The (p, ρ, T) Properties and Apparent Molar Volumes V_ϕ of LiBr + C_2H_5OH

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The (p, ρ, T) properties and apparent molar volumes (V_ϕ) of LiBr in ethanol at T = (273.15 to 398.15) K and pressures up to p = 100 MPa are reported. An empirical correlation for the density of (LiBr + C_2H_5OH) with pressure, temperature, and molality has been derived. The experiments were carried out at molalities m = (0.23351, 0.59717, 0.94988, 1.46165, 2.27186, 2.83298, and 3.36783) mol·kg^{-1} using lithium bromide.

Introduction

Absorption heat pumps perform heating of buildings or industrial installations by taking heat from a heat reservoir at low temperatures (e.g., environmental air or water) and "pumping" it via a cyclic process, with the help of an additional energy stream (often the electric power going into a fluid pump) and some additional heat flow, to a higher temperature level, where it is used as heating source. The simplest thermochemical compressor system consists of an absorber, a desorber, a solution pump, two heat exchangers, and two throttle valves. The efficiency of an absorption heat-transfer cycle is largely dependent on the physical and chemical properties of the heat-transfer fluids. Similar systems with the same principal parts are used as absorption refrigerators (e.g., in hotel rooms) because they work very quietly. The most serious problems with using conventional aqueous solutions of electrolytes have been discussed in our previous publications on investigations of methanol and ethanol as nonaqueous solvents.[1−4] This work is a continuation of our investigations of nonaqueous solutions for the absorption heat-transfer cycle. Applications of nonaqueous solvents as heat-transfer fluids in absorption heat transformer systems reduce these problems and can replace aqueous solutions at temperatures below the freezing point of water. Ethanol also has a freezing point below that of methanol, and this can help to increase the range over which these cycles can be used.

The pressure−density−temperature (p, ρ, T) properties and apparent molar volumes (V_ϕ) of LiBr in ethanol at T = (273.15 to 398.15) K and pressures up to p = 100 MPa are reported. An empirical correlation for the density of LiBr + C_2H_5OH with pressure, temperature, and molality has been derived.

In the literature analysis, we found only four studies[5−8] of the thermodynamic properties of LiBr in ethanol solutions at ambient pressure: In 1975, Uemura[5] investigated the specific gravity of LiBr + C_2H_5OH over the temperature range (278.15 to 333.15) K for mass fractions 100 w = 5 to 40.

In 1982, Glugla et al.[6] studied the partial molar volume of monovalent salts and polar molecules in organic solvents. High-volume injection and flow dilatometers were used during the experiments. The apparent molar volumes of LiBr in ethanol were measured at T = (298.15 and 323.15) K and m = (0.00167 to 2.8287) mol·kg^{-1}. The temperature bath used with this apparatus controlled the temperature fluctuations to within 0.001 K. The volume change was always less than 0.0001 mL and frequently less than 0.00005 mL. The partial molar volumes measured in solvents using this apparatus were accurate to better than ± 2 %.

In 2007, Zafarani-Moattar and Shekaari[7] measured the density of LiBr + ethanol solutions at T = 298.15 K with m = (0.0789 to 1.2642) mol·kg^{-1}. Measurements were carried out using a commercial density measurement apparatus (Anton Paar DSA 5000 densitometer). The uncertainty of the density measurement was reported to be ± 0.003 kg·m^{-3}.

In 2004, Marcus and Hefter[8] proposed values of the apparent molar volume at infinite dilution using various experimental data at ambient pressure. The apparent molar volume of LiBr in ethanol at infinite dilution at T = 298.15 K was analyzed, and $V_\phi^0 = -5.2$ cm^3·mol^{-1} was selected as the reference value.

The (p, ρ, T) properties of these solutions are not available in the literature.

Experimental Section

The (p, ρ, T) properties of LiBr + C_2H_5OH were studied using a high-pressure−high-temperature vibrating tube densiometer (DMA HPM).[9−11] Density measurements were based on the dependence of the oscillation frequency of a unilaterally fixed U-tube on its mass. The vibration U-tube material (Hastelloy C-276, nickel−molybdenum−chromium−tungsten alloy) was selected with the requirements that it show good corrosion resistance and be easily fabricated. The behavior of the vibrating tube can be described by a simple mathematical-physical mass−spring−damper model,[12] where the mass of the vibration tube (m) is equal to the sum of the mass of the tube in vacuum and the mass of liquid contained in it. The frequency of oscillation (f, in s^{-1}) is given by

$$f(T,p) = \frac{\omega_0}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{m_0 + \rho(T,p)V(T,p)}} \qquad (1)$$

where ω_0 is the angular frequency (rad·s^{-1}); k is the force constant (or spring constant) of the tube material (N·m^{-1}), which depends on the size and shape of the tube and is proportional to the Young's modulus of the tube material; m_0 is the mass of

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10.1021/je1003065
Published on Web 07/20/2010

the evacuated vibration tube (kg); $V(T, p)$ is the volume of the vibration tube (m^3); and $\rho(T, p)$ is the density of the liquid inside the vibration tube ($kg \cdot m^{-3}$). For a given force constant k, the sensitivity increases with increasing ratio of the mass of fluid to that of the tube, $\rho V/m_0$.

Measurement of the density of the liquid inside of the vibration tube can be achieved by measuring the period of vibration of the tube ($\tau = 1/f$), which from eq 1 is given by:

$$\tau(T, p) = 2\pi\sqrt{\frac{m_0 + \rho(T, p)V(T, p)}{k}} \quad (2)$$

The period depends on the elasticity and length of the tube. From eq 2 it is seen that the frequency of the harmonic oscillation of the vibration tube can be directly related to the density of the fluid:

$$\rho(T, p) = A_1(T, p) - B_1(T, p)\tau^2(T, p) \quad (3)$$

where $A_1(T, p) = -m_0/V(T, p)$ and $B_1(T, p) = -k/[4\pi^2 V(T, p)]$. The parameters $A_1(T, p)$ and $B_1(T, p)$ do not depend on the properties of the fluid to be measured. Thus, the instrument may be calibrated by measuring the period of oscillation for at least two substances of known density as calibration samples. To check the apparatus and procedures of the measurements and the accuracy of calibration before the apparatus was used in measurements on solutions, the densities of water (distillate),[13] methanol,[14−16] ethanol,[17−19] and NaCl(aq)[20,21] at various molalities were used as reference substances for the calibration of the installation. Measurements of the frequency of the evacuated oscillating tube as a function of temperature were performed after creation of a minimal pressure of (3 to 5) Pa within the tube.

Unfortunately, the parameters $A_1(T, p)$ and $B_1(T, p)$ depend strongly on temperature and pressure. Therefore, the parameters must be determined for each temperature and pressure separately, and the classical eq 3 must be extended to include additional temperature- and pressure-dependent terms. The following calibration equations containing 14 adjustable parameters were employed:[22]

$$A_1(T, p) = \sum_{i=0}^{3} d_i(T/K)^i + \sum_{j=1}^{2} e_j(p/MPa)^j + f(T/K)(p/MPa) \quad (4)$$

$$B_1(T, p) = \sum_{i=0}^{3} h_i(T/K)^i + \sum_{j=1}^{2} l_j(p/MPa)^j + n(T/K)(p/MPa) \quad (5)$$

where d_0, d_1, d_2, d_3, e_1, e_2, f, h_0, h_1, h_2, h_3, l_1, l_2, and n are parameters to be determined.

The temperature in the measuring cell was controlled using a thermostat (F32-ME, Julabo, Germany) with an error of ± 10 mK and measured using the (ITS-90) Pt100 thermometer (type 2141) with an experimental error of ± 15 mK. Pressure was generated using a pressure intensifier (model 37-6-30, HIP, USA) and measured using a pressure transmitter (model P-10, up to 100 MPa, WIKA Alexander Wiegand GmbH & Co., Germany) with an experimental uncertainty of 0.1 % of the full scale.

LiBr ($w > 0.998$) was obtained from Merck (Germany) and used without further purification. Before each experiment, the salt was dried for about 48 h in a special cell by heating it to 413.15 K under reduced pressure (3 to 5 Pa). Ethanol ($w > 0.998$) was obtained from Merck (Germany) and degassed by vacuum distillation using a 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 content < 50 ppm).

In order to prevent subsequent absorption of water, the preparation of the salt solutions was performed in a glovebox. For the preparation of samples, flasks with LiBr and ethanol were connected to a vacuum pump using a glass adapter. Before the valves of the flasks were opened, the air in the glass adapter was evacuated. Ethanol in the top flask streamed to the bottom flask containing LiBr under vacuum. The samples were obtained by successive dilutions of the concentrated solutions. The solutions were prepared by mass weighing using an electronic scale (ED224S, Sartorius, Germany) with a resolution of 0.0001 g.

Results and Discussion

In this work, the (p, ρ, T) properties and V_ϕ values of LiBr in ethanol for $T = (273.15$ to $398.15)$ K at pressures up to $p = 100$ MPa are reported. The experiments were carried out at $m = (0.23351, 0.59717, 0.94988, 1.46165, 2.27186, 2.83298$, and $3.36783)$ $mol \cdot kg^{-1}$ LiBr. The obtained (p, ρ, T) results are listed in Table 1.

The measured densities as a function of pressure and temperature were fitted to the following equation of state[1] from ref 23:

$$p/MPa = A(10^{-3}\rho/kg \cdot m^{-3})^2 + B(10^{-3}\rho/kg \cdot m^{-3})^8 + C(10^{-3}\rho/kg \cdot m^{-3})^{12} \quad (6)$$

in which the coefficients A, B, and C are functions of temperature and molalities m:

$$A = \sum_{i=1}^{3} T^i \sum_{j=0}^{3} a_{ij} m^j$$
$$B = \sum_{i=0}^{2} T^i \sum_{j=0}^{3} b_{ij} m^j \quad (7)$$
$$C = \sum_{i=0}^{2} T^i \sum_{j=0}^{3} c_{ij} m^j$$

The values of the parameters a_{ij}, b_{ij}, and c_{ij} in eqs 6 and 7 are given in Table 2. Equations 6 and 7 describe the experimental results as well as values extrapolated to $m = 0$ and interpolated between the $m = (0.23351$ to $3.36783)$ $mol \cdot kg^{-1}$ results with an average percent deviation of ± 0.023 %, a standard deviation of 0.261 $kg \cdot m^{-3}$, and an average absolute deviation of 0.198 $kg \cdot m^{-3}$.

Table 1. Experimental Values of Pressure (*p*), Density (*ρ*), and Temperature (*T*) for LiBr + C_2H_5OH

p/MPa	*ρ*/kg·m⁻³	*T*/K	*p*/MPa	*ρ*/kg·m⁻³	*T*/K	*p*/MPa	*ρ*/kg·m⁻³	*T*/K
			m/mol·kg^{-1} = 0.23351					
1.023	821.76	273.15	29.924	812.49	313.15	69.845	816.09	348.17
5.012	824.80	273.14	40.032	819.73	313.16	80.004	822.02	348.15
10.002	828.53	273.15	50.014	826.45	313.14	89.926	827.80	348.15
20.031	835.19	273.15	60.002	832.74	313.15	99.957	833.35	348.15
30.024	841.53	273.13	70.035	838.62	313.16	1.023	752.56	353.15
39.945	847.51	273.15	80.042	844.05	313.15	5.002	756.87	353.15
49.923	853.22	273.15	89.924	848.99	313.15	10.021	762.65	353.15
59.985	858.67	273.16	99.985	853.58	313.15	19.985	772.17	353.14
70.003	863.78	273.15	2.012	781.53	323.15	29.974	781.57	353.15
80.014	868.58	273.14	5.012	784.23	323.13	39.986	790.37	353.15
90.023	873.07	273.15	10.001	788.63	323.14	50.031	798.55	353.16
99.945	877.21	273.15	20.023	797.12	323.15	60.014	805.45	353.15
1.003	805.64	293.15	29.921	805.03	323.16	70.025	812.93	353.17
5.014	809.13	293.14	39.926	812.55	323.15	80.004	818.76	353.15
10.003	812.89	293.15	49.912	819.58	323.14	89.945	824.73	353.13
20.003	820.16	293.15	59.926	825.76	323.15	99.987	829.93	353.15
30.014	827.08	293.13	70.004	831.80	323.16	1.235	732.64	373.15
39.956	833.59	293.15	79.924	837.48	323.15	5.004	737.23	373.15
49.985	839.79	293.14	89.956	843.04	323.15	10.024	743.18	373.14
59.924	845.57	293.15	99.965	847.91	323.15	19.985	754.93	373.15
69.784	850.96	293.16	1.023	771.66	333.14	29.954	764.93	373.16
79.926	856.13	293.15	5.021	775.49	333.16	40.001	774.75	373.15
89.954	860.88	293.15	10.026	780.15	333.15	50.023	783.79	373.17
99.986	865.27	293.15	19.985	789.05	333.14	59.987	791.31	373.15
1.204	801.78	298.15	29.945	797.44	333.16	69.957	799.09	373.13
5.002	805.08	298.15	39.784	805.21	333.17	80.004	806.27	373.14
10.064	808.99	298.15	50.021	812.76	333.15	89.956	812.23	373.15
20.004	816.39	298.14	60.012	819.01	333.15	99.874	817.91	373.15
29.124	822.86	298.15	69.985	825.32	333.15	2.451	705.58	398.15
39.784	830.01	298.16	79.924	831.20	333.13	5.024	709.80	398.15
49.956	836.44	298.15	89.965	837.01	333.15	10.023	717.61	398.15
59.942	842.36	298.17	99.958	842.17	333.15	19.974	731.71	398.16
69.784	847.83	298.15	1.024	757.55	348.15	29.928	744.10	398.14
79.924	853.09	298.14	5.002	761.71	348.15	39.941	754.26	398.15
89.921	857.88	298.15	10.032	766.83	348.14	49.931	764.05	398.15
99.468	862.11	298.15	19.985	776.82	348.15	59.978	773.47	398.17
2.012	789.90	313.15	29.954	785.62	348.13	69.953	781.36	398.15
5.028	792.77	313.15	39.947	794.15	348.15	80.014	788.79	398.16
10.023	796.94	313.16	49.923	802.07	348.16	89.921	795.82	398.15
19.956	804.92	313.14	59.947	809.42	348.15	99.624	802.67	398.15
			m/mol·kg^{-1} = 0.59717					
1.306	845.06	273.18	29.958	834.89	313.15	70.013	838.69	348.16
4.686	847.38	273.18	39.844	841.83	313.15	80.021	844.82	348.15
9.917	850.91	273.18	49.963	848.54	313.15	89.957	850.38	348.14
19.964	857.46	273.17	59.831	854.67	313.15	99.985	855.43	348.15
29.993	863.70	273.17	69.997	860.59	313.15	2.037	777.89	353.16
39.918	869.58	273.17	79.828	865.90	313.15	5.143	781.10	353.13
49.994	875.26	273.16	89.993	870.99	313.15	10.149	786.15	353.17
59.884	880.54	273.16	99.841	875.52	313.15	20.259	796.52	353.14
69.990	885.63	273.16	1.026	803.74	323.15	29.993	804.77	353.14
80.091	890.43	273.17	5.021	807.24	323.15	40.152	813.43	353.15
89.993	894.84	273.17	10.023	811.53	323.15	49.993	821.26	353.15
100.098	899.04	273.18	19.945	819.71	323.16	60.225	828.81	353.15
1.504	829.09	293.17	29.978	827.54	323.15	69.979	835.44	353.15
4.938	831.68	293.17	39.926	834.87	323.17	80.139	841.77	353.15
10.061	835.46	293.15	50.001	841.84	323.15	89.993	847.35	353.16
19.905	842.47	293.16	59.974	848.31	323.18	100.098	852.48	353.18
29.993	849.31	293.15	69.923	854.32	323.15	2.757	759.44	373.14
39.912	855.69	293.15	79.954	859.95	323.13	5.125	762.20	373.16
49.993	861.83	293.15	90.021	865.14	323.15	10.201	767.99	373.14
59.817	867.48	293.14	99.745	869.74	323.15	20.555	780.15	373.13
69.979	872.97	293.14	2.100	796.01	333.15	29.993	788.87	373.14
79.675	877.88	293.14	5.223	798.91	333.15	40.172	798.56	373.16
89.926	882.72	293.15	10.112	803.35	333.13	49.979	807.22	373.16
99.971	887.12	293.16	20.295	812.23	333.16	59.801	815.22	373.17
1.141	824.73	298.09	29.996	820.22	333.16	69.994	822.13	373.15
5.221	827.89	298.15	40.191	828.11	333.17	79.738	829.02	373.14
9.947	831.46	298.18	49.994	835.21	333.16	89.934	835.63	373.15
20.192	838.95	298.16	60.159	841.68	333.15	99.866	840.98	373.15
29.993	845.75	298.15	69.994	847.73	333.16	2.804	733.32	398.15
39.830	852.23	298.15	80.063	854.04	333.16	5.071	736.75	398.17
49.963	858.53	298.15	89.993	859.28	333.16	9.730	743.51	398.17
59.998	864.41	298.13	100.035	864.08	333.16	19.941	757.12	398.16
69.931	869.87	298.15	1.002	781.38	348.15	29.996	769.06	398.15
80.151	875.11	298.15	5.412	785.83	348.15	40.001	779.67	398.14
89.963	879.79	298.15	10.035	790.37	348.14	49.993	789.19	398.15
99.874	884.17	298.15	19.902	799.98	348.16	59.907	797.77	398.17

Table 1 Continued

p / MPa	ρ / kg·m⁻³	T / K	p / MPa	ρ / kg·m⁻³	T / K	p / MPa	ρ / kg·m⁻³	T / K
1.459	812.65	313.19	29.914	809.07	348.14	69.979	805.77	398.15
4.759	815.39	313.09	39.945	816.93	348.15	79.787	813.07	398.15
9.792	819.49	313.11	50.012	824.77	348.14	89.994	820.32	398.15
19.554	827.15	313.13	59.956	831.96	348.15	99.863	827.19	398.14
				m/mol·kg^{-1} = 0.94988				
1.024	866.06	273.15	29.935	855.96	313.15	69.784	859.60	348.15
5.021	868.77	273.15	40.021	862.92	313.15	79.325	865.42	348.15
10.002	872.07	273.15	50.035	869.45	313.15	89.935	871.34	348.15
20.031	878.51	273.15	60.047	875.60	313.15	99.935	876.39	348.15
30.045	884.65	273.15	69.784	881.21	313.15	1.405	799.45	353.15
40.015	890.49	273.15	79.935	886.68	313.15	5.074	803.32	353.15
50.027	896.06	273.15	89.986	891.71	313.15	9.985	808.32	353.15
60.029	901.35	273.15	99.954	896.31	313.15	19.924	817.86	353.15
70.002	906.34	273.15	1.203	825.48	323.15	29.784	826.60	353.15
79.954	911.03	273.15	5.451	829.11	323.15	39.784	834.79	353.15
89.935	915.46	273.15	10.026	832.95	323.15	49.925	842.49	353.15
99.986	919.63	273.15	19.957	840.97	323.15	59.926	849.56	353.15
1.034	850.27	293.15	29.928	848.61	323.15	69.845	856.11	353.15
5.029	853.20	293.15	39.784	855.75	323.15	79.924	862.38	353.15
10.041	856.81	293.15	49.928	862.68	323.15	90.021	868.33	353.15
19.924	863.69	293.15	60.024	869.15	323.15	99.925	873.94	353.15
29.895	870.31	293.15	69.794	875.00	323.15	1.026	780.35	373.15
40.003	876.70	293.15	79.935	880.66	323.15	5.412	785.62	373.15
50.002	882.70	293.15	89.925	885.81	323.15	10.068	790.99	373.15
60.032	888.39	293.15	99.969	890.57	323.15	19.935	801.67	373.15
70.102	893.78	293.15	1.305	816.80	333.15	29.974	811.66	373.15
79.956	898.74	293.15	5.214	820.56	333.15	39.236	820.14	373.15
89.245	903.13	293.15	1.267	816.76	333.15	50.023	829.23	373.15
99.965	907.85	293.15	19.923	833.66	333.15	59.926	836.92	373.15
1.045	845.75	298.15	29.942	841.73	333.15	69.895	844.11	373.15
5.004	848.93	298.15	40.014	849.24	333.15	79.936	850.88	373.15
10.024	852.82	298.15	50.078	856.20	333.15	89.945	857.23	373.15
19.956	860.13	298.15	59.924	862.57	333.15	99.968	863.30	373.15
29.945	866.97	298.15	69.794	868.58	333.15	1.425	756.04	398.15
39.784	873.28	298.15	79.935	874.45	333.15	5.025	761.36	398.15
50.012	879.42	298.15	89.984	880.02	333.15	9.986	768.11	398.15
60.024	885.07	298.15	99.986	885.41	333.15	19.923	780.63	398.15
69.784	890.31	298.15	1.304	803.97	348.15	29.784	791.83	398.15
79.215	895.14	298.15	5.004	807.60	348.15	39.926	802.25	398.15
89.926	900.43	298.15	10.064	812.44	348.15	50.024	811.67	398.15
99.975	905.24	298.15	19.985	821.56	348.15	59.926	820.12	398.15
1.045	833.87	313.15	29.942	830.19	348.15	69.784	827.92	398.15
5.003	837.08	313.15	39.784	838.22	348.15	79.935	835.45	398.15
9.985	841.04	313.15	49.927	845.97	348.15	89.936	842.54	398.15
19.924	848.66	313.15	60.002	853.14	348.15	99.021	848.81	398.15
				m/mol·kg^{-1} = 1.46165				
2.048	896.66	273.15	29.979	885.66	313.15	69.784	888.55	348.16
5.195	898.75	273.16	39.715	892.26	313.16	79.956	894.65	348.15
9.742	901.73	273.17	49.925	898.82	313.15	89.932	900.39	348.15
20.115	908.30	273.18	59.623	904.69	313.15	99.845	905.92	348.15
29.966	914.27	273.18	69.928	910.56	313.15	1.217	830.74	353.13
39.973	920.07	273.19	79.877	915.87	313.15	5.043	834.64	353.11
49.922	925.55	273.18	89.926	920.86	313.15	9.980	839.50	353.10
60.091	930.87	273.18	99.649	925.34	313.16	19.703	848.50	353.10
69.993	935.78	273.18	1.035	855.48	323.15	29.947	857.25	353.10
80.129	940.52	273.18	5.106	859.08	323.15	39.836	865.06	353.10
89.963	944.86	273.18	10.065	863.30	323.15	49.993	872.50	353.10
99.708	948.89	273.20	20.003	871.29	323.16	60.279	879.53	353.10
1.999	881.23	293.13	29.975	878.73	323.15	69.928	885.72	353.10
5.005	883.38	293.13	39.954	885.66	323.14	80.053	891.89	353.09
9.790	886.75	293.12	49.926	892.13	323.15	89.979	897.68	353.10
19.962	893.68	293.13	59.957	898.25	323.15	99.915	903.29	353.10
29.997	900.21	293.13	70.002	904.07	323.14	2.369	814.46	373.14
40.468	906.69	293.13	79.923	909.56	323.15	5.019	817.48	373.15
49.901	912.25	293.13	89.956	914.93	323.16	9.909	822.87	373.16
60.137	917.97	293.14	99.957	920.17	323.15	20.097	833.45	373.17
69.979	923.18	293.14	2.291	848.63	333.11	29.993	842.95	373.17
79.914	928.13	293.15	5.163	851.27	333.12	40.176	851.97	373.19
89.963	932.84	293.15	9.932	855.51	333.11	49.993	860.02	373.17
99.824	937.16	293.15	20.223	864.16	333.10	59.977	867.61	373.15
1.341	876.32	298.16	29.979	871.75	333.11	69.979	874.66	373.15
5.308	879.29	298.13	39.966	878.97	333.12	79.993	881.25	373.16
9.947	882.69	298.17	49.993	885.74	333.12	89.924	887.37	373.16
20.358	890.05	298.19	59.791	891.94	333.12	99.791	893.10	373.17
29.993	896.53	298.15	69.993	898.03	333.12	2.214	790.21	398.15
39.801	902.81	298.12	79.815	903.61	333.12	5.252	795.21	398.13
49.922	908.93	298.12	89.925	909.13	333.12	10.085	801.33	398.12
60.144	914.77	298.11	100.027	914.48	333.12	19.859	812.89	398.15

Table 1 Continued

p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}	T/K
69.993	920.05	298.15	2.021	835.77	348.15	29.946	823.95	398.15
80.053	925.10	298.17	5.002	838.72	348.15	39.959	834.18	398.14
89.994	929.76	298.16	10.034	843.52	348.16	49.925	843.34	398.15
99.739	933.99	298.15	20.024	852.51	348.15	60.031	851.51	398.16
2.109	864.85	313.11	30.021	860.82	348.14	69.947	859.16	398.16
5.147	867.25	313.13	40.002	868.51	348.15	80.059	866.49	398.18
9.909	870.96	313.15	50.201	875.81	348.17	89.928	872.71	398.16
19.994	878.53	313.15	59.986	882.36	348.15	99.816	879.34	398.15
				m/mol·kg^{-1} = 2.27186				
1.948	941.72	273.17	29.993	931.18	313.14	69.784	932.62	348.15
4.590	943.92	273.09	40.450	937.95	313.14	79.624	938.32	348.14
10.177	947.50	273.15	49.925	943.67	313.15	89.931	944.08	348.15
20.349	953.97	273.17	59.995	949.40	313.16	99.945	949.54	348.15
29.947	959.72	273.17	69.943	954.83	313.16	1.827	878.19	353.16
40.359	965.49	273.19	80.160	960.11	313.17	5.076	881.19	353.16
49.964	970.63	273.17	89.963	965.03	313.17	10.028	886.04	353.13
59.570	975.51	273.15	100.029	969.91	313.18	20.124	895.23	353.13
69.980	980.49	273.15	1.032	901.60	323.15	29.947	902.89	353.13
79.857	985.04	273.15	5.024	905.02	323.15	39.486	909.80	353.14
89.925	989.55	273.15	10.002	909.13	323.15	49.994	916.93	353.14
100.090	994.02	273.16	19.956	916.87	323.16	60.014	924.01	353.14
1.430	926.33	293.17	29.986	924.09	323.15	69.979	929.91	353.14
4.902	928.89	293.17	39.945	930.75	323.14	80.071	936.01	353.14
10.030	932.58	293.17	49.921	937.00	323.15	89.993	941.40	353.14
19.789	939.24	293.17	60.002	942.94	323.16	99.992	946.74	353.13
29.946	945.75	293.17	69.794	948.43	323.15	1.353	860.50	373.17
40.161	951.90	293.17	79.953	953.90	323.15	4.985	864.78	373.18
49.963	957.45	293.17	89.926	959.13	323.15	9.782	870.51	373.18
60.025	962.80	293.18	99.985	964.32	323.15	19.637	879.78	373.19
69.979	967.88	293.18	2.335	895.03	333.13	29.927	888.82	373.19
79.838	972.67	293.19	5.177	897.13	333.15	39.864	896.99	373.19
89.964	977.54	293.17	10.272	902.05	333.09	49.979	904.77	373.15
99.958	982.14	293.17	20.737	910.39	333.18	59.597	911.69	373.12
2.166	922.88	298.19	29.993	917.22	333.18	69.993	918.69	373.12
5.165	925.09	298.18	40.158	924.19	333.18	79.585	924.75	373.11
9.642	928.25	298.18	49.954	930.45	333.18	89.994	930.92	373.14
20.184	935.31	298.20	60.271	936.65	333.18	99.892	936.43	373.16
29.950	941.76	298.15	69.979	942.19	333.18	1.833	839.10	398.18
39.933	947.93	298.12	79.359	947.33	333.18	4.702	842.75	398.22
49.993	953.69	298.12	89.994	952.98	333.17	9.704	848.87	398.14
60.039	959.15	298.12	99.907	958.17	333.15	20.117	860.65	398.14
69.983	964.25	298.13	1.003	881.25	348.15	29.993	870.74	398.13
79.970	969.11	298.15	5.004	885.02	348.15	39.724	879.80	398.12
89.925	973.93	298.13	10.021	890.16	348.16	49.958	888.51	398.12
99.589	978.52	298.10	19.956	898.47	348.14	59.977	896.37	398.12
1.319	910.08	313.11	29.784	906.12	348.16	69.928	903.66	398.12
4.863	912.94	313.11	39.925	913.47	348.14	79.836	910.54	398.11
9.982	916.81	313.14	49.921	920.25	348.15	89.963	917.33	398.15
20.135	924.35	313.14	59.932	926.65	348.16	99.619	923.71	398.19
				m/mol·kg^{-1} = 2.83298				
1.024	971.83	273.15	29.451	960.70	313.15	70.024	962.07	348.15
5.002	974.56	273.15	40.021	967.43	313.17	79.926	967.67	348.16
10.032	977.92	273.16	49.968	973.38	313.15	89.954	973.13	348.15
19.956	984.22	273.15	59.926	978.99	313.14	99.968	978.42	348.15
29.954	990.17	273.14	69.784	984.26	313.15	1.302	908.32	353.15
39.974	995.79	273.15	80.024	989.48	313.16	5.015	911.75	353.15
49.926	1001.06	273.14	89.925	994.32	313.15	9.986	916.20	353.14
60.021	1006.15	273.15	99.985	999.09	313.15	19.927	924.60	353.15
70.035	1010.98	273.15	1.023	931.78	323.15	30.024	932.51	353.16
80.061	1015.64	273.16	5.021	935.15	323.15	39.945	939.73	353.15
89.956	1020.12	273.15	9.995	939.18	323.15	49.965	946.54	353.14
99.986	1024.57	273.15	19.956	946.78	323.14	60.014	952.95	353.15
1.024	956.08	293.15	29.784	953.72	323.15	69.784	958.82	353.16
5.201	959.11	293.15	39.928	960.39	323.16	79.968	964.64	353.15
10.032	962.50	293.15	50.021	966.58	323.15	89.925	970.10	353.14
19.953	969.14	293.14	59.986	972.34	323.15	99.895	975.38	353.15
29.938	975.41	293.16	69.926	977.81	323.14	1.415	892.25	373.15
39.985	981.35	293.15	79.956	983.13	323.15	5.002	895.82	373.15
49.968	986.92	293.14	89.958	988.29	323.15	10.004	900.66	373.15
60.001	992.24	293.15	99.678	993.25	323.15	19.957	909.82	373.15
70.032	997.31	293.15	1.032	924.49	333.15	29.956	918.40	373.15
79.956	1002.13	293.15	5.026	927.90	333.14	39.984	926.44	373.15
89.958	1006.83	293.15	9.985	931.98	333.15	50.002	933.93	373.15
99.965	1011.42	293.15	19.968	939.71	333.16	59.924	940.87	373.15
1.023	951.93	298.15	29.965	946.88	333.15	69.784	947.33	373.15
5.004	954.84	298.14	40.021	953.59	333.14	80.021	953.61	373.15
9.986	958.39	298.16	49.925	959.77	333.15	89.926	959.33	373.15
19.935	965.15	298.15	59.945	965.67	333.16	99.845	964.74	373.15

Table 1 Continued

p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}	T/K
30.021	971.59	298.14	69.784	971.18	333.15	1.326	868.98	398.15
39.845	977.51	298.15	80.002	976.70	333.14	5.002	873.54	398.15
49.924	983.25	298.16	89.956	981.93	333.15	9.986	879.45	398.14
59.968	988.68	298.15	99.967	987.14	333.15	19.925	890.37	398.15
70.023	993.85	298.14	1.035	912.41	348.15	29.947	900.32	398.16
80.014	998.77	298.15	5.012	915.98	348.15	40.021	909.38	398.15
89.927	1003.47	298.15	9.989	920.29	348.14	49.956	917.53	398.14
99.968	1008.08	298.15	19.957	928.46	348.15	59.926	925.07	398.15
1.021	940.06	313.15	30.024	936.13	348.16	69.784	932.03	398.16
5.102	943.28	313.14	39.957	943.19	348.15	80.002	938.86	398.15
9.978	947.00	313.15	49.926	949.82	348.15	89.925	945.26	398.14
19.926	954.23	313.16	59.964	956.11	348.13	99.985	951.65	398.15
				m/mol·kg^{-1} = 3.36783				
1.537	1000.06	273.15	29.957	988.47	313.17	69.957	988.75	348.14
4.965	1002.30	273.18	40.159	994.86	313.17	79.924	994.30	348.15
10.114	1005.60	273.17	49.914	1000.58	313.17	89.923	999.65	348.15
20.027	1011.76	273.16	59.836	1006.06	313.18	99.934	1004.87	348.15
29.980	1017.69	273.16	69.925	1011.36	313.18	1.063	935.92	353.21
39.977	1023.39	273.16	79.843	1016.39	313.20	4.909	939.35	353.21
49.974	1028.82	273.17	89.986	1021.40	313.18	10.311	944.02	353.21
60.277	1034.14	273.18	99.603	1026.10	313.17	19.643	951.68	353.22
69.994	1038.90	273.18	1.032	959.14	323.15	30.003	959.64	353.21
79.725	1043.43	273.18	5.014	962.48	323.15	40.073	966.87	353.21
89.924	1047.90	273.17	10.058	966.55	323.16	49.925	973.50	353.21
99.951	1052.03	273.17	19.957	974.07	323.15	59.786	979.72	353.21
1.250	983.60	293.16	29.926	981.06	323.14	69.928	985.74	353.21
5.015	986.33	293.15	39.984	987.61	323.15	79.893	991.32	353.20
10.097	989.90	293.14	49.957	993.67	323.16	89.986	996.68	353.20
20.038	996.51	293.15	59.924	999.37	323.15	99.526	1001.50	353.20
29.978	1002.69	293.15	70.002	1004.85	323.14	2.208	920.02	373.12
39.654	1008.34	293.16	79.926	1010.05	323.15	5.044	922.80	373.12
49.936	1014.01	293.15	89.924	1015.15	323.15	10.014	927.55	373.13
59.950	1019.25	293.13	99.956	1020.21	323.15	19.844	936.43	373.12
69.946	1024.25	293.14	1.618	952.85	333.14	29.963	944.93	373.14
80.104	1029.17	293.15	5.051	955.66	333.19	39.934	952.72	373.14
89.989	1033.84	293.15	9.894	959.51	333.19	49.924	960.01	373.14
99.895	1038.46	293.15	19.918	967.06	333.18	60.080	966.95	373.14
2.703	980.82	298.18	29.946	974.09	333.18	69.925	973.28	373.14
5.041	982.47	298.18	39.652	980.47	333.18	80.063	979.45	373.14
9.735	985.72	298.18	49.993	986.85	333.18	89.993	985.20	373.14
19.511	992.17	298.18	59.593	992.46	333.18	99.876	990.71	373.14
29.936	998.66	298.18	69.927	998.21	333.18	2.012	896.84	398.15
40.157	1004.65	298.18	79.861	1003.51	333.18	5.023	900.37	398.16
49.943	1010.11	298.18	89.946	1008.74	333.18	9.911	905.89	398.15
59.916	1015.42	298.20	99.575	1013.64	333.17	19.987	916.46	398.14
69.994	1020.58	298.17	1.002	940.13	348.15	29.993	926.00	398.14
80.661	1025.85	298.13	5.024	943.65	348.15	39.727	934.47	398.13
89.985	1030.35	298.13	10.032	947.88	348.16	49.926	942.62	398.15
99.737	1034.98	298.12	19.956	955.83	348.14	60.122	950.15	398.16
1.995	968.15	313.17	29.985	963.31	348.15	69.957	956.94	398.16
5.344	970.84	313.17	39.978	970.26	348.15	79.919	963.47	398.16
10.286	974.66	313.17	49.952	976.77	348.16	89.993	969.83	398.16
19.807	981.61	313.17	60.024	982.97	348.15	100.000	976.03	398.15

The short empirical equation given by eq 8 can be used for the technical calculation of the (p, ρ, T) properties of ethanol solutions of LiBr:

$$p/\mathrm{MPa} = [d_0T + (d_1 + d_2m)T^2 + d_3T^3]\rho^2 + eT^2\rho^8 + [f_0m + f_1m^3 + (f_2 + f_3m^3)T + (f_4m + f_5m^2 + f_6m^3)T^2]\rho^{12} \tag{8}$$

Equation 8 describes the experimental results as well as values extrapolated to $m = 0$ and interpolated between the m = (0.23351 to 3.36783) mol·kg^{-1} results with an average percent deviation of ± 0.225 %, a standard deviation of 0.095 kg·m^{-3}, and an average absolute deviation of 1.993 kg·m^{-3}. The values of the coefficients in eq 8 are given in Table 3.

For the molality-dependence analysis of the experimental results, the (p, ρ, T) properties of ethanol from refs 17−19 were used. Figures 1 to 3, respectively, show plots of the pressure of LiBr + C_2H_5OH vs density at m = 1.46165 mol·kg^{-1} for various temperatures, the pressure vs density at T = 298.15 K for various molalities, and the deviation of the experimental density (ρ_{exp}) from the calculated density (ρ_{cal}) vs pressure for different temperatures and molalities,.

Table 2. Values of the Coefficients a_{ij}, b_{ij}, and c_{ij} in Equations 6 and 7

a_{ij}	b_{ij}	c_{ij}
$a_{10} = -2.90589$	$b_{00} = -854.902$	$c_{00} = 220.842$
$a_{11} = 0.109313$	$b_{01} = -725.491$	$c_{01} = 1345.81$
$a_{12} = -0.373513\cdot10^{-2}$	$b_{02} = 550.368$	$c_{02} = -821.217$
$a_{13} = 0.844221\cdot10^{-2}$	$b_{03} = -85.1256$	$c_{03} = 119.774$
$a_{20} = 0.88116\cdot10^{-2}$	$b_{10} = 7.71683$	$c_{10} = 2.77871$
$a_{21} = -0.334263\cdot10^{-3}$	$b_{11} = 3.53617$	$c_{11} = -11.3066$
$a_{22} = 0.328985\cdot10^{-3}$	$b_{12} = -3.1252$	$c_{12} = 5.7741$
$a_{23} = -0.145379\cdot10^{-3}$	$b_{13} = 0.487376$	$c_{13} = -0.786006$
$a_{30} = -0.603842\cdot10^{-5}$	$b_{20} = -0.427719\cdot10^{-2}$	$c_{20} = -0.0127063$
$a_{31} = -0.931409\cdot10^{-7}$	$b_{21} = -0.0102272$	$c_{21} = 0.0248023$
$a_{32} = -0.474398\cdot10^{-6}$	$b_{22} = 0.568101\cdot10^{-2}$	$c_{22} = -0.0108598$
$a_{33} = 0.226398\cdot10^{-6}$	$b_{23} = -0.7499\cdot10^{-3}$	$c_{23} = 0.13516\cdot10^{-2}$

Table 3. Values of the Coefficients d_i, e, and f_i in Equation 8

d_i	e	f_i
$d_0 = -2.3101169$	$e = 0.25848 \cdot 10^{-2}$	$f_0 = -178.144$
$d_1 = 0.82076 \cdot 10^{-2}$		$f_1 = 12.0626135$
$d_2 = -0.2343753 \cdot 10^{-3}$		$f_2 = 3.503227$
$d_3 = -0.703232 \cdot 10^{-5}$		$f_3 = -0.04860244$
		$f_4 = -0.813238 \cdot 10^{-2}$
		$f_5 = 0.33885335 \cdot 10^{-2}$
		$f_6 = -0.387565655 \cdot 10^{-3}$

The (p, ρ, T) properties of these solutions were used to derive various thermal and caloric properties. The isothermal compressibility κ_T can be calculated from the experimental (p, ρ, T) results for ethanol solutions of LiBr obtained using eqs 6 and 7 as follows:

$$\kappa_T = \frac{1}{2A\rho^2 + 8B\rho^8 + 12C\rho^{12}} \tag{9}$$

Calculated κ_T values for ethanol solutions of LiBr are given in the Supporting Information, and the values for $m = 2.27186$ mol·kg^{-1} are also shown in Figure 4.

Another thermal coefficient that can be calculated from the experimental (p, ρ, T) results for ethanol solutions of LiBr obtained using eqs 6 and 7 is the isobaric thermal expansibility (α_p):

$$\alpha_p = \frac{A' + B'\rho^6 + C'\rho^{10}}{2A + 8B\rho^6 + 12C\rho^{10}} \tag{10}$$

where A', B', and C' are the temperature derivatives of A, B, and C, which are given by:

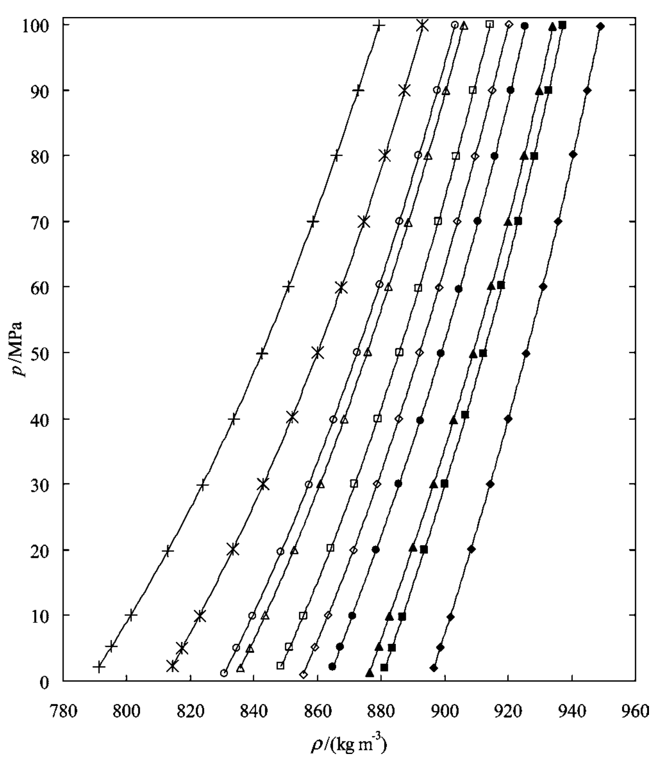

Figure 1. Plots of experimental at $m = 1.46165$ mol·kg^{-1}: ◆, 273.18 K; ■, 293.14 K; ▲, 298.15; ●, 313.15 K; ◇, 323.15 K; □, 333.12 K; △, 348.15 K; ○; 353.10 K; *, 373.16 K; +, 398.15 K. Solid lines were calculated using eqs 6 and 7.

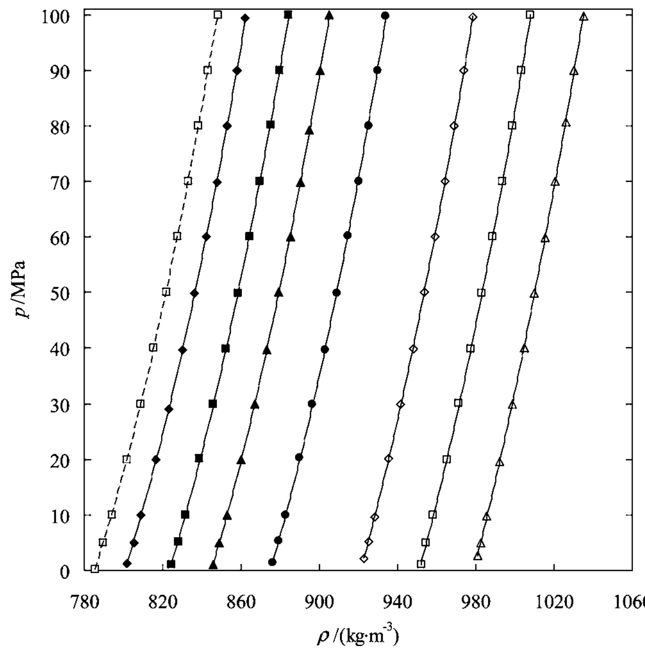

Figure 2. Plots of experimental pressure (p) of ethanol solutions of LiBr vs density (ρ) at $T = 298.15$ K: □, $m = 0$ (from refs 17−19); ◆, $m = 0.23351$ mol·kg^{-1}; ■, $m = 0.59717$ mol·kg^{-1}; ▲, $m = 0.94988$ mol·kg^{-1}; ●, $m = 1.46165$ mol·kg^{-1}; ◇, $m = 2.27186$ mol·kg^{-1}; △, $m = 2.83298$ mol·kg^{-1}; ○, $m = 3.36783$ mol·kg^{-1}. Lines were calculated using eqs 6 and 7.

$$A' = \sum_{i=1}^{3} iT^{i-1} \sum_{j=0}^{3} a_{ij} m^j$$

$$B' = \sum_{i=1}^{2} iT^{i-1} \sum_{j=0}^{3} b_{ij} m^j \tag{11}$$

$$C' = \sum_{i=1}^{2} iT^{i-1} \sum_{j=0}^{3} c_{ij} m^j$$

Calculated values of α_p for ethanol solutions of LiBr are given in the Supporting Information, and the values for $m = 0.59717$ mol·kg^{-1} are also shown in Figure 5.

The next important parameter for the investigation is the difference in specific heat capacities, $c_p - c_v$. Measuring the heat capacity at constant volume can be prohibitively difficult for liquids. That is, small temperature changes typically require large pressures to maintain a liquid at constant volume, so the containing vessel must be nearly rigid or at least very strong. Instead, it is easier to measure the heat capacity at constant pressure. Solving for the heat capacity at constant pressure using mathematical relationships derived from basic thermodynamic laws gives:

$$c_p = c_v + T\frac{(\partial p/\partial T)_\rho^{\ 2}}{\rho^2(\partial p/\partial \rho)_T} \tag{12}$$

where c_p and c_v are the heat capacities at constant pressure and volume, respectively. Using mathematical relationships for the isothermal compressibility κ_T and isobaric thermal expansibility α_p, we can find the following relationship:

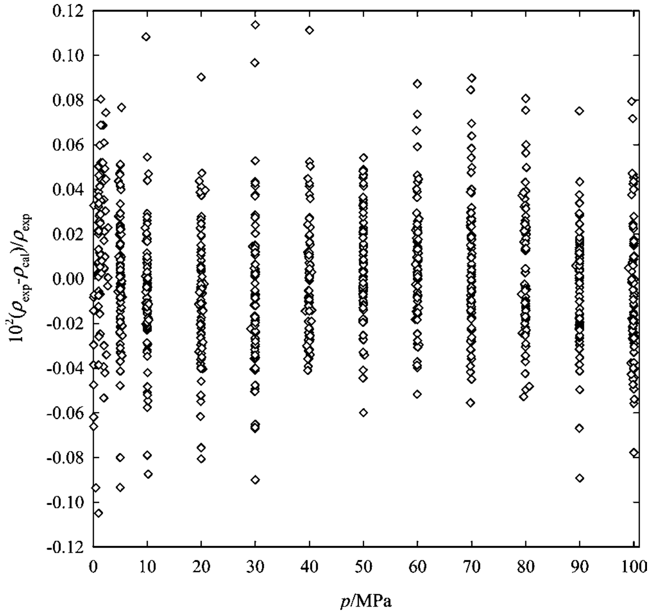

Figure 3. Plots of the relative deviation of the experimental density (ρ_{exp}) from the density calculated using eqs 6 and 7 (ρ_{cal}) vs pressure (p) at different temperatures and molalities.

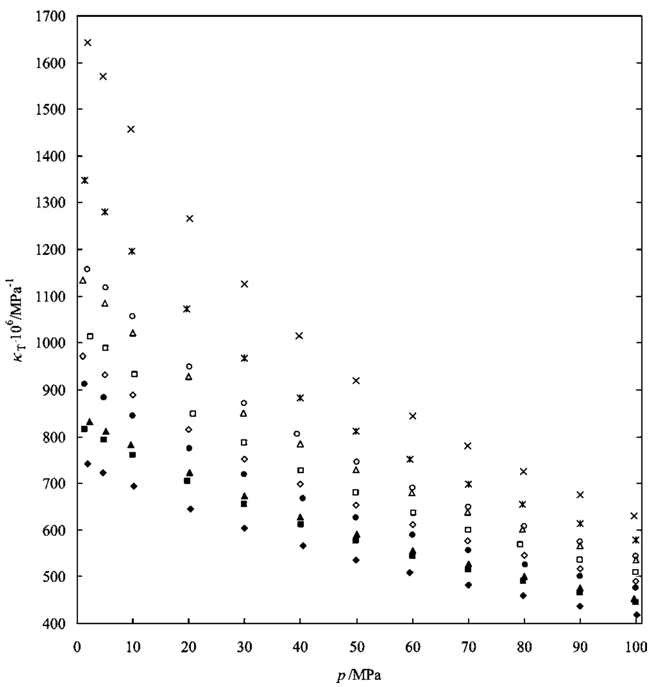

Figure 4. Plots of isothermal compressibility (κ_T) of ethanol solutions of LiBr vs pressure (p) at $m = 2.27186$ mol·kg^{-1}: ◆, 273.16 K; ■, 293.17 K; ▲, 298.15 K; ●, 313.15 K; ◇, 323.15 K; □, 333.16 K; △, 348.15 K; ○, 353.14 K; *, 373.16 K; ×, 398.15 K.

$$c_p - c_v = \frac{\alpha_p^{\,2} T}{\rho \kappa_T} \tag{13}$$

Calculated values of $c_p - c_v$ for ethanol solutions of LiBr are given in the Supporting Information.

The thermal pressure coefficient γ is calculated as the ratio of the isobaric thermal expansibility α_p to the isothermal compressibility κ_T at the same state parameters T and p:

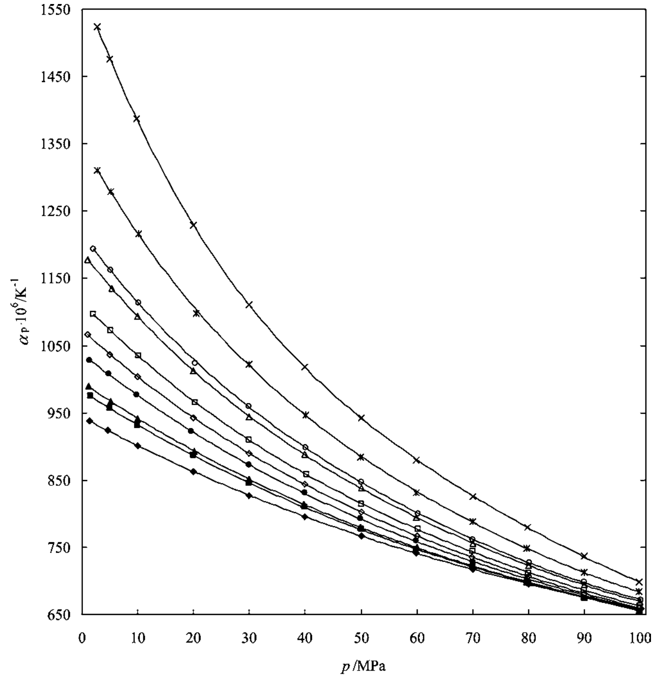

Figure 5. Plots of thermal expansibility (α_p) of ethanol solutions of LiBr vs pressure (p) at $m = 0.59717$ mol·kg^{-1}: ◆, 273.16 K; ■, 293.17 K; ▲, 298.15 K; ●, 313.15 K; ◇, 323.15 K; □, 333.16 K; △, 348.15 K; ○, 353.14 K; *, 373.16 K; ×, 398.15 K.

$$\gamma = \frac{\alpha_p}{\kappa_T} \tag{14}$$

Calculated values of γ for ethanol solutions of LiBr are given in the Supporting Information.

The internal pressure (p_{int}) is related to the thermal pressure coefficient γ and defined by the following relationship:

$$p_{int} \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\gamma - p = \frac{T\alpha_p}{\kappa_T} - p \tag{15}$$

Calculated values of p_{int} for LiBr + C_2H_5OH are given in the Supporting Information.

The apparent molar volume (V_ϕ) is the volume that would be attributed to the LiBr in the LiBr + C_2H_5OH solution if one assumes that the ethanol contributes the same volume it has in its pure state. The apparent molar volume is given by

$$V_\phi = \frac{V - n_1 V_1^0}{n_2} \tag{16}$$

where n_1 and n_2 are the numbers of moles of pure ethanol and LiBr, respectively, and V_1^0 is the molar volume of pure ethanol. In terms of the densities of LiBr + C_2H_5OH and pure ethanol at high temperatures and pressures, the apparent molar volume V_ϕ of LiBr in ethanol can be expressed as:

$$V_\phi = \frac{\rho_e - \rho_s}{m \rho_s \rho_e} + \frac{M}{\rho_s} \tag{17}$$

where ρ_e and ρ_s are the densities of ethanol and the solution, respectively, m is the molality of the LiBr + C_2H_5OH solution,

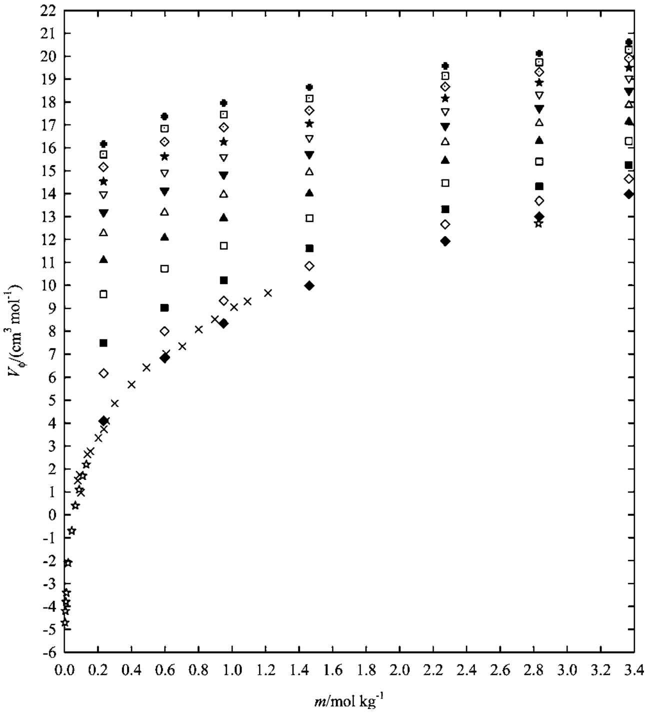

Figure 6. Plots of apparent molar volume (V_ϕ) of LiBr in ethanol vs molality (m) at $T = 298.15$ K: ◆, $p = 0.1$ MPa; ◇, $p = 5$ MPa; ■, $p = 10$ MPa; □, $p = 20$ MPa, ▲, $p = 30$ MPa; △, $p = 40$ MPa; ▼, $p = 50$ MPa; ▽, $p = 60$ MPa; ★, $p = 70$ MPa; dotted diamonds, $p = 80$ MPa; ⊡, $p = 90$ MPa; +, $p = 100$ MPa; ☆, $p = 0.1$ MPa[6], ×, $p = 0.1$ MPa[7].

and M is the molar mass of the dissolved LiBr. The calculations were carried out using the density results for ethanol and LiBr + C_2H_5OH at the same temperatures and pressures.

The maximum relative uncertainty[24] (δV_ϕ) in the V_ϕ determination for the investigated concentrations was $\delta V_\phi = 0.94$ %. Figure 6 shows plots of V_ϕ for LiBr in ethanol versus m at $T = 298.15$ K for various pressures.

The 18 density values of Zafarani-Moattar and Shekaari[7] for LiBr + ethanol solutions at $T = 298.15$ K and $p = 0.1$ MPa with $m = (0.0789$ to $1.2642)$ mol·kg^{-1} were compared with our results, and an average relative deviation of $\Delta\rho/\rho = \pm 0.0418$ % between the two sets of values was obtained. Our results are higher than those of Zafarani-Moattar and Shekaari.[7]

The calculated apparent molar volume results were compared with the available literature values. Only one point from the 11 determined results of Glugla et al.[6] for LiBr + ethanol solutions at $T = 298.15$ K and $p = 0.1$ MPa with $m = (0.00285$ to $2.82870)$ mol·kg^{-1} has the molality in the range of our measured molalities ($m = 2.8287$ mol·kg^{-1}), and it has a deviation of $\Delta V_\phi = \pm 0.282$ cm^3·mol^{-1} from our result at the same molality.

There are 12 apparent molar volume results of Zafarani-Moattar and Shekaari[7] for LiBr + ethanol solutions at $T = 298.15$ K and $p = 0.1$ MPa with $m = (0.00285$ to $2.82870)$ mol·kg^{-1} whose molalities fall in our measured molality interval [$m = (0.2348$ to $1.2146)$ mol·kg^{-1}], and they have an average deviation of $\Delta V_\phi = \pm 0.267$ cm^3·mol^{-1} with our results. Our results are higher than the results of Zafarani-Moattar and Shekaari.[7]

The apparent molar volume results from refs 6 and 7 at $T = 298.15$ K have been added to Figure 6 along with our results to provide a visual comparison.

Conclusion

For the first time, the (p, ρ, T) properties and apparent molar volumes V_ϕ of LiBr in ethanol for $T = (273.15$ to $398.15)$ K and pressures up to $p = 100$ MPa are reported. An empirical correlation of the density of the investigated solutions with composition, pressure, and temperature has been derived. The measured volumetric results are useful for absorption refrigeration machines and absorption heat pumps.

Supporting Information Available:

Calculated values of isothermal compressibility (κ_T), isobaric thermal expansibility (α_p), difference in isobaric and isochoric heat capacities ($c_p - c_v$), thermal pressure coefficient (γ), and internal pressure (p_{int}) for ethanol solutions of LiBr. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 29, 2010. Accepted July 1, 2010.

JE1003065