High Temperature and High Pressure Volumetric (Density and Apparent Molar Volumes) Properties of ($CaCl_2$ + C_2H_5OH) Solutions[†]

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The (p, ρ, T) and some derived volumetric properties such as apparent molar volumes V_ϕ of $CaCl_2$ in ethanol, isothermal compressibility, and thermal expansion coefficients of ($CaCl_2$ + C_2H_5OH) solutions at T = (298.15 to 398.15) K and pressures up to p = 40 MPa are reported. The density measurements were made at seven molalities of m = (0.09327, 0.17427, 0.43788, 0.68992, 0.98955, 1.26564, and 1.55045) mol·kg^{-1} of $CaCl_2$. An empirical correlation for the density of ($CaCl_2$ + C_2H_5OH) as a function of pressure, temperature, and molality has been developed. This equation of state was used to calculate other volumetric properties such as isothermal compressibility and thermal expansion coefficients. The derived values of apparent molar volumes were extrapolated to zero concentration to calculate the values of apparent molar volumes (or partial molar volumes) at infinite dilution.

Introduction

The efficiency of an absorption heat transfer cycle depends on the physical and chemical properties of the heat transfer fluid. The problems of using conventional aqueous solutions of electrolytes were discussed in our previous publications on methanol solutions of electrolytes.[1,2] This work is a continuation of the study of solutions of electrolytes for their future application as heat transfer fluids in absorption systems. These systems (alcohol solutions of electrolyte) could replace aqueous solutions at temperatures below the freezing point of water. Ethanol has a freezing temperature lower than methanol and can improve the circulation of heat transfer agents in the closed system.

A literature survey revealed that only two experimental data sets[3,4] are available for the density of $CaCl_2$ in ethanol solutions which cover very limited ranges of temperature (up to 343.15 K) and at pressure of 0.1 MPa only. Tashima and Arai[3] reported the densities of $CaCl_2$ + C_2H_5OH at temperatures T = (293.15 to 343.15) K, molalities m = (0 to 2.236) mol·kg^{-1}, and pressure of p = 0.1 MPa. The measurements were performed with a capped pycnometer. The uncertainty in the measured density was 0.4 kg·m^{-3}. The measured density data were used to develop a correlation equation as a function of temperature and molality. Sardroodi and Zafarani-Moattar[4] reported the densities of $CaCl_2$ + C_2H_5OH at temperatures of T = 298.15 K, m = (0.0015 to 3.3716) mol·kg$^{-1,}$ and p = 0.1 MPa using a vibration-tube densimeter (VTD). Apparent molar volumes were calculated from the experimental results. The uncertainty in the measured densities was estimated to be 0.01 kg·m^{-3}. No density data are available for $CaCl_2$ in ethanol solutions under high pressure.

The main objective of the paper is to provide accurate experimental density values for $CaCl_2$ + C_2H_5OH solutions at high temperatures (up to 398.15 K) and at high pressures (up to 40 MPa) for compositions up to 1.5505 mol·kg^{-1} using a vibrating-tube densimeter technique, which has been previously used for accurate measurements on other mixtures.[5−7] The present results considerably expand the temperature and pressure ranges in which density data for the solutions are available. We have also developed an equation of state for the $CaCl_2$ + C_2H_5OH solution which accurately reproduces the present density results.

Experimental

The (p, ρ, T) properties of $CaCl_2$ + C_2H_5OH solutions were studied using a high-pressure−high-temperature vibrating-tube densimeter DMA HPM. Since this method (apparatus, procedure of measurements, and calibration procedure) has been described fully in our previous publications,[5−8] it will not be necessary to give here the details bearing on the present experiments. The vibration tube (length 15 cm, the U radius is 1 cm, OD 6 mm, ID 2 mm, volume of the liquid in the tube was 2 cm^3) was made with corrosion resistance and good fabricability material (Hastelloy C-276, nickel−molybdenum−chromium−tungsten alloy). The measurements with a vibrating-tube densimeter are based on the dependence between the period of oscillation of a unilaterally fixed U-tube Hastelloy C-276 and its mass. The frequency of the harmonic oscillation of the tube can be directly related to the density of the fluid contained in the tube. The behavior of the vibrating tube can be described by the simple mathematical−physical model of the undamped spring-mass system.[11] The classical equation for vibrating-tube densimeters is

$$\rho = A - B\tau^2 \tag{1}$$

where A and B are the calibrating constants as a function of temperature and pressure and subscript 0 relates to the reference

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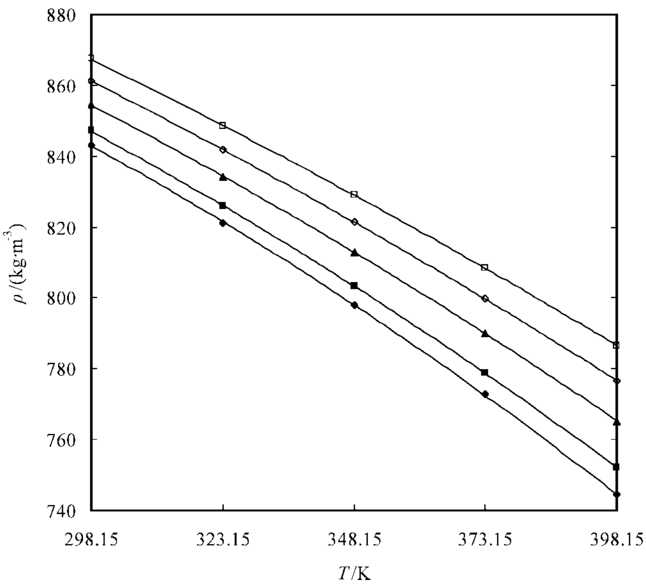

Figure 1. Measured values of density of $CaCl_2$ + C_2H_5OH solutions as a function of temperature along various isobars together with values calculated from eq 6 at a selected molality of $m = 0.1743\ mol \cdot kg^{-1}$. ♦, 0.101 MPa; ■, 10 MPa; ▲, 20 MPa; ○, 30 MPa; □, 40 MPa; −, calculated with eq 6.

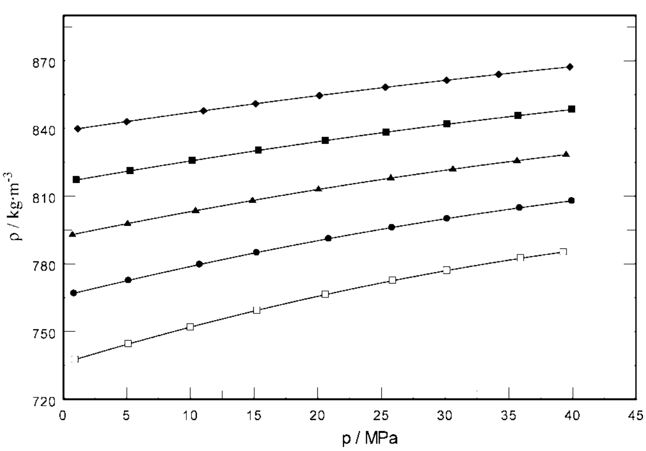

Figure 2. Measured values of density of $CaCl_2$ + C_2H_5OH solutions as a function of pressure along various isotherms together with values calculated from eq 6 at selected molality of $m = 0.6899\ mol \cdot kg^{-1}$. ♦, 298.15 K; ■, 323.15 K; ▲, 348.15 K; ●, 373.15 K; □, 398.15 K; −, calculated with eq 6.

fluid. The parameters A and B can be determined for each temperature and pressure using a minimum of two reference fluids (see our previous publications[5−8]).

For the pressure measurement, a pressure transducer (model P-10, WIKA, Switzerland) was used. The temperature was measured using the (ITS-90) Pt100 thermometer. To check the apparatus and procedures of the measurements and the uncertainty of calibration before engaging in measurements on solution, the density of triple-distilled water and reference fluid (methanol) was measured and compared with the values calculated from IAPWS[9] and IUPAC[10] formulations.

$CaCl_2$ ($w > 0.998$) was supplied from Merck, Germany, and was used without further purification. Before measurements, the salt was dried for about 48 h in a special cell by heating at 413.15 K and reduced pressure (10 Pa). To prevent absorption of water, preparation of salt solutions was performed in a glovebox. Ethanol ($w > 0.998$) was also supplied from Merck, Germany, and was degassed by vacuum distillation using a

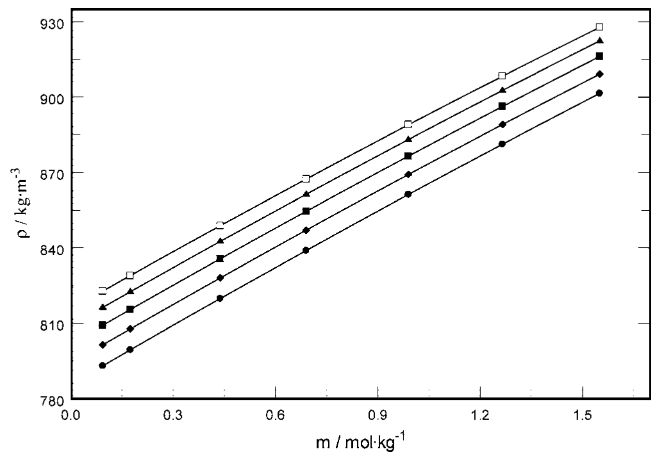

Figure 3. Measured values of density of $CaCl_2$ + C_2H_5OH solutions as a function of molality along various isobars together with values calculated from eq 6 at selected temperature of 298.15 K. ●, 0.1 MPa; ♦, 10 MPa; ■, 20 MPa; ▲, 30 MPa; □, 40 MPa; −, calculated with eq 6.

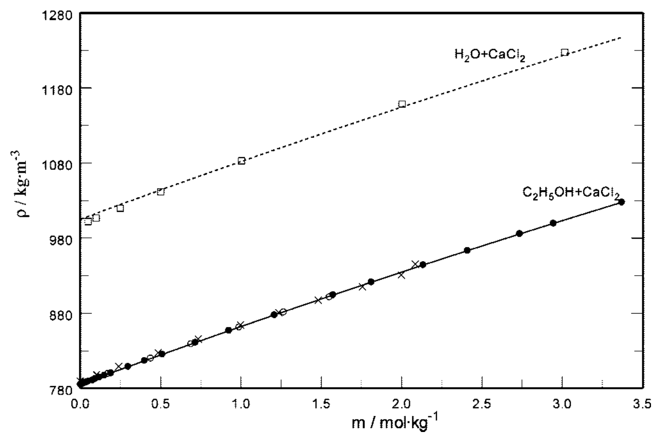

Figure 4. Comparison of the present results for the density of $CaCl_2$ + C_2H_5OH solutions with the data reported by other authors in the literature at atmospheric pressure and at temperature of 298.15 K together with values for H_2O + $CaCl_2$ solutions. ○, this work; ×, Tashima and Arai;[3] ●, Sardroodi and Zafarani-Moattar;[4] □, Gates and Wood[12] (H_2O + $CaCl_2$); −, calculated with eq 6; - - - -, derived by a parallel shift (by 220 $kg \cdot m^{-3}$) (ρ, m) curve for $CaCl_2$ + C_2H_5OH solution.

Vigreux column with a height of 90 cm. The final purity of the ethanol was checked by gas chromatography ($w > 0.999$) and Karl Fischer titration (water mass fraction $< 5 \cdot 10^{-5}$). The solutions were prepared by mass using an electronic scale with a resolution of 10^{-4} g. The uncertainty in the pressure and temperature measurements are 5 kPa and 15 mK, respectively. The uncertainty in density measurements is 0.01 $kg \cdot m^{-3}$ at low pressures (near atmospheric pressure) and 0.15 $kg \cdot m^{-3}$ at high pressures (the combined expanded uncertainty, coverage factor is $k = 2$). This leads to maximum relative uncertainties of 0.02 % for the performed measurements at high temperatures and high pressures.

Results and Discussion

Density. Measurements of the densities of $CaCl_2$ + C_2H_5OH solutions at seven molalities of m = (0.09327, 0.17427, 0.43788, 0.68992, 0.98955, 1.26564, and 1.55045) $mol \cdot kg^{-1}$ of $CaCl_2$ were made in the temperature range between (298.15 and 398.15) K and at pressures up to 40 MPa. The experimental temperature, density, pressure, and molality values for $CaCl_2$ + C_2H_5OH solutions are presented in Table 1 and shown in Figures 1 to 3 in (ρ, T), (ρ, m), and (ρ, p) planes. The present

Table 1. Experimental Values of Density, Pressure, Temperature, and Molality of $CaCl_2$ of ($CaCl_2$ + C_2H_5OH) Solutions

p/MPa	ρ/(kg·m^{-3})	p/MPa	ρ/(kg·m^{-3})	p/MPa	ρ/(kg·m^{-3})	p/MPa	ρ/(kg·m^{-3})	p/MPa	ρ/(kg·m^{-3})
				m = 0.09327 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
0.48	793.40	0.15	771.32	0.75	748.39	0.37	722.50	0.68	692.59
5.06	797.34	5.24	776.50	5.62	754.25	5.18	729.16	5.10	700.41
10.03	801.45	10.34	781.44	10.82	760.15	10.48	736.08	10.08	708.63
15.47	805.77	15.78	786.43	15.38	765.02	15.72	742.49	15.41	716.75
20.64	809.69	20.98	790.93	20.43	770.09	20.28	747.72	20.03	723.21
25.39	813.15	25.68	794.77	25.16	774.52	25.67	753.48	25.06	729.63
30.19	816.48	30.39	798.40	30.48	779.14	30.29	758.06	30.17	735.52
35.64	820.09	35.87	802.35	35.41	783.08	35.42	762.76	35.18	740.65
39.92	822.78	39.86	805.04	39.26	785.92	39.91	766.53	39.92	744.93
				m = 0.17427 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
0.28	800.14	0.24	777.83	0.89	755.18	0.68	728.72	1.03	700.75
6.58	804.98	5.06	782.74	5.09	760.16	5.06	735.26	5.07	707.51
11.33	808.85	10.48	787.98	10.48	766.21	10.74	743.09	10.54	716.08
15.72	812.29	15.62	792.67	15.76	771.77	15.25	748.79	15.29	722.99
20.49	815.89	20.64	796.99	20.48	776.42	20.64	754.98	20.14	729.54
25.82	819.73	25.87	801.22	25.62	781.15	25.18	759.68	24.98	735.56
31.46	823.58	30.38	804.64	30.42	785.25	30.41	764.51	30.78	742.10
35.34	826.11	35.92	808.56	35.86	789.53	35.87	768.88	35.46	746.84
40.18	829.13	39.94	811.21	39.97	792.50	39.74	771.57	39.79	750.79
				m = 0.43788 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
1.02	820.65	0.45	798.42	0.62	774.92	0.94	749.01	0.95	719.54
5.03	824.03	4.98	802.82	5.13	780.06	5.17	754.76	5.38	726.88
10.45	828.43	9.78	807.29	10.24	785.57	10.48	761.55	10.29	734.49
15.48	832.33	15.06	811.96	15.31	790.73	15.19	767.19	15.61	742.12
20.46	836.02	20.04	816.13	20.84	796.01	20.16	772.75	20.48	748.53
25.75	839.75	24.87	819.96	25.04	799.76	25.13	777.90	25.34	754.40
30.64	843.03	30.02	823.82	30.73	804.51	30.24	782.77	30.06	759.57
35.83	846.33	35.15	827.42	35.15	807.92	35.37	787.22	35.18	764.61
39.97	848.83	39.76	830.46	39.38	810.96	39.26	790.31	39.38	768.30
				m = 0.68992 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
1.17	839.86	1.06	817.18	0.75	792.97	0.87	766.95	0.97	737.62
5.01	843.06	5.30	821.26	5.08	797.87	5.15	772.70	5.16	744.53
11.05	847.88	10.18	825.76	10.41	803.58	10.74	779.75	10.02	752.01
15.12	850.99	15.37	830.30	14.89	808.11	15.21	785.01	15.24	759.43
20.13	854.64	20.64	834.66	20.06	813.01	20.86	791.16	20.62	766.40
25.31	858.24	25.39	838.36	25.74	818.02	25.84	796.14	25.89	772.57
30.12	861.41	30.18	841.89	30.61	821.98	30.15	800.10	30.14	777.06
34.21	863.97	35.76	845.73	35.64	825.77	35.84	804.85	35.94	782.51
39.77	867.27	39.94	848.42	39.49	828.45	39.94	807.94	39.29	785.29
				m = 0.98955 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
0.67	861.73	1.57	839.21	0.58	814.32	0.92	788.74	1.06	760.33
6.33	866.36	5.16	842.61	5.06	819.30	5.04	794.18	5.07	766.76
10.83	869.87	10.89	847.78	10.31	824.81	10.74	801.21	10.54	774.89
15.09	873.05	15.42	851.64	15.21	829.63	15.36	806.48	15.29	781.35
20.02	876.57	20.06	855.40	20.67	834.64	20.75	812.16	20.41	787.68
25.13	880.03	25.08	859.23	25.94	839.09	25.94	817.13	25.08	792.89
30.11	883.22	30.45	863.05	30.86	842.93	30.16	820.83	30.74	798.47
35.51	886.47	35.21	866.21	35.37	846.17	35.87	825.32	35.97	802.93
39.86	888.93	39.96	869.15	39.97	849.20	39.96	828.19	39.86	805.80
				m = 1.26564 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
0.26	881.44	0.31	857.30	0.27	833.32	0.42	808.17	0.62	780.71
5.06	885.32	5.07	861.31	5.06	837.99	4.98	813.49	5.18	786.93
10.85	889.78	10.06	865.40	10.45	843.06	9.78	818.85	10.06	793.27
14.86	892.71	15.41	869.66	15.84	847.95	15.26	824.65	15.62	800.09
20.08	896.35	19.98	873.20	19.98	851.59	20.03	829.44	20.08	805.26
25.41	899.86	24.86	876.87	25.06	855.90	25.41	834.54	25.64	811.31
30.06	902.74	30.07	880.67	30.61	860.42	29.98	838.62	30.03	815.79
35.91	906.14	35.16	884.27	35.48	864.22	35.07	842.89	35.74	821.22
39.98	908.34	39.87	887.49	39.96	867.59	39.97	846.74	39.92	824.91
				m = 1.55045 mol·kg^{-1}					
T = 298.15 K		T = 323.15 K		T = 348.15 K		T = 373.15 K		T = 398.15 K	
0.21	901.58	0.52	876.88	0.31	852.87	0.39	828.22	0.74	801.26
5.02	905.41	5.12	881.08	5.21	858.12	5.14	834.25	5.47	808.33
10.41	909.48	10.74	885.92	10.16	863.08	10.15	840.15	10.46	815.02
15.24	912.94	15.02	889.39	15.68	868.22	15.29	845.70	15.62	821.29
20.26	916.34	20.42	893.50	20.64	872.48	20.14	850.48	20.14	826.33
25.01	919.38	25.31	896.97	25.19	876.08	25.75	855.45	25.34	831.69
30.42	922.62	30.14	900.16	30.75	880.10	30.14	858.93	30.47	836.60
35.05	925.22	35.62	903.49	35.29	883.06	35.48	862.67	35.83	841.39
39.96	927.80	39.98	905.92	39.88	885.77	39.97	865.39	39.76	844.70

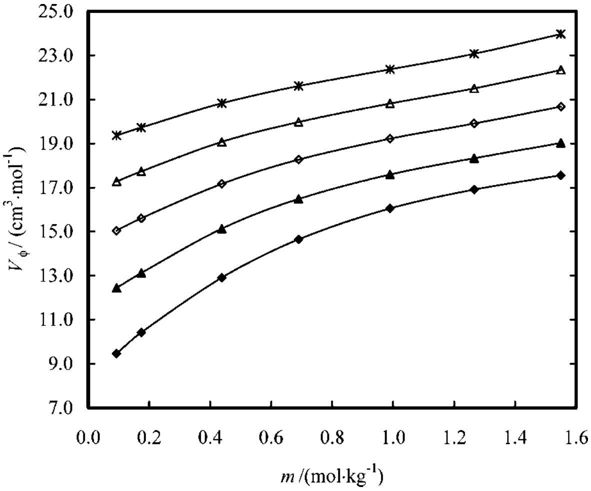

Figure 5. Apparent molar volume, V_ϕ, of $CaCl_2$ in ethanol as a function of molality, m, at selected isotherm of $T = 298.15$ K along various isobars. ♦, $p = 0.1$ MPa; ▲, $p = 10$ MPa; ◇, $p = 20$ MPa; Δ, $p = 30$ MPa; *, $p = 40$ MPa.

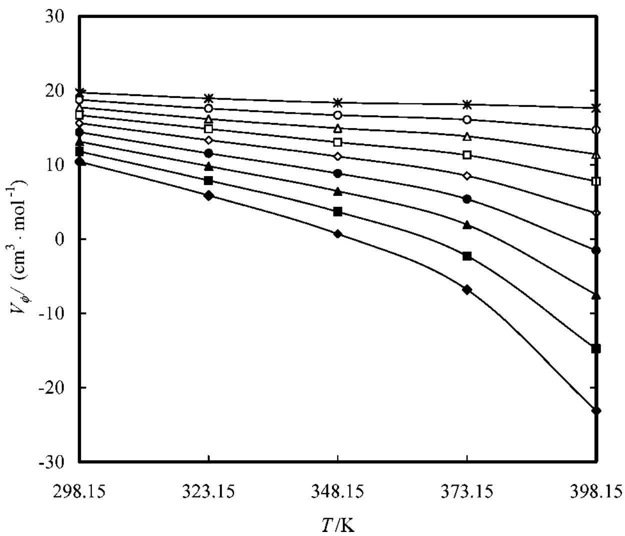

Figure 6. Apparent molar volumes, V_ϕ, of $CaCl_2$ in ethanol as a function of temperature at selected molality of $m = 0.17427$ mol·kg^{-1} for various isobars. ♦, $p = (0.101, 0.24, \text{and } 0.52)$ MPa; ■, $p = 5$ MPa; ▲, $p = 10$ MPa; ●, $p = 15$ MPa; ◇, $p = 20$ MPa; □, $p = 25$ MPa; △, $p = 30$ MPa; ○, $p = 35$ MPa; *, $p = 40$ MPa.

experimental values of density for $CaCl_2 + C_2H_5OH$ solutions at selected temperature of 298.15 K were compared with the data reported by Tashima and Arai[3] and Sardroodi and Zafarani-Moattar[4] (see Figure 4). The agreement (average absolute deviation, AAD) between the present results and those reported by Tashima and Arai[3] and Sardroodi and Zafarani-Moattar[4] are 0.50 % and 0.05 %, respectively. The data by Tashima and Arai[3] are systematically higher than the present by 0.5 %, while the data of Sardroodi and Zafarani-Moattar[4] are in excellent agreement with the present results. Figure 4 also shows the data reported by Gates and Wood[12] for $H_2O + CaCl_2$ solutions at the same pressure and temperature. As one can see from this figure, the densities of $H_2O + CaCl_2$ solutions are almost colinear with that of $CaCl_2 + C_2H_5OH$ (see dashed line in Figure 4). This is means that the (ρ, m) curve for $H_2O + CaCl_2$ can be derived by a parallel shift (by 220 kg·m^{-3}) (ρ, m) curve for $CaCl_2 + C_2H_5OH$ solution.

Apparent Molar Volumes. The measured densities for $CaCl_2 + C_2H_5OH$ solutions were used to calculate the apparent molar volumes V_ϕ of $CaCl_2$ in ethanol using the well-known relation

$$V_\phi = (\rho_0 - \rho_S)/(m\rho_S\rho_0) + M/\rho_S \tag{2}$$

where ρ_0 and ρ_S are densities of pure ethanol (calculated with the equation of state by Dillon and Penocello[13]) and the solutions, respectively; m is the molality of solution; and M is the molar mass of the dissolved $CaCl_2$. The derived values of the apparent molar volumes are given in Table 2 and shown in Figures 5 to 7 in different projections. The maximum relative uncertainty of the derived values of apparent molar volumes, δV_ϕ, is about $\delta V_\phi = 0.15$ % at high molalities and (2 to 3) % at low molalities.[14] Figure 7 compares the present apparent molar volumes of $CaCl_2$ in ethanol with the data reported by Sardroodi and Zafarani-Moattar.[4] In the same figure, the apparent molar volumes of $CaCl_2$ in water reported by Gates and Wood[12] are also presented. The data by Sardroodi and Zafarani-Moattar[4] at $m > 0.5$ molality are systematically lower {by about (1 to 1.2) cm^3·mol^{-1}} than the present values. Derived apparent molar volumes were fitted to the Pitzer ion-interaction relation[15] to calculate the values of apparent molar volumes at infinite dilution

$$V_\phi = V_\phi^0 + \nu|z_M z_X|A_V h(I) + 2\nu_M\nu_X RT[mB_{MX}^V + m^2(\nu_M z_M)C_{MX}^V] \tag{3}$$

where

$$h(I) = \ln(1 + bI^{1/2})/2b, A_V = -4RT\left(\frac{\partial A_\phi}{\partial P}\right)_T,$$

$$B_{MX} = \beta_{MX}^0 + 2\beta_{MX}^1[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]/\alpha^2 I,$$

$$B_{MX}^V(I) = \left(\frac{\partial B_{MX}}{\partial P}\right)_{T,I}, C_{MX} = C_{MX}^\phi/2|z_M z_X|^{1/2},$$

$$C_{MX}^V = \left(\frac{\partial C_{MX}}{\partial P}\right)_T, I = 0.5\sum_i m_i z_i^2$$

A_V and A_ϕ are the Debye−Hückel slope for the apparent molar volume and osmotic coefficient, respectively; $b = 1.2$ (kg·mol^{-1})$^{1/2}$; R= 8.3145 J·mol^{-1}·K^{-1}; B_{MX} and C_{MX} are the second and third virial coefficients; I is the ionic strength; z_i are the charges of the ions; $\alpha \approx 2$ kg$^{1/2}$·mol$^{-1/2}$ is the ion-interaction parameter specific to each solute (may be adjusted for each solute) and might remain the same for broad classes

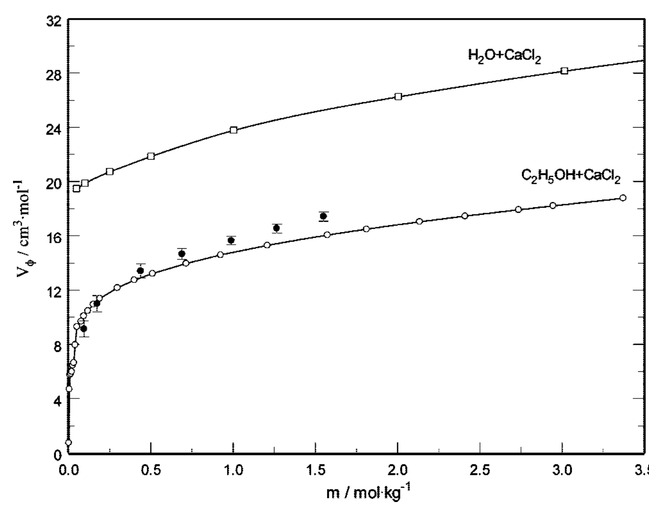

Figure 7. Comparison of the present results for the apparent molar volumes of $CaCl_2$ in ethanol with the data reported by other authors in the literature at atmospheric pressure and at a temperature of 298.15 K together with values for apparent molar volumes of $CaCl_2$ in water. ●, this work; ○, Sardroodi and Zafarani-Moattar;[4] □, Gates and Wood[12] ($H_2O + CaCl_2$); −, smothed curves.

Table 2. Apparent Molar Volumes, V_ϕ, of $CaCl_2$ in Ethanol

	V_ϕ/($cm^3 \cdot mol^{-1}$)						
	m/($mol \cdot kg^{-1}$)						
p/MPa	0.09327	0.17427	0.43788	0.68992	0.98955	1.26564	1.55045
	T = 298.15 K						
0.1	9.463	10.422	12.902	14.647	16.045	16.903	17.556
5	10.982	11.796	14.002	15.548	16.795	17.570	18.246
10	12.447	13.121	15.128	16.477	17.586	18.331	19.025
15	13.682	14.387	16.168	17.382	18.395	19.110	19.838
20	15.033	15.603	17.165	18.267	19.210	19.908	20.670
25	16.173	16.687	18.155	19.138	20.006	20.708	21.506
30	17.270	17.732	19.076	19.976	20.814	21.501	22.339
35	18.333	18.742	19.965	20.805	21.594	22.299	23.156
40	19.362	19.720	20.826	21.607	22.364	23.073	23.965
	T = 323.15 K						
0.1	4.434	5.873	9.844	12.892	15.670	17.366	18.084
5	6.585	7.884	11.526	14.272	16.790	18.320	18.998
10	8.644	9.810	13.098	15.635	17.948	19.357	20.011
15	10.435	11.553	14.593	16.928	19.076	20.409	21.054
20	12.321	13.313	16.058	18.207	20.228	21.494	22.136
25	13.790	14.820	17.391	19.409	21.329	22.544	23.200
30	15.372	16.180	18.637	20.587	22.404	23.600	24.253
35	16.730	17.579	19.874	21.723	23.469	24.631	25.299
40	18.209	18.933	21.068	22.821	24.500	25.629	26.313
	T = 348.15 K						
0.1	−1.001	0.716	5.761	9.543	12.852	14.684	15.107
5	2.106	3.702	8.152	11.516	14.430	16.027	16.382
10	5.064	6.442	10.383	13.409	16.018	17.442	17.764
15	7.499	8.844	12.417	15.172	17.560	18.858	19.163
20	10.000	11.131	14.350	16.869	19.055	20.262	20.561
25	11.846	13.026	16.082	18.416	20.461	21.610	21.922
30	13.971	14.936	17.779	19.943	21.856	22.952	23.268
35	15.661	16.677	19.297	21.364	23.180	24.228	24.563
40	17.462	18.354	20.797	22.711	24.455	25.471	25.824
	T = 373.15 K						
0.24	−9.188	−6.782	−0.390	4.199	7.929	9.703	9.679
5	−4.259	−2.256	3.234	7.163	10.301	11.714	11.573
10	0.236	1.947	6.640	9.979	12.636	13.777	13.567
15	3.874	5.378	9.552	12.487	14.778	15.735	15.506
20	7.313	8.516	12.221	14.801	16.793	17.600	17.372
25	10.200	11.293	14.594	16.894	18.664	19.375	19.160
30	12.761	13.840	16.737	18.837	20.428	21.065	20.863
35	15.025	16.078	18.745	20.621	22.079	22.654	22.493
40	17.380	18.126	20.596	22.332	23.663	24.192	24.050
	T = 398.15 K						
0.52	−26.666	−23.096	−13.359	−6.692	−1.542	0.742	0.569
5	−17.879	−14.753	−6.823	−1.398	2.672	4.277	3.805
10	−9.934	−7.481	−0.932	3.473	6.667	7.747	7.086
15	−3.599	−1.505	3.971	7.604	10.112	10.822	10.076
20	1.713	3.543	8.130	11.141	13.155	13.595	12.810
25	6.312	7.757	11.707	14.255	15.865	16.109	15.309
30	10.063	11.427	14.841	16.990	18.298	18.413	17.614
35	13.631	14.705	17.655	19.459	20.519	20.532	19.751
40	16.645	17.626	20.137	21.711	22.567	22.499	21.737

Table 3. Parameters of the Pitzer Ion-Interaction Model, Equation 3, as a Function of Temperature and Pressure

p	V_ϕ^0	A_V	$10^3 \cdot B_{MX}^V$	$10^6 \cdot C_{MX}^V$
(MPa)	($cm^3 \cdot mol^{-1}$)	($cm^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	($kg \cdot mol^{-1} \cdot MPa^{-1}$)	($kg^2 \cdot mol^{-2} \cdot MPa^{-1}$)
		T = 298.15 K		
0.1	4.644	22.435	0.375	32.02
5	6.985	18.482	0.411	7.85
10	8.987	15.826	0.446	4.91
15	10.600	14.209	0.446	1.53
20	12.554	11.138	0.574	1.10
25	14.010	9.615	0.614	0.72
30	15.454	7.900	0.686	0.58
35	16.854	6.222	0.763	0.52
40	18.219	4.545	0.846	0.55

of solutes.[15,16] Eq 3 combines the long-range Coulombic potential with the hard sphere (short-range) potential. Pitzer's model takes into account the size of the ions in the Coulombic part of the ion−ion potential, and as a consequence, the electrostatic part (second term in eq 3) differs from the Debye−Hückel equation. Pitzer's eq 3 describes quite well

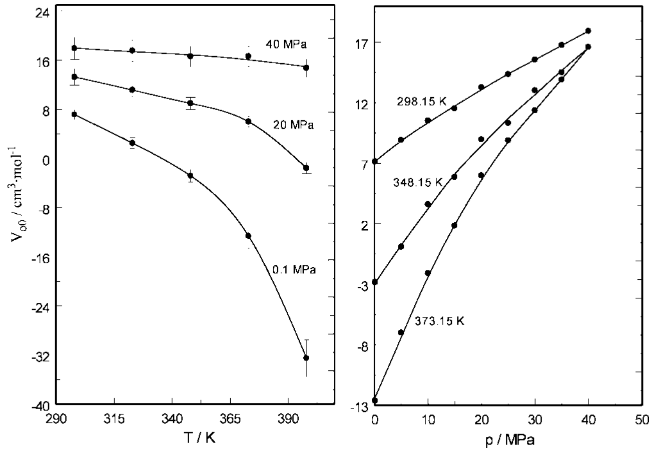

Figure 8. Apparent molar volumes of $CaCl_2$ in ethanol at infinite dilution as a function of temperature (left) at three selected isobars and as a function of pressure (right) at various temperatures. −, smothed curves.

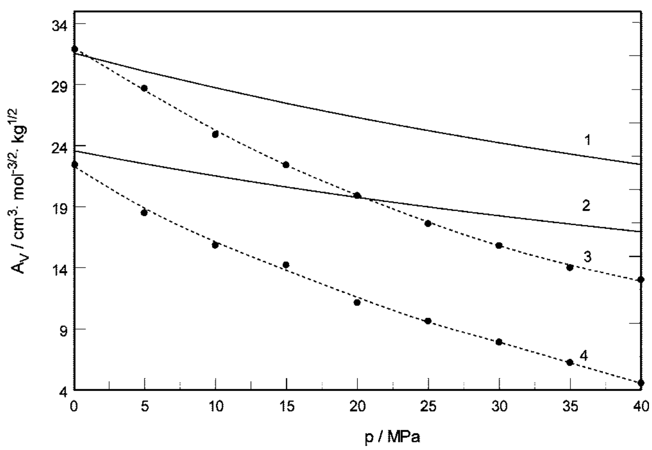

Figure 9. Comparison of the present results for the limiting Debye−Hückel slope for the apparent molar volume A_V with the values calculated from eq 4 at temperatures of (298.15 and 313.15) K. ●, this work (derived from apparent molar volumes); - - - -, smothed curves; −, calculated from eq 4. 1, 313.15 K; 2, 298.15 K (calculated from eq 4); 3, 313.15 K; 4, 298.15 K (from derived apparent molar volumes).

(standard deviations for each isotherm-isobar are varied within $0.8 \cdot 10^6$ to $1.2 \cdot 10^6$) the present apparent molar volume data over a wide range of temperature, pressure, and concentration, if one assumes that the coefficients $\beta^{(0)}$, $\beta^{(1)}$, and C^v are functions of pressure and temperature. As a rule, eq 3 is applied at fixed pressure p and temperature T. The derived values of the parameters of the Pitzer model for selected fixed temperature (298.15 K) and various pressures are given in Table 3. The infinite-dilution values of V_ϕ (or partial molar volumes V_2^∞) as a function of temperature (left) and pressure (right) are presented in Figure 8 along three selected pressures (0.1, 20, and 40) MPa and selected temperatures (298.15, 348.15, and 373.15) K. Note that V_ϕ and V_ϕ^0 (see Figures 5 to 8 and Tables 3 and 4) are slightly changed at low temperatures (below 350 K) and then sharply go to negative values, especially at low pressures. At high pressure (above 25 MPa), the values of apparent molar volumes are almost independent of temperature and positive. At low pressures (below 10 MPa) and high temperatures (above 348 K), the values of apparent molar volumes are negative. At high pressures (above 25 MPa) and at any measured temperatures (up to 398 K), the derived values of apparent molar volumes are almost constant (see Figure 6).

The values of the Debye−Hückel slope for the osmotic coefficient A_ϕ and apparent molar volume A_V can be calculated

Table 4. Apparent Molar Volume of $CaCl_2$ in Ethanol at Infinite Dilution as a Function of Temperature at Three Selected Pressures

T/K	V_ϕ^0/cm^3·mol^{-1}
	$p = 0.1$ MPa
298.15	4.644
323.15	2.503
348.15	−6.118
373.15	−12.63
398.15	−32.52
	$p = 20$ MPa
298.15	12.55
323.15	11.14
348.15	4.078
373.15	5.987
398.15	−1.577
	$p = 40$ MPa
298.15	18.312
323.15	17.557
348.15	12.851
373.15	16.604
398.15	14.721

from the isothermal compressibility, k_T, and pressure dependency of the dielectric constant of pure ethanol as

$$A_V = 6RTA_\phi\left[\left(\frac{\partial \ln D}{\partial p}\right)_T - \frac{k_T}{3}\right] \text{ and}$$

$$A_\phi = \frac{1}{3}(2\pi N_A\rho_0)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_0 DkT}\right)^{3/2} \quad (4)$$

where $N_A = 6.0222045 \cdot 10^{23}$ mol^{-1} is the Avogadro number; $e = 1.60217653 \cdot 10^{-19}$; C is the charge of the electron; $k = 1.3806505 \cdot 10^{-23}$ J·K^{-1} is the Boltzmann constant; and $\varepsilon_0 = 8.854188 \cdot 10^{-12}$ C^2·N·m^{-2} is the permittivity of the vaccum. The values of the dielectric constant D and pressure derivative $(\partial \ln D/\partial p)_T$ as a function of pressure were calculated using the Tait-type equation by Srinivasan and Kay[19]

$$D = \frac{D_0}{1 - A\ln[(B+p)/(B+1)]} \text{ and}$$

$$\left(\frac{\partial \ln D}{\partial p}\right)_T = AD/(B+p)D_0 \quad (5)$$

where D_0 is the dielectric constant of ethanol at 0.1 MPa. The pure ethanol properties (density, ρ_0, and isothermal compressibility, k_T) were calculated with the fundamental equation of state by Dillon and Penoncello.[13] The calculated results for the limiting Debye−Hückel slope for the apparent molar volume $A_V$were compared with the values derived from eq 3 by direct fitting to the present apparent molar volumes. As one can see from Figure 9, the agreement between the present results derived from measured molar volumes and the theoretical values is good (within (2 to 5) %) at at 0.1 MPa; however, at high pressures, the differences are very large. Parameter A_V is the limiting slope (at $m \rightarrow 0$, dilute solution) of the $V_\phi - m$ dependence along the isobar-isotherm. The present measurements mostly cover a higher concentration range. Therefore, the large differences between the present values of A_V and the theoretical prediction are caused by extrapolating our results to low concentration. The uncertainty of the extrapolating procedure is large because at low concetrations $V_\phi - m$ curves sharply change; i.e., small changes in concentration cause large changes in V_ϕ (see Figure 7). The values of the fitting parameters (V_ϕ^0, A_V, B_{MX}^V, C_{MX}^V) in eq 3 considerably depend on the concentration range where the experimental data are available. Thus, to accurately calculate the values of limiting slope A_V, the detailed measurements at low concentrations are needed (for dilute solutions, see for

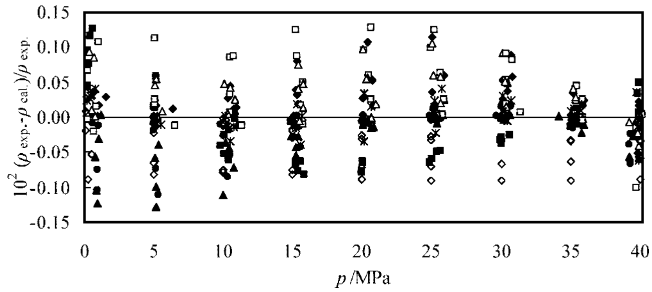

Figure 10. Percentage deviations, $\delta\rho = 100(\rho - \rho^{calcd}/\rho)$, of the present experimental densities for the $CaCl_2 + C_2H_5OH$ solutions from the values calculated with eq 6 as a function of pressure for various temperatures. ◇, $m = 0$; △, $m = 0.09327$ mol·kg^{-1}; □, $m = 0.17427$ mol·kg^{-1}; ●, $m = 0.43788$ mol·kg^{-1}; ▲, $m = 0.68992$ mol·kg^{-1}; ◆, $m = 0.98955$ mol·kg^{-1}; ■, $m = 1.26564$ mol·kg^{-1}; *, $m = 1.55045$ mol·kg^{-1}.

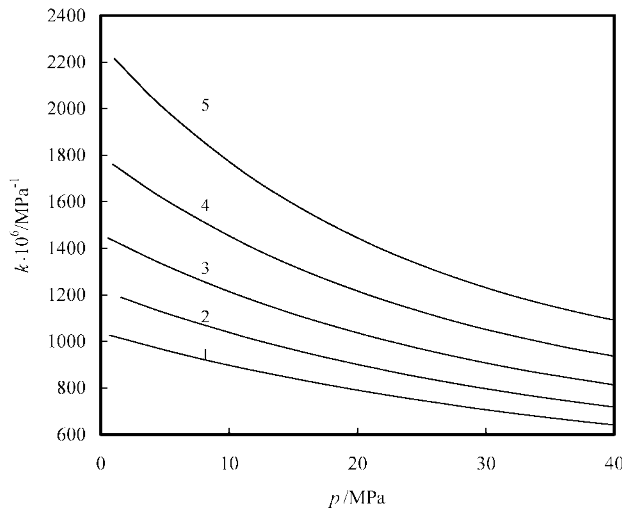

Figure 11. Isothermal compressibility, k, of $CaCl_2 + C_2H_5OH$ solutions as a function of pressure p along various isotherms at a selected molality of $m = 0.98955$ mol·kg^{-1} calculated with eq 6. 1, 298.15 K; 2, 323.15 K; 3, 348.15 K; 4, 373.15 K; 5, 398.15 K.

example, ref 4). Unfortunately, theory cannot accurately predict the range where eq 3 is valid. This is one of the reasons why the difference between A_V reported by various authors sometimes is large, although the agreement between the measured apparent molar volumes is within their uncertainties (see Figure 7). We tried to recalculate the values of fitting parameters (V_ϕ^0, B_{MX}^V, C_{MX}^V) at fixed A_V (by using theoretical values from eq 4). We found that the accuracies of the representation of the present experimental apparent molar volumes with eq 3 are nearly the same. Therefore, this confirms that the present derived apparent molar volumes of $CaCl_2$ in ethanol are in good agreement with Pitzer's theory. Our result for A_V at 298.15 K and 0.1 MPa, 22.435 cm^3·mol$^{-3/2}$·kg$^{1/2}$, is in good agreement with the value 23.873 cm^3·mol$^{-3/2}$·kg$^{1/2}$ reported by Sardroodi and Zafarani-Moattar[4] (derived from density measurements). Marcus and Hefter[20] also reported the value (26.17 cm^3·mol$^{-3/2}$·kg$^{1/2}$) of A_V at 298.15 K and 0.1 MPa which was calculated from the dielectric constant measurement data using the relation 4. We examined how the adjustable parameters (V_ϕ^0, A_V, B_{MX}^V, C_{MX}^V) of eq 3 depend on the fitting range. We found that if the fitting range is reduced, the value of the A_V is within 27.705 cm^3·mol$^{-3/2}$·kg$^{1/2}$, which is close to the value reported by Marcus and Hefter.[20] The values of $A_V$calculated with eq 4 also depend on the accuracy of the measured values of the dielectric constant, density, and isothermal compressibility of ethanol. Therefore, the reported values of A_V are in

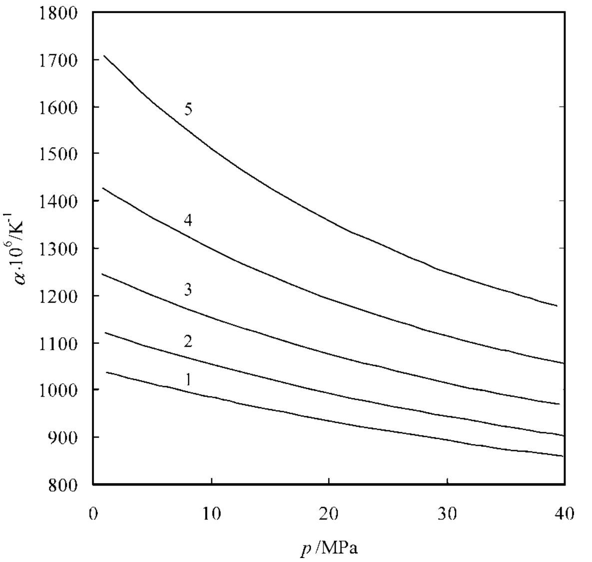

Figure 12. Thermal expansibilities, α, of $CaCl_2$ + C_2H_5OH solutions as a function of pressure p along various isotherms at selected molality of m = 0.68992 mol·kg^{-1} calculated with eq 6. 1, 298.15 K; 2, 323.15 K; 3, 348.15 K; 4, 373.15 K; 5, 398.15 K.

Table 5. Values of the Coefficients a_j, b_j, and c_i in Equation 6

a_i	b_i	c_j
$a_1 = -2.290444 \cdot 10^0$	$b_1 = 2.613913 \cdot 10^0$	$c_1 = 0.269527 \cdot 10^{-2}$
$a_2 = -0.029549 \cdot 10^0$	$b_2 = -2.223418 \cdot 10^0$	$c_2 = 0.271793 \cdot 10^{-2}$
$a_3 = 0.399296 \cdot 10^0$		
$a_4 = 0.655136 \cdot 10^{-2}$		
$a_5 = -0.724853 \cdot 10^{-3}$		
$a_6 = -0.383747 \cdot 10^{-5}$		

reasonable agreement with measured and predicted values reported in the literature.

Equation of State. Measured densities of $CaCl_2$ + C_2H_5OH were fitted to the equation of state

$$p = A\rho^2 + B\rho^8 + C\rho^{12} \tag{6}$$

where A, B, and C are the functions of temperature and molalities. The best description of the present density data for $CaCl_2$ + C_2H_5OH solution was achieved for the functions

$$A = (a_1 + a_2 m + a_3 m^2)T + (a_4 + a_5 m^2)T^2 + a_6 T^3$$

$$B = (b_1 + b_2 m)T$$

$$C = (c_1 + c_2 m)T^2$$

The derived values of the coefficients a_i, b_j, and c_i are given in Table 5. This equation was successfully used previously to represent measured densities for other binary solutions[1,2,17,18] and pure fluids.[8] Equation 6 reproduced our measured values of density for $CaCl_2$ + C_2H_5OH solution in the temperature range from (298 to 398) K and at molalities from (0 to 1.55045) mol·kg^{-1} for the pressures up to 40 MPa with an AAD = 0.05 %. The deviation plot is shown in Figure 10. The calculated values of the density together with experimental values are also presented in Figures 1 to 3. Equation 6 can be used to calculate the derived properties such as isothermal compressibility, $k = (1/\rho)(\partial p/\partial \rho)_{T,\mathrm{m}}^{-1}$, and thermal expansion coefficient, $\alpha = (1/\rho)(\partial p/\partial T)_{\rho,\mathrm{m}}(\partial p/\partial \rho)_{T,\mathrm{m}}^{-1}$. The calculated values of the isothermal compressibilities k and thermal expansibilities α are shown in Figures 11 and 12 as a function of pressure for various isotherms at selected composition.

Conclusion

New density measurements (p, ρ, T data) and derived properties such as apparent molar volumes V_ϕ of $CaCl_2$ in ethanol at T = (298.15 to 398.15) K, pressures up to p = 40 MPa, and molalities m = (0.09327, 0.17427, 0.43788, 0.68992, 0.98955, 1.26564, and 1.55045) mol·kg^{-1} of calcium chloride are reported. Measured densities were used to develop an accurate equation of state. The thermal expansivity, isothermal compressibility of solutions, and apparent molar volume of $CaCl_2$ in ethanol were calculated using the developed equation of state. The derived apparent molar volumes V_ϕ were used to calculate the apparent molar volumes (or partial molar volumes) at infinite dilution, V_ϕ^0. Derived values of V_ϕ and V_ϕ^0 do not vary significantly at low temperatures (below 350 K) and then sharply go to negative values at high temperatures. At high pressure, the values of apparent molar volumes (above 25 MPa) were almost independent of temperature and positive. At low pressures (below 10 MPa) and high temperatures (below 348 K), the values of apparent molar volumes are negative.

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Literature Cited

(1) Ihmels, E. C.; Safarov, J.; Hassel, E.; Gmehling, J. (p, ρ, T) properties, and apparent molar volumes V_ϕ of $ZnBr_2$ in methanol at T=(298.15 to 398.15) K and pressures up to p=40 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 1318–1326.
(2) Ihmels, E. C.; Safarov, J.; Hassel, E.; Gmehling, J. (p, ρ, T) properties, and apparent molar volumes V_ϕ of $CaCl_2$ in methanol at T=(298.15 to 398.15) K and pressures up to p=40 MPa. *J. Chem. Thermodyn.* **2006**, *38*, 224–229.
(3) Tashima, Y.; Arai, Y. Densities of Some Alcohols and Water Containing Calcium Chloride in the Region 20−70 °C. Relation With Salt Effect On Vapor−Liquid Equilibria. *Mem. Fac. Eng., Kyushu Univ.* **1981**, *41*, 217–232.
(4) Sardroodi, J. J.; Zafarani-Moattar, M. T. Apparent molal volumes of the solutions of $CaCl_2$ and $Ca(NO_3)_2$ in ethanol at 298.15: experimental data and correlation by local composition models. *Fluid Phase Equilib.* **2005**, *231*, 61–66.
(5) Abdulagatov, I. M.; Tekin, A.; Safarov, J.; Shahverdiyev, A.; Hassel, E. Densities, excess, apparent, and partial molar volumes of binary mixtures of ethanol + [BMIM][BF_4] as a function of temperature, pressure, and concentration. *Int. J. Thermophys.* **2008**, *29*, 505–533.
(6) Abdulagatov, I. M.; Tekin, A.; Safarov, J.; Shahverdiyev, A.; Hassel, E. High-pressure densities and derived volumetric properties (excess, apparent, and partial molar volumes) of binary mixtures of methanol+[BMIM][PF_6]. *J. Solution Chem.* **2008**, *37*, 801–833.
(7) Abdulagatov, I. M.; Tekin, A.; Safarov, J.; Shahverdiyev, A.; Hassel, E. Experimental study of the volumetric properties (density, apparent, partial, and excess molar volumes) of binary mixtures of Methanol+[BMIM][BF_4]. *J. Chem. Thermodyn.* **2008**, in press.
(8) Abdulagatov, I. M.; Safarov, J.; Aliyev, F.; Talibov, M.; Shahverdiyev, A.; Hassel, E. Experimental densities and derived properties of liquid propan-1-ol at temperatures from 298 to 423 K and at pressures up to 40 MPa. *Fluid Phase Equilib.* **2008**, *268*, 21–33.
(9) Wagner, W.; Pruβ, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.
(10) de Reuck, K. M.; Craven, R. J. B. *Methanol. International Thermodynamic Tables of the Fluid State-12*; Blackwell Scientific: Oxford, 1993.
(11) Kratky, O.; Leopold, H.; Stabinger, H. H. Dichtemessungen an Flüssigkeiten und Gasen auf 10^{-6} g/cm^3 bei 0.6 cm^3 Präparatvolumen. *Z. Angew. Phys.* **1969**, *27*, 273–277.
(12) Gates, J. A.; Wood, R. H. Density of aqueous solutions of NaCl, $MgCl_2$, KCl, NaBr, LiCl, and $CaCl_2$ from 0.05 to 5.0 mol/kg and 0.1013 to 40 MPa at 298.15 K. *J. Chem. Eng. Data* **1985**, *30*, 44–49.
(13) Dillon, H. E.; Penoncello, S. G. A Fundamental equation for calculation of the thermodynamic properties of ethanol. *Int. J. Thermophys.* **2004**, *25*, 321–335, 2.
(14) Abdulagatov, I. M.; Azizov, N. D. PVTx measurements and partial molar volumes for aqueous Li_2SO_4 solutions at temperatures from

297 to 573 K and pressures up to 40 MPa. *Int. J. Thermophys.* **2003**, *24*, 1581–1610.

(15) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(16) Bradley, D. J.; Pitzer, K. S. Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hueckel parameters to 350 °C and 1 kbar. *J. Phys. Chem.* **1979**, *83*, 1599–1603.

(17) Safarov, J. T. The investigation of the (p, ρ, T) and (p_s, ρ_s, T_s) properties of {(1-x)CH_3OH + xLiBr} for the application in absorption refrigeration machines and heat pumps. *J. Chem. Thermodyn.* **2003**, *35*, 1929–1937.

(18) Safarov, J. T.; Najafov, G. N.; Shahverdiyev, A. N.; Hassel, E. (p, ρ, T) and (p_s, ρ_s, T_s) properties, and apparent molar volumes V_ϕ of $LiNO_3$ (aq) in the 298.15−398.15 K temperature range and pressures to p=60 MPa. *J. Mol. Liq.* **2005**, *116*, 157–163.

(19) Srinivasan, K. R.; Kay, R. L. Structural considerations from dielectruc measurements on the aliphatic alcohols. *J. Solution Chem.* **1975**, *4*, 299–310.

(20) Marcus, Y.; Hefter, G. On the pressure and electrical filed dependencies of the relative permittivity of liquids. *J. Solution Chem.* **1999**, *28*, 575–592.

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