

**(p, ρ , T) AND (p_s, ρ _s, T_s) BEHAVIORS OF AQUEOUS
LITHIUM CHLORIDE SOLUTIONS**

Javid T. Safarov^{1,2}, Astan N. Shahverdiyev¹ and Sevil H. Huseynova¹

- ¹ Department: "Heat and Refrigeration Techniques", Azerbaijan Technical University, 370073, H. Javid Avn., 25. Baku, Azerbaijan, Tel: (994 12) 391432, Fax: (994 12) 383280, e-mail: javid_safarov@yahoo.com
- ² Institut fuer Thermodynamik, FB Maschinenbau, Universitaet Rostock, Albert-Einstein-Str.2, D-18059 Rostock, Germany, Tel: (49 381) 4983226, Fax: (49 381) 4983228, e-mail: javid_safarov@yahoo.com

ABSTRACT

The (p, ρ, T) and (p_s, ρ_s, T_s) behaviors of aqueous solutions of lithium chloride at the 0.04499; 0.12384; 0.18588; 0.25757 mole fractions, at the $298.15 \div 398.15$ K temperature interval and from bubble point pressure up to 60 MPa have been investigated in a constant volume piezometer installation in the department of "Heat and Refrigeration Techniques" of the Azerbaijan Technical University. The volume of piezometer (0.35013 dm^3) was determined at room temperature by the mass of water filling the vessel at an exactly measured temperature and moderate pressure in the range of 1 to 1.5 MPa.

The experimental uncertainties are $\Delta T = \pm 3 \text{ mK}$ for temperature, $\Delta p = \pm 5 \cdot 10^{-2} \text{ MPa}$ for high pressure and $\Delta p = \pm 5 \cdot 10^{-4} \text{ MPa}$ for atmospheric pressure, $\Delta \rho = \pm 3 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ for density.

An equation of state was derived for correlation of the experimental data of aqueous solutions of lithium chloride. The temperature and mole fraction dependence of the coefficients of the equation of states are described.

KEYWORDS: constant volume piezometer; equation of state; mole fraction; aqueous solutions of lithium chloride; temperature; pressure.

1. INTRODUCTION

The interest towards absorption refrigerating machines and heat pumps has increased considerably due to the extreme necessity of more effective use of heat; the creation of wasteless technology; and economy of fuel and energy resources. The number of investigations in this field has increased, concerning the processes and design of absorption refrigerating machines, and heat pumps.

Solutions for absorption refrigerating machines and absorption heat pumps widely apply the aqueous solutions of lithium chloride. In the aqueous solutions of lithium chloride, the mole fractions of water is determined by the content of lithium chloride, i.e. absorbent. The critical analysis of thermodynamic properties of aqueous solutions of lithium chloride for the application in the absorption refrigeration and heat pump systems were carried out in [1].

Also, the aqueous solutions of lithium chloride are used for the absorption of moisture from gases at the drying. For the analyse of full properties of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers it is necessary to know the thermodynamic properties, specially the (p, ρ, T) and (p_s, ρ_s, T_s) properties of these solutions. The purpose of this experimental investigation is to provide new values of density of aqueous solutions of lithium chloride in the high pressures and mole fractions.

The critical literature revision of the (p, ρ, T) and (p_s, ρ_s, T_s) properties, vapor pressure and other properties of the aqueous solutions of lithium chloride have been reported in several papers⁽²⁻⁷⁾. A lot of papers include a values in the atmospheric or low pressures. It is necessary to investigate these solutions over a wide range of state parameters in order to understand the properties of these solutions and provide accurate data for the absorption refrigerating machines and heat pumps.

The (p, ρ, T) and (p_s, ρ_s, T_s) values of Abdullayev⁽⁵⁾ covered the 298.15-598.15 K temperature, 0-40 MPa pressure and 4,7-41% mass. concentration interval. The investigations were carried out by the constant volume piezometer installation.

Panahov⁽⁶⁾ investigated the (p, ρ, T) properties of these solutions at the 298.15-623.15 K temperature, 0,1-35 MPa pressure and 1-20% mass concentration intervals by the hydrostatic weight method.

Holmes *et al*⁽⁸⁾ investigated the density of these solutions at the 498.15 and 523.15 K temperatures, 0,1-30 MPa pressure and 2,48-25,32% mass concentration intervals.

Gates *et al*⁽⁹⁾ carried out the density measurements of the aqueous solutions of lithium chloride at the 298.15 K temperature, 0,1013-40 MPa pressure and 0,21-17,5% mass concentration intervals.

The present paper describe the results of the experimental measurements to determine (p, ρ, T) and (p_s, ρ_s, T_s) properties of aqueous solutions of lithium chloride at the 298.15-398.15 K temperature range, at the 0.04499, 0.12384; 0.18588; 0.25757 mole fraction of lithium chloride and from bubble point pressure up to 60 MPa. The (p, ρ, T) and (p_s, ρ_s, T_s) properties of these solutions in a such pressure and mole fraction ranges of state parameters have been investigated for the first time.

2. Experimental

The measurements were carried out by using the experimental installation which realizes the method of a constant volume piezometer⁽¹⁰⁾. The developed experimental installation enables to derive (p, ρ, T) and (p_s, ρ_s, T_s) properties with high accuracy, as well as to perform experiments on isotherms, isochores, and isobars. The scheme of the experimental installation for the investigation of the (p, ρ, T) and (p_s, ρ_s, T_s) behaviors of aqueous lithium chloride solutions is showed in the Figure 1. Piezometer (3) volume was

determined at room temperature by the mass of water filling at an exactly measured temperature and moderate pressure of the order of 1 to 1.5 MPa and was $350.13 \times 10^{-6} \text{ m}^3$. At these conditions the density of ordinary water is known with high accuracy (0.001-0.003%) from the International Backbone Table for water⁽¹¹⁾. A spherical, thick-walled, high-pressure vessel manufactured of 1Cr18Ni9Ti grade stainless steel was used as the measuring device. The constant volume of the piezometer filled with the liquid under investigation was maintained by a mercury seal under visual observation. The piezometer ballast volume was determined both experimentally and by computation, and its value amounted to 0.1% of the working volume of the piezometer.

The thermostatic control of the piezometer was carried out by means of the liquid-filled thermostat. Glycerin was used for heat-transfer substance. An axial pump (13) was used to circulate the heat-transfer agent around the piezometer. The temperature was regulated by a VRT-2 thermoregulator (19) and measured by two TSN-25 platinum resistance thermometers (1) manufactured and calibrated at the All-Russian Research Institute for Physicotechnical and Radio-Engineering Measurements (VNIIFTRI) in Moscow, using the compensation method. The first thermometer was used for all the experiments and the second one was used for comparison. Difference of these two various thermometers was $\pm 1 \text{ mK}$. Pressure in the experiments was built up and measured by MP-6, MP-60 and MP-600 deadweight pressure gages of 0.05 accuracy class.

Thermodynamic equilibrium was usually attained within 3-5 h after the beginning of an experimental run. Reliability of the data obtained was verified after each run by a control measurement of (p, ρ, T) and (p_s, ρ_s, T_s) properties of water. Deviations of all the parameters did not exceed the tolerance given by [11].

The lithium chloride from Merck company (Germany) and the twice-distilled water were used for the preparation of the solutions. The solutions were prepared by weight in the analytically pure grade using a VLA-200 analytical balance.

Calculation of measurement deviations for experimental quantities was carried out according to the recommendations of meteorologic services⁽¹²⁾: $\Delta T = \pm 3$ mK for temperature, $\Delta p = \pm 5 \cdot 10^{-2} \cdot p$ for pressure, $\Delta \rho = \pm 3 \cdot 10^{-2} \cdot \rho$ for density.

3. Results

It was carried out the experimental measurements to determine the (p, ρ , T) and (p_s , ρ_s , T_s) properties of aqueous solutions of lithium chloride at the 298.15-398.15 K temperature range, at the 0.04499, 0.12384; 0.18588; 0.25757 mole fraction of lithium chloride and from bubble point pressure up to 60 MPa. The (p, ρ , T) values of the investigated solutions are listed in Table 1 and (p_s , ρ_s , T_s) values are listed in Table 2.

4. Correlation

Using standard thermodynamic analysis programs the equation of state (1) was used to describe the (p, ρ , T) and (p_s , ρ_s , T_s) properties of aqueous solutions of lithium chloride in the following form:

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

Here, A, B and C are coefficients and all are functions of temperature and mole fraction in the following form:

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

The a_{ij} , b_{ij} and c_{ij} are the coefficients of the polynomials and tabulated in table 3. The equation of state defined by equations (1) and (2) reproduces our experimental values with a deviation less than 0.07 %.

Eqn. (1) was derived by using the conditions of Putilov's molecular-kinetic theory⁽¹³⁾. The graphical analysis of temperature dependence of the coefficients of the equation has revealed that, at $T \rightarrow T_c$, $A \rightarrow 0$. Such a behavior of $A=f(T)$ has been explained [13] by the fact that, the first term on the right-hand side of (1), $A\rho^2$, is an attractive force or, in Putilov's terminology, attraction pressure; the second $B\rho^8$ and the third $C\rho^{12}$ terms are repulsive forces or repulsive pressure.

The data of water from reference [11] were used for the analysis of mole fraction dependence of the investigated solutions.

Figure 2 shows the temperature dependence of the density of aqueous solutions of lithium chloride at the $x=0.25757$ and figure 3 shows the pressure dependence of the density of aqueous solutions of lithium chloride at the $x=0.18588$.

5. Discussion

The results of the (p, ρ , T) properties of aqueous solutions of lithium chloride with the several sources of density data for a temperature range of 298.15-398.15 K were compared.

The comparison of data from [5] and present results show small deviations. The average deviation of these two data sets is ± 0.09 %. The maximum deviation is +0.18 %.

The deviation of the present results with values of Panahov⁽⁶⁾ is approximately ± 0.1 %. The max. deviation is -0.22 %.

Bogatykh⁽¹⁴⁾ had measured the density of aqueous solutions of lithium chloride at the atmosphere pressures and in 32-46 % mass concentration of lithium chloride. The comparison

of present values with [14] showed, that at the $x=0,18588$ mole fraction of lithium chloride the deviation of the values of [14] from present values is smaller approximately to 0.2% and at the $x=0.25757$ down that present values at the middle 0.3%.

6. Conclusion

The (p, ρ, T) and (p_s, ρ_s, T_s) properties of aqueous solutions of lithium chloride in a such pressure and mole fraction ranges have been investigated for the first time. The equation of state was derived for the correlation of the experimental data of aqueous solutions of lithium chloride. The theoretical analysis of a equation of state (1) was given.

Acknowledgments

Dr. Javid Safarov wish to thank the Alexander von Humboldt fellowship of Germany for the support of his research period at the Rostock University. The authors wish thank to prof. Egon Hassel (Germany), prof. Jean-Pierre Simonin (France), prof. Alexander Apelblat (Israel) and Dr. Laurel Watts (USA) for helpful references during the preparation of present paper.

The authors express appreciation to the Azerbaijan Technical University for support of all the experimental work.

LITERATURE

1. Karavan, S.V., Orekhov, I.I. *Kholodilaya texnika*, **1982**, 11, 32-34.
2. *Densities of Liquid Systems and Their Heat Capacities. Landolt-BBmstein Numerical Data and Functional Relationship in Science and Technology*. New Series. Hellwege, K. H.: editor. Springer-Veriag: Berlin. **1977**, 59-60.
3. Lobo, V. M. M. *Handbook of Electrolyte Solutions*. Part B. Elsevier Sci. Publ. Co.: Amsterdam. **1989**, 1198-1247.
4. Abdullayev, A.A. *The thermal properties and dynamic viscosity of aqueous solutions of halogens of lithium*, PhD dissertation, Baku, **1991**, 196 pp.
5. Panahov, I.A. *The experimental investigation of the density and viscosity of aqueous solutions of lithium, potassium and calcium chlorides*, PhD dissertation, Baku, **1992**, 177 pp.
6. Aseyev, G. G.; Zaytsev, I. D. *Volumetric Properties of Electrolyte Solutions, Estimation Methods and Experimental Data*. Begell House, Inc.: New York. **1996**, 261-279, 1026-1039.
7. Apelblat, A.; Manzurola, E. *J. Chem. Thermodynamics* **2001**, 33, 1133-1155.
8. Holmes, H.F., Mesmer, R.E. *J. Phys. Chem.* **1983**, 87, 1242-1255.
9. Gates, J. A.; Wood, R. H. *J. Chem. Eng. Data* **1985**, 30, 44-49.
10. Safarov, J.T. *Thermal properties of aliphatic alcohols and their mutual solutions*, PhD dissertation, Baku, **1993**, 200 pp.
11. S.L.Rivkin and A.A.Aleksandrov, *The thermodynamic properties of water and water vapor*, Energiya, USSR. **1975**, 80 pp.
12. S.G.Rabinovich, *Measuring Errors*, Energiya: USSR. **1978**, 261 pp.
13. K.A.Putilov, *The thermodynamics of simplest liquids. Studies in Thermodynamics*, Moscow, **1973**, p.105.
14. Bogatykh, S. A.; Evnovich, I. D. *Zh. Prikl. Khim.* **1965**, 38, 945-946.

Table 1

The (p, ρ , T) values of aqueous solutions of lithium chloride

x=0.04499								
	p, MPa							
T, K	0.1	5	10	20	30	40	50	60
298.15	1054.2	1056.1	1057.8	1061.8	1065.6	1069.6	1073.6	1077.3
323.15	1046.1	1047.7	1049.2	1053.0	1056.9	1060.2	1064.5	1068.2
348.15	1034.8	1036.4	1038.6	1042.5	1046.4	1050.4	1054.3	1058.3
373.15	1021.2	1023.5	1025.4	1029.4	1033.9	1037.8	1042.4	1046.4
398.15	-	1006.6	1008.9	1013.5	1017.9	1021.8	1026.2	1030.6
x=0.12384								
	p, MPa							
T, K	0.1	5	10	20	30	40	50	60
298.15	1145.4	1147.5	1149.1	1152.6	1156.4	1159.8	1163.6	1167.3
323.15	1136.0	1137.6	1139.4	1143.2	1146.9	1150.5	1154.5	1157.6
348.15	1125.6	1127.3	1129.3	1132.8	1136.6	1140.4	1144.2	1147.7
373.15	1113.3	1115.2	1117.2	1121.4	1125.6	1129.7	1133.8	1137.6
398.15	-	1102.4	1104.3	1108.4	1113.3	1117.4	1122.4	1126.6
x=0.18588								
	p, MPa							
T, K	0.1	5	10	20	30	40	50	60
298.15	1215.7	1217.4	1218.9	1222.1	1225.1	1228.7	1231.6	1234.5
323.15	1206.4	1208.1	1209.4	1213.0	1216.3	1219.5	1222.9	1226.3
348.15	1197.2	1198.4	1200.2	1203.6	1207.1	1210.5	1213.9	1217.4
373.15	1184.6	1186.4	1188.3	1192.3	1195.9	1199.4	1203.3	1207.3
398.15	-	1174.6	1176.6	1180.3	1184.5	1188.6	1192.5	1197.1
x=0.25757								
	p, MPa							
T, K	0.1	5	10	20	30	40	50	60
298.15	1290.1	1291.6	1293.3	1296.3	1300.4	1303.5	1306.9	1310.3
323.15	1281.4	1282.9	1284.2	1287.8	1291.3	1294.4	1298.1	1301.4
348.15	1271.8	1273.3	1275.1	1278.5	1281.8	1284.5	1288.4	1292.2
373.15	1259.8	1261.6	1263.4	1267.2	1270.6	1274.2	1277.9	1281.5
398.15	1247.6	1249.5	1251.5	1255.2	1259.2	1263.8	1267.4	1271.3

x - mole fraction of lithium chloride.

Table 2.

The (p_s , ρ_s , T_s) values of aqueous solutions of lithium chloride

$T_s=398.15$ K			
x	0.04499	0.12384	0.18588
p_s	0.2178	0.1654	0.1283
ρ_s	1004.5	1100.7	1172.9

Table 3.

Values of coefficients a_{ij} , b_{ij} and c_{ij} in the Eqn. (2)

a_{ij}	b_{ij}	c_{ij}
$a_{10}=-5.12589855$	$b_{00}=698.9742579$	$c_{00}=-251.8329201$
$a_{11}=64.616449$	$b_{01}=-9885.92628$	$c_{01}=4394.2858565$
$a_{12}=-351.74532978$	$b_{02}=15995.125199$	$c_{02}=-12182.666475$
$a_{13}=616.87128539$	$b_{03}=41204.61597$	$c_{03}=-2624.108386$
$a_{20}=0.00820533494$	$b_{10}=0.459453693$	$c_{10}=0.2532104275$
$a_{21}=-0.080680312555$	$b_{11}=-16.601931$	$c_{11}=0.291894177843$
$a_{22}=0.237078828235$	$b_{12}=243.4494685$	$c_{12}=-55.23079423446$
$a_{23}=-0.095329631939$	$b_{13}=-702.2590403$	$c_{13}=192.456463158$

Figure 1. The scheme of the experimental installation: 1 - platinum resistance thermometers; 2, 4, 16, 17 - electric heaters; 3 - piezometer; 5 - capillar tubes; 6, 14 - refrigerators; 7 - triangle; 8 - walves; 9 - vessel for the liquid; 10 - watching window; 11 - manometers; 12 - U-type tube; 13 - axial pump; 15 - propeller; 18 - potensometer; 19 - termoregulator.

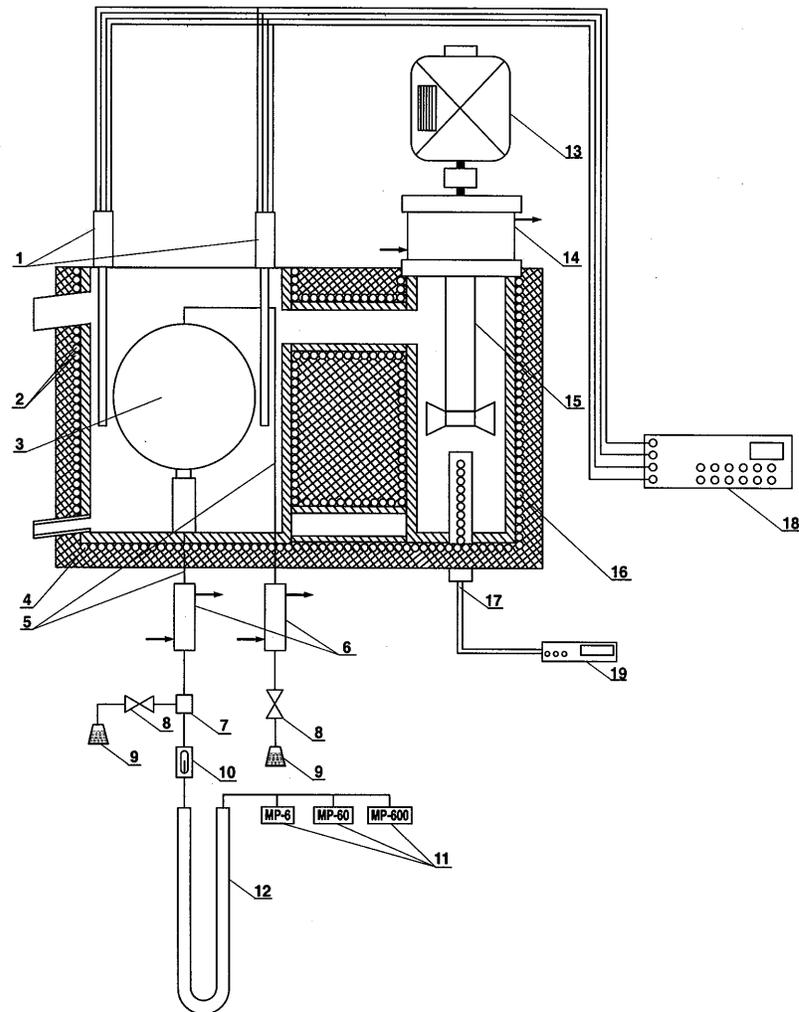


Figure 2. Temperature dependence of the density of aqueous solutions of lithium chloride at the $x=0.25757$ (x is mole fraction of lithium chloride).

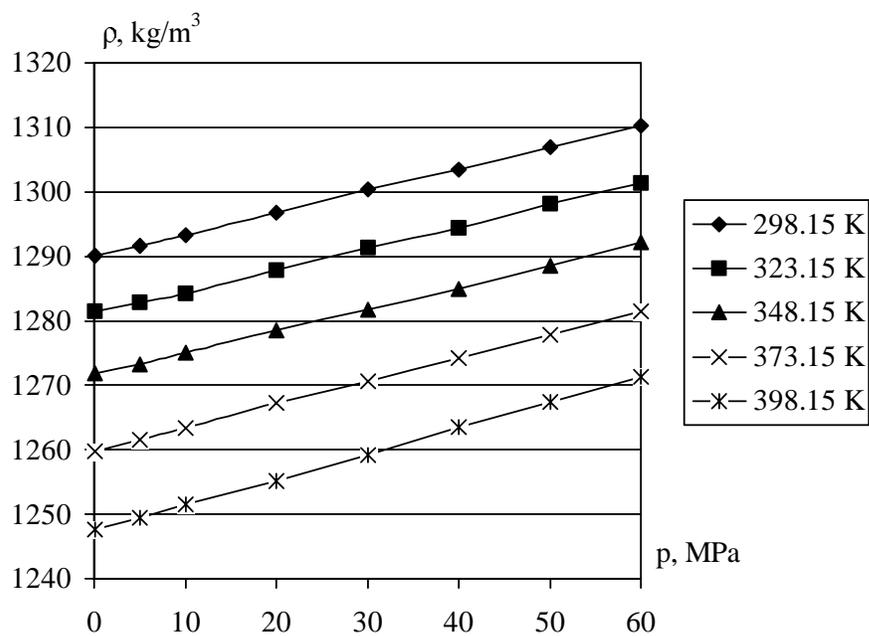


Figure 3. Pressure dependence of the density of aqueous solutions of lithium chloride at the $x=0.18588$ (x is mole fraction of lithium chloride).

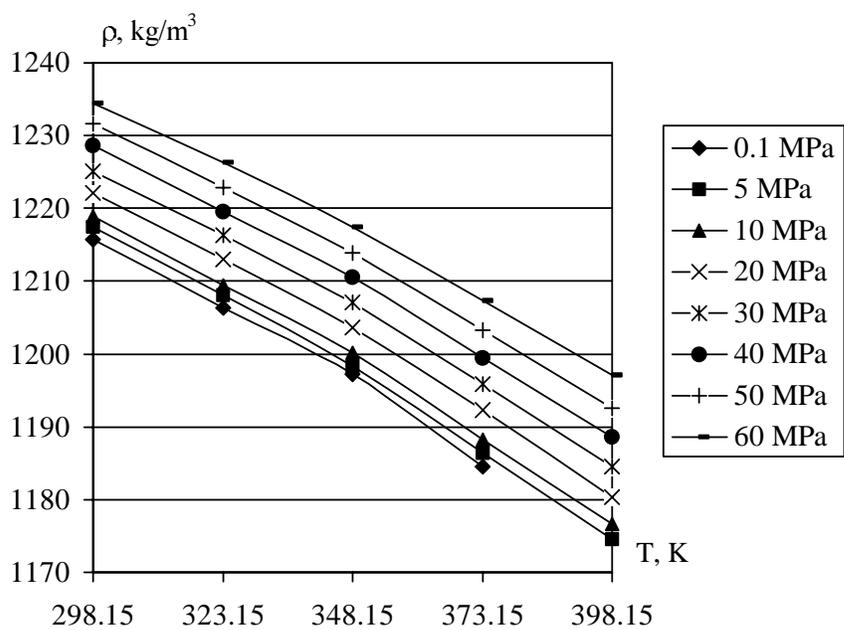


Figure 4. The deviation of experimental values from the calculations by equations (1) and (2) at the $x=0.12384$ mole fraction.

