

# Thermodynamics of Mixed Electrolyte Solutions. X. An Isopiestic Study of the Quaternary System $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ at 25°C

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*Activity coefficients in the aqueous quaternary system sodium chloride-potassium chloride-magnesium chloride were derived from isopiestic measurements at 25°C. The isopiestic data were treated by the various procedures of Scatchard, Friedman, and Reilly, Wood, and Robinson, and results obtained agreed fairly well with those obtained by pseudoternary transforms. Interaction parameters obtained indicated the preponderance of pairwise interactions. Excess Gibbs free energies of mixing were calculated.*

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**KEY WORDS:** Activity coefficients; osmotic coefficients; interaction parameters; excess Gibbs free energy of mixing;  $\text{NaCl}$ ;  $\text{KCl}$ ;  $\text{MgCl}_2$ .

## 1. INTRODUCTION

In a previous publication<sup>(1)</sup> dealing with the pseudoternary system  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$ , mean activity coefficients for magnesium chloride and excess Gibbs free energy of mixing were reported for mixtures in which  $n$  was taken equal to 1.3296. The present work deals with additional mixtures and provides enough data to compare the values of thermodynamic properties derived from isopiestic measurements<sup>(2)</sup> with those predicted by various methods.<sup>(3)</sup>

## 2. EXPERIMENTAL

Stock solutions of  $\text{MgCl}_2$  and  $\text{NaCl} \cdot n\text{KCl}$ , with  $n = 0.2552$  and  $4.0502$ , and their mixtures were prepared as previously reported.<sup>(1)</sup> The isopiestic

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apparatus and procedure have already been described.<sup>(1,4-7)</sup> The osmotic coefficients of the aqueous quaternary mixtures were isopiestically determined over an ionic strength range of 0.6 to 6 *m* at 25°C at constant molality ratios of NaCl to KCl.

### 3. RESULTS

The isopiestic data in the aqueous systems (NaCl·*n*KCl)–MgCl<sub>2</sub>–H<sub>2</sub>O for *n* = 0.2552 and 4.0502 are given in Tables I and II, respectively. The first

**Table I.** Observed and Calculated Osmotic Coefficients in the (NaCl·*n*KCl)–MgCl<sub>2</sub>–H<sub>2</sub>O System at 25°C (*n* = 0.2552)

<i>M<sub>r</sub></i>	<i>y<sub>B</sub></i>	<i>I</i>	$\phi_{\text{exp}}$	$\phi(\text{S})^a$	$\phi(\sqrt{I})^b$	$\phi(\text{W-R})^c$
0.540	0.2502	0.625	0.914	0.915	0.915	0.915
(0.9822)	0.5009	0.730	0.910	0.913	0.913	0.913
	0.7489	0.879	0.906	0.911	0.911	0.911
0.927	0.2502	1.059	0.934	0.931	0.931	0.930
(0.9693)	0.5009	1.231	0.938	0.940	0.940	0.939
	0.7489	1.458	0.948	0.953	0.953	0.953
1.691	0.2502	1.912	0.977	0.974	0.974	0.973
(0.9429)	0.5009	2.169	1.005	1.003	1.003	1.001
	0.7489	2.503	1.044	1.043	1.043	1.041
2.922	0.5652	3.721	1.138	1.135	1.134	1.132
(0.8964)	0.7195	3.992	1.189	1.184	1.184	1.183
	0.8391	4.247	1.233	1.234	1.234	1.233
	0.9275	4.442	1.276	1.278	1.278	1.277
3.199	0.3463	3.720	1.102	1.104	1.103	1.102
(0.8851)	0.5652	4.059	1.164	1.164	1.164	1.163
	0.7195	4.342	1.219	1.220	1.220	1.219
	0.8391	4.584	1.274	1.273	1.273	1.273
	0.9275	4.786	1.320	1.322	1.322	1.322
3.282	0.3463	3.814	1.109	1.111	1.110	1.109
(0.8817)	0.5652	4.157	1.173	1.173	1.173	1.172
	0.7195	4.435	1.232	1.229	1.229	1.229
	0.8391	4.685	1.286	1.285	1.285	1.285
3.577	0.3463	4.136	1.136	1.135	1.135	1.134
(0.8615)	0.5652	4.498	1.204	1.204	1.204	1.204
	0.8391	4.995	1.340			
	0.9275	5.201	1.393			
4.076	0.3463	4.697	1.178			
(0.8482)	0.5652	5.058	1.261			
	0.7195	5.357	1.334			
	0.8391	5.609	1.405			
	0.9275	5.805	1.470			

<sup>a</sup> The term  $\phi(\text{S})$  is calculated by Scatchard's method.

<sup>b</sup> The term  $\phi(\sqrt{I})$  is calculated by Friedman's method.

<sup>c</sup> The term  $\phi(\text{W-R})$  is calculated from Eq. (14).

**Table II.** Observed and Calculated Osmotic Coefficients in the (NaCl·*n*KCl)–MgCl<sub>2</sub>–H<sub>2</sub>O System at 25°C (*n* = 4.0502)

$M_r$	$y_B$	$I$	$\phi_{\text{exp}}$	$\phi(S)^a$	$\phi(\sqrt{I})^b$	$\phi(W-R)^c$
0.540 (0.9822)	0.2503	0.633	0.899	0.901	0.901	0.901
	0.4980	0.740	0.896	0.900	0.900	0.901
	0.7501	0.910	0.884			
0.927 (0.9693)	0.2503	1.084	0.912	0.909	0.909	0.910
	0.4890	1.256	0.917	0.920	0.920	0.922
	0.7501	1.478	0.937	0.939	0.030	0.940
1.691 (0.9429)	0.2503	1.983	0.942	0.938	0.938	0.939
	0.4980	2.230	0.976	0.970	0.969	0.972
	0.7501	2.560	1.021	1.021	1.020	1.022
2.106 (0.9277)	0.339	2.571	0.973	0.971	0.970	0.972
	0.7247	3.085	1.059	1.060	1.059	1.061
	0.8364	3.254	1.100	1.099	1.098	1.100
	0.9236	3.399	1.139	1.137	1.136	1.137
2.922 (0.9864)	0.3339	3.578	1.020	1.020	1.020	1.021
	0.5358	3.859	1.076	1.077	1.077	1.078
	0.7247	4.148	1.149	1.150	1.150	1.151
	0.8365	4.321	1.209	1.207	1.207	1.207
	0.9236	4.475	1.262	1.262	1.262	1.262
3.199 (0.8851)	0.3339	3.929	1.036	1.038	1.038	1.039
	0.5358	4.212	1.099	1.101	1.101	1.101
	0.7247	4.500	1.181	1.182	1.182	1.182
	0.8365	4.674	1.246	1.244	1.244	1.244
	0.9236	4.825	1.305	1.305	1.305	1.305
3.282 (0.8817)	0.3339	4.035	1.040	1.044	1.044	1.044
	0.5358	4.324	1.105	1.109	1.109	1.109
	0.7247	4.602	1.192	1.191	1.191	1.191
	0.8365	4.788	1.256	1.256	1.257	1.256
	0.9236	4.920	1.321			
3.577 (0.8695)	0.3339	4.390	1.062	1.062	1.062	1.062
	0.5358	4.689	1.132	1.133	1.134	1.133
	0.7247	4.972	1.225			
	0.8365	5.149	1.297			
	0.9236	5.270	1.370			
4.076 (0.8482)	0.3339	5.037	1.090			
	0.5358	5.320	1.175			
	0.7247	5.591	1.283			
	0.9236	5.885	1.444			

<sup>a</sup> The term  $\phi(S)$  is calculated by Scatchard's method.<sup>b</sup> The term  $\phi(\sqrt{I})$  is calculated by Friedman's method.<sup>c</sup> The term  $\phi(W-R)$  is calculated from Eq. (14).

column gives the molality of the NaCl reference solution and the water activity (in parentheses) obtained from Robinson and Stokes,<sup>(8)</sup> the second column gives the ionic strength fraction of the magnesium chloride,  $y_B = I_B/I = 3m_B/(m_A + 3m_B)$ , where  $m_A$  is the total molality of the pseudosalt  $\text{NaCl} \cdot n\text{KCl}$  and  $m_B$  is the molality of  $\text{MgCl}_2$ , and the third column gives  $I$ , the total ionic strength of the mixed salt solution. The property  $\phi$  is the observed molal osmotic coefficient of the solution.

#### 4. TREATMENT OF RESULTS

The excess Gibbs free energy of mixing in an asymmetric ternary system has been expressed<sup>(2)</sup> as

$$\Delta G^{\text{ex}}(y, I) = 2RTI \int_0^I \Delta d \ln \sqrt{I} \quad (1)$$

where  $\Delta$  is given by

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

and  $\phi(y, I)$ ,  $\phi(0, I)$ , and  $\phi(1, I)$  represent the osmotic coefficient of the mixed solution and the pure A and B solutions, respectively, at the same ionic strength  $I$ . Similarly, the mean activity coefficient  $\gamma_B$  for  $\text{MgCl}_2$  was expressed<sup>(2)</sup> as

$$\ln(\gamma_B/\gamma_B^\circ) = \Delta + (1 - y)[2\phi(0, I) - \phi(1, I) - 1] + (1 - y)^2 I g_0 \quad (3)$$

where  $g_0$  is Friedman's interaction coefficient<sup>(9)</sup> defined by

$$\Delta G^{\text{ex}}(y, I) = RTI^2 y_A y_B [g_0 + g_1(y_A - y_B) + \dots] \quad (4)$$

where  $g_i$  for  $i > 0$  are assumed to be negligible.

Since the pseudosalt  $\text{NaCl} \cdot n\text{KCl}$  behaves as a single compound<sup>(1)</sup> at constant  $n$ , the mean activity coefficients of  $\text{MgCl}_2$  in the mixed solution may be evaluated from the expression<sup>(7)</sup>

$$\ln(\gamma_B/\gamma_B^\circ) = \Delta + (1 - y)[2\phi(0, I) - \phi(1, I) - 1] + 2 \frac{1 - y}{y} \int_0^I \Delta d \ln \sqrt{I} \quad (5)$$

where all the parameters appearing on the right side of Eq. (5) are determined experimentally. The values obtained are given in Tables III and IV.

The experimental results reported in this paper were analyzed by various methods.

**Table III.** Calculated and Experimental Values of the Mean Activity Coefficients of  $\text{MgCl}_2$  in the  $(\text{NaCl} \cdot n\text{KCl})\text{--MgCl}_2\text{--H}_2\text{O}$  System ( $n = 4.0502$ ) at  $25^\circ\text{C}$

$y_B$	$I$	$\gamma_B(\text{W-R})^a$	$\gamma_B(\text{F})^b$	$\gamma_B(\text{S})^c$	$\gamma_B(\text{exp.})^d$
0.2503	0.633	0.470	0.469	0.467	0.467
0.4980	0.740	0.468	0.467	0.465	0.463
0.7500	0.901	0.467	0.466	0.465	0.455
0.2503	1.084	0.455	0.453	0.451	0.455
0.4980	1.256	0.461	0.458	0.457	0.456
0.7501	1.478	0.470	0.468	0.468	0.467
0.2503	1.983	0.475	0.470	0.468	0.474
0.4980	2.230	0.493	0.488	0.488	0.494
0.7501	2.560	0.521	0.518	0.518	0.519
0.3339	2.571	0.507	0.501	0.499	0.504
0.7247	3.085	0.559	0.555	0.555	0.556
0.8364	3.254	0.581	0.578	0.578	0.579
0.9236	3.399	0.601	0.600	0.600	0.601
0.3339	3.578	0.581	0.571	0.570	0.574
0.5358	3.859	0.619	0.610	0.610	0.611
0.7247	4.148	0.666	0.660	0.660	0.659
0.8365	4.321	0.700	0.696	0.696	0.698
0.9236	4.475	0.732	0.731	0.730	0.731
0.3339	3.929	0.612	0.602	0.601	0.603
0.5358	4.212	0.655	0.647	0.646	0.646
0.7247	4.500	0.709	0.703	0.703	0.703
0.8365	4.674	0.749	0.745	0.744	0.746
0.9236	4.825	0.786	0.784	0.784	0.784
0.3339	4.035	0.623	0.612	0.611	0.611
0.5358	4.324	0.668	0.659	0.658	0.657
0.7247	4.602	0.723	0.717	0.716	0.718
0.8365	4.788	0.766	0.761	0.761	0.761
0.3339	4.390	0.659	0.647	0.645	0.650
0.5358	4.689	0.711	0.702	0.700	0.702

<sup>a</sup> The term  $\gamma_B(\text{W-R})$  is predicted by the procedure of Reilly, Wood, and Robinson.

<sup>b</sup> The term  $\gamma_B(\text{F})$  is calculated by Friedman's method.

<sup>c</sup> The term  $\gamma_B(\text{S})$  is calculated by Scatchard's method.

<sup>d</sup> The term  $\gamma_B(\text{exp.})$  indicates experimental values.

1. The first method used is the neutral-electrolyte treatment of mixed salt solutions by Scatchard<sup>(10-12)</sup> which in an asymmetrical mixture of salt A ( $\text{NaCl} \cdot n\text{KCl}$ ), a 1-1 electrolyte, with a salt B of the 2-1 charge type ( $\text{MgCl}_2$ ) leads to the following expression for  $\Delta$ :

$$\Delta = \beta_0 y_A y_B + \beta_1 y_A y_B (y_A - y_B) \quad (6)$$

**Table IV.** Calculated and Experimental Values of the Mean Activity Coefficients of  $\text{MgCl}_2$  in the  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  System ( $n = 0.2552$ ) at  $25^\circ\text{C}$

$y$	$I$	$\gamma_B(\text{W-R})^a$	$\gamma_B(\text{F})^b$	$\gamma_B(\text{S})^c$	$\gamma_B(\text{exp.})^d$
0.2502	0.625	0.483	0.484	0.482	0.480
0.5009	0.730	0.477	0.478	0.477	0.474
0.7489	0.879	0.472	0.473	0.472	0.469
0.2502	1.059	0.474	0.475	0.473	0.473
0.5009	1.231	0.474	0.475	0.474	0.471
0.7489	1.458	0.478	0.478	0.478	0.474
0.2502	1.912	0.505	0.507	0.506	0.503
0.5009	2.169	0.515	0.517	0.516	0.515
0.7489	2.503	0.533	0.533	0.534	0.533
0.5652	3.721	0.659	0.659	0.659	0.658
0.7195	3.992	0.687	0.686	0.686	0.688
0.8391	4.247	0.717	0.715	0.715	0.714
0.9275	4.442	0.742	0.741	0.741	0.739
0.3463	3.720	0.671	0.674	0.673	0.661
0.5652	4.059	0.704	0.703	0.703	0.698
0.7195	4.342	0.736	0.734	0.734	0.731
0.8391	4.584	0.768	0.765	0.765	0.766
0.9275	4.786	0.797	0.795	0.795	0.794
0.3463	3.814	0.684	0.686	0.685	0.673
0.5652	4.157	0.718	0.717	0.717	0.711
0.7195	4.435	0.750	0.748	0.748	0.748
0.8391	4.685	0.784	0.782	0.781	0.782
0.3463	4.136	0.729	0.731	0.730	0.719
0.5652	4.498	0.770	0.768	0.767	0.761

<sup>a</sup> The term  $\gamma_B(\text{W-R})$  is predicted by the procedure of Reilly, Wood, and Robinson.

<sup>b</sup> The term  $\gamma_B(\text{F})$  is calculated by Friedman's method.

<sup>c</sup> The term  $\gamma_B(\text{S})$  is calculated by Scatchard's method.

<sup>d</sup> The term  $\gamma_B(\text{exp.})$  indicates experimental values.

where

$$\beta_0 = b_{01}I + b_{02}I^2 + b_{03}I^3 \quad (7)$$

$$\beta_1 = b_{12}I^2 + b_{13}I^3 \quad (8)$$

the  $b_{ij}$  parameters were evaluated from the measured osmotic coefficients by the least-squares method applied to Eq. (6),  $\beta_0$  and  $\beta_1$  being expressed by Eqs. (7) and (8). Some osmotic coefficients  $\phi$ , as can be noted in Tables I and II, were omitted in these calculations because the ionic strengths of the solutions exceeded that of the saturated solution of the reference salt. It was found that  $\Delta$  could be expressed by only two parameters (F test 95% level)

**Table V.** Parameters  $b_{0j}$  in Eq. (6) and  $A_i$  in Eq. (11) at 25°C

	$n = 0.2552$	$n = 4.0502$
$b_{01}$	0.6322	0.04860
$b_{02}$	-0.00812	-0.00793
$\sigma$	0.0026	0.0033
$A_2$	0.08372	0.06959
$A_3$	-0.02672	-0.02657
$\sigma$	0.0027	0.0034

in the (NaCl· $n$ KCl)–MgCl<sub>2</sub>–H<sub>2</sub>O systems. The values of the Scatchard coefficients which best reproduced the observed osmotic coefficients are given in Table V. The mean activity coefficient of the MgCl<sub>2</sub> is given by

$$\ln \gamma_B/\gamma_B^\circ = (1 - y)[b_{01}I + b_{02}I^2 + 2\phi(0, I) - \phi(1, I) - 1] + \frac{(1 - y)^2}{2} I^2 b_{02} \quad (9)$$

since

$$g_0 = b_{01} + \frac{1}{2}b_{02}I \quad (10)$$

The values calculated at experimental ionic strength are compared in Tables III and IV with those obtained earlier. Furthermore, calculated values of the activity and osmotic coefficients and the excess Gibbs free energy of mixing at rounded values of  $I$  are shown in Tables VI and VII.

2. In the second method, which is concerned with least-squares evaluation of the parameters  $A_i$  and  $B_i$ ,

$$\Delta = y_A y_B \left[ \sum_{i=2}^n A_i I^{i/2} + (y_A - y_B) \sum_{i=2}^n B_i I^{i/2} \right] \quad (11)$$

two coefficients,  $A_2$  and  $A_3$ , were found to be sufficient to best reproduce the experimental values of the osmotic coefficients in both systems. Their values are listed in Table V. It can be easily shown that

$$g_0 = A_2 + \frac{2}{3}A_3 I^{1/2} \quad (12)$$

leading to the following expression for the mean activity coefficient of MgCl<sub>2</sub> in the mixture:

$$\begin{aligned} \ln(\gamma_B/\gamma_B^\circ) = & (1 - y)[A_2 I + A_3 I^{3/2} + 2\phi(0, I) - \phi(1, I) - 1] \\ & + \frac{(1 - y)^2}{3} A_3 I^{3/2} \end{aligned} \quad (13)$$

**Table VI.** Osmotic  $\phi(S)$  and Mean Activity Coefficients  $\gamma_B(S)$  and Excess Gibbs Free Energies  $\Delta G^{\text{ex}}/RT$  in the  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  System ( $n = 0.2552$ ) at  $25^\circ\text{C}$  Calculated by the Scatchard Method

I	$\gamma_B$	$\phi(S)$	$-\log \gamma_B(S)$	$\Delta G^{\text{ex}}/RT$
1.0	0.0	0.926	0.324	0.0
	0.200	0.928	0.325	0.009
	0.400	0.928	0.326	0.014
	0.600	0.925	0.326	0.014
	0.800	0.917	0.327	0.009
	1.000	0.901	0.328	0.0
1.5	0.0	0.943	0.311	0.0
	0.200	0.950	0.314	0.021
	0.400	0.955	0.316	0.031
	0.600	0.958	0.318	0.031
	0.800	0.956	0.320	0.021
	1.000	0.947	0.322	0.0
2.0	0.0	0.964	0.285	0.0
	0.200	0.976	0.290	0.035
	0.400	0.987	0.294	0.053
	0.600	0.995	0.298	0.053
	0.800	0.999	0.301	0.305
	1.000	0.998	0.303	0.0
2.5	0.0	0.988	0.252	0.0
	0.200	1.005	0.259	0.053
	0.400	1.021	0.265	0.080
	0.600	1.034	0.270	0.080
	0.800	1.046	0.274	0.053
	1.000	1.053	0.277	0.0
3.0	0.0	1.015	0.214	0.0
	0.200	1.036	0.223	0.074
	0.400	1.057	0.230	0.110
	0.600	1.076	0.236	0.110
	0.800	1.095	0.241	0.074
	1.000	1.111	0.245	0.0
3.5	0.0	1.044	0.171	0.0
	0.200	1.069	0.182	0.096
	0.400	1.094	0.192	0.144
	0.600	1.120	0.199	0.144
	0.800	1.146	0.205	0.096
	1.000	1.173	0.209	0.0
4.0	0.0	1.074	0.126	0.0
	0.200	1.103	0.140	0.120
	0.400	1.133	0.150	0.180
	0.600	1.165	0.159	0.180
	0.800	1.199	0.165	0.120
	1.000	1.237	0.169	0.0
4.5	0.0	1.105	0.079	0.0
	0.200	1.138	0.095	0.146
	0.400	1.173	0.107	0.218
	0.600	1.211	0.116	0.218
	0.800	1.254	0.123	0.146
	1.000	1.304	0.126	0.0
5.0	0.0	1.137	0.031	0.0
	0.200	1.173	0.048	0.172
	0.400	1.213	0.061	0.258
	0.600	1.258	0.071	0.258
	0.800	1.310	0.078	0.172
	1.000	1.374	0.080	0.0



**Table VII.** Osmotic  $\phi(S)$  and Mean Activity Coefficients  $\gamma_B(S)$  and Excess Gibbs Free Energies  $\Delta G^{\text{ex}}/RT$  in the  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  System ( $n = 4.0502$ ) at  $25^\circ\text{C}$  Calculated by the Scatchard Method

I	$\gamma_B$	$\phi(S)$	$-\log \gamma_B(S)$	$\Delta G^{\text{E}}/RT$	I	$\gamma_B$	$\phi(S)$	$-\log \gamma_B(S)$	$\Delta G^{\text{E}}/RT$
1.0	0.0	0.903	0.350	0.0	0.600	1.031	0.267	0.079	
	0.200	0.906	0.346	0.007	0.800	1.067	0.257	0.053	
	0.400	0.908	0.341	0.011	1.000	1.111	0.245	0.0	
	0.600	0.909	0.337	0.011	3.5	0.0	0.965	0.262	0.0
	0.800	0.907	0.332	0.007	0.200	0.994	0.255	0.068	
	1.000	0.901	0.328	0.0	0.400	1.028	0.246	0.102	
1.5	0.0	0.910	0.349	0.0	0.600	1.066	0.235	0.102	
	0.200	0.919	0.344	0.015	0.800	1.113	0.223	0.068	
	0.400	0.927	0.339	0.023	1.000	1.173	0.209	0.0	
	0.600	0.935	0.333	0.023	4.0	0.0	0.982	0.231	0.0
	0.800	0.942	0.328	0.015	0.200	1.016	0.223	0.084	
	1.000	0.947	0.322	0.0	0.400	1.056	0.213	0.126	
2.0	0.0	0.920	0.336	0.0	0.600	1.103	0.201	0.126	
	0.200	0.935	0.330	0.026	0.800	1.161	0.186	0.084	
	0.400	0.950	0.324	0.039	1.000	1.237	0.169	0.0	
	0.600	0.965	0.318	0.039	4.5	0.0	0.999	0.199	0.0
	0.800	0.981	0.311	0.026	0.200	1.038	0.190	0.100	
	1.000	0.998	0.303	0.0	0.400	1.084	0.178	0.149	
2.5	0.0	0.934	0.315	0.0	0.600	1.140	0.164	0.149	
	0.200	0.953	0.309	0.039	0.800	1.210	0.146	0.100	
	0.400	0.974	0.303	0.058	1.000	1.304	0.126	0.0	
	0.600	0.997	0.295	0.058	5.0	0.0	1.016	0.167	0.0
	0.800	1.023	0.286	0.039	0.200	1.060	0.156	0.115	
	1.000	1.053	0.277	0.0	0.400	1.112	0.142	0.173	
3.0					0.600	1.177	0.125	0.173	
	0.200	0.973	0.284	0.053	0.800	1.261	0.104	0.115	
	0.400	1.000	0.276	0.079	1.000	1.374	0.080	0.0	

The values obtained at experimental ionic strengths are listed in Tables III and IV, while tabulated values of osmotic and activity coefficients and excess Gibbs free energy of mixing at rounded values are shown in Tables VIII and IX.

3. The method described by Reilly, Wood, and Robinson<sup>(13)</sup> has been successfully applied to the calculation of osmotic and mean activity coefficients in seawater and its concentrates<sup>(14)</sup> and in a pseudoternary system.<sup>(7)</sup> It will now be used in the prediction of osmotic and mean activity coefficients of the  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  systems. The calculation of the osmotic coefficient  $\phi$  depends upon Eq. (A-6) in ref. 13 and requires a knowledge of the osmotic

**Table VIII.** Osmotic  $\phi(F)$  and Mean Activity Coefficients  $\gamma_B(F)$  and Excess Gibbs Free Energy  $\Delta G^E/RT$  in the (NaCl- $n$ KCl)-MgCl<sub>2</sub>-H<sub>2</sub>O System ( $n = 0.2552$ ) Calculated by the Friedman Method

I	$y_B$	$\phi(F)$	$-\log \gamma_B(F)$	$\Delta G^E/RT$	I	$y_B$	$\phi(F)$	$-\log \gamma_B(F)$	$\Delta G^E/RT$
1.0	0.0	0.926	0.321	0.0	3.0	0.600	1.076	0.236	0.114
	0.200	0.928	0.323	0.011		0.800	1.094	0.242	0.076
	0.400	0.928	0.324	0.016		1.000	1.111	0.245	0.0
	0.600	0.925	0.326	0.016	3.5	0.0	1.044	0.169	0.0
	0.800	0.917	0.327	0.011		0.200	1.069	0.181	0.099
1.5	1.000	0.901	0.328	0.0		0.400	1.094	0.191	0.148
	0.0	0.943	0.308	0.0	4.0	0.600	1.119	0.199	0.148
	0.200	0.950	0.312	0.022		0.800	1.145	0.205	0.099
	0.400	0.955	0.315	0.033		1.000	1.173	0.209	0.0
	0.600	0.958	0.318	0.033	4.5	0.0	1.074	0.125	0.0
2.0	0.800	0.956	0.320	0.022		0.200	1.103	0.138	0.123
	1.000	0.947	0.0322	0.0		0.400	1.133	0.150	0.185
	0.0	0.964	0.282	0.0	5.0	0.600	1.165	0.159	0.185
	0.200	0.976	0.288	0.037		0.800	1.199	0.165	0.123
	0.400	0.986	0.293	0.056		1.000	1.237	0.169	0.0
2.5	0.600	0.994	0.297	0.056	5.5	0.0	1.105	0.078	0.0
	0.800	0.999	0.301	0.037		0.200	1.138	0.093	0.149
	1.000	0.998	0.303	0.0		0.400	1.173	0.106	0.223
	0.0	0.988	0.249	0.0	6.0	0.600	1.211	0.116	0.223
	0.200	1.005	0.257	0.056		0.800	1.254	0.122	0.149
3.0	0.400	1.020	0.264	0.083		1.000	1.304	0.126	0.0
	0.600	1.034	0.270	0.083	6.5	0.0	1.137	0.029	0.0
	0.800	1.045	0.274	0.056		0.200	1.174	0.046	0.176
	1.000	1.053	0.277	0.0		0.400	1.214	0.060	0.263
	0.0	1.015	0.211	0.0	7.0	0.600	1.259	0.070	0.263
3.5	0.200	1.036	0.221	0.076		0.800	1.311	0.077	0.176
	0.400	1.056	0.230	0.114		1.000	1.374	0.080	0.0

coefficients of NaCl, KCl, and MgCl<sub>2</sub> in pure solutions<sup>(1,15)</sup> and of the Scatchard interaction parameters  $b_{ij}$  in the systems NaCl-KCl-H<sub>2</sub>O,<sup>(16)</sup> NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O,<sup>(17)</sup> and KCl-MgCl<sub>2</sub>-H<sub>2</sub>O.<sup>(2)</sup> The values used for the osmotic coefficients of the salts and the required ionic strengths were checked by the Lietzke and Stoughton interpolation formula.<sup>(18)</sup> The expression for the osmotic coefficient  $\phi$  reads<sup>(7)</sup> as follows:

$$\phi = \frac{2E^{\text{Na}}}{m} \phi(0, \text{NaCl}) + \frac{2E^{\text{K}}}{m} \phi(0, \text{KCl}) + \frac{3E^{\text{Mg}}}{m} \phi(0, \text{MgCl}_2) \\ + \frac{E^{\text{Na}}E^{\text{K}}}{mI} \beta_0(\text{Na-K}) + \frac{3E^{\text{Na}}E^{\text{Mg}}}{2mI} \beta_0(\text{Na-Mg}) + \frac{3E^{\text{K}}E^{\text{Mg}}}{2mI} \beta_0(\text{K-Mg}) \quad (14)$$

**Table IX.** Osmotic  $\phi(F)$  and Mean Activity Coefficients  $\gamma_B(F)$  and Excess Gibbs Free Energy  $\Delta G^{\text{ex}}/RT$  in the  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  System ( $n = 4.0502$ ) at  $25^\circ\text{C}$  Calculated by the Friedman Method

I	$\gamma_B$	$\phi(F)$	$-\log \gamma_B(F)$	$\Delta G^E/RT$	I	$\gamma_B$	$\phi(F)$	$-\log \gamma_B(F)$	$\Delta G^E/RT$
1.0	0.0	0.903	0.347	0.0	3.5	0.600	1.030	0.267	0.084
	0.200	0.906	0.344	0.008		0.800	1.066	0.257	0.056
	0.400	0.909	0.340	0.012		1.000	1.111	0.245	0.0
	0.600	0.909	0.336	0.012		0.0	0.965	0.259	0.0
	0.800	0.907	0.332	0.008		0.200	0.994	0.253	0.071
1.5	1.000	0.901	0.328	0.0	4.0	0.400	1.027	0.245	0.107
	0.0	0.910	0.346	0.0		0.600	1.066	0.235	0.107
	0.200	0.919	0.342	0.017		0.800	1.113	0.223	0.071
	0.400	0.927	0.338	0.026		1.000	1.173	0.209	0.0
	0.600	0.935	0.333	0.026		0.0	0.982	0.229	0.0
2.0	0.800	0.942	0.328	0.017	4.5	0.200	1.016	0.222	0.087
	1.000	0.947	0.322	0.0		0.400	1.055	0.212	0.131
	0.0	0.920	0.333	0.0		0.600	1.102	0.200	0.131
	0.200	0.935	0.328	0.029		0.800	1.161	0.186	0.087
	0.400	0.949	0.323	0.043		1.000	1.237	0.169	0.0
2.5	0.600	0.965	0.317	0.043	5.0	0.0	0.999	0.197	0.0
	0.800	0.981	0.311	0.029		0.200	1.038	0.189	0.104
	1.000	0.998	0.303	0.0		0.400	1.084	0.177	0.156
	0.0	0.934	0.312	0.0		0.600	1.140	0.163	0.156
	0.200	0.953	0.308	0.042		0.800	1.211	0.146	0.104
3.0	0.400	0.974	0.302	0.062		1.000	1.304	0.126	0.0
	0.600	0.996	0.295	0.062		0.0	1.016	0.164	0.0
	0.800	1.022	0.286	0.042		0.200	1.060	0.154	0.120
	1.000	1.053	0.277	0.0		0.400	1.113	0.141	0.180
	0.0	0.949	0.287	0.0		0.600	1.178	0.124	0.180
3.5	0.200	0.973	0.282	0.056		0.800	1.262	0.104	0.120
	0.400	1.000	0.275	0.084		1.000	1.374	0.080	0.0

where  $E^M$  is the equivalent fraction of the cation,  $\phi(0, \text{MX})$  the osmotic coefficient of the pure MX aqueous solution, and  $m$  the total molality at the same total ionic strength. The quantity  $\beta_0(M_1-M_2)$  is the Scatchard interaction parameter in the mixture  $M_1X-M_2X$ .

The predicted values of the osmotic coefficients are compared in Tables I and II with the experimental data and other calculated values.

The expression for the mean activity coefficient of  $\text{MgCl}_2$  in the mixed solution has been previously given<sup>(7)</sup> as

$$\begin{aligned} \ln(\gamma_B/\gamma_B^\circ) = & \left(1 - \frac{3}{2} \frac{E^{\text{Mg}}}{I}\right) [1 - \phi(0, \text{MgCl}_2)] \\ & - \frac{2E^{\text{Na}}}{I} [1 - \phi(0, \text{NaCl})] - \frac{2E^{\text{K}}}{I} [1 - \phi(0, \text{KCl})] \\ & + E^{\text{Na}} \left\{ g_0(\text{Mg-Na}) + E^{\text{Mg}} \frac{\partial}{\partial I} [g_0(\text{Mg-Na})] \right\} \\ & + E^{\text{K}} \left\{ g_0(\text{Mg-K}) + E^{\text{Mg}} \frac{\partial}{\partial I} [g_0(\text{Mg-K})] \right\} \\ & + \frac{2}{3} E^{\text{Na}} E^{\text{K}} \frac{\partial}{\partial I} [g_0(\text{K-Na})] \end{aligned} \quad (15)$$

where  $g_0(\text{M}_1\text{-M}_2)$  refers to the mixed  $\text{M}_1\text{X-M}_2\text{X}$  system.

**Table X.** Predicted Osmotic and Mean Activity Coefficients in the System  $(\text{NaCl} \cdot n\text{KCl})\text{-AgCl}_2\text{-H}_2\text{O}$  ( $n = 0.2552$ )

I	$\gamma_B$	$\phi$	$-\log \gamma_{\text{NaCl}}$	$-\log \gamma_{\text{KCl}}$	$-\log \gamma_{\text{MgCl}_2}$	I	$\gamma_B$	$\phi$	$-\log \gamma_{\text{NaCl}}$	$-\log \gamma_{\text{KCl}}$	$-\log \gamma_{\text{MgCl}_2}$
1.0	0.0	0.925	0.187	0.211	0.323	3.0	0.600	1.073	0.134	0.193	0.237
	0.200	0.927	0.182	0.206	0.325		0.800	1.092	0.123	0.181	0.242
	0.400	0.927	0.178	0.201	0.326		1.000	1.111	0.112	0.168	0.245
	0.600	0.924	0.173	0.196	0.326	3.5	0.0	1.043	0.144	0.218	0.176
	0.800	0.916	0.168	0.190	0.327		0.200	1.067	0.135	0.207	0.185
	1.000	0.901	0.163	0.185	0.328		0.400	1.091	0.126	0.196	0.193
1.5	0.0	0.942	0.189	0.223	0.311		0.600	1.117	0.115	0.184	0.200
	0.200	0.949	0.183	0.216	0.314		0.800	1.144	0.104	0.171	0.205
	0.400	0.954	0.177	0.210	0.316		1.000	1.173	0.092	0.157	0.209
	0.600	0.956	0.171	0.203	0.319	4.0	0.0	1.073	0.125	0.210	0.132
	0.800	0.955	0.165	0.196	0.320		0.200	1.101	0.116	0.199	0.143
	1.000	0.947	0.158	0.188	0.322		0.400	1.131	0.106	0.187	0.151
2.0	0.0	0.964	0.184	0.228	0.287		0.600	1.162	0.095	0.174	0.159
	0.200	0.975	0.177	0.220	0.291		0.800	1.197	0.083	0.160	0.165
	0.400	0.985	0.170	0.212	0.295		1.000	1.237	0.069	0.144	0.169
	0.600	0.993	0.162	0.203	0.298	4.5	0.0	1.104	0.105	0.201	0.085
	0.800	0.998	0.154	0.194	0.301		0.200	1.137	0.096	0.189	0.097
	1.000	0.998	0.146	0.185	0.303		0.400	1.172	0.085	0.176	0.107
2.5	0.0	0.988	0.174	0.227	0.255		0.600	1.210	0.073	0.162	0.115
	0.200	1.003	0.166	0.219	0.261		0.800	1.253	0.059	0.147	0.121
	0.400	1.018	0.158	0.209	0.266		1.000	1.304	0.045	0.131	0.126
	0.600	1.032	0.150	0.199	0.271	5.0	0.0	1.135	0.084	0.190	0.037
	0.800	1.043	0.140	0.189	0.274		0.200	1.173	0.073	0.178	0.049
	1.000	1.053	0.131	0.178	0.277		0.400	1.214	0.062	0.164	0.059
3.0	0.0	1.014	0.160	0.224	0.218		0.600	1.260	0.049	0.150	0.068
	0.200	1.034	0.152	0.214	0.225		0.800	1.312	0.035	0.133	0.075
	0.400	1.054	0.143	0.204	0.232		1.000	1.374	0.019	0.116	0.080

**Table XI.** Predicted Osmotic and Mean Activity Coefficients in the (NaCl·*n*KCl)–MgCl<sub>2</sub>–H<sub>2</sub>O System at 21°C (*n* = 4.0502)

I	Y <sub>B</sub>	φ	-log γ <sub>NaCl</sub>	-log γ <sub>KCl</sub>	-log γ <sub>MgCl<sub>2</sub></sub>
1.0	0.0	0.903	0.200	0.217	0.345
	0.200	0.907	0.193	0.211	0.342
	0.400	0.910	0.186	0.205	0.338
	0.600	0.911	0.178	0.198	0.335
	0.800	0.908	0.171	0.192	0.331
	1.000	0.901	0.163	0.185	0.328
1.5	0.0	0.910	0.209	0.232	0.342
	0.200	0.920	0.199	0.224	0.339
	0.400	0.929	0.189	0.215	0.335
	0.600	0.937	0.179	0.206	0.331
	0.800	0.943	0.168	0.197	0.326
	1.000	0.947	0.158	0.188	0.322
2.0	0.0	0.920	0.210	0.239	0.327
	0.200	0.936	0.198	0.229	0.323
	0.400	0.951	0.186	0.219	0.319
	0.600	0.967	0.173	0.208	0.314
	0.800	0.982	0.160	0.197	0.309
	1.000	0.998	0.146	0.185	0.303
2.5	0.0	0.934	0.207	0.241	0.306
	0.200	0.954	0.193	0.230	0.301
	0.400	0.976	0.178	0.218	0.297
	0.600	0.999	0.163	0.205	0.291
	0.800	1.024	0.147	0.192	0.284
	1.000	1.053	0.131	0.178	0.277
3.0	0.0	0.949	0.200	0.241	0.279
	0.200	0.974	0.184	0.228	0.275
	0.400	1.002	0.168	0.214	0.269
	0.600	1.033	0.150	0.200	0.262
	0.800	1.068	0.132	0.185	0.254
	1.000	1.111	0.112	0.168	0.245
3.5	0.0	0.965	0.192	0.238	0.250
	0.200	0.995	0.174	0.224	0.245
	0.400	1.029	0.155	0.209	0.239
	0.600	1.068	0.135	0.193	0.230
	0.800	1.114	0.114	0.175	0.220
	1.000	1.173	0.092	0.157	0.209
4.0	0.0	0.982	0.181	0.233	0.219
	0.200	1.016	0.162	0.218	0.213
	0.400	1.056	0.141	0.202	0.205
	0.600	1.103	0.118	0.184	0.195
	0.800	1.161	0.095	0.165	0.183
	1.000	1.237	0.069	0.144	0.169
4.5	0.0	0.999	0.169	0.227	0.187
	0.200	1.038	0.148	0.212	0.180
	0.400	1.084	0.125	0.194	0.170
	0.600	1.140	0.100	0.175	0.158
	0.800	1.210	0.074	0.154	0.143
	1.000	1.304	0.045	0.131	0.126
5.0	0.0	1.016	0.157	0.221	0.154
	0.200	1.060	0.134	0.204	0.146
	0.400	1.112	0.109	0.186	0.134
	0.600	1.177	0.081	0.165	0.119
	0.800	1.260	0.051	0.142	0.101
	1.000	1.374	0.019	0.116	0.080

The predicted values are listed in Tables III and IV, and tabulated values of the osmotic and mean activity coefficients for NaCl, KCl, and  $\text{MgCl}_2$  are given in Tables X and XI using the following expression, where  $M_i$  refers to either KCl or NaCl:

$$\begin{aligned} \ln(\gamma_{M_i}/\gamma_{M_i}^\circ) = & \left(1 - \frac{E^{M_i}}{I}\right)[1 - \phi(0, M_i\text{Cl})] - \left(1 - \frac{E^{M_j}}{I}\right)[1 - \phi(0, M_j\text{Cl})] \\ & - \frac{3}{4} \frac{E^{M_g}}{I} [1 - \phi(0, \text{MgCl}_2)] + \frac{3}{4} E^{M_j} E^{M_g} \frac{\partial}{\partial I} [g_0(M_j - \text{Mg})] \\ & + \frac{1}{2} E^{M_j} \left\{ g_0(M_i - M_j) + \frac{\partial}{\partial I} [g_0(M_i - M_j)] \right\} \\ & + \frac{3}{4} E^{M_g} \left\{ g_0(M_i - \text{Mg}) + E^{M_i} \frac{\partial}{\partial I} [g_0(M_i - \text{Mg})] \right\} \end{aligned} \quad (16)$$

4. Other methods were also used. Results obtained by the ion component methods of Scatchard<sup>(3a)</sup> indicate that the quality of the fit is about the same as that obtained by the neutral electrolyte treatment<sup>(19)</sup> and did not result in a great improvement. The alternative treatment of Pitzer<sup>(20)</sup> is similar to that offered by Scatchard<sup>(10)</sup> [ $\Delta = y_A y_B (Dm + Em^2)$ ] and will be considered in a forthcoming article.<sup>(21)</sup>

## 5. DISCUSSION

The various methods of calculating the mean activity coefficients of  $\text{MgCl}_2$  in the system  $(\text{NaCl} \cdot n\text{KCl})\text{-MgCl}_2\text{-H}_2\text{O}$  are compared in Table XII where the  $\gamma_B^{\text{trace}}$  activity coefficients are listed over the molal ionic strength range 1–5. The average deviations observed in  $\gamma^{\text{trace}}$  values are reasonable, and those predicted by the Reilly, Wood, and Robinson method (RWR)<sup>(13)</sup> are systematically higher than the others at ionic strengths above 3 *m*. This was expected<sup>(7)</sup> since their treatment correctly accounts for only all pairwise interactions.<sup>(3)</sup> Additional support may be found in the decreasing values of  $g_0$  with increasing ionic strength as noted in Table XIII. The interactions between two ions which contribute to a common-ion charge-asymmetric mixture have been calculated by Friedman<sup>(9)</sup> and include contributions from all possible pairs and indicate the importance of ion-pair interactions prevailing in the mixture.

The expression

$$g_0 = (0.456 \ln I - A - \frac{2}{3} A_3 I^{1/2}) \exp(-10I^2) + A_2 - \frac{2}{3} A_3 I^{1/2} \quad (17)$$

**Table XII.** Values of  $\gamma_B^{\text{trace}}$  Calculated by Various Methods

<i>I</i>	<i>n</i> = 0.2552			<i>n</i> = 4.0502		
	$\gamma_B^{\text{tr}}(\text{S})^a$	$\gamma_B^{\text{tr}}(\text{F})^b$	$\gamma_B^{\text{tr}}(\text{W-R})^c$	$\gamma_B^{\text{tr}}(\text{S})$	$\gamma_B^{\text{tr}}(\text{F})$	$\gamma_B^{\text{tr}}(\text{W-R})$
1.0	0.475	0.478	0.475	0.447	0.450	0.452
1.5	0.489	0.492	0.488	0.448	0.451	0.455
2.0	0.518	0.522	0.517	0.462	0.465	0.471
2.5	0.559	0.563	0.556	0.484	0.487	0.495
3.0	0.611	0.615	0.606	0.513	0.516	0.526
3.5	0.674	0.677	0.666	0.547	0.551	0.562
4.0	0.747	0.751	0.738	0.587	0.591	0.604
4.5	0.832	0.836	0.821	0.632	0.636	0.650
5.0	0.931	0.935	0.919	0.682	0.686	0.701

<sup>a</sup> The letter (S) denotes Scatchard's method.<sup>b</sup> The letter (F) denotes Friedman's method.<sup>c</sup> The letters (W-R) denote Reilly, Wood, and Robinson's method.

which has been obtained<sup>(2,7)</sup> by a stochastic description of a two-structure model,<sup>(22)</sup> agrees with Friedman's new derivation<sup>(23)</sup> of the higher limiting law which requires that as  $I \rightarrow 0$ ,  $g_0$  goes to  $-\infty$  as  $\ln I$ . It may be used for the extrapolation of  $g_0$  below the experimental range, and values obtained for  $g_0$  and  $\gamma_B^{\text{trace}}$  in the entire NaCl-KCl-MgCl<sub>2</sub>-H<sub>2</sub>O system are compared in Table XIV with those previously obtained<sup>(2)</sup> in the KCl-MgCl<sub>2</sub>-H<sub>2</sub>O system. As the concentration decreases, the values of  $g_0$  tend to be identical

**Table XIII.** Values of  $g_0$  Calculated by the Methods of Scatchard (S) and Friedman (F)

<i>I</i>	<i>n</i> = 0.2552		<i>n</i> = 4.0502	
	$g_0(\text{S})$	$g_0(\text{F})$	$g_0(\text{S})$	$g_0(\text{F})$
1.0	0.059	0.066	0.045	0.052
1.5	0.057	0.062	0.043	0.048
2.0	0.055	0.059	0.041	0.045
2.5	0.053	0.056	0.039	0.042
3.0	0.051	0.053	0.037	0.039
3.5	0.049	0.050	0.035	0.036
4.0	0.047	0.048	0.033	0.034
4.5	0.045	0.046	0.031	0.032
5.0	0.043	0.044	0.029	0.030

**Table XIV.** Predicted Values of  $g_0$  and  $\gamma_B^{\text{trace}}$  at Lower Ionic Strengths

$I$	$n = 4.0502$		$n = 0.2552$		$\gamma_B^{\circ a}$
	$g_0$	$\gamma_B^{\text{tr}}$	$g_0$	$\gamma_B^{\text{tr}}$	
1.0	0.052	0.448	0.066	0.476	0.470
0.9	0.053	0.451	0.067	0.476	0.472
0.8	0.054	0.454	0.068	0.477	0.474
0.7	0.053	0.459	0.067	0.479	0.478
0.6	0.048	0.465	0.062	0.483	0.484
0.5	0.026	0.470	0.039	0.485	0.493
0.4	-0.038	0.473	-0.027	0.486	0.506
0.3	-0.188	0.476	-0.179	0.486	0.526
0.2	-0.472	0.492	-0.467	0.499	0.558
0.1	-0.944	0.553	-0.943	0.558	0.620

<sup>a</sup> Values of  $\gamma_B^{\text{trace}}$  in the KCl-MgCl<sub>2</sub>-H<sub>2</sub>O system.

as expected. The effect of NaCl on  $\gamma^{\text{trace}}$  tends to decrease, however, more slowly in mixed than pure solutions, thereby pointing to higher association than in a pure MgCl<sub>2</sub> solution.

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