

(p , ρ , T) Properties and Apparent Molar Volumes V_ϕ of ZnCl_2 in CH_3OH E. C. Ihmels[†] and J. T. Safarov^{*‡}

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The (p , ρ , T) properties and apparent molar volumes V_ϕ of ZnCl_2 in methanol at $T = (298.15 \text{ to } 398.15) \text{ K}$ and pressures up to $p = 40 \text{ MPa}$ are reported. An empirical correlation for the density of the ($\text{ZnCl}_2 + \text{CH}_3\text{OH}$) with pressure, temperature, and molality has been derived. For the solutions the experiments were carried out at molalities $m = (0.13476, 0.47677, 0.80178, 1.03861, 1.97685, \text{ and } 5.36750) \text{ mol}\cdot\text{kg}^{-1}$ of zinc chloride.

Introduction

The efficiency of an absorption refrigeration cycle is largely dependent on the physical and chemical properties of the heat transfer fluids. These systems work with the heat transfer fluid, which contains two working pairs, usually water/salt solutions, which are used with evaporator temperatures above $0 \text{ }^\circ\text{C}$ due to freezing of the refrigerant (water).

The most serious problems by using the conventional aqueous solutions of electrolytes were discussed in our previous publications of the investigation of methanol solutions of electrolytes.^{1,2} Using methanol as a refrigerant in absorption systems reduces these problems and can replace aqueous solutions at temperatures below the freezing point of water.

In the present work, the (p , ρ , T) properties and apparent molar volumes V_ϕ of the ZnCl_2 in methanol at $T = (298.15 \text{ to } 398.15) \text{ K}$ and pressures up to $p = 40 \text{ MPa}$ are reported. An empirical correlation for the density of the ($\text{ZnCl}_2 + \text{CH}_3\text{OH}$) with pressure, temperature, and molality has been derived. The (p , ρ , T) properties and apparent molar volumes of ZnCl_2 in methanol solutions were not available in the literature.

Experimental Section

The (p , ρ , T) properties were investigated using a high pressure–high temperature vibrating-tube densimeter.^{2,3} The observed reproducibility and estimated maximum uncertainty of the density measurements between $T = (298.15 \text{ to } 398.15) \text{ K}$ and up to $p = 40 \text{ MPa}$ is within $\rho = \pm 0.05 \text{ kg}\cdot\text{m}^{-3}$ and $\rho = \pm 0.2 \text{ kg}\cdot\text{m}^{-3}$, respectively. This leads to maximum relative uncertainties of $\pm 0.03 \%$ for the performed measurements for the solutions. For the pressure measurement, a pressure transducer (model PDCR 922 up to 60 MPa, from Druck, Leicester, England) is used. The accuracy after calibration with a dead-weight pressure gauge was estimated to be better than $\pm 6 \text{ kPa}$. The calibrated (ITS-90) Pt100 temperature sensors installed show a resolution of $\pm 3 \text{ mK}$ and an accuracy of $\pm 30 \text{ mK}$, while the thermostat has a stability of $\pm 20 \text{ mK}$.

ZnCl_2 ($w > 0.998$) was supplied from Merck, Germany, and was used without further purification. Before experiment, the

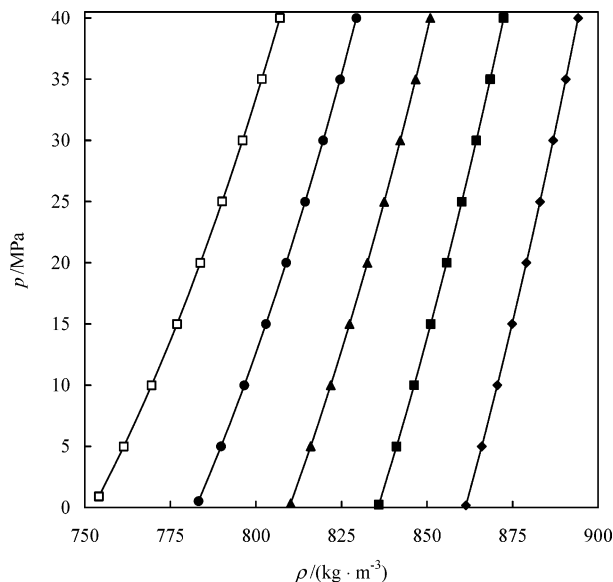


Figure 1. Plot of experimental density ρ of methanol solutions of ZnCl_2 vs pressure p at $m = 0.80178 \text{ mol}\cdot\text{kg}^{-1}$: \blacklozenge , 298.27 K; \blacksquare , 323.23 K; \blacktriangle , 348.27 K; \bullet , 373.29 K; \square , 398.32 K.

salt was dried about 72 h in a special cell by heating at 413.15 K and reduced pressure. To prevent absorption of water, preparation of salt solutions has been performed in a glovebox. The samples were obtained by successive dilutions of the concentrated solutions. Methanol ($w > 0.998$) was supplied from the Carl Roth Company and was degassed by vacuum distillation using a Vigreux column with a height of 90 cm. The final purity of the methanol was checked by gas chromatography ($w > 0.999$) and Karl Fischer titration (water content $< 50 \text{ ppm}$). The solutions were prepared by mass using an electronic scale with resolution of 0.0001 g.

Results and Discussion

In this work, the (p , ρ , T) properties and apparent molar volumes V_ϕ of ZnCl_2 in methanol at $T = (298.15 \text{ to } 398.15) \text{ K}$, at pressures up to $p = 40 \text{ MPa}$ are reported. The experiments were carried out at $m = (0.13476, 0.47677, 0.80178, 1.03861, 1.97685, \text{ and } 5.36750) \text{ mol}\cdot\text{kg}^{-1}$ of ZnCl_2 . The obtained (p , ρ , T) results are listed in Table 1.

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Table 1. Experimental (p , ρ , T) Results of the ($\text{ZnCl}_2 + \text{CH}_3\text{OH}$)

p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	
$m = 0.13476 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.27 \text{ K}$			$T = 323.24 \text{ K}$			$T = 348.27 \text{ K}$			$T = 373.30 \text{ K}$	
0.205	801.32	0.209	777.17	0.308	752.15	0.533	725.48	0.893	695.88	
5.004	805.97	4.990	782.51	4.989	758.25	4.995	732.41	4.994	703.77	
10.000	810.57	10.003	787.77	9.993	764.30	9.985	739.51	9.984	712.39	
15.010	814.96	14.999	792.71	14.999	769.95	15.001	746.08	14.988	720.18	
20.007	819.13	20.000	797.39	19.998	775.25	19.986	752.14	19.984	727.30	
24.999	823.11	24.994	801.85	24.994	780.25	24.992	757.83	25.003	733.89	
30.002	826.95	29.993	806.09	29.998	785.01	29.985	763.18	29.996	740.01	
34.993	830.61	35.007	810.14	34.998	789.52	35.008	768.23	34.993	745.75	
40.006	834.16	39.997	814.00	39.998	793.81	39.993	773.04	39.989	751.12	
$m = 0.47677 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.28 \text{ K}$			$T = 323.23 \text{ K}$			$T = 348.26 \text{ K}$			$T = 373.29 \text{ K}$	
0.188	833.84	0.207	808.23	0.320	782.80	0.527	755.90	0.908	726.55	
4.994	838.00	4.985	813.47	4.983	788.73	4.990	762.64	4.981	734.09	
10.004	841.99	9.994	818.67	9.998	794.70	9.984	769.58	9.983	742.44	
14.982	845.90	14.982	823.55	14.985	800.24	14.985	776.00	14.993	750.05	
20.018	849.66	19.995	828.21	19.989	805.48	19.987	781.98	19.994	757.02	
25.032	853.57	24.999	832.65	24.996	810.44	24.985	787.59	24.992	763.47	
30.004	857.56	29.987	836.86	29.985	815.14	30.012	792.89	30.005	769.51	
34.993	862.15	35.003	840.94	34.987	819.64	34.987	797.89	34.992	775.14	
39.997	866.01	39.994	844.83	40.007	823.94	40.000	802.68	40.002	780.53	
$m = 0.80178 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.27 \text{ K}$			$T = 323.23 \text{ K}$			$T = 348.27 \text{ K}$			$T = 373.29 \text{ K}$	
0.170	861.37	0.233	835.94	0.328	810.17	0.523	783.25	0.907	754.11	
4.996	865.98	4.983	841.09	4.999	816.01	4.994	789.83	4.988	761.40	
9.995	870.53	10.002	846.25	9.992	821.86	9.984	796.61	9.984	769.52	
15.000	874.88	15.002	851.11	14.985	827.35	15.005	802.94	14.994	776.95	
20.001	879.03	19.999	855.74	19.994	832.56	20.005	808.85	19.982	783.77	
24.988	883.01	24.989	860.16	24.989	837.48	24.990	814.38	25.006	790.16	
30.004	886.87	29.989	864.40	29.987	842.17	29.997	819.65	29.994	796.10	
34.992	890.56	34.998	868.48	34.988	846.66	34.983	824.61	35.011	801.72	
39.997	894.15	39.995	872.40	39.999	850.97	39.991	829.37	39.992	807.01	
$m = 1.03861 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.28 \text{ K}$			$T = 323.23 \text{ K}$			$T = 348.27 \text{ K}$			$T = 373.29 \text{ K}$	
0.203	881.26	0.220	855.22	0.330	829.39	0.536	802.51	0.904	773.50	
4.985	885.56	4.994	860.28	4.994	835.08	4.988	808.88	5.004	780.59	
9.997	889.93	10.005	865.32	10.000	840.82	9.995	815.55	9.993	788.48	
14.987	894.12	14.999	870.09	14.987	846.22	15.009	821.76	14.985	795.70	
19.985	898.15	20.003	874.64	20.003	851.34	20.001	827.53	19.982	802.38	
25.003	902.02	24.990	878.98	24.994	856.19	24.989	832.97	24.984	808.61	
30.007	905.80	30.007	883.18	30.014	860.81	29.993	838.14	29.996	814.47	
34.983	909.40	34.989	887.17	34.990	865.23	34.984	843.03	35.010	819.97	
39.991	912.90	39.991	891.04	39.991	869.48	39.990	847.71	39.997	825.19	
$m = 1.97685 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.27 \text{ K}$			$T = 323.24 \text{ K}$			$T = 348.27 \text{ K}$			$T = 373.29 \text{ K}$	
0.205	959.59	0.230	931.65	0.305	904.26	0.527	876.84	0.905	848.36	
5.014	963.97	4.993	936.57	4.984	909.72	5.003	882.85	4.985	854.80	
9.996	968.35	9.985	941.48	9.985	915.25	9.986	889.12	9.999	862.15	
14.997	972.58	14.998	946.20	14.992	920.51	15.009	895.06	15.019	868.94	
19.989	976.63	19.999	950.72	19.986	925.50	20.012	900.64	19.996	875.28	
24.993	980.56	24.989	955.05	24.987	930.28	25.001	905.94	25.009	881.23	
29.990	984.35	29.990	959.23	29.990	934.86	29.988	910.98	29.990	886.89	
35.014	988.04	35.001	963.27	34.985	939.27	34.997	915.82	35.014	892.27	
39.994	991.58	39.997	967.17	39.993	943.53	39.997	920.45	39.988	897.37	
$m = 5.36750 \text{ mol}\cdot\text{kg}^{-1}$										
$T = 298.27 \text{ K}$			$T = 323.24 \text{ K}$			$T = 348.27 \text{ K}$			$T = 373.29 \text{ K}$	
0.200	1205.67	0.209	1172.87	0.335	1141.63	0.535	1112.11	0.899	1083.75	
4.983	1209.53	4.999	1177.21	4.982	1146.29	4.986	1117.02	5.002	1088.78	
9.992	1213.48	9.997	1181.61	9.992	1151.14	10.002	1122.33	9.988	1094.64	
14.995	1217.30	15.002	1185.89	15.020	1155.81	14.990	1127.43	15.018	1100.25	
19.988	1221.03	19.998	1190.03	20.001	1160.36	20.008	1132.37	20.003	1105.62	
24.996	1224.68	24.989	1194.06	25.001	1164.74	25.001	1137.12	24.989	1110.77	
29.994	1228.21	30.001	1197.99	30.011	1169.01	29.994	1141.72	29.999	1115.75	
34.996	1231.68	34.987	1201.80	34.990	1173.15	34.986	1146.17	35.003	1120.56	
39.994	1235.10	39.995	1205.55	39.984	1177.19	39.995	1150.53	39.994	1125.22	

Using a program for standard thermodynamic analysis to describe the (p , ρ , T) properties of methanol solutions of ZnCl_2 , the equation of state (eq 1) from ref 1 was used:

$$p = A\rho^2 + B\rho^8 + C\rho^{12} \quad (1)$$

The coefficients of eq 1 (A , B , and C) are functions of temperature and molalities m :

$$A = \sum_{i=1}^4 T^i \sum_{j=0}^6 a_{ij} m^j \quad (2)$$

$$B = \sum_{i=0}^3 T^i \sum_{j=0}^6 b_{ij} m^j \quad (3)$$

$$C = \sum_{i=0}^3 T^i \sum_{j=0}^6 c_{ij} m^j \quad (4)$$

The a_{ij} , b_{ij} , and c_{ij} are the coefficients of the polynomials, and they are given in Table 2. Equations 1 to 4 are described our experimental results with $\pm 0.006\%$ average deviation. During the molality m dependence of experimental results, the (p , ρ , T) properties of methanol from ref 2 were used. The statistical,

Table 2. Values of the Coefficients a_{ij} , b_{ij} , and c_{ij} in Equations 1 to 4

a_{ij}	b_{ij}	c_{ij}
$a_{10} = -3.2320574273$	$b_{00} = -1477.925642552$	$c_{00} = -1380.64064$
$a_{11} = 31.1317287076$	$b_{01} = 286352.1656083$	$c_{01} = -494179.9917153526$
$a_{12} = -421.992228948$	$b_{02} = -2651482.16388571$	$c_{02} = 4679325.534965326$
$a_{13} = 1042.4065547565$	$b_{03} = 6135248.272333951$	$c_{03} = -10845143.9673409$
$a_{14} = -952.592801854$	$b_{04} = -5528630.590143065$	$c_{04} = 9756652.812321812$
$a_{15} = 339.898612167$	$b_{05} = 1969416.312510314$	$c_{05} = -3469682.188901562$
$a_{16} = -36.500223852878$	$b_{06} = -211560.332348847$	$c_{06} = 372375.69140993$
$a_{20} = 1.40111335262 \cdot 10^{-2}$	$b_{10} = 12.130167272$	$c_{10} = 19.552432301$
$a_{21} = -8.10758 \cdot 10^{-2}$	$b_{11} = -2765.71218910273$	$c_{11} = 4517.45214244155$
$a_{22} = 1.6862214$	$b_{12} = 26010.72725075362$	$c_{12} = -43212.4546402518$
$a_{23} = -4.35497186$	$b_{13} = -60377.39067149046$	$c_{13} = 100344.112888808$
$a_{24} = 4.009522573$	$b_{14} = 54444.49307483342$	$c_{14} = -90316.41207528222$
$a_{25} = -1.43034389078$	$b_{15} = -19395.45094714807$	$c_{15} = 32121.92666262618$
$a_{26} = 0.1534603705$	$b_{16} = 2083.45052993937$	$c_{16} = -3447.480837585364$
$a_{30} = -2.30426 \cdot 10^{-5}$	$b_{20} = -1.812152 \cdot 10^{-2}$	$c_{20} = -7.443132332 \cdot 10^{-2}$
$a_{31} = -2.0394195 \cdot 10^{-4}$	$b_{21} = 8.508135242$	$c_{21} = -13.361786362$
$a_{32} = -2.527559864 \cdot 10^{-4}$	$b_{22} = -80.96712412515407$	$c_{22} = 128.73553972$
$a_{33} = 1.602673 \cdot 10^{-3}$	$b_{23} = 188.3622675198797$	$c_{23} = -299.3369197708$
$a_{34} = -1.6178404 \cdot 10^{-3}$	$b_{24} = -169.9367631086781$	$c_{24} = 269.51208602198$
$a_{35} = 5.75543597306 \cdot 10^{-4}$	$b_{25} = 60.54255859374153$	$c_{25} = -95.8612056870612$
$a_{36} = -6.10858737 \cdot 10^{-5}$	$b_{26} = -6.503394322434008$	$c_{26} = 10.28840125167783$
$a_{40} = 1.6126218 \cdot 10^{-8}$	$b_{30} = 1.0961 \cdot 10^{-5}$	$c_{30} = 8.544351 \cdot 10^{-5}$
$a_{41} = 5.276624 \cdot 10^{-7}$	$b_{31} = -8.467978661416 \cdot 10^{-3}$	$c_{31} = 1.288067662334561 \cdot 10^{-2}$
$a_{42} = -3.289147786 \cdot 10^{-6}$	$b_{32} = 8.11769955405 \cdot 10^{-2}$	$c_{32} = -0.1246624482824$
$a_{43} = 6.867150914471 \cdot 10^{-6}$	$b_{33} = -0.1891254685$	$c_{33} = 0.2900941008840552$
$a_{44} = -6.078608884437 \cdot 10^{-6}$	$b_{34} = 0.17067851958934$	$c_{34} = -0.2612296506270426$
$a_{45} = 2.171218215735 \cdot 10^{-6}$	$b_{35} = -6.0808567190033 \cdot 10^{-2}$	$c_{35} = 9.291544596564023 \cdot 10^{-2}$
$a_{46} = -2.34086431973426 \cdot 10^{-7}$	$b_{36} = 6.531880767726 \cdot 10^{-3}$	$c_{36} = -9.972100295663517 \cdot 10^{-3}$

Table 3. Statistical, Absolute, and Average Deviations of Equations 1 to 4

molality, $m/(\text{mol}\cdot\text{kg}^{-1})$	standard deviation ^a	absolute deviation ^b	maximum absolute deviation	average percent deviation ^c
0.13476	0.002	0.008	0.03	0.0011
0.47677	0.033	0.180	0.60	0.0222
0.80178	0.001	0.007	0.02	0.0009
1.03861	0.003	0.015	0.06	0.0018
1.97685	0.002	0.008	0.03	0.0008
5.36750	0.006	0.036	0.09	0.0032

^{a-c} The equations of deviations are available in ref 2.

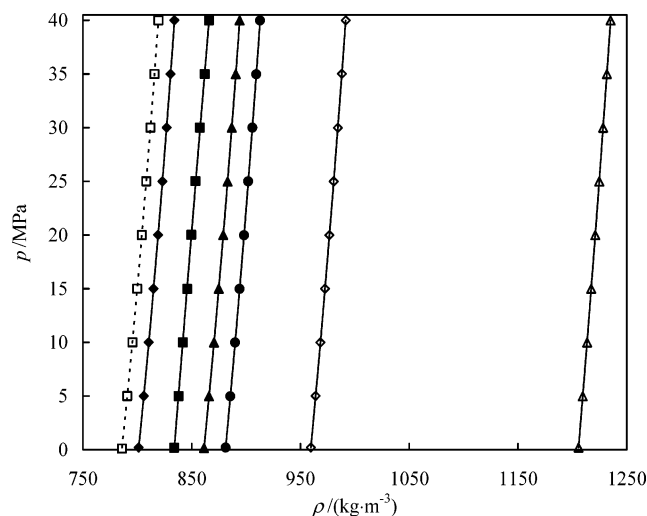


Figure 2. Plot of experimental density ρ of methanol solutions of ZnCl_2 vs pressure p at $T = 298.15$ K: \square , $m = 0$ (from ref 3); \blacklozenge , $m = 0.13476$ $\text{mol}\cdot\text{kg}^{-1}$; \blacksquare , $m = 0.47677$ $\text{mol}\cdot\text{kg}^{-1}$; \blacktriangle , $m = 0.80178$ $\text{mol}\cdot\text{kg}^{-1}$; \bullet , $m = 1.03861$ $\text{mol}\cdot\text{kg}^{-1}$; \blacklozenge , $m = 1.97685$ $\text{mol}\cdot\text{kg}^{-1}$; \blacktriangle , $m = 5.36750$ $\text{mol}\cdot\text{kg}^{-1}$; $-$, calculated by eqs 1 to 4.

absolute, and average deviations of fitting by eqs 1 to 4 are presented in Table 3. Figures 1 to 3 show the plot of pressure of the ($\text{ZnCl}_2 + \text{CH}_3\text{OH}$) versus density at $m = 0.80178$

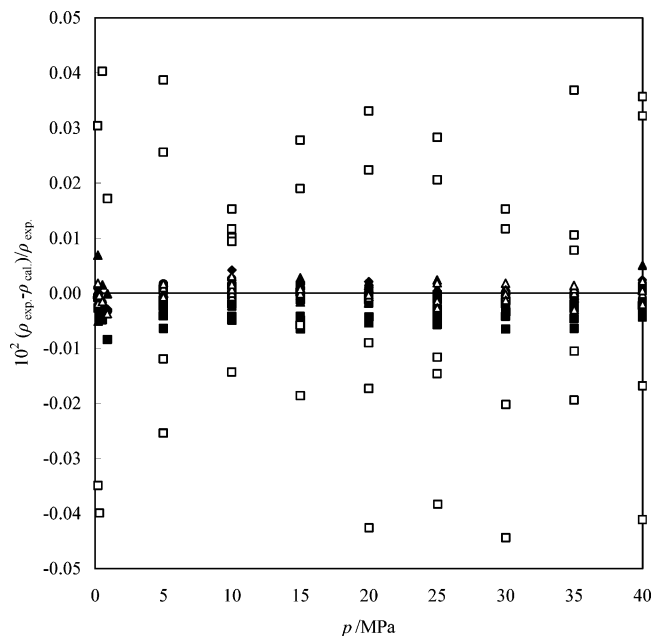


Figure 3. Plot of deviations of experimental density ρ_{exp} from the calculated by eqs 1 to 4 density ρ_{cal} vs pressure p : \triangle , $m = 0.13476$ $\text{mol}\cdot\text{kg}^{-1}$; \square , $m = 0.47677$ $\text{mol}\cdot\text{kg}^{-1}$; \bullet , $m = 0.80178$ $\text{mol}\cdot\text{kg}^{-1}$; \blacktriangle , $m = 1.03861$ $\text{mol}\cdot\text{kg}^{-1}$; \blacklozenge , $m = 1.97685$ $\text{mol}\cdot\text{kg}^{-1}$; \blacksquare , $m = 5.36750$ $\text{mol}\cdot\text{kg}^{-1}$.

$\text{mol}\cdot\text{kg}^{-1}$, pressure versus density at $T = 298.15$ K, and deviations of experimental density from calculated density versus pressure.

The graphical analysis of the temperature dependence of the coefficients of eq 1 revealed that, at $T \rightarrow T_c$, $A \rightarrow 0$. Such a behavior of $A = f(T)$ may be explained by the fact that, according to Putilov,⁵ the first term on the right-hand side of eq 1, $A\rho^2$, is the attractive force (attractor pressure), and the second and third terms are the repulsive force (repulsive pressure). As the temperature rises, the spacing between molecules increases, which contributes to a decrease in the attractive force. As the attractive force tends to zero ($A \rightarrow 0$),

Table 4. Apparent Molar Volumes V_ϕ (cm³·mol⁻¹) of the ZnCl₂ in CH₃OH

p /MPa	m /(mol·kg ⁻¹)					
	0.13476	0.47677	0.80178	1.03861	1.97685	5.36750
$T = 298.15$ K						
0.101	-11.171	10.806	19.137	22.167	25.530	30.493
5	-8.834	13.870	20.230	23.401	26.376	31.074
10	-6.588	16.336	21.201	24.502	27.143	31.603
15	-4.673	18.149	22.060	25.465	27.812	32.074
20	-2.959	19.426	22.816	26.296	28.402	32.493
25	-1.317	20.283	23.479	27.062	28.927	32.874
30	0.034	20.672	24.069	27.723	29.396	33.214
35	1.330	20.668	24.592	28.313	29.814	33.520
40	2.575	20.346	25.069	28.850	30.196	33.799
$T = 323.15$ K						
0.101	-14.393	9.255	18.392	21.641	25.436	30.539
5	-11.314	12.434	19.863	23.135	26.554	31.283
10	-8.623	14.917	21.140	24.436	27.526	31.945
15	-6.197	16.790	22.260	25.543	28.378	32.526
20	-4.012	18.148	23.217	26.514	29.115	33.037
25	-2.167	19.015	24.040	27.358	29.756	33.488
30	-0.411	19.573	24.796	28.085	30.325	33.893
35	1.270	19.773	25.455	28.745	30.834	34.254
40	2.883	19.755	26.040	29.329	31.294	34.578
$T = 348.15$ K						
0.37	-18.728	7.415	15.937	19.196	23.982	29.870
5	-14.963	10.483	17.878	21.098	25.459	30.822
10	-11.701	13.141	19.617	22.818	26.802	31.704
15	-8.517	15.258	21.154	24.302	27.954	32.467
20	-6.019	16.937	22.428	25.551	28.938	33.128
25	-3.663	18.278	23.540	26.648	29.791	33.707
30	-1.552	19.337	24.504	27.604	30.540	34.217
35	0.334	20.164	25.371	28.446	31.192	34.671
40	2.251	20.839	26.15	29.212	31.784	35.074
$T = 373.15$ K						
0.54	-27.493	4.320	11.014	14.593	20.414	27.873
5	-22.301	7.041	13.775	17.195	22.512	29.191
10	-17.525	9.549	16.317	19.603	24.460	30.434
15	-13.501	11.729	18.401	21.612	26.080	31.487
20	-10.018	13.624	20.178	23.311	27.437	32.386
25	-7.015	15.306	21.704	24.782	28.612	33.163
30	-4.322	16.800	23.001	26.060	29.615	33.839
35	-2.034	18.125	24.131	27.180	30.497	34.431
40	0.132	19.333	25.149	28.170	31.264	34.953
$T = 398.15$ K						
0.94	-40.270	-5.442	2.832	6.946	14.011	24.051
5	-33.134	-1.506	6.804	10.642	17.025	25.882
10	-26.008	2.561	10.661	14.311	20.002	27.734
15	-20.377	6.027	13.743	17.243	22.385	29.258
20	-15.626	9.070	16.264	19.686	24.348	30.529
25	-11.643	11.757	18.381	21.735	25.990	31.612
30	-8.212	14.173	20.159	23.480	27.377	32.535
35	-5.273	16.356	21.677	25.004	28.574	33.337
40	-2.512	18.368	23.026	26.347	29.610	34.038

molecules under the effect of the repulsive force are capable of displacement. The extent of their displacement is defined only by the density of the substance (i.e., external pressure). As a result, the aggregate state changes. Note that the form of eq 1 was derived from Putilov's molecular kinetic theory.⁵

The apparent molar volumes V_ϕ of ZnCl₂ in methanol were defined⁶ by eq 5 and are listed in Table 4:

$$V_\phi = (\rho_m - \rho_s) / (m\rho_s\rho_m) + M/\rho_s \quad (5)$$

where ρ_m and ρ_s are densities of methanol and solutions, m is the molality of solution, and M is the molar mass of the dissolved ZnCl₂. The calculations were carried out using the density results of methanol and solution at the same temperatures and pressures.

The maximum relative uncertainty⁴ δV_ϕ in the V_ϕ determination by the investigated concentrations are as follows: δV_ϕ

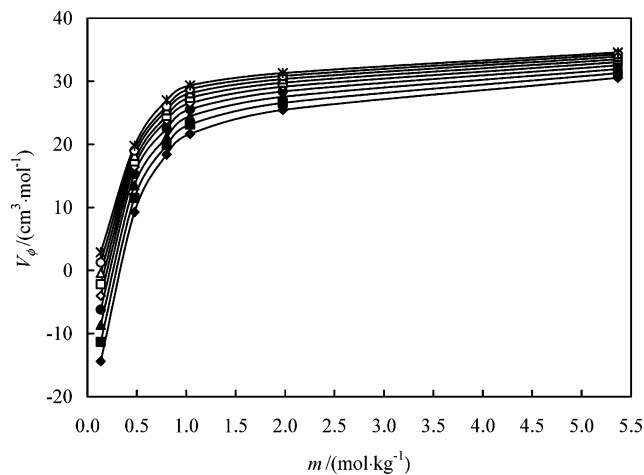


Figure 4. Plot of V_ϕ of ZnCl₂ in methanol vs m at $T = 323.15$ K: \blacklozenge , $p = 0.1$ MPa; \blacksquare , $p = 5$ MPa; \blacktriangle , $p = 10$ MPa; \bullet , $p = 15$ MPa; \diamond , $p = 20$ MPa; \square , $p = 25$ MPa; \triangle , $p = 30$ MPa; \circ , $p = 35$ MPa; $*$, $p = 40$ MPa.

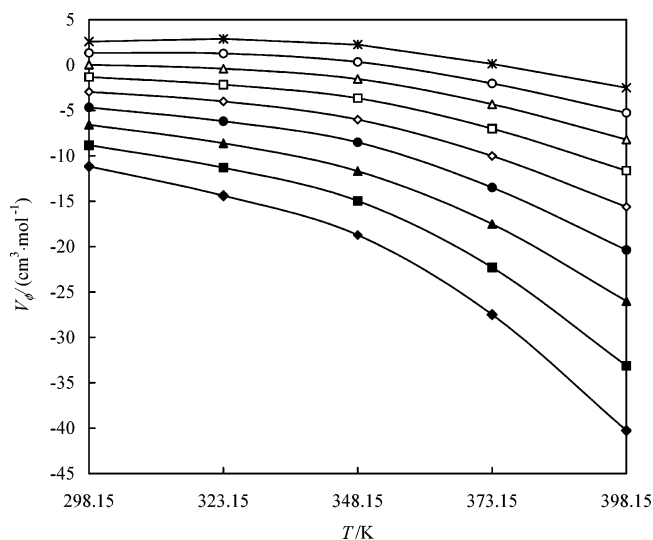


Figure 5. Plot of apparent molar volumes V_ϕ of ZnCl₂ in methanol vs temperature T at $m = 0.13476$ mol·kg⁻¹: \blacklozenge , $p = (0.1, 0.34, 0.54, \text{ and } 0.94)$ MPa; \blacksquare , $p = 5$ MPa; \blacktriangle , $p = 10$ MPa; \bullet , $p = 15$ MPa; \diamond , $p = 20$ MPa; \square , $p = 25$ MPa; \triangle , $p = 30$ MPa; \circ , $p = 35$ MPa; $*$, $p = 40$ MPa.

=(3.12, 1.01, 0.62, 0.49, 0.27, and 0.10) %, respectively. Figure 4 show the plot of the apparent molar volumes V_ϕ of ZnCl₂ in methanol versus m at $T = 323.15$ K and various pressures. Figure 5 shows the plot of the apparent molar volumes V_ϕ of ZnCl₂ in methanol versus T at $m = 0.13476$ mol·kg⁻¹ and various pressures.

Conclusion

For the first time, the (p, ρ, T) properties and apparent molar volumes V_ϕ of ZnCl₂ in methanol at $T = (298.15 \text{ to } 398.15)$ K and pressures up to $p = 40$ MPa are reported. An empirical correlation for the density of investigated solutions with composition, pressure, and temperature has been derived. The measured volumetric results are useful for the absorption refrigeration machines and heat pumps.

Literature Cited

- (1) Safarov, J. T. The investigation of the (p, ρ, T) and (p_s, ρ_s, T_s) properties of $\{(1-x)\text{CH}_3\text{OH} + x\text{LiBr}\}$ for the application in absorption refrigeration machines and heat pumps. *J. Chem. Thermodyn.* **2003**, *35*, 1929–1937.

- (2) 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.
- (3) Ihmels, E. C.; Gmehling, J. Densities of toluene, carbon dioxide, carbonyl sulfide, and hydrogen sulfide over a wide temperature and pressure range in the sub- and supercritical state. *Ind. Eng. Chem. Res.* **2001**, *40*, 4470–4477.
- (4) 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.
- (5) Putilov, K. A. Thermodynamics of simplest liquids. *Issledovaniya po Termodinamike* (Thermodynamic Studies); Nauka: Moscow, 1973; p 105.
- (6) Millero, F. J. The molal volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.

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