Thermodynamics of Aqueous Reciprocal Salt Systems. V. Isopiestic Determination of Osmotic and Activity Coefficients of the System Mg^{2+}, K^+/Cl^-, Br^- // H_2O at 100.3 °C

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Isopiestic measurements have been performed for mixed aqueous solutions of the two reciprocal salt pairs $MgCl_2-KBr$ and $MgBr_2-KCl$ and for all common ion subsystems of the reciprocal system Mg^{2+}, K^+/Cl^-, Br^- // H_2O at 100.3 °C. As reference solution $CaCl_{2(aq)}$ was used. From the experimentally determined isopiestic ratios the deviation of the osmotic coefficients from additivity at constant total ionic strength has been evaluated. By applying the ion-interaction approach (Pitzer's equation), activity coefficients of the salt components were calculated for mixed solutions of the reciprocal salt pairs. Both the deviation of the osmotic coefficients from additivity and the variation of the salt activity coefficients, $\gamma_\pm$, are discussed in relation to the Gibbs energy of the corresponding metathetical reaction between the reciprocal salt pairs.

Recently it was shown that the concentration dependence of the salt activity coefficients of an aqueous reciprocal salt system is related to the Gibbs energy of the corresponding metathetical reaction.[1-3] Moreover, the deviation of the osmotic coefficients from additivity seems to bear a close relation to the Gibbs energy of the exchange reaction.[3]

The recently published results concern aqueous reciprocal salt systems consisting of I–I electrolytes.[2,3] It is the aim of this contribution to investigate a reciprocal system which contains electrolytes of the II–I charge type. For the system Mg^{2+}, K^+/Cl^-, Br^- // H_2O, including all common ion subsystems, osmotic and salt activity coefficients 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.[4,5]

Mixed solutions were prepared from stock solutions of the pure salt components. The same stock solutions were used as in the previous investigation.[5]

Results and discussion

Osmotic coefficients. The experimentally determined osmotic molalities are summarized in Tables 1–5: while Tables

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1–3 contain the results of the common ion subsystems, the isopiestic molalities of the two reciprocal systems are given in Tables 4 and 5. The third column of each table contains the molality of the reference solution ($CaCl_{2(aq)}$), which is an average of triplicate samples. No results were accepted unless triplicates agreed within 0.1 % in molality. In general the agreement was better than ±0.03 %. In the second column water activities are given, calculated by using the compilation established by Ananthaswamy and Atkinson.[6] Osmotic coefficients were calculated by applying eqn. (1),

$$\varphi_{MX} = 3\varphi_{CaCl_2} m_{CaCl_2} / (\Sigma\, \nu_{MX} m_{MX}) \tag{1}$$

where m is the molality and ν_{MX} is the number of ions of the electrolyte MX.

The isopiestic molalities of the mixed solutions have been determined at different ionic strength fractions y_B. For a mixture of the system Salt 1 (A) – Salt 2 (B) – H_2O y_B is defined by eqn. (2), in which I is given by eqn. (3), where

$$y_B = I_B / (I_A + I_B) \tag{2}$$

$$I = \frac{1}{2} \sum_i m_i\, z_i^2 \tag{3}$$

z_i is the charge number of the ion i.

Osmotic coefficients as a function of the ionic strength fraction at two different constant total ionic strengths ($I = 4$ mol kg^{-1} H_2O and $I = 8$ mol kg^{-1} H_2O) were evaluated by interpolating the experimentally determined osmotic coef-

Table 1. Isopiestic molalities (in mol kg^{-1} H$_2$O) of the system MgCl$_2$–KCl–H$_2$O at 100.3 °C.

Run	a_w	CaCl$_2$	y_{KCl}							
			0.57985	0.43739	0.37696	0.22649	0.18669	0.14423	0.12425	0.03391
10.1	0.70240	3.7742	$-^a$	6.3459	5.9861	5.0377	4.7796	4.4954	4.3593	3.7422
10.2	0.72614	3.5470	6.5781	5.8799	5.5626	4.7095	4.4788	4.2187	4.0969	3.5302
10.3	0.75445	3.2738	5.9389	5.3399	5.0637	4.3200	4.1165	3.8859	3.7772	3.2711
10.4	0.76714	3.1500	5.6519	5.0943	4.8371	4.1423	3.9508	3.7348	3.5956	3.1325
10.5	0.80588	2.7627	4.7867	–	4.1477	3.5908	3.4352	3.2597	3.1755	2.7766
10.6	0.80896	2.7312	4.7164	4.2922	4.0925	3.5458	3.3930	3.2211	3.1386	2.7453
10.7	0.82691	2.5442	4.3191	3.9439	–	3.2842	3.1470	2.9923	2.9187	2.5627
11.1	0.84249	2.3773	3.9764	3.6421	–	3.0534	2.9294	2.7891	2.7207	2.3975
10.8	0.84352	2.3660	3.9453	3.6171	3.4751	3.0336	2.9120	2.7740	2.7072	2.3865
11.2	0.85391	2.2515	3.7171	3.4146	3.2866	2.8772	2.7643	2.6348	2.5720	2.2731
11.4	0.86015	2.1813	3.5716	3.2864	3.1527	2.7775	2.6693	2.5478	2.4877	2.2029
11.5	0.88396	1.9030	3.0255	2.8014	2.6955	2.3960	2.3091	2.2101	2.1609	1.9256
11.3	0.89304	1.7915	2.8153	2.6136	2.5182	2.2458	2.1662	2.0756	2.0310	1.8148
11.7	0.92006	1.4373	2.1638	2.0255	1.9602	1.7692	1.7126	1.6488	1.6158	1.4582
11.6	0.92278	1.3992	2.0957	1.9637	1.8999	1.7179	1.6637	1.6023	1.5710	1.4190

^{a}KCl saturation.

Table 2. Isopiestic molalities (in mol kg^{-1} H$_2$O) of the system MgBr$_2$–KBr–H$_2$O at 100.3 °C.

Run	a_w	CaCl$_2$	y_{KBr}							
			0.76708	0.62894	0.42832	0.33389	0.28975	0.20456	0.14387	0.09267	0.04689
51.2	0.61041	4.6681	$-^a$	$-^a$	$-^a$	$-^a$	6.1923	5.4922	4.9915	4.5716	4.2002
51.1	0.66520	4.1307	$-^a$	$-^a$	6.3897	5.7512	5.4451	4.8622	4.4424	4.0848	3.7670
50.1	0.67372	4.0487	$-^a$	7.4885	–	5.6177	5.3298	4.7659	4.3596	4.0098	3.6974
50.2	0.70385	3.7602	7.5063	6.8087	–	5.1795	4.9217	4.4157	4.0502	3.7359	3.4530
50.3	0.76651	3.1562	5.9261	5.4446	4.6609	4.2528	4.0589	–	3.3931	3.1446	2.9212
51.3	0.79599	2.8632	5.2223	4.8114	4.1524	3.8137	3.6477	3.3166	3.0711	2.8555	2.6591
50.4	0.84553	2.3441	4.0354	3.7606	3.3018	3.0531	2.9322	2.6908	2.5036	2.3399	2.1892
51.4	0.87754	1.9799	–	3.0627	2.7183	2.5321	2.4399	2.2502	2.1057	1.9768	1.8571
50.5	0.88662	1.8707	3.0433	2.8628	2.5515	2.3794	2.2941	2.1226	1.9887	1.8686	1.7571
51.5	0.91674	1.4828	2.3004	2.1739	1.9626	1.8456	1.7856	1.6636	1.5689	1.4829	1.4013

^{a}KBr saturation.

Table 3. Isopiestic molalities (in mol kg^{-1} H$_2$O) of the systems MgCl$_2$–MgBr$_2$–H$_2$O and KCl–KBr–H$_2$O at 100.3 °C.

Run	a_w	CaCl$_2$	MgCl$_2$–MgBr$_2$–H$_2$O: y_{MgBr_2}					KCl–KBr–H$_2$O: y_{KBr}			
			0.8191	0.68011	0.52592	0.34725	0.14175	0.81717	0.66575	0.46116	0.26728
60.4	0.55584	5.2378	4.2506	–	4.3497	4.4122	4.4829	–	–	–	–
60.3	0.60994	4.6729	3.8734	3.9159	3.9633	4.0200	4.0851	–	–	–	–
60.2	0.67735	4.0139	3.3962	3.4321	3.4730	3.5234	3.5812	–	–	–	–
60.1	0.70621	3.7377	3.1844	3.2186	3.2572	3.3027	3.3579	8.5850	8.6451	8.7521	$-^a$
61.1	0.73740	3.4388	2.9520	2.9816	3.0178	–	3.1112	7.6049	7.6573	7.7340	7.8047
61.4	0.80184	2.8039	2.4372	2.4610	2.4908	2.5265	2.5681	5.6992	5.7375	5.7985	5.8461
61.3	0.82007	2.6161	2.2823	2.3052	2.3323	2.3653	2.4040	5.1889	5.2234	5.2751	5.3159
61.2	0.84592	2.3397	2.0537	2.0738	2.0981	2.1270	2.1617	4.4718	4.4995	4.5393	4.5752
60.5	0.84659	2.3324	2.0446	2.0721	2.0914	2.1210	2.1560	4.4724	4.4921	4.5311	4.5690
60.6	0.87833	1.9706	–	1.7636	1.7801	–	–	3.5783	3.5986	3.6280	3.6530
61.5	0.89485	1.7690	1.5718	1.5872	1.6046	1.6265	1.6513	3.1028	3.1198	3.1518	3.1738
61.6	0.94068	1.1361	1.0299	1.0383	1.0484	1.0608	1.0747	1.7984	1.8074	1.8199	1.8359

^{a}Saturation.

Table 4. Isopiestic molalities (in mol kg^{-1} H$_2$O) of the system MgCl$_2$-KBr-H$_2$O at 100.3 °C.

Run	a_w	CaCl$_2$	y_{KBr}								
			0.78104	0.59310	0.43331	0.34615	0.25064	0.18226	0.11614	0.09202	0.04506
30.1	0.66952	4.0890	$-^a$	7.4992	6.5639	6.0289	5.4167	4.9611	4.5157	4.3481	4.0220
31.2	0.67357	4.0502	$-^a$	7.4055	6.4882	5.9578	5.3598	4.9126	4.4726	4.3092	3.9855
31.1	0.68584	3.9325	8.0884	7.1338	6.2659	5.7658	5.1937	4.7665	4.3467	4.1887	3.8772
31.3	0.69869	3.8096	7.7473	6.8556	6.0333	5.5594	5.0199	4.6135	–	4.0625	3.7645
31.4	0.71418	3.6615	7.3280	6.5111	5.7500	5.3109	4.8038	4.4272	4.0532	3.9076	3.6262
30.3	0.74749	3.3414	6.4899	5.7999	5.1592	4.7889	4.3548	4.0248	3.6962	3.5720	3.3257
30.2	0.77533	3.0694	5.7922	5.2169	4.6687	4.3491	3.9697	3.6821	3.3924	3.2828	3.0640
31.5	0.79502	2.8730	5.3038	4.7994	4.3162	4.0303	3.6915	3.4339	3.1746	3.0725	2.8726
31.6	0.83717	2.4348	4.2823	3.9152	3.5565	3.3407	3.0830	2.8842	2.6817	2.6018	2.4436
32.1	0.86524	2.1234	3.5968	3.3140	3.0325	2.8595	2.6543	2.4933	2.3270	2.2635	2.1307
32.2	0.87134	2.0528	3.4461	3.1805	2.9162	2.7533	2.5570	2.4054	2.2474	2.1869	2.0608
32.3	0.92211	1.4086	2.1772	2.0403	1.9007	1.8116	1.7050	1.6191	1.5291	1.4941	1.4197
32.4	0.93595	1.2081	1.8167	1.7111	1.6022	1.5319	1.4479	1.3796	1.3075	1.2794	1.2191
32.5	0.95742	0.8639	1.2361	1.1742	1.1095	1.0670	1.0163	0.9739	0.9291	0.9117	0.8734

^{a}KBr saturation.

Table 5. Isopiestic molalities (in mol kg^{-1} H$_2$O) of the system MgBr$_2$-KCl-H$_2$O at 100.3 °C.

Run	a_w	CaCl$_2$	y_{KCl}								
			0.72531	0.56586	0.47682	0.33158	0.24729	0.18748	0.11051	0.10230	0.04171
40.1	0.71604	3.6437	7.3923	6.5575	6.0543	5.1713	4.6497	4.2670	3.7764	3.7251	–
41.1	0.73113	3.4990	6.9830	6.2039	5.7528	4.9377	4.4455	4.0884	3.6269	3.5780	3.2113
40.2	0.74150	3.3992	6.7196	5.9945	5.5554	4.7751	4.3097	3.9658	3.5250	3.4791	3.1234
40.3	0.74725	3.3438	6.5692	5.8755	5.4472	4.6864	4.2327	3.9009	3.4680	3.4235	3.0748
41.2	0.81656	2.6527	4.8489	4.3925	4.1198	3.6109	3.2948	3.0614	2.7483	2.7162	2.4617
40.4	0.83235	2.4865	4.4553	4.0603	3.8098	3.3565	3.0725	2.8585	2.5752	2.5440	2.3105
40.5	0.87806	1.9738	3.3255	3.0672	2.9023	2.5938	2.3938	2.2428	2.0399	2.0181	1.8453
40.6	0.90884	1.5890	2.5471	2.3709	2.2580	2.0408	1.8986	1.7897	1.6408	1.6250	1.4953
41.3	0.90892	1.5880	2.5475	2.3674	2.2563	2.0413	1.8988	1.7894	1.6397	1.6231	1.4948
40.7	0.92983	1.2986	1.9999	1.8755	1.7946	1.6384	1.5331	1.4522	1.3397	1.3276	1.2291
41.4	0.93375	1.2409	1.8963	1.7796	1.7046	1.5585	1.4619	1.3864	1.2801	1.2685	1.1761
41.5	0.94450	1.0765	1.6043	1.5122	1.4533	1.3372	1.2587	1.1973	1.1108	1.1012	1.0250
41.7	0.95981	0.8225	1.1783	1.1182	1.0800	1.0031	–	0.9086	0.8492	0.8425	0.7892
41.6	0.96097	0.8020	1.1482	1.0861	1.0495	0.9759	–	0.8855	0.8271	0.8209	0.7693

ficients. For that purpose the experimental data were fitted to equations of the form of eqn. (4). The experimentally

$$\varphi(y = \text{const.}) = a_0 + a_1 I + a_2 I^2 + a_3 I^3 \tag{4}$$

determined osmotic coefficients scatter around these smooth curves with maximum deviations of 0.002 in φ. This is less than the estimated uncertainty of 0.2 % of the experimentally determined isopiestic molalities.

The deviation of the osmotic coefficients from additivity at constant total ionic strength is given by eqn. (5), where

$$\Delta\varphi = \varphi_{interp} - [(1 - y_B)\varphi°_A + y_B \varphi°_B]; \quad I = \text{const.} \tag{5}$$

φ_{interp} represents the interpolated osmotic coefficient of the mixed solution, and $\varphi°_A$ and $\varphi°_B$ are the osmotic coefficients of the pure binary solutions at the same ionic strength as the mixed solution. The osmotic coefficients $\varphi°_A$ and $\varphi°_B$ were calculated at $I = 4$ mol kg^{-1} H$_2$O and $I = 8$ mol kg^{-1} H$_2$O by using the extended ion-interaction approach and the parameters given in our previous publication.[5] For the pure KCl solution an extrapolation of the experimental results to $I = 8$ mol kg^{-1} was necessary because of the limited solubility of KCl, which is lower than 8 mol kg^{-1} H$_2$O at 100.3 °C.

The deviation of the osmotic coefficients from additivity for two different total ionic strengths is plotted against the ionic strength fraction for the common ion subsystems and the reciprocal systems in Fig. 1.

For the systems with common cation (in particular the potassium halide system) the deviations from additivity are very small (about one order of magnitude smaller than in the systems with a common anion). While for the magnesium halide system [Fig. 1(a)] the sign of the deviation
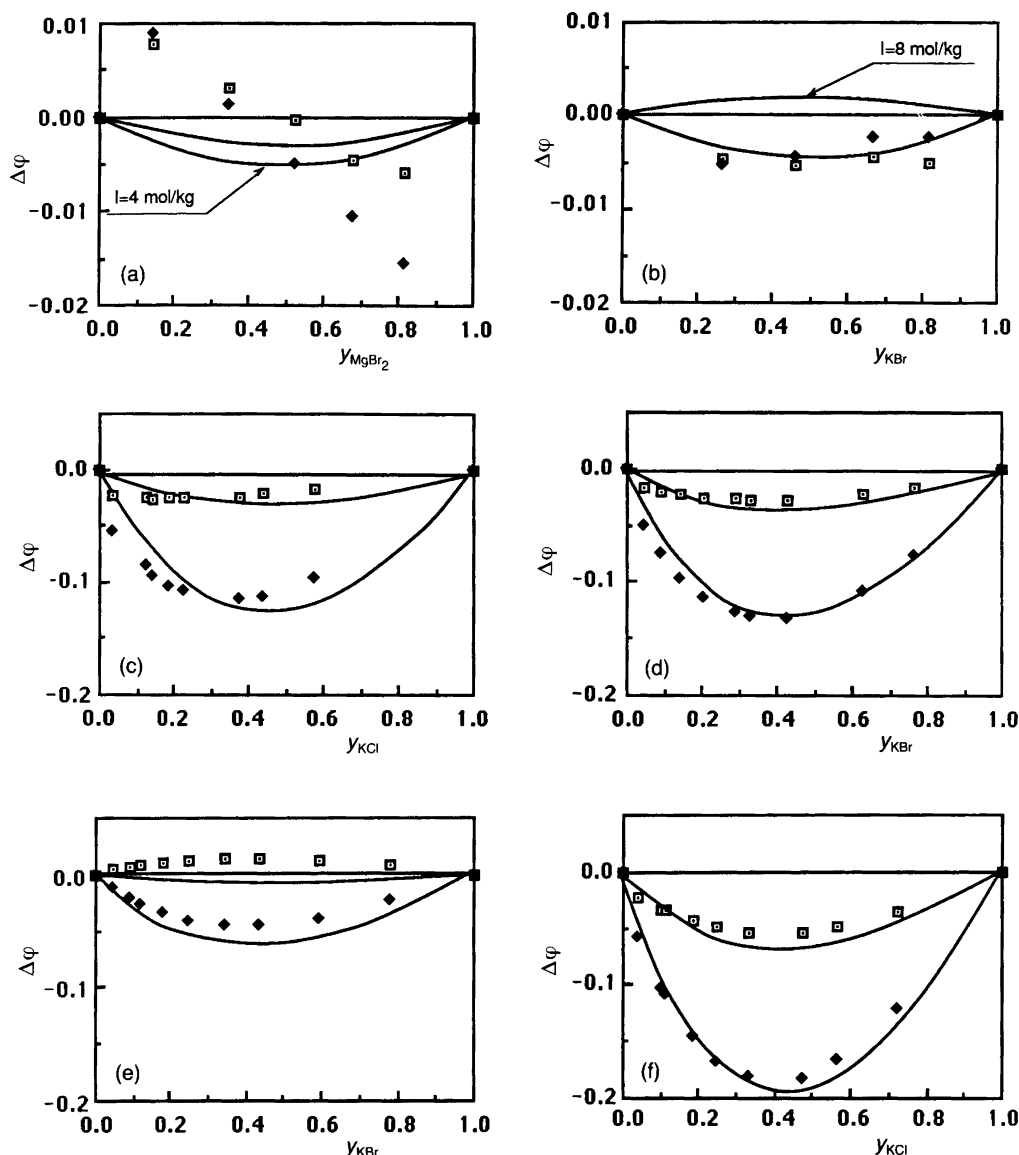
Fig. 1. Deviation of the osmotic coefficients from additivity according to eqn. (3) at 100.3 °C for the systems, (a) $MgCl_2-MgBr_2-H_2O$, (b) $KCl-KBr-H_2O$, (c) $MgCl_2-KCl-H_2O$, (d) $MgBr_2-KBr-H_2O$, (e) $MgCl_2-KBr-H_2O$ and (f) $MgBr_2-KCl-H_2O$. The points were evaluated by interpolating the experimentally determined osmotic coefficients, while the solid lines were calculated by using the ion-interaction approach [eqn. (4)]. □, $I = 4$ mol kg^{-1}; ◆, $I = 8$ mol kg^{-1}; (————) Pitzer's equation.

from additivity changes, the potassium halide system [Fig. 1(b)] shows negative deviations in φ over the whole range of the ionic strength fraction.

The systems with a common anion [Figs. 1(c) and (d)] show very similar mixing behaviour even when considering quantities. With increasing ionic strength the deviation from additivity becomes more negative in both systems. A minimum occurs around an ionic strength fraction y_{KX} of about 0.4. This ionic strength fraction represents a molar ratio of the salt components of 1:1.

The plots for the two reciprocal salt pairs [Figs. 1(e) and (f)] show a very interesting feature. According to the exchange reaction (I) $MgCl_2$ and KBr are the stable salt pair

$$MgCl_2 + 2KBr \rightarrow MgBr_2 + 2KCl$$
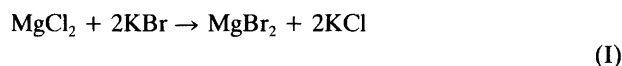
$$\Delta G_{ex}° = 31.03 \text{ kJ mol}^{-1} \text{ at } 25 °C$$

(I)

at 25 °C. The influence of the Gibbs energy of the exchange reaction on the deviation plots is demonstrated in the different behaviour of the two reciprocal systems. While for the unstable pair ($MgBr_2-KCl$) the deviation from additivity in the osmotic coefficients is increased compared to the systems with common anion, for the stable pair ($MgCl_2-KBr$) a compensation effect occurs. For this system the deviation of the osmotic coefficients from additivity is much smaller, and even becomes positive at low ionic

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strengths. It seems to be obvious that the contribution of the Gibbs energy of the exchange reaction to the excess Gibbs energy of mixing has an opposite sign for the two reciprocal salt pairs.

This behaviour of the reciprocal salt pairs with regard to $\Delta\varphi$ can be compared with former results of reciprocal salt systems consisting of 1-1 electrolytes. The opposite was found for the systems $LiNO_3-NaCl-H_2O$ and $LiCl-NaNO_3-H_2O$, respectively.[3] Mixed solutions of the stable pair ($LiNO_3-NaCl$) cause negative deviations, and vice versa the unstable pair cause positive deviations from additivity in φ.

For total ionic strengths up to $I = 8$ mol kg^{-1} H_2O the ion-interaction approach (Pitzer's equation) should be applicable. The general equations for osmotic and activity coefficients are defined below. The equations are identical with the form presented by Kim and Frederick[7] or by Harvie and Weare.[8]

$$\varphi - 1 = \frac{2}{\Sigma m_i} \left[\frac{-A^\varphi I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B^\varphi_{ca} + ZC_{ca}) \right.$$

$$+ \sum_{c<c'} \sum m_c m_{c'} \left(\Phi^\varphi_{cc'} + \sum_a m_a \psi_{cc'a} \right)$$

$$\left. + \sum_{a<a'} \sum m_a m_{a'} \left(\Phi^\varphi_{aa'} + \sum_c m_c \psi_{aa'c} \right) \right] \quad (6)$$

$$\ln \gamma_{MX} = |z_M z_X| F$$

$$+ \left(\frac{2\nu_M}{\nu} \right) \sum_a m_a \left[B_{Ma} + \frac{Z}{2} C_{Ma} + \left(\frac{\nu_X}{\nu_M} \right) \Phi_{Xa} \right]$$

$$+ \left(\frac{2\nu_X}{\nu} \right) \sum_c m_c \left[B_{cX} + \frac{Z}{2} C_{cX} + \left(\frac{\nu_M}{\nu_X} \right) \Phi_{Mc} \right]$$

$$+ \nu^{-1} \sum_c \sum_a m_c m_a [2\nu_M z_M C_{ca} + \nu_M \psi_{cMa} + \nu_X \psi_{acX}]$$

$$+ \sum_{c<c'} \sum m_c m_{c'} \left(\frac{\nu_X}{\nu} \right) \psi_{cc'X} + \sum_{a<a} \sum m_a m_{a'} \left(\frac{\nu_M}{\nu} \right) \psi_{aa'M} \quad (7)$$

where

$$F = -A^\varphi \left(\frac{I^{1/2}}{1 + b I^{1/2}} + \frac{2}{b} \ln (1 + b I^{1/2}) \right)$$

$$+ \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<c'} \sum m_c m_{c'} \Phi'_{cc'} + \sum_{a<a'} \sum m_a m_{a'} \Phi'_{aa'}$$

$$Z = \sum_i m_i |z_i|$$

$$I = \tfrac{1}{2} \sum_i m_i z_i^2$$

$$B_{MX}^\varphi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp (-\alpha I^{1/2})$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} f(\alpha I^{1/2})$$

$$B'_{MX} = \beta_{MX}^{(1)} f'(\alpha I^{1/2})/I$$

with

$$f(\chi) = 2[1 - (1 + \chi) \exp (-\chi)]/\chi^2$$

and

$$f'(\chi) = -2[1 - (1 + \chi + \tfrac{1}{2}\chi^2) \exp (-\chi)]/\chi^2$$

$$C_{MX} = C^\varphi_{MX}/2[|z_M z_X|]^{1/2}$$

A^φ is the Debye–Hückel coefficient for osmotic coefficients (0.4609 at 100.3 °C)[9] and $\alpha = 2$ and $b = 1.2$. The subscripts M, c and c' refer to cations having a charge number z_M corresponding to stoichiometric coefficients ν_M and X, a and a' to anions having a charge number z_X and stoichiometric coefficients ν_X, respectively.

The mixed electrolyte's second virial coefficients Φ_{ij} are defined by eqns. (8)–(10), where θ_{ij} is an adjustable

$$\Phi^\varphi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) + I\,{}^E\theta'_{ij}(I) \quad (8)$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (9)$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I) \quad (10)$$

parameter for each anion–anion and cation–cation pair. The third virial coefficients ψ_{ijk} are assumed to be independent of ionic strength. The higher-order electrostatic terms ${}^E\theta_{ij}(I)$ and ${}^E\theta'_{ij}(I)$ are given by eqns. (11) and (12),

$${}^E\theta_{MN}(I) = \frac{z_M z_N}{4I} \left(J0(X_{MN}) - \tfrac{1}{2}J0(X_{MM}) - \tfrac{1}{2}J0(X_{NN}) \right) \quad (11)$$

$${}^E\theta'_{MN}(I) = \frac{z_M z_N}{8I^2} \left(J1(X_{MN}) - \tfrac{1}{2}J1(X_{MM}) - \tfrac{1}{2}J1(X_{NN}) \right)$$

$$- \frac{{}^E\theta_{MN}}{I} \quad (12)$$

where $X_{MN} = 6 z_M z_N A^\varphi I^{1/2}$. If $z_M = z_N$ then ${}^E\theta_{MN}(I) = {}^E\theta'_{MN}(I) = 0$. The terms $J0(X)$ and $J1(X)$ were calculated using the expressions given by Pitzer.[10]

The binary parameters $\beta^{(0)}$, $\beta(1)$ and C^φ were evaluated from the isopiestic molalities presented in our previous publication,[5] and are given together with standard deviations in Table 6. Only experimental data up to the concentrations shown in Table 6 have been used to determine $\beta^{(0)}$, $\beta^{(1)}$ and C^φ. To evaluate the mixing parameters θ_{ij} and ψ_{ijk}

Table 6. Pitzer's coefficients and standard deviations σ_φ of the binary systems at 100.3 °C.

Parameter	System			
	MgCl$_2$–H$_2$O	MgBr$_2$–H$_2$O	KCl–H$_2$O	KBr–H$_2$O
$\beta^{(0)}$	0.327726	0.407698	0.0743736	0.0890834
$\beta^{(1)}$	2.231857	2.219082	0.299123	0.356430
$C^\varphi \times 10^3$	−1.10342	−3.20727	−3.71431	−4.72819
$\sigma^\varphi \times 10^3$	1.3	1.0	1.3	1.9
I_{max}	8.8	8.0	7.0	8.7

Table 7. Pitzer's mixing parameters of the system Mg^{2+}, K$^+$ / Cl$^-$, Br$^-$ // H$_2$O at 100.3 °C.

i	j	k	$\theta_{i,j}$	$\psi_{i,j,k}$
Mg	K	Cl	0	−0.0153±0.0004
Mg	K	Br		−0.0132±0.0005
Cl	Br	Mg	−0.0103±0.0048	0.0032±0.0023
Cl	Br	K		0.0014±0.0008

all data of the four common ion subsystems (Tables 1–3) with total ionic strengths $I \leq 8$ mol kg^{-1} H$_2$O were used for an overall fit. The parameters are given in Table 7. The parameter θ_{MgK} is not significant, and hence it was set equal to zero. The standard deviation σ^φ for the overall fit is 0.0088. This is about four times larger than the estimated uncertainty of the experimentally determined osmotic coefficients.

By application of eqn. (6) and the parameters given in Tables 6 and 7, $\Delta\varphi$ was calculated as a function of y for all systems with total ionic strengths $I = 4$ and $I = 8$ mol kg^{-1} H$_2$O. The results are plotted as solid lines in Fig. 1. In general the calculated and the experimental results agree reasonably well. The deviation between the calculated and the experimental results in both the common anion subsystems and the reciprocal systems does not differ significantly, although the solid lines for the two reciprocal salt pairs in Fig. 1 are real predictions. For the two common cation subsystems the deviation of the osmotic coefficients from additivity is of the same order of magnitude as the standard deviation for the overall fit. Hence the real behaviour of these two systems can not be reflected by the model equation.
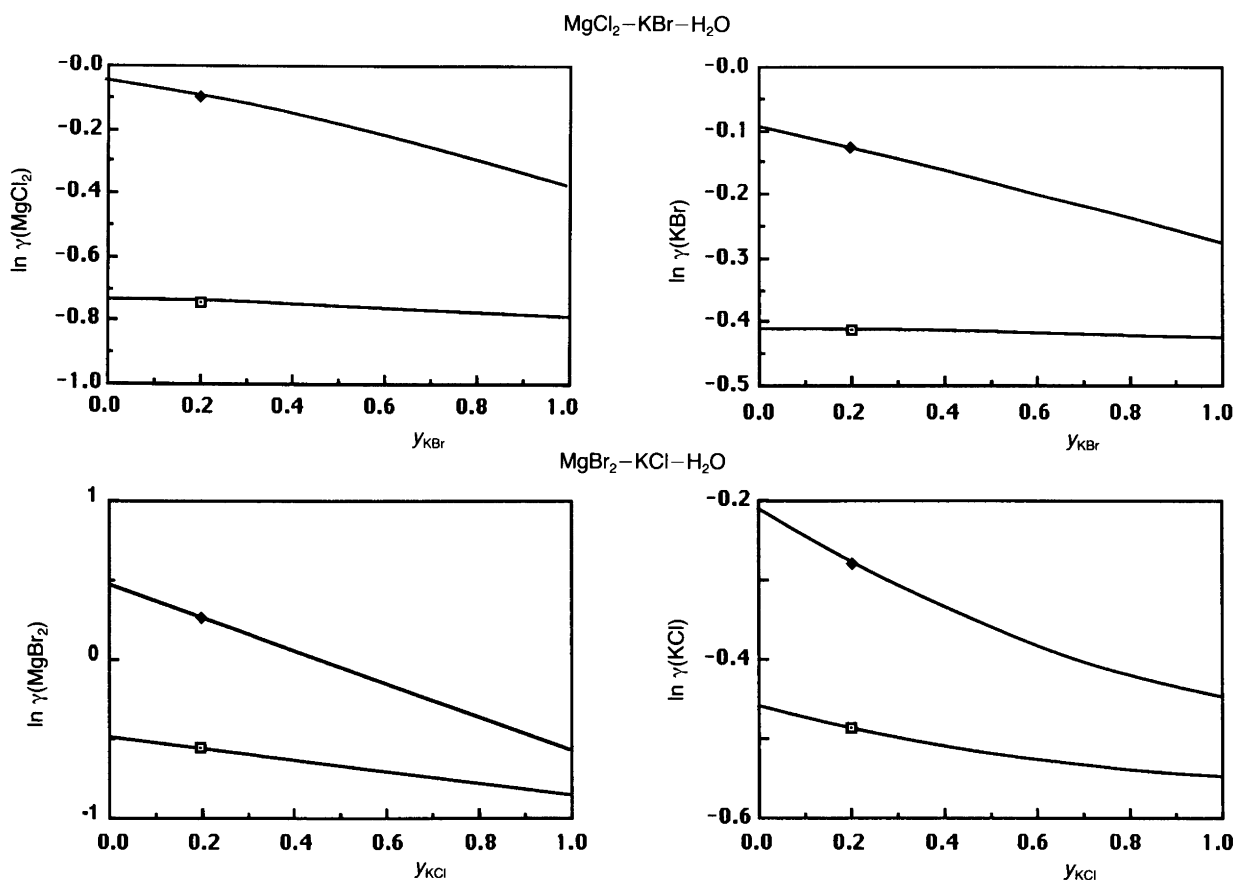

Fig. 2. Dependence of the mean molal salt activity coefficients In $\gamma_\pm$ on the ionic strength fraction in mixed solutions of the reciprocal salt pairs MgCl$_2$–KBr–H$_2$O and MgBr$_2$–KCl–H$_2$O at constant total ionic strength $I = 4$ and $I = 8$ mol kg^{-1} H$_2$O at 100.3 °C. The salt activity coefficients were calculated by using the ion-interaction approach [eqn. (5)]. Points are for identification of the curves only ($\square$, $I = 4$ mol kg^{-1}; $\blacklozenge$, $I = 8$ mol kg^{-1}).

Salt activity coefficients. The mean molal activity coefficients for each electrolyte in mixed solutions of the two reciprocal salt pairs have been calculated using eqn. (5). The results for two levels of constant total ionic strength ($I = 4$ and 8 mol kg^{-1} H$_2$O) are plotted in Fig. 2.

The pattern reflects the expected behaviour. The salt activity coefficients $\gamma_\pm$ decrease for the stronger hydrating salt and increase for the weaker hydrating salt if pure binary solutions of both salts with equal ionic strength are mixed.

The different sign of the slope for ln $\gamma_\pm = f(y)$ as given in Fig. 2 can be predicted by the empiricial rule for the variation of activity coefficients in such systems as discussed earlier.[1-3] According to this empirical rule the slope is governed by the change in the Gibbs energy of the exchange reaction $\Delta G°_{ex}$ [reaction (I)] and the difference in the standard Gibbs energy of solution of both salts. For the system Mg^{2+}, K$^+$/Cl$^-$, Br$^-$//H$_2$O the latter difference is up to five times larger than the value of the Gibbs energy of the exchange reaction. Hence the differences in hydration properties dominate the behaviour of the mixed solutions.

References

1. Grjotheim, K. and Voigt, W. *Acta Chem. Scand., Ser. A 40* (1986) 91.
2. Voigt, W., Dittrich, A., Haugsdal, B. and Grjotheim, K. *Acta Chem. Scand. 44* (1990) 12.
3. Voigt, W., Haugsdal, B. and Grjotheim, K. *Acta Chem. Scand. 44* (1990) 311.
4. Grjotheim, K., Voigt, W., Haugsdal, B. and Dittrich A. *Acta Chem. Scand., Ser. A 42* (1988) 470.
5. Fanghänel, T. and Grjotheim, K. *Acta Chem. Scand. 44* (1990). *In press.*
6. Ananthaswamy, J. and Atkinson, G. *J. Chem. Eng. Data 30* (1985) 120.
7. Kim, H.-T. and Frederick, W. J., Jr. *J. Chem. Eng. Data 33* (1988) 278.
8. Harvie, C. E. and Weare, J. H. *Geochim. Cosmochim. Acta 44* (1980) 981.
9. Ananthaswamy, J. and Atkinson, G. *J. Chem. Eng. Data 29* (1984) 81.
10. Pitzer, K. S. *J. Solution Chem. 4* (1975) 249.