

# Thermodynamics of Reciprocal Salt Systems. III. Isopiestic Determination of the Osmotic and Activity Coefficients of the System $\text{Li}^+$ , $\text{Na}^+//\text{Cl}^-,\text{NO}_3^- - \text{H}_2\text{O}$ at $100.3^\circ\text{C}$

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Isopiestic measurements have been performed for mixed solutions of  $\text{LiNO}_3\text{--NaCl}$ ,  $\text{LiCl--NaNO}_3$ ,  $\text{NaCl--NaNO}_3$  and  $\text{LiNO}_3\text{--NaNO}_3$  at  $T = 100.3^\circ\text{C}$ .  $\text{CaCl}_2\text{--H}_2\text{O}$  was used as reference system. The concentration range which could be investigated varied between 1–8 and 1–15 mol  $\text{kg}^{-1}$  depending on the salt composition. Osmotic coefficients  $\Phi$  and activity coefficients  $\gamma_{\pm}$  of the salt components in the non-common ion mixtures were calculated. The deviation of  $\Phi$  from additivity seems to be related to the change in Gibbs energy of the corresponding metathetical reaction between the reciprocal salt pairs. The application of Pitzer's equation and an empirical rule to predict the variation of  $\gamma_{\pm}$  are discussed.

From an earlier discussion of the correlations between the thermodynamic behaviour of aqueous and high-temperature molten reciprocal salt systems,<sup>1</sup> we became interested in systematic investigations of activity coefficients in such aqueous mixtures. Only a few experimental data for aqueous reciprocal salt systems at moderately high concentrations can be found in the literature. Recently, we reported results of isopiestic measurements of the systems  $\text{LiNO}_3\text{--NaBr--H}_2\text{O}$  and  $\text{LiBr--NaNO}_3\text{--H}_2\text{O}$  at  $100.3^\circ\text{C}$ .<sup>2</sup> In this work, analogous systems have been investigated with  $\text{Cl}^-$  instead of  $\text{Br}^-$  as the halide anion. In addition, the common ion subsystems  $\text{LiNO}_3\text{--LiCl--H}_2\text{O}$ ,  $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$  and  $\text{LiNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$  have been measured.

## Experimental

The apparatus and experimental procedure are described in a previous paper.<sup>3</sup> In brief, an aluminium container was loaded with a set of 12 vitreous carbon cups containing the solutions. Three of the cups contained solutions of the reference salt  $\text{CaCl}_2$ . Isopiestic equilibrium was reached within 48 h at  $T = 100.3^\circ\text{C}$ . Then the cups were closed under equilibrium conditions and the whole apparatus allowed to cool to room temperature. Final weights of the cups were determined on an analytical balance. Runs were not accepted unless the molality difference between the triplicates of  $\text{CaCl}_2$  solution was less than 0.1 %.

Mixed solutions of desired compositions were prepared

from stock solutions of the pure salts. For  $\text{LiCl}$  and  $\text{LiNO}_3$  the stock solutions were the same as in the prior investigations.<sup>2,3</sup> New stock solutions were prepared for the sodium salts. All salts were of reagent grade as specified previously.<sup>2,3</sup>

## Results and discussion

*Osmotic coefficients.* The experimental results are summarized in Tables 1–6. Tables 1–3 contain the isopiestic molalities for the investigated reciprocal salt solutions. The results of the common ion subsystems  $\text{LiCl--LiNO}_3\text{--H}_2\text{O}$ ,  $\text{NaCl--NaNO}_3\text{--H}_2\text{O}$  and  $\text{LiNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$  are listed in Tables 4–6. For the fourth subsystem,  $\text{LiCl--NaCl--H}_2\text{O}$ , Holmes and Mesmer<sup>4</sup> have published isopiestic data at elevated temperatures.

In the first column of each table the molality of the reference solutions,  $\text{CaCl}_2$ , is given. Normally, these values are averages from triplicate samples. The osmotic coefficients,  $\Phi_x$ , of the alkali salt solutions were calculated from the isopiestic molalities by means of eqn. (1).

$$\Phi_x = \frac{3m_{\text{CaCl}_2}}{2m_x} \Phi_{\text{CaCl}_2} \quad (1)$$

For the calculation of  $\Phi_{\text{CaCl}_2}$  the empirical equation and parameter set recommended by Ananthaswamy and Atkinson<sup>5</sup> were used. Quadratic interpolation was applied in order to obtain  $\Phi_x$  as a function of the molality fraction  $y$  at constant total molality.

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Table 1. Isopiestic molalities  $m$  of  $\{(1-y)\text{LiCl} + y\text{NaNO}_3\}$ (aq) at 100.3°C.

CaCl <sub>2</sub>	$y = 0.11062$	0.20600	0.32856	0.44971	0.58074	0.71671	0.84803
1.0675	1.5363	1.5466	1.5636	1.5864	1.6146	1.6514	1.6939
1.4037	—	2.0996	2.1324	2.1729	2.2272	2.2972	2.3798
1.4214	2.1085	2.1284	2.1619	2.2027	2.2486	2.3332	2.4174
2.0414	3.1729	3.2227	3.3030	3.4019	3.5349	3.7096	3.9236
2.5444	4.0778	4.1637	4.3038	4.4704	4.6992	5.0056	5.3895
2.9112	4.7509	4.8732	5.0653	5.3014	5.6248	6.0560	6.6047
3.6133	—	6.2651	6.5905	6.9862	—	8.2888	9.2451
3.8659	6.5308	6.7773	7.1627	7.6355	8.2846	9.1633	10.3060

Table 2. Isopiestic molalities  $m$  of  $\{(1-y)\text{LiCl} + y\text{NaNO}_3\}$ (aq) at 100.3°C.

CaCl <sub>2</sub>	$y = 0$	0.20082	0.40286	0.60116	0.79951
1.6664	2.4939	2.5482	2.6357	2.7574	2.9304
1.9959	3.0450	3.1343	3.2698	3.4575	3.7276
2.5556	4.0111	4.1764	4.4224	4.7706	5.2789
2.8642	4.5499 <sub>s</sub>	4.7706	5.0978	5.5591	6.2442
3.3624	5.4213	5.7500	6.2355	6.9244	7.9564
3.7052	6.0147	6.4369	7.0518	7.9258	9.2478
4.2673	6.9677	7.5628	8.4241	9.6452	11.4997
4.5629	7.4582	8.1529	9.1572	10.5856	12.7480
5.0479	8.2379	9.1201	10.3793	12.1669	14.8966

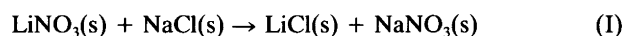
The variation of  $\Phi_x$  along sections of constant total molality  $m$  is best characterized by its deviation from additivity according to eqn. (2), where  $\Phi_A^\circ$  and  $\Phi_B^\circ$  stand for the

$$\Delta\Phi = \Phi_x - (1-y)\Phi_A^\circ - y\Phi_B^\circ \quad (2)$$

osmotic coefficients of the pure binary solutions at the same molality as the mixed solution. The latter was calculated at the desired molality using our own regression equation given earlier.<sup>2,3</sup>

Fig. 1 shows a plot of  $\Delta\Phi$  for both reciprocal salt pairs at total molalities of 2, 3 and 5 mol kg<sup>-1</sup> (H<sub>2</sub>O). The evaluated points lie on smooth curves with a scattering well below the estimated error limit of 0.3%. This error also includes uncertainties due to numerical manipulations of the data.

An interesting feature of the curves is the different signs of  $\Delta\Phi$  for the two pairs LiNO<sub>3</sub>-NaCl and LiCl-NaNO<sub>3</sub>. Considering the change in Gibbs energy  $\Delta_{\text{ex}}G^\circ$  due to reaction (I), the crystalline salts LiNO<sub>3</sub> and NaCl represent the stable pair at 298 K.



$$\Delta_{\text{ex}}G^\circ = 13.9 \text{ kJ mol}^{-1}$$

Thus, it can be stated that mixing solutions of the stable pair causes negative deviations from additivity (curves 1-3). The curves are symmetric. The deviations increase with total molality, reaching ca. 4% of the absolute value of  $\Phi$  at  $m = 5 \text{ mol kg}^{-1}$  (H<sub>2</sub>O). The opposite situation is found for solutions of the unstable pair LiCl-NaNO<sub>3</sub>.

Table 3. Isopiestic molalities  $m$  of  $\{(1-y)\text{LiNO}_3 + y\text{NaCl}\}$ (aq) at 100.3°C.

CaCl <sub>2</sub>	$y = 0.12430$	0.24029	0.35225	0.47455	0.59509	0.73505	0.84254
0.74465	1.0445	1.0515	—	1.0646	1.0696	1.0745	1.0777
0.84469	—	—	1.2155	1.2244	1.2304	—	1.2407
1.2019	1.7815	1.7952	1.8096	1.8261	1.8374	—	1.8551
1.4486	2.2008	2.2251	2.2484	2.2677	2.2843	2.3026	2.3111
1.9955	3.2241	3.2681	3.3070	3.3443	3.3707	3.3937	3.4038
2.2055	3.6477	3.6995	3.7476	3.7900	3.8144	—	3.8551
2.6421	4.5779	4.6507	—	4.7674	4.8061	4.8323	4.8415
2.9726	5.3258	5.4085	5.4815	5.5511	5.5931	5.6312	5.6253
3.3754	6.2723	6.3802	6.4752	6.5581	6.6002	—	6.6387
3.7247	7.1366	7.2629	7.3690	7.4632	7.5262	7.5636	7.5604

Table 4. Isopestic molalities  $m$  of  $\{(1-y)\text{LiCl} + y\text{NaNO}_3\}(\text{aq})$  at 100.3°C.

$\text{CaCl}_2$	$y = 0.19964$	0.40085	0.59906	0.80064	0
1.1144	1.5962	1.6004	1.6043	1.6129	1.5968
1.3095	1.9103	1.9141	1.9213	1.9313	1.9050
1.6664	2.4993	2.5173	2.5288	2.5478	2.4939
1.9716	3.0203	3.0442	2.0738	3.1066	3.0037
1.9959	3.0608	3.0856	3.1139	3.1504	3.0450
2.5367	4.0203	4.0756	4.1396	4.2113	3.9787
2.5556	4.0528	4.1065	4.1703	4.2468	4.0111
2.8642	4.6121	4.6905	4.7800	4.8870	4.5499
3.0236	4.9048	5.0006	5.1064	5.2301	4.8288
3.3632	5.5365	5.6536	5.7979	5.9677	5.4213
3.4229	5.6394	5.7782	5.9303	6.1081	5.5263
3.7052	6.1596	6.3282	6.5168	6.7415	6.0147
3.7182	6.1827	6.3572	6.5503	6.7729	6.0361
4.2673	7.1859	7.4361	7.7104	8.0344	6.9677
4.56295	7.7162	8.0112	8.3366	8.7240	7.4582
5.0479	8.5726	8.9459	9.3699	9.8522	8.2379
5.9770	10.1237	10.6468	11.2394	11.9582	9.6330

(curves 4–6). The values of  $\Delta\Phi$  are positive. At  $m = 3$  and  $5 \text{ mol kg}^{-1} (\text{H}_2\text{O})$  data sets from measurements made 9 months later using new stock solutions (○) can be compared with former results (●). The agreement is within the estimated error limit of 0.3%. Curves 4–6 show that by increasing the total molality, the maximum values of  $\Delta\Phi$  are reached at ca.  $3 \text{ mol kg}^{-1} (\text{H}_2\text{O})$ . A further increase of  $m$  drops the height of the maximum again, and the curve becomes asymmetric in form.

This behaviour of  $\Delta\Phi$  can be compared with  $\Delta\Phi$  for the corresponding common ion mixtures plotted in Fig. 2. The

 Table 5. Isopestic molalities  $m$  of  $\{(1-y)\text{NaCl} + y\text{NaNO}_3\}(\text{aq})$  at 100.3°C.

$\text{CaCl}_2$	$y = 0.19958$	0.41222	0.59951	0.79969
1.1144	1.7317	1.7578	1.7837	1.8148
1.3095	2.0956	2.1374	2.1838	2.2329
1.9716	3.4629	3.5825	3.7077	3.8664
2.5367	4.7898	5.0293	5.2803	5.6045
3.0236	6.0508	6.4368	6.8390	7.3740
3.4230	7.1787	7.7116	8.2709	9.0177
3.7182	–	8.7105	9.4051	10.3200

 Table 6. Isopestic molalities  $m$  of  $\{(1-y)\text{LiNO}_3 + y\text{NaNO}_3\}(\text{aq})$  at 100.3°C.

$\text{CaCl}_2$	$y = 0.19044$	0.39351	0.58305	0.78233
0.81688	1.1696	1.1989	1.2128	–
1.3008	1.9705	2.0352	2.0961	–
2.1948	3.7436	3.9481	4.1625	4.4127
3.0052	5.6250	6.0481	6.5114	7.0988
3.8140	7.7577	8.4992	9.3184	–
4.2803	9.0863	10.0373	11.1120	–
4.9738	11.1280	12.4264	13.9317	15.9266
5.3961	12.3572	13.8925	15.6716	18.2597

deviations from additivity in the common ion system are much smaller than for the reciprocal one. The absolute values of  $\Delta\Phi$  at  $m = 3 \text{ mol kg}^{-1} (\text{H}_2\text{O})$  are below 0.003, and therefore are not plotted in Fig. 2.  $\text{LiNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$  represents the common ion system with the largest absolute values of  $\Delta\Phi$ .

Within the concentration range considered in Fig. 1 Pitzer's ion interaction equation should be applicable.<sup>6</sup> In terms of this equation,  $\Delta\Phi$  of a mixed solution of the two salts AX and BY can be expressed by eqn. (3).

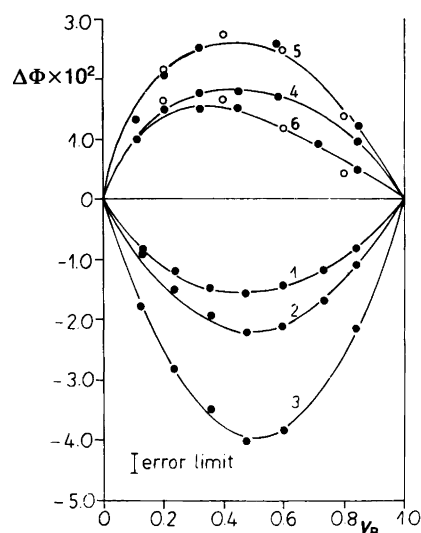


Fig. 1. Deviation of osmotic coefficients from additivity according to eqn. (2) for solutions of reciprocal salt pairs at 100.3°C.  $\text{LiNO}_3\text{--NaCl}$ : (1)  $m = 2$ , (2)  $m = 3$ , (3)  $m = 5$ ;  $\text{LiCl--NaNO}_3$ : (4)  $m = 2$ , (5)  $m = 3$ , (6)  $m = 5$ . (○, ● denote solutions prepared from different stock solutions);  $m/\text{mol kg}^{-1} (\text{H}_2\text{O})$ .

$$\begin{aligned} \Delta\Phi = & (1-y)ym\{[B_{BX}^\Phi + B_{AY}^\Phi - B_{AX}^\Phi - B_{BY}^\Phi \\ & + m(C_{BX}^\Phi + C_{AY}^\Phi - C_{AX}^\Phi - C_{BY}^\Phi)] \\ & + [\Theta_{AB} + \Theta_{XY} + m(1-y)(\psi_{ABX} + \psi_{AXY}) \\ & + my(\psi_{ABY} + \psi_{BXY})]\} \end{aligned} \quad (3)$$

The subscripts A, B, X and Y specify the corresponding combinations of cations  $A^+$  and  $B^+$  and anions  $X^-$  and  $Y^-$ . The term in the first square bracket represents the contribution arising from the second,  $B_{ij}^\Phi$ , and third,  $C_{ij}^\Phi$ , virial coefficients of the pure solutions of AX, BY, AY and BX. While  $C_{ij}^\Phi$  is considered to be a constant, the second virial coefficient depends on total molality according to eqn. (4).

$$B_{ij}^\Phi = \beta_{ij}^{(0)} + \beta_{ij}^{(1)} \exp(-2m^{1/2}) \quad (4)$$

The empirical parameters  $\beta_{ij}^{(0)}$ ,  $\beta_{ij}^{(1)}$  and  $C_{ij}^\Phi$ , must be determined from a fit of experimental data in the pure binary solutions using eqn. (5), where  $A^\Phi$  is the Debye-Hückel

$$\varphi = -\frac{A^\Phi m^{1/2}}{1 + 1.2m^{1/2}} + mB_{ij}^\Phi + m^2C_{ij}^\Phi \quad (5)$$

parameter. The second square bracket in eqn. (3) contains Pitzer's mixing parameters, which can be determined from isopiestic data of the common ion subsystems AX-BX, AX-AY, BX-BY and AY-BY. The system  $\text{Li}^+, \text{Na}^+//\text{Cl}^-, \text{NO}_3^- - \text{H}_2\text{O}$  is one of the few 1-1 valence systems without a common ion for which the complete set of parameters

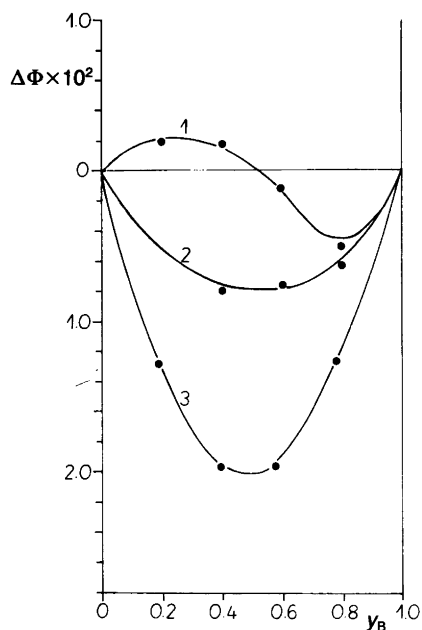


Fig. 2. Deviation of osmotic coefficients from additivity according to eqn. (2) for mixed solutions with a common ion at 100.3°C and  $m = 5 \text{ mol kg}^{-1} (\text{H}_2\text{O})$ : (1)  $\text{LiCl-LiNO}_3$ , (2)  $\text{NaCl-NaNO}_3$ , (3)  $\text{LiNO}_3\text{-NaNO}_3$ .

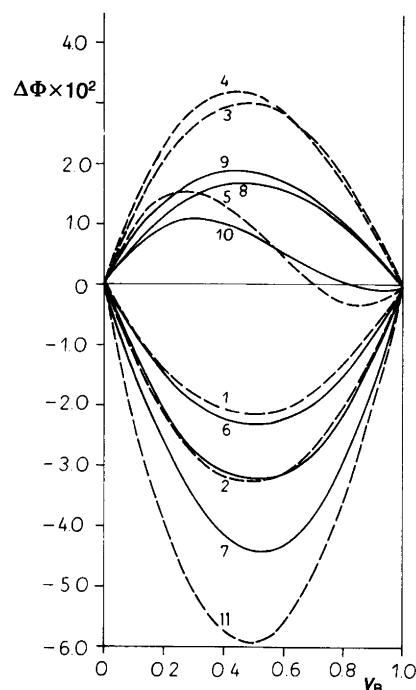


Fig. 3. Deviation of osmotic coefficients from additivity as calculated from Pitzer's equations, (---) at 25°C and (—) at 100.3°C.  $\text{LiNO}_3\text{-NaCl}$ : (1,6)  $m = 2$ , (2)  $m = 3$ , (7, 11)  $m = 5$ ;  $\text{LiCl-NaNO}_3$ : (3,8)  $m = 2$ , (4,9)  $m = 3$ , (5,10)  $m = 5$ ;  $m/\text{mol kg}^{-1} (\text{H}_2\text{O})$ .

of eqn. (3) is known at  $T = 25.0^\circ\text{C}$ .<sup>5</sup> Using these parameters and calculating  $\Delta\Phi$  by means of eqn. (3) results in the curves drawn as dotted lines in Fig. 3. The essential features of the curves correspond to the experimental curves in Fig. 1. Only the absolute values of  $\Delta\Phi$  are larger than those found at  $T = 100.3^\circ\text{C}$ . In order to describe our experimental curves by means of eqn. (3) we estimated the necessary Pitzer parameters using our own experimental data of the binary and common ion ternary subsystems at 100.3°C. Since Pitzer's equation should be applied up to a maximum molality of ca.  $6 \text{ mol kg}^{-1} (\text{H}_2\text{O})$ , only data for  $m < 7 \text{ mol kg}^{-1} (\text{H}_2\text{O})$  were selected. Data of the pure solutions  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{LiNO}_3$ <sup>3</sup> and  $\text{NaNO}_3$ ,<sup>2</sup> reported earlier, were fitted against eqn. (5). The adjusted coefficients and the standard deviations of  $\Phi$  are listed in Table 7. The mixing parameters  $\Theta_{ij}$  and  $\psi_{ijk}$  were estimated by means of eqn. (6) applied to the osmotic coefficients  $\Phi$  of mixed solutions having the common ion  $k$ .

Table 7. Pitzer's ion-interaction coefficients  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^\Phi$  and standard deviation  $\sigma(\Phi)$  of the osmotic coefficient at 100.3°C<sup>a</sup>

Salt	$\beta^{(0)}$	$\beta^{(1)}$	$C^\Phi \times 10^3$	$\sigma_\Phi \times 10^3$
$\text{LiNO}_3$	0.1449(6)	0.3675(60)	-7.59(11)	1.24
$\text{LiCl}$	0.1431(1)	0.2990(30)	-0.237(10)	0.06
$\text{NaNO}_3$	0.05275(121)	0.3920(117)	-4.62(19)	2.02
$\text{NaCl}$	0.1057(5)	0.3072(59)	-4.00(10)	1.12

<sup>a</sup>( ) within the table denotes uncertainty in the last digits.

$$\Phi = (1-y)\Phi_{ik}^* + Y\Phi_{jk}^* + ym\Theta_{ij} + y(1-y)m^2\psi_{ijk} \quad (6)$$

$\Phi_{ik}^*$  and  $\Phi_{jk}^*$  are the osmotic coefficients of the pure binary solutions calculated from eqn. (5) and the parameters in Table 7. The set of mixing parameters obtained in this way is given in Table 8. The uncertainty of the parameters is quite large, especially for the system LiCl–LiNO<sub>3</sub>–H<sub>2</sub>O. Therefore a complete optimization of the  $\Theta_{ij}$  was not attempted. Recalculation of  $\Delta\Phi$  with the parameters from Tables 7 and 8 (with  $\Theta_{\text{Cl,NO}_3} = 8.81 \times 10^{-3}$  and  $\Theta_{\text{Li,Na}} = -1.00 \times 10^{-3}$ ) yields the curves drawn as solid lines in Fig. 3. Qualitative and quantitative features of these curves are close to those in Fig. 1. The maximum differences of  $\Delta\Phi$  between the experimental curves in Fig. 1 and the calculated one in Fig. 3 are 0.01. Thus, we conclude that the larger values of  $\Delta\Phi$  calculated for  $T = 25.0^\circ\text{C}$  reflect the true behaviour of the system.

*Activity coefficients.* Since the isopiestic molalities given in Tables 1–6 exceed the validity range of Pitzer's ion interaction model, the McKay–Perring method<sup>7,8</sup> was used to calculate the mean ionic activity coefficients of the salt components. The numerical procedure remained the same as that described previously.<sup>2</sup> In essence, the calculation is based on eqns. (7)–(9), which are formulated for the case of 1–1 valence-type electrolytes.

$$\ln\gamma_A = \ln\Gamma_A + \ln R_A + y^2 \int_0^{m\Phi} (b/M_A)d(m\Phi) \quad (7)$$

$$\ln\gamma_B = \ln\Gamma_B + \ln R_B + (1-y)^2 \int_0^{m\Phi} (b/M_A)d(m\Phi) \quad (8)$$

$$R_A = 1 - ay - by^2 = M_A/m \quad (9)$$

The subscripts A and B denote salts A and B, and  $\Gamma_A$  and  $\Gamma_B$  are the activity coefficient of a pure solution of A ( $y = 0$ ) and B ( $y = 1$ ), respectively, having the same total molality,  $m$ , as the mixed solutions.

The results of our calculations are presented in Figs. 4 and 5. Two levels of total molalities were selected:  $m = 2$  and  $m = 5 \text{ mol kg}^{-1}$  (H<sub>2</sub>O).

The variations of  $\ln\gamma_{\pm}$  follow the same pattern as in the

Table 8. Pitzer's mixing parameters obtained from fitting against eqn. (6) for the system Li<sup>+</sup>, Na<sup>+</sup>//Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>–H<sub>2</sub>O at 100.3°C.

System	$\Theta_{ij} \times 10^3$	$\psi_{ijk} \times 10^3$	$\sigma(\Phi) \times 10^3$
LiCl–LiNO <sub>3</sub>	$1.73 \pm 5.01$	$-0.60 \pm 0.99$	4.5
NaCl–NaNO <sub>3</sub>	$8.81 \pm 1.86$	$-3.36 \pm 0.39$	1.6
LiNO <sub>3</sub> –NaNO <sub>3</sub>	$-1.00 \pm 0.37$	$-1.36 \pm 0.72$	3.1
LiCl–NaCl <sup>a</sup>	$-5.42 \pm 3.81$	0	–

<sup>a</sup>From eqn. (10) of Ref. 4.

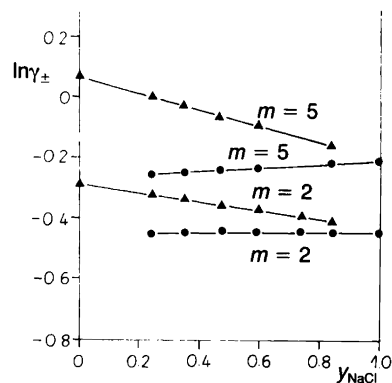


Fig. 4. Composition dependence of  $\ln\gamma_{\pm}$  in the system LiNO<sub>3</sub>–NaCl–H<sub>2</sub>O at constant total molalities of  $m = 2$  and  $5 \text{ mol kg}^{-1}$  (H<sub>2</sub>O) at  $T = 100.3^\circ\text{C}$ .  $\blacktriangle$ ,  $\ln\gamma_{\pm}$  (LiNO<sub>3</sub>);  $\bullet$ ,  $\ln\gamma_{\pm}$  (NaCl).

analogous mixtures with Br<sup>-</sup> instead of Cl<sup>-</sup>.<sup>2</sup> Except for  $\ln\gamma_{\pm}(\text{NaNO}_3)$ , the activity coefficients of all the other salt components decrease linearly when mixing solutions of the corresponding reciprocal salts. Thus, the results of the present work support the fact that in mixed solutions of LiNO<sub>3</sub> and sodium halide (stable pairs) the mean ionic activity coefficients are lower than in their pure binary solutions at the same molality (Fig. 4). This is valid up to the highest concentration at which measurements were made. As discussed earlier,<sup>2</sup> this contradicts our empirical rule for the variation of activity coefficients in such systems. According to this rule [eqn. (10)] the variation of the activity coefficient of a salt AX is governed by the change in Gibbs energy  $\Delta_{\text{ex}}G^\circ$  due to reaction (I) and the difference in standards Gibbs energy of solution of both salt components,  $\Delta_s G_{\text{AX}}^\circ$  and  $\Delta_s G_{\text{BY}}^\circ$ , respectively.

$$\Delta = \ln\gamma_{\text{AX}} = \Delta_{\text{ex}}G^\circ + (\Delta_s G_{\text{AX}}^\circ - \Delta_s G_{\text{BY}}^\circ) \quad (10)$$

Positive values of  $\Delta$  predict increasing activity coefficients of AX considering mixing with a solution of BY at constant

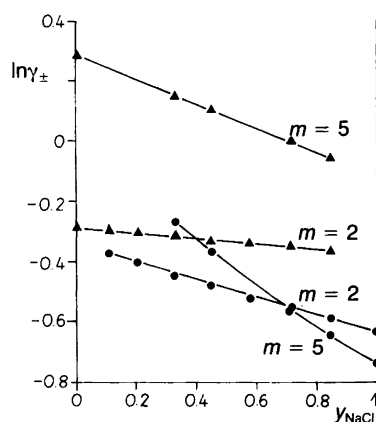


Fig. 5. Composition dependence of  $\ln\gamma_{\pm}$  in the system LiCl–NaNO<sub>3</sub>–H<sub>2</sub>O at constant total molalities of  $m = 2$  and  $5 \text{ mol kg}^{-1}$  (H<sub>2</sub>O) at  $T = 100.3^\circ\text{C}$ .  $\blacktriangle$ ,  $\ln\gamma_{\pm}$  (LiCl);  $\bullet$ ,  $\ln\gamma_{\pm}$  (NaNO<sub>3</sub>).

total molality.<sup>1</sup> With values of  $\Delta_s G_{\text{LiNO}_3}^\circ = -23.4 \text{ kJ mol}^{-1}$  and  $\Delta_s G_{\text{NaCl}}^\circ = -9.0 \text{ kJ mol}^{-1}$  at  $T = 25.0^\circ\text{C}$ ,<sup>9</sup> eqn. (10) predicts curves with slopes of opposite sign to those shown in Fig. 4.

In the near future we intend to give a more thorough discussion of the thermodynamic behaviour of aqueous reciprocal systems within the framework of a quasi-lattice approach.

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