CaCl$_2$–H$_2$O in the Supercritical and Two-Phase Ranges[1]

C. S. Oakes,[2,3] R. J. Bodnar,[4] J. M. Simonson,[5] and K. S. Pitzer[2]

Critical temperatures (T_c) and densities (ρ_c) for aqueous CaCl$_2$ solutions were measured using two different optical techniques. Measurements of T_c were made using sealed silica capillaries containing 0.3, 0.5, 1.0, and 2.0 molal CaCl$_2$(aq) solutions. The T_c values from these measurements are 661, 666, 678, and 738 K, respectively. Critical temperatures were also determined from measured homogenization temperatures and the observed mode of homogenization (i.e., to the liquid or vapor phase or by fading of the meniscus) in synthetic fluid inclusions. Critical temperatures determined by the second method for 1.0, 2.0, and 3.0 molal CaCl$_2$(aq) solutions are 680, 739, and 838 K, respectively. The T_c for 4.0 molal CaCl$_2$(aq) was found to be in excess of 933 K. The capillary-tube measurements yield approximate values of the critical density ρ_c, but do not give the critical pressure P_c. Approximate values of P_c are available, however, from other sources.

KEY WORDS: aqueous solution; calcium chloride; critical line; supercritical properties.

1. INTRODUCTION

The critical properties of aqueous salt solutions are important because they provide information on the pressure and temperature limits of the region of immiscibility and because they are the thermodynamic anchor points at which equations of state must meet certain constraints (e.g., the

---

compressibility becomes infinite, etc.). The system $CaCl_2-H_2O$ is of interest practically and geologically and intrinsically as a 2–1-type electrolyte. The available sources of critical properties of $CaCl_2(aq)$ are Marshall and Jones [1], Tkachenko and Schmulovich [2], and Tkachenko [3]. Marchall and Jones [1] present critical temperature data for 0.1–1.8 molal $CaCl_2(aq)$, while Tkachenko and Schmulovich [2] graphically present liquid–vapor equilibrium data at 673, 773, and 873 K from which the respective critical pressures and molalities may be interpolated. In this paper we present new measurements of the critical temperatures for aqueous $CaCl_2$ solutions of up to 3.0 molal and estimates of the critical densities and pressures for solutions up to 2.0 and 3.0 molal, respectively.

2. MEASUREMENTS

2.1. Capillary-Tube Method

The equipment used was nearly identical to that described by Marshall et al. [4] although the method of sample preparation was modified so that more information could be obtained from the experiment. Note that the apparatus used for this study was not the same as that used by Marshall and Jones [1].

Several 50-mm segments of fused silica tubing (3 mm OD, 1 or 1.5 mm ID) were cleaned and fused at one end. A measured volume of a given solution was injected into one of the tubes with a 100-μl syringe and then centrifuged to drive any solution which had wicked up the capillary tube down to the sealed end of the tube. During injection solution tended to wick up between the syringe needle and the inner wall of the capillary, but this effect was minimized by withdrawing the syringe tip ahead of the meniscus as solution was injected. The open end of the capillary was then closed by fusing with an oxyacetylene torch. Boiling off of solution was prevented by wrapping all but the end to be sealed with a moistened paper towel. The newly sealed end was then oxyacetylene-welded to a silica rod (approximately 12 mm by 3 mm). The rod extended out of the tube furnace during the experiment and was connected to the tip of an engraving tool via a flexible rubber sleave. The solution in the capillary could then be agitated to minimize density gradients by periodically switching on the engraving tool. Before inserting the tube assembly into the furnace the total enclosed length of the capillary and the length of the solution-filled portion were measured. From these measurements and the density of the solution at 298 K, an estimate of the solution's critical density (ρ_c) could also be made. The inside diameters of each of the capillaries were assumed to be constant along their entire length. The interior length was measured from the tip of

the terminal cone of one end to the base of the terminal cone of the opposite end. The length of the liquid-filled portion was measured from the base of the meniscus to a point approximately half the distance between the base and the tip of the terminal cone. Solution densities at 298 K were taken from Oakes et al. [5].

An aluminum tube-furnace (~ 10 in. in length) wound externally with heating coils and sheathed both internally and externally with fused silica tubing was used to heat the capillaries. Once inserted into the furnace, with the long dimension perpendicular to the direction of gravity, the capillary could be observed with a low-power microscope through an elongated port machined through the aluminum tube. Heating of the sample was accomplished by radiative and conductive heat transfer. Temperature was measured with an iron-constantan thermocouple which rested on the capillary and could be moved freely along the length of the capillary to determine the magnitude of the thermal gradients in the furnace. The temperature variation along the capillary varied by as much as 3 K, which is taken as the precision of these measurements. The thermocouple was calibrated at 647 K using a capillary containing a critical volume of distilled, deionized water.

Because the inner diameters of the capillaries were small and the solutions' viscosity sufficiently high, the meniscus remained approximately parallel to the direction of gravity to temperatures nearing the critical temperature. For capillary fillings at or very near ρ_c the strength of the meniscus and viscosity decreased as T_h was approached, so that the liquid phase pooled in the bottom of the horizontally mounted capillary. Filling densities greater than ρ_c homogenized to the liquid phase and filling densities less than ρ_c homogenized to the vapor phase. Though the length of the sample made it difficult to determine whether or not there was a 1:1 volume ratio of liquid to vapor at homogenization, we estimate that the accuracy and precision of measurements made via this method are equivalent to those made using the fluid inclusion technique.

2.2. Synthetic Fluid Inclusion Method

The T_c measurements of CaCl₂(aq) were also made by the synthetic-fluid-inclusion method. This is also a bracketing technique in which solution is trapped within quartz which has been recrystallized in the presence of a fluid at hyperambient pressures and temperatures. In this case, isobaric experiments bracketed the critical isochore for a given CaCl₂(aq) molality producing fluid inclusions with varying liquid–vapor ratios at room temperture. Then T_c was determined by microthermometric analysis and observation of phase changes analogous to those described previously for

Table I. Critical Properties of CaCl$_2$(aq) Obtained from the Capillary-Tube^a Method

m (mol·kg^{-1})	Capillary length (mm)	Liquid length (mm)	ρ^a (g·cm^{-3})	T_c (K)	ρ_c (g·cm^{-3})
0.3	39.5	18.5	1.026	661	0.48$_1$
0.5	41.0	20.5	1.040	666	0.52$_0$
1.0	38.5	21.5	1.082	678	0.60$_4$
2.0	43.5	26.5	1.156	738	0.70$_4$

^{a} ρ is the solution density at 298 K; ρ_c is the critical density (uncertainties are $\geqslant 5\%$).

the capillary technique. The technique is described in detail by Bodnar and Sterner [6] and Knight and Bodnar [7] and the results for CaCl$_2$(aq) are described by Oakes et al. [8]; hence further details are omitted here.

3. RESULTS

The T_c for 0.3, 0.5, 1.0, and 2.0 mol·kg^{-1} CaCl$_2$(aq) solutions was measured using the capillary-tube technique, while T_c for solutions of 0.5, 1.0, 2.0, and 3.0 mol·kg^{-1} was measured using the synthetic-fluid-inclusion technique. Attempts at measuring T_c for 2.6 and 4.0 mol·kg^{-1} solutions were made using the capillary and synthetic-fluid-inclusion techniques, respectively. In the former experiments the capillary tubes could not withstand the internal pressures, and in the latter case T_c exceeded the upper operating limit of the fluid inclusion heating stage (i.e., $T_c > 973$ K).

The T_c measurements made using the capillary technique are shown in Table I along with the relevant tube and liquid lengths, solution densities at 298 K (ρ^a), and ρ_c estimates based on these measurements. The uncertainty of ρ_c is estimated to be at least $\pm 5\%$. Estimates of T_c and the associated uncertainties based on the synthetic-fluid-inclusion measurements are shown in Table II.

Table II. T_c Estimates Based on the Synthetic-Fluid-Inclusion Data

m CaCl$_2$ (mol·kg^{-1})	T_c (K)
0.5	668 ± 10
1.0	679 ± 3
2.0	739 ± 7
3.0	838 ± 20
4.0	>935

4. DISCUSSION

   Figure 1 shows the T_c data from this study, values interpolated from the liquid–vapor equilibrium data of Tkachenko and Schmulovich [2] and Tkachenko [3] (reproduced in Table III), and the smoothed data of Marshall and Jones [1] plotted against molality. Marshall and Jones' data show a relatively rapid increase in T_c in the dilute range below 0.5 mol · kg^{-1} followed by a much less pronounced increase to 676 K at their highest molality of 1.8. In contrast, the T_c data from this study and those extrapolated from Tkachenko and Schmulovich [2] and Tkachenko [3] define a sigmoidal curve which increases rapidly over the entire
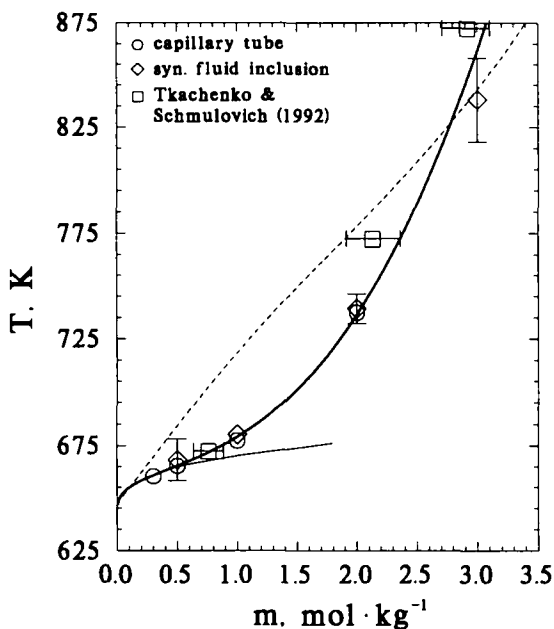

Fig. 1. Experimentally determined critical temperature of CaCl$_2$(aq) plotted versus molality. Vertical error bars are used where the precision of T_c is in excess of the symbol heights. The data of Tkachenko and Schmulovich [2] were collected at constant temperature, so the temperature error is probably within the size of the symbols; the molalities, however, were determined by graphical interpolation of the vapor–liquid equilibria data [3] and may be in error by as much as 0.4 mol · kg^{-1} at 773 and 873 K. The dark solid curve is drawn to aid the eye and its placement is a compromise between the data from this paper and those extrapolated from Tkachenko [3]. The dashed curve shows T_c for NaCl(aq) as given by the equation of Knight and Bodnar [7].

molality range to 3.0 mol·kg^{-1}. The critical temperatures from this study and those extrapolated from Tkachenko [3] are always higher than the results from Marshall and Jones. At less than ∼0.75 mol·kg^{-1} the difference appears to be insignificant, but the difference in T_c between the value of Marshall and Jones at 1.8 mol·kg^{-1} and our curve is greater than 40 K.

Also shown on Fig. 1, as a dashed curve, is the critical line for NaCl(aq). While both critical lines have monotonically positive slopes and qualitative curvature patterns, the detailed forms differ considerably and the slope above 2.0 mol·kg^{-1} is much greater for CaCl$_2$(aq). Figure 2 shows the critical pressures of CaCl$_2$(aq) and NaCl(aq). The points for CaCl$_2$(aq) are based on extrapolations of the data of Tkachenko [3] as reproduced in Table III, while the curve for NaI(aq) is based on the graphs and tables of Anderko and Pitzer [9]. As for the temperature, we find a much greater slope for CaCl$_2$(aq) than for NaCl(aq) at the higher molalities. The fluid-inclusion measurements reported elsewhere [8] also

Table III.   Experimental Liquid–Vapor Equilibrium Pressures and Composition Data[a]

673 K			773 K			873 K		
P (bars)	m_{vap}	m_{liq}	P (bars)	m_{vap}	m_{liq}	P (bars)	m_{vap}	m_{liq}
311.3	0.364		800.0		3.100	1324.1	2.216	
311.1		1.238	794.4	1.304		1323.9		3.975
308.8		1.529	787.6	1.194		1313.5	1.717	
308.7	0.200		782.8		3.830	1307.0		4.940
307.3	0.156		770.8		4.188	1298.7	1.383	
305.6		1.725	769.9	1.092		1297.3		5.146
304.9	0.121		760.6	0.948		1288.1	1.217	
303.4		1.915	751.5		4.698	1285.9		5.804
302.5	0.091		747.4		4.752	1277.3	1.105	
300.4	0.070		741.1	0.798		1262.0	1.049	
300.0		2.113	732.8		5.130	1260.0		6.994
297.2	0.057		723.9	0.667		1252.7	0.909	
295.3	0.051		712.0	0.585		1235.9	0.760	7.292
288.9		2.774				1216.7	0.620	
288.5	0.043							
284.8		3.008						
282.4		3.095						
278.9	0.035							
271.0	0.032							

[a] From Tkachenko [3], reproduced with permission, and converted from the original wt% to molality CaCl$_2$ in mol·kg^{-1}.
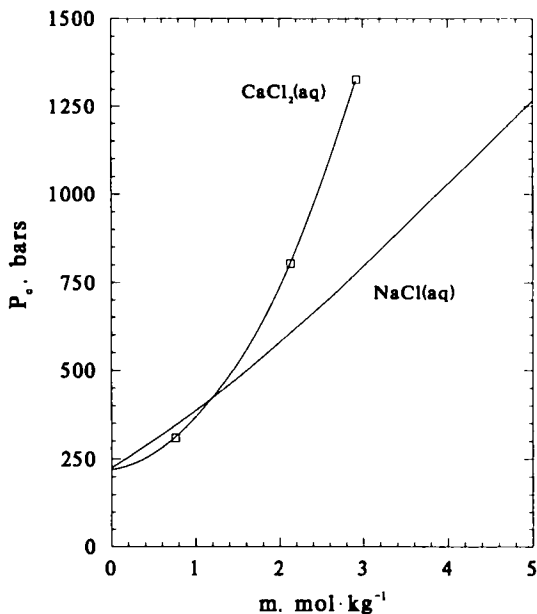
Fig. 2. Plot of P_c against molality for CaCl₂(aq) and NaCl(aq). The squares represent pressures at corresponding molalities interpolated from the 673, 773, and 873 K data of Tkachenko [3], while the curve for NaCl(aq) was taken from Anderko and Pitzer [9].

provide information concerning the critical pressure, but it is less precise and will not be discussed here. Figure 3 shows the vapor–liquid phase behavior at 673 K for both CaCl₂(aq) and NaCl(aq). The critical mole fraction and pressure are considerably greater for CaCl₂(aq), but the shapes of the curves are very similar. The dependence of the difference in mole fraction on pressure can be expressed by

$$(X'' - X') = \text{const} \cdot (P_c - P)^\beta \tag{1}$$

For neutral-molecule fluids both theory and experiment indicate that β is near 1/3, whereas fluids dominated by ionic forces show a pattern corresponding to $\beta = 1/2$ [10]. Bischoff and Rosenbauer [11] showed that NaCl(aq) conformed to Eq. (1) with $\beta = 1/2$ at 673 K and higher temperature. As the critical point of pure water, 647 K, is approached the pattern shifts; this was discussed by Harvey and Levelt Sengers [12] and By Pitzer and Tanger [13].
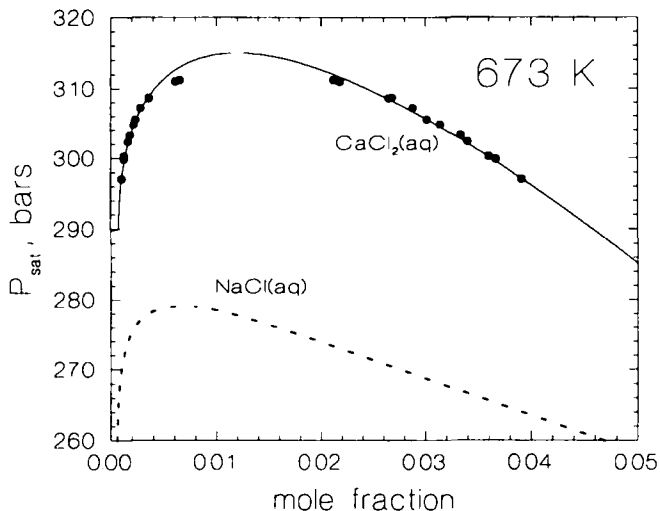
Fig. 3. Vapor-liquid equilibrium composition at 673 K for (—) CaCl₂(aq) and ( ) NaCl(aq). The points for CaCl₂(aq) are taken from Tkachenko [3], while the curve is consistent with Eq. (1).

Figure 4 tests the conformity of CaCl₂(aq) as well as NaCl(aq) to Eq. (1) with $\beta = 1/2$ at 673 and 773 K. While the measurements for CaCl₂(aq) are less precise than those for NaCl(aq), they are equally consistent with $\beta = 1/2$.

Comparison of CaCl₂(aq) with NaCl(aq) on a molal or mole fraction basis is appropriate since there is little ionization, due to the small dielectric constant of the solvent at the critical density of the solution. The obvious difference is that of the multipolar moments. NaCl has a large dipole moment, whereas CaCl₂, a linear Cl–Ca–Cl molecule, has no dipole but a large quadrupole moment. The interactions of these with the smaller dipole of H_2O are undoubtedly important. The comprehensive equation of state for NaCl–H_2O of Anderko and Pitzer [9] was based on the theory for a mixed fluid of dipolar molecules, and a similar study is being initiated for CaCl₂–H_2O as a mixture of quadrupoles with dipoles. This study may explain the differences between these two systems. Another possible complication is hydrolysis, which is known to be significant, but not a major factor for NaCl(aq) [14]. Much less is known for CaCl₂(aq), but the report of Tkachenko and Schmulovich [2] indicates some hydrolysis with extra Cl in the vapor phase, but not a major effect. Further investigation of hydrolysis in CaCl₂(aq) solutions at near critical conditions is needed.
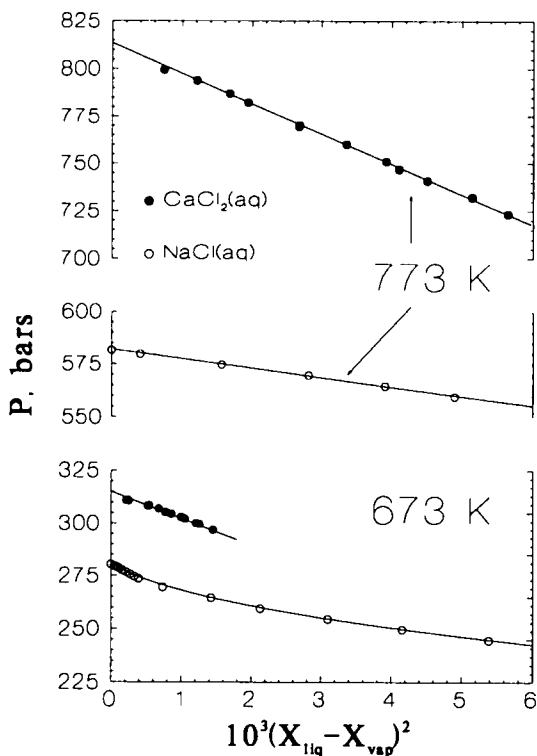
Fig. 4. Tests of Eq. (1); see text for details.

ACKNOWLEDGMENTS

REFERENCES

1. W. L. Marshall and E. V. Jones, *J. Inorg. Nucl. Chem.* **36**:2313 (1974).
2. S. I. Tkachenko and K. I. Schmulovich, *Dokl. Akad. Nauk SSSR* **326**:1055 (1992).
3. S. I. Tkachenko, personal communication (1993).
4. W. L. Marshall, H. W. Wright, and C. H. Secoy, *J. Chem. Ed.* **31**:34 (1954).
5. C. S. Oakes, J. M. Simonson, and R. J. Bodnar, *J. Chem. Eng. Data* **35**:304 (1990).
6. R. J. Bodnar and S. M. Sterner, *Geochim. Cosmochim. Acta* **49**:1855 (1985).

7. C. L. Knight and R. J. Bodnar, *Geochim. Cosmochim. Acta* **53**:3 (1989).
8. C. S. Oakes, R. J. Bodnar, J. M. Simonson, and K. S. Pitzer, *Geochim. Cosmochim. Acta* **58**:2421 (1994).
9. A. Anderko and K. S. Pitzer, *Geochim. Cosmochim. Acta* **57**:1657 (1993).
10. K. S. Pitzer, *Acc. Chem. Res.* **23**:333 (1990).
11. J. L. Bischoff and R. J. Rosenbauer, *Geochim. Cosmochim. Acta* **52**:2121 (1988).
12. A. H. Harvey and J. M. H. Levelt Sengers, *Chem. Phys. Lett.* **156**:415 (1989).
13. K. S. Pitzer and J. C. Tanger IV, *Chem. Phys. Lett.* **156**:418 (1989).
14. F. J. Armelli and J. W. Tester, *Fluid Phase Equilibria* **84**:123 (1993).