# Investigations of the $(p, \rho, T)$ Properties and Apparent Molar Volumes $V_\phi$ of the $LiCl + C_2H_5OH$ Solutions

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The $(p, \rho, T)$ properties and apparent molar volumes $V_\phi$ of LiCl in ethanol 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 $(LiCl + C_2H_5OH)$ with pressure, temperature, and molality has been derived. The experiments were carried out at molalities of $m = (0.10487, 0.30229, 0.58732, 1.22211, 2.02242, \text{ and } 2.87989)$ mol·kg$^{-1}$ using lithium chloride.

## Introduction

An absorption heat transfer performs cooling and/or heating by using outside air as a radiation source and an absorption source. It is similar to a vapor-compression device except that compression is accomplished in the absorption heat pump through the use of a thermochemical compressor. The simple thermochemical compressor consists of an absorber, a solution pump, a heat exchanger, and a desorber.

The efficiency of an absorption heat transfer cycle is largely dependent on the physical and chemical properties of the heat transfer fluids. The most serious problems by using the conventional aqueous solutions of electrolytes were discussed in our previous publications on the investigation of methanol solutions of electrolytes.[1,2] In the present work, we begin to analyze the thermal properties of ethanol solutions of electrolytes for their future application as heat transfer fluids in absorption heat transfer systems, where they can replace aqueous solutions at temperatures below the freezing point of water. Ethanol has a lower freezing point than methanol, and this effect can help the optimal circulation of the heat transfer agent in the closed system.

In the present work, the $(p, \rho, T)$ properties and apparent molar volumes $V_\phi$ of LiCl in ethanol 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 $(LiCl + C_2H_5OH)$ with pressure, temperature, and molality has been derived.

Few works [3–8] with density measurements and apparent molar volumes of LiCl in ethanol solutions are available in the literature. $(p, \rho, T)$ properties of these solutions were not available in the literature. Butler and Less[3] studied the refractive index, density, and partial molar volume of these solutions at $T = 291.15$ K, $m = (0 \text{ to } 1.2339)$ mol·kg$^{-1}$, and $p = 0.1$ MPa. Density results were measured by a silika pycnometer with 15 c.c. capacity. Vosburgh et al.[4] investigated the density and apparent molar volume of LiCl in ethanol at $T = 298.05$ K, $m = (0.276 \text{ to } 0.87708)$ mol·kg$^{-1}$, and $p = 0.1$ MPa. Temperature was measured with a thermometer calibrated by the N.P.L. with ± 0.01 °C. Density was measured by a pycnometer with 33 c.c. capacity. Millero[5] in 1971 fully analyzed the apparent molar volumes of electrolytes in various substances. Using the available previous research works, he found the apparent molar volume of LiCl in ethanol at infinite dilution. Kawaizumi and Zana[6] studied the partial molal volumes of ions in organic solvents from ultrasonic vibration potentials and density measurements. The apparent molar volume of LiCl in ethanol at infinite dilution was determined and compared with the results from ref 3. Glugla et al.[7] investigated 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 LiCl in ethanol were measured at $T = 298.15$ K, $m = (0.00196 \text{ to } 2.2998)$ mol·kg$^{-1}$, and $p = 0.1$ MPa. The temperature bath used with this apparatus controlled temperature fluctuation to within 0.001 °C. The volume change was always less than 0.0001 mL and frequently less than 0.00005 mL. The partial molar volumes measured in aprotic solvents with this apparatus were precise to better than ± 2 %. In 2004, Marcus and Hefter[8] carried out a full literature analysis of investigations of thermodynamic

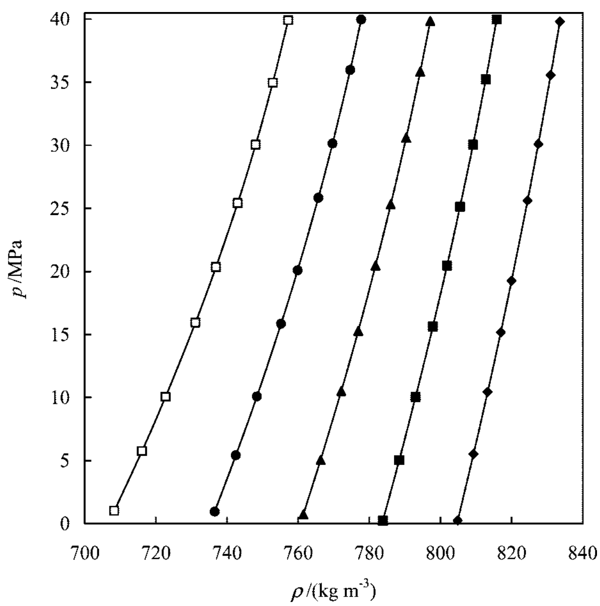


**Figure 1.** Plot of experimental density $\rho$ of ethanol solutions of LiCl versus pressure $p$ at $m = 0.58732$ mol·kg$^{-1}$: ♦, 298.15 K; ■, 323.15 K; ▲, 348.15 K; ●, 373.15 K; □, 398.15 K; ___ calculated by eqs 5 to 8.

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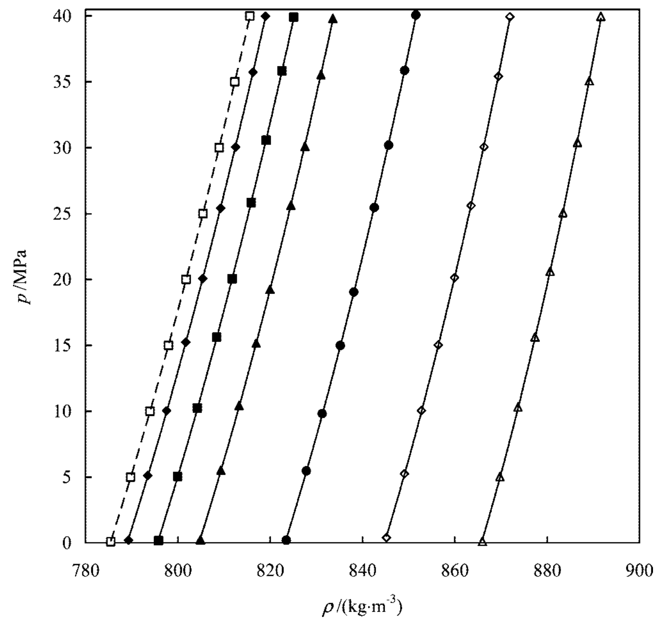


**Figure 2.** Plot of experimental density $\rho$ of ethanol solutions of LiCl versus pressure $p$ at $T$ = 298.15 K: □, $m$ = 0 (from refs 14 to 16); ♦, $m$ = 0.10487 $\text{mol}\cdot\text{kg}^{-1}$; ■, $m$ = 0.30229 $\text{mol}\cdot\text{kg}^{-1}$; ▲, $m$ = 0.58732 $\text{mol}\cdot\text{kg}^{-1}$; ●, $m$ = 1.22211 $\text{mol}\cdot\text{kg}^{-1}$; ◇, $m$ = 2.02242 $\text{mol}\cdot\text{kg}^{-1}$; Δ, $m$ = 2.87989 $\text{mol}\cdot\text{kg}^{-1}$; __ calculated by eqs 5 to 8.

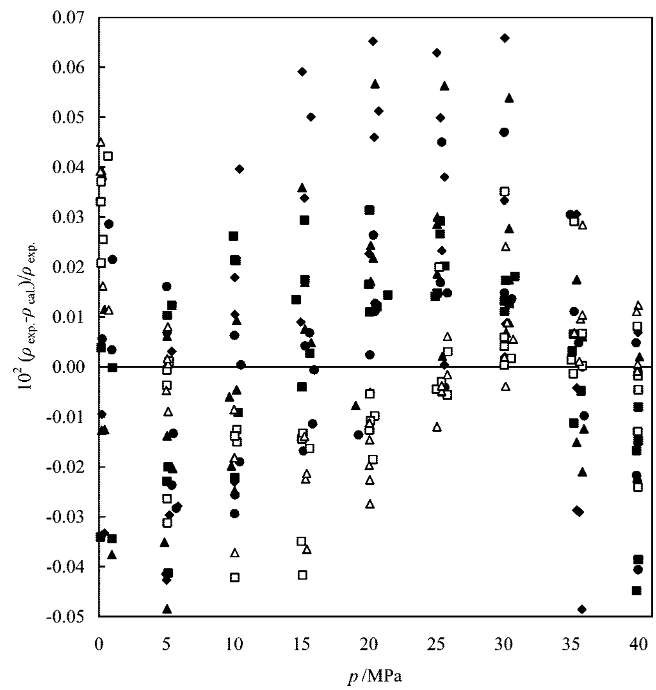


**Figure 3.** Plot of deviations of experimental density $\rho_{exp}$ from density calculated $\rho_{cal}$ by eqs 5 to 8 versus pressure $p$: Δ, $m$ = 0.10487 $\text{mol}\cdot\text{kg}^{-1}$; □, $m$ = 0.30229 $\text{mol}\cdot\text{kg}^{-1}$; ●, $m$ = 0.58732 $\text{mol}\cdot\text{kg}^{-1}$; ▲, $m$ = 1.22211 $\text{mol}\cdot\text{kg}^{-1}$; ♦, $m$ = 2.02242 $\text{mol}\cdot\text{kg}^{-1}$; ■, $m$ = 2.87989 $\text{mol}\cdot\text{kg}^{-1}$.

properties of LiCl + ethanol solutions from previous years. The apparent molar volumes at infinite dilution at $T$ = 298.15 K were analyzed, and $V_\phi^0 = -4.9\ \text{cm}^3\cdot\text{mol}^{-1}$ was selected as the reference value.

## Experimental Section

The ($p$, $\rho$, $T$) properties were investigated using a modified high-pressure−high-temperature Anton-Paar vibrating-tube densimeter (model DMA 5000).[9] This instrument is very suitable for fast and precise measurements of the density of liquids in wide temperature and pressure ranges. The principle of a vibrating tube densimeter is in the phenomena in which the vibrating period of the unilaterally fixed U-tube changes with the density of the sample fluid. In this method, the vibration period $\tau$ of the U-shape tube completely filled with the sample liquid is measured, and then the densities $\rho$ of the sample liquid are computed by applying a principle of a fixed relation between $\tau$ and $\rho$. The liquid sample is a part of the vibrating system affecting directly its mass and thus also its resonant frequency. Due to the complexity of the geometry of the vibrating tube, it requires calibration with a reference fluid of well-known density. This method is suited to precisely measure the difference between the density of the liquid and reference fluid. The precision of the density measurements with the instrument is

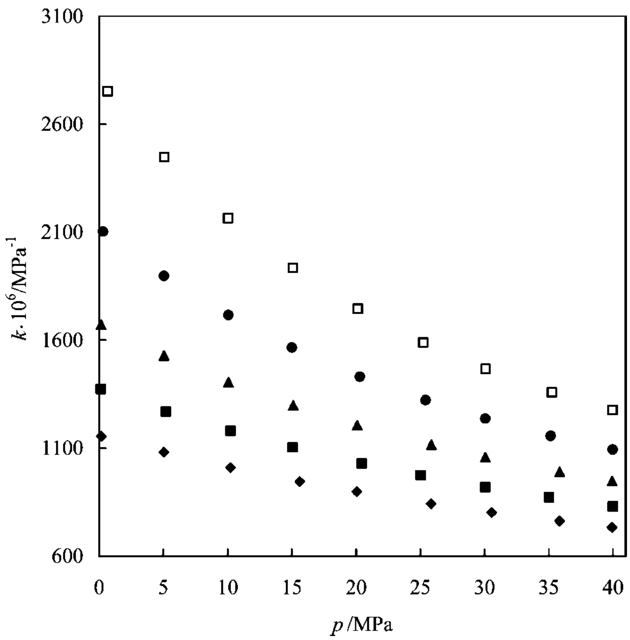


**Figure 4.** Plot of isothermal compressibility $k\cdot10^6/\text{MPa}^{-1}$ of ethanol solutions of LiCl versus pressure $p$ at $m$ = 0.30229 $\text{mol}\cdot\text{kg}^{-1}$: ♦, 298.15 K; ■, 323.15 K; ▲, 348.15 K; ●, 373.15 K; □, 398.15 K.

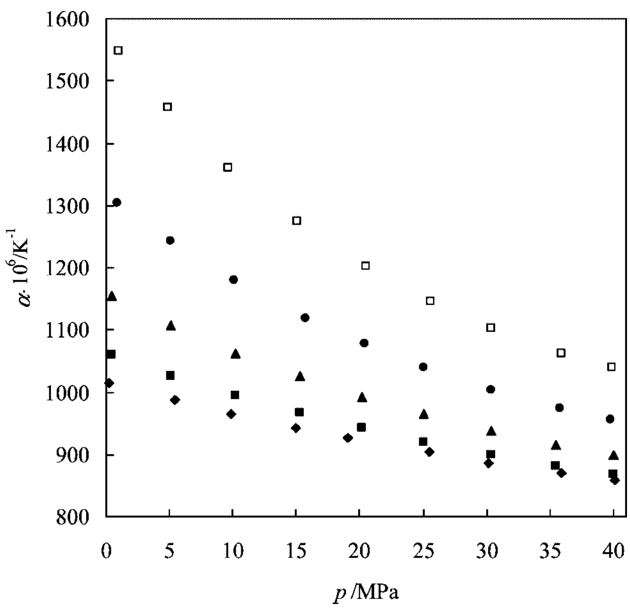


**Figure 5.** Plot of thermal expansibilities $\alpha\cdot10^6/\text{K}^{-1}$ of ethanol solutions of LiCl versus pressure $p$ at $m$ = 1.22211 $\text{mol}\cdot\text{kg}^{-1}$: ♦, 298.15 K; ■, 323.15 K; ▲, 348.15 K; ●, 373.15 K; □, 398.15 K.

**Table 1. Experimental ($p$, $\rho$, $T$) Results of ($LiCl + C_2H_5OH$)**

| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
|---|---|---|---|---|---|
| $m$ = 0.10487 mol·kg$^{-1}$ | | | | | |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.21 | 789.29 | 0.14 | 743.86 | 0.74 | 688.68 |
| 5.12 | 793.51 | 5.08 | 749.63 | 5.01 | 695.99 |
| 10.03 | 797.57 | 10.06 | 755.18 | 10.45 | 704.75 |
| 15.24 | 801.71 | 15.41 | 760.81 | 15.42 | 712.20 |
| 20.06 | 805.39 | 20.06 | 765.44 | 20.09 | 718.73 |
| 25.41 | 809.29 | 25.84 | 770.86 | 25.84 | 726.13 |
| 30.06 | 812.53 | 30.71 | 775.12 | 30.15 | 731.22 |
| 35.71 | 816.28 | 35.24 | 778.84 | 35.86 | 737.37 |
| 39.98 | 818.97 | 39.93 | 782.45 | 39.86 | 741.26 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.12 | 767.47 | 0.29 | 717.74 | | |
| 5.14 | 772.47 | 5.14 | 724.52 | | |
| 10.02 | 777.11 | 10.08 | 731.05 | | |
| 15.32 | 781.93 | 15.42 | 737.69 | | |
| 20.04 | 786.01 | 20.08 | 743.13 | | |
| 25.06 | 790.15 | 25.41 | 748.94 | | |
| 30.15 | 794.13 | 30.26 | 753.85 | | |
| 35.61 | 798.15 | 35.84 | 759.05 | | |
| 39.94 | 801.15 | 39.91 | 762.54 | | |
| $m$ = 0.30229 mol·kg$^{-1}$ | | | | | |
| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.18 | 795.82 | 0.17 | 751.06 | 0.68 | 696.61 |
| 5.04 | 799.96 | 5.06 | 756.68 | 5.07 | 704.02 |
| 10.24 | 804.22 | 10.07 | 762.15 | 10.06 | 711.93 |
| 15.62 | 808.44 | 15.12 | 767.36 | 15.09 | 719.36 |
| 20.05 | 811.77 | 20.09 | 772.20 | 20.14 | 726.27 |
| 25.84 | 815.92 | 25.86 | 777.45 | 25.23 | 732.68 |
| 30.56 | 819.15 | 30.06 | 781.03 | 30.07 | 738.24 |
| 35.84 | 822.58 | 35.84 | 785.62 | 35.24 | 743.62 |
| 39.91 | 825.10 | 39.94 | 788.64 | 39.97 | 748.04 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.14 | 774.35 | 0.31 | 725.29 | | |
| 5.21 | 779.31 | 5.06 | 731.82 | | |
| 10.23 | 784.00 | 10.07 | 738.32 | | |
| 15.06 | 788.31 | 15.02 | 744.36 | | |
| 20.45 | 792.88 | 20.31 | 750.38 | | |
| 25.04 | 796.57 | 25.41 | 755.77 | | |
| 30.06 | 800.40 | 30.06 | 760.33 | | |
| 35.02 | 803.97 | 35.16 | 764.94 | | |
| 39.98 | 807.32 | 39.96 | 768.90 | | |
| $m$ = 0.58732 mol·kg$^{-1}$ | | | | | |
| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.25 | 804.88 | 0.74 | 761.48 | 1.02 | 708.33 |
| 5.52 | 809.31 | 5.06 | 766.32 | 5.74 | 716.08 |
| 10.44 | 813.28 | 10.53 | 772.13 | 10.06 | 722.74 |
| 15.17 | 816.95 | 15.29 | 776.89 | 15.96 | 731.15 |
| 19.25 | 819.98 | 20.48 | 781.78 | 20.35 | 736.90 |
| 25.64 | 824.52 | 25.32 | 786.04 | 25.42 | 742.99 |
| 30.11 | 827.53 | 30.61 | 790.37 | 30.05 | 748.05 |
| 35.56 | 831.01 | 35.84 | 794.33 | 34.95 | 752.88 |
| 39.82 | 833.60 | 39.86 | 797.14 | 39.92 | 757.22 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.24 | 783.81 | 0.96 | 736.55 | | |
| 5.03 | 788.42 | 5.42 | 742.51 | | |
| 10.05 | 793.02 | 10.09 | 748.41 | | |
| 15.62 | 797.87 | 15.85 | 755.19 | | |
| 20.47 | 801.87 | 20.09 | 759.84 | | |
| 25.14 | 805.52 | 25.84 | 765.68 | | |
| 30.06 | 809.15 | 30.15 | 769.70 | | |
| 35.22 | 812.74 | 35.98 | 774.65 | | |
| 39.97 | 815.82 | 39.97 | 777.73 | | |

**Table 1. (Continued)**

| $m = 1.22211\ mol \cdot kg^{-1}$ | | | | | |
|---|---|---|---|---|---|
| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.21 | 823.50 | 0.42 | 780.84 | 0.96 | 731.58 |
| 5.47 | 827.84 | 5.06 | 785.85 | 4.86 | 737.73 |
| 9.82 | 831.28 | 10.21 | 791.09 | 9.68 | 744.82 |
| 14.99 | 835.20 | 15.28 | 795.92 | 15.06 | 752.07 |
| 19.04 | 838.14 | 20.14 | 800.25 | 20.47 | 758.65 |
| 25.46 | 842.57 | 25.07 | 804.33 | 25.62 | 764.26 |
| 30.19 | 845.65 | 30.41 | 808.41 | 30.41 | 768.90 |
| 35.87 | 849.13 | 35.42 | 811.91 | 35.95 | 773.57 |
| 40.07 | 851.57 | 39.97 | 814.81 | 39.94 | 776.48 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.41 | 802.86 | 0.84 | 757.56 | | |
| 5.07 | 807.19 | 5.06 | 762.98 | | |
| 10.20 | 811.76 | 10.06 | 769.02 | | |
| 15.29 | 816.02 | 15.74 | 775.35 | | |
| 20.15 | 819.88 | 20.34 | 780.06 | | |
| 25.06 | 823.57 | 25.08 | 784.55 | | |
| 30.42 | 827.32 | 30.41 | 789.12 | | |
| 35.41 | 830.59 | 35.84 | 793.28 | | |
| 39.96 | 833.36 | 39.82 | 796.01 | | |
| $m = 2.02242\ mol \cdot kg^{-1}$ | | | | | |
| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.41 | 845.20 | 0.15 | 803.25 | 0.74 | 758.72 |
| 5.23 | 849.07 | 4.96 | 808.25 | 5.03 | 765.06 |
| 10.05 | 852.76 | 10.03 | 813.19 | 10.42 | 772.34 |
| 15.03 | 856.40 | 14.96 | 817.67 | 15.06 | 778.00 |
| 20.12 | 859.94 | 20.03 | 821.94 | 20.74 | 784.18 |
| 25.61 | 863.54 | 25.42 | 826.11 | 25.61 | 788.80 |
| 30.08 | 866.32 | 30.16 | 829.46 | 30.09 | 792.51 |
| 35.41 | 869.43 | 35.61 | 832.94 | 35.81 | 796.49 |
| 39.94 | 871.92 | 39.96 | 835.44 | 39.94 | 798.83 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.23 | 824.57 | 0.32 | 781.71 | | |
| 5.41 | 829.25 | 5.86 | 788.43 | | |
| 10.08 | 833.25 | 10.09 | 793.18 | | |
| 15.23 | 837.42 | 15.72 | 799.00 | | |
| 20.41 | 841.36 | 20.31 | 803.31 | | |
| 25.31 | 844.84 | 25.05 | 807.37 | | |
| 30.01 | 847.97 | 30.06 | 811.20 | | |
| 35.42 | 851.30 | 35.41 | 814.80 | | |
| 39.97 | 853.89 | 39.97 | 817.45 | | |
| $m = 2.87989\ mol \cdot kg^{-1}$ | | | | | |
| $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) | $p$/MPa | $\rho$/(kg·m$^{-3}$) |
| $T$ = 298.15 K | | $T$ = 348.15 K | | $T$ = 398.15 K | |
| 0.12 | 865.97 | 0.54 | 825.55 | 1.01 | 785.44 |
| 5.04 | 869.78 | 5.14 | 829.96 | 5.07 | 790.37 |
| 10.32 | 873.67 | 10.08 | 834.46 | 10.14 | 796.07 |
| 15.64 | 877.37 | 15.06 | 838.73 | 15.28 | 801.31 |
| 20.61 | 880.65 | 20.07 | 842.77 | 20.01 | 805.83 |
| 25.08 | 883.43 | 25.64 | 846.96 | 25.32 | 810.70 |
| 30.41 | 886.56 | 30.84 | 850.58 | 30.07 | 814.57 |
| 35.09 | 889.13 | 35.19 | 853.39 | 34.98 | 818.00 |
| 39.98 | 891.64 | 39.86 | 856.19 | 39.98 | 821.90 |
| $T$ = 323.15 K | | $T$ = 373.15 K | | | |
| 0.18 | 845.88 | 0.98 | 805.91 | | |
| 5.41 | 850.34 | 5.14 | 810.39 | | |
| 10.08 | 854.11 | 9.98 | 815.52 | | |
| 15.24 | 858.04 | 14.62 | 819.69 | | |
| 20.06 | 861.48 | 21.42 | 825.53 | | |
| 25.30 | 864.98 | 24.94 | 828.37 | | |
| 30.07 | 867.94 | 30.15 | 832.41 | | |
| 35.21 | 870.90 | 35.74 | 836.30 | | |
| 39.86 | 873.36 | 39.98 | 839.22 | | |

**Table 2. Values of the Coefficients $a_{ij}$, $b_{ij}$, and $c_{ij}$ in Equations 5 to 8**

| $a_{ij}$ | $b_{ij}$ | $c_{ij}$ |
|---|---|---|
| $a_{10} = -1.360094$ | $b_{00} = -1419.63206381$ | $c_{00} = 1724.38987323$ |
| $a_{11} = -0.0510372$ | $b_{01} = 587.21071$ | $c_{01} = -1357.667957$ |
| $a_{12} = 0.15135715$ | $b_{02} = 275.65116767$ | $c_{02} = -532.3577943$ |
| $a_{13} = -0.06578586$ | $b_{03} = -271.34232$ | $c_{03} = 605.31548324$ |
| $a_{14} = 0.0118697$ | $b_{04} = 44.5829$ | $c_{04} = -108.611242$ |
| $a_{20} = 0.002760349$ | $b_{10} = 5.730492$ | $c_{10} = -2.293768$ |
| $a_{21} = 0.16961 \cdot 10^{-5}$ | $b_{11} = -2.19719472$ | $c_{11} = 3.3961916$ |
| $a_{22} = -0.145706 \cdot 10^{-3}$ | $b_{12} = -1.428243344$ | $c_{12} = 2.633988$ |
| $a_{23} = 0.250216 \cdot 10^{-4}$ | $b_{13} = 1.249180504$ | $c_{13} = -2.45685$ |
| $a_{24} = -0.614345 \cdot 10^{-5}$ | $b_{14} = -0.21176755$ | $c_{14} = 0.4390121444$ |

**Table 3. Standard, Absolute, and Average Deviations of Equations 5 to 8**

| molality, $m$/(mol·kg$^{-1}$) | standard deviation[a] | absolute deviation[a] | maximum absolute deviation | average percent deviation[a] |
|---|---|---|---|---|
| 0.10487 | 0.03095 | 0.14165 | 0.46 | 0.01910 |
| 0.30229 | 0.02407 | 0.12001 | 0.40 | 0.01602 |
| 0.58732 | 0.02308 | 0.12157 | 0.38 | 0.01583 |
| 1.22211 | 0.03768 | 0.18973 | 0.54 | 0.02417 |
| 2.02242 | 0.06915 | 0.34834 | 0.63 | 0.04323 |
| 2.87989 | 0.02900 | 0.16087 | 0.45 | 0.01916 |

[a] The equations of deviations are available in ref 1.

about 0.01 kg·m$^{-3}$, although for glass tubes at low pressures the uncertainty in density measurements is about 0.001 kg·m$^{-3}$. The precision of the method is limited by the calibration procedure.

The behavior of the vibrating tube can be described by the simple mathematical−physical model of the undamped spring-mass system.[10] The tube is filled with a sample of interest and vibrates perpendicular to its plane in an electromagnetic field. The frequency of the harmonic oscillation of the tube can be directly related to the density of the fluid contained in the tube. The characteristic period of the vibrator, $\tau$ ($\mu$s), is oscillating at its resonance frequency in the fundamental harmonic mode[11]

$$\tau = 2\pi\left(\frac{m_t + \rho V_t}{C}\right)^{1/2} \quad (1)$$

where $\tau$ is the period of oscillation of the vibration tube ($\mu$s); $m_t$ is the mass of the empty vibrating tube (kg); $V_t$ is the volume of the vibrating tube (m$^3$); $\rho$ is the sample density (kg·m$^{-3}$); and $C$ is the spring constant (N·m$^{-1}$), which depends on the size and shape of the tube and is proportional to Yong's modulus of the tube material.

From written explicitly as eq 1, the density can be

$$\rho = A - B\tau^2 \quad (2)$$

where

$$B(T, P) = -\frac{C(T, P)}{4\pi^2 V_T(T, P)}$$

and

$$A(T, P) = -\frac{m_t}{V_T(T, P)}$$

The parameters $A$ and $B$ can be determined by substance calibration measuring the period of oscillation of at least two substances of known density (in this work, water and methanol). Unfortunately, the parameters $A$ and $B$ are highly temperature dependent and also pressure dependent. Therefore, the parameters must be determined for each temperature and pressure separately, or like in this work, the classical equation must be expanded with temperature- and pressure-dependent terms. For measurements at $T$ = (298.15 to 398.15) K and up to $p$ = 40 MPa, an extended calibration equation with 14 significant parameters is employed[12]

$$A = \sum_i a_i(T/\mathrm{K})^i + \sum_j b_j(p/\mathrm{MPa})^j + c(T/\mathrm{K})(p/\mathrm{MPa}) \quad (3)$$

$$B = \sum_i d_i(T/\mathrm{K})^i + \sum_j e_j(p/\mathrm{MPa})^j + f(T/\mathrm{K})(p/\mathrm{MPa}) \quad (4)$$

where $a_0$, $a_1$, $a_2$, $a_3$, $b_1$, $b_2$, $c$, $d_0$, $d_1$, $d_2$, $d_3$, $e_1$, $e_2$, and $f$ are parameters of the extended vibrating tube equations.

The observed reproducibility and estimated maximum uncertainty of the density measurements between $T$ = (298.15 and 398.15) K and up to $p$ = 40 MPa is within $\rho = \pm$ 0.05 kg·m$^{-3}$ and $\rho = \pm$ 0.2 kg·m$^{-3}$, respectively. This leads to maximum relative uncertainties of ± 0.03 % for the performed measurements for the solutions. For the pressure measurement, a pressure transducer (S-10, WIKA Alexander Wiegand GmbH & Co., Germany) was used. The precision after calibration with a dead weight pressure gauge was estimated to be better than ± 5 kPa. The calibrated (ITS-90) Pt100 temperature sensors installed show a resolution of ± 3 mK and a precision of ± 30 mK, while the thermostat has a stability of ± 20 mK.

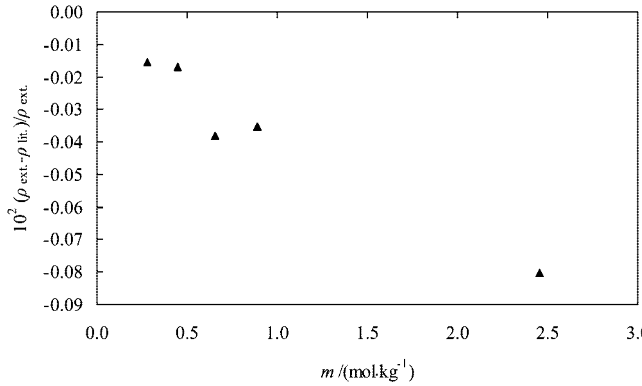


**Figure 6.** Plot of deviations of extrapolated density $\rho_{ext}$ of this work from the literature values of ref 4 vs molality $m$ at $T$ = 298.05 K.

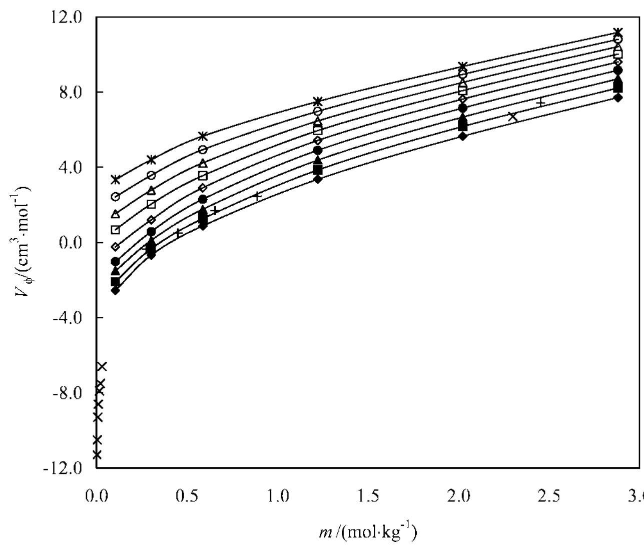


**Figure 7.** Plot of $V_\phi$ of LiCl in ethanol versus $m$ at $T$ = 298.15 K: ♦, $p$ = 0.1 MPa; ■, $p$ = 5 MPa; ▲, $p$ = 10 MPa; ●, $p$ = 15 MPa; ◇, $p$ = 20 MPa; □, $p$ = 25 MPa; Δ, $p$ = 30 MPa; ○, $p$ = 35 MPa; *, $p$ = 40 MPa; +, $T$ = 298.05 K and $p$ = 0.1 MPa [ref 3]; x, $p$ = 0.1 MPa [ref 7]; the calculated points are connected with solid lines only for the visual comparios.

**Table 4. Isothermal Compressibilities $k \cdot 10^6$/MPa$^{-1}$ of (LiCl + $C_2H_5OH$)**

| $m$ = 0.10487 mol·kg$^{-1}$ | | | $m$ = 0.30229 mol·kg$^{-1}$ | | | $m$ = 0.58732 mol·kg$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ | $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ | $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ |
| | | | | $T$ = 298.15 K | | | | |
| 0.21 | 1186 | 1056 | 0.18 | 1155 | 1043 | 0.25 | 1117 | 1030 |
| 5.12 | 1108 | 1020 | 5.04 | 1081 | 1010 | 5.52 | 1041 | 997 |
| 10.03 | 1039 | 988 | 10.24 | 1010 | 977 | 10.44 | 977 | 969 |
| 15.24 | 974 | 956 | 15.62 | 945 | 947 | 15.17 | 923 | 944 |
| 20.06 | 919 | 930 | 20.05 | 898 | 924 | 19.25 | 880 | 924 |
| 25.41 | 866 | 903 | 25.84 | 842 | 897 | 25.64 | 821 | 896 |
| 30.06 | 824 | 881 | 30.56 | 802 | 876 | 30.11 | 784 | 878 |
| 35.71 | 779 | 858 | 35.84 | 762 | 855 | 35.56 | 744 | 858 |
| 39.98 | 748 | 841 | 39.91 | 733 | 841 | 39.82 | 716 | 844 |
| | | | | $T$ = 323.15 K | | | | |
| 0.12 | 1423 | 1177 | 0.14 | 1373 | 1152 | 0.24 | 1313 | 1119 |
| 5.14 | 1314 | 1130 | 5.21 | 1269 | 1107 | 5.03 | 1220 | 1079 |
| 10.02 | 1222 | 1088 | 10.23 | 1180 | 1066 | 10.05 | 1135 | 1042 |
| 15.32 | 1135 | 1047 | 15.06 | 1104 | 1032 | 15.62 | 1053 | 1005 |
| 20.04 | 1066 | 1015 | 20.45 | 1029 | 997 | 20.47 | 991 | 976 |
| 25.06 | 1002 | 984 | 25.04 | 974 | 970 | 25.14 | 937 | 951 |
| 30.15 | 944 | 955 | 30.06 | 919 | 943 | 30.06 | 887 | 928 |
| 35.61 | 889 | 927 | 35.02 | 872 | 919 | 35.22 | 841 | 905 |
| 39.94 | 851 | 907 | 39.98 | 830 | 898 | 39.97 | 804 | 887 |
| | | | | $T$ = 348.15 K | | | | |
| 0.14 | 1741 | 1337 | 0.17 | 1671 | 1300 | 0.74 | 1573 | 1246 |
| 5.08 | 1590 | 1272 | 5.06 | 1529 | 1240 | 5.06 | 1457 | 1196 |
| 10.06 | 1459 | 1214 | 10.07 | 1405 | 1185 | 10.53 | 1331 | 1141 |
| 15.41 | 1339 | 1160 | 15.12 | 1298 | 1137 | 15.29 | 1237 | 1099 |
| 20.06 | 1249 | 1119 | 20.09 | 1206 | 1094 | 20.48 | 1148 | 1059 |
| 25.84 | 1152 | 1073 | 25.86 | 1116 | 1052 | 25.32 | 1077 | 1025 |
| 30.71 | 1083 | 1039 | 30.06 | 1058 | 1024 | 30.61 | 1010 | 993 |
| 35.24 | 1026 | 1011 | 35.84 | 990 | 990 | 35.84 | 953 | 966 |
| 39.93 | 973 | 984 | 39.94 | 947 | 969 | 39.86 | 915 | 947 |
| | | | | $T$ = 373.15 K | | | | |
| 0.29 | 2199 | 1558 | 0.31 | 2103 | 1512 | 0.96 | 1962 | 1438 |
| 5.14 | 1976 | 1465 | 5.06 | 1897 | 1425 | 5.42 | 1785 | 1362 |
| 10.08 | 1787 | 1384 | 10.07 | 1716 | 1347 | 10.09 | 1628 | 1294 |
| 15.42 | 1616 | 1309 | 15.02 | 1566 | 1280 | 15.85 | 1467 | 1222 |
| 20.08 | 1491 | 1252 | 20.31 | 1431 | 1219 | 20.09 | 1367 | 1177 |
| 25.41 | 1369 | 1196 | 25.41 | 1322 | 1168 | 25.84 | 1253 | 1124 |
| 30.26 | 1275 | 1151 | 30.06 | 1237 | 1127 | 30.15 | 1181 | 1090 |
| 35.84 | 1183 | 1107 | 35.16 | 1157 | 1089 | 35.98 | 1099 | 1050 |
| 39.91 | 1126 | 1078 | 39.96 | 1093 | 1057 | 39.97 | 1051 | 1026 |
| | | | | $T$ = 398.15 K | | | | |
| 0.74 | 2884 | 1878 | 0.68 | 2753 | 1821 | 1.02 | 2568 | 1733 |
| 5.01 | 2569 | 1750 | 5.07 | 2448 | 1695 | 5.74 | 2269 | 1607 |
| 10.45 | 2245 | 1614 | 10.06 | 2165 | 1575 | 10.06 | 2044 | 1510 |
| 15.42 | 2006 | 1511 | 15.09 | 1935 | 1475 | 15.96 | 1797 | 1400 |
| 20.09 | 1821 | 1429 | 20.14 | 1746 | 1390 | 20.35 | 1648 | 1332 |
| 25.84 | 1636 | 1345 | 25.23 | 1589 | 1318 | 25.42 | 1506 | 1266 |
| 30.15 | 1520 | 1291 | 30.07 | 1467 | 1261 | 30.05 | 1398 | 1215 |
| 35.86 | 1394 | 1231 | 35.24 | 1358 | 1208 | 34.95 | 1304 | 1169 |
| 39.86 | 1320 | 1195 | 39.97 | 1276 | 1168 | 39.92 | 1225 | 1131 |

| $m$ = 1.22211 mol·kg$^{-1}$ | | | $m$ = 2.02242 mol·kg$^{-1}$ | | | $m$ = 2.87989 mol·kg$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ | $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ | $p$/MPa | $k \cdot 10^6$/MPa$^{-1}$ | $\alpha \cdot 10^6$/K$^{-1}$ |
| | | | | $T$ = 298.15 K | | | | |
| 0.21 | 1052 | 1015 | 0.41 | 974 | 989 | 0.12 | 901 | 959 |
| 5.47 | 981 | 987 | 5.23 | 916 | 967 | 5.04 | 847 | 936 |
| 9.82 | 929 | 966 | 10.05 | 864 | 946 | 10.32 | 796 | 913 |
| 14.99 | 873 | 943 | 15.03 | 816 | 927 | 15.64 | 750 | 893 |
| 19.04 | 834 | 926 | 20.12 | 772 | 910 | 20.61 | 713 | 875 |
| 25.46 | 779 | 903 | 25.61 | 731 | 893 | 25.08 | 683 | 861 |
| 30.19 | 743 | 887 | 30.08 | 700 | 880 | 30.41 | 651 | 846 |
| 35.87 | 705 | 870 | 35.41 | 668 | 866 | 35.09 | 626 | 833 |
| 40.07 | 680 | 859 | 39.94 | 644 | 856 | 39.98 | 602 | 822 |
| | | | | $T$ = 323.15 K | | | | |
| 0.42 | 1211 | 1060 | 0.23 | 1110 | 1000 | 0.18 | 1024 | 958 |
| 5.06 | 1130 | 1027 | 5.41 | 1030 | 970 | 5.41 | 954 | 931 |
| 10.21 | 1050 | 995 | 10.08 | 966 | 946 | 10.08 | 899 | 908 |
| 15.28 | 982 | 967 | 15.23 | 905 | 922 | 15.24 | 845 | 886 |
| 20.14 | 925 | 942 | 20.41 | 852 | 900 | 20.06 | 801 | 868 |
| 25.07 | 874 | 920 | 25.31 | 808 | 882 | 25.30 | 759 | 850 |

**Table 4. (Continued)**

| $m = 1.22211$ mol·kg$^{-1}$ | | | $m = 2.02242$ mol·kg$^{-1}$ | | | $m = 2.87989$ mol·kg$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| $p$/MPa | $k\cdot10^6$/MPa$^{-1}$ | $\alpha\cdot10^6$/K$^{-1}$ | $p$/MPa | $k\cdot10^6$/MPa$^{-1}$ | $\alpha\cdot10^6$/K$^{-1}$ | $p$/MPa | $k\cdot10^6$/MPa$^{-1}$ | $\alpha\cdot10^6$/K$^{-1}$ |
| 30.41 | 826 | 899 | 30.01 | 770 | 867 | 30.07 | 726 | 835 |
| 35.42 | 786 | 881 | 35.42 | 732 | 851 | 35.21 | 694 | 821 |
| 39.97 | 754 | 867 | 39.97 | 704 | 839 | 39.86 | 669 | 810 |
| | | | | $T = 348.15$ K | | | | |
| 0.41 | 1441 | 1154 | 0.15 | 1298 | 1054 | 0.54 | 1179 | 979 |
| 5.07 | 1329 | 1108 | 4.96 | 1198 | 1015 | 5.14 | 1099 | 950 |
| 10.20 | 1222 | 1063 | 10.03 | 1107 | 980 | 10.08 | 1024 | 922 |
| 15.29 | 1133 | 1025 | 14.96 | 1032 | 950 | 15.06 | 958 | 896 |
| 20.15 | 1059 | 993 | 20.03 | 966 | 923 | 20.07 | 901 | 874 |
| 25.06 | 995 | 965 | 25.42 | 906 | 899 | 25.64 | 845 | 851 |
| 30.42 | 935 | 938 | 30.16 | 861 | 880 | 30.84 | 800 | 833 |
| 35.41 | 887 | 916 | 35.61 | 817 | 861 | 35.19 | 767 | 819 |
| 39.96 | 849 | 899 | 39.96 | 787 | 848 | 39.86 | 736 | 806 |
| | | | | $T = 373.15$ K | | | | |
| 0.84 | 1763 | 1305 | 0.32 | 1542 | 1147 | 0.98 | 1350 | 1016 |
| 5.06 | 1614 | 1242 | 5.86 | 1382 | 1085 | 5.14 | 1257 | 983 |
| 10.06 | 1465 | 1179 | 10.09 | 1282 | 1045 | 9.98 | 1161 | 948 |
| 15.74 | 1326 | 1118 | 15.72 | 1169 | 999 | 14.62 | 1089 | 921 |
| 20.34 | 1232 | 1077 | 20.31 | 1094 | 968 | 21.42 | 996 | 886 |
| 25.08 | 1150 | 1040 | 25.05 | 1028 | 940 | 24.94 | 954 | 870 |
| 30.41 | 1073 | 1004 | 30.06 | 969 | 916 | 30.15 | 899 | 848 |
| 35.84 | 1007 | 974 | 35.41 | 918 | 893 | 35.74 | 848 | 828 |
| 39.82 | 967 | 955 | 39.97 | 882 | 878 | 39.98 | 813 | 813 |
| | | | | $T = 398.15$ K | | | | |
| 0.96 | 2262 | 1549 | 0.74 | 1889 | 1300 | 1.01 | 1575 | 1080 |
| 4.86 | 2044 | 1457 | 5.03 | 1702 | 1226 | 5.07 | 1457 | 1040 |
| 9.68 | 1822 | 1361 | 10.42 | 1514 | 1150 | 10.14 | 1333 | 996 |
| 15.06 | 1624 | 1274 | 15.06 | 1385 | 1096 | 15.28 | 1230 | 959 |
| 20.47 | 1466 | 1202 | 20.74 | 1258 | 1042 | 20.01 | 1149 | 929 |
| 25.62 | 1345 | 1146 | 25.61 | 1172 | 1005 | 25.32 | 1068 | 898 |
| 30.41 | 1254 | 1103 | 30.09 | 1107 | 977 | 30.07 | 1009 | 875 |
| 35.95 | 1169 | 1063 | 35.81 | 1043 | 949 | 34.98 | 959 | 856 |
| 39.94 | 1119 | 1039 | 39.94 | 1007 | 932 | 39.98 | 906 | 835 |

LiCl ($w > 0.998$) was supplied from Merck, Germany, and was used without further purification. Before the experiment, the salt was dried in a special cell by prolonged heating at $T = 413.15$ K and the vacuum being renewed by pumping at frequent intervals for 24 h prior to use. To prevent absorption of water, preparation of salt solutions was performed in a glovebox. The samples were obtained by successive dilutions of the concentrated solutions. Ethanol ($w > 0.998$) was supplied from Carl Roth, Germany, and was 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). The solutions were prepared by mass using an electronic scale with a resolution of 0.0001 g.

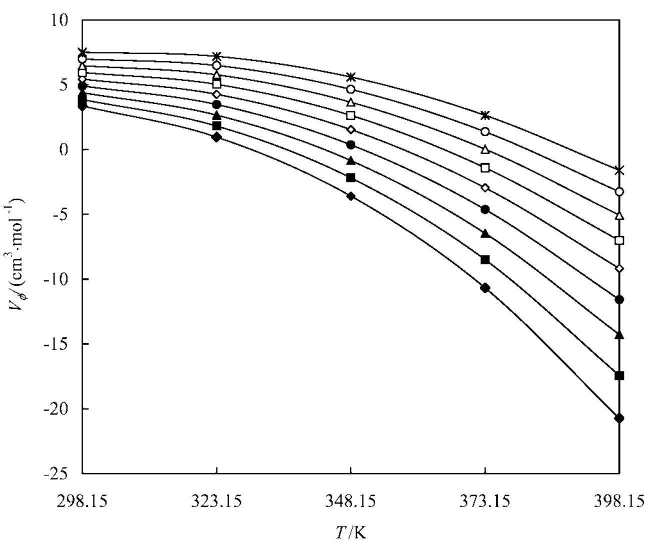


**Figure 8.** Plot of apparent molar volumes $V_\phi$ of LiCl in ethanol versus temperature $T$ at $m = 1.22211$ mol·kg$^{-1}$: ♦, $p = (0.101, 0.24,$ and $0.52)$ MPa; ■, $p = 5$ MPa; ▲, $p = 10$ MPa; ●, $p = 15$ MPa, ◇, $p = 20$ MPa; □, $p = 25$ MPa; Δ, $p = 30$ MPa; ○, $p = 35$ MPa; *, $p = 40$ MPa; the calculated points are connected with solid lines only for the visual showing.

## Results and Discussion

In this work, the ($p$, $\rho$, $T$) properties and apparent molar volumes $V_\phi$ of LiCl in ethanol at $T = (298.15$ to $398.15)$ K, at

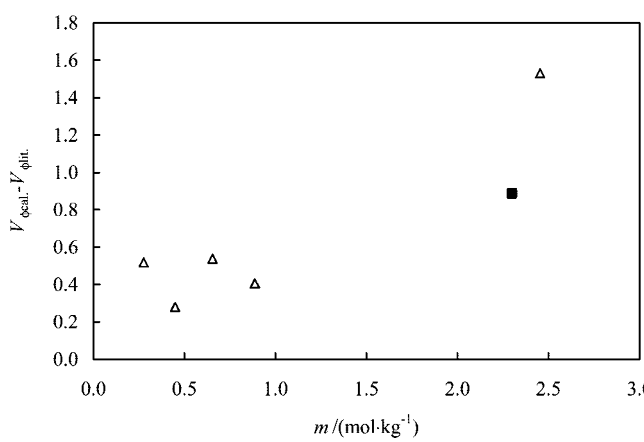


**Figure 9.** Plot of deviations of calculated results of apparent molar volume $V_{\phi\text{calcd}}$ of LiCl in ethanol from the literature values $V_{\phi\text{lit}}$ versus molality $m$: Δ, ref 4 at $T = 298.05$ K; and ■, ref 7 at $T = 298.15$ K.

**Table 5. Apparent Molar Volumes $V_\phi$/($cm^3 \cdot mol^{-1}$) of LiCl in $C_2H_5OH$**

| | $m$/($mol \cdot kg^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| $p$/MPa | 0.10487 | 0.30229 | 0.58732 | 1.22211 | 2.02242 | 2.87989 |
| | | | $T$ = 298.15 K | | | |
| 0.101 | −2.550 | −0.680 | 0.882 | 3.359 | 5.649 | 7.715 |
| 5 | −2.090 | −0.340 | 1.265 | 3.854 | 6.168 | 8.220 |
| 10 | −1.509 | 0.110 | 1.765 | 4.382 | 6.670 | 8.705 |
| 15 | −1.020 | 0.570 | 2.295 | 4.902 | 7.153 | 9.167 |
| 20 | −0.230 | 1.200 | 2.908 | 5.427 | 7.627 | 9.605 |
| 25 | 0.680 | 2.040 | 3.552 | 5.947 | 8.078 | 10.024 |
| 30 | 1.530 | 2.782 | 4.228 | 6.463 | 8.516 | 10.421 |
| 35 | 2.430 | 3.570 | 4.937 | 6.977 | 8.942 | 10.808 |
| 40 | 3.340 | 4.400 | 5.654 | 7.502 | 9.364 | 11.180 |
| | | | $T$ = 323.15 K | | | |
| 0.101 | −5.670 | −4.100 | −2.126 | 0.952 | 3.574 | 5.946 |
| 5 | −5.040 | −3.350 | −1.354 | 1.811 | 4.402 | 6.688 |
| 10 | −4.350 | −2.590 | −0.532 | 2.651 | 5.177 | 7.378 |
| 15 | −3.600 | −1.840 | 0.336 | 3.469 | 5.914 | 8.025 |
| 20 | −2.650 | −0.800 | 1.195 | 4.255 | 6.592 | 8.617 |
| 25 | −1.460 | 0.102 | 2.132 | 5.028 | 7.249 | 9.184 |
| 30 | −0.260 | 1.254 | 3.066 | 5.764 | 7.870 | 9.713 |
| 35 | 1.250 | 2.478 | 3.999 | 6.478 | 8.457 | 10.210 |
| 40 | 2.660 | 3.774 | 4.960 | 7.184 | 9.028 | 10.689 |
| | | | $T$ = 348.15 K | | | |
| 0.101 | −11.002 | −9.150 | −7.118 | −3.592 | −0.489 | 2.537 |
| 5 | −10.003 | −7.937 | −5.760 | −2.185 | 0.833 | 3.681 |
| 10 | −8.910 | −6.822 | −4.410 | −0.856 | 2.032 | 4.720 |
| 15 | −7.650 | −5.545 | −3.100 | 0.358 | 3.130 | 5.653 |
| 20 | −6.240 | −4.101 | −1.760 | 1.534 | 4.143 | 6.515 |
| 25 | −4.750 | −2.604 | −0.446 | 2.625 | 5.079 | 7.296 |
| 30 | −2.923 | −0.996 | 0.822 | 3.650 | 5.951 | 8.022 |
| 35 | −0.740 | 0.617 | 2.076 | 4.643 | 6.763 | 8.698 |
| 40 | 1.001 | 2.238 | 3.320 | 5.592 | 7.536 | 9.332 |
| | | | $T$ = 373.15 K | | | |
| 0.24 | −19.601 | −17.215 | −14.779 | −10.684 | −7.032 | −3.107 |
| 5 | −17.702 | −15.374 | −12.571 | −8.504 | −4.974 | −1.323 |
| 10 | −16.001 | −13.386 | −10.441 | −6.470 | −3.108 | 0.284 |
| 15 | −13.903 | −11.281 | −8.405 | −4.632 | −1.440 | 1.706 |
| 20 | −11.304 | −9.171 | −6.504 | −2.958 | 0.039 | 2.962 |
| 25 | −9.000 | −6.982 | −4.661 | −1.415 | 1.379 | 4.090 |
| 30 | −6.694 | −4.824 | −2.924 | 0.024 | 2.608 | 5.116 |
| 35 | −4.201 | −2.687 | −1.252 | 1.367 | 3.735 | 6.054 |
| 40 | −1.801 | −0.800 | 0.391 | 2.637 | 4.791 | 6.921 |
| | | | $T$ = 398.15 K | | | |
| 0.52 | −32.002 | −28.643 | −25.277 | −20.742 | −16.802 | −11.887 |
| 5 | −28.402 | −25.100 | −21.874 | −17.430 | −13.605 | −9.077 |
| 10 | −25.003 | −22.002 | −18.517 | −14.284 | −10.620 | −6.462 |
| 15 | −22.301 | −18.926 | −15.538 | −11.572 | −8.088 | −4.262 |
| 20 | −19.101 | −15.897 | −12.846 | −9.176 | −5.906 | −2.373 |
| 25 | −16.004 | −12.850 | −10.306 | −7.015 | −3.968 | −0.705 |
| 30 | −13.005 | −10.300 | −7.955 | −5.064 | −2.242 | 0.766 |
| 35 | −9.701 | −7.700 | −5.772 | −3.258 | −0.677 | 2.086 |
| 40 | −7.202 | −5.500 | −3.709 | −1.599 | 0.741 | 3.284 |

pressures up to $p$ = 40 MPa, are reported. The experiments were carried out at $m$ = (0.10487, 0.30229, 0.58732, 1.22211, 2.02242, and 2.87989) $mol \cdot kg^{-1}$ of LiCl. The obtained ($p$, $\rho$, $T$) results are listed in Table 1.

Using a program for standard thermodynamic analysis to describe the ($p$, $\rho$, $T$) properties of ethanol solutions of LiCl, the equation of state (1) from ref 13 was used

$$p = A\rho^2 + B\rho^8 + C\rho^{12} \tag{5}$$

where the coefficients of eq 5, $A$, $B$, and $C$ are functions of temperature and molalities $m$

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

$$B = \sum_{i=0}^{1} T^i \sum_{j=0}^{4} b_{ij} m^j \tag{7}$$

$$C = \sum_{i=0}^{1} T^i \sum_{j=0}^{4} c_{ij} m^j \tag{8}$$

$a_{ij}$, $b_{ij}$, and $c_{ij}$ are the coefficients of the polynomials, and they are given in Table 2. Equations 5 to 8 describe the experimental and interpolated results between the $m$ = (0 and 2.87989) $mol \cdot kg^{-1}$ molality interval with ± 0.03 % average deviation. During the molality $m$ dependence analysis of experimental results, the ($p$, $\rho$, $T$) properties of ethanol from refs 14 to 16 were used for $m$ = 0. The standard, absolute, and average deviations of fitting by eqs 5 to 8 are presented in Table 3. Figures 1 to 3 show the plot of pressure of (LiCl + $C_2H_5OH$) versus density at $m$ = 0.58732 $mol \cdot kg^{-1}$, 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 5 revealed that, at $T \rightarrow T_c$, $A \rightarrow 0$. Such behavior of $A = f(T)$ may be explained by the fact that, according to Putilov,[17] the first term on the right-hand side of eq 5, $A\rho^2$, 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 ($A \rightarrow 0$), 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 5 was derived from Putilov's molecular-kinetic theory.

The $(p, \rho, T)$ properties of these solutions can be used to derive the isothermal compressibilities $k \cdot 10^6/\mathrm{MPa}^{-1}$ and thermal expansibilities $\alpha \cdot 10^6/\mathrm{K}^{-1}$. These properties were calculated from eqs 5 to 8

$$k = (1/\rho)(\partial p/\partial \rho)_T^{-1} \quad (9)$$

$$\alpha = (1/\rho)(\partial p/\partial T)(\partial p/\partial \rho)_T^{-1} \quad (10)$$

$$k = 1/(2A\rho^2 + 8B\rho^8 + 12C\rho^{12}) \quad (11)$$

$$\alpha = (A' + B'\rho^6 + C'\rho^{10})/(2A + 8B\rho^6 + 12C\rho^{10}) \quad (12)$$

where $A'$, $B'$, and $C'$ are the derivatives of $A$, $B$, and $C$ in the following form

$$A' = \sum_{i=1}^{2} iT^{i-1} \sum_{j=0}^{4} a_{ij} m^j, \quad B' = \sum_{j=0}^{4} b_{1j} m^j, \quad C' = \sum_{j=0}^{4} c_{1j} m^j \quad (13)$$

The calculated values of the isothermal compressibilities $k \cdot 10^6/\mathrm{MPa}^{-1}$ and thermal expansibilities $\alpha \cdot 10^6/\mathrm{K}^{-1}$ are given in Table 4 and shown in Figures 4 and 5.

There are two publications[3,4] presenting the density results of these solutions. The experimental density results of Butler and Lees[3] were measured at $T = 291.15$ K, and this temperature point is outside of our temperature interval. In this case, our results were not compared with the results from ref 3. The experimental investigations of thermal properties of LiCl + $C_2H_5OH$ solutions at $T = 298.04$ K were carried out by Vosburgh et al.[4] using a pycnometer method. The comparison of our extrapolated results to $T = 298.05$ K results with the results from ref 4 showed $\pm$ 0.037 % average deviation (Figure 6). Our values are mainly higher than the results of ref 4.

The apparent molar volumes $V_\phi$ of LiCl in ethanol were defined by eq 14 and are listed in Table 5

$$V_\phi = (\rho_e - \rho_s)/(m\rho_s\rho_e) + M/\rho_s \quad (14)$$

where $\rho_e$ and $\rho_s$ are densities of ethanol and the solutions, respectively; $m$ is the molality of solution; and $M$ is the molar mass of the dissolved LiCl. The calculations were carried out using the density results of ethanol and solution at the same temperatures and pressures.

The maximum relative uncertainties[18] $\delta V_\phi$ in the $V_\phi$ determination by the investigated concentrations are $\delta V_\phi$ = (0.38, 0.13, 0.07, 0.03, 0.02, and 0.01) %, respectively. Figure 7 shows the plot of the apparent molar volumes $V_\phi$ of LiCl in ethanol versus $m$ at $T = 298.15$ K and various pressures together with literature results. Figure 8 gives the plot of the apparent molar volumes $V_\phi$ of LiCl in ethanol versus $T$ at $m = 1.22211$ $\mathrm{mol \cdot kg^{-1}}$ and various pressures.

The apparent molar volume results were compared with available literature values. The one value of ref 4 was compared with our extrapolated value of apparent molar volume at $T = 298.05$ K, and $\Delta V_\phi = \pm$ (0.89 $\mathrm{cm^3 \cdot mol^{-1}}$) absolute deviation was found. The five values of apparent molar volume from ref 7 were compared with our calculated values at $T = 298.15$ K, and $\Delta V_\phi = \pm$ 0.65 ($\mathrm{cm^3 \cdot mol^{-1}}$) absolute deviation was found. The apparent molar volume results of ref 4 at $T = 298.05$ K and ref 7 at $T = 298.15$ K were added to Figure 7 for visual comparison, and deviation of calculated results from refs 4 and 7 are shown in Figure 9.

The nonavailability of dielectric permittivity data of ethanol in the literature at the experimental pressures and temperature intervals in this work has made it impossible to calculate the apparent molar volume of these solutions in infinite dilution and compare them with the literature results (refs 5, 6, and 8).

## Conclusion

For the first time, the $(p, \rho, T)$ properties and apparent molar volumes $V_\phi$ of LiCl in ethanol at $T$ = (298.15 to 398.15) K and pressures up to $p$ = 40 MPa are reported. An empirical correlation for the density of the investigated solutions with composition, pressure, and temperature has been derived. The thermal expansivity, isothermal compressibility of solutions, and apparent molar volume of LiCl in ethanol were calculated from the $(p, \rho, T)$ properties at the above-mentioned state parameter intervals in the first time. The experimental $(p, \rho, T)$ properties and calculated apparent molar volumes $V_\phi$ of LiCl in ethanol were compared with the few literature results, and good agreement was found. The measured volumetric results are useful for absorption refrigeration machines and heat pumps.

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