Thermodynamics of Aqueous Reciprocal Salt Systems. VI. Isopiestic Determination of Osmotic Coefficients in Mixtures of Chlorides, Bromides and Nitrates of Lithium, Sodium, Potassium and Cesium at 100.3 °C

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Osmotic coefficients of four pure binary aqueous systems [CsCl(aq), CsBr(aq), $CsNO_3$(aq) and KNO_3(aq)] and of 16 aqueous mixtures of reciprocal salt pairs at an ionic strength fraction y_B = 0.5 have been determined by means of isopiestic measurements at 100.3 °C. From the results reported in this contribution and by using previously published data the change of the osmotic coefficients while mixing pure aqueous salt solutions of a reciprocal salt pair $\Delta\varphi$ (the deviation of the osmotic coefficients from additivity) was calculated for 36 aqueous reciprocal salt pairs, which can be formed from the chlorides, bromides and nitrates of lithium, sodium, potassium and cesium at an ionic strength fraction of y_B = 0.5 and at different total molalities. $\Delta\varphi$ is discussed in terms of predictions made from a simple quasi-lattice model. According to this model $\Delta\varphi$ of an aqueous reciprocal salt pair mainly depends on an energy parameter $\Delta_{ex} G°$, the Gibbs energy of the corresponding metathetical exchange reaction.

From the experimental results a correlation between $\Delta\varphi$ and $\Delta_{ex} G°$ is suggested. In particular, for the simple halide systems (chloride–bromide systems) the model is fulfilled qualitatively. The situation in the nitrate systems is more complex. For aqueous halide–nitrate systems the model is contradicted at low concentrations. Obviously this is due to ion-pair formation between NO_3^- and the alkali–metal ions, which is not considered in our model.

It became evident from our previous results concerning the thermodynamic behaviour of aqueous reciprocal salt systems[1–4] that the Gibbs energy of the corresponding exchange reaction $\Delta_{ex} G°$ is related to the concentration dependence of osmotic and salt activity coefficients. In particular, the deviation of the osmotic coefficients from additivity seems to be in close relation to the Gibbs energy of the exchange reaction. For aqueous reciprocal salt pairs, which are formed from I–I valence-type electrolytes, symmetrical curves with a maximum deviation in φ from additivity at an ionic strength fraction y_B of about 0.5 have been obtained.[2,3] To determine whether $\Delta\varphi$ is correlated to the Gibbs energy of the exchange reaction it would be worthwhile to compare different aqueous reciprocal salt systems from the viewpoint of this interesting feature. Unfortunately, very little is known about the thermodynamic properties of aqueous reciprocal salt systems, and the complete experimental investigation of the thermodynamic properties of a reciprocal salt system, including all binary and common ion ternary sub-systems, is very extensive.[2–4]

However, to answer the question as to whether there is a correlation between $\Delta\varphi$ and $\Delta_{ex} G$ it should be sufficient to know, in addition to the properties of the pure binary systems, the osmotic coefficients of the reciprocal mixtures at an ionic strength fraction y_B of 0.5.

Starting from that idea we wish to investigate all aqueous reciprocal salt pairs which can be formed from the chlorides, bromides and nitrates of lithium, sodium, potassium and cesium. Among the 12 binary systems and 36 reciprocal salt pairs that can be formed from the above-mentioned electrolytes, eight binary and two reciprocal systems (the four salt pairs $LiCl-NaNO_3$, $LiNO_3-NaCl$, $LiBr-NaNO_3$ and $NaBr-LiNO_3$) had been investigated previously at 100.3 °C.[2,3,5,6] Hence, in this contribution osmotic coefficients of four pure binary systems [CsCl(aq), CsBr(aq), $CsNO_3$(aq) and KNO_3(aq)] and of 16 reciprocal salt pairs (at an ionic strength fraction y_B = 0.5) have been determined by means of isopiestic measurements at 100.3 °C.

Experimental

The isopiestic method used and the accompanying experimental procedure are described in detail in previous publications.[5,6] Stock solutions were prepared from: $CaCl_2$, cal-

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Table 1. Isopiestic molalities and water activities of aqueous CsCl, CsBr, CsNO$_3$ and KNO$_3$ at 100.3 °C.

Run	a_w	m_{CaCl_2}	m_{CsCl}	m_{CsBr}	m_{CsNO_3}	m_{KNO_3}
100.4	0.630 02	4.4730	11.8506	–	–	–
111.5	0.677 99	4.0077	–	–	–	21.2072
90.5	0.681 81	3.9711	–	10.7506	–	–
100.3	0.700 40	3.7932	9.3804	–	–	–
111.4	0.702 77	3.7706	–	–	–	18.6600
90.4	0.730 95	3.5008	–	8.8729	–	–
111.3	0.754 50	3.2734	–	–	–	13.8922
111.2	0.773 09	3.0915	–	–	–	12.3653
90.3	0.776 46	3.0582	–	7.2638	–	–
100.2	0.783 72	2.9862	6.7195	–	–	–
70.2	0.786 88	2.9547	–	–	–	11.2824
111.1	0.790 55	2.9179	–	–	–	11.0329
90.2	0.797 84	2.8445	–	6.5401	–	–
71.3	0.804 05	2.7815	6.0845	–	–	9.9682
70.1	0.817 06	2.6475	5.6887	5.8851	–	9.0813
90.1	0.822 18	2.5940	–	5.7286	–	–
100.1	0.826 80	2.5454	5.4053	–	–	–
110.2	0.843 25	2.3690	–	–	7.2124	–
91.1	0.861 00	2.1717	–	–	6.1849	–
110.3	0.864 15	2.1358	–	–	6.0012	–
112.1	0.871 51	2.0508	–	–	5.5837	–
71.1	0.873 59	2.0265	3.9855	4.0599	–	5.4717
110.4	0.883 07	1.9137	–	–	4.9615	–
101.1	0.888 38	1.8492	–	–	–	4.6828
101.2	0.889 55	1.8349	–	–	–	4.6091
112.2	0.904 37	1.6476	–	–	3.8747	–
91.3	0.921 41	1.4184	–	–	3.0786	–
101.3	0.927 25	1.3358	–	–	–	2.7675
111.7	0.928 96	1.3112	–	–	–	2.6955
112.3	0.932 05	1.2661	–	–	2.6010	–
72.1	0.934 13	1.2353	2.1236	2.1344	2.5115	2.4577
91.4	0.944 52	1.0746	–	–	2.0564	–
72.2	0.949 68	0.9934	1.6286	1.6308	1.8483	1.8066
72.3	0.959 33	0.8306	1.3138	1.3137	1.4544	1.4218
72.4	0.968 12	0.6726	1.0322	1.0286	1.1152	1.0915

cium chloride-2-hydrate, p.a. (Merck, D.); CsCl, CsNO$_3$, KNO$_3$, NaCl, NaBr and LiBr, purum p.a. (Fluka AG, CH); CsBr and KCl, puriss. p.a. (Fluka AG, CH); and LiCl, purum p.a. (Merck, D.).

All salts were dissolved in deionized water. The final compositions of the stock solutions were determined by drying ca. 2 g of solution in a vitreous carbon cup. Duplicate determinations agreed within 0.05 % or better. Mixed solutions were prepared from the stock solutions of the pure salt components.

Results

All experimental results are summarized in Table 1 and Tables 3–6. The isopiestic molalities have been corrected according to the amount of water in the vapour phase at equilibrium temperature and pressure. The system CaCl$_2$–H$_2$O has been chosen as a reference system. The compilation established by Ananthaswamy and Atkinson[7] was used to calculate the osmotic coefficients and water activities, respectively. The molalities of the reference solution [CaCl$_2$(aq)] are averages of triplicate samples. No

results were accepted unless triplicates agreed within 0.1 % in molality. The isopiestic molalities of the binary systems (Table 1) and of the reciprocal mixtures (Tables 3–6) usually represent mean values of two individual measuring points, with a maximum deviation of 0.05 % from the values given in the tables.

Binary systems. Osmotic coefficients φ_{MX} were calculated from the isopiestic molalities m_{MX} in Table 1 by applying eqn. (1).

$$\varphi_{MX} = 3\varphi_{CaCl_2} \, m_{CaCl_2}/2 \, m_{MX} \tag{1}$$

To estimate osmotic coefficients at rounded molalities the experimental data are described by the application of an extension of the ion-interaction approach.[7] The dependence of the osmotic coefficients φ on molality is given by eqn. (2), which is adopted for I–I valence type electrolytes

$$\varphi - 1 = f^\varphi + mB^\varphi_{MX} + m^2 C^\varphi_{MX} + m^3 D^\varphi_{MX}$$

$$+ m^4 E^\varphi_{MX} + m^5 F^\varphi_{MX} \tag{2}$$

Table 2. Parameters of eqn. (2) and standard deviations σ_φ at 100.3 °C.

Parameter	System				
	CsCl-H₂O	CsBr-H₂O	CsNO₃-H₂O	KNO₃-H₂O	KNO₃-H₂O
$\beta(0)\times10^2$	6.168 77	5.878 76	-0.605 453	-0.560 512	-0.583 933
$\beta(1)$	0.162 337	0.208 794	0.213 946	0.347 362	0.347 042
$C_\varphi\times10^3$	-3.075 32	-3.995 70	-0.294 551	-0.996 715	-0.821 669
$D_\varphi\times10^5$	5.405 35	9.788 77	0	7.501 43	4.358 83
$E_\varphi\times10^6$	0	0	0	-1.560 65	0
F_φ	0	0	0	0	0
$\sigma_\varphi\times10^3$	1.3	1.3	0.9	1.3	1.3
I_{max}	12	11	8	22	13

and in which f^φ is given by eqn. (3) (where $I = m$) and B^φ_{MX}

$$f^\varphi = -A^\varphi\,I^{1/2}\,/\,(1 + b\,I^{1/2}) \tag{3}$$

$$B^\varphi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp -X \tag{4}$$

is given by eqn. (4) (where $X = \alpha\,I^{1/2}$, $\alpha = 2$ and $b = 1.2$). A^φ is the Debye–Hückel coefficient for the osmotic coefficient (0.4609 at 100.3 °C)[8] and $\beta^{(0)}$, $\beta^{(1)}$, C^φ, $D^\prime$, E^φ and F^φ are adjustable parameters.
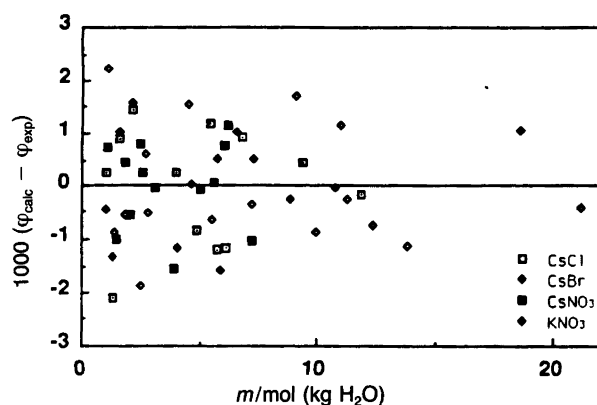

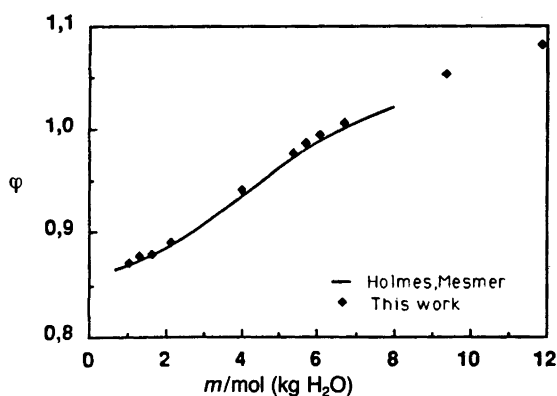*Fig. 1.* Deviation plot of the experimental osmotic coefficients Δ_{exp} from eqn. (2).

Fig. 2. Comparison of different data for osmotic coefficients of aqueous CsCl at 100.3 °C.

The coefficients estimated by non-linear regression are listed in Table 2 together with standard deviations and maximum ionic strengths. For KNO₃(aq) two different fits of the experimental data have been carried out. As well as one overall fit up to maximum molalities of ca. 22 mol KNO₃ (kg⁻¹ H₂O), data up to maximum molalities of about 13 mol kg⁻¹ have been fitted separately. Molalities of about 10 mol (kg⁻¹ H₂O) are sufficient for further evaluations in the reciprocal systems.

In Fig. 1 the calculated and experimentally determined osmotic coefficients are compared for each of the four systems. The deviations are less than 0.002 in φ. Only two points slightly exceed this limit.

In Fig. 2 our experimental results for CsCl(aq) are compared with the compilation published by Holmes and Mesmer.[9] We find slightly higher osmotic coefficients within the whole concentration interval investigated. The mean deviation is ca. 0.005 in φ within the concentration range for which the compilation is valid. The maximum deviation occurs at the highest molalities.

To our knowledge, osmotic coefficients for CsBr(aq) and CsNO₃(aq) at elevated temperatures have not previously been published.

Reciprocal mixtures. The isopiestic molalities of 16 reciprocal mixtures have been determined at an ionic strength fraction y_B of ca. 0.5. The results are presented in Tables 3–6, where the ionic strength fraction y_B is defined by eqn. (5), with A and B denoting the two salt components.

$$y_B = m_B/(m_A + m_B) \tag{5}$$

Osmotic coefficients were calculated by applying eqn. (1), where φ_{MX} and m_{MX} are the osmotic coefficients and the total isopiestic molality of the reciprocal mixture, respectively.

For all 36 reciprocal salt pairs which can be formed from combinations of the ions Cl⁻, Br⁻, NO₃⁻, Li⁺, Na⁺, K⁺ and Cs⁺ the deviation of the osmotic coefficients from additivity was calculated at $y_B = 0.5$ according to eqn. (6). φ°_A and

$$\Delta\varphi = \varphi_m - 0.5\,(\varphi^\circ_A + \varphi^\circ_B) \tag{6}$$

Table 3. Isopiestic molalities [in mol (kg^{-1} H$_2$O)] and water activities of mixed solutions of the reciprocal salt pairs NaBr–CsNO$_3$, KCl–CsBr, KCl–CsNO$_3$ and KNO$_3$–CsBr at 100.3 °C.

Run	a_w	$m(CaCl_2)$	$m(NaBr-CsNO_3)$ $Y_{CsNO_3} = 0.492\,40$	$m(KCl-CsBr)$ $Y_{CsBr} = 0.497\,19$	$m(KCl-CsNO_3)$ $Y_{CsNO_3} = 0.502\,34$	$m(KNO_3-CsBr)$ $Y_{CsBr} = 0.498\,76$
81.3	0.951 60	0.9620	1.5603	1.5265	1.6231	1.6176
81.2	0.935 15	1.2201	2.0958	2.0336	2.1993	2.1931
81.1	0.916 01	1.4929	2.7244	2.6148	2.8835	2.8788
81.4	0.896 55	1.7476		3.1965	3.5810	3.5830
80.2	0.894 92	1.7681	3.4195	3.2422	3.6411	3.6482
80.1	0.878 94	1.9633	3.9531	3.7230		
81.6	0.878 68	1.9664		3.7300	4.2318	4.2459
80.3	0.844 52	2.3552	5.1087	4.7202	5.5062	5.5582
80.4	0.801 03	2.8122	6.6379	6.0205	7.2657	7.3600
81.7	0.784 92	2.9743	–[a]	6.5383	–[a]	8.0561
81.8	0.783 31	2.9904	–[a]	6.5834	–[a]	8.1202

[a]Saturation.

Table 4. Isopiestic molalities [in mol (kg^{-1} H$_2$O)] and water activities of mixed solutions of the reciprocal salt pairs NaBr–KNO$_3$, NaBr–KCl, NaCl–CsNO$_3$ and NaCl–CsBr at 100.3 °C.

Run	a_w	$m(CaCl_2)$	$m(NaBr-KNO_3)$ $Y_{KNO_3} = 0.495\,57$	$m(NaBr-KCl)$ $Y_{KCl} = 0.493\,05$	$m(NaCl-CsNO_3)$ $Y_{CsNO_3} = 0.499\,06$	$m(NaCl-CsBr)$ $Y_{CsBr} = 0.500\,93$
91.4	0.944 62	1.0746	1.7401	1.6499	1.8023	1.7085
91.3	0.921 41	1.4184	2.4631	2.2908	2.5729	2.3880
91.2	0.884 19	1.9003	3.6293	3.2769	3.8260	3.4396
91.1	0.861 00	2.1717	4.3796	3.8822	4.6485	4.0908
90.1	0.822 18	2.5940	5.6522	4.8743	6.0453	5.1613
90.2	0.797 84	2.8445	6.4786	5.4944	6.9615	5.8325
90.3	0.776 46	3.0582	7.2136	6.0404	7.7711	6.4223
90.4	0.730 95	3.5008	8.8412	7.2237	9.5770	7.7001
90.5	0.681 81	3.9711	10.7134	8.5692	11.6826	9.1450

Table 5. Isopiestic molalities [in mol (kg^{-1} H$_2$O)] and water activities of mixed solutions of the reciprocal salt pairs NaCl–KNO$_3$, LiBr–CsNO$_3$, LiBr–KNO$_3$ and LiBr–KCl at 100.3 °C.

Run	a_w	$m(CaCl_2)$	$m(NaCl-KNO_3)$ $Y_{KNO_3} = 0.500\,17$	$m(LiBr-CsNO_3)$ $Y_{CsNO_3} = 0.500\,32$	$m(LiBr-KNO_3)$ $Y_{KNO_3} = 0.499\,19$	$m(LiBr-KCl)$ $Y_{KCl} = 0.499\,75$
101.4	0.953 56	0.9293	1.4791	1.4354	1.3962	1.3598
101.3	0.927 25	1.3358	2.3244	2.2252	2.1419	2.0561
101.1	0.888 38	1.8492	3.5988	3.3783	3.2124	3.0183
100.1	0.826 80	2.5454	5.7128	5.2005	4.8792	4.4428
100.2	0.783 72	2.9862	7.2868	6.4836	6.0502	5.3984
100.3	0.700 40	3.7932	10.6391	9.0235	8.3745	7.2328
100.4	0.630 02	4.4730	13.9622	11.2930	10.4288	8.8310

$\varphi^{\circ}{}_B$ represent the osmotic coefficients of the pure binary solutions at the same total molality as for the mixture with φ_m. A graphical presentation of the results is given in Figs. 3–5, where $\Delta\varphi$ is plotted against the total molality of the mixtures. $\Delta\varphi$ can be interpreted as the change of the osmotic coefficients on mixing the pure salt solutions.

Calculations of $\Delta\varphi$ were carried out at rounded molalities from $m = 1$ mol (kg^{-1} H$_2$O) to 8 mol (kg^{-1} H$_2$O). For interpolations of φ_m the experimental data of every mixture were fitted to a cubic polynomial. The maximum deviation

between experimental data and the smoothed curves did not exceed 0.002 in φ. The osmotic coefficients φ° of the the 12 pure binary solutions were calculated at rounded molalities by using eqn. (2) and the coefficients evaluated in this work (Table 2) or given in previous publications (CsCl, CsBr, CsNO$_3$, KNO$_3$: this work; KCl, KBr: Fanghänel and Grjotheim;[6] LiCl, LiNO$_3$, NaCl: Grjotheim *et al.*;[9] NaBr, NaNO$_3$, LiBr: Voigt *et al.*[2]).

At $y_B = 0.5$ for a mixed solution of I–I electrolytes (AX + BY) φ_m is equal to φ_m of a solution of AY and BX at the

Table 6. Isopiestic molalities [in mol (kg^{-1} H$_2$O)] and water activities of mixed solutions of the reciprocal salt pairs LiCl–NaBr, LiCl–KNO$_3$, LiCl–CsBr and LiCl–CsNO$_3$ at 100.3 °C.

Run	a_w	m(CaCl$_2$)	m(LiCl–NaBr) $Y_{NaBr} = 0.500\ 32$	m(LiCl–KNO$_3$) $Y_{KNO_3} = 0.499\ 81$	m(LiCl–CsBr) $Y_{CsBr} = 0.499\ 87$	m(LiCl–CsNO$_3$) $Y_{CsNO_3} = 0.500\ 03$
112.4	0.953 40	0.9319	1.3230	1.4354	1.4141	1.4631
112.3	0.932 05	1.2661	1.8542	2.0458	2.0195	2.1168
111.7	0.928 96	1.3112	1.9260	2.1344	2.1012	2.2060
112.2	0.904 37	1.6476	2.4949	2.8357	2.7710	2.9513
110.4	0.883 07	1.9137	2.9599	3.4335	3.3268	3.5889
112.1	0.871 51	2.0508	3.2032	3.7627	3.6296	3.9376
110.3	0.864 15	2.1358	3.3554	3.9672	3.8172	4.1595
110.2	0.843 25	2.3690	3.7747	4.5496	4.3423	4.7863
111.1	0.790 55	2.9179	4.8041	6.0610	5.6497	6.3915
111.2	0.773 09	3.0915	5.1282	6.5587	6.0680	6.9116
110.1	0.768 22	3.1394	5.2261	6.7135	6.2039	
111.3	0.754 50	3.2734	5.4674	7.0928	6.5138	7.4728
111.4	0.702 77	3.7706	6.4208	8.6496	7.7730	9.1228
111.5	0.677 99	4.0077	6.8592	9.4101	8.3766	9.9236
111.6	0.653 65	4.2422	7.3141	10.1848	8.9767	10.7278

same total molality. Therefore, on the basis of the experimental data of the 20 reciprocal pairs reported in paper Parts II and III together with this paper, φ_m of the remaining 16 non-common ion combinations are also known at y_B = 0.5. Small deviations of the actual composition from y_B = 0.5 have been neglected. The resulting uncertainties in $\Delta\varphi$ were estimated to be smaller than 0.001. For the systems LiBr–NaNO$_3$, NaBr–LiNO$_3$, LiCl–NaNO$_3$ and NaCl–
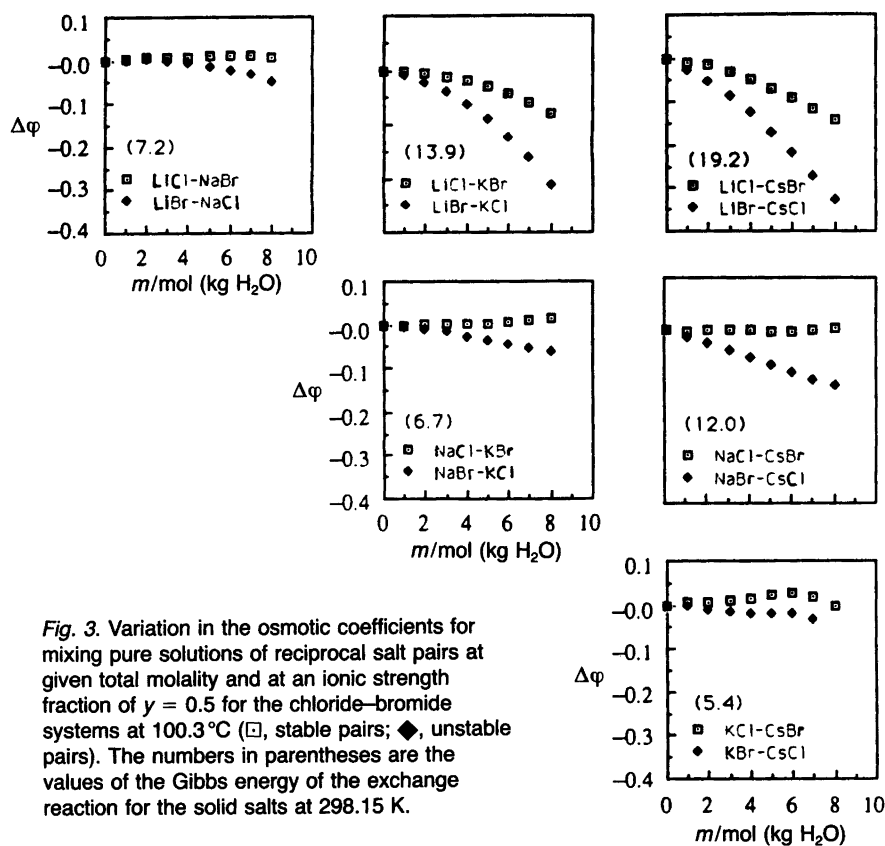

Fig. 3. Variation in the osmotic coefficients for mixing pure solutions of reciprocal salt pairs at given total molality and at an ionic strength fraction of y = 0.5 for the chloride–bromide systems at 100.3 °C (□, stable pairs; ◆, unstable pairs). The numbers in parentheses are the values of the Gibbs energy of the exchange reaction for the solid salts at 298.15 K.
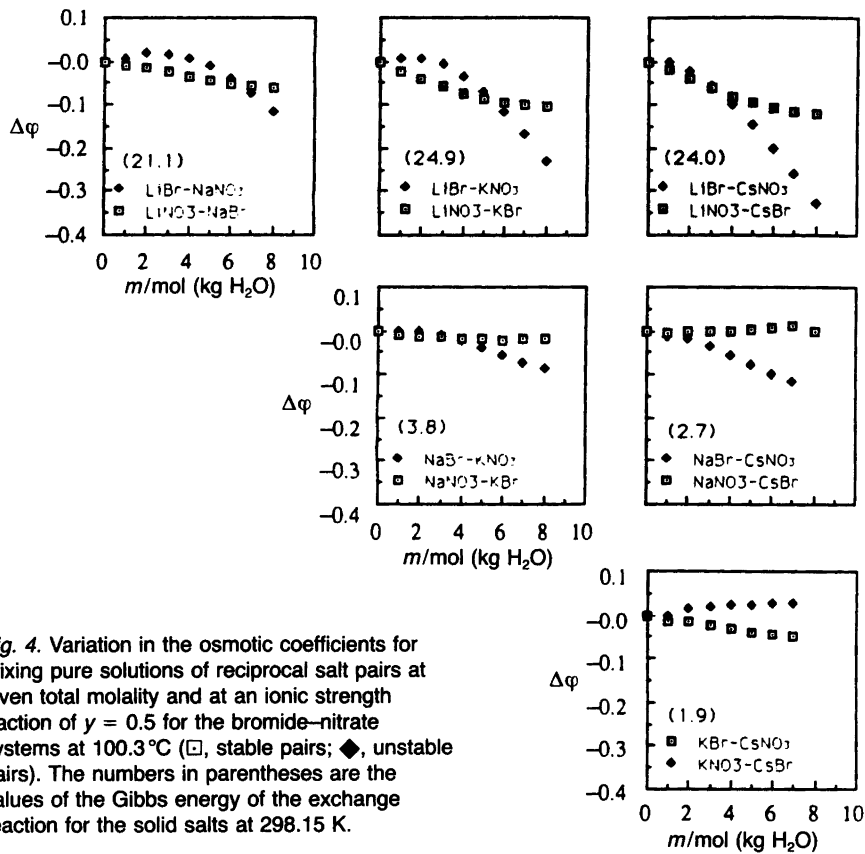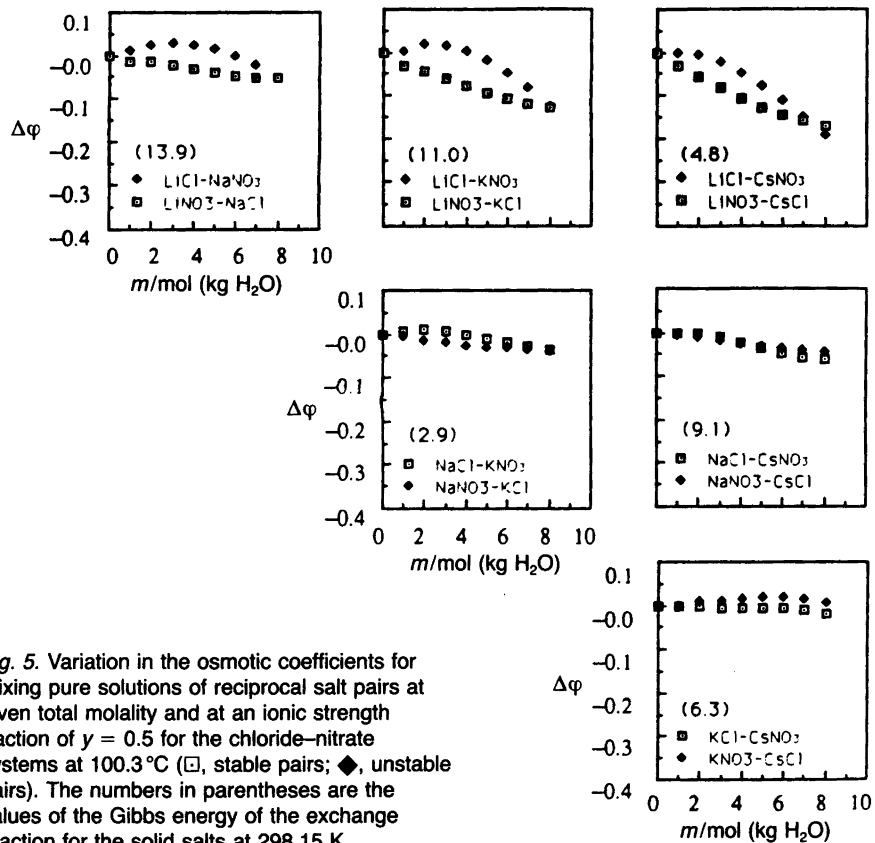
Fig. 4. Variation in the osmotic coefficients for mixing pure solutions of reciprocal salt pairs at given total molality and at an ionic strength fraction of $y = 0.5$ for the bromide–nitrate systems at 100.3 °C ($\square$, stable pairs; $\blacklozenge$, unstable pairs). The numbers in parentheses are the values of the Gibbs energy of the exchange reaction for the solid salts at 298.15 K.

Fig. 5. Variation in the osmotic coefficients for mixing pure solutions of reciprocal salt pairs at given total molality and at an ionic strength fraction of $y = 0.5$ for the chloride–nitrate systems at 100.3 °C ($\square$, stable pairs; $\blacklozenge$, unstable pairs). The numbers in parentheses are the values of the Gibbs energy of the exchange reaction for the solid salts at 298.15 K.

$LiNO_3$ the dependence of φ on y_B had been investigated at different ionic strengths.[2,3] Thus, we used these results to interpolate φ_m at $y_B = 0.5$ for these pairs. Thereby, the values of φ_m of $LiBr$–$NaNO_3$ should be equal to those of $NaBr$–$LiNO_3$. At $y_B = 0.5$ the average deviation in φ_m between solutions of corresponding reciprocal pairs was $\bar{\Delta} = 0.0046$ in the bromide–nitrate system and $\bar{\Delta} = 0.0026$ in the chloride–nitrate system.

Discussion

In Figs. 3–5 plots of $\Delta\varphi$ are presented separately for the anion combination chloride–bromide (Fig. 3), chloride–nitrate (Fig. 4) and bromide–nitrate (Fig. 5). First let us consider the chloride–bromide mixture (Fig. 3). Every diagram contains two plots: one for the mixtures of the stable pair (□) and one for the corresponding unstable pair (◆). A salt pair is termed stable when the standard Gibbs energy $\Delta_{ex}G°$ for the metathetical reaction (exchange reaction) (I) is positive.

$$AX + BY \rightarrow AY + BX \qquad \Delta_{ex}G° > 0 \qquad (I)$$
stable pair \qquad unstable pair

Values of $\Delta_{ex}G°$ of reaction (I) were calculated from standard formation data at 298.15 K,[10] and are given as values in parentheses within each diagram. The anhydrous crystalline salts have been chosen as standard state.

From the plots in Fig. 3 a correlation between $\Delta_{ex}G°$ and $\Delta\varphi$ is clearly suggested. For all bromide–chloride systems the $\Delta\varphi$ values of the unstable pairs (◆) are negative. The plots of the corresponding stable pairs (□) are shifted toward more positive values. Except for the systems with the Li^+–K^+ and Li^+–Cs^+ combinations, the absolute values for the mixtures of the stable pairs are also positive. With

increasing molality the plots of corresponding pairs diverge. This tendency correlates with the magnitude of $\Delta_{ex}G°$. We observe the largest distance between the two curves for the system Li^+,Cs^+ / Cl^-,Br^- // H_2O with $\Delta_{ex}G°$ = 19.2 kJ mol^{-1}.

These facts are in agreement with predictions made from a simple quasi-lattice model, which will be shown briefly in the following.

For a system consisting of the cations A^+ and B^+, the anions X^- and Y^-, and H_2O, the important interactions can be summarized as in Table 7. The number of pairs in the second column of Table 7 results from considering a random distribution of cations and anions each in its own sublattice. The water molecules are assumed to be distributed in equal portions in the cation and anion sublattices. The latter assumption is a consequence of local electroneutrality at molar water/salt ratios less than the mean coordination number z, i.e. in the concentration range of molten salt hydrates. Horsak[11] introduced this condition successfully in the modelling of liquidus curves in mixed salt solvates. In order to avoid a serious complexity in our expressions, we also apply this assumption to more dilute solutions.

Specifying a solution of salts $(AX + BY)$ in water (which implies $N_a = N_x$, $N_B = N_y$), summation over all products of specific interaction energy, ε_i, with the number of pairs, N_i^*, leads to an expression or the total energy as in eqn. (8).

$$e = \frac{z}{N_H/2+N_A+N_B}\left[(N_A)^2\varepsilon_1 + (N_B)^2\varepsilon_2 + N_AN_B(\varepsilon_3 + \varepsilon_4)\right.$$
$$\left. + N_A\frac{N_H}{2}(\varepsilon_5 + \varepsilon_7) + N_B\frac{N_H}{2}(\varepsilon_6 + \varepsilon_8) + \left(\frac{N_H^2}{2}\right)\varepsilon_9\right] \qquad (8)$$

Introduction of the salt component fraction y_i, the molar water/salt ratio r and the mole number n_i instead of molecule numbers N_i yields eqn. (9), where E_i denotes molar

$$E = z\frac{n_A + n_B}{(r/2) + 1}\left(-y_A^2\Delta_{ex}E + y_A(E_3 + E_4 - 2E_2)\right.$$

$$+ y_A(r/2)(E_5 + E_7 - E_6 - E_8) \qquad (9)$$

$$\left. + (r/2)(E_6 + E_8) + (r/2)^2 E_9 + E_2\right)$$

energies and $\Delta_{ex}E$ can be identified with the energy change of a metathetical reaction (I). According to eqn. (9), the total energies of pure water $E_H°$ and the salts at infinite dilution, E_{AX}^∞ and E_{BY}^∞, are given by eqns. (10)–(12).

$$E_H° = z (r/2) (n_A + n_B) E_9 \qquad (10)$$

$$E_{AX}^\infty = z(n_A+n_B)y_A(E_5+E_7) \qquad (11)$$

Table 7. Ion–ion and ion–water interactions considered within a quasi-lattice model.

Type of interaction	No. of pairs at random distribution [a]	Specific interaction energy
A–X	$N_AN_X{}^*z / \Sigma = N_1{}^*$	ε_1
B–Y	$N_BN_Y{}^*z / \Sigma = N_2{}^*$	ε_2
A–Y	$N_AN_Y{}^*z / \Sigma = N_3{}^*$	ε_3
B–X	$N_BN_X{}^*z / \Sigma = N_4{}^*$	ε_4
A–H_2O	$\frac{1}{2}N_AN_H{}^*z / \Sigma = N_5{}^*$	ε_5
B–H_2O	$\frac{1}{2}N_BN_H{}^*z / \Sigma = N_6{}^*$	ε_6
X–H_2O	$\frac{1}{2}N_YN_H{}^*z / \Sigma = N_7{}^*$	ε_7
Y–H_2O	$\frac{1}{2}N_XN_H{}^*z / \Sigma = N_8{}^*$	ε_8
H_2O–H_2O	$\frac{1}{4}N_HN_H{}^*z / \Sigma = N_9{}^*$	ε_9

Total number of pairs $\Sigma = (N_H/2) + N_A + N_B$

Total energy $e = \sum_{i=1}^{9} N_i\varepsilon_i$

[a] Subscript H denotes H_2O.

$$E_{BY}^{\infty} = z\,(n_A + n_B)\,(1 - y_A)\,(E_6 + E_8) \tag{12}$$

The excess energy of the solution is defined by eqn. (13).

$$E^E = E - n_H E_H^{\,\circ} - n_A E_{AX}^{\infty} - n_B E_{BY}^{\infty} \tag{13}$$

Inserting eqns. (9)–(12) into eqn. (13) gives eqn. (14).

$$E^E = z\,\frac{n_A + n_B}{(r/2)+1}\left[- y_A^{\,2}\Delta_{ex}E \right.$$

$$+ y_A\,(E_3 + E_4 + E_6 + E_8 - 2E_2 - E_5 - E_7) \tag{14}$$

$$\left. - (r/2)E_9 + E_2 - E_6 - E_8 \right]$$

The energy parameters in parentheses in eqn. (14) can be substituted by energy changes due to lattice reactions for ion recombination, reaction (I), and hydration, reactions (II) and (III).

$$AX + H_2O\text{–}H_2O \rightarrow A(H_2O) + X(H_2O) \quad \Delta E_{AX}^{\,H} \tag{II}$$

$$BY + H_2O\text{–}H_2O \rightarrow B(H_2O) + Y(H_2O) \quad \Delta E_{BY}^{\,H} \tag{III}$$
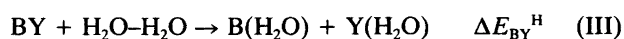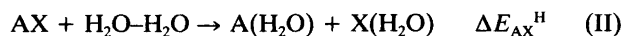
Then the expression in parentheses is given by eqn. (15),

$$(E_3 + E_4 + E_6 + E_8 - 2E_2 - E_5 - E_7) =$$

$$-\Delta_{ex}E + (\Delta E_{AX}^{\,H} - \Delta E_{BY}^{\,H}) \tag{15}$$

setting $G_i = E_i$, which means that neglecting the excess entropy and volume changes, the right-hand side of eqn. (15) corresponds to the empirical term for predictions of activity coefficient variations introduced earlier.[1]

From the partial derivative of eqn. (14) with respect to water, using the usual thermodynamic relations and taking $G_i = E_i$, eqn. (16) is obtained for the osmotic coefficients.

$$RT\varphi = \frac{zm}{1 + (2m^2 M_H/1000)}\left(-y_A^2\Delta_{ex}G^{\circ} + y_A\,(-\Delta_{ex}G^{\circ}\right.$$

$$+ \Delta G_{AX}^{\,H} - \Delta G_{BY}^{\,H}) + E_2 - E_6 - E_8 + \frac{E_9}{(1000/M_H)^2}\Bigg)$$

$$- \frac{1000RT}{2mM_H}\ln\frac{(500/M_H)}{(500/M_H) + m} \tag{16}$$

Applying eqn. (16) to φ_m, φ_A°, φ_B° and introducing these expressions into the definition equation of $\Delta\varphi$ [eqn. (6)], yields the final relation [eqn. (17)], in which all but one of

$$\Delta\Phi = \frac{zm}{1 + (2m^2 M_H/1000)} \tag{17}$$

the energy parameters have disappeared. This formula pre-

dicts values of $\Delta\varphi$ for mixed solutions of the two corresponding reciprocal pairs, which are equal in magnitude and opposite in sign. This is confirmed by our results of the chloride–bromide mixtures, although formula (17) is not fulfilled quantitatively. The $\Delta\varphi$ values of stable pairs seem to be too small, and in mixed solutions of either LiCl–KBr or LiCl–CsBr they are even negative. This reflects the deviation of the solution structure from the simplifying presumption of random distribution introduced into the model. One important reason for such deivations is due to different hydration affinities of the cations. These differences are largest for the cation pair Li^+–Cs^+.

Considering the results of the nitrate-containing mixtures (Figs. 4 and 5), a contradiction to the expectations from formula (17) becomes evident. For almost all nitrate mixtures the $\Delta\varphi$ curves start with an opposite order: $\Delta\varphi$(unstable pair) > $\Delta\varphi$(stable pair). However, at high molalities in all systems a crossing-over occurs towards the predicted order in $\Delta\varphi$. Only two systems ($Na^+,K^+/Cl^-,NO_3^-/H_2O$ and $K^+,Cs^+/Br^-,NO_3^-/H_2O$) do not follow this pattern. However, the $\Delta_{ex}G^{\circ}$ values of 2.9 and 1.9 kJ mol^{-1}, respectively, are near the limit of uncertainty, so that a correlation with $\Delta_{ex}G^{\circ}$ cannot be expected.[1]

Unfortunately, the molality of the crossing point is often as high as the maximum concentration we could investigate at a temperature of 100 °C, because of limited solubility. Thus for these systems measurements in the range of hydrated melts, where a molten salt-like lattice model represents a more natural basis, should be of particular interest.

The difference in behaviour of the nitrate mixtures, compared with the chloride–bromide mixtures, is obviously a consequence of ion-pair formation between NO_3^- and the alkali-metal cations, which is known from spectroscopic investigations[12,13] and has not been considered in our model.

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