Thermodynamics of Mixed Electrolyte Solutions. IX. Calculation of the Osmotic and Activity Coefficients in a Pseudoternary System (NaCl–nKCl)–MgCl$_2$–H$_2$O at 298.15°K

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The equation of Reilly, Wood, and Robinson was used to predict the osmotic coefficient of a pseudoternary system (NaCl–nKCl)–MgCl$_2$–H$_2$O over a molal ionic strength range of 1.0 to 5.0 moles-kg^{-1}. The results are in close agreement with experimental data at most ionic strengths. The standard deviation in the osmotic coefficients over the entire concentration range lies within 0.0035. The predicted values of the mean activity coefficients are in good agreement with those obtained by the treatments of both Scatchard and Friedman. Mean activity coefficients for the other components were also predicted.

1. INTRODUCTION

There has been considerable progress recently in the calculation of the properties of aqueous solutions containing more than one salt,[1–6] namely, the prediction of excess Gibbs free energy of mixing and osmotic and mean activity coefficients. Such calculations require the values of the osmotic and mean activity coefficients of each salt in its own solution or in each binary common ion mixture from which the interaction parameters of each pair of

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salts may be evaluated. These calculations will be applied to a pseudoternary system, $(NaCl + nKCl) + MgCl_2 + H_2O$, and the results compared with those obtained by standardized recalculations of the experimental data previously reported.[7]

2. TREATMENT OF EXPERIMENTAL DATA

It has been shown previously[8] that in a ternary system such as the $KCl + MgCl_2 + H_2O$ mixture the excess Gibbs free energy of mixing $\Delta G^{ex}(y, I)$ is given by

$$\Delta G^{ex}(y, I) = 2RT(I/I°) \int_0^I \Delta/\sqrt{I}\, d\sqrt{I} \tag{1}$$

where

$$\Delta = (1 + y_A)\phi(y, I) - 2y_A\phi(0, I) - y_B\phi(1, I) \tag{2}$$

and $\phi(y, I)$, $\phi(0, I)$, and $\phi(1, I)$ represent the osmotic coefficients of the mixed salts and the pure KCl (A) and pure $MgCl_2$ (B) solutions, respectively, at the same ionic strength I, and $I°$ is a standard value of ionic strength taken as 1 mole-kg^{-1}.

Assuming that the pseudosalt $(NaCl + nKCl)$ behaves as a single compound, the experimental results[7] expressed by Eq. (2) for Δ can be treated by two methods.[8]

1. The neutral-electrolyte treatment of mixed salt solutions by Scatchard[9-11] leads to the following expression for Δ:

$$\Delta = \beta_0 y_A y_B + \beta_1(y_A - y_B) \tag{3}$$

in which

$$\beta_0 = b_{01}(I/I°) + b_{02}(I/I°)^2 + b_{03}(I/I°)^3 \tag{4}$$

$$\beta_1 = b_{12}(I/I°)^2 + b_{13}(I/I°)^3 \tag{5}$$

The values of the Scatchard coefficient previously reported,[7] $b_{01} = 0.0879$, $b_{02} = -0.0299$, $b_{03} = 0.0031$, $b_{12} = 0.0006$, and $b_{13} = 0.0$, reproduced the observed osmotic coefficients within a standard deviation in ϕ of $\sigma = 0.0028$. It was of interest to see how well the results could be fitted by setting $\beta_1 = 0$. Using a more sophisticated least-squares method, all the experimental data could be fitted by adjusting only the terms in β_0. Only two parameters, $b_{01} = 0.05316$ and $b_{02} = -0.00813$, were found to be needed to best reproduce the experimental osmotic coefficients within a standard deviation in ϕ of $\sigma = 0.0031$. Since the former and latter σ values do not differ significantly, the b_{0j} parameters obtained in this paper will be used to recalculate the values of $\phi(S)$, which are compared with the experimental values in Table I. The first

Table I. Experimental and Calculated Values of the Osmotic Coefficients in the $(NaCl + nKCl) + MgCl_2 + H_2O$ System at 298.15°K

y_B	I, mole-kg^{-1}	$\phi_{(exp)}{}^a$	$\phi_{(S)}{}^b$	$\phi_{(F)}{}^c$	$\phi_{(W-R)}{}^d$
0.1393	0.639	0.909	0.906	0.907	0.907
0.4389	0.762	0.909	0.906	0.907	0.907
0.5994	0.847	0.911	0.907	0.907	0.908
0.8678	1.048	0.912	0.911	0.912	0.912
0.1393	0.996	0.912	0.912	0.913	0.913
0.4389	1.179	0.918	0.922	0.923	0.924
0.5994	1.296	0.931	0.930	0.931	0.932
0.7350	1.419	0.941	0.940	0.940	0.941
0.8678	1.576	0.947	0.953	0.953	0.954
0.1393	1.790	0.932	0.936	0.936	0.937
0.2856	1.916	0.945	0.950	0.950	0.951
0.5994	2.244	0.987	0.991	0.991	0.993
0.7350	2.422	1.013	1.016	1.016	1.018
0.8678	2.622	1.045	1.049	1.049	1.050
0.1393	1.863	0.942	0.939	0.939	0.940
0.2856	1.997	0.954	0.954	0.954	0.955
0.5994	2.329	1.001	0.997	0.996	0.999
0.7350	2.509	1.029	1.024	1.023	1.025
0.1393	2.392	0.962	0.960	0.960	0.960
0.2856	2.545	0.982	0.980	0.980	0.982
0.4389	2.722	1.008	1.006	1.006	1.008
0.7350	3.139	1.079	1.077	1.077	1.079
0.8678	3.357	1.127	1.124	1.123	1.125
0.3076	3.398	1.027	1.028	1.028	1.030
0.5094	3.677	1.078	1.079	1.079	1.081
0.6576	3.911	1.125	1.128	1.128	1.131
0.7880	4.117	1.184	1.181	1.181	1.183
0.8588	4.259	1.216	1.218	1.218	1.220
0.3076	3.582	1.037	1.038	1.038	1.040
0.5094	3.870	1.090	1.093	1.092	1.095
0.6576	4.097	1.143	1.144	1.144	1.147
0.7880	4.313	1.202	1.201	1.201	1.203
0.1359	3.484	1.013	1.008	1.008	1.009
0.5094	4.009	1.101	1.102	1.102	1.105
0.6576	4.238	1.157	1.156	1.156	1.159
0.7880	4.458	1.218	1.215	1.216	1.218
0.1359	3.961	1.026	1.030	1.030	1.031
0.3076	4.181	1.071	1.072	1.073	1.075
0.5094	4.473	1.136	1.136	1.136	1.139
0.6576	4.716	1.197	1.197	1.197	1.201

[a] Experimental data from ref. 7.
[b] Calculated from Eq. (3) with $b_{01} = 0.5316$ and $b_{02} = -0.00813$.
[c] Calculated from Eq. (6) with $A_2 = 0.07613$ and $A_3 = -0.02781$.
[d] Calculated from Eq. (7) using the parameters listed in Table II.

column gives the ionic-strength fraction of the magnesium chloride, $y_B = I_B/I = 3m_B/(m_A + m_B)$, where m_A is the molality of the pseudosalt $(NaCl \cdot nKCl)$ and m_B the molality of $MgCl_2$ in the mixed solution; the second column gives the total ionic strength, and the third column the experimental osmotic coefficient ϕ^{exp}; in the succeeding columns calculated values are presented.

2. The second method is concerned with the expression

$$\frac{\Delta}{y_A y_B} = \sum_{i=2}^{n} A_i (I/I^\circ)^{i/2} \tag{6}$$

which arises from the limiting behavior of the osmotic coefficient.[8,12] Here again only two coefficients, $A_2 = 0.07613$ and $A_3 = -0.02781$, were deemed to be sufficient to reproduce the experimental data within a standard deviation of 0.0031 in $\phi(F)$, as can be seen in Table I.

3. PREDICTION OF OSMOTIC COEFFICIENTS

Robinson and Wood have shown[4] that osmotic and mean activity coefficients in seawater and its concentrates may be calculated over a molal ionic strength range of 0.5 to 6.0 mole-kg^{-1} at 25°C. The results obtained for the osmotic coefficients agreed closely with experimental data at ionic strengths below 5 mole-kg^{-1}. The calculation of the osmotic coefficient ϕ depends upon Eq. (A-6) in ref. 3 and requires a knowledge of the osmotic coefficients of NaCl, KCl, and MgCl$_2$ in their own solutions[7,13] and of the Scatchard interaction parameters b_{ij} in the systems NaCl–KCl–H$_2$O,[14] NaCl–MgCl$_2$–H$_2$O,[15] and KCl–MgCl$_2$–H$_2$O,[8,16] which are listed in Table II. The values of the osmotic coefficients of the pure salts used at the required ionic strength were checked with the Lietzke and Stoughton interpolation formula.[17]

For the system NaCl–KCl–MgCl$_2$–H$_2$O Eq. (A-6) in ref. 3 becomes

$$\phi = \frac{2E^{Na}}{(m/m^\circ)} \phi(0, NaCl) + \frac{2E^K}{(m/m^\circ)} \phi(0, KCl) + \frac{3E^{Mg}}{2(m/m^\circ)} \phi(0, MgCl_2)$$

$$+ \frac{E^{Na}E^K}{(mI/m^\circ I^\circ)} \beta (Na\text{–}K) + \frac{3}{2} \frac{E^{Na}E^{Mg}}{(mI/m^\circ I^\circ)} \beta (Na\text{–}Mg)$$

$$+ \frac{3}{2} \frac{E^K E^{Mg}}{(mI/m^\circ I^\circ)} \beta (K\text{–}Mg) \tag{7}$$

where E^M is the equivalent fraction of the metal ion, $\phi(0, MX)$ is the osmotic coefficient of the pure MX salt solution at the molal ionic strength I, m is the molality, and β is the Scatchard interaction parameter in the mixture M_1M_2X.

Table II. Values of Scatchard Parameters b_{ij} at 298.15°K
in Ternary Systems

System	b_{01}	b_{02}	b_{03}
NaCl–KCl–H$_2$O	−0.02530	−0.00299	0.0
NaCl–MgCl$_2$–H$_2$O	0.06540	−0.00880	0.000637
KCl–MgCl$_2$–H$_2$O	0.05722	−0.01219	0.0

The calculated values of the osmotic coefficients $\phi_{(W-R)}$[3] are compared in Table I with the experimental data and those values obtained by the procedures of Scatchard and Friedman. The agreement between the predicted values $\phi_{(W-R)}$ of the osmotic coefficient and the observed values ϕ_{exp} is good, with the average difference in ϕ being 0.0020 over the whole concentration range and within a standard deviation of 0.0035.

4. PREDICTION OF ACTIVITY COEFFICIENTS

It has already been shown that the mean activity coefficient of MgCl$_2$ (B) in a ternary system is given by the expression[8]

$$\ln(\gamma_B/\gamma_B^\circ) = \Delta + (1 - y)[2\phi(0, I) - \phi(1, I) - 1] + (1 - y)^2(I/I^\circ)g_0 \quad (8)$$

where g_0 is Friedman's pair-interaction coefficient defined in Eq. (9):

$$\Delta G^{ex}(y, I) = RT(I/I^\circ)^2 y(1 - y)[g_0 + g_1(1 - 2y) + \cdots] \quad (9)$$

Since the g_1 contribution to the excess Gibbs free energy is negligible, it follows from Eq. (1) that

$$g = \frac{2 \cdot I^\circ}{y(1 - y)I} \int_0^I \frac{\Delta}{\sqrt{I}} d\sqrt{I} \quad (10)$$

which leads to the experimental evaluation of the activity coefficient

$$\ln(\gamma_B/\gamma_B^\circ) = \Delta + (1 - y)[2\phi(0, I) - \phi(1, I) - 1] + 2\frac{1 - y}{y} \int_0^I \frac{\Delta}{\sqrt{I}} d\sqrt{I} \quad (11)$$

since all the quantities appearing on the right side of Eq. (11) are experimental.

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[3] We are indebted to Prof. Wood, who provided us with a Fortran IV program for performing these calculations on our systems.

Table III.   Calculated and Experimental
Values of the Mean Activity Coefficients of
$MgCl_2$ in the Mixed Solutions

y_B	$I/mol\ kg^{-1}$	$\gamma_B(W-R)$ [a]	$\gamma_B(F)$ [b]	$\gamma_B(S)$ [c]	$\gamma_B(exp)$ [d]
0.1393	0.639	0.473	0.473	0.470	0.472
0.4389	0.762	0.470	0.469	0.467	0.469
0.5994	0.847	0.468	0.468	0.467	0.469
0.8678	1.048	0.468	0.468	0.468	0.468
0.1393	0.996	0.462	0.460	0.457	0.457
0.4389	1.179	0.465	0.463	0.461	0.458
0.5994	1.296	0.467	0.466	0.465	0.465
0.7350	1.419	0.471	0.470	0.470	0.470
0.8678	1.576	0.477	0.477	0.476	0.473
0.1393	1.790	0.479	0.475	0.471	0.468
0.2856	1.916	0.485	0.481	0.479	0.475
0.5994	2.244	0.505	0.501	0.501	0.498
0.7350	2.422	0.518	0.515	0.515	0.513
0.8678	2.622	0.534	0.532	0.533	0.530
0.1393	1.863	0.482	0.478	0.474	0.477
0.2856	1.997	0.489	0.485	0.482	0.482
0.5994	2.329	0.510	0.506	0.506	0.509
0.7350	2.509	0.524	0.521	0.520	0.524
0.1393	2.392	0.510	0.505	0.501	0.503
0.2856	2.545	0.521	0.515	0.513	0.514
0.4389	2.722	0.535	0.529	0.528	0.529
0.7350	3.139	0.573	0.569	0.569	0.570
0.8678	3.357	0.598	0.595	0.595	0.598
0.3076	3.398	0.590	0.581	0.578	0.577
0.5094	3.677	0.621	0.612	0.611	0.610
0.6576	3.911	0.650	0.642	0.642	0.639
0.7880	4.117	0.681	0.675	0.674	0.677
0.8588	4.259	0.703	0.699	0.698	0.697
0.3076	3.582	0.608	0.598	0.595	0.594
0.5094	3.870	0.641	0.631	0.630	0.628
0.6576	4.097	0.672	0.664	0.663	0.663
0.7880	4.313	0.706	0.700	0.699	0.701
0.1359	3.484	0.598	0.587	0.583	0.589
0.5094	4.009	0.657	0.647	0.645	0.644
0.6576	4.238	0.690	0.681	0.680	0.681
0.7880	4.458	0.726	0.719	0.719	0.721
0.1359	3.961	0.647	0.633	0.629	0.624
0.3076	4.181	0.673	0.659	0.657	0.655
0.5094	4.473	0.715	0.702	0.700	0.700
0.6576	4.716	0.756	0.744	0.743	0.743

[a] $\gamma_B(W-R)$, predicted by Reilly, Wood, and Robin-
son procedure using Eq. (14).

[b] $\gamma_B(F)$, calculated by Friedman method using param-
eters in Table II [Eq. (13)].

[c] $\gamma_B(S)$, calculated by Scatchard method using param-
eters in Table II [Eq. (12)].

[d] $\gamma_B(exp)$, experimental values [Eq. (11)].

Calculated values of the mean activity coefficient were obtained from

$$\ln(\gamma_B/\gamma_B^\circ) = (1 - y)[b_{01}(I/I^\circ) + b_{02}(I/I^\circ)^2 + 2\phi(0, I) - \phi(1, I) - 1]$$

$$- \frac{(1 - y)^2}{2} (I/I^\circ)^2 b_{02} \tag{12}$$

$$\ln(\gamma_B/\gamma_B^\circ) = (1 - y)[A_2(I/I^\circ) + A_3(I/I^\circ)^{3/2} + 2\phi(0, I) - \phi(1, I) - 1]$$

$$- \frac{(1 - y)^2}{3} (I/I^\circ)^{3/2} A_3 \tag{13}$$

Equations (12) and (13) are obtained when Δ and g_0 are expressed in terms of the fitted parameters b_{0j} and A_i, respectively. The values obtained may be compared with those calculated using the Reilly, Wood, and Robinson equation (A-9)[3] which for $MgCl_2$ reads as follows:

$$\ln(\gamma_B/\gamma_B^\circ) = \left[1 - \tfrac{3}{2}\frac{E^{Mg}}{I/I^\circ}\right][1 - \phi(0, MgCl_2)]$$

$$- \frac{2E^{Na}}{I/I^\circ}[1 - \phi(0, NaCl)] - \frac{2E^{K}}{I/I^\circ}[1 - \phi(0, KCl)]$$

$$+ E^{Na}\left\{g_0(Mg\text{–}Na) + E^{Mg}\frac{\partial}{\partial I}[g_0(Mg\text{–}Na)]\right\}$$

$$+ E^{K}\left\{g_0(Mg\text{–}K) + E^{Mg}\frac{\partial}{\partial I}[g_0(Mg\text{–}K)]\right\}$$

$$+ \tfrac{2}{3}E^{Na}E^{K}\frac{\partial}{\partial I}[g_0(Na\text{–}K)] \tag{14}$$

All the values are listed in Table III and seem to agree with each other within the experimental error.

Calculated values of the osmotic coefficient and mean activity coefficient of $MgCl_2$ and excess Gibbs free energy of mixing obtained according to the two methods of calculation are given in Tables IV and V, respectively. Predicted mean activity coefficients of all the components are presented in Table VI (Method of Reilly, Wood, and Robinson).

5. DISCUSSION

The various methods of calculating the mean activity coefficients of $MgCl_2$ in the system $NaCl + nKCl + MgCl_2 + H_2O$ are summarized in Table VII where the γ^{trace} activity coefficients are given over the molal ionic strength range 1 to 5 moles-kg^{-1}. The average deviations observed in γ^{trace} values are reasonable, and those given by the Reilly, Wood, and Robinson

Table IV. Calculated Values of Osmotic and Mean Activity Coefficients and Excess Gibbs Free Energy at 25°C (Friedman's Method)

I/mol kg^{-1}	y_B	ϕ(F)	$-\log\gamma_B$(F)	$\Delta G^E/RT$	I/mol kg^{-1}	y_B	ϕ(F)	$-\log\gamma_B$(F)	$\Delta G^E/RT$
1.0	0.0	0.910	0.338	0.0	3.0	0.0	0.970	0.262	0.0
	0.200	0.914	0.336	0.009		0.200	0.993	0.262	0.063
	0.400	0.915	0.335	0.014		0.400	1.018	0.261	0.095
	0.600	0.915	0.333	0.014		0.600	1.045	0.257	0.095
	0.800	0.911	0.330	0.009		0.800	1.075	0.252	0.063
	1.000	0.901	0.328	0.0		1.000	1.111	0.245	0.0
1.5	0.0	0.920	0.333	0.0	3.5	0.0	0.990	0.230	0.0
	0.200	0.929	0.332	0.019		0.200	1.018	0.230	0.081
	0.400	0.937	0.330	0.029		0.400	1.048	0.228	0.122
	0.600	0.943	0.328	0.029		0.600	1.083	0.224	0.122
	0.800	0.946	0.325	0.019		0.800	1.123	0.217	0.081
	1.000	0.947	0.322	0.0		1.000	1.173	0.209	0.0
2.0	0.0	0.935	0.316	0.0	4.0	0.0	1.011	0.195	0.0
	0.200	0.948	0.315	0.032		0.200	1.043	0.195	0.100
	0.400	0.961	0.313	0.048		0.400	1.080	0.193	0.150
	0.600	0.974	0.311	0.048		0.600	1.122	0.187	0.150
	0.800	0.986	0.307	0.032		0.800	1.173	0.180	0.100
	1.000	0.998	0.303	0.0		1.000	1.237	0.169	0.0
2.5	0.0	0.951	0.291	0.0	4.5	0.0	1.032	0.159	0.0
	0.200	0.970	0.291	0.047		0.200	1.069	0.158	0.119
	0.400	0.989	0.289	0.070		0.400	1.112	0.155	0.179
	0.600	1.008	0.287	0.070		0.600	1.162	0.148	0.179
	0.800	1.030	0.282	0.047		0.800	1.224	0.139	0.119
	1.000	1.053	0.277	0.0		1.000	1.304	0.126	0.0
					5.0	0.0	1.053	0.121	0.0
						0.200	1.095	0.120	0.139
						0.400	1.144	0.116	0.208
						0.600	1.203	0.107	0.208
						0.800	1.277	0.096	0.139
						1.000	1.374	0.080	0.0

method (RWR)[3] are systematically higher than the others at ionic strengths higher than 3 moles-kg^{-1}. This is to be expected since their treatment correctly accounts for all pairwise interactions only[3] but does not explicitly allow for the triplet-formation contribution which increases with increasing ionic strength. This is further illustrated by the values of g_0 in Table VII which decrease at increasing concentrations. The interactions between two ions which contribute to a charge asymmetric mixture with a common ion have been calculated by Friedman,[6] and it has been shown that in this kind of mixture all possible pairs contribute.

The quantity g_0 may be extrapolated below the experimental range using the expression[8]

$$g_0 = [0.456 \ln(I/I^\circ) - A_2 - \tfrac{2}{3}A_3(I/I^\circ)^{1/2}] \exp[-10(I/I^\circ)^2]$$
$$+ A_2 - \tfrac{2}{3}A_3(I/I^\circ)^{1/2} \tag{15}$$

obtained by a stochastic description of a two-structure model.[19] It obeys the higher limiting law which requires that as $I \to 0$, g_0 goes to $-\infty$ as $\ln(I/I^\circ)$. This agrees with Friedman's new derivation[20] of the higher limiting law in a mixture of electrolyte A (1, 1 charge type) with electrolyte B (1, 2 or 2, 1 charge type).

The values of g_0 and γ_B^{trace} of $MgCl_2$ in the mixture over the molal ionic strength of 0.1 to 1 mole-kg^{-1} are compared in Table VIII with those obtained previously[8] in the $KCl + MgCl_2 + H_2O$ system. As concentration decreases, the values tend to be identical as expected, and the effect of NaCl on γ_B^{trace} lessens with decreasing ionic strength. Values of γ_B^{trace} decrease slowly at low I, pointing to higher association in mixed solution than in pure $MgCl_2$ solutions.

Table V. Calculated Values of Osmotic and Mean Activity Coefficients and Excess Gibbs Free Energy at 25°C (Scatchard's Method)

I/mol kg^{-1}	y_B	$\phi(S)$	$-\log\gamma_B(S)$	$\Delta G^E/RT$	I/mol kg^{-1}	y_A	$\phi(S)$	$-\log\gamma_b(S)$	$\Delta G^E/RT$
1.0	0.0	0.910	0.341	0.0	3.0	0.0	0.970	0.266	0.0
	0.200	0.913	0.339	0.008		0.200	0.993	0.265	0.059
	0.400	0.915	0.336	0.012		0.400	1.018	0.262	0.088
	0.600	0.914	0.334	0.012		0.600	1.045	0.257	0.088
	0.800	0.910	0.331	0.008		0.800	1.075	0.252	0.059
	1.000	0.901	0.328	0.0		1.000	1.111	0.245	0.0
1.5	0.0	0.920	0.337	0.0	3.5	0.0	0.990	0.234	0.0
	0.200	0.929	0.334	0.017		0.200	1.018	0.232	0.076
	0.400	0.936	0.332	0.025		0.400	1.048	0.229	0.114
	0.600	0.942	0.329	0.025		0.600	1.083	0.224	0.114
	0.800	0.946	0.325	0.017		0.800	1.123	0.217	0.076
	1.000	0.947	0.322	0.0		1.000	1.173	0.209	0.0
2.0	0.0	0.935	0.320	0.0	4.0	0.0	1.011	0.199	0.0
	0.200	0.948	0.318	0.029		0.200	1.043	0.197	0.094
	0.400	0.961	0.315	0.043		0.400	1.080	0.194	0.142
	0.600	0.974	0.312	0.043		0.600	1.122	0.188	0.142
	0.800	0.986	0.308	0.029		0.800	1.173	0.180	0.094
	1.000	0.998	0.303	0.0		1.000	1.237	0.169	0.0
2.5	0.0	0.951	0.296	0.0	4.5	0.0	1.032	0.162	0.0
	0.200	0.970	0.294	0.043		0.200	1.069	0.161	0.113
	0.400	0.989	0.291	0.064		0.400	1.111	0.157	0.169
	0.600	1.009	0.287	0.064		0.600	1.162	0.149	0.169
	0.800	1.030	0.282	0.043		0.800	1.224	0.139	0.113
	1.000	1.053	0.277	0.0		1.000	1.304	0.126	0.0
					5.0	0.0	1.053	0.125	0.0
						0.200	1.095	0.123	0.131
						0.400	1.143	0.118	0.197
						0.600	1.202	0.109	0.197
						0.800	1.276	0.096	0.131
						1.000	1.374	0.080	0.0

Table VI. Predicted Values of Osmotic and Mean Activity Coefficients at 25°C (Reilly, Wood, and Robinson's Method)

$I/\text{mol kg}^{-1}$	γ_B	ϕ	$-\log\gamma_{NaCl}$	$-\log\gamma_{KCl}$	$-\log\gamma_{MgCl_2}$
1.0	0.0	0.910	0.195	0.215	0.337
	0.200	0.914	0.189	0.209	0.335
	0.400	0.916	0.182	0.203	0.333
	0.600	0.916	0.176	0.197	0.332
	0.800	0.911	0.170	0.191	0.330
	1.000	0.901	0.163	0.185	0.328
1.5	0.0	0.920	0.201	0.228	0.330
	0.200	0.930	0.193	0.221	0.329
	0.400	0.938	0.184	0.213	0.328
	0.600	0.944	0.176	0.205	0.326
	0.800	0.948	0.167	0.197	0.324
	1.000	0.947	0.158	0.188	0.322
2.0	0.0	0.935	0.200	0.235	0.312
	0.200	0.949	0.190	0.226	0.311
	0.400	0.963	0.180	0.216	0.310
	0.600	0.976	0.169	0.206	0.308
	0.800	0.988	0.158	0.196	0.306
	1.000	0.998	0.146	0.185	0.303
2.5	0.0	0.951	0.194	0.236	0.286
	0.200	0.971	0.183	0.226	0.286
	0.400	0.991	0.170	0.215	0.285
	0.600	1.011	0.158	0.203	0.283
	0.800	1.031	0.144	0.191	0.280
	1.000	1.053	0.131	0.178	0.277

$I/\text{mol kg}^{-1}$	γ_B	ϕ	$-\log\gamma_{NaCl}$	$-\log\gamma_{KCl}$	$-\log\gamma_{MgCl_2}$
3.0	0.0	0.970	0.185	0.234	0.256
	0.200	0.994	0.172	0.223	0.256
	0.400	1.020	0.158	0.210	0.255
	0.600	1.047	0.144	0.197	0.253
	0.800	1.077	0.128	0.183	0.250
	1.000	1.111	0.112	0.168	0.245
3.5	0.0	0.990	0.173	0.230	0.222
	0.200	1.019	0.159	0.218	0.222
	0.400	1.050	0.144	0.204	0.221
	0.600	1.085	0.128	0.190	0.219
	0.800	1.125	0.110	0.174	0.215
	1.000	1.173	0.092	0.157	0.209
4.0	0.0	1.011	0.160	0.225	0.186
	0.200	1.045	0.144	0.211	0.186
	0.400	1.082	0.128	0.196	0.185
	0.600	1.125	0.109	0.180	0.181
	0.800	1.175	0.090	0.163	0.176
	1.000	1.237	0.069	0.144	0.169
4.5	0.0	1.032	0.145	0.218	0.149
	0.200	1.071	0.128	0.203	0.148
	0.400	1.115	0.110	0.187	0.146
	0.600	1.165	0.090	0.170	0.141
	0.800	1.227	0.068	0.151	0.135
	1.000	1.304	0.045	0.131	0.126
5.0	0.0	1.053	0.129	0.210	0.110
	0.200	1.097	0.111	0.195	0.109
	0.400	1.146	0.091	0.178	0.105
	0.600	1.207	0.069	0.159	0.099
	0.800	1.280	0.045	0.138	0.091
	1.000	1.374	0.019	0.116	0.080

Table VII. Values of g_0 and γ_B^{trace} Calculated by Various Methods[a]

I, mole-kg^{-1}	$g_0(S)$	$g_0(F)$	$\gamma_B^{\text{tr}}(S)$	$\gamma_B^{\text{tr}}(F)$	$\gamma_B^{\text{tr}}(W\text{-}R)$
1.0	0.049	0.057	0.456	0.460	0.461
1.5	0.047	0.053	0.460	0.465	0.467
2.0	0.045	0.050	0.479	0.483	0.488
2.5	0.043	0.047	0.506	0.511	0.517
3.0	0.041	0.044	0.542	0.547	0.555
3.5	0.039	0.041	0.584	0.589	0.599
4.0	0.037	0.039	0.633	0.638	0.651
4.5	0.035	0.037	0.688	0.694	0.710
5.0	0.033	0.035	0.749	0.756	0.776

[a] The letter S refers to Scatchard's method, F to Friedman's method, and W–R to Reilly, Wood, and Robinson's method.

Table VIII. Calculated Values of g_0 and γ_B^{trace} in the KCl (A) + MgCl$_2$ (B) + H$_2$O and (NaCl + nKCl) (A) + MgCl$_2$ (B) + H$_2$O Systems[a]

I, mole-kg^{-1}	g_0 (1)	g_0 (2)	γ_B^{trace} (1)	γ_B^{trace} (2)	γ_B° (3)
1.0	0.063	0.058	0.450	0.456	0.470
0.9	0.965	0.059	0.453	0.458	0.472
0.8	0.066	0.059	0.456	0.461	0.474
0.7	0.066	0.059	0.461	0.465	0.478
0.6	0.061	0.054	0.466	0.470	0.484
0.5	0.039	0.032	0.471	0.475	0.493
0.4	−0.026	−0.033	0.474	0.477	0.506
0.3	−0.178	−0.184	0.476	0.480	0.526
0.2	−0.466	−0.470	0.491	0.494	0.588
0.1	−0.942	−0.943	0.553	0.555	0.620

[a] The number 1 refers to the KCl + MgCl$_2$ + H$_2$O system (ref. 8), 2 to the NaCl + KCl + MgCl$_2$ + H$_2$O system, and 3 to the MgCl$_2$ + H$_2$O system (refs. 7, 8, and 13).

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