

# Thermodynamics of Aqueous Reciprocal Salt Systems. II. Isopiestic Determination of the Osmotic and Activity Coefficients in $\text{LiNO}_3\text{-NaBr-H}_2\text{O}$ and $\text{LiBr-NaNO}_3\text{-H}_2\text{O}$ at $100.3^\circ\text{C}$

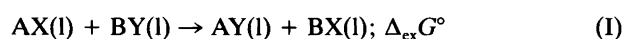
W. Voigt,<sup>a</sup> A. Dittrich,<sup>b</sup> B. Haugsdal<sup>b</sup> and K. Grjotheim<sup>b,\*</sup>

<sup>a</sup>Department of Chemistry, Bergakademie Freiberg, Leipziger Strasse, 9200 Freiberg, G.D.R. and <sup>b</sup>Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

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Isopiestic vapour pressure measurements have been performed at  $100.3^\circ\text{C}$  on mixed aqueous solutions of the reciprocal salt pairs  $\text{LiNO}_3\text{-NaBr}$  and  $\text{LiBr-NaNO}_3$ . A concentration range of  $1\text{-}8\text{ mol kg}^{-1}$  (in some cases up to  $12\text{ mol kg}^{-1}$ ) has been explored. The mean ionic activity coefficients of the salt components have been evaluated by the method of McKay and Perring. In addition, new osmotic coefficient data of the pure binary solutions of  $\text{LiBr}$ ,  $\text{NaBr}$  and  $\text{NaNO}_3$  are reported and described by an extended form of Pitzer's ion-interaction equation.

For molten mixtures of reciprocal salt pairs it is well-known that the composition dependence of activity coefficients is related to the Gibbs energy  $\Delta_{\text{ex}}G^\circ$  of the corresponding exchange reaction of the pure liquid components, reaction (I).<sup>1</sup>



In the most simple situation, i.e. considering only the nearest cation-anion interactions, the activity coefficients in a mixture of the salts AX and BY are given by eqn. (1), where  $X$  denotes the mole fraction of the salt.

$$\ln\gamma_{\text{AX}} = X_{\text{BY}}^2(\Delta_{\text{ex}}G^\circ/RT) \quad (\text{1})$$

$$\ln\gamma_{\text{BY}} = X_{\text{AX}}^2(\Delta_{\text{ex}}G^\circ/RT)$$

More expanded formulas describing the excess Gibbs energy or activity coefficients in multicomponent molten salt mixtures also contain terms similar to eqn. (1), thus taking into consideration interactions between salt components with non-common ions.<sup>2</sup>

Recently, we have also shown that in aqueous systems the concentration dependence of the salt activity coefficient is related to the Gibbs energy of the exchange reaction (I).<sup>3</sup> The difference in the standard Gibbs energies of solution,  $\Delta_s G_{ij}^\circ$ , was introduced as a correction term for specific hydration effects. Thus eqn. (2) was quite successful in predicting the direction of activity coefficient variations at

constant total molarity for a large number of 1-1 electrolyte mixtures.<sup>3</sup>

$$RT\ln\gamma_{\text{AX}} \sim \Delta_{\text{ex}}G^\circ + (\Delta_s G_{\text{AX}}^\circ - \Delta_s G_{\text{BY}}^\circ) \quad (\text{2a})$$

$$RT\ln\gamma_{\text{BY}} \sim \Delta_{\text{ex}}G^\circ + (\Delta_s G_{\text{BY}}^\circ - \Delta_s G_{\text{AX}}^\circ) \quad (\text{2b})$$

More reliable thermodynamic data for aqueous reciprocal salt systems are needed in order to develop and test this approach quantitatively. Especially useful in this respect would be activity coefficient data for all components of a simple 1-1 valence type mixture at high and constant total molality.

In this paper we report isopiestic determinations of osmotic coefficients of the reciprocal pairs  $\text{LiNO}_3\text{-NaBr}$  and  $\text{LiBr-NaNO}_3$ . The component of lowest solubility,  $\text{NaBr}$ , and the binary subsystem having the highest water activity,  $\text{NaNO}_3\text{-H}_2\text{O}$ , are the limiting factors for the concentration range which can be investigated by the isopiestic method. At a temperature of  $100.3^\circ\text{C}$  a concentration range of  $1\text{-}8\text{ mol kg}^{-1}$   $\text{H}_2\text{O}$  has been covered; in certain composition ranges  $12\text{ mol kg}^{-1}$   $\text{H}_2\text{O}$  was reached.

## Experimental

The apparatus and experimental procedure have been described earlier.<sup>4</sup> In brief, isopiestic equilibrium was established between 12 cups placed inside an aluminium container. Three of these cups contained the reference solution ( $\text{CaCl}_2$ ). The construction of the container allowed the cups to be closed under conditions of equilibrium. The temperature was controlled within the limit of  $\pm 0.05\text{ K}$  using a thermostat filled with a glycerol-water mixture.

\* To whom correspondence should be addressed.

Table 1. Compositions of stock solutions (g salt/g solution).

Salt	Date of analysis			
	26.01.87	15.03.87	05.05.87	01.07.87
CaCl <sub>2</sub>	0.46137 <sup>a</sup>	0.46219 <sup>b</sup> 0.46219 <sup>c</sup>	0.46137 <sup>a</sup>	0.46150 <sup>a</sup>
LiBr	0.57547 <sup>a</sup>	0.57506 <sup>c</sup>	–	0.57496 <sup>a</sup>
LiNO <sub>3</sub>	0.42420 <sup>a</sup>	0.42423 <sup>d</sup>	–	0.42568 <sup>a</sup>
NaBr	0.48109 <sup>e</sup>	–	0.48115 <sup>a</sup>	0.48112 <sup>a</sup>
NaNO <sub>3</sub>	0.47049 <sup>e</sup>	–	0.47049 <sup>a</sup>	0.47059 <sup>a</sup>

<sup>a</sup>Determined by drying of ca. 2 g solution. <sup>b</sup>Complexometric titration of Ca<sup>2+</sup> using EDTA. <sup>c</sup>Argentometric determination of Cl<sup>-</sup>. <sup>d</sup>Water content determined by the Karl Fischer method. <sup>e</sup>Prepared by weighing anhydrous salt and water.

*Substances.* The same procedures and analytical methods as in Ref. 4 were used to prepare and analyze stock solutions. Besides the reagent grade salts given in Ref. 4, the salts LiBr, NaBr and NaNO<sub>3</sub> were of purum p.a. quality from Fluke AG, Buchs, Switzerland. Table 1 shows the concentrations of the stock solution as a function of storage time. Variations in the concentrations are close to the limits of analytical accuracy.

## Results

*Osmotic Coefficient.* Measurements were performed with mixed solutions of LiNO<sub>3</sub>-NaBr and LiBr-NaNO<sub>3</sub>, includ-

Table 2. Isopiestic molalities (mol kg<sup>-1</sup> H<sub>2</sub>O) of the system: LiNO<sub>3</sub>-NaBr-H<sub>2</sub>O at 100.3 °C.

Run	$m_{\Phi}^a$	CaCl <sub>2</sub>	$y(\text{NaBr})$								
			0	0.12674	0.24995	0.3746	0.47143	0.62798	0.75014	0.87529	1.000
3.3	19.528	5.9548	12.6058	12.6304	12.6270	12.5762	12.5314	12.3930	12.2545	12.1147	–
3.2	18.833	5.7977	12.2120	12.2480	12.2522	12.2119	12.1643	12.0276	11.8982	11.7447	11.5935
3.1	18.110	5.6361	11.8149	11.8540	11.8663	11.8294	11.7860	11.6531	11.5232	11.3705	11.2012
2.1	17.203	5.4359	11.3010	11.3563	11.3746	11.3445	11.2978	11.1801	11.0489	10.8935	10.7145
7.1	15.637	5.0929	10.4404	10.4967	10.5152	10.5063	10.4779	10.3632	10.2377	10.0650	9.8543
1	12.566	4.4156	8.7103	8.7889	8.8262	8.8252	8.8071	8.7196	8.6158	8.4799	8.3125
5.1	11.304	4.1283	7.9872	8.0749	8.1030	8.1100	8.1014	8.0219	7.9441	7.8111	–
2.2	9.3868	3.6723	6.8590	6.9315	6.9738	6.9865	6.9818	6.9329	6.8626	6.7700	–
3.4	6.8185	3.0016	5.2850	5.3465	5.3793	5.3985	5.4045	5.3797	5.3388	5.2838	5.2122
5.2	5.7819	2.7005	4.6166	4.6654	4.7004	4.7199	4.7281	4.7094	4.6903	4.6420	–
6.1	4.6199	2.3317	3.8412	3.8810	3.9094	3.9289	3.9378	3.9341	3.9146	3.8841	3.8473
5.3	3.4304	1.9058	3.0001	–	3.0509	3.01661	3.07404	3.0722	3.0669	3.0525	–
6.2	1.8725	1.2259	1.7937	1.8079	1.8194	1.8251	1.8309	1.8334	1.8312	1.8269	1.8195
7.2	0.97607	0.7219	1.0043	1.0110	1.0109	1.0140	1.0186	1.0174	1.0161	1.0139	1.0121
7.3	0.77760	0.5920	0.8126	–	0.8176	0.8206	0.8202	0.8214	0.8209	0.8197	0.8184

$$^a m_{\Phi} = (3/2)m_{\text{CaCl}_2}\varphi_{\text{CaCl}_2}$$

Table 3. Isopiestic molalities (mol kg<sup>-1</sup> H<sub>2</sub>O) of the system: LiBr-NaNO<sub>3</sub>-H<sub>2</sub>O at 100.3 °C.

Run	$m_{\Phi}^a$	CaCl <sub>2</sub>	$y(\text{NaNO}_3)$								
			0	0.12786	0.24992	0.37493	0.50167	0.64772	0.74938	0.82516	1.000
10.1	18.488	5.7204	8.3060	8.9551	9.7254	10.70975	11.9864	13.95605	–	17.54705	–
14.2	13.016	4.5162	6.75345	7.1611	7.6438	8.2631	9.0541	10.2654	11.38555	12.4305	15.9904
13.1	12.232	4.3401	6.5012	6.8707	7.3247	7.8922	8.6209	9.7325	10.7559	11.7112	14.94565
14.1	10.751	3.9995	6.0038	6.3202	6.6941	7.1722	7.7822	8.7068	9.5459	10.3347	12.9704
10.3	7.2046	3.1084	4.6345	4.8171	5.0337	5.3035	5.6558	6.1624	–	7.0389	8.3764
11.1	5.7988	2.7055	3.9937	4.1322	4.2908	4.4909	4.7425	5.11035	5.43345	5.7266	6.6425
11.2	2.8210	1.6607	2.3545	2.4579	–	2.5270	2.6096	2.72705	2.8251	2.9101	3.1543
13.2	2.1160	1.3453	1.8799	–	1.9400	1.9841	2.0371	2.1137	2.17465	2.2238	–
14.3	1.5925	1.0807	1.4832	1.5027	1.5234	1.5496	1.5846	1.6310	–	1.6988	–
11.3	1.5081	1.0349	–	1.4416	1.4611	1.4821	1.5144	1.5544	1.5871	1.6162	1.6905
11.4	1.1643	0.8918	1.1429	1.1510	1.1603	1.1752	1.1939	1.2203	1.2407	1.2592	1.2076
13.3	0.89725	0.67128	0.89952	0.90779	0.91502	0.92647	0.93951	0.95703	0.97010	0.98392	1.0138

$$^a m_{\Phi} = (3/2)m_{\text{CaCl}_2}\varphi_{\text{CaCl}_2}$$

ing the pure binary solutions. The isopiestic molalities are listed in Tables 2 and 3. In the third column the molalities of the reference solutions of  $\text{CaCl}_2$  are presented; they are average values of triplicates. The maximum deviation within one triplicate is less than 0.1 %, except in runs 7.3, 10.3 and 13.3 with, respectively, 0.19, 0.13 and 0.15 % deviation. The absence of a value in some parts of the tables is mainly due to accidents during the handling of the cups.

From the product  $m\varphi$ , listed in the second columns of Tables 2 and 3, the osmotic coefficient,  $\varphi$ , can easily be calculated for any value of the molality fraction  $y$  within one row. The product  $m\varphi$  itself was calculated from eqn. (3). In this equation the subscript R specifies the reference electrolyte and  $v_i$  denotes the number of ions constituting the stoichiometric formula of salt  $i$ .

$$v_i m_i \varphi = v_R m_R \varphi_R \quad (3)$$

The osmotic coefficient of the reference  $\text{CaCl}_2$  solution,  $\varphi_R$ , was evaluated from the recommended equation of Ananthaswamy and Atkinson,<sup>5</sup> eqns. (4a) and (4b).

$$\begin{aligned} \varphi - 1 = & |z_+ z_-| f + 2 \left( \frac{v_+ v_-}{v} \right) m B + \\ & \frac{2(v_+ v_-)^{3/2}}{v} m^2 C + \frac{2(v_+ v_-)^2}{v} m^3 D + \\ & \frac{2(v_+ v_-)^{5/2}}{v} m^4 E + \frac{2(v_+ v_-)^3}{v} m^5 F \end{aligned} \quad (4a)$$

$$\begin{aligned} m \gamma_{\pm} = & |z_+ z_-| f' + \frac{2(v_+ v_-)}{v} m B' + \\ & \frac{3(v_+ v_-)^{3/2}}{v} m^2 C + \frac{8}{3} \frac{(v_+ v_-)^2}{v} m^3 D + \\ & \frac{10}{4} \frac{(v_+ v_-)^{5/2}}{v} m^4 E + \frac{12}{5} \frac{(v_+ v_-)^3}{v} m^5 F \end{aligned} \quad (4b)$$

where

$$f = -A I^{1/2} (1 + 1.2 I^{1/2})$$

$$f' = -A \left( \frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2 I^{1/2}) \right)$$

$$B = \beta^{(0)} + \beta^{(1)} \exp(-2I^{1/2})$$

$$B' = 2\beta^{(0)} + 2\beta^{(1)} [1 - (1 + 2I^{1/2} - 2I) \exp(-2I^{1/2})] / 4I$$

$$v = v_+ + v_-$$

$$I = \frac{1}{2} m (v_+ z_+^2 + v_- z_-^2)$$

with  $z_i$  denoting the charges of ions and with  $v_+$  and  $v_-$  denoting the number of cations and anions constituting the salt component. The Debye-Hückel parameter,  $A$ , was taken from Ref. 6.

For subsequent calculations it was advantageous to use an analytical expression for the concentration dependence of the osmotic and activity coefficients of the pure binary solutions. For this purpose eqns. (4a) and (4b) were applied again. In order to obtain reliable estimates of the empirical coefficients  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C$ ,  $D$ ,  $E$  and  $F$ , additional isopiestic experiments were carried out for pure solutions of each of  $\text{LiBr}$ ,  $\text{NaBr}$  and  $\text{NaNO}_3$ . The experimental data are given in Table 4. By fitting the osmotic coefficients of the pure solution in Table 4, and of the mixtures in Tables 2 and 3 (in columns 4 and 12), against eqn. (4a), the coefficients listed in Table 5 were obtained. The corresponding coefficients of  $\text{LiNO}_3$  solutions were reported earlier.<sup>4</sup>

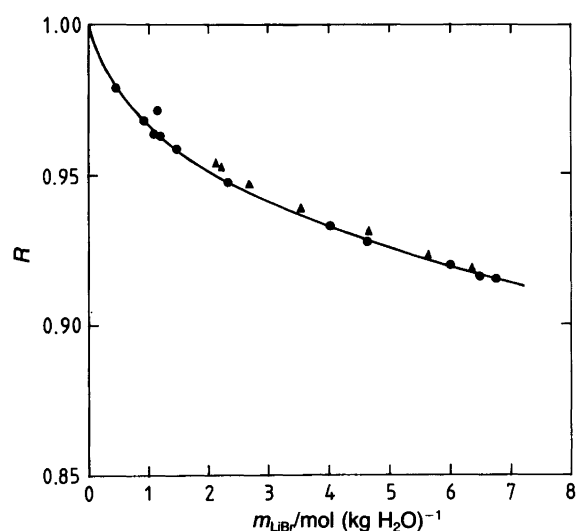
Our data for  $\text{LiBr}$  can be compared with results from Braunstein's measurements at the same temperature.<sup>7</sup> Braunstein used  $\text{LiCl}$  as the reference electrolyte. In Fig. 1 the isopiestic ratios  $R = (m_{\text{LiBr}}/m_{\text{LiCl}})$ , calculated from Braunstein's data, are plotted together with our values versus the  $\text{LiBr}$  molality. Thereby, our data points were derived from independent series of isopiestic measurements for  $\text{LiCl}$  and  $\text{LiBr}$  with  $\text{CaCl}_2$  as reference electrolyte. The molality of  $\text{LiCl}$ ,  $m_{\text{LiCl}}$ , which would be in isopiestic equilibrium with a given  $\text{LiBr}$  solution, was calculated

Table 4. Osmotic coefficients,  $\varphi$ , of the pure solutions of, respectively,  $\text{LiBr}$ ,  $\text{NaBr}$  and  $\text{NaNO}_3$  at 100.3°C.

$\text{LiBr/mol kg}^{-1} \text{H}_2\text{O}$	$\varphi$	$\text{NaBr/mol kg}^{-1} \text{H}_2\text{O}$	$\varphi$	$\text{NaNO}_3/\text{mol kg}^{-1} \text{H}_2\text{O}$	$\varphi$
1.2130	1.0365	10.618	1.6032	12.224	0.83330
1.2126	1.0369	7.9993	1.4961	7.5040	0.86611
1.0688	1.0198	6.9459	1.4353	4.2568	0.89065
0.69415	0.97238	3.5790	1.1790	2.5020	0.89532
0.46438	0.94689	3.2951	1.1539	1.7569	0.89256
		1.2783	0.98355	1.4101	0.89162
		0.81500	0.95186	1.2226	0.89156
		0.71550	0.94337	0.86968	0.89201
		0.47284	0.92994	0.49225	0.89328

Table 5. Empirical coefficients of eqns. (4a) and (4b) and standard deviation,  $\sigma$ , of the experimental osmotic coefficients at 100.3°C.

System	$\beta^{(0)}$	$\beta^{(1)}$	$10^3C$	$10^4D$	$10^6E$	$10^7F$	$10^4\sigma$
LiBr-H <sub>2</sub> O	0.17736	0.31897	-1.7302	2.8266	-	-	8.4
NaBr-H <sub>2</sub> O	0.12475	0.37284	-1.5442	-2.9196	8.008	-	7.2
NaNO <sub>3</sub> -H <sub>2</sub> O	0.07092	0.30471	-12.585	10.785	-46.236	7.9	5.8

Fig. 1. Concentration dependence of the ratio  $R = (m_{\text{LiBr}}/m_{\text{LiCl}})$  for LiCl solutions in isopiestic equilibrium at 100.3°C;  $\Delta$ , Braunstein;<sup>7</sup>  $\bullet$ , this work.

by the simultaneous solution of eqns. (5) and (4a) for  $\varphi_{\text{LiCl}}$ , where  $a_w$  is the water activity of the CaCl<sub>2</sub> solution in isopiestic equilibrium with the LiBr solution. The coefficients of LiCl in eqn. (4a), given in Ref. 4, are valid up to a concentration of 6.3 mol kg<sup>-1</sup>. Up to this concentration the maximum deviation of Braunstein's values from our smoothed curve is less than 0.4%.

$$\varphi_{\text{LiCl}} = - \frac{1000 \ln a_w}{2 \times m_{\text{LiCl}} \times 18.0152} \quad (5)$$

$$\ln \gamma_{\pm}(A) = \ln \Gamma_A + \ln(M_A/m) + \int_0^{m\varphi} [(1/m^2)(dm/d\ln y_B)_{m\varphi} + (1/m) - (1/M_A)] d(m\varphi) \quad (6)$$

**Salt Activity Coefficients.** The McKay-Perring method<sup>8</sup> was applied to calculate the salt activity coefficients in the mixed solutions. The evaluation procedure was similar to that suggested by Robinson.<sup>9</sup> For a solution containing the salts A and B, the mean ionic activity coefficient of A can be calculated by means of eqn. (6), where  $\Gamma_A$  and  $M_A$  denote the salt activity coefficient and the molality of the pure solution of A at the same water activity as the mixed

solution of a total molality  $m$ . Eqn. (7) was used to describe the dependence of  $m$  on the molality fraction  $y_B$  at constant  $m\varphi$ .

$$M_A/m = 1 - aY_B - by_B^2 \quad (7)$$

Substitution of eqn. (7) into eqn. (6) gives eqn. (8) for the integral term.

$$\int_0^{m\varphi} ( ) d(m\varphi) = y_B^2 \int_0^{m\varphi} (b/M_A) d(m\varphi) \quad (8)$$

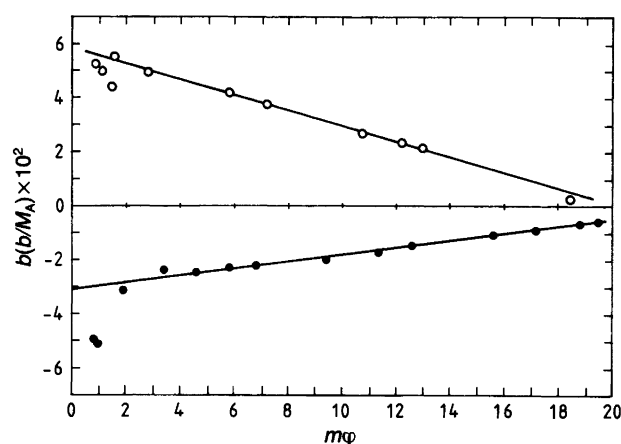
At the same values of water activity and  $m\varphi$ , respectively, the activity coefficient of the second salt B is given by eqn. (9).

$$\ln \gamma_{\pm}(B) = \ln \Gamma_B + \ln(M_B/m) + (1-y_B)^2 \int_0^{m\varphi} (b/M_A) d(m\varphi) \quad (9)$$

The evaluation of the integrals in eqns. (8) and (9) requires an expression for the dependence of  $(b/M_A)$  on the product  $(m\varphi)$ . The plots in Fig. 2 show that the formulation of a linear dependence should be appropriate. The best straight lines according to these plots are described by eqns. (10) and (11).

$$\text{For LiBr-NaNO}_3: 10^4 (b/M_A) = 580 - 28.43M_A\varphi \quad (10)$$

$$\text{For LiNO}_3\text{-NaBr: } 10^4 (b/M_A) = -300 + 12.245m\varphi \quad (11)$$

Fig. 2. Plots of the function  $(b/M_A) = f(m\varphi)$  within the integral of eqn. (8), versus  $m\varphi$ ;  $\bullet$ , LiNO<sub>3</sub>-NaBr-H<sub>2</sub>O;  $\circ$ , LiBr-NaNO<sub>3</sub>-H<sub>2</sub>O.

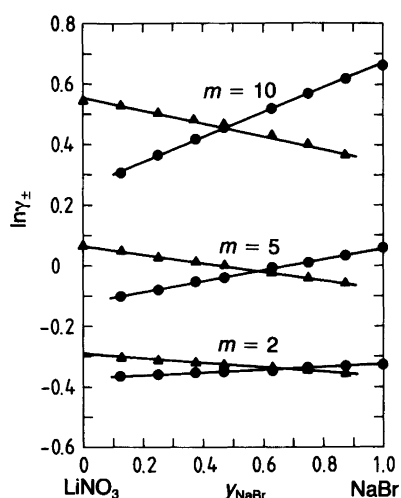


Fig. 3. Composition dependence of  $\ln\gamma_{\pm}$  at constant total molalities  $m = 2, 5$  and  $10$ ;  $\bullet$ ,  $\ln\gamma_{\pm}(\text{NaBr})$ ;  $\blacktriangle$ ,  $\ln\gamma_{\pm}(\text{LiNO}_3)$ .

At values of  $m\phi$  below 2.0 the uncertainty in  $(b/M_A)$  grows rapidly, as was reported earlier for the system  $\text{NaCl-KCl}$ .<sup>9</sup> In addition to the enhanced scattering in the system  $\text{LiNO}_3\text{-NaBr}$ , a tendency toward more negative values of  $(b/M_A)$  is revealed. The influence of this deviation from the straight line defined by eqn. (11) is not important for the final results. This was estimated by additional calculations, whereby the integral of eqn. (8) was split into two parts, applying eqn. (12) to represent the integrand at  $m\phi < 3.4304$ .

$$10^4 (b/M_A) = -600 + 107.1m\phi \quad (12)$$

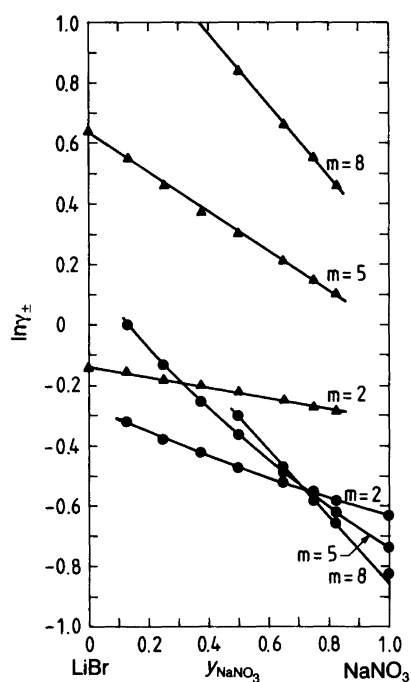


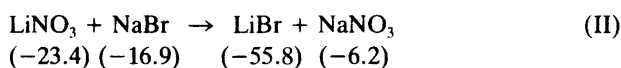
Fig. 4. Composition dependence of  $\ln\gamma_{\pm}$  at constant total molalities  $m = 2, 5$  and  $8$ ;  $\bullet$ ,  $\ln\gamma_{\pm}(\text{NaNO}_3)$ ;  $\blacktriangle$ ,  $\ln\gamma_{\pm}(\text{LiBr})$ .

The first two terms of eqns. (6) and (9) were calculated by means of eqns. (4a) and (4b).

Summation of all three terms in eqns. (6) and (9) provides the activity coefficients of the salts A and B at the molality fractions  $y_B$  and total molalities  $m$  given in Tables 2 and 3. A quadratic Lagrange interpolation routine was applied to obtain the composition dependence of  $\ln\gamma_{\pm}$  at constant and rounded-off values of the total molality. A graphical representation of the results is given in Figs. 3 and 4. Three total molalities, representative for the validity range of the evaluation procedure, have been selected.

## Discussion

The two diagrams in Figs. 3 and 4 characterize the variation of the mean ionic activity coefficients by the mixing of a pure solution of the reciprocal pairs  $\text{LiNO}_3\text{-NaBr}$  (Fig. 3) and  $\text{LiBr-NaNO}_3$  (Fig. 4) with constant ionic strength. Both pairs are related by the exchange reaction shown in reaction (II).



$$\text{with } \Delta_{\text{ex}}G^\circ(298 \text{ K}) = 21.1 \text{ kJ mol}^{-1}.$$

The standard Gibbs energy of reaction  $\Delta_{\text{ex}}G^\circ$  refers to the pure crystalline salts as standard state. Below the chemical formula the value of the standard Gibbs energy of solution is given for each salt.<sup>10</sup> According to eqn. (2) the appropriate combination of  $\Delta_{\text{ex}}G^\circ$  and  $\Delta_s G^\circ$  yields the factors of proportionality of the logarithmic activity coefficients shown in eqn. (13).

$$\ln\gamma_{\pm}(\text{LiNO}_3) \sim 21.1 + (-23.4 + 16.9) = 14.6 \quad (13a)$$

$$\ln\gamma_{\pm}(\text{NaBr}) \sim 21.1 + (-16.9 + 23.4) = 27.6 \quad (13b)$$

$$\ln\gamma_{\pm}(\text{LiBr}) \sim -21.1 + (-55.3 + 6.2) = -70.0 \quad (13c)$$

$$\ln\gamma_{\pm}(\text{NaNO}_3) \sim -21.1 + (-6.2 + 55.3) = 28.2 \quad (13d)$$

When pure solutions are mixed at constant total molality, positive values predict increasing activity coefficients and negative values decreasing activity coefficients. The variation of  $\ln\gamma_{\pm}$  in Fig. 3 is contrary to this prediction. Earlier we stated that  $\text{LiNO}_3\text{-NaBr}$  represents one of the few examples in which eqn. (2) does not apply at a total molality of  $1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ . With the present results it becomes evident that this statement is true for molalities as high as  $10 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ . Obviously, in this instance the specific hydration effects are not adequately reflected by the difference in  $\Delta_s G^\circ$ . Unfortunately, there are no reliable data for  $\Delta_s G^\circ$  at 373 K for  $\text{LiNO}_3$  and  $\text{LiBr}$ . However, the differences in  $\Delta_s G^\circ$  of the corresponding salt pairs will not be changed to such an extent that the signs of the factors given

in eqns. (13a)–(13d) become invalid at higher temperatures.

On the other hand, the strong decrease of  $\ln\gamma_{\pm}(\text{LiBr})$  and the increase of  $\ln\gamma_{\pm}(\text{NaNO}_3)$  are in agreement with the predictions in eqns. (13c) and (13d). Thus, the present experimental results confirm the unusual behaviour of activity coefficients in systems containing nitrate and halide anions as discussed recently.<sup>3</sup>

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