Thermodynamics of Aqueous Reciprocal Salt Systems. III. Isopiestic Determination of Osmotic and Activity Coefficients of Aqueous $MgCl_2$, $MgBr_2$, KCl and KBr at 100.3 °C

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Osmotic coefficient of aqueous $MgCl_2$, $MgBr_2$, KCl and KBr were determined by means of isopiestic measurements at 100.3 °C. By applying the extended ion-interaction approach (Pitzer's equation) salt activity coefficients are calculated. The experimentally determined osmotic coefficients of aqueous $MgCl_2$, KCl and KBr are in reasonably good agreement with literature data. Osmotic coefficients for $MgBr_2$(aq) at temperatures higher than 25 °C have not been published in the literature before.

In an earlier publication the correlation between the thermodynamic behaviour of molten and aqueous reciprocal salt systems was discussed.[1] For aqueous reciprocal salt systems very few data are available at moderate and high concentrations. Recently osmotic coefficients of aqueous reciprocal salt pairs with I–I charge type electrolytes at 100.3 °C were published.[2,3] We wish to continue the systematic study of aqueous reciprocal salt pairs with the investigation of a system which contains electrolytes of the II–I charge type. For this goal the system Mg^{2+}, K^+/Cl^-, Br^-/H_2O was chosen. For internal consistency of the data set first osmotic coefficients and salt activity coefficients of the four binary sub-systems were determined by means of isopiestic measurements at 100.3 °C. In a succeeding paper the results of mixed electrolyte solutions of the above-mentioned reciprocal system will be discussed.

Experimental

Apparatus and procedure. A detailed description of the isopiestic method used and the accompanying experimental procedure was given in a previous publication.[4] In brief, 12 vitreous carbon cups with polished, mirror-like surfaces to their upper edges (to ensure they were tight) containing the solutions were used. The cups were placed in an aluminium block inside an aluminium container. Of the 12 cups three contained the reference solution [$CaCl_2$(aq)]. After isopiestic equilibrium was reached (48 h) the cups were closed under equilibrium conditions and the whole apparatus was cooled to room temperature. The cups were opened in a small chamber under reduced pressure to avoid splashing of the solution. Thereafter their weights were determined.

Substances. Stock solutions were prepared from: $CaCl_2$, calcium chloride-2-hydrate, p.a. (Merck, FRG); $MgCl_2$, magnesium chloride-6-hydrate, purum p.a. (Fluka AG, CH); $MgBr_2$, magnesium bromide-6-hydrate, purum p.a. (Fluka AG, CH);KCl, puriss. p.a. (Fluka AG, CH) and KBr, puriss. p.a. (Fluka AG, CH).

All salts were dissolved in de-ionized water. The final compositions of the $MgCl_2$ and $MgBr_2$ solutions were determined analytically by means of both complexometric titration of the Mg^{2+} with EDTA and argentometric titration of the halide. The mean values of both methods agreed within ±0.1 %. The water contents of the potassium halide and of the $CaCl_2$ stock solutions were determined by the drying of about 2 g of solution. Duplicate determinations agreed within 0.05 % or better.

Each solution was stored in a polyethylene bottle in an individual closed glass container. Several checks of the composition after some weeks showed that the changes were within the limits of accuracy.

Results and discussion

The system $CaCl_2$–H_2O has been chosen as reference system. The compilation established by Ananthaswarmy and Atkinson[5] was used to calculate the osmotic coefficients and water activities, respectively.

The experimental results are summarized in Table 1. Isopiestic molalities m as well as water activities a_w are presented. The isopiestic molalities have been corrected according to the amount of water in the vapour phase at equilibrium temperature and pressure and represent the mean values of at least two individual measuring points with a maximum deviation of ±0.05 % from the values given in Table 1. The last digit of the values in Table 1 is usually not significant. It is only given to avoid round-off

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Table 1. Isopiestic molalities and water activities of aqueous $MgCl_2$, $MgBr_2$, KCl and KBr.

Run	a_w	m_{CaCl_2}	m_{MgCl_2}	m_{MgBr_2}	m_{KCl}	m_{KBr}
20.6	0.34458	8.8690	6.3789	5.8292	–	–
20.5	0.37971	7.9254	6.0004	5.4890	–	–
21.4	0.62547	4.5164	4.0373	3.6900	–	–
21.3	0.67279	4.0576	3.6789	3.3615	–	–
21.2	0.69538	3.8412	3.5027	3.2003	–	–
21.1	0.69588	3.8365	3.4986	3.1964	–	8.8075
20.1	0.69776	3.8185	3.4816	3.1808	–	8.7466
20.2	0.76658	3.1555	2.9213	2.6693	6.9769	6.6589
20.4	0.82278	2.5878	2.4212	2.2136	5.2947	5.0688
20.3	0.84300	2.3717	2.2276	2.0386	4.7057	4.5117
22.1	0.87243	2.0401	1.9272	1.7663	3.8477	3.6935
22.2	0.89055	1.8225	1.7273	1.5859	3.3168	3.1904
22.3	0.91643	1.4872	1.4189	1.3088	2.5610	2.4724
22.4	0.93718	1.1896	1.1423	1.0585	1.9448	1.8855
22.5	0.95184	0.9580	0.92475	0.8617	1.5016	1.4610

errors. The isopiestic molalities are accurate to better than 0.2 %, based on the reproducibility of the isopiestic measurements and the accuracy of the analytical determinations.

Osmotic coefficients φ_{MX} were calculated by applying eqn. (1), in which m is the molality and ν_{MX} is the number of ions of the electrolyte MX.

$$\varphi_{MX} = 3\varphi_{CaCl_2} m_{CaCl_2} / \nu_{MX} m_{MX} \quad (1)$$

The standard deviation for the osmotic coefficients of the reference solution [$CaCl_2$(aq)] is 0.023, as given by Ananthaswarmy and Atkinson.[5]

To describe the experimental data an extension of the ion interaction approach was applied.[5] Equations for the concentration dependence of the osmotic coefficients φ and the salt activity coefficients γ can be formulated in terms of eqns. (2) and (3) for a I–I or I–II charge type electrolyte consisting of ν_M cations of charge z_M and ν_X anions of charge z_X.

$$\varphi - 1 = |z_M z_X| f^{\varphi} + [2(\nu_M \nu_X)/\nu] m B_{MX}^{\varphi} + [2(\nu_M \nu_X)^{3/2}/\nu] m^2 C_{MX}^{\varphi} + [2(\nu_M \nu_X)^2/\nu] m^3 D_{MX}^{\varphi} + [2(\nu_M \nu_X)^{5/2}/\nu] m^4 E_{MX}^{\varphi} + [2(\nu_M \nu_X)^3/\nu] m^5 F_{MX}^{\varphi} \quad (2)$$

$$\ln \gamma_{MX} = |z_M z_X| f^{\gamma} + [2(\nu_M \nu_X)/\nu] m B_{MX}^{\gamma} + [3(\nu_M \nu_X)^{3/2}/\nu] m^2 C_{MX}^{\varphi} + [8(\nu_M \nu_X)^2/3\nu] m^3 D_{MX}^{\varphi} + [10(\nu_M \nu_X)^{5/2}/4\nu] m^4 E_{MX}^{\varphi} + [12(\nu_M \nu_X)^3/5\nu] m^5 F_{MX}^{\varphi} \quad (3)$$

where:

$$f^{\varphi} = -A_{\varphi} I^{1/2}/(1+bI^{1/2}); I = \tfrac{1}{2} \sum_i m_i z_i^2$$

$$f^{\gamma} = -A_{\varphi}\{[I^{1/2}/(1+bI^{1/2})] + [2\ln(1+bI^{1/2})/b]\}$$

$$B_{MX}^{\varphi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-x)$$

$$B_{MX}^{\gamma} = 2\beta_{MX}^{(0)} + 2\beta_{MX}^{(1)}[1-(1+x-x^2/2)\exp(-x)]/x^2$$

$$x = \alpha I^{1/2},\ \alpha = 2.0,\ b = 1.2$$

A_{φ} is the Debye–Hückel parameter for osmotic coefficients given by Ananthaswamy and Atkinson,[6] m is the molality of the electrolyte and $\beta^{(0)}$, $\beta^{(1)}$, C^{φ}, D^{φ}, E^{φ} and F^{φ} are adjustable parameters.

The coefficients estimated by non-linear regression are listed in Table 2, together with standard deviations. For the magnesium halide systems the complete set of six parameters was necessary to describe the experimental results within the limits of accuracy, while for the potassium halide systems four parameters are sufficient.

In Fig. 1 the calculated and experimentally determined osmotic coefficients are compared for each of the four systems. The deviation of the experimentally determined osmotic coefficients from the curves fitted is less than 0.001. Only a very few points exceed this limit.

Salt activity coefficients were calculated by applying eqn.

Table 2. Parameters of eqn. (1) and standard deviations σ^{φ}.

Parameter	System			
	$MgCl_2$–H_2O	$MgBr_2$–H_2O	KCl–H_2O	KBr–H_2O
$\beta^{(0)}$	0.318 426	0.387 078	0.083 9617	0.097 7107
$\beta^{(1)}$	2.200 047	2.285 439	0.225 765	0.291 471
$C^{\varphi} \times 10^2$	1.357 22	2.223 87	−0.675 497	−0.749 366
$D^{\varphi} \times 10^3$	−7.015 17	−11.434	0.248 651	0.229 223
$E^{\varphi} \times 10^3$	1.274 66	2.099 20	0	0
$F^{\varphi} \times 10^5$	−7.314 78	−12.581 2	0	0
$\sigma^{\varphi} \times 10^3$	0.8	1.0	0.5	1.0

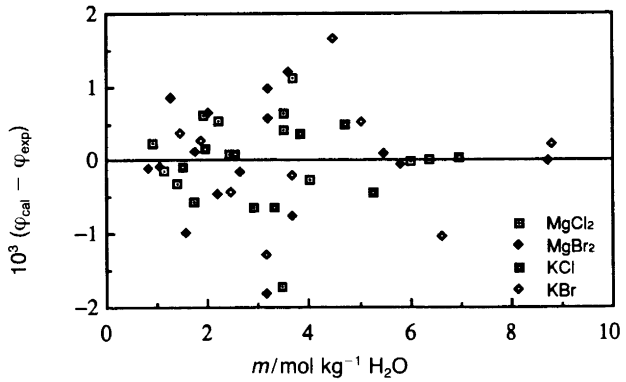

Fig. 1. Deviation plot of the experimental osmotic coefficients φ_{exp} from eqn. (1)

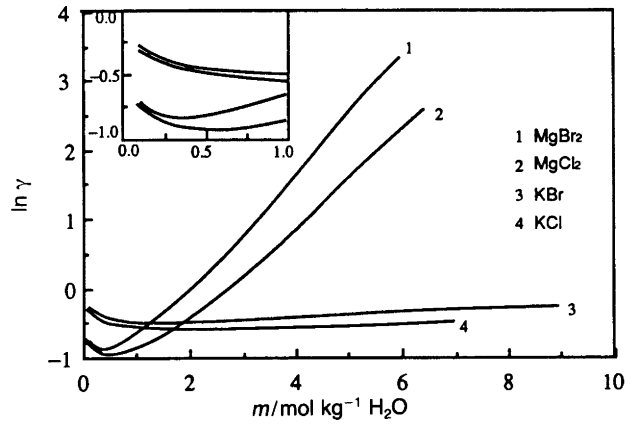

Fig. 2. Calculated salt activity coefficients ln γ for $MgBr_2$(aq), $MgCl_2$(aq), KBr(aq) and KCl(aq) at 100.3 °C. (Insert: enlargement of the concentration range between 0 and 1 mol kg^{-1} H_2O.)

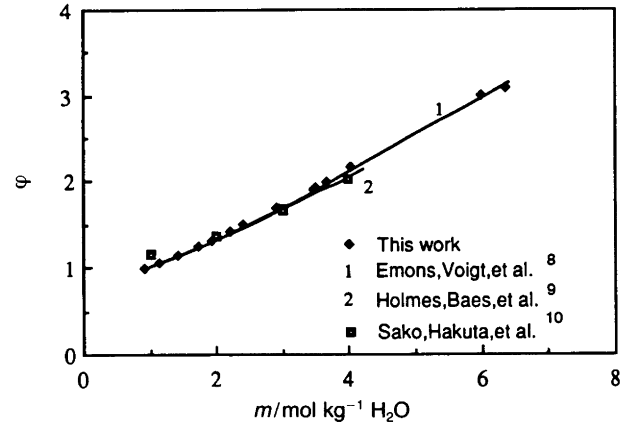

Fig. 3. Comparison of different data for osmotic coefficients of aqueous $MgCl_2$ at 100.3 °C.

(3) and the coefficients given in Table 2. In Fig. 2 ln γ vs. Molality is plotted for all four systems.

The comparison between experimentally determined osmotic coefficients for aqueous $MgCl_2$, KCl and KBr with

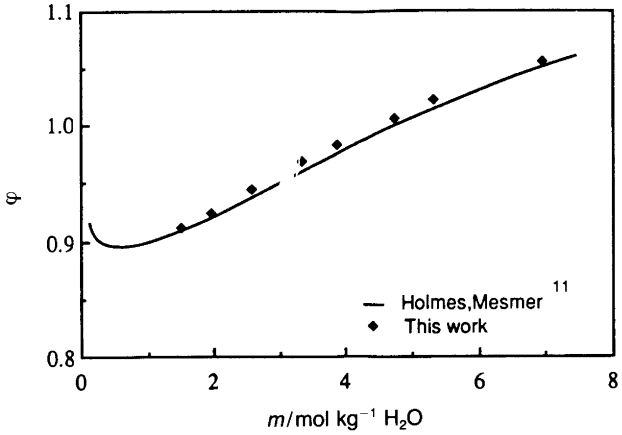

Fig. 4. Comparison of different data for osmotic coefficients of aqueous KCl at 100.3 °C.

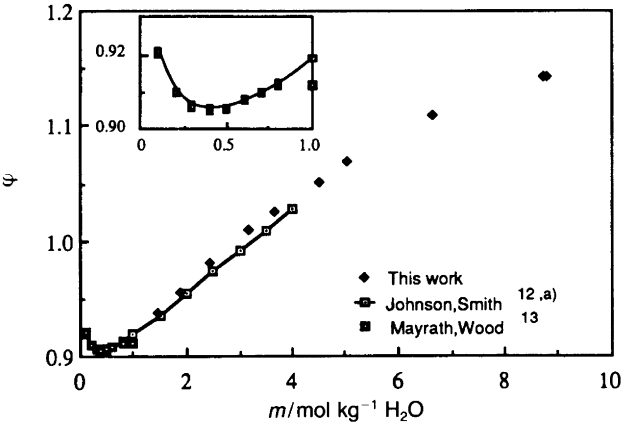

Fig. 5. Comparison of different data for osmotic coefficients of aqueous KBr at 100.3 °C. (Insert: enlargement of the concentration range between 0 and 1 mol kg^{-1} H_2O.) The symbol a) denotes data from Robinson and Stokes.[14]

literature data is shown in Figs. 3–5. Osmotic coefficients for $MgBr_2$(aq) are known at 25 °C only.[7]

Our osmotic coefficients for $MgCl_2$(aq) (Fig. 3) agree reasonably well with the fitted literature data given by Emons *et al.*[8] We find systematically higher values (≈ 0.03 in φ). As already pointed out by Emons *et al.*[8] the osmotic coefficients determined by Holmes *et al.*[9] show relatively large deviations from almost all other literature data, in particular at high molalities. In addition, osmotic coefficients calculated from vapour pressure measurements of Sako *et al.*[10] are plotted in Fig. 3.

The agreement of our experimental results for aqueous KCl solution with the compilation established by Holmes and Mesmer[11] is good (Fig. 4). The mean deviation of the osmotic coefficients is about 0.007 (maximum deviation 0.01).

Experimental data for KBr(aq) are known in a limited concentration range only (up to 4 mol kg^{-1}). The mean deviation of the osmotic coefficients for aqueous KBr solution (Fig. 5) calculated from the measurement of the

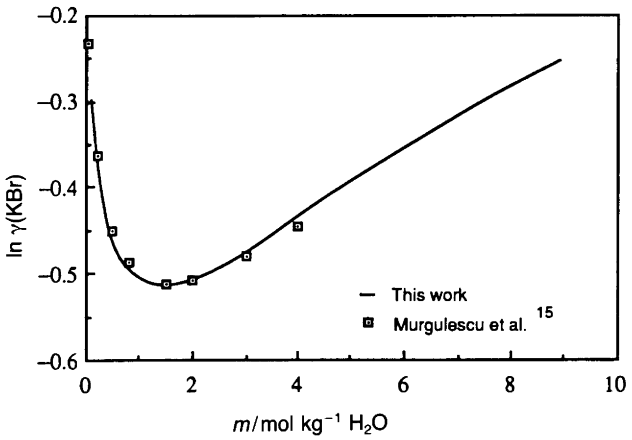

Fig. 6. Comparison of activity coefficients of aqueous KBr with the literature data by Murgulescu and Vilcu[15] at 100.3 °C.

boiling point evaluation by Johnson and Smith[12] from our data is about 0.005. In addition, osmotic coefficients published by Mayrath and Wood[13] from their measurements of the enthalpies of solution are plotted in Fig. 5.

Margulescu and Vilcu[15] have published activity coefficients for aqueous KBr calculated from their measurements of boiling point elevations. The excellent agreement of these data with our calculated activity coefficients within the limited concentration range is demonstrated in Fig. 6 (mean deviation in $\ln \gamma \approx 0.005$).

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