

# Thermodynamics of Mixed Electrolyte Solutions. XI. An Isopiestic Study of the Quaternary System NaCl-KCl-CaCl<sub>2</sub>-H<sub>2</sub>O at 25°C

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Received May 23, 1979; revised October 9, 1979

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*Osmotic and activity coefficients in the aqueous quaternary system sodium chloride-potassium chloride-calcium 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. The results obtained showed good agreement with those obtained by pseudo-ternary 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; NaCl:KCl:CaCl<sub>2</sub>.

## 1. INTRODUCTION

Many investigations on the thermodynamics of ternary aqueous solutions of mixed electrolytes have been carried out but relatively fewer studies have been made on mixtures of three or more salts, which are representative of natural brines. Alkali and alkaline earth chlorides prevailing in many geochemical brines led to our previous investigations of the quaternary system NaCl-KCl-MgCl<sub>2</sub>-H<sub>2</sub>O.<sup>(1-3)</sup> The present work deals with a system of the same charge type: NaCl-KCl-CaCl<sub>2</sub>-H<sub>2</sub>O. A few measurements on the latter system were made by Kirgintsev and Luk'yanov,<sup>(4)</sup> but it has been stated<sup>(5)</sup> that their procedure has no theoretical base.

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## 2. EXPERIMENTAL

Sodium chloride and potassium chloride (Fluka purissimum) were recrystallized twice from conductivity water and dried to constant weight at 200°C. Stock solutions were prepared by weight and their concentrations were determined gravimetrically by precipitated silver chloride. The constant-salt-ratio mixtures were prepared by weight from the stock solutions and diluted by weight. The mixtures of the two alkali chlorides were treated as a pseudobinary salt  $\text{NaCl} \cdot n\text{KCl}$ ,<sup>(3)</sup> where  $n = 0.3330$ , 1.0001, and 3.0005. Recrystallization of calcium chloride does not significantly reduce its alkali content.<sup>(6)</sup> Accordingly, purification was carried out by adding ammonium carbonate and washing the resulting precipitate well. The calcium carbonate formed was dissolved in HCl, and the solution obtained was concentrated by evaporation. This stock solution was analyzed gravimetrically for chloride.

The isopiestic apparatus and procedure have been described previously.<sup>(1)</sup> The osmotic coefficients were determined isopiastically over an ionic strength range of 0.9–5.7 mole-kg<sup>-1</sup> at 25°C. The reference salt was NaCl.

## 3. RESULTS

The isopiestic data are given in Tables I–III. The first column gives the molality of the NaCl reference solution and the water activity (in parentheses)

**Table I.** Observed and Calculated Osmotic Coefficients in the  $(\text{NaCl} \cdot n\text{KCl})\text{--CaCl}_2\text{--H}_2\text{O}$  System at 25°C ( $n = 0.3330$ )

$m_r$	$y_B$	$I$	$\phi_{\text{exp}}$	$\phi(S)^a$
0.9834	0.2501	1.1045	0.926	0.927
(0.9671)	0.5002	1.3242	0.931	0.932
1.9798	0.2501	2.2674	0.980	0.980
(0.9320)	0.5002	2.5757	1.007	1.005
	0.7502	2.9788	1.045	1.041
2.1997	0.2501	2.5169	0.994	0.994
(0.9238)	0.5002	2.8475	1.025	1.023
	0.7502	3.2756	1.069	1.065
2.5211	0.2501	2.8840	1.013	1.015
(0.9116)	0.5002	3.2471	1.050	1.051
	0.7502	3.7114	1.102	1.101
3.0421	0.2501	3.4750	1.049	1.051
(0.8910)	0.5002	3.8847	1.094	1.096
	0.7502	4.3993	1.160	1.160
3.5013	0.2501	3.9944	1.082	1.084
(0.8721)	0.5002	4.4358	1.136	1.137
	0.7502	4.9809	1.214	1.212
4.1002	0.5002	5.1605	1.190	1.191
(0.8464)	0.7502	5.7460	1.283	1.282

<sup>a</sup>  $\phi(S)$  indicates values calculated by Scatchard's method.

**Table II.** Observed and Calculated Osmotic Coefficients in the (NaCl·*n*KCl)–CaCl<sub>2</sub>–H<sub>2</sub>O System at 25°C (*n* = 1.0001)

$m_r$	$y_B$	$I$	$\phi_{\text{exp}}$	$\phi(S)^a$
0.8143	0.2499	0.9496	0.910	0.911
(0.9730)	0.5000	1.1058	0.912	0.913
	0.7500	1.3221	0.916	0.917
1.3066	0.5000	1.7421	0.948	0.942
(0.9561)	0.7500	2.0481	0.968	0.962
1.9803	0.2499	2.3154	0.960	0.962
(0.9320)	0.5000	2.6231	0.989	0.990
	0.7500	3.0174	1.032	1.030
2.6003	0.2499	3.0417	0.996	0.997
(0.9085)	0.5000	3.4129	1.035	1.036
	0.7500	3.8744	1.095	1.096
2.8539	0.2499	3.3403	1.011	1.011
(0.8985)	0.5000	3.7319	1.056	1.056
	0.7500	4.2122	1.123	1.122
3.4776	0.2499	4.0870	1.048	1.050
(0.8731)	0.5000	4.5234	1.105	1.106
	0.7500	5.0423	1.190	1.190
3.9857	0.2499	4.6973	1.081	1.082
(0.8514)	0.5000	5.1642	1.147	1.146
	0.7500	5.7060	1.246	1.245

<sup>a</sup>  $\phi(S)$  indicates values calculated by Scatchard's method.

obtained from Hamer and Wu.<sup>(7)</sup> The second column gives the ionic strength fraction of the calcium chloride,  $y_B = I_B/I = 3m_B/m_A + 3m_B$ , where  $m_A$  is the total molality of the salt (NaCl·*n*KCl) and  $m_B$  the molality of CaCl<sub>2</sub> in the mixed salt solution. The third column gives  $I$ , the total ionic strength of the mixed salt solution;  $\phi$  is the observed 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

**Table III.** Observed and Calculated Osmotic Coefficients in the (NaCl·*n*KCl)–CaCl<sub>2</sub>–H<sub>2</sub>O System at 25°C (*n* = 3.0005)

<i>m<sub>r</sub></i>	<i>y<sub>B</sub></i>	<i>I</i>	<i>φ<sub>exp</sub></i>	<i>φ(S)<sup>a</sup></i>
0.8613	0.2502	1.0144	0.903	0.905
(0.9714)	0.5003	1.1792	0.906	0.908
	0.7497	1.4049	0.913	0.916
1.5988	0.2502	1.8918	0.929	0.930
(0.9458)	0.5003	2.1611	0.949	0.950
	0.7497	2.5099	0.981	0.983
2.2009	0.2502	2.6158	0.957	0.956
(0.9238)	0.5003	2.9485	0.990	0.989
	0.7497	3.3605	1.043	1.041
2.7796	0.2502	3.3157	0.988	0.984
(0.9015)	0.5003	3.7007	10.32	1.029
	0.7497	4.1594	1.102	1.100
3.3012	0.2502	3.9710	1.013	1.012
(0.8804)	0.5003	4.3990	1.066	1.067
	0.7497	4.8876	1.152	1.154
3.4995	0.2502	4.2235	1.022	1.023
(0.8722)	0.5003	4.6635	1.080	1.082
	0.7497	5.1538	1.173	1.175
3.9841	0.2502	4.8351	1.050	1.049
(0.8515)	0.5003	5.3037	1.116	1.116

<sup>a</sup> *φ(S)* indicates values calculated by Scatchard's method.

strength *I*. Table IV gives the parameters of two-component systems (binary solutions) for evaluation of the osmotic coefficients as a function of *I* from the equation<sup>(7,8)</sup>

$$\phi = 1 + \frac{I}{\nu m} \frac{2S}{A^3 I} \left( L - 2 \ln L - \frac{1}{L} \right) + BI + CI^2 + DI^3 \quad (3)$$

where  $L = 1 + A\sqrt{I}$  and  $S = -1.17082$  at 25°C. Values of  $\phi(0, I)$  in Eq. (2) for the pseudobinary salt A were obtained from the parameters reported for the binary solutions NaCl–H<sub>2</sub>O and KCl–H<sub>2</sub>O (Table IV), and the ternary mixture<sup>(9)</sup> NaCl–KCl–H<sub>2</sub>O (Table V). Values of  $\phi(1, I)$  were obtained from the parameters of the CaCl–H<sub>2</sub>O system<sup>(8)</sup> using Eq. (3).

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

a. The first method used is the neutral electrolyte treatment of mixed salt solutions by Scatchard<sup>(10–13)</sup> which in an asymmetrical mixture of salt A

**Table IV.** Parameters for Two-Component (Ref. 8) Systems (Binary Solutions)

Electrolyte solution	$A$	$B \times 10^2$	$C \times 10^3$	$D \times 10^4$	$\sigma^2 \times 10^6$
NaCl	1.45397	2.23565	9.30838	-5.36209	0.12
KCl	1.30752	-0.35919	7.17091	-5.67500	1.46
CaCl <sub>2</sub>	1.61291	4.56577	8.57310	-2.73800	4.03

(NaCl· $n$ KCl), a 1-1 electrolyte, with a salt B of the 2-1 charge type (MgCl<sub>2</sub>) leads to the following expression for  $\Delta$ :

$$\Delta = \beta_0 y_A y_B + \beta_1 y_A y_B (y_A - y_B) \quad (4)$$

where

$$\beta_0 = b_{01}I + b_{02}I^2 + b_{03}I^3 \quad (5)$$

$$\beta_1 = b_{12}I^2 + b_{13}I^3 \quad (6)$$

the  $b_{ij}$  parameters were evaluated from the measured osmotic coefficients by the least-squares method applied to Eq. (4),  $\beta_0$  and  $\beta_1$  being expressed by Eqs. (5) and (6). It was found that  $\Delta$  could be expressed by only two parameters (F test 95% level) as in the (NaCl· $n$ KCl)-MgCl<sub>2</sub>-H<sub>2</sub>O systems<sup>(3)</sup>; hence

$$\frac{\Delta}{y_A y_B} = b_{01}I + b_{02}I^2 \quad (7)$$

b. In the second method, which is involved with the least-squares evaluations of the parameters in the equation<sup>(14,15)</sup>

$$\Delta = y_A y_B \sum_{i=2} A_i I^{i/2} \quad (8)$$

**Table V.** Parameters for Three-Component Systems (Ternary Solutions)

Parameter	System		
	NaCl-KCl (ref. 6)	NaCl-CaCl <sub>2</sub> (ref. 12)	KCl-CaCl <sub>2</sub> (ref. 13)
$b_{01}$	-0.02530	0.07030	0.03332
$b_{02}$	-0.00299	-0.02250	-0.01036
$b_{03}$	0.0	0.00235	0.0
$b_{12}$	0.0	0.00405	0.0
$b_{13}$	0.0	-0.00050	0.0
$\sigma$	0.0008	0.0011	0.0021

**Table VI.** The Parameters  $b_{ij}$  and  $A_i$  for the  $\text{NaCl} \cdot n\text{KCl} - \text{CaCl}_2 - \text{H}_2\text{O}$  System

$n$	$b_{01}$	$b_{02}$	$\sigma$	$A_2$	$A_3$	$\sigma$
0.3330	0.0470	-0.0070	0.0018	0.0729	-0.0272	0.0019
1.0001	0.0494	-0.0088	0.0022	0.0808	-0.0338	0.0021
3.0005	0.0438	-0.0093	0.0019	0.0730	-0.0336	0.0022

two coefficients  $A_2$  and  $A_3$  were found to be sufficient to best reproduce the experimental values of the osmotic coefficients of the pseudoternary system  $(\text{NaCl} - n\text{KCl}) - \text{CaCl}_2 - \text{H}_2\text{O}$ .

Table VI gives the parameters  $b_{ij}$  and  $A_i$  with the standard deviation  $\sigma$  for the present system. From these parameters we have recalculated<sup>(15)</sup> the values of the osmotic coefficients which are given in the fifth and sixth columns of Tables I-III. From the respective equations<sup>(15)</sup> activity coefficients, excess Gibbs free energies of mixing, and Friedman interaction parameters can also be evaluated using the parameters in Table VI.

c. The method described by Reilly, Wood, and Robinson<sup>(16)</sup> (RWR) has been applied successfully to the calculation of  $\phi$  and  $\gamma$  in seawater and its concentrates<sup>(17)</sup> and in the quaternary  $\text{NaCl} - \text{KCl} - \text{MgCl}_2 - \text{H}_2\text{O}$  system.<sup>(1)</sup> We shall now use it to predict values of  $\phi$  and  $\gamma$  in the present system. The calculations require a knowledge of parameters in binary aqueous solutions of  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$ <sup>(8)</sup> (Table IV), and of the three-component parameters  $b_{ij}$  in ternary systems  $\text{NaCl} - \text{KCl} - \text{H}_2\text{O}$ ,<sup>(9)</sup>  $\text{NaCl} - \text{CaCl}_2 - \text{H}_2\text{O}$ ,<sup>(18)</sup> and  $\text{KCl} - \text{CaCl}_2 - \text{H}_2\text{O}$ <sup>(19)</sup> (Table V). The predicted values of the osmotic coefficients (at experimental ionic strengths) showed good agreement when compared with the experimental data and other calculated values.

## 5. DISCUSSION

The various methods of calculating the mean activity coefficients of  $\text{CaCl}_2$  in the system  $\text{NaCl} - n\text{KCl} - \text{CaCl}_2 - \text{H}_2\text{O}$  are compared in Table VIII, where the  $\gamma_{\text{B}}^{\text{trace}}$  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>(16)</sup> (Table VII) are usually higher than the others at ionic strengths above 3 *m*. This was expected<sup>(15)</sup> since their treatment correctly accounts for only all pairwise interactions.<sup>(16)</sup>

The interactions between two ions which contribute to a common ion-charge-asymmetrical mixture have been calculated by Friedman.<sup>(20)</sup> They include contributions from all possible pairs and indicate the importance of ion-pair interactions prevailing in the mixture. The parameter  $g_0$  representing

Table VII. Mean Activity Coefficients in the NaCl-*n*KCl-CaCl<sub>2</sub>-H<sub>2</sub>O System at 25°C Predicted by the RWR Method<sup>(16)</sup>

I	y <sub>B</sub>	n = 0.3330			n = 1.0001			n = 3.0005		
		γ CaCl <sub>2</sub>	γ NaCl	γ KCl	γ CaCl <sub>2</sub>	γ NaCl	γ KCl	γ CaCl <sub>2</sub>	γ NaCl	γ KCl
1.0	0.0	0.464	0.649	0.615	0.451	0.641	0.611	0.439	0.633	0.607
	0.2	0.461	0.655	0.619	0.451	0.648	0.616	0.441	0.642	0.613
	0.4	0.458	0.661	0.624	0.451	0.656	0.622	0.444	0.651	0.620
	0.6	0.456	0.667	0.629	0.451	0.664	0.627	0.447	0.661	0.626
	0.8	0.454	0.674	0.634	0.452	0.672	0.633	0.450	0.671	0.633
	1.0	0.453	0.681	0.640	0.453	0.681	0.640	0.453	0.681	0.640
2.0	0.0	0.492	0.652	0.591	0.466	0.636	0.584	0.443	0.620	0.578
	0.2	0.482	0.660	0.597	0.463	0.647	0.591	0.445	0.634	0.586
	0.4	0.475	0.669	0.603	0.461	0.659	0.599	0.447	0.649	0.595
	0.6	0.468	0.678	0.610	0.459	0.671	0.607	0.451	0.665	0.605
	0.8	0.463	0.687	0.617	0.459	0.684	0.616	0.455	0.681	0.615
	1.0	0.459	0.698	0.626	0.459	0.698	0.626	0.459	0.698	0.626
3.0	0.0	0.560	0.687	0.595	0.518	0.660	0.586	0.479	0.636	0.576
	0.2	0.543	0.696	0.601	0.511	0.675	0.593	0.481	0.654	0.586
	0.4	0.529	0.706	0.608	0.506	0.690	0.602	0.484	0.674	0.596
	0.6	0.516	0.717	0.616	0.502	0.706	0.612	0.488	0.695	0.608
	0.8	0.508	0.728	0.625	0.501	0.723	0.623	0.494	0.718	0.622
	1.0	0.502	0.741	0.637	0.502	0.741	0.637	0.502	0.741	0.637
4.0	0.0	0.661	0.742	0.614	0.594	0.702	0.600	0.534	0.666	0.587
	0.2	0.634	0.752	0.619	0.583	0.720	0.608	0.536	0.690	0.597
	0.4	0.611	0.763	0.626	0.575	0.738	0.617	0.540	0.715	0.609
	0.6	0.593	0.775	0.635	0.570	0.758	0.629	0.548	0.742	0.623
	0.8	0.580	0.788	0.646	0.569	0.779	0.643	0.558	0.771	0.640
	1.0	0.571	0.803	0.659	0.571	0.803	0.659	0.571	0.803	0.659
5.0	0.0	0.797	0.814	0.641	0.692	0.757	0.622	0.603	0.707	0.605
	0.2	0.757	0.825	0.646	0.677	0.779	0.630	0.607	0.736	0.615
	0.4	0.725	0.837	0.653	0.667	0.801	0.640	0.615	0.767	0.629
	0.6	0.698	0.851	0.662	0.662	0.826	0.653	0.627	0.802	0.645
	0.8	0.680	0.865	0.674	0.662	0.853	0.669	0.645	0.840	0.665
	1.0	0.668	0.882	0.689	0.668	0.882	0.689	0.668	0.882	0.689

these interactions can be expressed in our system either by the Scatchard equation<sup>(13)</sup>

$$g_0 = b_{01} + \frac{1}{2}b_{02}I \quad (9)$$

or by the modified Friedman equation<sup>(15)</sup>

$$g_0 = A_2 + \frac{2}{3}A_3I^{1/2} \quad (10)$$

Table IX gives  $g_0$  at various ionic strengths calculated from Eqs. (9) and (10).

It has been reported<sup>(9)</sup> that in an aqueous mixture of potassium and sodium chlorides,  $K^+-K^+$  and  $Na^+-Na^+$  interactions tend to be replaced by  $K^+-Na^+$  interactions, as indicated by negative  $g_0$  values. The addition of a solution of  $CaCl_2-H_2O$  to form a quaternary system does not change this

**Table VIII.** Values of Trace Activity Coefficients  $\gamma_B^{\text{tr}}$  in the (NaCl- $n$ KCl)-CaCl<sub>2</sub>-H<sub>2</sub>O System Calculated by Various Methods

<i>I</i>	<i>n</i> = 0.3330			<i>n</i> = 1.0001			<i>n</i> = 3.0005		
	$\gamma_B^{\text{tr}}(\text{S})$	$\gamma_B^{\text{tr}}(\text{F})$	$\gamma_B^{\text{tr}}(\text{RWR})$	$\gamma_B^{\text{tr}}(\text{S})$	$\gamma_B^{\text{tr}}(\text{F})$	$\gamma_B^{\text{tr}}(\text{RWR})$	$\gamma_B^{\text{tr}}(\text{S})$	$\gamma_B^{\text{tr}}(\text{F})$	$\gamma_B^{\text{tr}}(\text{RWR})$
1.0	0.457	0.462	0.464	0.448	0.454	0.451	0.438	0.443	0.439
1.5	0.461	0.467	0.470	0.448	0.455	0.452	0.433	0.439	0.435
2.0	0.480	0.487	0.491	0.461	0.469	0.466	0.441	0.447	0.443
2.5	0.507	0.515	0.521	0.483	0.491	0.489	0.456	0.463	0.458
3.0	0.544	0.552	0.560	0.511	0.519	0.518	0.477	0.483	0.479
3.5	0.587	0.596	0.607	0.544	0.553	0.553	0.502	0.508	0.505
4.0	0.638	0.648	0.661	0.583	0.593	0.594	0.531	0.538	0.534
4.5	0.697	0.707	0.725	0.627	0.637	0.640	0.563	0.570	0.567
5.0	0.764	0.775	0.797	0.675	0.686	0.692	0.598	0.605	0.603



**Table IX.** Values of  $g_0$  for the (NaCl- $n$ KCl)-CaCl<sub>2</sub>-H<sub>2</sub>O Quaternary System

$I$	$g_0(S)^a$			$g_0(F)^b$		
	$n = 0.3$	$n = 1.0$	$n = 3.0$	$n = 0.3$	$n = 1.0$	$n = 3.0$
1.0	0.044	0.045	0.039	0.055	0.058	0.051
2.0	0.040	0.041	0.035	0.047	0.049	0.041
3.0	0.037	0.036	0.030	0.041	0.042	0.034
4.0	0.033	0.032	0.025	0.037	0.036	0.028
5.0	0.030	0.027	0.021	0.032	0.030	0.023

<sup>a</sup>  $g_0(S)$  is calculated from Eq. (9).<sup>b</sup>  $g_0(F)$  is calculated from Eq. (10).

tendency, as shown by positive values of  $g_0$  in the quaternary system. This indicates the preponderance of already present pairwise interactions. However, the slight decrease of  $g_0$  with the ionic strength may be due to possible triplet interactions. Comparison with the NaCl-KCl-MgCl<sub>2</sub>-H<sub>2</sub>O<sup>(2-3)</sup> system shows that both systems behave similarly. The expression

$$g_0 = (0.456 \ln I - A_2 - \frac{2}{3}A_3I^{1/2})e^{-10I^2} + A_2 + \frac{2}{3}A_3I^{1/2} \quad (11)$$

obtained by a stochastic description of a two-structure model,<sup>(15)</sup> includes the higher limiting law which requires that, in a mixture of electrolyte A (1:1 charge

**Table X.** Values of  $g_0$  and Trace Activity Coefficients  $\gamma_B^{\text{tr}}$  in the (NaCl- $n$ KCl)-CaCl<sub>2</sub>-H<sub>2</sub>O System Calculated for a Two-Structure Model

$I$	$n = 0.3330$		$n = 1.0001$		$n = 3.0005$	
	$g_0$	$\gamma_B^{\text{tr}}$	$g_0$	$\gamma_B^{\text{tr}}$	$g_0$	$\gamma_B^{\text{tr}}$
1.0	0.055	0.460	0.058	0.451	0.051	0.441
0.9	0.055	0.461	0.059	0.453	0.052	0.444
0.8	0.056	0.464	0.060	0.457	0.053	0.448
0.7	0.056	0.468	0.060	0.462	0.053	0.454
0.6	0.051	0.473	0.055	0.468	0.048	0.461
0.5	0.029	0.477	0.034	0.473	0.027	0.467
0.4	-0.035	0.480	-0.031	0.476	-0.037	0.471
0.3	-0.186	0.482	-0.183	0.478	-0.187	0.475
0.2	-0.471	0.496	-0.469	0.493	-0.471	0.491
0.1	-0.944	0.556	-0.943	0.554	-0.944	0.553

type) with electrolyte B (2:1 or 1:2 charge type),<sup>(20)</sup> as  $I \rightarrow 0$ ,  $g_0$  goes to  $-\infty$  as in  $I$ . It may be used for the extrapolation of  $g_0$  below the experimental range. Values obtained for  $g_0$  and the trace mean activity coefficients of calcium chloride in the range  $I = 0.1$ – $1.0$  are given in Table X. As the concentration decreases, the values of  $g_0$  tend to be identical as expected. These could possibly be checked with future potentiometric measurements by using a suitable ion-specific electrode.

## 6. CONCLUSION

Results in systems of the type  $\text{NaCl-KCl-MCl}_2\text{-H}_2\text{O}$ , where M is  $\text{Mg}$ ,<sup>(1-3)</sup>  $\text{Ca}$  (this work and refs. 4 and 14), or  $\text{Ba}$ ,<sup>(16)</sup> seem to confirm that thermodynamic properties of multicomponent systems can be predicted from those of the simpler binary and ternary solutions.

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