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The System NaCl–$CaCl_2$–H_2O. 2. Densities for Ionic Strengths of 0.1–19.2 mol·kg^{-1} at 298.15 and 308.15 K and at 0.1 MPa

Charles S. Oakes,*,† **John M. Simonson,**‡ **and Robert J. Bodnar**†

Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Densities for ternary solutions in the system NaCl–$CaCl_2$–H_2O were measured with a vibrating-tube densimeter at 298.15 ± 0.09 and 308.15 ± 0.03 K and 0.1 MPa and over a range of ionic strengths from 0.1 to 19.2 mol·kg^{-1}. The present results are in excellent agreement with previously published data for the NaCl–H_2O binary and are in very good agreement with the more precise of the available data for the $CaCl_2$–H_2O binary at 298.15 K. Very large discrepancies between the results of the three most recent reports of densities for the $CaCl_2$–H_2O system at 308.15 K are resolved here, improving both the accuracy and precision for this system. Most significantly, the results reported here substantially expand the volumetric data base for ternary solutions. On the basis of the results of this study, most of the previously reported 308.15 K density data in the ternary system appear to contain large errors. We have evaluated the data within the framework of the Pitzer formalism and obtain new values for the ion interaction and mixing parameters for this ternary system. In addition to the parameters determined from the binary end-member solutions, it was found that only θ^{v}_{NaCa} was needed to represent the ternary results.

Introduction

Data on the physical properties of the ternary system NaCl–$CaCl_2$–H_2O are of particular importance in the processing and disposal of brines produced from industrial processes, chemical manufacture, and petroleum and geothermal reservoirs. In order to satisfy the need for this data, we have begun a program to determine the volumetric and phase equilibrium properties for this system over a wide range of pressures and temperatures. In this work densities in the ternary system NaCl–$CaCl_2$–H_2O were measured at 298.15 and 308.15 K over the range of ionic strengths 0.1–19.2 mol·kg^{-1} by using a vibrating-tube densimeter. In succeeding papers, experimental investigations of this system will be extended to substantially higher pressures and temperatures using a combination of vibrating-tube densimetry and synthetic fluid inclusion techniques.

The present work was undertaken to provide an accurate means of analysis of the compositions of NaCl–$CaCl_2$–H_2O solutions in equilibrium with ice for the first paper in this series (*1*). The only prior density determinations for this system were made by Kumar et al. (*2*) and Kumar and Atkinson (*3*) to maximum ionic strengths of 20.0 mol·kg^{-1} at 298.15 K and 5 mol·kg^{-1} at 308.15 K. Monnin (*4*) has shown that these two works (*2*, *3*) are of low precision and that the 308.15 K $CaCl_2$–H_2O data are inaccurate.

Density measurements were made over a range of ionic strengths (I) from 0.10 to 19.2 mol·kg^{-1} along the two binaries and five pseudobinaries (i.e. lines of constant ionic strength fraction; $y_B = 3m\,CaCl_2/\{3m\,CaCl_2 + m\,NaCl\}$). The data have been modeled within the framework of the Pitzer ion-interaction formalism. From this approach we can evaluate the effects of mixing of charge types at high ionic strengths, i.e., determine the magnitude of the mixing parameters θ^{v}_{NaCa} and ψ^{v}_{NaCaCl}.

Experimental Method

Binary stock solutions were prepared from distilled, deionized water and reagent grade NaCl(aq) and $CaCl_2$(aq) (Fisher Scientific and Baker). With the exception of the $y_B = 0.8$ stock, pseudobinary stocks were prepared by mixing measured masses of 3.6685 mol·kg^{-1} $CaCl_2$(aq) and 5.1339 mol·kg^{-1} NaCl(aq) solutions. The $y_B = 0.8$ stock solution was prepared by adding anhydrous NaCl and water to a 6.4110 mol·kg^{-1} $CaCl_2$–H_2O stock solution. Small (15-cm^3) aliquots for the density determinations were prepared by weight dilution of the concentrated binary and pseudobinary stocks. Some of the NaCl(aq) samples were prepared in the 15-cm^3 sample bottles by mixing known masses of water and anhydrous NaCl. The compositions of the binary stocks were determined by mass difference between aliquots of solution and the masses of anhydrous salt residue after drying. The 6.4110 mol·kg^{-1} $CaCl_2$(aq) stock was used to extend the range of compositions for the $y_B = 1.0$ binary to $I = 19.2$ mol·kg^{-1}. All solution compositions were corrected to masses under vacuum.

Relative densities were measured with a vibrating-tube densimeter (Paar DMA60 and 602HP remote cell with a borosilicate-glass tube) at nominal temperatures of 298 and 308 K. The densimeter tube was thermostated with a refrigerated circulating bath. Sample bottles (15-cm^3 high-density polyethylene) were stored in the thermostat for a minimum of 2 h before being introduced into the vibrating tube. The temperature of the tube ranged from 298.15 to 298.24 K and from 308.12 to 308.15 K over the course of the experiments. No detectable error was introduced by temperature drift (always $\leq$0.004 K·h^{-1}). The temperatures of the circulating bath and U-tube were monitored with separate resistance bridges and platinum resistance thermometers accurate within 0.01 K.

The U-tube's vibrational frequency during any given run was read to ±1 ppm. Agreement between period measurements of the same sample run on different dates was usually within 40 ppm; however, disagreements as large as 200 ppm were noted for some samples. The larger of these errors was probably due to contamination, while the lower value appears to represent the real limit on the reproducibility of these measurements. It was found that successive measurements on different aliquots of the same sample gave average periods for each measurement larger than the preceding one, with no indication that a limit was being approached. The cause of this phenomenon is uncertain but may be due to adsorption of salt on the walls of the U-tube or evaporation of solution near the end of the sampling capillary. In any case, the problem was minimized by running samples in the direction of increasing dilution and by flushing the tube with 1 tube volume of sample (preceded by a small plug of air) prior to recording the period. This was repeated for each sample until the average period passed through a minimum (usually requiring three analyses for any solution composition). The minimum average period was

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† Virginia Polytechnic Institute and State University.
‡ Oak Ridge National Laboratory.

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used to determine the density of the sample. The period of vibration (τ) of a fluid-filled tube can be converted to density (ρ) through

$$\rho = A(\tau^2 - B) \qquad (1)$$

where A and B are instrument constants dependent on the U-tube mass, volume, and spring constant. The constant A is determined through

$$A = (\tau_1{}^2 - \tau_2{}^2)/(\rho_1 - \rho_2) \qquad (2)$$

where τ_1 and τ_2 are the vibration periods of the U-tube when filled with two fluids of known density ρ_1 and ρ_2. Distilled, deionized water and NaCl(aq) (5.552 mol·kg^{-1}) were used for the determination of constants A and B. The densities of water and the NaCl(aq) standard were calculated from the Haar et al. (*5*) equation of state and the ion-interaction treatment of Rogers and Pitzer (*6*) and Pitzer et al. (*7*), respectively. Calibrations were performed frequently, and the period measurements for water and 5.552 mol·kg^{-1} NaCl(aq) were plotted as functions of time and temperature. In both cases the relationships were linear for the small range in temperature and time over which the experiments were run. The density of each sample was determined by using the period counts of the standards for the date and temperature at which the experimental sample was run.

The NaCl(aq) standard solution was prepared separately from our experimental samples to remove one potential source of artificial bias in the NaCl–H$_2$O binary system densities.

Results and Model Equations

Densities calculated from eqs 1 and 2 were used to determine mean apparent molar volumes V_ϕ through

$$V_\phi = \frac{-1000(\rho_s - \rho_w)}{\rho_s \rho_w \sum\limits_{MX} m_{MX}} + \frac{\sum\limits_{MX} m_{MX} M_{MX}}{\rho_s \sum\limits_{MX} m_{MX}} \qquad (3)$$

where ρ_s is the experimental solution density, ρ_w is the density of water, m_{MX} is the molality of salt MX, and M_{MX} is the formula weight. Sample molalities, densities, temperatures, and values of V_ϕ are listed in Table I.

The ion-interaction model developed by Pitzer (*7*), and applied to volumetric data by Rogers and Pitzer (*6*), has been shown to describe accurately the thermodynamic properties of aqueous electrolyte systems over wide ranges of temperature, pressure, and solution composition. For this reason and for ease of comparison with earlier investigations, the results of Table I have also been modeled with this treatment.

For a solution containing salts with a common anion, the Pitzer expression for apparent molar volume is

$$V_\phi = \frac{1}{\sum\limits_{M} m_{MX}} \Bigg\{ \sum_{M} m_{MX} \bar{V}^\circ{}_{MX} + \frac{A_v I}{b} \ln(1 + bI^{1/2}) + 2RT\Big[m_X \sum_{M} (m_M B^v_{MX} + m_X m_M C^v_{MX} + m_X{}^2 m_M D^v_{MX}) + \sum_{i<j} (m_i m_j \theta^v_{ij} + \tfrac{1}{2} m_i m_j m_X \psi^v_{ijX})\Big]\Bigg\} \qquad (4)$$

A_v is the limiting slope for the apparent molar volume at 298.15 and 308.15 K as defined by Bradley and Pitzer (*8*); B^v, C^v, and D^v are the second, third, and fourth virial coefficients; θ^v_{ij} and ψ^v_{ijX} are the binary and ternary mixing parameters (e.g. i = Na$^+$, j = Ca^{2+}, X = Cl$^-$), respectively; m_{MX}, m_M, and m_X are the molalities of salt MX, cations M, and anions X; $\bar{V}^\circ{}_{MX}$ is the partial molar volume of salt MX at infinite dilution; R = 83.1441 cm^3·bar·mol^{-1}·K^{-1}; and T is the absolute temperature (K). The value of b is 1.2 kg$^{1/2}$·mol$^{-1/2}$. The volumetric second virial coefficient is given by

$$B^v_{MX} = \beta^{(0)v}_{MX} + 2\beta^{(1)v}_{MX}[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \qquad (5)$$

where α = 2.0 kg$^{1/2}$·mol$^{-1/2}$, $\beta^{(0)v}_{MX} = (\partial \beta^{(0)}_{MX}/\partial p)_T$, and $\beta^{(1)v}_{MX} = (\partial \beta^{(1)}_{MX}/\partial p)_T$. The third and fourth virial coefficients are defined as $C^v_{MX} = {}^1/_2(\partial C^\varphi/\partial p)_T$ and $D^v_{MX} = {}^1/_2(\partial D^\varphi/\partial p)_T$ where C^φ and D^φ are the third and fourth virial parameters for the osmotic coefficient.

The data were fit to eq 4 at 298.15 and 308.15 K by using a linear least-squares regression technique. Initial attempts to fit the data through only the third virial coefficient were unsatisfactory; however, inclusion of the fourth virial coefficient for CaCl$_2$ improved the fit dramatically. The ternary mixing parameter (Ψ^v_{NaCaCl}) was not statistically defined, leaving only θ^v_{NaCa} to be determined from the ternary solution results. The B^v_{NaCl} coefficient includes only the $\beta^{(0)v}$ interaction parameter ($\beta^{(1)v}_{NaCl} = 0$), while the $B^v_{CaCl_2}$ coefficient includes both $\beta^{(0)v}$ and $\beta^{(1)v}$. The fitted values of $\bar{V}^\circ{}_{MX}$, the virial coefficients, and the binary mixing parameter (θ^v_{NaCa}) are listed in Table II.

Though the data were not obtained under strictly isothermal conditions at 298.15 and 308.15 K, the errors introduced in ρ and V_ϕ by modeling the data on an isothermal basis are very small. For example, the largest temperature deviation from 298.15 K was 0.09 K, noted along the NaCl–H$_2$O binary. With use of the fit by Rogers and Pitzer (*6*) for the NaCl–H$_2$O binary as a standard, these temperature deviations introduce errors in V_ϕ generally less than 0.04 cm^3·mol^{-1}, while the largest error in ρ is only 129 ppm (at 5.258 mol·kg^{-1}). The mean deviation of our data from Rogers and Pitzer (*6*) is 0.02 cm^3·mol^{-1} in V_ϕ and −19 ppm in ρ. Because most of our data differ from 298.15 or 308.15 K by less than 0.04 K and the interlaboratory precision of density measurements (Figures 1–4) is usually worse than the precision shown in Figure 5 and 6, we consider

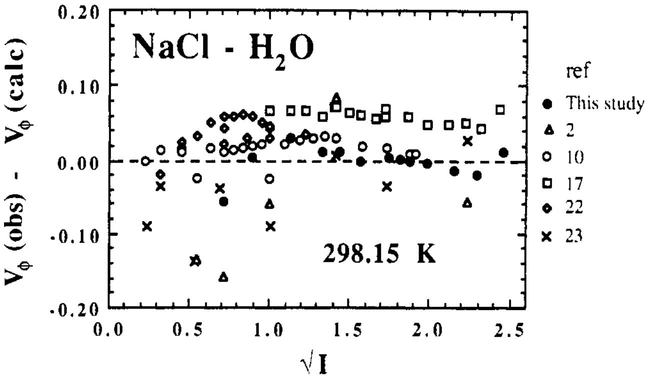

Figure 1. Residual apparent molar volumes at 298.15 K for the NaCl–H$_2$O binary from previously published studies compared to the results of this study.

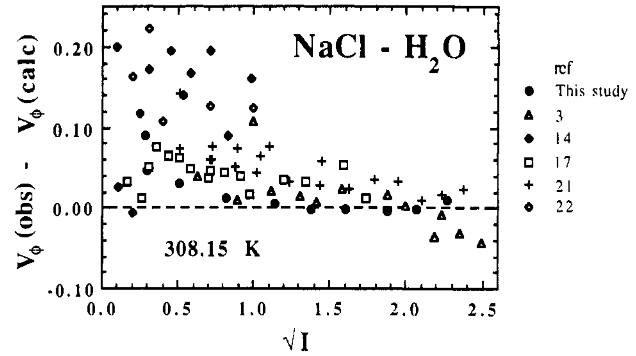

Figure 2. Residual apparent molar volumes at 308.15 K for the NaCl–H$_2$O binary from previously published studies compared to the results of this study.

Table I. Experimental Densities ρ and Mean Apparent Molar Volumes V_ϕ of Aqueous Solutions of NaCl and $CaCl_2$ at Ionic Strength I and Ionic Fraction y_B

I, mol·kg^{-1}	T, K	ρ, g·cm^{-3}	V_ϕ,[a] cm^3·mol^{-1}	I, mol·kg^{-1}	T, K	ρ, g·cm^{-3}	V_ϕ,[a] cm^3·mol^{-1}
298 K							
y_B = 0.0000							
6.0398	298.234	1.195 285	21.352	2.4718	298.226	1.088 403	19.636
5.2576	298.228	1.173 879	21.048	2.0564	298.228	1.074 233	19.357
4.6308	298.230	1.155 881	20.798	1.7533	298.228	1.063 639	19.128
3.9459	298.229	1.135 448	20.448	1.2656	298.239	1.046 051	18.738
3.5342	298.228	1.122 758	20.277	0.7974	298.242	1.028 575	18.254
3.2809	298.229	1.114 787	20.137	0.5042	298.226	1.017 296	17.845
3.0416	298.229	1.107 129	19.999				
y_B = 0.2883							
6.3863	298.180	1.195 040	21.926	2.1330	298.178	1.071 922	19.697
5.5927	298.181	1.174 149	21.614	1.6677	298.179	1.056 517	19.331
5.0532	298.183	1.159 437	21.385	1.3804	298.175	1.046 783	19.073
4.6782	298.176	1.149 008	21.205	1.0063	298.174	1.033 818	18.702
4.0540	298.176	1.131 114	20.896	0.5908	298.172	1.019 000	18.230
3.4272	298.176	1.112 520	20.551	0.3930	298.175	1.011 778	17.965
2.8633	298.176	1.095 215	20.205	0.1918	298.175	1.004 331	17.524
2.3792	298.178	1.079 880	19.882	0.1235	298.174	1.001 754	17.412
y_B = 0.5199							
7.1045	298.167	1.204 214	22.937	1.7857	298.165	1.056 753	19.935
6.6843	298.169	1.193 830	22.776	1.5466	298.162	1.049 143	19.713
6.4650	298.167	1.188 374	22.682	1.2583	298.156	1.039 829	19.435
5.7282	298.169	1.169 530	22.369	1.0734	298.157	1.033 765	19.236
5.1163	298.169	1.153 422	22.079	0.8492	298.158	1.026 321	18.991
4.5642	298.167	1.138 497	21.794	0.6340	298.157	1.019 072	18.736
3.8781	298.169	1.119 374	21.409	0.4198	298.157	1.011 767	18.411
3.3450	298.167	1.104 405	20.932	0.2095	298.157	1.004 473	17.996
2.7820	298.165	1.087 436	20.700	0.2082	298.157	1.004 429	17.986
2.2781	298.166	1.072 125	20.331	0.1038	298.154	1.000 758	17.676
y_B = 0.7091							
8.2580	298.169	1.223 809	24.322	2.0531	298.162	1.061 862	20.680
7.3979	298.170	1.203 750	23.967	1.5325	298.163	1.046 103	20.186
6.7933	298.171	1.189 243	23.698	1.2083	298.163	1.036 094	19.828
5.9260	298.162	1.167 816	23.279	0.9934	298.165	1.029 357	19.574
5.1992	298.163	1.149 273	22.890	0.7302	298.165	1.020 997	19.228
4.5099	298.162	1.131 150	22.490	0.4704	298.165	1.012 622	18.817
3.7260	298.162	1.109 895	21.977	0.2385	298.163	1.005 015	18.468
3.2238	298.160	1.095 869	21.622	0.1301	298.165	1.001 436	17.849
2.6386	298.163	1.079 111	21.172				
y_B = 0.8669							
8.9201	298.184	1.231 121	26.041	2.4788	298.166	1.071 020	21.952
8.6079	298.184	1.224 219	25.897	2.0002	298.167	1.057 408	21.483
7.5355	298.167	1.199 892	25.379	1.7009	298.161	1.048 736	21.186
6.7849	298.167	1.182 309	24.980	1.4085	298.161	1.040 175	20.837
6.0131	298.166	1.163 702	24.542	1.1060	298.161	1.031 170	20.487
5.1203	298.167	1.141 489	23.991	0.8295	298.156	1.022 845	20.089
4.3846	298.166	1.122 606	23.492	0.5388	298.160	1.013 958	19.611
3.6734	298.167	1.103 845	22.951	0.2737	298.161	1.005 734	18.987
2.9477	298.167	1.084 097	22.367	0.1256	298.161	1.001 067	18.564
y_B = 0.8860							
9.7363	298.161	1.247 823	26.642	6.5234	298.167	1.175 222	25.044
9.0446	298.174	1.232 868	26.336	6.1709	298.158	1.166 746	24.835
8.0992	298.172	1.211 856	25.885	5.7768	298.161	1.157 127	24.595
7.4755	298.167	1.197 600	25.568				
y_B = 1.0000							
19.2372	298.156	1.408 609	33.093	5.3034	298.194	1.140 986	25.699
17.9940	298.154	1.390 500	32.503	4.5702	298.196	1.122 791	25.115
16.5597	298.154	1.368 145	31.838	3.8247	298.197	1.103 786	24.474
15.2697	298.206	1.346 842	31.227	3.0576	298.198	1.083 655	23.770
15.1962	298.154	1.345 565	31.199	2.9967	298.198	1.082 038	23.705
13.9218	298.153	1.323 188	30.608	2.7246	298.197	1.074 758	23.416
12.1749	298.210	1.290 633	29.774	2.0073	298.171	1.055 126	22.689
11.1663	298.211	1.270 848	29.276	1.4469	298.176	1.039 461	21.934
9.6855	298.197	1.240 461	28.510	1.0797	298.181	1.028 982	21.386
7.7967	298.198	1.199 415	27.420	1.0110	298.181	1.026 992	21.307
7.5012	298.201	1.192 751	27.234	0.5355	298.184	1.013 130	20.383
7.2336	298.192	1.186 651	27.066	0.4305	298.184	1.010 020	20.153
5.8452	298.194	1.154 126	26.104				

Table I (Continued)

I, mol·kg^{-1}	T, K	ρ, g·cm^{-3}	V_ϕ,^{a} cm^3·mol^{-1}	I, mol·kg^{-1}	T, K	ρ, g·cm^{-3}	V_ϕ,^{a} cm^3·mol^{-1}
308 K							
y_B = 0.0000							
5.1339	308.124	1.165 082	21.395	1.2931	308.120	1.043 229	19.340
4.2755	308.124	1.140 383	21.053	0.6693	308.120	1.020 187	18.765
3.5039	308.122	1.117 048	20.703	0.2617	308.120	1.004 479	18.237
2.5694	308.120	1.087 200	20.206	0.0879	308.120	0.997 590	17.903
1.9075	308.120	1.064 897	19.790	0.0844	308.120	0.997 446	17.868
y_B = 0.2883							
6.3863	308.136	1.189 878	22.274	1.0063	308.138	1.030 228	19.318
5.0532	308.136	1.154 445	21.794	0.3930	308.136	1.008 508	18.669
3.4272	308.136	1.107 995	21.014	0.1235	308.136	0.998 634	18.334
2.1330	308.136	1.067 866	20.215				
y_B = 0.5199							
7.1045	308.131	1.198 988	23.323	1.2583	308.129	1.036 229	20.041
5.1163	308.129	1.148 682	22.503	0.8492	308.129	1.022 901	19.635
4.5642	308.128	1.133 875	22.235	0.4198	308.131	1.008 539	19.068
2.7820	308.131	1.083 302	21.205	0.1038	308.129	0.997 680	18.410
y_B = 0.7091							
8.2580	308.128	1.218 603	24.711	1.5324	308.128	1.042 513	20.759
5.9260	308.131	1.163 107	23.697	0.4704	308.126	1.009 422	19.419
3.7260	308.124	1.105 700	22.446	0.2386	308.126	1.001 909	19.027
y_B = 0.8669							
8.9201	308.132	1.225 849	26.491	2.4788	308.132	1.067 258	22.496
6.7849	308.133	1.177 623	25.408	1.1060	308.131	1.027 810	21.046
4.3846	308.132	1.118 388	23.978	0.2737	308.129	1.002 617	19.651
y_B = 0.8860							
9.7363	308.124	1.242 354	27.103	6.5234	308.127	1.170 626	25.476
9.0446	308.124	1.227 817	26.737	6.1709	308.126	1.152 687	25.035*
8.0992	308.126	1.206 955	26.300				
y_B = 1.0000							
19.2372	308.153	1.402 105	33.495	5.3034	308.144	1.136 814	26.153
17.9940	308.145	1.384 147	32.910	4.5420	308.147	1.117 994	25.595
15.1962	308.146	1.339 614	31.614	2.9967	308.141	1.078 330	24.194
13.9218	308.154	1.317 430	31.027	1.7850	308.142	1.045 452	23.001
11.0055	308.153	1.262 402	29.617	1.0110	308.141	1.023 715	21.863
10.5171	308.149	1.252 542	29.381	0.2820	308.140	1.002 475	20.596
7.6215	308.144	1.190 797	27.770				

[a] The datum masked by an asterisk was excluded from the final fit.

Table II. Fitting Parameters for the Mean Apparent Molar Volume of Aqueous Solutions of NaCl and $CaCl_2$ at 298.15 and 308.15 K and at 0.1 MPa[a]

T, K	$\bar{V}^\circ_{NaCl}$, cm^3·mol^{-1}	$\bar{V}^\circ_{CaCl_2}$, cm^3·mol^{-1}	$10^5\beta^{(0)v}_{NaCl}$, kg·mol^{-1}·MPa^{-1}	$10^5\beta^{(0)v}_{CaCl_2}$, kg·mol^{-1}·MPa^{-1}	$10^5\beta^{(1)v}_{CaCl_2}$, kg·mol^{-1}·MPa^{-1}	$10^7C^v_{NaCl}$, kg^2·mol^{-2}·MPa^{-1}	$10^6C^v_{CaCl_2}$, kg^2·mol^{-2}·MPa^{-1}	$10^8D^v_{CaCl_2}$, kg^3·mol^{-3}·MPa^{-1}	$10^6\theta^v_{NaCa}$, kg·mol^{-1}·MPa^{-1}
298.15	16.6299	17.5302	1.271 96	1.981 78	−5.998 66	−6.883 50	−1.070 32	3.902 70	−2.108 94
308.15	17.2575	18.1570	0.977 85	1.737 67	−8.903 12	−5.121 91	−0.902 795	3.351 60	−1.025 26

[a] From eq 4: I = 0–19.2m.

the errors in V_ϕ and ρ from the temperature variations in our experiment as insignificant.

The regressed data from this study are presented as residuals $\{V_\phi(\text{obs}) - V_\phi(\text{calc})\}$ in Figures 5 and 6. As shown in these figures, most of the present results are represented within ±0.05 cm^3·mol^{-1}, corresponding to a maximum uncertainty in ρ of approximately 400 ppm. Only samples with $I < 1.0$ mol·kg^{-1} show fit deviations greater than ±0.10 cm^3·mol^{-1}, and these were given reduced weights in the fitting routine. The maximum deviations of V_ϕ from eq 4 are −0.24 cm^3·mol^{-1} at 298.15 K and 0.20 cm^3·mol^{-1} at 308.15 K. The standard deviations of the fits are 0.056 and 0.061 cm^3·mol^{-1} at 298.15 and 308.15 K, respectively.

Comparison with Previous Studies

Several investigations of the volumetric properties of binary aqueous solutions of NaCl and $CaCl_2$ have been made at 298.15 K for concentrations to saturation. References to these studies and evaluations of the data are presented by Rogers and Pitzer (*6*), Monnin (*4*), and Majer et al. (*9*). In contrast, densities for $NaCl–CaCl_2–H_2O$ solutions have been measured

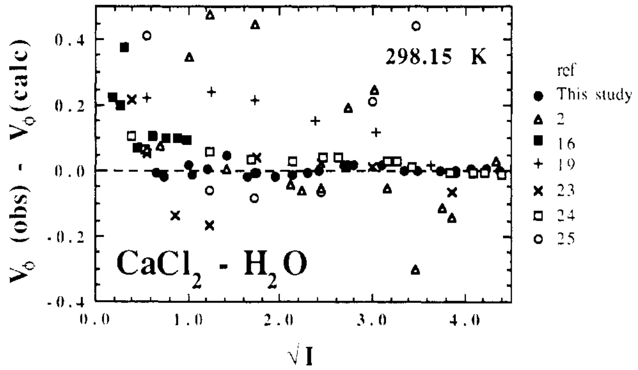

Figure 3. Residual apparent molar volumes at 298.15 K for the $CaCl_2–H_2O$ binary from previously published studies compared to the results of this study.

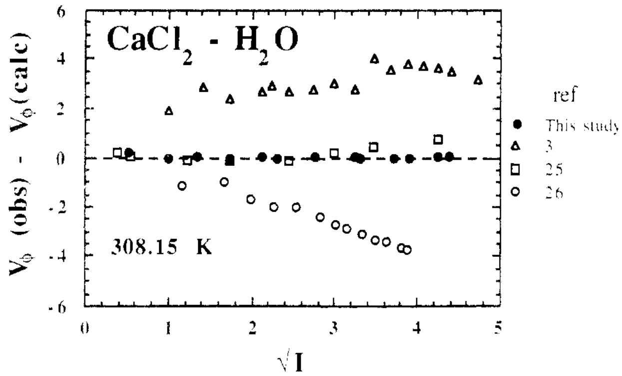

Figure 4. Apparent molar volumes at 308.15 K for the $CaCl_2$–H_2O binary from previously published studies compared to the results of this study. Note that the scale of the vertical axis is an order of magnitude greater than that in Figure 3. Two data points from ref 25 and three from ref 3 plot off of the figure.

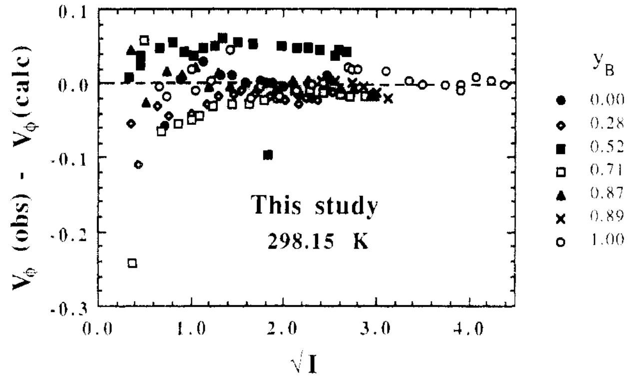

Figure 5. Residual apparent molar volumes from this study at 298.15 K $\{V_\phi(\mathrm{obs}) - V_\phi(\mathrm{calc})\}$ along constant y_B pseudobinaries in the system $NaCl$–$CaCl_2$–H_2O plotted against $\sqrt{I}$. $V_\phi(\mathrm{calc})$ was obtained from eq 4.

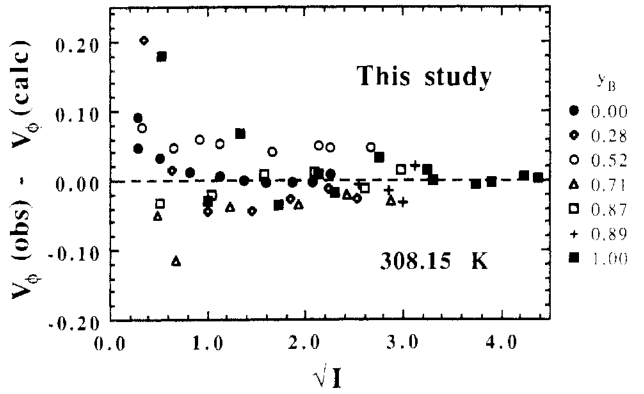

Figure 6. Residual apparent molar volumes from this study at 308.15 K along constant y_B pseudobinaries in the system $NaCl$–$CaCl_2$–H_2O plotted against $\sqrt{I}$.

only by Kumar et al. (*2*) and Kumar and Atkinson (*3*) at 278.15–308.15 K and 0.1 MPa.

NaCl–H₂O. Figures 1 and 2 show our results and the results of several previous studies compared to V_ϕ values determined from eq 4. At 298.15 K our results (Figure 1) are in excellent agreement with those of Vaslow (*10*) and in fairly good agreement with most of the available data at $I > 1.0$ mol·kg^{-1}. The largest discrepancy between our 298.15 K results and the previously published data are at $I < 1.0$ mol·kg^{-1}; as noted in text above, these samples carried less weight in the fit of eq 4. As will be subsequently shown, the agreement between sets of available results for this system at 298.15 K is better than generally observed for other aqueous electrolytes.

Table III. Comparison of the Partial Molar Volumes (cm³·mol⁻¹) of NaCl and CaCl₂ at Infinite Dilution

$\bar{V}^\circ_{\mathrm{NaCl}}$		$\bar{V}^\circ_{\mathrm{CaCl_2}}$		
298 K	308 K	298 K	308 K	ref
16.63	17.26	17.53	18.16	this study
16.72		18.86		2
16.58	17.30	18.53	19.50	3
		17.42	17.79	4
16.68	17.26			6
16.63				10
		17.78		11
16.61				12
16.61	17.16	17.84	18.32	13
16.62	17.28			14
16.62				15
		17.65		16
	17.30			17
		16.1		18
		17.2		19
		18.05		20
16.68	17.29			21

Our 308.15 K results (Figure 2) are also in excellent agreement with previously published data for concentrations at $I > 1.0$ mol·kg^{-1}, and again the interlaboratory precision is good for $I > 1.0$ mol·kg^{-1}. Conversely, both the intra- and interlaboratory results at $I < 1.0$ mol·kg^{-1} have much lower precision. The bulk of the data, however, appear to suggest that there is a positive tail that converges to values derived from eq 4 as salinity increases. This would seem to imply that the $\bar{V}^\circ_{\mathrm{NaCl}}$ value fitted to eq 4 is too low, but Table III indicates that $\bar{V}^\circ_{\mathrm{NaCl}}$ determined from this study is in good agreement with most of the previously published values.

At both temperatures the data from the present study were initially fit by using $\bar{V}^\circ_{\mathrm{NaCl}}$, $\beta^{(0)V}_{\mathrm{NaCl}}$, and C^V_{NaCl} from Rogers and Pitzer (*6*); however, the fit was slightly improved by allowing these parameters to float.

CaCl₂–H₂O. Though the 298.15 K data (Figure 3) are much better than those at 308.15 K (Figure 4), the intra- and interlaboratory precision for this system at both temperatures is much worse than for the $NaCl$–H_2O binary. At 298.15 K our data and those of Perron et al. (*24*) are in excellent agreement at $I > 1.0$ mol·kg^{-1}. Though the data of Gates and Wood (*23*) are less precise, their data also agree very well. The data of Kumar et al. (*2*), Isono (*25*), and Alekhin (*19*), conversely, are of low precision and show substantial differences with our results.

Similarly to the behavior observed in the $NaCl$–H_2O binary, the data of Perron et al. (*16*, *24*) and Gates and Wood (*23*) imply that our 298.15 K $\bar{V}^\circ_{\mathrm{CaCl_2}}$ value is somewhat low as compared with earlier studies. Table III shows that this may indeed be the case; however, the range of $\bar{V}^\circ_{\mathrm{CaCl_2}}$ from various laboratories is so wide that a conclusive assessment cannot be made.

In contrast to the 298.15 K data, very few data are available at 308.15 K, and where there are data, the interlaboratory agreement is extremely poor. Figure 4 shows that the deviations between our fit and the data of Romankiw and Chou (*26*) and Kumar and Atkinson (*3*) are as large as 10%. The agreement between our data and those if Isono (*25*) is much better but shows deviations from our 308.15 K results that are very similar to those at 298.15 K. The similarity in the shapes of the residual plots of Isono's 298.15 and 308.15 K data when plotted at the same scale suggests that there was a systematic difference between his results and those reported here.

NaCl–CaCl₂–H₂O. Prior to this study, density determinations for this ternary had been made in only one laboratory (*2*, *3*). Parts a and b of Figure 7 show the residuals for these two data sets plotted against ionic fraction for solutions of constant ionic strength. As noted in text above, the data of Kumar et al. (*2*) at 298.15 K have fair internal precision, and the agreement of

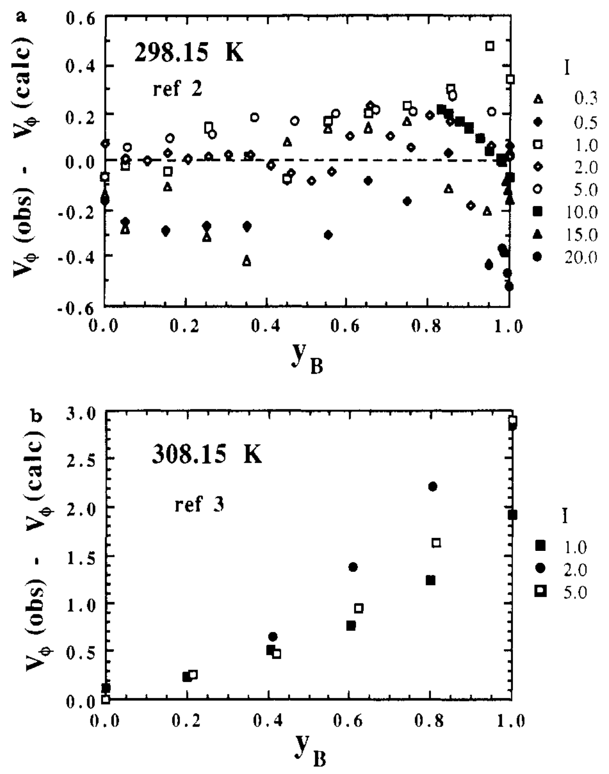

Figure 7. (a,b) Residual apparent molar volumes at 298.15 and 308.15 K, respectively, from refs 2 and 3. The data are plotted as residuals against y_B because the data were collected at constant ionic strength rather than at constant ionic fraction, as was done in this study. Again note the order of magnitude difference along the vertical axis in Figure 7b. All deviations of ref 3 from eq 4 were positive.

those results with the data from the present study is acceptable. The 308.15 K data of Kumar and Atkinson (*3*), in contrast, not only have poor internal precision but also show a strong discordance with the results of this study. The fact that their data (*3*) systematically diverge from the present results with increasing ionic strength and ionic fraction strongly suggests that there may have been substantial error in the determination of the concentration of their $CaCl_2$(aq) stock solution.

The inclusion of θ^v_{NaCa} has a significant effect on the calculated values of V_ϕ for $I > 4$ mol·kg^{-1}. Without this parameter the residuals for each pseudobinary tail away from 0.0 beginning at $I = 2.25$ mol·kg^{-1}. The inclusion of θ^v_{NaCa} improves the fit so that nearly all of the residuals are ≤ 0.05 cm^3·mol^{-1} versus residuals that are systematically negative and reach deviations of -1.0 to -1.5 cm^3·mol^{-1} at $I = 9.0$ mol·kg^{-1}.

Conclusion

Densities of aqueous solutions of NaCl and $CaCl_2$ were measured at 298.15 and 308.15 K for the range of ionic strengths up to 19.2 mol·kg^{-1}. The precision of the measurements is within 0.05 mol·kg^{-1} for V_ϕ and 250 ppm for ρ at both temperatures. The measurements are in good agreement with the more precise measurements previously made by others along both binaries. The ternary data are in acceptable agreement with the previously published data at 298.15 K; however, there are substantial differences between the results of this study and the previously published data (*3*) at 308.15 K. Because of the good agreement between the binary data of this study with the more precise of the previously published data, it is likely that the ternary results of this study are more accurate than the results of Kumar and Atkinson (*3*).

The results of the present study are accurately represented by the Pitzer ion-interaction model with the addition of $D^v_{CaCl_2}$ to the usual B^v and C^v terms for both salts. Fits of thermodynamic properties of most aqueous electrolytes using the Pitzer formalism generally do not require terms beyond the third virial coefficient. However, other fits of $CaCl_2$-bearing solutions by the Pitzer ion-interaction model have also required tertiary or higher order terms; e.g., Atkinson and Ananthaswamy (*27*) found it necessary to include terms through the sixth virial coefficient for their temperature-dependent activity and osmotic coefficient fit for the $CaCl_2$–H_2O binary.

The ternary data require only the θ^v_{NaCa} term, implying that ternary mixing interactions are insignificant to the volumetric properties of this system at these conditions.

Registry No. $CaCl_2$, 10043-52-4; NaCl, 7647-14-5.

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