hydrochloric acid in the hydrogen chloride-alkali metal perchlorate-water systems at 25 °C.
1: HCl-$LiClO_4$-H_2O System (○: This work).
2: HCl-$NaClO_4$-H_2O System (⊖: This work, ◑: Bates, *et al.*,[4] ●: Prue, *et al.*[5]).
3: HCl-$KClO_4$-H_2O System (□: Bates, *et al.*[4]).

with the parameters mentioned also agree with the experimental results within about 5%.

In the treatments of the activity coefficients in the three-component systems, *i.e.*, in the solutions containing two electrolytes, the method based on Eq. (1) is similar to the Harned-rule[15] in form. However, the Harned-rule is restricted to the treatments of the three-component systems; furthermore, its parameters are treated as the functions of the ionic strength, while the parameters, $a_{i(12)}$, in Eq. (1) may be treated independently of the ionic strength and the coexisting ions other than 1, 2, and *i* ions because Eq. (1) has been derived on the assumption that the short-range forces may be independent of the ionic strength. As a result, this method may be expanded to treatments of solutions containing more than two electrolytes.

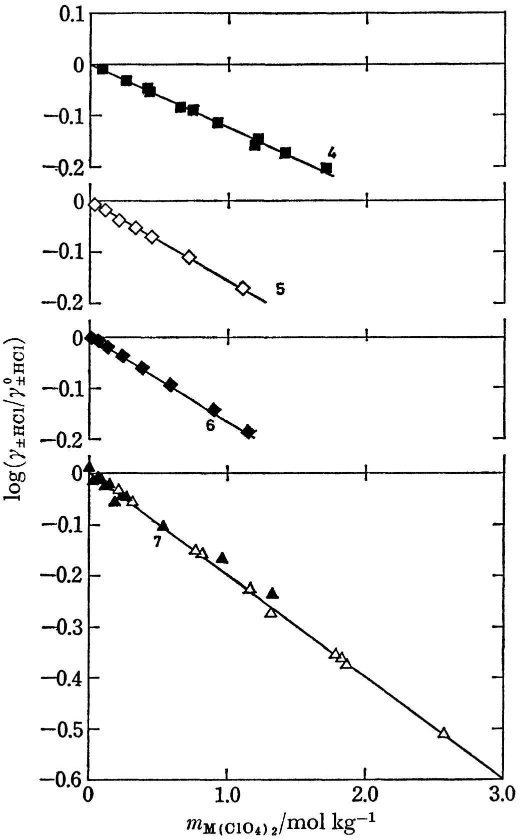

Fig. 2. Activity coefficients of hydrochloric acid in the hydrogen chloride-alkaline earth metal perchlorate-water systems at 25 °C.
4: HCl-$Mg(ClO_4)_2$-H_2O System (■: This work).
5: HCl-$Ca(ClO_4)_2$-H_2O System (◇: Stokes, *et al.*[6]).
6: HCl-$Sr(ClO_4)_2$-H_2O System (◆: Weeks[7]).
7: HCl-$Ba(ClO_4)_2$-H_2O System (△: This work, ▲: Weeks[7]).

TABLE 4. ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN THE FOUR-COMPONENT SYSTEMS AT 25 °C

m_1/mol kg^{-1}	m_2/mol kg^{-1}	m_3/mol kg^{-1}	I_T[a)]/mol kg^{-1}	E/mV	$\gamma_{\pm HCl}$ (exptl)	$\gamma^0_{\pm HCl}$	$\gamma_{\pm HCl}$ (calcd)	Dev./%
		(A)	HCl(1)-$LiClO_4$(2)-$NaClO_4$(3)-H_2O System					
0.4503	1.4143	0.5396	2.4042	258.92	1.090	1.121	1.069	−1.9
0.4610	1.0096	1.0523	2.5229	258.20	1.079	1.155	1.067	−1.1
0.4730	0.5560	1.5887	2.6177	257.12	1.074	1.187	1.060	−1.3
0.9756	1.4395	0.4940	2.9091	212.13	1.250	1.285	1.230	−1.6
1.0107	0.8278	0.8728	2.7113	215.20	1.137	1.218	1.140	0.3
1.0293	0.5035	1.6568	3.1896	208.99	1.260	1.393	1.238	−1.7
		(B)	HCl(1)-$NaClO_4$(2)-$Ba(ClO_4)_2$(3)-H_2O System					
0.4793	1.8108	0.5100	3.8201	252.04	1.170	1.674	1.168	−0.2
0.4793	0.4118	1.0126	3.9289	258.01	1.042	1.727	1.053	1.1
0.4793	1.5257	1.0062	5.0236	245.55	1.328	2.397	1.357	2.2
0.9692	0.5231	0.5121	3.0286	222.43	1.030	1.328	1.012	−1.7
0.9692	1.4651	0.4226	3.7021	213.90	1.216	1.617	1.203	−1.1
0.9692	0.3969	0.9096	4.0949	216.40	1.158	1.815	1.162	0.3
1.4630	0.8105	0.2170	2.9245	195.63	1.149	1.290	1.104	−3.9
1.4630	0.5189	0.5134	3.5221	193.08	1.208	1.529	1.165	−3.6
1.4630	0.4479	0.9292	4.6985	185.68	1.395	2.175	1.375	−1.4

a) Total ionic strength.

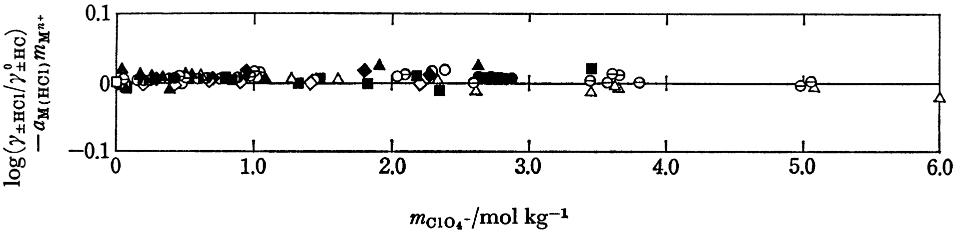

Fig. 3. Determination of parameter for perchlorate ion, $a_{ClO_4(HCl)}$. Symbols are identical with those in Figs. 1 and 2.

TABLE 5. ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN THE FIVE-COMPONENT SYSTEM, $HCl(1)-LiClO_4(2)-NaClO_4(3)-Ba(ClO_4)_2(4)-H_2O$, AT 25 °C

m_1 / mol kg^{-1}	m_2 / mol kg^{-1}	m_3 / mol kg^{-1}	m_4 / mol kg^{-1}	I_T[a] / mol kg^{-1}	E / mV	$\gamma_{\pm HCl}$ (exptl)	$\gamma^0_{\pm HCl}$	$\gamma_{\pm HCl}$ (calcd)	Dev. / %
0.4626	0.8731	0.9302	0.2815	3.1104	254.78	1.150	1.357	1.111	−3.4
0.4636	0.8290	1.2928	0.1870	3.1464	252.91	1.190	1.371	1.143	−3.9
0.4690	0.5701	0.7797	0.7994	4.2170	249.35	1.260	1.881	1.229	−2.5
0.4791	0.2283	0.5967	0.5687	3.0102	259.57	1.011	1.320	0.973	−3.8
1.0286	0.5151	0.4827	0.4922	3.5030	212.52	1.177	1.519	1.167	−0.8
1.0324	0.4490	0.8280	0.2967	3.1995	213.68	1.146	1.397	1.147	0.1

a) Total ionic strength.

As a matter of course, it seems that the short-range forces may be independent of the ionic strength; the results in a previous[12] and in this one show that indeed the $a_{i(12)}$ values are approximately independent of the ionic strength over a wide range and that the effects on $a_{i(12)}$ of the coexisting ions other than 1, 2, and i ions can generally be ignored. Moreover, the parameters which can be determined easily in the simpler systems containing three or four ions may be applied to the more complicated systems. It should also be noted that this method may be used, with errors in estimation within about 5%, over a wide range of ionic strengths. Although the examinations using this method in this work were made only on the activity coefficients of hydrochloric acid, yet this method may be useful in evaluating that of the other strong electrolytes in multicomponent electrolyte solutions. The method based on Eq. (1) may, therefore, be a convenient one for evaluating the activity coefficients in multicomponent electrolyte solutions for use in engineering calculations.

References

1) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York (1958).

2) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed. (revised), Butterworths, London (1968).

3) H. S. Harned and R. A. Robinson, "Multicomponent Electrolyte Solutions," Pergamon Press, London (1968).

4) S. J. Bates and J. W. Urmston, *J. Am. Chem. Soc.*, **55**, 4058 (1933).

5) J. E. Prue and A. J. Read, *J. Chem. Soc.*, *A*, **1966**, 1812.

6) J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, **67**, 2242 (1963).

7) I. A. Weeks, *Aust. J. Chem.*, **20**, 2367 (1967).

8) G. Scatchard, R. M. Rush, and J. S. Johnson, *J. Phys. Chem.*, **74**, 3876 (1970).

9) P. J. Reilly, R. H. Wood, and R. A. Robinson, *J. Phys. Chem.*, **75**, 1305 (1971).

10) K. S. Pitzer, *J. Phys. Chem.*, **77**, 268 (1973).

11) K. Teruya and I. Nakamori, *Technol. Rep. Kyushu Univ.*, **48**, 267 (1975).

12) K. Teruya, T. Mori, and I. Nakamori, *Kagaku Kogaku Ronbunshu*, **2**, 91 (1976).

13) K. Teruya, T. Mori, K. Shiraogawa, F. Noguchi, and I. Nakamori, *Technol. Rep. Kyushu Univ.*, **48**, 507 (1975).

14) R. G. Bates and V. E. Vower, *J. Res. Nat. Bur. Stand.*, **53**, 283 (1954).

15) H. S. Harned, *J. Am. Chem. Soc.*, **57**, 1865 (1935).