Density and Apparent Molar Volume of Aqueous $CaCl_2$ at 323–600 K

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The difference in density between pure water and $CaCl_2$(aq) has been measured with a vibrating tube densimeter at molalities from 0.05 to 6.4 mol kg^{-1}, temperatures from 323 to 600 K, and pressures up to 40 MPa. The results were fitted to a cubic spline surface in three dimensions (P, T, and m). The data extend the range of experimental data for $CaCl_2$(aq) to 600 K.

Introduction

As part of a continuing investigation of the thermodynamic properties of aqueous solutions at high temperatures, a densimeter based on the vibrating tube principle was recently constructed in our laboratory (*1*). The densimeter has previously been used to measure densities of aqueous NaCl, KCl, NaBr, LiCl, $MgCl_2$, and $CaCl_2$ at 298.15 K and pressures up to 40 MPa (*2*). In this paper, we present measurements of the densities of aqueous $CaCl_2$ at temperatures from 323 to 600 K and pressures up to 40 MPa.

Experimental Section

The densimeter has been described in detail elsewhere (*1*–*3*). It is a vibrating U-tube type densimeter which is used to measure the differences in density between an aqueous solution and pure water at a given temperature and pressure. In this experiment, the change in density Δd is given by

$$\Delta d = d - d_o = K(\tau^2 - \tau_o^2) \tag{1}$$

where the subscript o refers to pure water (the reference fluid), τ is the period of vibration of the U tube, and K is a calibration constant determined at each temperature. In a typical experiment degassed, distilled deionized water was pumped through the densimeter at 0.75 cm^3 min^{-1} to establish a reference base line. A Rheodyne 7010 HPLC injection valve was employed to introduce a 6-mL sample of solution into the flowing stream. As the sample passed through the instrument, a sample plateau was measured, which was followed by a return to the water base line. The average of the two water base lines was used in calculating the density differences. The temperature of the densimeter block was maintained constant to 0.001 K and was measured by a Burns Engineering platinum resistance thermometer, Model XPPOG5-2-5B, and an ESI Model PVD300 Kelvin bridge with a rated accuracy of 0.02%. The accuracy of the temperature measured in this fashion was estimated to be ±0.08 K at 300 K and ±0.3 K at 600 K. The system pressure was maintained with a Circle Seal BPR21 series back-pressure regulator and monitored with an in-line McDaniel 0.25% test gauge with an accuracy of 0.3 MPa.

At each temperature, the system was calibrated with water and nitrogen (*1*). Since the dependence of the calibration constant on pressure has previously been shown to be negligible (*1*), calibrations were performed with nitrogen at low pressure and water at high pressure.

Solutions were prepared with Fisher Scientific Co. ACS-certified calcium chloride dihydrate, lot no. 730805. A stock solution was prepared from which all final solutions were prepared by careful mass dilutions. The stock solution was determined gravimetrically to 0.2%. As a check, the densities of the $CaCl_2$ solutions were measured at 298.15 K and atmospheric pressure. The molalities calculated from the densities given by Perron, Roux, and Desnoyers (*4*) agreed within 0.2%.

Results and Discussion

Table I gives the results of the present measurements of relative densities. The precision of the experiments estimated by the reproducibility of the duplicate measurement is better than 0.050 kg m^{-3} at 450 K and below. At 550 K the precision is somewhat worse, and at 600 K the precision is much worse. At 600 K the densimeter block temperature was perturbed by the most concentrated $CaCl_2$ solutions. The perturbations became so dramatic at the highest pressure that the runs could not be performed. Upon cooling, a small leak was discovered near the heat exchanger. Such a leak could explain the problem of block control since the heat of vaporization of pure water and concentrated $CaCl_2$(aq) are quite different. Although the precision of the low concentration $CaCl_2$ data seem to be unaffected by the leak, the accuracy of the $CaCl_2$ data should be considered to be on the order of 1.0 kg m^{-3} at 600 K and 38 MPa.

The values of Δd in Table I were fit to a three-dimensional cubic spline surface in the same way that we have previously fit a three-dimensional apparent molar heat capacity surface in three dimensions (*3*, *5*). The knot values and positions for the cubic spline surface of Δd are given in Table II. From these knot values, successive spline interpolation in each of the three dimensions (m, T, and P) gives the value of Δd at any T, P, and m within the range of the experimental data. The values of the knots in Table II were found by using a nonlinear least-squares routine to adjust the knots to the values giving a minimum in the sum of the squares of the differences between the calculated and experimental values of Δd. At zero molality Δd was constrained to be zero and the second derivative end conditions were also varied in order to give a minimum in the sum of the squares of the errors. The end conditions are also given in Table II. It was found that the concentration dependence could be represented by four knots at 0, 0.1, 1.5, and 6.45 mol kg^{-1}, together with a second derivative end condition at the most concentrated knot. Increasing the number of concentration knots did not significantly improve the fit.

The temperature dependence was found to be adequately represented by four equally spaced knots with second derivative end conditions included. The data of Gates and Wood (*2*) at 298 K were included in the fit to extend the low-temperature range. The pressure dependence was represented by just two knots, implying a linear pressure dependence. This assumption of linearity in pressure is accurate below 500 K. However, at 550 K, Δd for $CaCl_2$ exhibits a noticeable curvature versus pressure, and errors on the order of 0.8 kg m^{-3} occur as seen

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Table I. Values of the Difference in Density, Δd, for Aqueous $CaCl_2$ at Various Temperatures, Pressures, and Molalities

P/MPa	m/(mol kg^{-1})	Δd/(kg m^{-3})	δ^a/(kg m^{-3})	P/MPa	m/(mol kg^{-1})	Δd/(kg m^{-3})	δ^a/(kg m^{-3})
T = 323.16 K							
0.101	6.4244	403.17	0.058	20.370	6.4244	401.16	0.030
0.101	6.4244	402.95	0.275	20.370	6.4244	401.20	−0.013
0.101	5.0100	338.34	−0.023	20.240	5.0100	336.37	0.087
0.101	5.0100	338.38	−0.066	20.240	5.0100	336.37	0.083
0.101	3.1970	235.47	0.247	20.240	3.1970	233.87	0.349
0.101	3.1970	235.49	0.222	20.170	3.1970	233.89	0.333
0.101	1.0240	85.32	−0.061	20.170	1.0240	84.58	0.000
0.101	1.0240	85.27	−0.061	20.240	1.0240	84.56	0.025
0.101	1.0240	85.27	−0.008	20.240	1.0240	84.58	0.000
0.101	0.5246	44.92	0.157	20.240	0.5246	44.52	0.172
0.101	0.5246	44.89	0.179	20.170	0.5246	44.52	0.176
0.101	0.2722	23.78	0.078	20.170	0.2722	23.58	0.076
0.101	0.2722	23.78	0.079	20.170	0.2722	23.58	0.076
0.101	0.1014	8.98	0.019	20.170	0.1014	8.90	0.022
0.101	0.1014	8.97	0.029	20.170	0.1014	8.90	0.019
0.101	0.0497	4.43	−0.008	20.240	0.0497	4.42	−0.037
0.101	0.0497	4.46	−0.040	20.240	0.0497	4.41	−0.029
T = 323.05 K							
37.540	6.4244	399.42	0.070	37.470	0.5246	44.25	0.111
37.540	6.4244	399.42	0.070	37.470	0.5246	44.26	0.104
37.540	5.0100	334.91	−0.040	37.470	0.2722	23.34	0.128
37.540	5.0100	334.93	−0.054	37.470	0.2722	23.43	0.042
37.540	3.1970	232.58	0.356	37.470	0.1014	8.80	0.049
37.470	3.1970	232.57	0.376	37.470	0.1014	8.80	0.049
37.470	1.0240	84.14	−0.130	37.470	0.0497	4.35	−0.003
37.470	1.0240	84.08	−0.078	37.470	0.0497	4.35	−0.006
T = 349.16 K							
1.000	6.4244	399.39	−0.024	20.310	1.0240	84.51	−0.177
1.000	6.4244	399.46	−0.095	20.310	0.5246	44.53	0.106
1.000	5.0100	335.68	−0.049	20.310	0.5246	44.64	−0.005
1.000	5.0100	335.66	−0.031	20.310	0.2722	23.63	0.018
1.000	3.1970	234.37	−0.129	20.310	0.2722	23.67	−0.023
1.000	3.1970	234.40	−0.157	20.310	0.1014	9.06	−0.132
1.000	1.0240	85.27	−0.288	20.310	0.1014	8.91	0.012
1.000	1.0240	85.25	−0.267	20.310	0.0497	4.46	−0.072
1.000	0.5246	44.95	0.048	39.890	6.4244	395.60	0.080
1.000	0.5246	44.95	0.052	39.890	6.4244	395.65	0.026
1.000	0.2722	23.83	0.015	39.890	5.0100	332.05	−0.048
1.000	0.2722	23.83	0.012	39.890	5.0100	332.05	−0.048
1.000	0.1014	9.02	−0.024	39.820	3.1970	231.46	−0.230
1.000	0.1014	9.04	−0.041	39.820	3.1970	231.44	−0.206
1.000	0.0497	4.48	−0.056	39.820	1.0240	83.90	−0.223
1.000	0.0497	4.46	−0.039	39.820	1.0240	83.89	−0.219
20.370	6.4244	397.71	−0.183	39.820	0.5246	44.15	0.131
20.310	6.4244	397.68	−0.149	39.820	0.5246	44.14	0.134
20.310	5.0100	333.95	−0.126	39.750	0.2722	23.48	−0.025
20.310	5.0100	333.97	−0.147	39.750	0.2722	23.46	−0.004
20.310	3.1970	232.98	−0.231	39.680	0.1014	8.82	0.032
20.310	3.1970	232.95	−0.210	39.680	0.0497	4.44	−0.095
20.310	1.0240	84.50	−0.162				
T = 399.85 K							
1.690	6.4244	402.74	−0.043	20.370	1.0240	87.11	0.077
1.690	6.4244	402.57	0.128	20.310	1.0240	87.01	0.180
1.690	6.4244	402.77	−0.075	20.370	0.5246	46.19	0.067
1.690	5.0100	339.46	−0.019	20.370	0.5246	46.15	0.105
1.690	5.0100	339.49	−0.047	20.370	0.2714	24.53	−0.069
1.690	3.1970	239.23	0.048	20.440	0.2714	24.58	−0.118
1.690	3.1970	239.21	0.069	20.310	0.1014	9.37	−0.102
1.690	1.0240	88.21	0.004	20.370	0.1014	9.28	−0.019
1.690	1.0240	88.22	−0.006	20.370	0.0497	4.64	−0.092
1.690	0.5246	46.75	0.094	20.310	0.0497	4.66	−0.112
1.690	0.5246	46.65	0.191	40.160	6.4244	397.12	−0.042
1.690	0.2714	24.89	−0.117	40.160	6.4244	397.12	−0.050
1.690	0.2714	24.92	−0.148	40.300	5.0100	334.32	−0.093
1.690	0.1014	9.29	0.093	40.230	5.0100	334.13	0.110
1.690	0.1014	9.43	−0.042	40.370	5.0100	334.24	−0.023
1.690	0.0497	4.45	0.163	40.440	3.1970	234.82	0.006
1.690	0.0497	4.69	−0.078	40.370	3.1970	234.75	0.090
20.170	6.4244	399.79	0.202	40.030	1.0240	86.03	0.071
20.170	6.4244	399.98	0.018	40.100	1.0240	86.09	0.008
20.370	5.0100	336.73	0.185	40.160	0.5246	45.56	0.080
20.370	5.0100	336.85	0.073	40.300	0.5246	45.53	0.111
20.370	3.1970	237.03	0.107	40.370	0.2714	24.23	−0.109
20.370	3.1970	236.98	0.151	40.510	0.2714	24.24	−0.121

Table I (Continued)

P/MPa	m/(mol kg^{-1})	Δd/(kg m^{-3})	δ^a/(kg m^{-3})	P/MPa	m/(mol kg^{-1})	Δd/(kg m^{-3})	δ^a/(kg m^{-3})
40.580	0.1014	9.29	−0.155	40.640	0.0497	4.60	−0.112
40.640	0.1014	9.21	−0.077	40.710	0.0497	4.58	−0.099
T = 450.13 K							
3.550	6.4244	415.01	0.029	3.480	0.2722	26.92	−0.070
3.550	6.4244	415.06	−0.019	3.410	0.1014	10.33	−0.156
3.550	6.4244	415.08	−0.037	3.410	0.1014	10.32	−0.152
3.550	5.0100	351.05	−0.088	3.410	0.0497	5.16	−0.162
3.550	5.0100	351.05	−0.087	3.410	0.0497	5.15	−0.155
3.550	5.0100	351.11	−0.148	11.340	5.0100	349.13	0.215
3.550	3.1970	249.94	0.045	11.340	5.0100	349.21	0.139
3.550	3.1970	249.97	0.015	11.340	1.0240	93.14	−0.062
3.550	1.0240	93.90	−0.170	11.340	1.0240	93.11	−0.035
3.550	1.0240	93.89	−0.159	11.270	0.2722	26.66	0.004
3.480	0.5246	50.20	0.222	11.270	0.2722	26.67	−0.005
3.480	0.5246	50.18	0.243	20.310	6.4244	411.07	−0.031
3.480	0.2722	26.88	−0.026	20.310	6.4244	410.53	0.502
T = 449.75 K							
20.310	6.4244	411.14	−0.223	20.440	0.1014	10.12	−0.119
20.310	6.4244	411.10	−0.183	20.440	0.1014	10.18	−0.174
20.310	5.0100	347.45	−0.071	20.440	0.0497	5.01	−0.092
20.310	5.0100	347.45	−0.067	20.440	0.0497	5.05	−0.130
20.310	3.1970	246.86	0.077	29.130	1.0240	91.69	−0.148
20.310	3.1970	246.85	0.088	29.130	1.0240	91.70	−0.159
20.310	1.0240	92.44	−0.166	29.060	5.0100	345.68	−0.092
20.310	1.0240	92.43	−0.152	29.060	5.0100	345.68	−0.094
20.310	0.5246	49.31	0.301	29.060	0.2722	26.11	0.098
20.310	0.5246	49.29	0.324	29.060	0.2722	26.07	0.132
20.440	0.2722	26.40	0.016	38.160	6.4244	406.67	−0.005
20.440	0.2722	26.35	0.070				
T = 548.05 K							
10.860	0.0497	7.22	−0.722	24.720	3.1970	282.79	0.650
10.860	0.0497	7.28	−0.784	24.720	3.1970	282.67	0.767
10.860	0.1014	13.95	−0.748	24.720	5.0100	390.98	1.067
10.860	0.1014	13.92	−0.725	24.720	5.0100	391.04	1.005
10.860	0.2722	35.06	−0.539	24.720	1.0240	110.62	0.851
10.860	0.2722	35.07	−0.546	24.720	6.4244	460.06	0.463
10.860	0.5246	63.83	0.032	24.720	6.4244	459.54	0.991
10.860	0.5246	63.84	0.025	24.720	5.0100	391.10	0.941
10.790	1.0240	116.06	0.187	37.060	0.0497	6.20	−0.330
10.860	1.0240	116.11	0.116	37.060	0.0497	6.24	−0.373
10.790	3.1970	292.92	−0.682	37.060	0.1014	12.44	−0.516
10.860	3.1970	292.93	−0.736	37.060	0.1014	12.50	−0.582
10.860	5.0100	403.23	−0.930	37.060	0.2722	31.71	−0.404
10.860	6.4244	471.94	−0.846	37.060	0.2722	31.73	−0.423
24.650	0.0497	6.62	−0.453	37.060	0.5246	58.29	−0.018
24.650	0.0497	6.57	−0.408	37.060	0.5246	58.30	−0.021
24.720	0.1014	12.93	−0.407	37.060	1.0240	107.20	0.032
24.720	0.1014	12.93	−0.410	37.060	1.0240	107.39	−0.156
24.720	0.2722	33.03	−0.210	37.400	3.1970	276.01	−0.581
24.720	0.2722	33.03	−0.213	37.400	3.1970	276.15	−0.723
24.720	0.5246	60.42	0.483	37.400	5.0100	383.36	−0.697
24.720	0.5246	60.50	0.405	37.400	5.0100	383.19	−0.530
24.720	1.0240	111.01	0.461	37.400	6.4244	451.44	−0.585
24.720	1.0240	110.89	0.576	37.400	6.4244	451.15	−0.287
T = 597.45 K							
20.650	0.0151	3.19	−0.805	20.650	6.4244	519.22	−0.448
20.650	0.0151	3.14	−0.760	20.650	6.4244	518.49	0.289
20.650	0.0497	8.69	−0.868	38.780	0.0151	2.42	−0.251
20.650	0.0497	8.60	−0.777	38.780	0.0151	2.36	−0.192
20.650	0.1014	16.77	−0.890	38.780	0.0497	7.36	−0.250
20.650	0.1014	16.75	−0.871	38.780	0.0497	7.39	−0.276
20.650	0.2722	41.84	−0.570	38.780	0.1014	14.64	−0.253
20.650	0.2722	41.92	−0.648	38.780	0.1014	14.53	−0.143
20.650	0.5246	75.50	0.101	38.850	0.2722	36.70	0.126
20.650	0.5246	75.42	0.181	38.850	0.2722	36.62	0.204
20.650	1.0240	134.61	0.527	38.920	0.5246	66.32	0.042
20.650	1.0240	134.33	0.805	38.920	0.5246	66.39	−0.030
20.650	3.1970	329.55	−1.028	38.920	1.0240	120.32	−0.068
20.650	3.1970	328.29	0.227	38.920	1.0240	120.11	0.138
20.650	5.0100	447.28	−0.264	38.920	1.0240	120.34	−0.091
20.650	5.0100	446.22	0.800				

[a] δ is the Δd calculated by cubic spline interpolation of the knots and end conditions in Table II minus the experimental Δd.

Table II. Knot Positions and Knot Values for the Cubic Spline Representation of $\Delta d/(\mathrm{kg\ m^{-3}})$ as a Function of T, P, and m[a]

$m/(\mathrm{mol\ kg^{-1}})$	*b*	T = 298.15 K	T = 400.00 K	T = 500.00 K	T = 600.00 K	*b*
			P = 20.0 MPa			
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1000	1.7	8.904	9.141	10.988	15.938	11.3
1.5000	43.2	122.305	122.823	140.370	185.180	85.4
6.4500	79.4	410.072	401.069	432.696	525.951[c]	149.5
d		−5.94	−5.95	−5.34	3.43	
			P = 40.0 MPa			
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1000	0.6	8.768	9.011	10.569	14.294	12.3
1.5000	35.9	121.089	121.362	135.734	177.966[c]	142.2
6.4500	68.3	407.377	398.138	425.948	453.164[c]	−230.1
d		−5.42	−6.02	6.64	−310	

[a] This fit is a representation of 353 data points. The sum of the squares of the residuals is 32.7, resulting in a standard error of the fit of 0.330 kg $\mathrm{m^{-3}}$. The minimum sum of the squares is 2.44. [b] These columns contain the second derivative end conditions multiplied by 10000, $(\partial^2\Delta d/\partial T^2) \times 10^4$ kg $\mathrm{m^{-3}\ K^{-2}}$. [c] Since there are no experimental results at 600 K above 3.2 mol $\mathrm{kg^{-1}}$ at 20 MPa or above 1.0 mol $\mathrm{kg^{-1}}$ at 40 MPa, the spline surface is unreliable above these molalities. [d] These rows give the second derivative end condition at m = 6.450 mol $\mathrm{kg^{-1}}$, $(\partial^2\Delta d/\partial m^2) \times 10^4$.

in Table I. Unfortunately, a measured pressure curvature at one temperature does not justify fitting with a pressure curvature at all temperatures. The data at 600 K were run at only two pressures, and thus, there is no measure of the nonlinearity at this temperature. A better pressure representation will have to await a more detailed study. The cubic spline surface is a representation of 350 data points, and the standard error of the fit is 0.33 kg $\mathrm{m^{-3}}$. The standard error of the data below 500 K is 0.16 kg $\mathrm{m^{-3}}$. The decrease in the quality of the fit above 500 K is due to the pressure dependence of Δd, together with the experimental problems at 600 K. Since at 600 K there are no experimental results above 3.2 mol $\mathrm{kg^{-1}}$ at 20 MPa or above 1.0 mol $\mathrm{kg^{-1}}$ at 40 MPa, the spline surface is unreliable above these molalities.

Ellis (*6*) has measured thermal expansions for aqueous $\mathrm{CaCl_2}$ from 323 to 473 K at 0.05–1.0 mol $\mathrm{kg^{-1}}$ at 2 MPa. The temperature dependence of Ellis' data is in excellent agreement with that calculated from our spline surface at temperatures up to and including 448 K. At 473 K the density values calculated here are 0.5 kg $\mathrm{m^{-3}}$ higher than the values of Ellis at 0.5 and 1.0 mol $\mathrm{kg^{-1}}$. This is approximately 3 times the sum of the estimated errors for both data sets. Romankiw and Chou (*7*) have measured aqueous $\mathrm{CaCl_2}$ densities using a vibrating tube densimeter at 298 to 318 K. Their results are not compatible with our measurements. The previous measurements at 298.1 K with this instrument compared well with those of Perron, Roux, and Desnoyers (*4*). Zhang and Frantz (*8*) determined homogenization temperatures for synthetic $\mathrm{CaCl_2(aq)}$ fluid inclusions at high temperature and pressure. The combination of their data with the previous measurements of Rodnyanskii et al. (*9*, *10*) of the density at the saturation pressure allows the calculation of density as a function of T and P from 300 to 700 °C. Using the equations of Zhang and Frantz (there is a misprint in their eq 21) corrected for the expansion of quartz, we can calculate densities at 326.85 °C for comparison with the present spline surface. The differences are, for m = 0.5 mol $\mathrm{kg^{-1}}$, −17 and −24 kg $\mathrm{m^{-3}}$ at 20 and 40 MPa and, for m = 1.0 mol $\mathrm{kg^{-1}}$, +1 and −9 kg $\mathrm{m^{-3}}$ at 20 and 40 MPa. These differences are within the expected accuracy of the saturation density as estimated by Potter and Clyne (*10*) (±10 kg $\mathrm{m^{-3}}$ from 250 to 300 °C with larger errors above 300 °C).

The data presented here significantly extend the range and quality of volumetric properties of aqueous $\mathrm{CaCl_2}$. These data allow the calculation of the pressure dependence of free energies, enthalpies, and heat capacities. The data at 600 K are not as accurate as can be obtained from the present instrumentation.

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