

Densities and apparent molar volumes of concentrated aqueous LiCl solutions at high temperatures and high pressures

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Abstract

A constant-volume piezometer immersed in a precision liquid thermostat was used to measure the densities of aqueous LiCl solutions from 0.129 to 15.498 mol kg⁻¹, 291.25 to 607.71 K, and 0.961 to 30.55 MPa. The total uncertainties of density, pressure, temperature, and composition measurements were estimated to be less than 0.06%, 0.05%, 15 mK, and 0.015%, respectively. Apparent molar volumes ϕ_V were derived using measured values of density for the solutions and for pure water. The apparent molar volumes were extrapolated to zero concentration to yield partial molar volumes at infinite dilution \bar{V}_2^∞ . The temperature, pressure, and concentration dependence of apparent molar volumes were studied. All experimental and derived properties (apparent and partial molar volumes) were compared with experimental values reported in the literature. The maximum apparent and partial molar volumes at temperatures around 315–400 K, depending on concentration and pressure, was determined.

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1. Introduction

Aqueous solutions of electrolytes at high temperatures and high pressures play a major role in both natural and industrial processes and in waste disposal (Pitzer, 1993). Accurate volumetric (density, apparent and partial molar volumes) data of aqueous solutions is crucial for understanding industrial and natural processes. In many

applications (chemical engineering and geochemistry), these processes occur at high temperatures and high pressures. Surface and oceanic waters are near room temperature, similar aqueous solutions are present at high temperatures and high pressures in deep geological formations. Aqueous systems also arise in steam-power generation, geothermal power plants, hydrothermal synthesis, seawater desalination processes, and other industrial operations at high temperatures and high pressures. The oceans and underground waters are the largest reservoirs of aqueous electrolyte solutions. Thus, there is great practical interest in the thermodynamic properties of aqueous salt solutions at these conditions.

The dominant solutes are often simple electrolytes such as NaCl, KCl, LiCl, CaCl₂, MgCl₂, and Na₂SO₄

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with lesser amounts of potassium salt, carbonates, borates, etc. LiCl is one of the dominant components of many aqueous fluids (natural fluids). LiCl concentration can be similar to that of NaCl in some Li-rich pegmatites (London, 1985; Lagache and Sebastian, 1991; Wood and Williams-Jones, 1993) or in magmatic fluids associated with Li-rich leucogranites (Cuney et al., 1992). Volumetric properties of LiCl-rich brines are important in understanding deep seated geochemical processes. Although most saline groundwaters are dominated by NaCl, Li is one of the next most important cation after Na, and Cl is the dominant anion. LiCl-rich brines also may play a role in seafloor hydrothermal systems at mid-ocean ridges. Therefore, the thermodynamic behavior of aqueous LiCl solutions over a wide range of temperatures and pressures is of considerable interest in chemical oceanography and geochemistry. In addition, the volumetric data are also of relevance for understanding the properties of geothermal brines, high temperature corrosion processes, and the scaling of boiler systems. The H₂O+LiCl system is very important in many geological processes. LiCl is the primary solution in most hydrothermal and metasomatic fluids. The importance of LiCl in deep brines of the Earth's crust and its reactivity in fluid–rock interaction is becoming increasingly recognized. The thermodynamic properties of the H₂O+LiCl are important to understanding these interactions and deep seated geochemical processes. Groundwater encountered in deep wells drilled in crystalline rocks are also commonly high in saline brines in which Li⁺ is one of the dominant cation.

To use H₂O+LiCl solutions effectively, it is necessary to know their fundamental *PVTx* relationships and other derived properties (apparent and partial molar volumes) at high temperatures and high pressures. However, *PVTx* data for the H₂O+LiCl system under high pressure and at high temperatures are scarce. The development of an equation of state depends on experimental data, from which empirical parameters can be obtained. Theoretical modeling of the H₂O+LiCl

system serves as an example for other ionic systems of 1:1 charge-type electrolytes. Obviously there is a need for a thorough study of the volumetric properties of LiCl (aq) at high temperatures and high pressures. The main objective of this paper is to provide reliable experimental volumetric (density, apparent and partial molar volumes) properties for LiCl(aq) solutions at high temperatures and high pressures. The present measurements focused on the temperature range from 291 to 608 K, at pressures up to 31 MPa, and at molalities up to 15.5 mol kg⁻¹. The present results considerably expand the temperature, pressure, and concentration ranges in which densities and apparent and partial molar volumes for aqueous LiCl are available. We also give a comprehensive analysis of the available experimental volumetric data for LiCl(aq) to estimate the reliability of the published data. Most reported experimental data on the volumetric properties of LiCl(aq) cover near ambient temperatures and atmospheric pressure. The volumetric properties (density, apparent and partial molar volumes) of LiCl(aq) have been studied by many authors (Green, 1908; Baxter and Wallace, 1916; Sudgen, 1926; Jones and Bradshaw, 1932; Lanman and Mair, 1933; Scott et al., 1934; Scott and Bridger, 1935; Paranjpe and Rajderkar, 1935; Nickels and Allmand, 1937; Suhrmann and Wiederich, 1953; Lengyel et al., 1964; Bogatykh and Evnovich, 1965; Ellis, 1966; Vaslow, 1966; Millero and Drost-Hansen, 1968; Wirth and Lo Surdo, 1968; Ostroff et al., 1969; Vaslow, 1969; Postnikov, 1970; Mashovets et al., 1971; Choi and Bonner, 1973; Fortier et al., 1974; Millero et al., 1977; Out and Los, 1980; Isono, 1980, 1985; Maksimova et al., 1987; Wimby and Berntsson, 1994; Jahagirdar et al., 2000; Apelblat and Manzurova, 2001; Vercher et al., 2003; Brown et al., 2004) at atmospheric pressure and at ambient and low temperatures. Several authors (Gorbachev et al., 1974; Gates and Wood, 1985; Majer et al., 1989; Abdullaev et al., 1990; Abdullaev, 1991; Pepinov et al., 1989; Pepinov, 1992) reported the volumetric data (density, apparent

Table 1

Summary of the density measurements for aqueous LiCl solutions at high temperatures and high pressures

First author	Year	Method	Uncertainty	Temperature (K)	Pressure (MPa)	Concentration (mol kg ⁻¹)
Gorbachev	1974	HW	0.15% to 0.20%	313 to 553	10	0.001 to 1.5
Gates	1985	VTD	0.1% to 0.2%	298	0.1 to 40	0.05 to 5.0
Majer	1989	VTFD	0.02 to 0.53 kg m ³	322 to 550	0.8 to 33	0.05 to 3.00
Pepinov	1989, 1991	HW	0.15%	298 to 623	0.1 to 30	0.56 to 12.28
Abdullaev	1990, 1991	CVP	0.65%	298 to 598	5 to 40	2.8 to 28.5
This work	2005	CVP	0.06%	291 to 608	0.1 to 31	0.13 to 15.50

VTFD—vibrating-tube flow densimeter; VTD—vibrating-tube densimeter; CVP—constant-volume piezometer; HW— hydrostatic weighing method.

and partial molar volumes) in the fairly wide range of temperature and pressure. Table 1 shows all available density data sets for binary $\text{H}_2\text{O}+\text{LiCl}$ solutions at high temperatures and high pressures. In this table the first author is given together with the method employed, uncertainty of the measurements, and the temperature, pressure, and concentration ranges. Some of the reported densities are inaccurate and inconsistent. As one can see from Table 1, the uncertainty of the data reported by Abdullaev et al. (1990), Abdullaev (1991) is 0.65% (almost 10 times higher than present measurements).

It is apparent that experimental data at high temperature, and high pressure, are scarce. Thus, the primary objective of this work was to expand the existing database to high temperatures, high pressures, and high concentrations. The extensive volumetric data for LiCl (aq) have been reviewed on several occasions (Gates and Wood, 1985; Majer et al., 1989; Apelblat and Manzurolo, 2001; Brown et al., 2004) and do not need to be discussed here. Several compilations of the volumetric properties of LiCl(aq) at atmospheric pressure exist in the literature (Lobo and Quaresma, 1981; Aseyev and Zaytsev, 1996). However, new data have appeared since these works were completed. Lobo and Quaresma (1981) and Aseyev and Zaytsev (1996) reported a comprehensive review of LiCl(aq) volumetric measurements made between 1908 and 1994, except for a few missing works. Therefore, here we will briefly review only the works that were published recently. We also included some missing data from theses and local publications which are difficult to obtain for most readers.

Majer et al. (1989) studied the volumetric properties (density differences between the densities of LiCl(aq) and pure water and apparent molar volumes) of LiCl(aq) from 0.05 to 3 mol kg^{-1} , 322 to 550 K, and 0.8 to 32.6 MPa by using a vibrating-tube flow densimeter. The uncertainty of the temperature, pressure, and density difference measurements were 0.05–0.15 K, 0.1 MPa, and 0.02–0.53 kg m^{-3} , respectively. The uncertainty in derived apparent molar volumes is within 0.1 to 1.9 $\text{cm}^3 \text{ l}^{-1}$ depending on temperature. Wimby and Bertsson (1994) reported new experimental density data for LiCl (aq) over a temperature range 293.15–343.15 K at concentrations between 0.3001 and 0.4539 mass fraction. Measurements were performed with a vibrating-tube densimeter. The uncertainty in temperature and density measurements was 0.05 K and 0.1 kg m^{-3} , respectively. Apelblat and Manzurolo (2001) reported the three densities (0.1009, 0.4932, and 1.0009 mol kg^{-1}) for LiCl(aq) in the temperature range from 278.15 to 338.15 K. These data were used to evaluate the

apparent molar volumes. Measurements were made with a commercial densimeter such as vibrating tube with built-in thermoelectrical module for heating and cooling the sample in a thermostated U-tube. The uncertainty in

Table 2

Experimental values of density, temperature, apparent molar volume, and concentration of $\text{H}_2\text{O}+\text{LiCl}$ solutions at atmospheric pressure

T (K)	ρ (kg m^{-3})	ϕ_v ($\text{cm}^3 \text{ mol}^{-1}$)
<i>m</i> = 0.129 (mol kg^{-1})		
297.85	1000.2	18.51
304.75	998.35	17.52
314.23	994.9	18.31
326.95	989.3	18.86
335.55	985.2	17.08
348.05	977.9	19.08
<i>m</i> = 0.847 (mol kg^{-1})		
295.55	1017.55	18.56
301.15	1016.05	18.61
305.95	1014.55	18.65
318.35	1009.75	18.82
329.15	1005.00	18.60
337.55	1000.95	18.23
<i>m</i> = 1.236 (mol kg^{-1})		
289.85	1027.9	18.34
298.75	1025.7	18.54
316.55	1019.3	18.83
338.95	1009.6	17.90
359.90	997.90	17.00
<i>m</i> = 2.592 (mol kg^{-1})		
289.85	1056.62	18.99
298.75	1054.21	19.17
316.55	1047.91	19.26
338.95	1037.98	18.90
359.90	1027.43	17.99
<i>m</i> = 5.827 (mol kg^{-1})		
289.85	1114.72	20.17
298.75	1112.18	20.27
316.55	1106.41	20.23
338.95	1097.98	19.82
359.90	1088.67	19.19
<i>m</i> = 10.062 (mol kg^{-1})		
289.85	1179.88	20.66
298.75	1177.14	20.75
316.55	1171.13	20.76
338.95	1163.13	20.49
359.90	1154.65	20.06
<i>m</i> = 15.498 (mol kg^{-1})		
294.85	1249.06	20.93
306.00	1245.06	21.01
320.75	1239.60	21.02
331.05	1235.80	20.96
352.05	1227.48	20.75

Table 3

Experimental values of pressure, density, apparent molar volume, temperature, and concentration of H₂O+LiCl solutions

<i>T</i> (K)	<i>P</i> (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)	<i>T</i> (K)	<i>P</i> (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)
<i>m</i> = 0.129 (mol kg ⁻¹)				<i>m</i> = 0.847 (mol kg ⁻¹)			
318.00	26.713	1004.3	21.27	326.75	6.9500	1008.9	18.87
318.00	18.868	1001.1	20.73	326.75	11.608	1010.7	19.11
318.00	8.9830	997.0	20.04	326.75	23.105	1015.4	19.27
318.00	1.1370	993.6	20.02	326.75	30.552	1018.4	19.36
348.90	19.613	985.7	20.35	349.18	4.1060	996.3	17.91
348.90	15.769	984.3	18.50	349.18	11.952	999.5	18.21
348.90	8.0810	981.1	17.50	349.18	22.064	1003.8	18.26
348.90	1.5890	978.3	17.06	349.18	28.210	1006.1	18.60
398.17	23.928	953.7	18.23	423.55	8.1060	945.1	12.04
398.17	19.849	952.1	15.30	423.55	14.032	948.3	12.16
398.17	13.141	949.0	13.98	423.55	20.075	951.1	12.80
398.17	2.8440	943.9	13.78	423.55	24.230	953.2	12.96
447.67	24.026	909.9	19.16	448.95	6.0360	921.5	7.710
447.67	17.162	906.7	11.02	448.95	11.140	924.4	8.260
447.67	7.8260	901.4	6.910	448.95	24.006	931.5	9.410
447.67	3.0990	898.3	7.760	485.55	11.061	887.1	1.230
–	–	–	–	485.55	14.995	890.0	1.620
–	–	–	–	485.55	21.234	893.9	3.020
–	–	–	–	485.55	27.632	898.0	4.010
<i>m</i> = 1.236 (mol kg ⁻¹)				<i>m</i> = 2.592 (mol kg ⁻¹)			
292.25	2.452	1028.5	18.37	306.37	2.452	1052.7	19.28
292.25	8.414	1031.0	18.55	306.37	7.366	1054.7	19.34
292.25	16.985	1034.6	18.75	306.45	2.942	1052.9	19.27
292.25	22.712	1037.0	18.86	306.45	7.845	1054.7	19.41
310.31	2.353	1022.8	18.75	306.45	16.91	1057.6	19.81
310.31	8.492	1025.1	19.06	306.45	22.56	1059.6	19.96
310.31	12.402	1026.5	19.29	348.10	2.275	1034.3	18.64
310.31	18.401	1028.9	19.43	348.10	8.081	1036.5	18.79
325.28	2.118	1016.6	18.62	348.10	16.08	1039.6	18.94
325.28	7.296	1018.6	18.82	348.10	25.01	1042.6	19.26
325.28	15.926	1022.0	19.05	360.32	2.687	1027.6	18.29
325.28	23.124	1024.9	19.15	360.32	7.257	1029.4	18.40
348.12	2.765	1005.5	17.89	373.43	2.608	1020.5	17.43
348.12	11.219	1009.0	18.07	373.43	9.709	1023.3	17.65
348.12	18.221	1011.8	18.26	373.43	19.52	1027.0	17.98
348.12	22.065	1013.3	18.37	373.43	25.40	1029.0	18.24
<i>m</i> = 1.2363 (mol kg ⁻¹)				<i>m</i> = 2.592 (mol kg ⁻¹)			
356.91	20.206	1007.0	18.50	398.06	3.2560	1005.3	15.78
356.91	17.215	1005.7	18.50	398.06	12.749	1009.2	16.18
356.91	11.278	1003.4	18.24	398.06	21.398	1012.5	16.51
356.91	8.065	1002.0	18.22	398.06	26.635	1014.6	16.78
398.12	27.361	984.0	15.71	409.61	4.3150	997.2	15.17
398.12	20.829	981.3	15.32	409.61	11.925	1000.8	15.37
398.12	16.907	979.5	15.23	409.61	19.205	1004.0	15.63
398.12	7.512	975.3	14.80	409.61	27.035	1007.2	15.96
398.12	2.687	973.2	14.47	423.69	26.144	997.7	14.52
398.46	5.217	973.5	15.11	423.69	22.379	995.7	14.51
398.46	11.278	976.5	15.17	423.69	17.064	993.4	14.24
398.46	18.503	979.7	15.49	423.69	11.101	990.8	13.92
423.64	2.53	953.0	11.84	423.69	2.6870	986.7	13.41
423.64	13.317	959.0	11.95	447.96	3.5110	968.3	10.75
423.64	20.182	961.6	13.01	447.96	9.4730	971.4	11.15
423.64	27.949	965.0	13.68	447.96	16.985	975.0	11.71
443.02	4.805	937.2	9.660	447.96	21.732	977.2	12.05

(continued on next page)

Table 3 (continued)

T (K)	P (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)	T (K)	P (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)
443.02	12.16	941.4	10.04	447.96	28.439	980.0	12.62
448.04	3.511	932.5	8.200	470.37	4.236	949.2	7.63
448.04	8.904	935.5	8.710	470.37	12.748	953.9	8.50
448.04	12.906	937.6	9.180	531.89	5.629	888.2	-8.18
448.04	19.613	941.1	9.790	531.89	8.728	890.8	-7.20
479.74	7.021	903.0	3.230	531.89	14.405	896.0	-5.90
479.74	11.356	906.0	3.700	601.78	12.415	804.0	-
479.74	17.50	909.7	4.750	601.78	16.181	809.1	-56.9
479.74	25.30	914.5	5.700	601.78	20.496	816.0	-49.44
524.61	9.552	853.8	-10.27	-	-	-	-
524.61	13.553	858.1	-9.820	-	-	-	-
524.61	19.065	862.5	-7.820	-	-	-	-
583.88	10.611	771.0	-66.81	-	-	-	-
583.88	12.984	775.7	-63.09	-	-	-	-
$m = 2.047$ (mol kg ⁻¹)				$m = 5.827$ (mol kg ⁻¹)			
306.65	9.023	1043.4	19.55	302.25	1.373	1111.4	20.33
306.65	18.134	1047.2	19.62	302.25	10.04	1114.3	20.49
306.65	23.405	1049.1	19.78	302.25	19.69	1117.4	20.67
306.65	29.035	1051.0	20.01	302.25	29.40	1120.6	20.82
324.52	7.035	1035.5	19.46	307.17	4.315	1111.1	20.34
324.52	8.012	1036.2	19.32	307.17	9.885	1113.1	20.41
324.52	11.120	1037.4	19.39	348.37	0.961	1093.8	19.66
324.52	17.956	1040.1	19.49	348.37	11.51	1097.3	19.86
324.52	28.231	1043.7	19.82	348.37	21.08	1100.4	20.04
399.45	9.410	994.5	15.56	348.37	27.77	1102.5	20.17
399.45	13.953	996.5	15.72	356.05	4.158	1091.5	19.47
399.45	26.034	1001.5	16.22	356.05	8.728	1093.0	19.57
423.90	7.035	975.5	13.24	397.81	1.549	1069.4	17.54
423.90	13.235	978.6	13.47	397.81	7.590	1071.5	17.74
423.90	27.324	984.7	14.34	397.81	16.75	1074.7	18.01
449.05	6.025	954.7	10.06	397.81	23.69	1077.0	18.21
449.05	20.234	962.1	11.06	401.63	2.687	1066.9	17.51
449.05	27.065	965.3	11.62	401.63	5.002	1067.8	17.57
483.97	11.032	926.4	4.390	401.63	8.983	1069.3	17.68
483.97	14.985	928.7	4.960	448.25	2.354	1038.8	13.86
483.97	20.820	932.0	5.770	448.25	8.826	1041.5	14.21
483.97	28.065	936.1	6.610	448.25	18.95	1045.3	14.77
-	-	-	-	448.25	25.01	1047.3	15.13
-	-	-	-	449.37	4.491	1038.5	13.96
-	-	-	-	449.37	9.061	1040.4	14.21
-	-	-	-	477.10	5.394	1019.7	10.99
-	-	-	-	477.10	9.807	1021.8	11.32
-	-	-	-	477.10	11.905	1022.7	11.49
-	-	-	-	502.70	6.041	1000.9	7.25
-	-	-	-	502.70	9.140	1002.3	7.66
-	-	-	-	502.70	11.643	1003.3	8.01
-	-	-	-	537.29	9.885	974.3	0.61
-	-	-	-	537.29	13.062	976.0	1.33
$m = 10.062$ (mol kg ⁻¹)				$m = 15.498$ (mol kg ⁻¹)			
291.25	2.452	1180.8	20.65	306.39	2.844	1246.1	21.01
291.25	5.708	1181.8	20.70	306.39	6.453	1247.2	21.03
291.25	11.925	1183.6	20.79	306.39	11.555	1248.7	21.07
291.25	21.575	1186.4	20.93	354.78	3.824	1226.9	20.79
299.21	3.668	1178.1	20.80	354.78	10.454	1228.9	20.85
299.21	9.765	1180.0	20.87	354.78	14.925	1230.3	20.88
323.17	1.863	1169.4	20.73	389.51	4.648	1211.9	20.17
323.17	7.273	1171.0	20.80	389.51	9.963	1213.7	20.22

Table 3 (continued)

<i>T</i> (K)	<i>P</i> (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)	<i>T</i> (K)	<i>P</i> (MPa)	ρ (kg m ⁻³)	ϕ_V (cm ³ mol ⁻¹)
323.17	13.239	1172.8	20.87	389.51	13.958	1214.9	20.27
323.17	22.555	1175.4	20.99	418.62	4.805	1197.7	19.41
349.25	5.296	1160.8	20.36	418.62	11.846	1200.0	19.52
349.25	14.651	1164.1	20.43	418.62	14.843	1200.9	19.57
373.59	2.314	1149.8	19.68	449.61	4.315	1181.8	18.21
291.25	2.452	1180.8	20.65	449.61	13.141	1185.0	18.41
373.59	6.806	1151.1	19.76	449.61	16.643	1186.2	18.48
373.59	12.082	1152.7	19.85	502.46	5.884	1151.7	15.19
373.59	21.163	1155.3	20.01	502.46	12.651	1154.3	15.55
384.63	5.786	1145.5	19.43	502.46	15.858	1155.4	15.71
384.63	12.258	1147.7	19.53	532.15	9.708	1134.4	12.73
423.80	2.275	1125.8	17.60	532.15	11.356	1135.1	12.87
423.80	6.276	1127.0	17.73	532.15	13.054	1135.7	13.02
423.80	12.160	1129.0	17.89	557.08	11.258	1118.9	9.61
423.80	18.378	1130.9	18.07	557.08	15.926	1121.2	10.23
423.80	25.242	1133.0	18.25	557.08	17.923	1122.1	10.48
429.74	5.472	1122.8	17.49	593.56	12.003	1093.8	1.20
429.74	11.434	1125.0	17.64	593.56	15.436	1095.4	2.57
448.09	2.687	1112.7	16.19	593.56	17.836	1096.4	3.40
448.09	6.531	1113.9	16.35	–	–	–	–
448.09	13.396	1116.3	16.61	–	–	–	–
448.09	21.398	1118.9	16.90	–	–	–	–
448.09	28.106	1120.9	17.14	–	–	–	–
469.32	17.152	1104.7	15.43	–	–	–	–
469.32	12.651	1102.9	15.25	–	–	–	–
469.32	5.786	1099.9	14.96	–	–	–	–
498.07	14.455	1085.2	12.94	–	–	–	–
498.07	10.689	1083.7	12.67	–	–	–	–
498.07	7.178	1082.0	12.44	–	–	–	–
533.15	9.140	1058.4	8.03	–	–	–	–
533.15	11.543	1060.1	8.28	–	–	–	–
533.15	15.592	1062.0	8.78	–	–	–	–
533.15	19.790	1064.0	9.26	–	–	–	–
564.24	10.297	1037.0	1.51	–	–	–	–
564.24	12.160	1038.2	1.97	–	–	–	–
564.24	18.142	1041.4	3.35	–	–	–	–
607.71	14.710	1003.2	-15.71	–	–	–	–
607.71	18.633	1006.3	-12.23	–	–	–	–
607.71	23.830	1010.2	-8.85	–	–	–	–

density measurement is less than $\pm 10^{-5}$ g·cm⁻³. Brown et al. (2004) reported measured values of the density and apparent molar volumes for aqueous LiCl solutions at molalities from 0.02 to 1.0 mol kg⁻¹ and at a pressure of 0.35 MPa at temperatures between 278.15 and 368.15 K. Measurements were made with a vibrating-tube densimeter. The derived values of the apparent molar volumes agreed with the values reported in the literature within 0.02 to 1.08 cm³ mol⁻¹. The densities and apparent molar volumes of LiCl(aq) were measured by Vercher et al. (2003) at four temperatures (288.15, 298.15, 308.15, and 318.15 K) over a large range of concentrations by using an oscillating-tube densimeter. The uncertainty of the density measurements was 0.1 kg m⁻³. Abdullaev et al. (1990), Abdullaev (1991) used the same technique (constant volume piezometer) to

measure the densities of LiCl(aq) over a temperature range from 298.15 to 598.15 K and at pressures up to 40 MPa for concentrations from 5 to 40 mass%. The authors claim an uncertainty in the density measurements of 0.65%. Pepinov et al. (1989), Pepinov (1992) used a hydrostatic weighing technique to measure the densities of LiCl(aq) in the temperature range from 298.15 to 623.15 K at pressures up to 30 MPa and at concentrations from 1 to 20 mass%. The uncertainty of the measured density values is 0.15%.

2. Experimental apparatus and procedures

The experimental apparatus used for the present density measurements is the same as that used for measurements on aqueous MgCl₂, BaCl₂, Na₂SO₄,

K_2SO_4 , $MgSO_4$, $NaNO_3$, $Zn(NO_3)_2$, and $LiNO_3$ solutions at high temperatures and high pressures. The apparatus and procedures that were described previously (Abdulagatov and Azizov, 2003a,b, 2004a, b,c,d,e, 2003/2004; Azizov et al., 1996; Azizov and Akhundov, 1997, 1998) were used without modification. Since the apparatus, the design and construction of the piezometer, the experimental procedure, and the uncertainty estimates have been described in detail in several previous publications, they will only be briefly reviewed here. The PVT_x properties of aqueous lithium chloride solutions were measured with a constant-volume method, which gives a maximum uncertainty of 0.06% for the density. The main parts of the apparatus consisted of a piezometer, a separating U-shape capillary tube filled with mercury, a liquid thermostat, heaters, a temperature regulator, and a platinum resistance thermometer (PRT). The volume of the piezometer at 298.15 K and at atmospheric pressure (0.1 MPa) is $95.545 \pm 0.02 \text{ cm}^3$. Two capillaries (upper and lower) with IDs of 0.5 mm are soldered to the ends of the piezometer. The capillaries had small noxious (ballast) volumes, 0.15%

of the piezometer volume. A correction for the inactive (noxious) volume was introduced using the density of the solution at room temperature. The temperature inside the thermostat was maintained uniformly within 0.02 K with the aid of a high precision temperature regulator. The piezometer is located vertically in the liquid thermostat with an internal volume of 0.02 m^3 . Three heaters were used to regulate the thermostat temperature. Two heaters were mounted outside the thermostat (on the bottom and side of thermostat) and another one inside the thermostat near the piezometer. The temperature of the thermostated liquid was measured with a 10Ω platinum resistance thermometer. The sample temperature was detected with a precision of $\pm 0.015 \text{ K}$. The pressure of the sample (solution) was measured with a pressure gauge with a range from 0.6 to 60 MPa. The average uncertainty in pressure measurements is 0.015%, and the maximum uncertainty is 0.05%. After thermal equilibration, density measurements along the isotherms were made, starting from a maximum pressure of 31 MPa. Subsequent measurements at lower pressures and densities were made after

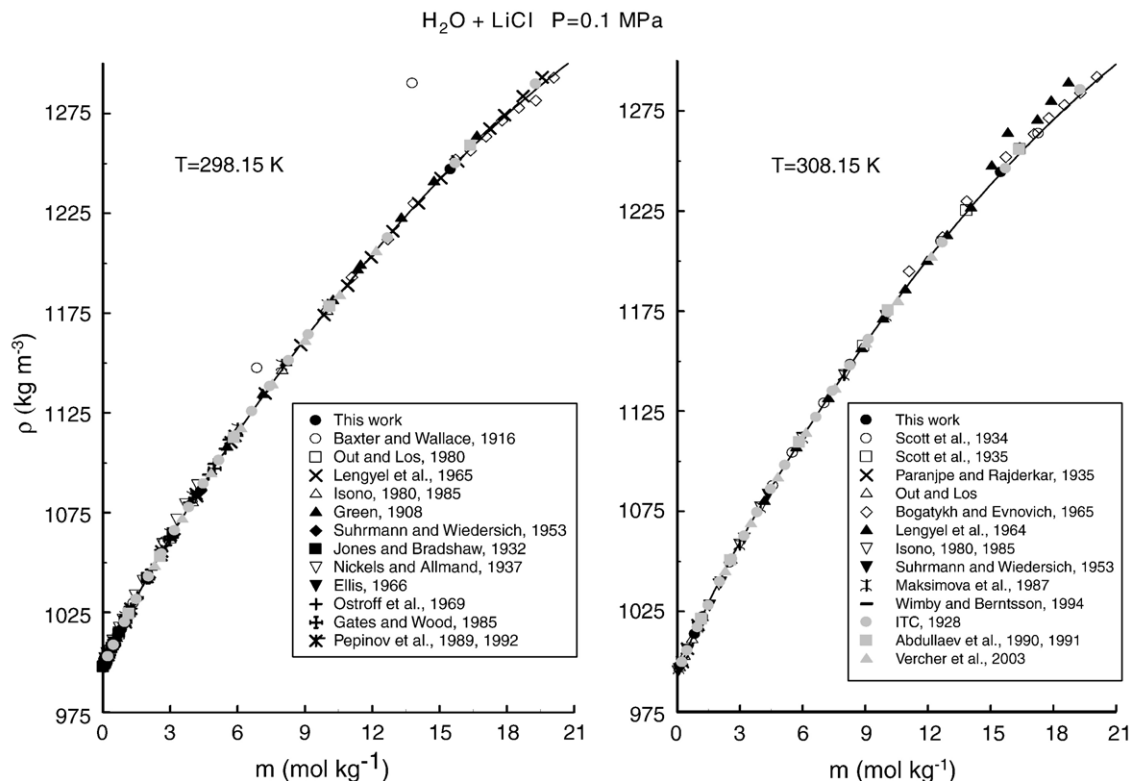


Fig. 1. Experimental and calculated densities ρ of $H_2O+LiCl$ solutions as a function of composition m along selected isotherms at atmospheric pressure.

extracting small amounts of sample from the piezometer through an upper capillary and valve. The extracted samples were collected in a separate collector and weighed within an uncertainty of 0.05 mg using a high-precision balance.

The density of the sample (ρ_i) at a given temperature T and pressure P was obtained from measurements of the following: M , mass of the solution, and V_{PT} , volume of the of the piezometer as

$$\rho_i = M_i/V_{PT}, \quad (1)$$

$$M_i = M_{\text{tot}} - M_{\text{coll}}, \quad M_{\text{tot}} = M_1 + M_2 + M_3 + \dots + M_N, \quad (2)$$

where M_i ($i=1, N$) is the current mass of sample in the piezometer, M_{coll} is the mass of the sample extracted from the piezometer and stored in the collector during the runs, M_{tot} is the total mass of sample in the piezometer before extractions, N is the number of extractions, and V_{PT} is the volume of the piezometer at a given temperature and pressure. The mass of the sample in the piezometer was corrected for the noxious (inactivated) volumes (volumes of the capillaries at room temperature and in the transitional zones) and evaporation of the sample during extraction. The

temperature dependence of the piezometer volume at fixed pressure was calculated as

$$\Delta V_T = V_{T0}[1 + 3\alpha(T-T_0)], \quad (3)$$

where V_{T0} is the volume of the piezometer at an initial reference temperature T_0 , and $\alpha=1.3 \times 10^{-5} \text{ K}^{-1}$ is the thermal expansion coefficient of the piezometer material (stainless steel 1X18H9T). The pressure dependence of the piezometer volume ΔV_P was calculated by using the Lave formula (Keyes and Smith, 1933). The final equation for the piezometer volume is

$$V_{PT} = V_{298} + \Delta V_T + \Delta V_P, \quad (4)$$

where $V_{298}=94.545 \pm 0.02 \text{ cm}^3$ at a temperature of 298 K and pressure of 0.1 MPa. The value of V_{298} was previously calibrated from the known density of a standard fluid (pure water, IAPWS formulation, Wagner and Pruß, 2002). The uncertainty in the piezometer volume at given temperature T and pressure P was less than 0.038%. In total, the noxious volume is about 0.15% of the piezometer volume. The uncertainty of the mass of solution is estimated to be 0.007%. The experimental

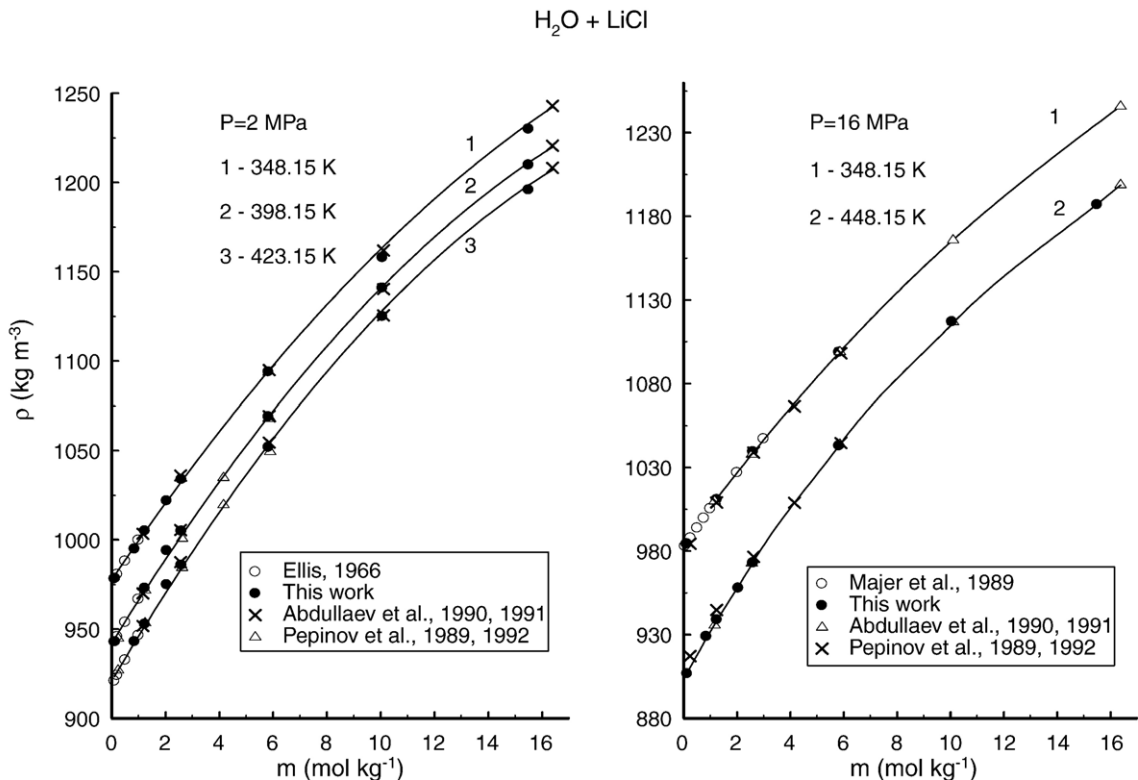


Fig. 2. Experimental densities ρ of $\text{H}_2\text{O} + \text{LiCl}$ solutions as a function of composition m along selected isotherms at 2 and 16 MPa.

uncertainty in the concentration is estimated to be 0.014%. Based on a detailed analysis of all sources of uncertainty likely to affect the determination of the density with the present method, the combined standard uncertainty of the measured density is 0.06%.

To check and confirm the accuracy of the method and procedure of the measurements, density measurements were made with pure water at two selected isobars of 10 and 38 MPa. The comparisons of the present experimental data for pure water measured using the same experimental apparatus with those calculated from the accurate equation of state of water (IAPWS formulation, Wagner and Pruβ, 2002) shows that the agreement at isobars of 10 and 38 MPa are 0.028% and 0.048%, respectively. At atmospheric pressure the AAD (average absolute deviation, $ADD = (100/N) \sum_{i=1}^N |(\rho^{\text{exp}} - \rho^{\text{cal}}) / \rho^{\text{exp}}|_i$ where N is the number of experimental points) between the measured values and IAPWS (Wagner and Pruβ, 2002) calculated values are about 0.02%. This excellent agreement between the present data for pure water and IAPWS (Wagner and Pruβ, 2002) calculations demonstrates the reliability of the present measurements for H₂O+LiCl solutions.

The H₂O+LiCl solutions were prepared from chemically pure LiCl (Merck, PA grade, >99.0 mass%) and doubly-distilled water. Eight stock solutions were prepared by mass using an analytical balance (VLA-200) with a precision of $\pm 5 \times 10^{-8}$ kg. The accuracy of the molalities of all LiCl solutions was 0.25%.

3. Results and discussion

Measurements of the PVT_x relationships of the aqueous LiCl solutions were performed at eight (0.129, 0.847, 1.236, 2.047, 2.592, 5.827, 10.062, and 15.498 mol kg⁻¹) compositions for temperatures between 291.25 and 607.71 K. The pressure ranged from 0.1 to 30.55 MPa. The experimental results are presented in Tables 2 and 3. These tables also include apparent molar volumes, derived from present density data as discussed below. Some selected experimental results are shown in Figs. 1–5 as projections in the ρ - m , ρ - T , and ρ - P planes, together with values reported by other researchers.

We compared our density results for LiCl(aq) with the literature data at atmospheric and high pressures. Occasionally, the comparison of the present density results with other data, especially at high temperatures and pressures, are difficult because of temperature,

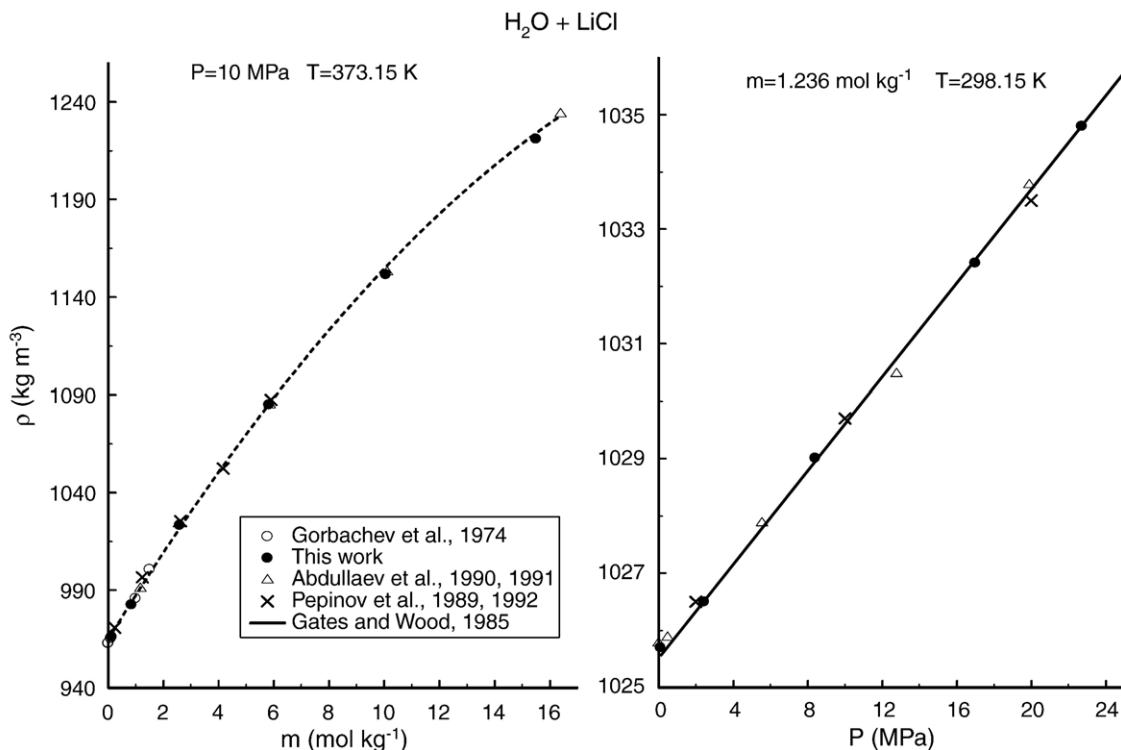


Fig. 3. Experimental densities ρ of H₂O+LiCl solutions as a function of composition m and pressure along the two selected isotherms and at a pressure of 10 MPa and a concentration of 1.236 mol kg⁻¹.

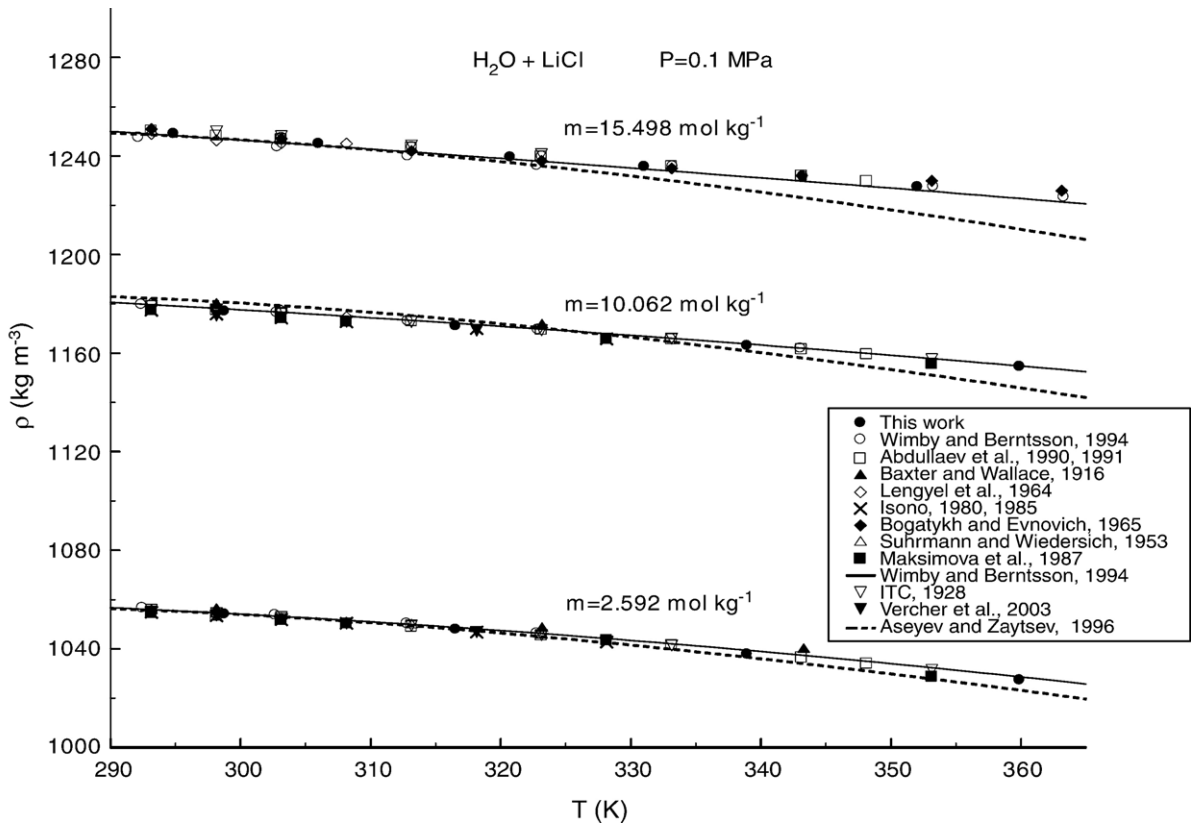


Fig. 4. Experimental densities ρ of $\text{H}_2\text{O} + \text{LiCl}$ solutions as a function of temperature T along the three selected compositions and at atmospheric pressure.

pressure, and concentration differences between the measurements. Therefore, to comparison the present density data with the values reported by other authors, we used an interpolating procedure (analytical method). The present results of (P, ρ, T, m) measurements for $\text{H}_2\text{O} + \text{LiCl}$ solutions were represented by the following equation

$$V_{\text{sol}} = A + B\Delta T + C\Delta T^2 + D\Delta T^7, \quad (5)$$

where V_{sol} is the specific volume of the solution in $\text{cm}^3 \text{g}^{-1}$ (density is $\rho_{\text{sol}} = 1/V_{\text{sol}}$), and $\Delta T = T - 273.15$, where T is the temperature in K. The pressure and concentration dependences of the specific volume V_{sol} of solution have been taken into account through the coefficients $A(P, m)$, $B(P, m)$, and $D(P, m)$ as a polynomial function of pressure P and concentration m

$$\begin{aligned} A &= \sum_{i=0}^2 \sum_{j=0}^3 a_{ij} P^i m^j, & B &= \sum_{i=0}^2 \sum_{j=0}^3 b_{ij} P^i m^j, \\ C &= \sum_{i=0}^2 \sum_{j=0}^3 c_{ij} P^i m^j, & D &= \sum_{i=0}^2 \sum_{j=0}^3 d_{ij} P^i m^j, \end{aligned} \quad (6)$$

where P is the pressure in MPa, and m is the concentration in mol kg^{-1} . Eq. (5) represents the present experimental densities for the solution with an average absolute deviation of 0.065%, which is very close to the experimental uncertainty (0.06%). Derived values of the coefficients a_{ij} , b_{ij} , c_{ij} and d_{ij} in Eq. (6) are given in Table 4. This equation is valid in the temperature range from 291 to 608 K, pressures up to 30 MPa, and concentrations up to 15.5 mol kg^{-1} . Eq. (5) was used in our previous publications (Abdulagatov and Azizov, 2003b, 2004a,b,d, in press-b) to correlate the (P, ρ, T, m) measurements for other aqueous electrolyte solutions ($\text{H}_2\text{O} + \text{LiNO}_3$, $\text{H}_2\text{O} + \text{Li}_2\text{SO}_4$, $\text{H}_2\text{O} + \text{H}_3\text{BO}_3$, and $\text{H}_2\text{O} + \text{NaClO}_4$).

Fig. 1 demonstrates the concentration dependence of density of $\text{LiCl}(\text{aq})$ along the two temperatures (298.15 and 308.15 K) at atmospheric pressure reported by various researchers together with the present results. As one can see from Fig. 1, all the available data sets reported by various authors are reasonably consistent, except the data by Baxter and Wallace (1916). Figs. 2 and 3 show the ρ - m dependence of the present density results along the selected isotherms (348.15, 398.15,

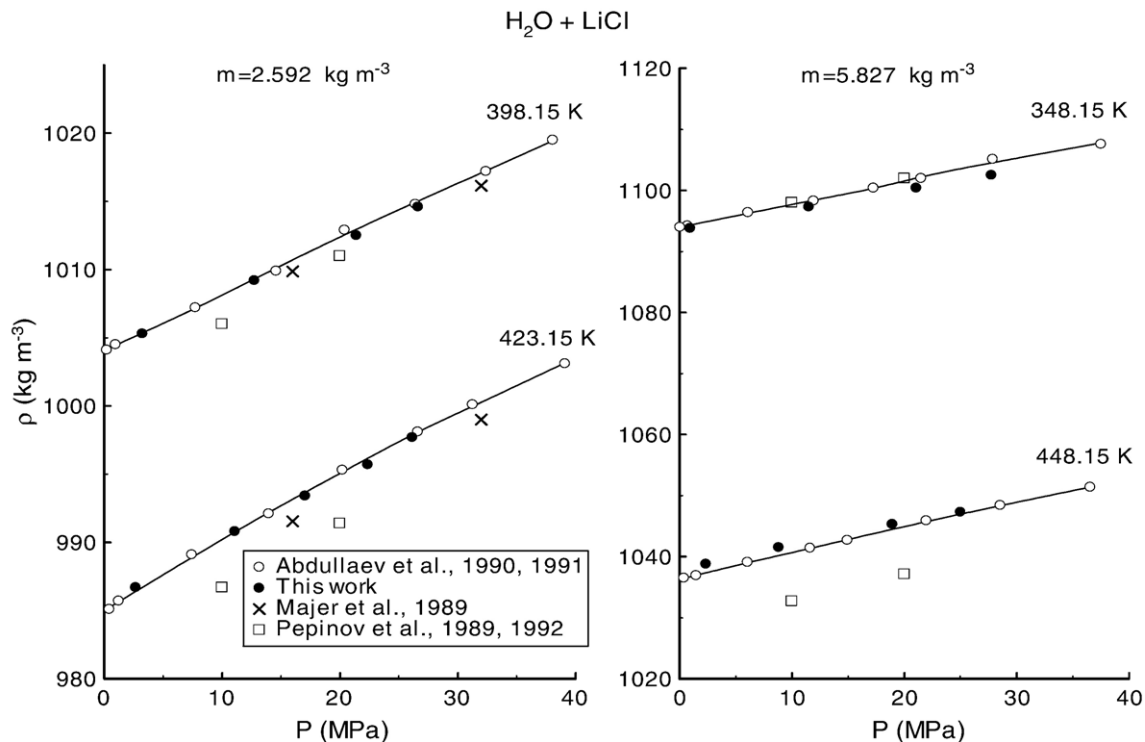


Fig. 5. Experimental densities ρ of $\text{H}_2\text{O} + \text{LiCl}$ solutions as a function of pressure P along the selected isotherms and at two constant concentrations of 2.592 and 5.827 mol kg^{-1} .

423.15, and 448.15 K) at high pressures (2, 10, and 16 MPa) together with the data reported by other authors. The agreement between different data sets is good. Fig. 4 shows the ρ - T plot for the various data sources together with the present data along the three constant

compositions (2.592, 10.062, and 15.498 mol kg^{-1}). As this figure demonstrates, almost all of the available data sets are good consistent each other. Fig. 4 also includes the values of density calculated with a correlation by Wimby and Bertsson (1994) and Aseyev and Zaytsev

Table 4
Parameters a_{ij} , b_{ij} , c_{ij} , and d_{ij} for Eq. (6)

i	$j=0$	$j=1$	$j=2$	$j=3$
a_{ij}				
0	0.995600×10^0	-2.2741×10^{-2}	1.03115×10^{-3}	-2.5349×10^{-5}
1	-3.44877×10^{-4}	-1.3036×10^{-5}	2.8408×10^{-6}	-9.6510×10^{-8}
2	-5.52161×10^{-6}	2.93994×10^{-6}	-2.98044×10^{-7}	8.80656×10^{-9}
b_{ij}				
0	1.635300×10^{-4}	1.87287×10^{-5}	-3.7139×10^{-6}	1.6687×10^{-7}
1	-1.53634×10^{-6}	7.40541×10^{-7}	-1.20766×10^{-8}	-1.6560×10^{-9}
2	1.562400×10^{-7}	-6.38938×10^{-8}	4.4175×10^{-9}	-6.1034×10^{-11}
c_{ij}				
0	3.058300×10^{-6}	-5.7949×10^{-7}	5.5846×10^{-8}	-1.85102×10^{-9}
1	-4.28981×10^{-9}	-8.20353×10^{-10}	-2.7049×10^{-10}	2.0343×10^{-11}
2	-7.39490×10^{-10}	3.11236×10^{-10}	-1.94687×10^{-11}	1.67117×10^{-13}
d_{ij}				
0	3.198990×10^{-19}	-6.65218×10^{-20}	4.31927×10^{-21}	-8.4241×10^{-23}
1	-2.26097×10^{-20}	1.05554×10^{-20}	-1.2964×10^{-21}	4.58560×10^{-23}
2	1.287500×10^{-21}	-7.3877×10^{-22}	9.84280×10^{-23}	-3.62636×10^{-24}

(1996). The pressure dependence of the present density data and the data reported in the literature by Majer et al. (1989); Pepinov et al. (1989), and Abdullaev et al. (1990), Abdullaev (1991) at high temperatures and high pressures for the two selected compositions is depicted in Fig. 5. The AAD between the present density values and the data published by other authors at atmospheric pressure and at high pressures are given in Table 5. The agreement between present and published data at atmospheric pressure is excellent. All measurements by the other authors deviate from the present data with an AAD within 0.08% to 0.32%. The present density data agree with the data of Wimby and Berntsson (1994), Majer et al. (1989), Gates and Wood (1985), Abdullaev et al. (1990), Abdullaev (1991), Isono (1980), (1985), Pepinov et al. (1989), ITC (1928), Vercher et al. (2003), Gorbachev et al. (1974), Green (1908), Lengyel et al. (1964), Jones and Bradshaw (1932), Ostroff et al. (1969), Out and Los (1980), and Suhrmann and Wiederich (1953), generally all within 0.015% to 0.070% at atmospheric pressure. The data of Nickels and Allmand (1937) are consistently 0.323% higher than the present values and other published data. The AAD at temperatures of 298.15 and 308.15 K are

0.112% for the data of Maksimova et al. (1987); 0.218% for the data of Bogatykh and Evnovich (1965); 0.115% for the data of Ellis (1966); and 0.275% for the data of Scott et al. (1934), Scott and Bridger (1935). The deviations between published and the present data at high pressures and high temperatures are within 0.007% to 0.075%, except the data reported by Pepinov et al. (1989). These data are systematically lower than our result by 0.25% at temperatures to 448.15 K. The maximum deviation of up to 0.8% is found at high temperatures ($T=448.15$ K) and high concentrations ($m=5.827$ mol kg⁻¹). Excellent agreement within 0.007% (maximum deviation is 0.013%) is found between the present data and the data reported by Gates and Wood (1985) at pressures up to 30 MPa and at temperature of 298.15 K. The data of Majer et al. (1989) agree with our results within 0.048% to 0.101% at temperatures up to 423.15 K and at pressure of 16 MPa. Good agreement within 0.021% to 0.096% is observed between the data reported by Abdullaev et al. (1990), Abdullaev (1991) at temperatures to 448.15 K and at pressures to 30 MPa. This excellent agreement between the present density data and the data reported by other authors for LiCl(aq) confirms the reliability and high accuracy of the present measurements and the correct operation of the instrument. This generally good agreement provides some confidence in the experimental values of Tables 2 and 3.

Table 5
Comparison of the present density results with those from the literature

First author	AAD (%)	Max. dev. (%)
<i>At atmospheric pressure</i>		
Wimby (1994)	0.050	0.100
Majer (1989)	0.038	0.070
Gates (1985)	0.055	0.140
Abdullaev (1990, 1991)	0.008	0.017
Pepinov (1989)	0.015	0.026
Maksimova (1987)	0.112	0.220
ITC (1928)	0.029	0.052
Vercher (2003)	0.039	0.049
Isono (1980, 1985)	0.070	0.110
Bogatykh (1965)	0.218	0.330
Gorbachev (1974)	0.022	0.028
Lengyel (1964)	0.051	0.090
Green (1908)	0.063	0.195
Jones (1932)	0.057	0.086
Nickels (1937)	0.322	0.360
Ellis (1966)	0.115	0.120
Ostroff (1969)	0.023	0.025
Scott (1934, 1935)	0.275	0.450
Out (1980)	0.047	0.060
Suhrmann (1953)	0.086	0.230
<i>At high pressures</i>		
Majer (1989)	0.075	0.140
Abdullaev (1990, 1991)	0.067	0.200
Pepinov (1989)	0.253	0.517
Gates (1985)	0.007	0.013
Gorbachev (1974)	0.016	0.021

The measured densities were used to calculate the apparent molar volumes ϕ_V for each solution. In the limit of infinite dilution, the apparent molar volume of the solute $\phi_V(P, T, m \rightarrow 0)$ becomes equal to the partial molar volume ($\lim_{m \rightarrow 0} \phi_V = \phi_V^0 = \bar{V}_2^\infty$). The values of the apparent ϕ_V and partial \bar{V}_2^∞ molar volumes are very useful tools for understanding the interactions occurring in aqueous solutions. Studies of the apparent and partial molar volumes of electrolyte solutions are used to examine ion–solvent, ion–ion, and solvent–solvent (structural) interactions, i.e., provide useful information on the nature of the interaction between dissolved ions and molecules of a solvent (water). In this work the apparent molar volumes ϕ_V were calculated from measured solution densities ρ_{sol} and pure water densities ρ_0 by the usual relationship

$$\phi_V = \frac{(\rho_0 - \rho_{\text{sol}})}{m\rho_{\text{sol}}\rho_0} + \frac{M}{\rho_{\text{sol}}}, \quad (7)$$

where M is the molecular mass of the salt, and are the densities of solution and pure water, respectively, and m is the solution molality (mol kg⁻¹). The derived values of ϕ_V are given in Tables 2 and 3 and are shown in Figs. 6–10. The uncertainty in derived values of ϕ_V depends

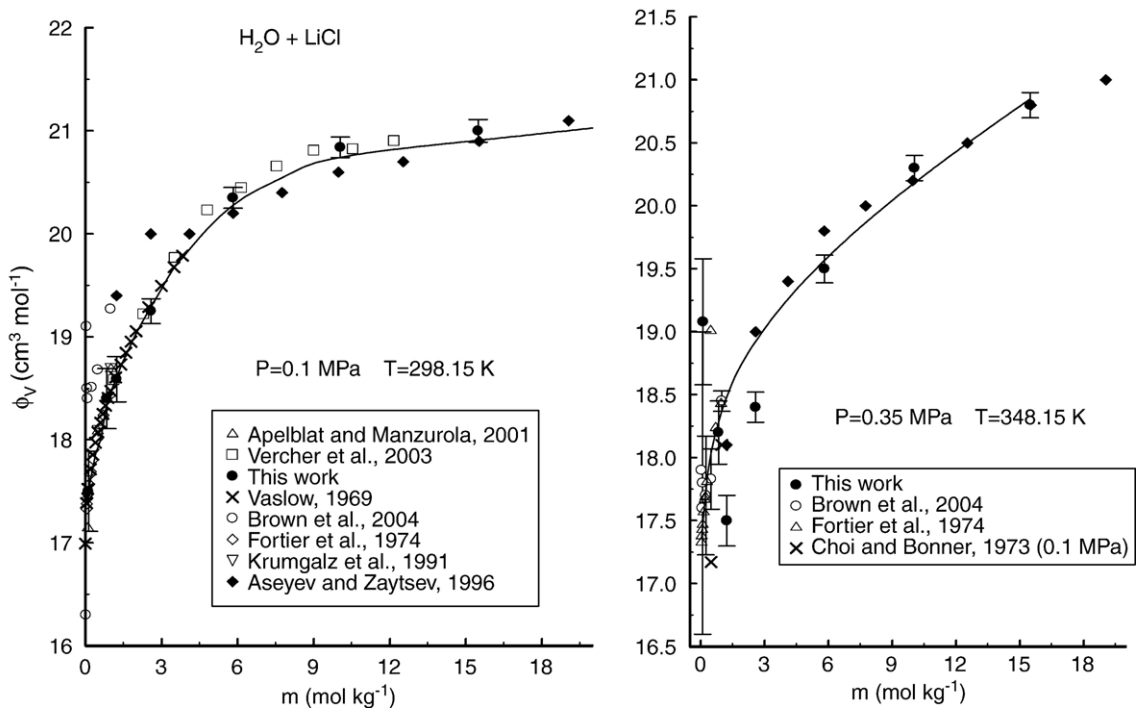


Fig. 6. Apparent molar volumes ϕ_V for LiCl as a function of molality m at two selected isobars (0.1 and 0.35 MPa) and selected temperatures (298.15 and 348.15 K).

strongly on m , T , and ρ_{sol} and ρ_0 . The accuracy of the derived values of ϕ_V was assessed by analyzing the sensitivity of Eq. (7) to the experimental uncertainties of

the measured quantities (m , T , ρ_{sol}) (see our previous publication [Abdulagatov and Azizov, 2003b, 2004a, in press-b](#)). The maximum relative uncertainty in the

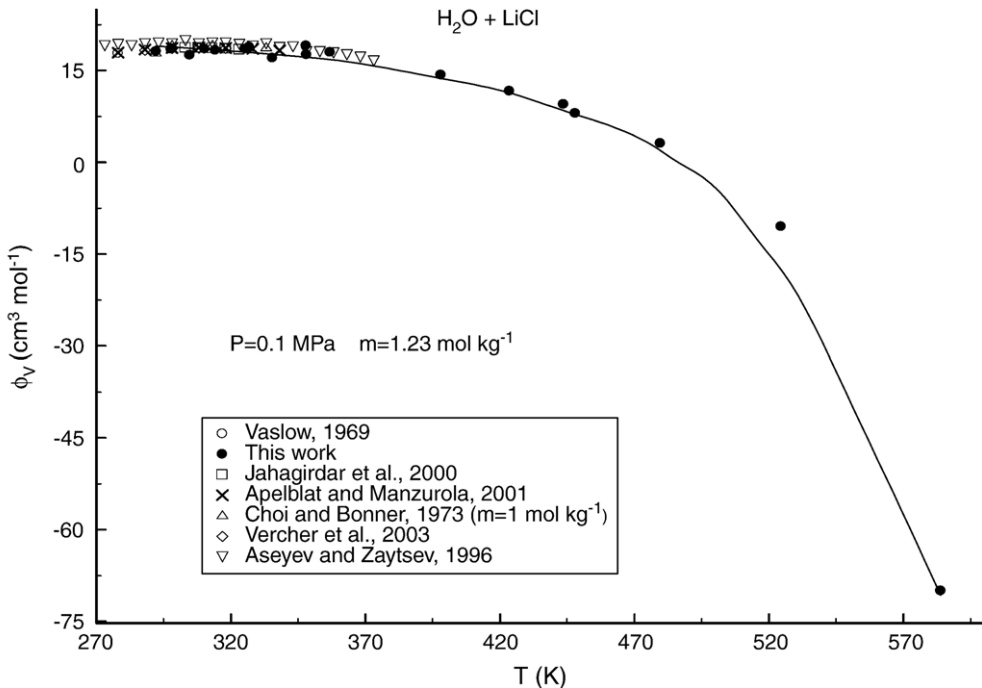


Fig. 7. Apparent molar volume ϕ_V for LiCl as a function of temperature T for a composition of 1.23 mol kg^{-1} and at atmospheric pressure.

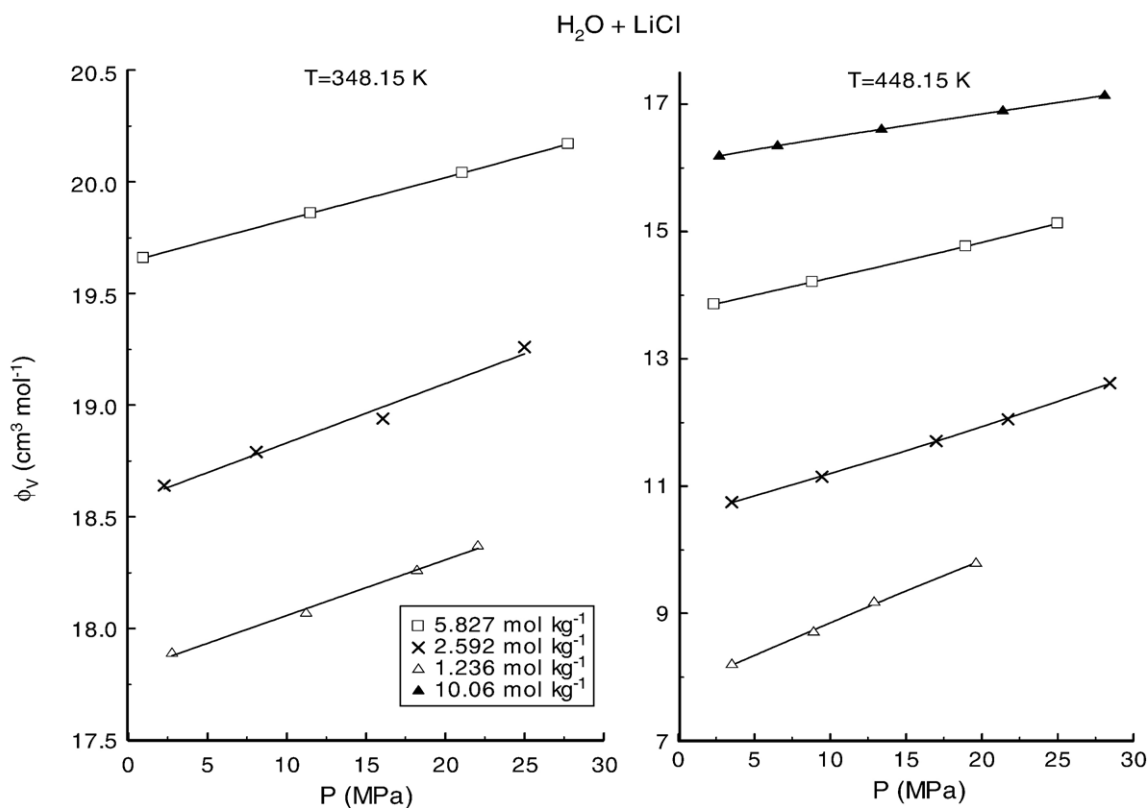


Fig. 8. Apparent molar volume ϕ_V for LiCl as a function of pressure P at constant concentrations for selected temperatures (348.15 and 448.15 K).

apparent molar volume determination is about 10% at dilute solution ($m < 0.1 \text{ mol kg}^{-1}$) and 0.04% to 2.0% at high concentrations ($m > 1.0 \text{ mol kg}^{-1}$).

Figs. 6–8 illustrate concentration, temperature, and pressure dependences of derived values of the apparent molar volume ϕ_V . As Fig. 6 shows, the apparent molar volume ϕ_V rises rapidly with concentration at low concentrations (below 5 mol kg^{-1}). The data reported in this work indicate that ϕ_V can be increased by 30% over the first 5 mol kg^{-1} , then to increase less rapidly (by 2–3%) at higher concentrations (see Figs. 6 and 9). All of the ϕ_V data sets reported by various authors shows good agreement, except the data by Brown et al. (2004). These data are 2–4% higher than the present and other published data at temperature of 298.15 K, while at a temperature of 348.15 K these data agree with the data by Fortier et al. (1974), but are still systematically higher than the present data and the data of Choi and Bonner (1973). As Fig. 7 shows, the apparent molar volume ϕ_V increases with temperature, passes through a maximum near 315–400 K (depending on pressure and concentration), and decreases at higher temperatures. At temperatures above 480 K ϕ_V becomes negative. The dependence of ϕ_V on temperature increases significantly

above 480 K (see Fig. 7). As Fig. 7 illustrate, the agreement between the present and other apparent molar volume data sets is good. Almost all available reported values of ϕ_V cover (see Fig. 7) very limited temperatures range (between 278 and 340 K). The apparent molar volume was found to increase almost linearly with pressure (see Fig. 8). As one can see from Fig. 8, the apparent molar volume ϕ_V is not affected much (5–9%) by pressure. However, at high temperatures (above 480 K) and low concentrations (below 5 mol kg^{-1}), the pressure significantly (up to 30%) influences ϕ_V . Fig. 9 compare the present results for ϕ_V at two selected pressures (16 and 17.13 MPa) and temperatures (298.15 and 348.15 K) with the values measured by other authors (Majer et al., 1989; Gates and Wood, 1985). As this figure demonstrates our apparent molar volume data shows good agreement within 2% and 0.45% with the data reported by Majer et al. (1989) and Gates and Wood (1985), respectively. Good agreement within 0.48% is found between the present apparent molar volumes and the data reported by Vaslow (1969) (maximum deviation is 0.77%). The recently reported data by Vercher et al. (2003) and the data by Apelblat and Manzurola (2001) deviate from the present values of apparent molar

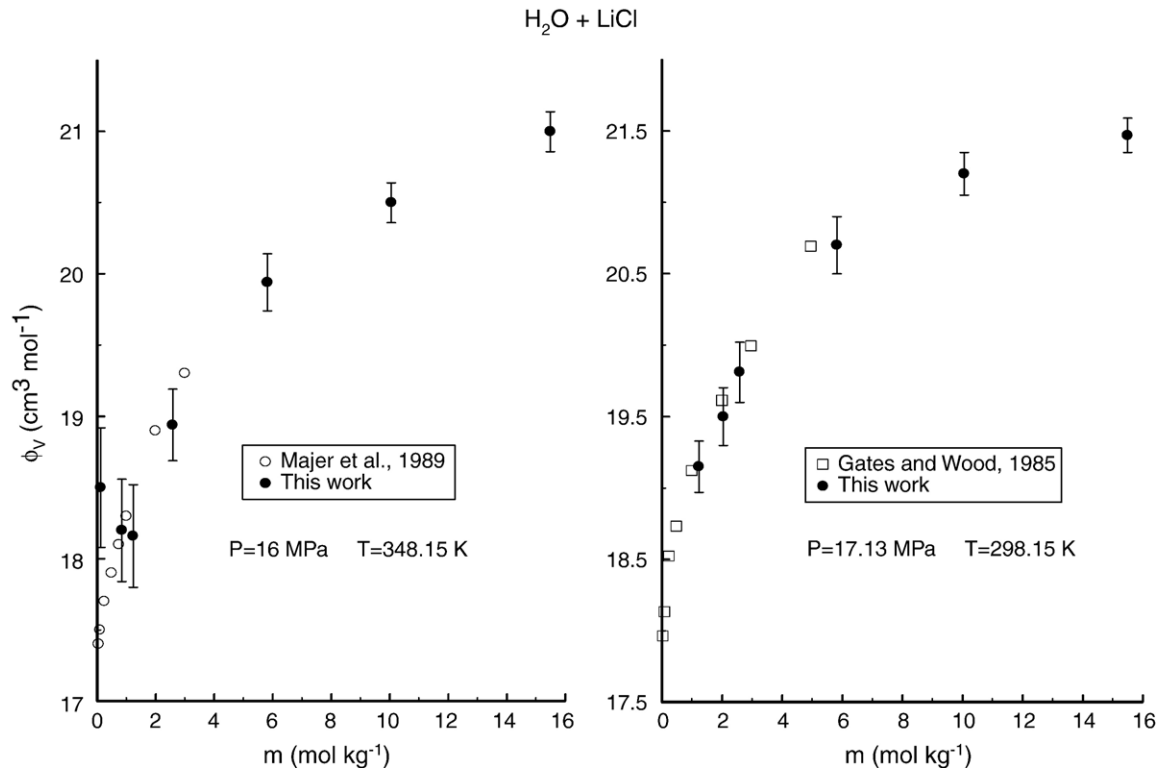


Fig. 9. Comparison of the present results for the apparent molar volume ϕ_V for LiCl with the values reported in the literature at two selected pressures and temperatures.

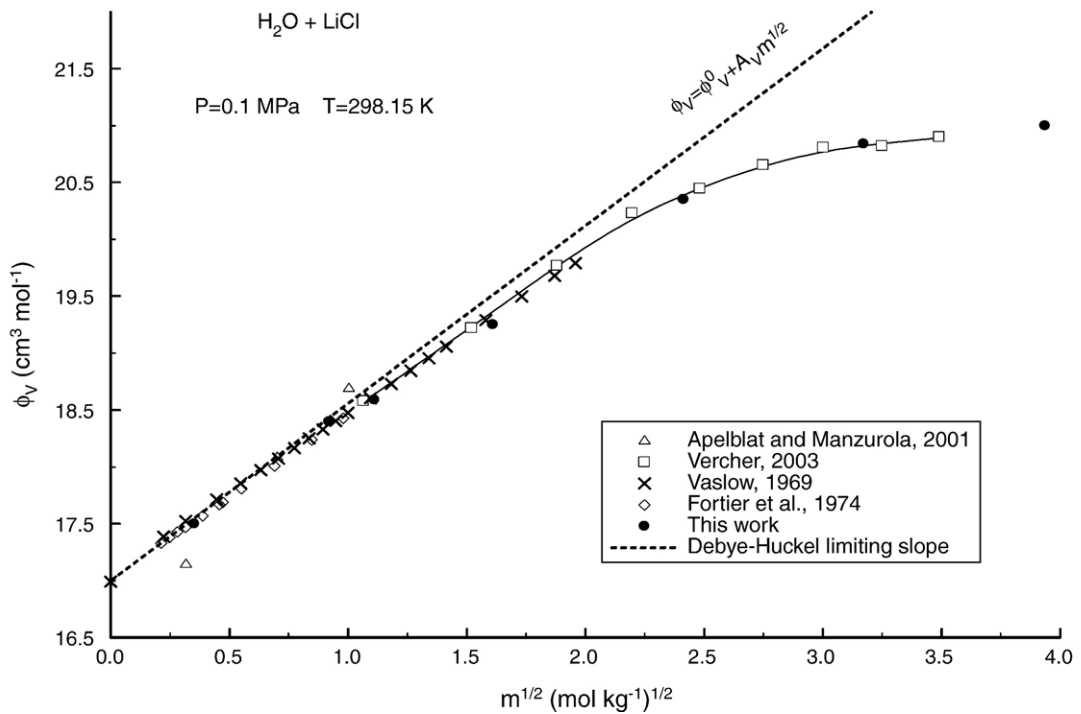


Fig. 10. Apparent molar volume ϕ_V for LiCl as a function of the square root of molality $m^{1/2}$ at atmospheric pressure and 298.15 K.

Table 6

Comparison of the present apparent molar volumes ϕ_V ($\text{cm}^3 \text{mol}^{-1}$) with those from the literature at 298.15 K and atmospheric pressure

m (mol kg^{-1})	This work	Apelblat and Manzurola, 2001	Krumgalz et al., 1996	Vaslow, 1969	Vercher et al., 2003	Fortier et al., 1974
0.1	17.47	17.15	17.44	17.52	–	17.47
0.5	18.04	18.09	18.07	18.07	–	18.03
1.0	18.49	18.69	18.50	18.48	18.50	18.46

volumes at atmospheric pressure and at temperatures of (298.15 and 348.15 K) within 0.42% and 1.05%, respectively. The data reported by Brown et al. (2004) were 3–4% higher than the present results. Good agreement within 0.25% is also found between the present data and the values reported by Fortier et al. (1974) at a temperature of 298.15 K and at atmospheric pressure, while at 348.15 K and at 0.35 MPa the deviations reach of up to 3.5%. The data reported by Choi and Bonner (1973) are 2.5% higher than the present results. This is still good because at low concentrations (dilute solution, $m < 0.1 \text{ mol kg}^{-1}$) the uncertainty of the derived values of the apparent molar volume is about 10%. The comparison between the present value of the apparent molar volume at 298.15 K and at 0.1 MPa and the value reported by other authors in the literature is given in Table 6. As one can see from this table, the agreement between the present results and those reported in the literature is within 0.15%. Only two data points reported by Apelblat and Manzurola (2001) at compositions 0.1 and 1.5 m show the deviation within 1.07% to 1.87%. This is still within their uncertainty.

The derived apparent molar volumes ϕ_V for LiCl(aq) have been used to calculate the values of the apparent molar volume ϕ_V^0 (or infinite-dilution partial molar volume \bar{V}_2^∞) at infinite dilution at various temperatures and pressures. Of more fundamental interest (for example to study ion–solvent interactions), are the partial molar volumes of the electrolyte at infinite

dilution \bar{V}_2^∞ (where ion–ion interactions vanish). The standard procedure for calculating ϕ_V^0 or \bar{V}_2^∞ is to extrapolate ϕ_V to infinite dilution ($m \rightarrow 0$), based on the extended Redlich–Mayer relation (Pearce and Hopson, 1937; Redlich and Mayer, 1964; Roux et al., 1978)

$$\phi_V = \phi_V^0 + A_V \sqrt{m} + bm + dm^{3/2}, \quad (8)$$

where $A_V = kw^{3/2}$ is the Debye–Hückel limiting slope and w and k are expressed as

$$k = N^2 e^3 \left(\frac{8\pi}{1000D^3 RT} \right)^{1/2} \left(\frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right) \text{ and} \\ w = 0.5 \sum_i \nu_i Z_i^2 \quad (9)$$

e is the electric charge, D is the dielectric constant of the solvent, N is Avogadro's number, ν_i is the number of ions of species i formed from one molecule of dissociating salt, Z_i is the charge on species i , m is the molality, β is the compressibility of the solvent, and b and d are the empirical coefficients. The limiting slope depends only on temperature and the physical properties (dielectric constant D and compressibility β) of the solvent (pure water IAPWS standard, Fernandez et al., 1997). As a rule, this relationship is applied at fixed pressure P and temperature T . The infinite-dilution values of ϕ_V (\bar{V}_2^∞) are obtained by extrapolating Eq. (8) to zero concentration ($m \rightarrow 0$). Fig. 10 shows the apparent molar volumes ϕ_V for LiCl reported by various authors as a function of the square root of the

Table 7

The infinite-dilution values of the partial molar volume ($\bar{V}_2^\infty, \text{cm}^3 \text{mol}^{-1}$) of LiCl in water as derived by Eq. (8)

$P = 0.1 \text{ (MPa)}$					
289.85 (K)	298.75 (K)	304.75 (K)	316.55 (K)	338.95 (K)	359.19 (K)
16.451	17.371	16.93	17.518	16.269	14.965
$P = 16 \text{ (MPa)}$					
348.90 (K)	398.17 (K)	447.67 (K)	485.55 (K)	524.61 (K)	593.56 (K)
17.575	13.034	6.010	–3.911	–23.106	–75.18
$P = 20 \text{ (MPa)}$					
348.90 (K)	398.17 (K)	447.67 (K)	–	–	–
16.746	14.565	6.392	–	–	–

molality $m^{1/2}$ at atmospheric pressure and 298.15 K. Our values for ϕ_V at high concentration together with the data by other authors at low concentrations were fitted to Eq. (8) for the fixed temperatures and pressures. For our calculations we have used the theoretical values of the Debye–Hückel limiting slope recommended by Majer et al. (1989), Bradley and Pitzer (1979) and Fernandez et al. (1997). The treatment of all the present results has been based on least-squares fits of all results using Eq. (8) from 0.129 to 15.498 mol kg⁻¹. The derived results of the partial molar volumes \bar{V}_2^∞ for the various temperatures and pressures are given in Table 7. The comparison between our results for ϕ_V^0 (or \bar{V}_2^∞) and more accurate data reported by other authors at two pressures (0.1 and 16 MPa) is given in Fig. 11. Most data in the literature show satisfactory agreement within 1.5% to 5% with the present results for ϕ_V^0 . Our values are within about 1.41% of the data reported recently by Apelblat and Manzurola (2001) at atmospheric pressure. The data by Ellis (1966) and by Choi and Bonner (1973) shows the deviation from the present results within 2.2%, while the recent data of Brown et al. (2004) agree with our data to within 5%. The data reported by Majer et al. (1989) were extrapolated to atmospheric pressure to compare with our data. These values of ϕ_V^0 agree with the present data within 7.5%, while the data by

Table 8

Comparison of the present apparent molar volumes ϕ_V^0 at infinite dilution with those from the literature at 298.15 K and atmospheric pressure

Reference	ϕ_V^0 , (cm ³ mol ⁻¹)
This work	17.17
Vercher et al., 2003	17.59
Krumgalz et al., 1996	16.87
Apelblat and Manzurola, 2001	16.45
Vaslow, 1969	16.99
Ellis, 1966	16.60
Out and Los, 1980	16.81
Desnoyers et al., 1969	16.91
Millero and Drost-Hansen, 1968	16.96
Fajans and Johnson, 1942	17.10
Gucker, 1933	17.06
Scott, 1931	17.00
Glueckauf, 1965	16.85
Hirakawa et al., 1989	18.20
Fortier et al., 1974	17.13
Choi and Bonner, 1973	17.03
Majer et al., 1989	16.73
Brown et al., 2004	16.20
Redlich and Rosenfeld, 1931	16.92
Geffcken, 1931	17.06

Jahagirdar et al. (2000) systematically higher by 8% than the present results. As Fig. 11 shows, the agreement between the present data for ϕ_V^0 is consistent (within

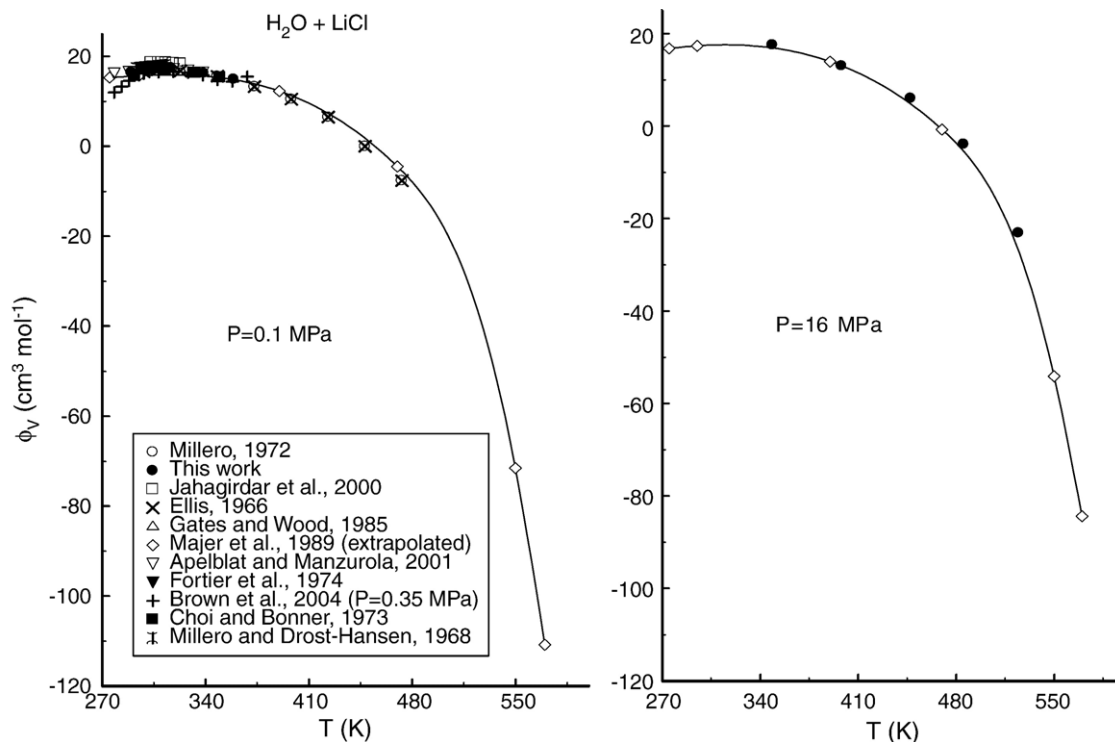


Fig. 11. Comparison between the present apparent molar volumes at infinite dilution ϕ_V^0 and the data reported by other authors in the literature. The solid curve guides the eye.

7%) with the data by Majer et al. (1989) at pressure of 16 MPa. Table 8 shows the comparison between the present value of the ϕ_V^0 and the value derived by other authors at 298.15 K and at 0.1 MPa. Most reported data deviate from our results within 1.15%. Good agreement within 0.5% is found between the present value of ϕ_V^0 and the data reported by Fajans and Johnson (1942), Gucker (1933), Fortier et al. (1974), Choi and Bonner (1973), Choi and Bonner (1973), while the data by Apelblat and Manzurola (2001), Hirakawa et al. (1989); and Brown et al. (2004) deviate from the present result within 4% to 6%. This is still expectable because the uncertainty of ϕ_V^0 is within 5% to 10%.

4. Conclusions

Densities of eight (0.129, 0.847, 1.236, 2.047, 2.592, 5.827, 10.062, and 15.498 mol kg⁻¹) binary aqueous LiCl solutions have been measured with a constant-volume piezometer immersed in a precision liquid thermostat. Measurements were made at pressures up to 30.55 MPa. The range of temperature was 291.25 to 607.71 K. Good agreement (within 0.01% to 0.1%) is found between the present density measurements for the solution and the data sets reported by other authors in the literature. The measured densities were used to calculate the apparent and partial molar volumes for each solution. The temperature, pressure, and concentration dependences of the density, apparent and partial molar volumes were studied. The maximum of the apparent molar volumes at temperature around 315–400 K depending on concentration and pressure was found.

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