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Determination of Ion Activity Coefficients from the Measurement of Membrane Concentration Potentials—Activity Behavior of Alkali-metal Cations in Aqueous Solutions at 25°C

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The membrane concentration potentials across a permselective sulfonated polystyrene collodion-base membrane were measured with aqueous solutions of alkali-metal salts at 25.0°C. By assuming the ideal behavior of the membrane, the activity coefficients of the critical cations were determined from the membrane concentration potentials at ionic strengths higher than 0.01. The ion activity coefficients of alkali-metal cations were found to follow the order $Li^+ > Na^+ > K^+$ for the chlorides, nitrates, perchlorates, and sulfates. The order of activity coefficients of Na^+ in different halide solutions was bromide>chloride>fluoride. Considerable differences were observed between the individual and mean activity coefficients at ionic strengths higher than 0.01. The individual ion activity coefficients determined from the experimental data were analysed by means of the extended Debye-Hückel equation.

The application of permselective membranes, *i.e.*, membranes of highest ionic selectivity and high permeability, to the determination of ion activities has been suggested and demonstrated by Sollner and his collaborators.[1-3] Among various ion-selective membranes, some of them being available on market, Sollner's permselective collodion-base membranes seem to be the best for theoretical activity studies because of their ideal characteristics over a considerable range of concentration.

This study deals with the measurement of membrane concentration potentials with aqueous solutions of some alkali-metal salts across a permselective sulfonated polystyrene collodion-base membrane, and shows the applicability of the method to the study of ion activity behavior. The individual activity coefficients of the critical cations determined from the membrane concentration potentials will be discussed on the basis of theoretical activity equations.

Experimental

Permselective Sulfonated Polystyrene Collodion-base Membrane. Test-tube-shaped sulfonated polystyrene collodion-base membranes were prepared by the method proposed by Sollner and Neihof,[4,5] and a membrane of the best quality was employed throughout this study. The ohmic resistance of the membrane, being measured in a 0.1 M potassium chloride solution at 1000 Hz, was 50 ohms cm². The ionic selectivity of the membrane was examined by measuring the rates of exchange of critical and non-critical ions across the membrane.[5,6] The anion leak after five hours was found to be less than 0.5% of actual cation movement in a 0.5 M KNO_3/membrane/0.5 M NH_4Cl system whose bi-ionic potential was about 5.2 mV.

Solutions. All solutions were made from analytical reagent grade chemicals and redistilled water.

Measurement of Membrane Concentration Potentials. For the determination of membrane concentration potentials, the electromotive force of a cell,

$$\text{SCE(I)/sat. KCl-agar bridge/soln. }(c)\text{/membrane/}$$
$$\text{soln. }(c')\text{/salt. KCl-agar bridge/SCE(I}')\qquad(1)$$

was measured by a precision potentiometer (Model P-1, Yokogawa Electric Works). The concentration ratio $c:c'=2:1$ was used. In each experimental run, the solutions were renewed after 20 min from the

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1) K. Sollner, *Ann. N. Y. Acad. Sci.*, **57**, 177 (1953).

2) K. Sollner, S. Dray, E. Grim and R. Neihof, "Ion Transport Across Membranes," ed. H. T. Clarke, Academic Press, New York (1954), p. 144.

3) K. Sollner, *Ann. N. Y. Acad. Sci.*, **148**, 154 (1968).

4) K. Sollner and R. Neihof, *Arch. Biochem. Biophys.*, **33**, 166 (1951).

5) R. Neihof, *J. Phys. Chem.*, **58**, 916 (1954).

6) H. P. Gregor and K. Sollner, *ibid.*, **50**, 53 (1946).

construction of the cell, and then several readings of the electromotive force were made at a 10 min-interval. Stable electromotive forces were established within 10 min with the membrane which had been saturated with the critical ions by prior ion exchange. The reproducibility of the individual measurements was better than ±0.05 mV, except at the ionic strengths lower than 0.01. All measurements were carried out in a a water thermostat of 25.0±0.1°C.

Results and Discussion

The electromotive force, E, of the concentration cell represented by (1) is given by

$$E = E_{\mathrm{M}} + \Delta E_{\mathrm{SCE}} + E_{\mathrm{L}} \tag{2}$$

where E_{M} is the membrane concentration potential, ΔE_{SCE}, the asymmetry of electrode potentials of the two saturated calomel electrodes, and E_{L}, the sum of liquid junction potentials at sat. KCl-agar bridge/soln. (c) and soln. (c')/sat. KCl-agar bridge. In order to obtain the membrane concentration potential from the raw experimental data, the electromotive force of the cell should be corrected for ΔE_{SCE} and E_{L}.[3] The value of ΔE_{SCE} was determined directly from the electromotive force measurement of a cell, SCE (I)/sat. KCl-agar bridge/sat. KCl/sat. KCl-agar bridge/SCE (I′), while the liquid junction potentials were calculated by using Henderson's equation[7] and ionic mobility data. The accuracy of E_{M} thus obtained is considered to be of the order of ±0.1 mV because of the uncertainty in estimating liquid junction potentials. Table 1 presents the membrane concentration potentials with aqueous solutions of alkali-metal salts at various concentrations.

The following analysis of the membrane concentration potentials is based upon the assumption of virtually ideal selectivity of the membrane. The extremely small leak of anions across the membrane provides a strong evidence to support the fulfilment of this assumption in the present systems.

Theoretically, the membrane concentration potential of a concentration chain, soln. (c)/membrane/soln. (c'), with an ideal negative membrane is given by a Nernst-type equation,

$$\begin{aligned} E_{\mathrm{M}} &= \frac{\boldsymbol{R}T}{z_{+}\boldsymbol{F}}\ln\frac{a_{+}}{a_{+}{}'} \\ &= \frac{\boldsymbol{R}T}{z_{+}\boldsymbol{F}}\left(\ln\frac{c_{+}}{c_{+}{}'} + \ln\frac{y_{+}}{y_{+}{}'}\right) \end{aligned} \tag{3}$$

where z_{+}, a_{+}, c_{+} and y_{+} are the valency, activity, molar concentration, and activity coefficient on the molarity basis, respectively, of the critical cation. Thus the ratio of activity coefficients of the critical cation at two different concentrations, c and c', can be determined from the membrane concentration potential:

$$\ln\frac{y_{+}}{y_{+}{}'} = \frac{z_{+}\boldsymbol{F}}{\boldsymbol{R}T}E_{\mathrm{M}} - \ln\frac{c_{+}}{c_{+}{}'} \tag{4}$$

Figures 1—5 show the experimental relationship between $\log(y_{+}/y_{+}{}^{\mathrm{st}})$ and $I^{1/2}$, where I is the ionic strength on the molarity scale, y^{+}, the ion activity coefficient at a given value of I, and $y_{+}{}^{\mathrm{st}}$, the ion activity coefficient at the ionic strength I^{st} chosen for standard; in the present study, I^{st} being equal to 0.01 for 1 : 1 electrolytes and 0.015 for 1 : 2 electrolytes, respectively. The behavior of mean ionic activity coefficients, $y_{\pm}$, of the salts[8] is also

TABLE 1. MEMBRANE CONCENTRATION POTENTIALS, E_{M} (mV),* WITH AQUEOUS SOLUTIONS OF ALKALI-METAL SALTS ACROSS THE PERMSELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANE AT 25.0°C
(Concentration ratio, $c : c' = 2 : 1$)

Salt	$c : c'$ (M)							
	0.01: 0.005	0.02: 0.01	0.04: 0.02	0.08: 0.04	0.16: 0.08	0.32: 0.16	0.64: 0.32	1.28: 0.64
LiCl	16.8**	16.3**	16.5	16.7	16.5	16.6	17.0	17.5
NaCl	16.9**	16.6	16.6	16.4	16.2	16.0	16.1	16.1
KCl	16.7**	16.6	16.5	16.2	15.9	15.2	15.0	14.3
NaF	16.2**	16.4**	16.4	16.2	15.9	15.4	14.7	—
NaBr	17.0**	16.8	16.5	16.6	16.3	16.4	16.4	16.7
$LiNO_3$	16.7**	16.4**	16.9	17.0	17.2	17.7	18.5	19.9
$NaNO_3$	16.9**	16.8	16.8	16.4	16.4	16.1	15.6	14.6
KNO_3	16.8**	16.6	16.6	15.8	15.8	14.6	13.4	11.6
$NaClO_4$	16.8**	16.8**	16.7	16.6	16.4	—	—	—
$KClO_4$	17.0**	17.0	16.1	15.8	—	—	—	—
Na_2SO_4	16.4	16.3	16.0	15.8	15.4	14.9	14.1	—
K_2SO_4	16.1**	16.1	16.0	15.6	15.1	14.5	—	—

* Corrected for ΔE_{SCE} and E_{L}; accuracy, ±0.1 mV.
** Accuracy, ±0.2 mV.

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[7] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold, New York (1939), Chap. 13.

shown in the figures for comparison. The data at ionic strengths below 0.01 are not subject to the discussion because of their relatively low accuracy.

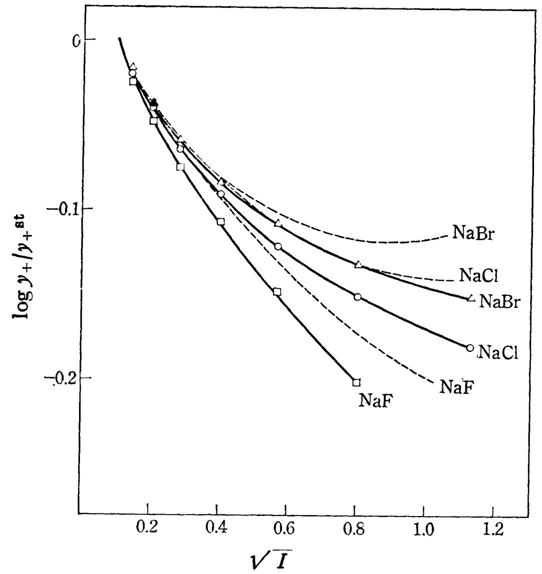

Fig. 1. Behavior of individual and mean activity coefficients with changing ionic strength at 25.0°C: solid lines for $\log(y_+/y_+^{\rm st})$ and broken lines for $\log(y_\pm/y_\pm^{\rm st})$; —□— (NaF), —○— (NaCl), —△— (NaBr). The ionic strength chosen for standard: $I^{\rm st}=0.01$.

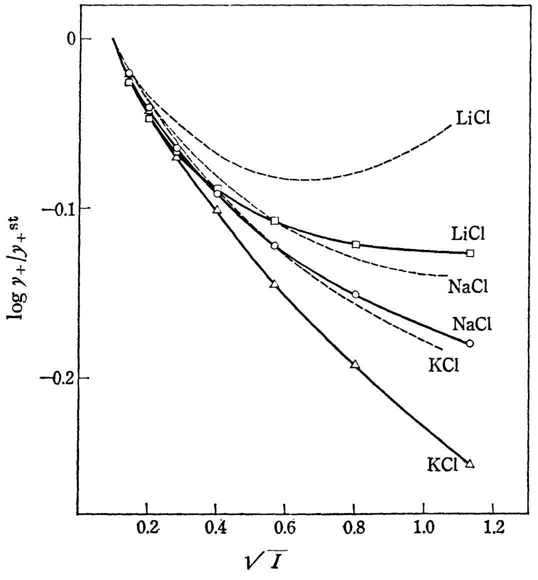

Fig. 2. Behavior of individual and mean activity coefficients with changing ionic strength at 25.0°C: solid lines for $\log(y_+/y_+^{\rm st})$ and broken lines for $\log(y_\pm/y_\pm^{\rm st})$; —□— (LiCl), —○— (NaCl), —△— (KCl). The ionic strength chosen for standard: $I^{\rm st}=0.01$.

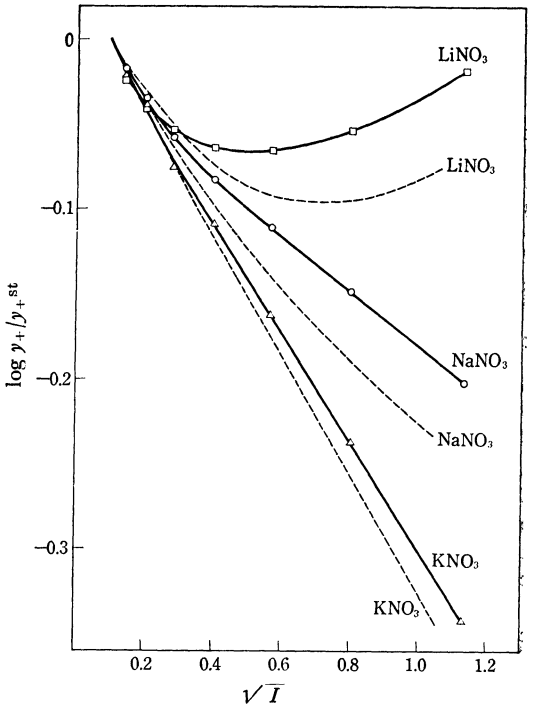

Fig. 3. Behavior of individual and mean activity coefficients with changing ionic strength at 25.0°C: solid lines for $\log(y_+/y_+^{\rm st})$ and broken lines for $\log(y_\pm/y_\pm^{\rm st})$; —□— ($LiNO_3$), —○— ($NaNO_3$), —△— ($KNO_3$). The ionic strength chosen for standard: $I^{\rm st}=0.01$.

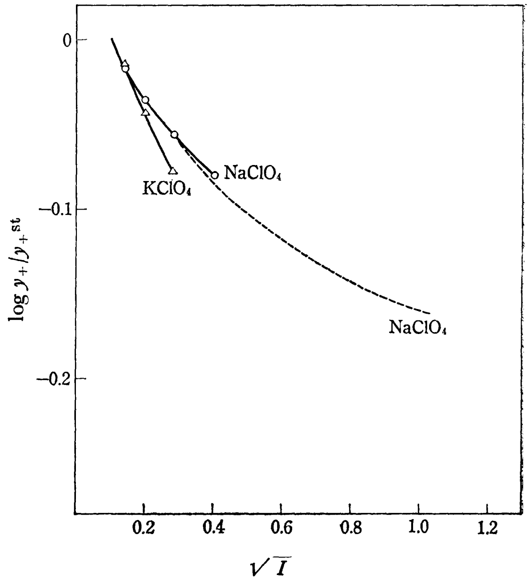

Fig. 4. Behavior of individual and mean activity coefficients with changing ionic strength at 25.0°C: solid lines for $\log(y_+/y_+^{\rm st})$ and broken lines for $\log(y_\pm/y_\pm^{\rm st})$; —○— ($NaClO_4$), —△— ($KClO_4$). The ionic strength chosen for standard: $I^{\rm st}=0.01$.

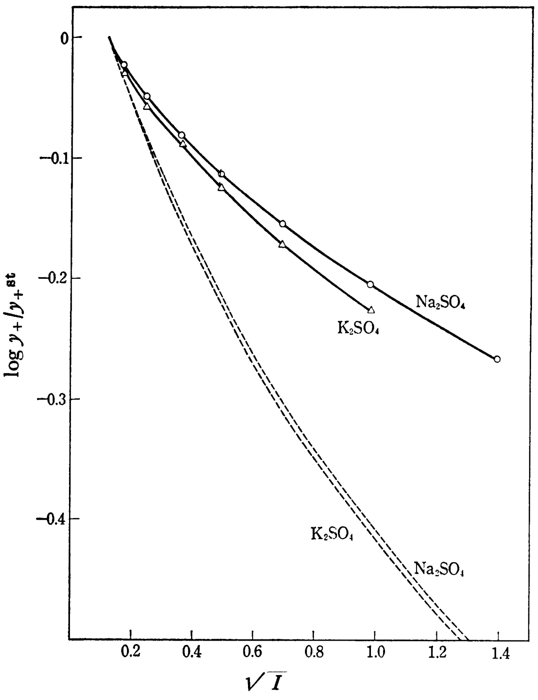

Fig. 5. Behavior of of individual and mean activity coefficients with changing ionic strength at 25.0°C: solid lines for $\log(y_+/y_+^{\mathrm{st}})$ and broken lines for $\log(y_\pm/y_\pm^{\mathrm{st}})$: —○— ($Na_2SO_4$), —△— ($K_2SO_4$). The ionic strength chosen for standard: $I^{\mathrm{st}}=0.015$.

From these figures the following remarks can be made about the behavior of the individual ion activity coefficients with changing ionic strength.

(i) The individual activity coefficient curves of the cations follow the order of $Li^+ > Na^+ > K^+$ for the chlorides, nitrates, perchlorates, and sulfates. The order of the curves for Na^+ of different halides is bromide>chloride>fluoride. These sequences are consistent with those observed for the mean ionic activity coefficients of alkali-metal salts.[9]

(ii) Considerable differences between the individual and mean activity coefficients arise at ionic strengths higher than 0.01, which indicates the specific effect of individual ions on their activity behavior.

The determination of individual ion activity coefficients requires the introduction of a non-thermodynamic assumption. The activity coefficients of the critical cations at relatively low ionic strengths ($I \lesssim 0.01$) can be given with reasonable accuracy by the Debye-Hückel equation (5),

$$\log y_+ = \frac{-z_+^2 A\sqrt{I}}{(1+Ba_+^\circ\sqrt{I})} \tag{5}$$

where A and B are the Debye-Hückel constants, and a_+° is the ion-size parameter. Estimating y_+^{st} by Eq. (5) with suitable values of a_+°, we can determine the individual activity coefficients of the critical cations at higher ionic strengths from the experimental data according to the following relation,

$$\log y_+ = \log\frac{y_+}{y_+^{\mathrm{st}}} - \frac{z_+^2 A\sqrt{I^{\mathrm{st}}}}{(1+Ba_+^\circ\sqrt{I^{\mathrm{st}}})} \tag{6}$$

The numerical values used in the calculation are as follows: $A=0.5116$ and $B=0.3292\times10^8$ on the molarity basis at 25°C; $a_+^\circ=6$, 4.5 and 3 (10^{-8} cm) for Li^+, Na^+ and K^+, respectively.[10] The individual ion activity coefficients, y_+, of Li^+, Na^+ and K^+ thus obtained for various salts are summarized in Table 2. The uncertainty in the y_+-values is estimated to be $\pm1\%$.

In most cases the deviation of the experimentally determined activity coefficients, y_+, from the Debye-Hückel values, $(y_+)_{\mathrm{DH}}$, calculated by Eq. (5) increases with increasing ionic strength as shown in Fig. 6. It is expected that the experimental results at higher ionic strengths can be reproduced with smaller deviations by using the extended Debye-Hückel equation (7) with a linear term,

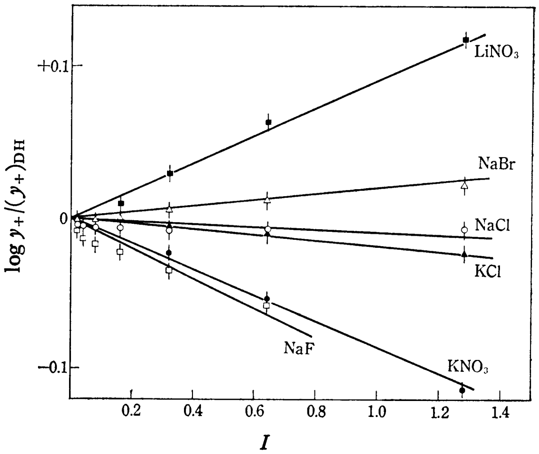

Fig. 6. Deviation of the experimentally determined activity coefficients, y_+, from the Debye-Hückel values, $(y_+)_{\mathrm{DH}}$, as a function of ionic strength: —□— (NaF), —○— (NaCl), —△— (NaBr), —▲— (KCl), —●— (KNO_3), —■— ($LiNO_3$).

$$\log y_+ = \frac{-z_+^2 A\sqrt{I}}{(1+Ba_+^\circ\sqrt{I})} + b_+ I \tag{7}$$

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8) For example: R. Parsons, "Handbook of Electrochemical Constants," Table 19, Butterworths, London (1959).

9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1965), p. 219.

10) G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, Elsevier, Amsterdam (1951), p. 680.

TABLE 2. INDIVIDUAL ACTIVITY COEFFICIENTS OF THE CRITICAL CATIONS IN AQUEOUS SOLUTIONS OF ALKALI-METAL SALTS AT DIFFERENT CONCENTRATIONS (25.0°C)

Salt	Concn. (M)								
	0.005	0.01	0.02	0.04	0.08	0.16	0.32	0.64	1.28
LiCl	—	0.91* (0.91)	0.86 (0.88)	0.81 (0.85)	0.78 (0.81)	0.74 (0.77)	0.71 (0.73)	0.69 (0.69)	0.68 (0.66)
NaCl	—	0.90* (0.90)	0.86 (0.87)	0.82 (0.83)	0.78 (0.79)	0.73 (0.74)	0.68 (0.69)	0.64 (0.64)	0.60 (0.59)
KCl	—	0.90* (0.90)	0.86 (0.86)	0.82 (0.82)	0.77 (0.77)	0.71 (0.71)	0.64 (0.64)	0.58 (0.57)	0.50 (0.50)
NaF	—	0.90* (0.90)	0.85 (0.87)	0.81 (0.83)	0.76 (0.78)	0.71 (0.72)	0.64 (0.65)	0.57 (0.56)	—
NaBr	—	0.90* (0.90)	0.87 (0.87)	0.82 (0.83)	0.79 (0.79)	0.74 (0.76)	0.70 (0.71)	0.67 (0.67)	0.64 (0.65)
$LiNO_3$	—	0.91* (0.91)	0.86 (0.88)	0.83 (0.85)	0.80 (0.82)	0.78 (0.80)	0.78 (0.78)	0.80 (0.79)	0.87 (0.86)
$NaNO_3$	—	0.90* (0.90)	0.87 (0.87)	0.83 (0.83)	0.79 (0.79)	0.75 (0.74)	0.70 (0.69)	0.64 (0.63)	0.57 (0.57)
KNO_3	—	0.90* (0.90)	0.86 (0.86)	0.82 (0.82)	0.76 (0.76)	0.70 (0.69)	0.62 (0.61)	0.52 (0.52)	0.41 (0.41)
$NaClO_4$	—	0.90*	0.87	0.83	0.79	0.75	—	—	—
$KClO_4$	—	0.90*	0.87	0.81	0.75	—	—	—	—
Na_2SO_4	0.89* (0.89)	0.84 (0.85)	0.79 (0.80)	0.74 (0.75)	0.68 (0.70)	0.62 (0.63)	0.55 (0.56)	0.48 (0.47)	— —
K_2SO_4	0.88* (0.88)	0.82 (0.84)	0.77 (0.79)	0.72 (0.73)	0.66 (0.66)	0.59 (0.59)	0.52 (0.51)	—	—

* y_+^{st} determined by Eq. (5) with the ion-size parameters given in Table 3.
The values in parentheses are the activity coefficients calculated by Eq. (7) with the parameters given in Table 3.

TABLE 3. ION-SIZE PARAMETER, a_+°, AND b_+-PARAMETER OF THE EXTENDED DEBYE-HÜCKEL EQUATION (7) FOR THE CRITICAL CATIONS OF VARIOUS SALTS (25°C)

Critical cation	Salt	$10^8 a_+^\circ$ (cm)*	b_+**	Range of I examined
Na^+	NaF	4.5	−0.10	0.01—0.64
	NaCl		−0.01	0.01—1.28
	NaBr		+0.02	0.01—1.28
	$NaNO_3$		(−0.02)***	0.01—1.28
	$NaClO_4$		****	0.01—0.16
	Na_2SO_4		−0.05	0.015—1.92
K^+	KCl	3.0	−0.02	0.01—1.28
	KNO_3		−0.09	0.01—1.28
	$KClO_4$		****	0.01—0.08
	K_2SO_4		−0.04	0.015—0.94
Li^+	LiCl	6.0	(0)***	0.01—1.28
	$LiNO_3$		+0.09	0.01—1.28

* Assumed.
** Determined from the plot of $[\log y_+ - \log(y_+)_{DH}]$ vs. I.
*** The $[\log y_+ - \log(y_+)_{DH}]$ vs. I plot was not linear.
**** Not determined because of a narrow range of I.

where b_+ is another adjustable parameter. Rough estimates of parameters b_+ for each cation of given salts were obtained from the slope of the plot of $[\log y_+ - \log(y_+)_{DH}]$ against I (Fig. 6), and are presented in Table 3.

The individual ion activity coefficients calculated by Eq. (7) with a_+°- and b_+-parameters given in Table 3 are presented in parentheses in Table 2. The agreement between the experimental and calculated values is reasonable except for the LiCl-system in which an appreciable deviation of the $[\log y_+ - \log(y_+)_{DH}]$ vs. I plot from linearity was observed. A better fit may be expected by adjusting both parameters, a_+° and b_+; such a trial, however, will be meaningless unless more accurate data are available for analysis.