August, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(8), 1921—1926 (1974) 1921

Estimation of Individual Ionic Activity Coefficients from Conductivity Data on Strong Electrolytes in Dilute Aqueous Solutions

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(Received April 22, 1974)

The individual ionic activity coefficients of strong electrolytes in dilute aqueous solutions are derived from the ionic conductivity data, using the Debye-Hückel-Onsager theory of strong electrolyte solutions. The mean activity coefficients computed by the present method are in good agreement with the experimental values in most of the uni-univalent and some of the uni-multivalent electrolytes studied, which demonstrates the validity of the method in deriving the individual ionic activity coefficients. Comparisons are made of the values of individual activity coefficients of various ions in dilute aqueous solutions of strong electrolytes, as determined by different methods including measurements of potential differences across membranes at varying concentrations. The influence of the ion of opposite sign on the individual ionic activity coefficient has been observed.

The individual ionic activity coefficient is an important and useful quantity in the study of various phenomena in electrolyte solutions. Thermodynamics provides methods of determining mean activity coefficients of electrolytes, but it can offer no theoretical or experimental approach to the determination of individual ionic activity coefficients. Non-thermodynamic assumptions must be introduced in the calculation of individual ionic activity coefficients. Typical conventions used for computing ionic activities have been discussed in detail by Bates and Alfenaar.[1)]

In solutions of low ionic strength ($I \leq 0.1$ M), individual ionic activity coefficients can be calculated with reasonable accuracy from the Debye-Hückel equation, if appropriate ion-size parameters are assumed. In his classical tabulation of ion-size parameters, Kielland[2)] employed the so-called Stokes radius calculated from the ionic conductivity at infinite dilution. The application of conductivity data to the determination of ion-size parameters in the activity equation was suggested by Fuoss and Accascina.[3)] Justice *et al.*[4)] discussed the self-consistency of the Debye-Hückel theory of activity coefficients and the Fuoss-Onsager theory of electrolytic conductivity, and justified the use of conductivity data in the estimation of activity coefficients of electrolytes in dilute solutions ($I \leq 0.1$ M). Their study, however, was restricted to mean activity coefficients of electrolytes. The possibility of computing individual ionic activity coefficients from conductivity data has not been discussed.

In this paper, individual ionic activity coefficients are derived from ionic conductivity data, based upon the Debye-Hückel-Onsager theory of strong electrolyte solutions. The results are compared with the individual ionic activity coefficients calculated by various conventions[1)] and with some experimental values obtained from membrane-potential measurements.

Theoretical

The Debye-Hückel-Onsager theory[5)] of strong electrolyte solutions gives the following expressions for the individual ionic activity coefficient $\gamma_{+(-)}$ and ionic conductivity $\lambda_{+(-)}$, respectively, of the cation (anion) in a solution of a single electrolyte*:

$$\log \gamma_{+(-)} = -A^* z^2_{+(-)} \chi^{-1}_{+(-)} \tag{1}$$

$$\lambda_{+(-)} = \lambda^\infty_{+(-)} - (\alpha^* \lambda^\infty_{+(-)} + \beta^* |z_{+(-)}|) \chi^{-1}_{+(-)} \tag{2}$$

where $z_{+(-)}$ is the charge number, $\lambda^\infty_{+(-)}$ the ionic conductivity at infinite dilution, the coefficients A^*, α^*, and β^* are given in Table 1, and $\chi_{+(-)}$ is the distance parameter that determines the potential due to the environment of the given central ion. According to the Debye-Hückel theory, $\chi_{+(-)}$ is given by

$$\chi_{+(-)} = a_{+(-)} + \kappa^{-1} \tag{3}$$

where $a_{+(-)}$ is the distance of closest approach and κ^{-1} is often called the thickness of the ionic atmosphere. In the following treatment, however, it is not necessary to know the explicit expression for the quantity $\chi_{+(-)}$.

Eliminating $\chi_{+(-)}$ from Eqs. (1) and (2), we obtain

$$\log \gamma_{+(-)} = -\frac{A^* z^2_{+(-)}}{\alpha^* \lambda^\infty_{+(-)} + \beta^* |z_{+(-)}|} (\lambda^\infty_{+(-)} - \lambda_{+(-)}) \tag{4}$$

which relates the individual ionic activity coefficient to the ionic conductivity. Similarly, for the mean activity coefficient $\gamma_\pm$ of a completely dissociated electrolyte, we obtain

$$\log \gamma_\pm = -\frac{A^* |z_+ z_-|}{\alpha^* \Lambda^\infty + \beta^* (z_+ + |z_-|)} (\Lambda^\infty - \Lambda) \tag{5}$$

where Λ is the equivalent conductivity of the electrolyte.

Eq. (1) (the Debye-Hückel approach) and Eq. (2) (the Onsager-Robinson-Stokes approach) are less rigorous than more advanced theoretical expressions,[5)] but do fit with reasonable accuracy the experimental data on mean activity coefficients and conductivities of completely dissociated electrolytes in aqueous solutions of ionic strengths below 0.1 M. The use of Eqs. (1) and (2) also has the following practical advantages for the present purpose:

(i) The equations can be combined in a straightforward way to give the expressions (4) and (5) for activity coefficients in terms of conductivity data.

(ii) The application of Eq. (2) is not restricted to solutions of symmetrical electrolytes, whereas some advanced conductivity equations (such as the Fuoss-Onsager equation) can be used only in solutions of

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* The difference in activity coefficients due to the different concentration scales is ignored throughout the present paper.

TABLE 1. EXPRESSIONS FOR A^*, α^* AND β^* IN Eqs. (1) AND (2), AND THEIR NUMERICAL VALUES IN AQUEOUS SOLUTIONS OF 25 °C ($\varepsilon=78.30$, $\eta=0.008903$ poise)

Theoretical expression[a]	Numerical value in aq. soln. of 25 °C
$A^* = \dfrac{e^2}{2\varepsilon kT(\ln 10)}$	1.554×10^{-8} cm
$\alpha^* = \dfrac{\lvert z_+z_-\rvert e^2}{3\varepsilon kT}\,\dfrac{q}{1+\sqrt{q}}$	$2.3858\times10^{-8}\lvert z_+z_-\rvert\dfrac{q}{1+\sqrt{q}}$ cm
$\beta^* = \dfrac{F^2}{6\pi\eta N_A}$	$92.11\times10^{-8}\ \Omega^{-1}\,\text{cm}^3\,\text{mol}^{-1}$
$q = \dfrac{\lvert z_+z_-\rvert}{z_+ + \lvert z_-\rvert}\,\dfrac{\lambda_+^\infty+\lambda_-^\infty}{z_+\lambda_-^\infty + \lvert z_-\rvert\lambda_+^\infty}$	

a) The symbols used have their usual meaning.

TABLE 2. COMPARISON OF THE CALCULATED AND EXPERIMENTAL MEAN ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25 °C (calc.: calculated from the conductivity data by the present method)

A. Uni-univalent and uni-bivalent electrolytes.

Electrolyte		Equivalent concentration $c^*(=\nu zc)^{a)}$/mol dm^{-3}				Ref.	Electrolyte		Equivalent concentration $c^*(=\nu zc)^{a)}$/mol dm^{-3}				Ref.
		0.01	0.02	0.05	0.1				0.01	0.02	0.02	0.1	
HCl	calc.	0.894	0.862	0.810	0.763		KNO_3	calc.	0.892	0.855	0.792	0.735	
	exp.	0.905	0.876	0.830	0.796	5, 8		exp.	0.898	0.862	0.799	0.739	8
LiCl	calc.	0.901	0.869	0.817	0.772		$AgNO_3$	calc.	0.895	0.857	0.792	0.732	
	exp.	0.895	0.865	0.819	0.790	8		exp.	0.897	0.860	0.793	0.734	8
NaCl	calc.	0.901	0.869	0.817	0.772		$Na(CH_3COO)$	calc.	0.901	0.869	0.816	0.769	
	exp.	0.902	0.871	0.819	0.778	5, 8		exp.	—	—	—	0.791	8
KCl	calc.	0.899	0.867	0.815	0.772		$K(CH_3COO)$	calc.	0.919	0.888	0.836	0.780	
	exp.	0.902	0.869	0.816	0.770	8		exp.	—	—	—	0.796	5
NH_4Cl	calc.	0.900	0.866	0.809	0.761		Na_2SO_4	calc.	0.758	0.694	0.601	0.531	
	exp.	0.896	0.862	0.808	0.770	8		exp.	0.778	0.714	(0.615)[b]	0.536	8
KBr	calc.	0.901	0.872	0.822	0.777		K_2SO_4	calc.	0.745	0.675	0.582	0.513	
	exp.	0.906	0.876	0.824	0.778	8		exp.	0.777	0.711	(0.610)[b]	0.525	8
KI	calc.	0.901	0.870	0.821	0.782		$CaCl_2$	calc.	0.779	0.722	0.643	0.584	
	exp.	0.903	0.872	0.820	0.778	8		exp.	0.789	0.731	(0.645)[b]	0.583	8
HNO_3	calc.	0.887	0.858	0.807	0.758		$MgCl_2$	calc.	0.783	0.726	0.648	0.587	
	exp.	0.902	0.871	0.823	0.791	8		exp.	—	—	—	—	

B. Lanthanum salts.

Electrolyte		Molarity c/mol dm^{-3}				Ref.	Electrolyte		Molarity c/mol dm^{-3}			
		0.005	0.01	0.02	0.03				0.005	0.01	0.02	0.03
$LaCl_3$	calc.	0.611	0.543	0.479	0.444		$La(NO_3)_3$	calc.	0.606	0.531	0.465	0.429
	exp.	0.631	0.556	0.480	0.436	6		exp.	—	—	—	—
$LaBr_3$	calc.	0.628	0.563	0.502	0.470		$La(ClO_4)_3$	calc.	0.645	0.582	0.526	0.494
	exp.	0.638	0.567	0.490	0.449	6		exp.	—	—	—	—

a) Equivalent concentration c^* is defined by $c^*=\nu zc$, where c is the molarity and $\nu z=\nu_+z_+=\nu_-\lvert z_-\rvert$.

b) Interpolated values.

symmetrical electrolytes.

In this connection, it is important to remember that the formal expression for χ is not required in the derivation of Eqs. (4) and (5); these relations are satisfied if the effect of ionic interaction (considering only the Debye-Hückel type) on the activity and conductivity is expressed by the common parameter χ in Eqs. (1) and (2).

Results and Discussion

Equivalent Conductivities and Transport Numbers. Knowledge of equivalent conductivities and transport numbers is necessary in order to determine activity coefficients by using Eqs. (4) and (5). Ionic conductivities $\lambda_{+(-)}$ can be obtained from the equivalent conductivity Λ of the electrolyte and the transport numbers $t_{+(-)}$ of the ions according to the equation

$$\lambda_{+(-)} = t_{+(-)}\Lambda \tag{6}$$

In the following calculations we used the conductivities and transport numbers reported by Spedding and Atkinson[6] (for the lanthanum salts) and those given in the Landolt-Börnstein Tables[7] (for the other electrolytes).

Mean Activity Coefficients of Strong Electrolytes. The validity of the present method of computing activity coefficients from conductivity data was examined by comparing the mean activity coefficients calculated by using Eq. (5) with the experimental data available in literature.[5,6,8] The results obtained with a variety of strong electrolytes are given in Table 2.

It is seen that the calculated activity coefficients o the majority of uni-univalent electrolytes are in good agreement with the experimental values at ionic strengths below 0.1 M. The agreement is also good for calcium chloride and for lanthanum chloride and bromide in solutions where $I \leq 0.1$ M. Some deviation of the calculated values from the experimental data is observed in solutions of hydrochloric and nitric acids. From the 62 sets of data in Table 2, the correlation between $\gamma_{\pm\mathrm{calc}}$ and $\gamma_{\pm\mathrm{exp}}$ is given by

$$\gamma_{\pm\mathrm{calc}} = -0.00193 + 0.993\ \gamma_{\pm\mathrm{exp}}$$

with

$$S = 0.0112,\quad S_a = 0.00858,\quad S_b = 0.0111$$

where S, S_a, and S_b are the standard deviations for $\gamma_\pm$, the intercept, and the slope, respectively.

Individual Activity Coefficients of Ions. Examination of the results given in Table 2 shows Eq. (4) to give reasonably good estimates of individual ionic activity coefficients in dilute solutions ($I \leq 0.1$ M). Table 3 presents the individual activity coefficients of various ions calculated by using Eq. (4) in aqueous electrolyte solutions of 25 °C.

It follows from the results in Table 3 that:

(i) In chloride solutions the individual activity coefficients of univalent cations increase in the order $H^+ < NH_4^+ < K^+ < Na^+ < Li^+$. This sequence of the alkali-metal cations is consistent with that obtained from potential measurements using a permselective membrane.[9] The activities of calcium and magnesium ions are almost the same in chloride solutions.

(ii) The values of $\gamma(H^+)$ are practically equal in chloride and nitrate solutions.

(iii) In solutions of a given ionic strength, $\gamma(K^+)$ varies with the nature of the anion, increasing in the order $SO_4^{2-} < NO_3^- < Cl^- < Br^- \lesssim CH_3COO^- < I^-$.

(iv) The values of $\gamma(La^{3+})$ increase in the following order: $NO_3^- \simeq Cl^- < Br^- < ClO_4^-$.

(v) The individual activity coefficient of chloride ion is almost the same in solutions of HCl, LiCl, NaCl, KCl, NH_4Cl, $CaCl_2$ and $MgCl_2$ of a given ionic strength ($I \leq 0.1$ M). In Fig. 1, $\log \gamma(Cl^-)$ is plotted as a function of $I^{1/2}$; the theoretical lines calculated from the Debye-Hückel limiting equation and from the Scatchard equation (*cf.* Eq. (8)) are also shown. Smaller values of $\gamma(Cl^-)$ observed in $LaCl_3$-solutions suggest the existence of some specific interaction between La^{3+} and Cl^-.

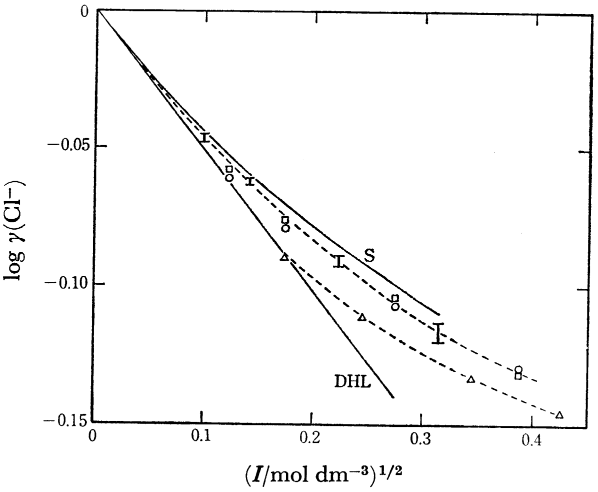

Fig. 1. Individual activity coefficients of chloride ion as a function of $I^{1/2}$ in aqueous solutions of uni-univalent and uni-multivalent electrolytes at 25 °C. I, uni-univalent electrolytes (HCl, LiCl, NaCl, KCl and NH_4Cl); ○, $CaCl_2$; □, $MgCl_2$; △, $LaCl_3$. DHL, Debye-Hückel limiting slope; S, theoretical line by the Scatchard equation.

(vi) The values of $\gamma(NO_3^-)$ increase in the order $Ag^+ < K^+ < H^+$.

(vii) The activity of sulfate ion is almost the same in solutions of Na_2SO_4 and K_2SO_4 ($I \leq 0.15$ M).

Comparison of Individual Ionic Activity Coefficients Calculated by Different Methods. The following non-thermodynamic conventions have been commonly adopted in the estimation of individual ionic activities.[1]

The MacInnes Convention. MacInnes[10] assumes that

$$\gamma(K^+) = \gamma(Cl^-) = \gamma_\pm(KCl) \tag{7}$$

in aqueous solutions of potassium chloride. It is also assumed that the activity of chloride ion in the presence of various univalent cations is independent of the nature of the cation at any concentration.

The pH Convention. In this convention[1,11] the individual activity coefficient of chloride ion in dilute aqueous solutions ($I \leq 0.1$ M) is assumed to be given by the Scatchard equation[12]

Table 3. Individual activity coefficients of ions in aqueous solutions of strong electrolytes at 25 °C, as computed from the ionic conductivity data

A. Individual activity coefficients of cations.

Ion	Electrolyte	Equivalent concentration $c^*(=\nu zc)$/mol dm^{-3}			
		0.01	0.02	0.05	0.1
H^+	HCl	0.893	0.861	0.809	0.761
	HNO_3	0.897	0.862	0.808	0.762
Li^+	LiCl	0.903	0.872	0.822	0.779
Na^+	NaCl	0.902	0.871	0.821	0.777
	$Na(CH_3COO)$	0.901	0.869	0.816	0.768
	Na_2SO_4	0.860	0.817	0.754	0.705
K^+	KCl	0.900	0.868	0.816	0.773
	KBr	0.899	0.869	0.820	0.778
	KI	0.901	0.870	0.822	0.784
	KNO_3	0.895	0.858	0.796	0.740
	$K(CH_3COO)$	0.924	0.891	0.839	0.780
	K_2SO_4	0.845	0.799	0.733	0.681
NH_4^+	NH_4Cl	0.901	0.868	0.811	0.763
Ag^+	$AgNO_3$	0.902	0.867	0.806	0.752
Ca^{2+}	$CaCl_2$	0.635	0.552	0.444	0.370
Mg^{2+}	$MgCl_2$	0.635	0.551	0.450	0.384
La^{3+}	$LaCl_3$	0.281	0.207	0.149	0.121
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
	$LaBr_3$	0.295	0.222	0.163	0.135
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
	$La(NO_3)_3$	0.281	0.204	0.147	0.120
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
	$La(ClO_4)_3$	0.307	0.233	0.176	0.146
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$

B. Individual activity coefficients of anions.

Ion	Electrolyte	Equivalent concentration $c^*(=\nu zc)$/mol dm^{-3}			
		0.01	0.02	0.05	0.1
Cl^-	HCl	0.896	0.864	0.813	0.770
	LiCl	0.899	0.867	0.814	0.766
	NaCl	0.900	0.868	0.814	0.768
	KCl	0.899	0.867	0.815	0.771
	NH_4Cl	0.899	0.865	0.808	0.758
	$CaCl_2$	0.869	0.833	0.782	0.743
	$MgCl_2$	0.875	0.840	0.786	0.738
	$LaCl_3$	0.814	0.774	0.737	0.716
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
Br^-	KBr	0.904	0.874	0.823	0.777
	$LaBr_3$	0.823	0.787	0.752	0.735
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
NO_3^-	HNO_3	0.864	0.848	0.804	0.748
	KNO_3	0.889	0.851	0.788	0.730
	$AgNO_3$	0.889	0.848	0.778	0.713
	$La(NO_3)_3$	0.799	0.753	0.710	0.685
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
ClO_4^-	$La(ClO_4)_3$	0.838	0.804	0.774	0.757
		$(c^*=0.015)$	$(c^*=0.03)$	$(c^*=0.06)$	$(c^*=0.09)$
CH_3COO^-	$Na(CH_3COO)$	0.901	0.869	0.816	0.770
	$K(CH_3COO)$	0.915	0.883	0.833	0.782
SO_4^{2-}	Na_2SO_4	0.591	0.503	0.383	0.303
	K_2SO_4	0.586	0.490	0.376	0.300

$$\log \gamma(\mathrm{Cl}^-) = -\frac{A\sqrt{I}}{1+1.5\sqrt{I}} \tag{8}$$

where A is the Debye-Hückel limiting slope.

The Valance-relationship Convention. According to this convention,[1] the activity coefficients of ions are related as in the Debye-Hückel limiting law. In the case of an unsymmetrical electrolyte MA_2, for example, the relationship between $\gamma(M^{2+})$, $\gamma(A^-)$ and $\gamma_\pm(MA_2)$ is given by

$$\gamma(M^{2+}) = \gamma(A^-)^4 = \gamma_\pm(MA_2)^2 \tag{9}$$

For uni-univalent electrolytes the relationship is simply

$$\gamma_+ = \gamma_- = \gamma_\pm \tag{10}$$

which is equivalent to the assumption proposed by Guggenheim.[13]

If the individual activity coefficients of chloride ion at varying ionic strengths are defined either by the MacInnes convention or by the pH convention, the individual activity coefficients of other ions can be calculated in the following way:[1] *e.g.*, for the univalent cation M^+ and anion A^- of the electrolyte MA

$$\log \gamma(M^+) = 2 \log \gamma_\pm(\mathrm{MCl}) - \log \gamma(\mathrm{Cl}^-)$$

$$\log \gamma(A^-) = \log \gamma(\mathrm{Cl}^-) + 2 \log \frac{\gamma_\pm(\mathrm{MA})}{\gamma_\pm(\mathrm{MCl})}$$

and for the univalent anion A^- of the salt MA_2

TABLE 4. COMPARISON OF INDIVIDUAL ACTIVITY COEFFICIENTS OF VARIOUS IONS IN AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES AT IONIC STRENGTH OF 0.1 M AND AT 25 °C, AS COMPUTED BY DIFFERENT METHODS

Electrolyte	Ion	MacInnes-convention	pH-convention	Valence-convention	Present method	Exp.[9]
HCl	H^+	0.823	0.816	0.796	0.761	—
	Cl^-	0.770	0.777	0.796	0.770	—
HNO_3	H^+	0.823	0.816	0.791	0.762	—
	NO_3^-	0.760	0.767	0.791	0.748	—
LiCl	Li^+	0.811	0.804	0.790	0.779	0.76
	Cl^-	0.770	0.777	0.790	0.766	0.82
NaCl	Na^+	0.786	0.779	0.778	0.777	0.76
	Cl^-	0.770	0.777	0.778	0.768	0.80
$Na(CH_3COO)$	Na^+	0.786	0.779	0.791	0.768	—
	CH_3COO^-	0.796	0.803	0.791	0.770	—
KCl	K^+	0.770	0.763	0.770	0.773	0.75
	Cl^-	0.770	0.777	0.770	0.771	0.79
KBr	K^+	0.770	0.763	0.772	0.778	—
	Br^-	0.774	0.781	0.772	0.777	—
KI	K^+	0.770	0.763	0.778	0.784	—
	I^+	0.786	0.793	0.778	0.781	—
KNO_3	K^+	0.770	0.763	0.739	0.740	—
	NO_3^-	0.709	0.716	0.739	0.730	—
$K(CH_3COO)$	K^+	0.770	0.763	0.796	0.780	—
	CH_3COO^-	0.823	0.830	0.796	0.782	—
NH_4Cl	NH_4^+	0.770	0.763	0.770	0.763	—
	Cl^-	0.770	0.777	0.770	0.758	—
$AgNO_3$	Ag^+	—	—	0.734	0.752	—
	NO_3^-	—	—	0.734	0.713	—
Na_2SO_4	Na^+	0.786	0.779	0.763	0.733	0.75
	SO_4^{2-}	0.319	0.325	0.339	0.350	0.35
K_2SO_4	K^+	0.770	0.763	0.757	0.710	0.73
	SO_4^{2-}	0.317	0.323	0.328	0.340	0.35
$CaCl_2$	Ca^{2+}	0.401	0.394	0.384	0.415	0.42[a]
	Cl^-	0.770	0.777	0.787	0.765	0.75[a]
$MgCl_2$	Mg^{2+}	—	—	—	0.423	—
	Cl^-	0.770	0.777	—	0.765	—
$LaCl_3$	La^{3+}	0.137	0.133	0.125	0.162	—
	Cl^-	0.770	0.777	0.794	0.745	—
$LaBr_3$	La^{3+}	—	—	0.134	0.180	—
	Br^-	—	—	0.800	0.762	—
$La(NO_3)_3$	La^{3+}	—	—	—	0.162	—
	NO_3^-	—	—	—	0.720	—
$La(ClO_4)_3$	La^{3+}	—	—	—	0.190	—
	ClO_4^-	—	—	—	0.783	—

a) *Estimated from the figure given in Ref. 1.*

$$\log \gamma(\mathrm{A}^-) = \log \gamma(\mathrm{Cl}^-) + \frac{3}{2} \log \frac{\gamma_\pm(\mathrm{MA}_2)}{\gamma_\pm(\mathrm{MCl}_2)}$$

In this derivation of individual ionic activity coefficients, it is assumed that $\gamma(\mathrm{Cl}^-)$ and $\gamma(\mathrm{M}^+$ or $\mathrm{M}^{2+})$ are independent of the nature of the ions of opposite sign present in the solution.

Application of all the conventions mentioned above more or less ignores the nature of the ions. On the other hand, the present method takes into account the nature of the ions as revealed by their characteristic ionic conductivities, and should give more reasonable estimates of individual ionic activity coefficients.

Table 4 compares the activity coefficients of various ions in aqueous solutions at ionic strength of 0.1 M, as determined by the different methods discussed earlier. The experimental values for cations in Table 4 were derived from potential measurements with a permselective membrane[9]; the experimental data were standardized at an ionic strength of 0.01 M or 0.015 M (in case of $\mathrm{Na_2SO_4}$ and $\mathrm{K_2SO_4}$). The experimental values for anions were calculated from those for the cations and those for the mean activity coefficients of the corresponding electrolytes. The membrane-potential measurements involve some error due to the difficulty of eliminating liquid-junction potentials; the uncertainty in the present experimental values is estimated to be between 1 and 5% most in cases.

Further experimental data will be required before it can be decided whether the present method gives more reliable estimates of individual ionic activity coefficients than the other conventions. From Table 4, however, it is already seen that the present method gives the best fit to the experimental values in the cases of calcium chloride and of sodium and potassium sulfates, where the other conventions result in appreciably different values.

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