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PVTx Measurements and Partial Molar Volumes for Aqueous Li_2SO_4 Solutions at Temperatures from 297 to 573 K and at Pressures up to 40 MPa

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Densities of four aqueous Li_2SO_4 solutions (0.0944, 0.2798, 0.6115, 0.8850 $mol \cdot kg^{-1}$) have been measured in the liquid phase with a constant-volume piezometer immersed in a precision liquid thermostat. Measurements were made for ten isotherms between 297 and 573 K. The range of pressure was from 3.9 to 40 MPa. The total uncertainty of density, pressure, temperature, and concentration measurements were estimated to be less than 0.06%, 0.05%, 10 mK, and 0.014%, respectively. The reliability and accuracy of the experimental method was confirmed with measurements on pure water for two isobars at 10 and 38 MPa. Experimental and calculated (IAPWS formulation) densities for pure water show excellent agreement within their experimental uncertainties (average absolute deviation within 0.02 to 0.05%). Saturated liquid densities were determined by extrapolating experimental P-ρ data to the vapor pressure at fixed temperature and composition using an interpolating equation. Apparent and partial molar volumes were derived using measured densities for aqueous solutions and pure water. Derived apparent molar volumes were extrapolated to zero concentration to yield partial molar volumes of electrolyte (Li_2SO_4) at infinite dilution. The temperature, pressure, and concentration dependences of partial and apparent molar volumes were studied. A polynomial type of equation of state for specific volume was obtained as a function of temperature, pressure, and composition by a least-squares method using the experimental data. The average absolute deviation (AAD) between measured and calculated values from this polynomial equation for density was 0.02%. Measured values

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of solution density, and apparent and partial molar volumes were compared with data reported in the literature by other authors.

KEY WORDS: apparent molar volume; aqueous solution; density; equation of state; lithium sulfate; partial molar volume; water.

1. INTRODUCTION

The thermodynamic properties of aqueous solutions over a wide range of temperatures and concentrations are of great interest for different branches of science and industrial operations at high temperatures and high pressures. Aqueous systems play a significant role not only in chemical industry and technological processes but also in nature, e.g., geothermal systems and in biological processes of living organisms. Oceans and underground waters are the largest reservoirs of aqueous electrolyte solutions. Li^+ and SO_4^{2-} are important components of natural fluids, and a knowledge of their aqueous solution thermodynamic properties is important in understanding various geochemical processes, such as those related to subsurface brines, seafloor vents, geothermal energy production, and mineral scaling problems. Therefore, additional experimental and theoretical studies of the thermophysical properties of aqueous systems at high temperatures and high pressures are very important for many industrial processes and for design calculations, heat and mass transfer, fluid flow, development and utilization of geothermal energy, etc. However, a lack of reliable data over wide temperature, pressure, and concentration ranges makes it necessary to estimate missing properties by empirical and semi-empirical methods. New experimental data for $PVTx$ properties of aqueous systems at high temperatures and high pressures are needed to improve and extend the range of validity of available estimation and correlation methods that are capable of reproducing the experimental density data and to develop new more reliable prediction techniques of $PVTx$ behavior at these conditions. From measured values of $PVTx$ it is also possible to evaluate apparent and partial molar volumes and other derived thermodynamic properties. Only limited experimental $PVTx$ data of water + salt solutions over a wide range of temperatures, pressures, and concentrations are available in the literature.

The main objective of the paper is to provide new reliable experimental $PVTx$ data for aqueous lithium sulfate solutions at high temperatures (up to 573 K) and high pressures (up to 40 MPa) which can be used to develop theoretical models and for application in the new technologies. This work is a part of a continuing program on the volumetric properties of electrolytes in aqueous solutions. In previous studies [1–8] we have measured the densities of aqueous $MgCl_2$, $BaCl_2$, Na_2SO_4, K_2SO_4,

$Zn(NO_3)_2$, $NaNO_3$, and $LiNO_3$ solutions. The present results considerably expand the temperature and pressure ranges in which *PVTx* data for aqueous Li_2SO_4 solutions are available. *PVTx* properties for aqueous Li_2SO_4 solutions have been previously studied only at atmospheric pressure and over narrow temperature (up to 590 K) and concentration ranges [9–16]. Sometimes the reported densities are inaccurate and inconsistent.

Kaminsky [10] reported density data for $H_2O + Li_2SO_4$ solutions at atmospheric pressure at temperatures from 15.1 to 42.5°C and at compositions between 0.00085 to 0.17348 $mol \cdot l^{-1}$. Measurements were made by means of pycnometers, which were calibrated on distilled water. The uncertainty in the density measurements is about $(2 \text{ to } 6) \times 10^{-6}\ g \cdot cm^{-3}$ at low concentrations and $10^{-5}\ g \cdot cm^{-3}$ at high concentrations. The results of the measurements were represented by a correlation equation as a power series in terms of $m^{1/2}$, where m is the methanol composition.

Maksimova et al. [14] reported density data for $H_2O + Li_2SO_4$ solutions at six temperatures 20, 30, 40, 60, 80, and 90°C and concentrations between 1 and 24 mass%. The measurements were made by means of pycnometers, which were calibrated with distilled water. The experimental uncertainty of the density measurements was $\pm 2 \times 10^{-4}\ g \cdot cm^{-3}$. Puchkov et al. [16] measured the densities of $H_2O + Li_2SO_4$ solutions at temperatures up to 315°C with an uncertainty of $\pm 3 \times 10^{-3}\ g \cdot cm^{-3}$. They used the hydrostatic weighing method.

Pearce and Eckstrom [11] reported vapor-pressure, density, and partial molar volume data for aqueous solutions of lithium sulfate at 298.15 K. The densities of the solutions were measured by means of a 100 ml. pycnometer. The uncertainty in density measurements is about $10^{-6}\ g \cdot cm^{-3}$. Using measured values of density, the apparent molar volumes were calculated. Derived values of the apparent molar volumes ϕ_V were described by the equation,

$$\phi_V = 12.9093 + 8.47832 m^{1/2} + 0.204579 m, \tag{1}$$

where m is the concentration in $mol \cdot kg^{-1}$. This equation was used to calculate the partial molar volumes of solute (Li_2SO_4) $\bar{V}_2$ by employing Gucker's equation [17].

Novotný and Sohnel [18] have critically evaluated and correlated existing density data [12, 13] for binary $H_2O + Li_2SO_4$ solutions. They reported an equation which expressed the densities of aqueous Li_2SO_4 solutions as a function of concentration (c) and temperature (t)

$$\rho = \rho_{H_2O} + Ac + Bct + Cct^2 + Dc^{3/2}, \tag{2}$$

where ρ_{H_2O} is the density of pure water, c is the concentration in $mol \cdot dm^{-3}$, t is the temperature in °C, and A, B, C, D are adjustable parameters. Equation (2), theoretically substantiated [19], can be used for calculating densities of $H_2O + Li_2SO_4$ solutions at concentrations up to saturation.

Aseyev and Zaytsev [20, 21] represented available experimental density data from the literature for $H_2O + Li_2SO_4$ solutions by polynomial type correlation equation.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus used for the present *PVT* measurements is the same as that used for measurements on aqueous $MgCl_2$, $BaCl_2$, Na_2SO_4, K_2SO_4, $NaNO_3$, $Zn(NO_3)_2$, and $LiNO_3$ solutions. The apparatus and procedures that were described previously [1–8] 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 [6–8], they will be only briefly reviewed here. The *PVTx* properties of aqueous lithium sulfate solutions were measured with a constant-volume method, which gives an uncertainty of 0.06% for the density.

The apparatus used is schematically shown in Fig. 1. The main parts of the apparatus consisted of a piezometer (1), separating U-shape capillary tube filled with mercury (5), a liquid thermostat (7), heaters (10) and (11), temperature regulator (12), and platinum resistance thermometer (PRT) (13). The volume of the piezometer at 298 K and at atmospheric pressure (0.1 MPa) is $95.545 \pm 0.02\ cm^3$. Two capillaries (upper-2 and lower-3, see Fig. 1) 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. These capillaries lead to the room temperature zone and are connected with the pressure gauge through a separating U-shape capillary tube filled with mercury and oil and with a valve located outside the thermostat. A correction for the inactive ("dead" or noxious) volume was introduced using the density of the solution at room temperature.

The temperature inside the thermostat was maintained uniform within 0.02 K with the aid of a high precision temperature regulator. The piezometer is located vertically in the liquid thermostat. The cylindrical thermostat with an internal volume of $0.02\ m^3$ was made from stainless steel. Pure water was used as a liquid in the thermostat at temperatures to 350 K, glycerin at temperatures from 350 to 448 K, and a molten salt mixture (45% KNO_3 and 55% $NaNO_3$, the melting point of this mixture is 410 K) at temperatures above 448 K. The liquid in the thermostat was

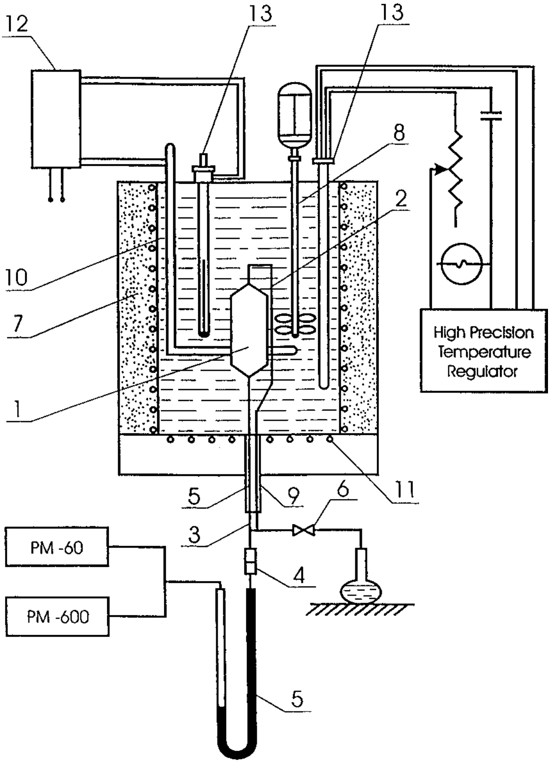

Fig. 1. Schematic diagram of the experimental *PVTx* apparatus. 1, piezometer; 2, upper capillary; 3, lower capillary; 4, viewing window; 5, separating U-shape capillary tube with mercury; 6, valve; 7, liquid-filled thermostat; 8, pump with mixer; 9, tube; 10, side heater; 11, bottom heater; 12, temperature regulator; 13, PRT.

vigorously circulated by a stirrer driven by a motor. 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 thermostat liquid was measured with a 10 Ω platinum resistance thermometer. The sample temperature (ITS-90) was detected with a precision of ±0.01 K. The pressure of the sample (solution) was measured with a dead-weight pressure gauge range from 0.6 to 60 MPa. The average uncertainty in pressure measurements is 0.015%, and the maximum uncertainty is 0.05%. The sample in the piezometer was heated in the thermostat until its temperature reached the prescribed value and the pressure reached a maximum value of 40 MPa. After thermal equilibration, $PVTx$ measurements along isotherms were made, starting from a maximum pressure of 40 MPa. Subsequent measurements at lower pressures and densities were made after 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

$$\begin{aligned} \rho_i &= M_i / V_{PT}, \\ M_i &= M_{\text{tot}} - M_{\text{coll}}, \\ M_{\text{tot}} &= M_1 + M_2 + M_3 + \cdots + M_N, \end{aligned} \tag{3}$$

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 ("dead" or inactivated) volumes (volumes of the capillaries in the room temperature and transitional zones) and evaporation of the sample during extraction. The temperature dependence of the piezometer volume at fixed pressure was calculated as

$$\Delta V_T = V_{T_0}[1 + 3\alpha(T - T_0)], \tag{4}$$

where V_{T_0} 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 [22]. The final equation for the piezometer volume is

$$V_{PT} = V_{298} + \Delta V_T + \Delta V_P, \tag{5}$$

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 [23, 24]). The uncertainty in the piezometer volume calculation can be estimated as

$$\delta V_{PT} = \delta(V_{298}) + \delta(\Delta V_T) + \delta(\Delta V_P), \tag{6}$$

where $\delta(V_{298}) = 0.002\%$, $\delta(\Delta V_T) = 0.016\%$, and $\delta(\Delta V_P) = 0.02\%$. Therefore, the value of δV_{PT} was less than 0.038%. Because of a small, "dead volume" of capillaries, etc. outside the autoclave, minor corrections had to be applied. These were based on the assumption that the dead volume remained completely filled with liquid sample at 25°C. The piezometer noxious volume was determined both experimentally and by calculation. 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 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, *PVT* measurements were made with pure water. Table I provides 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 [23, 24]). As one can see from Table I, the agreement between IAPWS [23, 24] and the present results along isobars of 10 and 38 MPa are 0.028 and 0.048%, respectively. At atmospheric pressure the AAD between measured and IAPWS [23, 24] calculated values is about 0.02%. No systematic trend of the deviations was found for pure water. This excellent agreement between the present data for pure water and IAPWS [23, 24] calculations demonstrates the reliability of the present measurements for $H_2O + Li_2SO_4$ solutions.

The $H_2O + Li_2SO_4$ solutions were prepared from chemically pure Li_2SO_4 (Merck GR, > 99.5 mass%) and doubly-distilled water. The solutions were prepared gravimetrically using an analytical balance (VLA-200) with a precision of $\pm 5 \times 10^{-8}$ kg.

Table I. Comparisons Between Experimental and Calculated Densities for Pure Water

T (K)	ρ ($kg \cdot m^{-3}$) This work	ρ ($kg \cdot m^{-3}$) IAPWS [23]	$\delta\rho$ (%) Deviation	T (K)	ρ ($kg \cdot m^{-3}$) This work	ρ ($kg \cdot m^{-3}$) IAPWS [23]	$\delta\rho$ (%) Deviation
	$P = 10$ MPa (AAD = 0.028%)				$P = 38$ MPa (AAD = 0.048%)		
323.15	992.1	992.3	+0.02	323.15	1003.5	1004.0	+0.05
373.15	962.8	962.9	+0.01	373.15	974.5	975.2	+0.07
423.15	922.8	922.3	−0.05	423.15	937.5	936.9	−0.06
473.15	870.9	870.9	+0.00	473.15	889.8	889.7	−0.01
523.15	805.2	805.7	+0.06	523.15	832.5	832.6	+0.01
573.15	715.5	715.3	−0.03	573.15	761.1	761.8	+0.09

3. RESULTS AND DISCUSSION

Measurements of the density for the aqueous Li_2SO_4 solutions were performed along ten isotherms between 297 and 573 K for four compositions, namely, 0.0944, 0.2798, 0.6115, and 0.8850 $mol \cdot kg^{-1}$. The pressure range was from 3.9 to 40 MPa. The experimental temperature, density, pressure, and concentration values are presented in Tables II and III. Some selected experimental results are shown in Figs. 2 to 6 as projections of isopleth-isotherm (constant composition and constant temperature), isobar-isotherm (constant pressure and constant temperature), and isopleth-isobar (constant concentration and constant pressure) curves in the P-ρ, ρ-m, and ρ-T spaces together with values calculated from IAPWS [23, 24] for pure water (see Figs. 3 and 6). The density of $H_2O + Li_2SO_4$ solutions was measured as a function of pressure at constant temperature.

The present results for densities of $H_2O + Li_2SO_4$ solutions at atmospheric pressure (see Table III) can be directly compared with experimental values reported in the literature and calculated with various correlation equations. For example, Figs. 5 to 7 contains the values of density calculated from correlations by Aseyev and Zaytsev [20, 21] and Novotný and Sohnel [18] and data by Pearce and Eckstrom [11] and Maksimova et al. [14]. Figure 5 shows comparisons of the present density measurements for $H_2O + Li_2SO_4$ solutions at atmospheric pressure for the composition of 0.0944 $mol \cdot kg^{-1}$ with values calculated from correlation equations

Table II. Experimental Densities, Pressures, Temperatures, and Concentrations of $H_2O + Li_2SO_4$ Solutions

P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)
$m = 0.0944\ mol \cdot kg^{-1}$									
297.95 K		323.15 K		348.15 K		373.15 K		398.15 K	
36.24	1020.9	39.04	1012.6	36.73	999.0	38.06	983.8	36.40	965.5
30.26	1018.5	31.93	1009.8	30.75	996.7	30.89	980.9	30.84	963.1
20.94	1014.8	20.43	1005.2	21.12	992.9	20.93	976.7	21.04	958.8
11.23	1010.4	10.49	1001.0	11.23	988.8	10.33	972.2	11.47	954.3
4.94	1007.9	5.20	998.8	4.97	986.1	5.30	970.0	5.25	951.2
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.95	946.8	37.65	924.1	37.94	899.5	37.61	842.5	38.63	773.1
30.85	942.9	31.57	920.7	31.20	895.3	31.69	837.3	31.30	763.3
20.84	937.9	22.25	915.3	22.10	889.2	22.45	828.7	22.10	749.3
10.27	932.3	12.00	909.1	11.39	881.9	12.33	818.5	15.89	740.1
5.63	929.9	6.13	905.9	5.92	877.9	6.41	812.2	12.11	731.2

Table II. *(Continued)*

P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)	P (MPa)	ρ ($kg \cdot m^{-3}$)
$m = 0.2798\ mol \cdot kg^{-1}$									
309.57 K		323.15 K		348.15 K		373.15 K		398.15 K	
39.53	1034.5	38.74	1028.8	35.10	1014.6	38.05	1001.0	35.49	982.0
30.10	1031.1	30.84	1025.8	29.77	1012.7	30.97	998.2	30.26	980.0
20.21	1027.2	20.94	1021.8	20.70	1009.2	20.67	994.0	21.02	976.0
10.74	1023.4	10.42	1017.4	10.90	1005.3	10.84	989.9	11.47	971.5
4.76	1021.1	5.04	1015.2	5.01	1002.8	5.21	987.5	4.76	968.3
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.05	963.8	37.87	942.2	36.77	917.9	38.89	863.9	39.65	796.6
30.53	960.3	30.96	938.6	31.00	914.4	31.73	858.1	31.83	786.9
20.68	955.6	22.41	933.7	21.76	908.4	21.96	849.3	21.57	772.1
10.42	950.6	12.25	927.9	11.72	901.8	12.53	840.3	16.73	763.9
4.89	947.8	5.74	924.3	6.03	897.9	6.33	834.1	12.78	757.5
306.68 K		323.15 K		348.15 K		373.15 K		398.15 K	
37.12	1063.4	38.75	1057.2	37.79	1044.1	39.05	1031.9	36.89	1011.7
30.02	1060.7	30.45	1053.9	30.10	1041.5	30.49	1028.3	30.28	1009.2
21.04	1057.5	20.92	1050.0	20.63	1038.0	20.49	1024.2	21.61	1005.5
10.64	1053.6	10.42	1045.6	10.98	1034.1	10.82	1020.2	11.39	1001.1
3.96	1050.9	4.95	1043.2	5.01	1031.8	5.29	1017.8	5.35	998.5
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.62	993.6	37.87	972.3	37.38	949.0	38.10	896.2	38.51	830.7
30.92	990.3	29.69	968.3	31.04	945.4	31.49	891.1	32.22	823.3
20.84	985.9	21.76	964.1	21.43	939.6	22.08	883.2	22.59	810.5
10.41	981.3	11.96	958.7	11.55	933.5	11.96	874.3	15.44	800.5
5.39	979.1	5.43	955.2	5.62	929.4	5.78	868.3	11.35	793.4
$m = 0.8850\ mol \cdot kg^{-1}$									
305.40 K		323.15 K		348.15 K		373.15 K		398.15 K	
38.20	1086.4	38.95	1078.4	35.00	1065.3	38.95	1053.5	36.39	1034.4
30.51	1083.6	30.65	1075.1	25.94	1062.1	30.85	1050.6	30.35	1032.1
21.04	1080.2	20.64	1071.1	16.06	1058.5	20.83	1047.0	20.78	1028.2
11.23	1076.7	10.83	1067.0	9.84	1056.1	10.39	1043.3	10.74	1024.4
4.86	1074.3	5.39	1064.7	5.09	1054.3	5.46	1041.6	5.43	1022.4
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.64	1017.6	37.04	996.1	36.63	973.2	37.65	921.5	38.28	857.4
30.64	1014.4	30.84	992.9	30.84	970.1	31.73	916.9	30.88	849.2
20.94	1010.6	21.04	988.4	21.61	964.8	22.45	909.9	22.55	838.7
10.82	1006.6	11.58	983.3	12.29	959.1	12.21	901.1	15.43	828.1
5.73	1004.6	5.21	979.8	5.58	954.5	6.45	895.9	12.41	823.9

Table III. Experimental Densities of $H_2O + Li_2SO_4$ Solutions at Atmospheric Pressure

m (mol·kg^{-1})							
0.0944		0.2798		0.6115		0.8850	
T (K)	ρ (kg·m^{-3})	T (K)	ρ (kg·m^{-3})	T (K)	ρ (kg·m^{-3})	T (K)	ρ (kg·m^{-3})
295.35	1006.40	295.95	1023.40	296.25	1052.19	296.25	1075.13
302.45	1004.29	297.15	1023.16	301.15	1050.60	300.85	1073.61
322.95	996.07	307.75	1019.52	308.15	1048.17	315.15	1068.11
–	–	322.95	1013.00	322.45	1042.05	323.55	1064.19

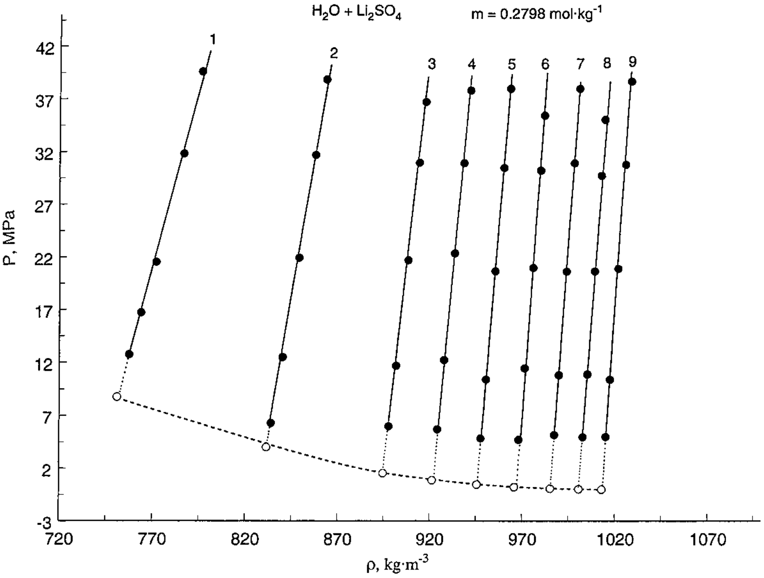

Fig. 2. Pressure P of $H_2O + Li_2SO_4$ solutions as a function of density ρ along various isotherms for fixed composition of 0.2798 mol·kg^{-1}. 1, 573.15 K; 2, 523.15 K; 3, 473.15 K; 4, 448.15 K; 5, 423.15 K; 6, 398.15 K; 7, 373.15 K; 8, 348.15 K; 9, 323.15 K; (- - -), vapor-pressure curve calculated from correlation by Aseyev [25]; ○, extrapolated values of vapor pressure; (——), calculated from Eq. (14).

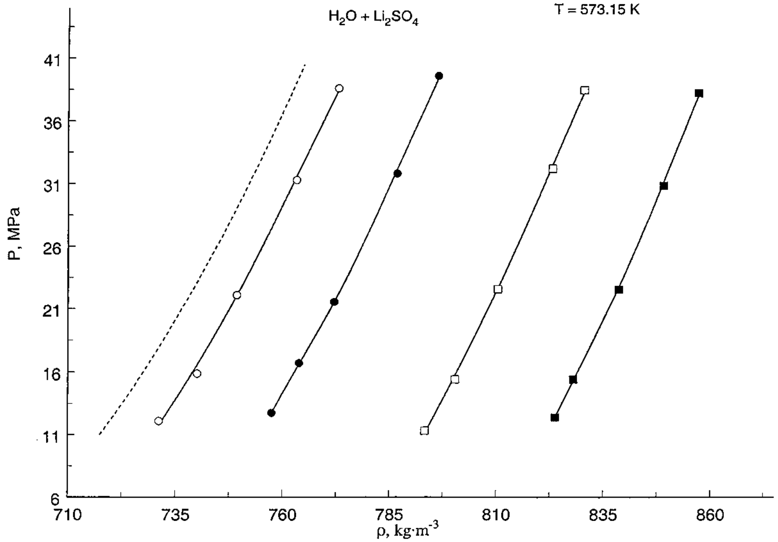

Fig. 3. Pressure P of $H_2O + Li_2SO_4$ solutions as a function of density ρ along selected isotherm of 573.15 K for various compositions together with values of density for pure water. ○, $m = 0.0944\ mol \cdot kg^{-1}$; □, $m = 0.6115\ mol \cdot kg^{-1}$; ■, $m = 0.8850\ mol \cdot kg^{-1}$; ●, $m = 0.2798\ mol \cdot kg^{-1}$; (- - -), pure water IAPWS [23, 24].

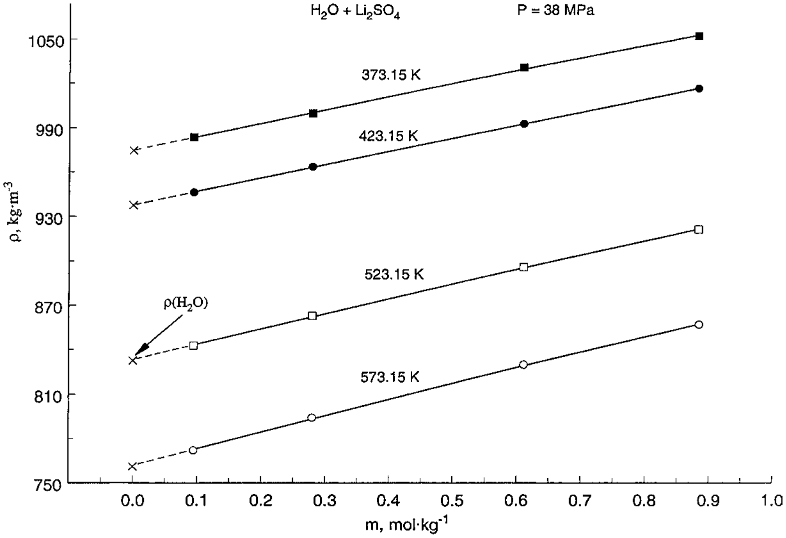

Fig. 4. Density ρ of $H_2O + Li_2SO_4$ solutions as a function of composition m along selected isotherms for isobar of 38 MPa. ×, values of density for zero concentration ($m = 0$, pure water values); solid curves are values calculated with Eq. (14).

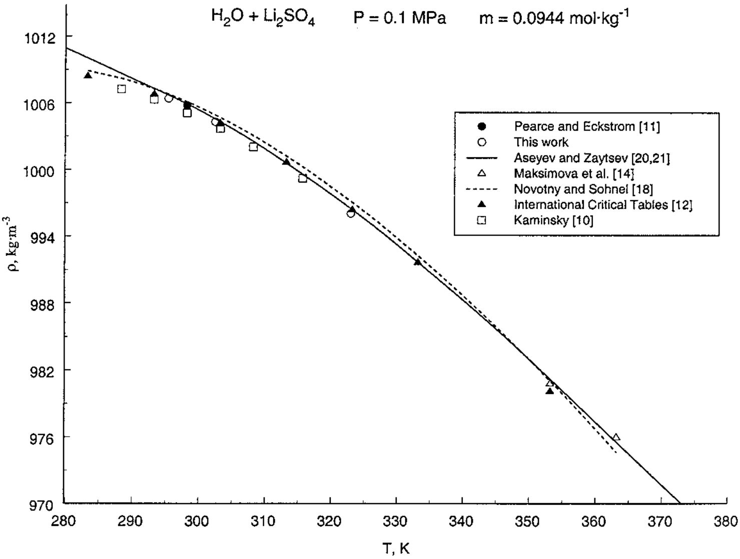

Fig. 5. Density ρ of $H_2O + Li_2SO_4$ solution as a function of temperature T at atmospheric pressure together with values calculated with correlation equations and data reported in the literature by various authors.

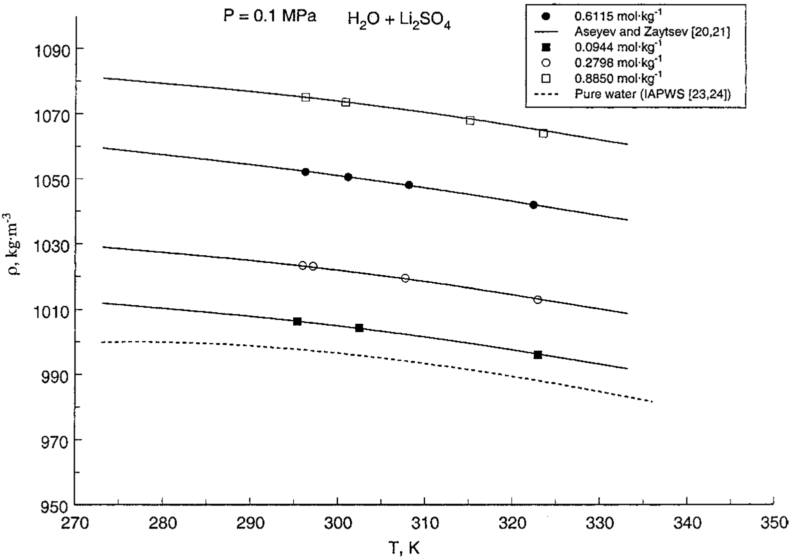

Fig. 6. Density ρ of $H_2O + Li_2SO_4$ solutions as a function of temperature T at atmospheric pressure together with values calculated with correlation by Aseyev and Zaytsev [20, 21] and IAPWS [23, 24] formulation for pure water.

reported by Novotný and Sohnel [18] (Eq. (2)) and by Aseyev and Zaytsev [20, 21]. The average absolute deviation (AAD) for Novotny and Sohnel [18] and Aseyev and Zaytsev [20, 21] calculated values of density are 0.050 and 0.058%, respectively. As one can see from Fig. 5 the data reported by Maksimova et al. [14], by Pearce and Eckstrom [11], and from the International Critical Tables [12] show good consistency. Figure 6 shows comparisons between the present density measurements and the values calculated from the Aseyev and Zaytsev [20, 21] correlation for various concentrations. The AAD for the various compositions range from 0.018 to 0.067%. Figure 7 shows comparisons of the concentration dependence of the present density measurements and the data reported by various authors at 298.15 K and atmospheric pressure. This figure contains also the values calculated with the correlation by Novotný and Sohnel [18] (Eq. (2)) and by Aseyev and Zaytsev [20, 21]. As Fig. 7 shows, the agreement between various data sets is good (deviations of about 0.05%). Figures 5 to 7 illustrate that our data are reasonably consistent with the literature at atmospheric pressure.

By extrapolation of the *P*-ρ curves to the vapor pressure curve calculated with the correlation equation, reported by Aseyev [25] for each

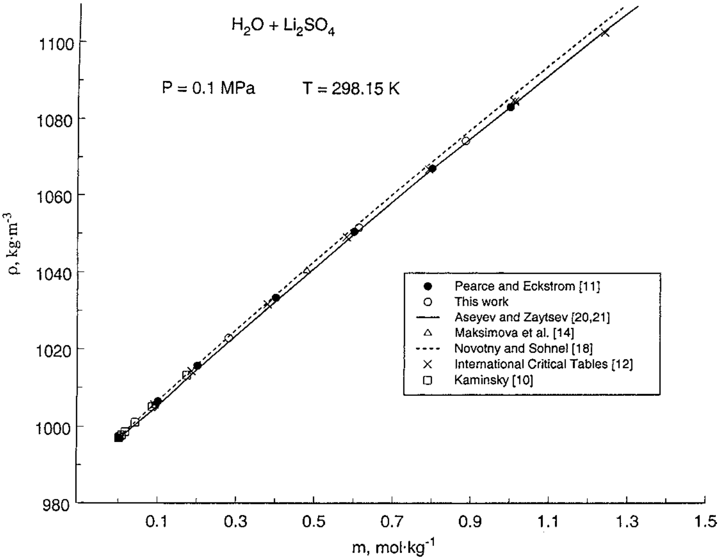

Fig. 7. Density ρ of $H_2O + Li_2SO_4$ solutions as a function of composition *m* along selected isotherm of 298.15 K at atmospheric pressure together with values calculated with correlation equations and data reported in the literature by various authors.

fixed temperature and composition, values of density on the liquid-vapor coexistence curve were derived from the present measurements. The results are presented in Table IV and in Fig. 8 together with values of saturated density for pure water calculated from the IAPWS [23, 24] equation of state. Because the experimental P-ρ isotherms are almost linear, the extrapolation is reliable. The uncertainty in the derived values of saturated density for $H_2O + Li_2SO_4$ solutions is 0.05 to 0.1%.

The measured solution density results were used to calculate the apparent ϕ_V and partial $\bar{V}_2$ molar volumes for each solution. In the limit of infinite dilution, the apparent molar volume of the solute $\phi_V(P, T, m \to 0)$ becomes equal to the partial molar volume $\bar{V}_2^{\infty}(\lim_{m \to 0} \phi_V = \bar{V}_2^{\infty})$. The values of the apparent molar volume ϕ_V of an electrolyte may provide essential information on the interaction between dissolved ions and molecules of a solvent. Apparent ϕ_V and partial $\bar{V}_2$ molar volumes of electrolyte solutions are a very useful tool to study structural interactions (ion-ion, ion-solvent, and solvent-solvent) occurring in solutions. The concentration dependence of the apparent and partial molar volumes of electrolytes can be used to study ion-ion interactions. Millero [26], Fajans and Johnson [27], and Zen [28] compiled partial molar volumes of electrolytes at infinite dilution. We examine the partial and apparent molar volumes of aqueous Li_2SO_4 solutions at infinite dilution as a function of temperature and pressure.

From the experimental values of molar volumes $V_m(P, T, x)$ for $H_2O + Li_2SO_4$ solutions and the corresponding values for pure water $V_m(P, T, 0)$, the values of apparent $\phi_V(P, T, x)$ molar volumes are defined as [29–31]

$$x\phi_V(P, T, x) = V_m(P, T, x) - (1-x)\, V_m(P, T, 0). \tag{7}$$

Apparent molar volumes show a change in molar volume as the composition is changed from that of the pure first component (pure water $V_m(P, T, 0)$) to mole fraction x of the second component (salt, Li_2SO_4). The apparent molar volumes ϕ_V were calculated from measured solution densities ρ_{sol} and pure water densities ρ_0 by the following relationship [32, 33]:

$$\phi_V = \frac{1000(\rho_0 - \rho_{sol})}{m\rho_{sol}\,\rho_0} + \frac{M_2}{\rho_{sol}}, \tag{8}$$

where M_2 is the molar mass of the salt, ρ_{sol} and ρ_0 are the densities of solution and pure water, respectively, and m is the solution molality ($mol \cdot l^{-1}$). Water densities used for transforming the measured values of

Table IV. Temperature, Pressures, Densities, and Compositions at the Liquid-Vapor Coexistence Curve for Aqueous Li_2SO_4 Solutions

T_S (K)	P_S (MPa)	ρ_S ($kg \cdot m^{-3}$)	P_S (MPa)	ρ_S ($kg \cdot m^{-3}$)	P_S (MPa)	ρ_S ($kg \cdot m^{-3}$)	P_S (MPa)	ρ_S ($kg \cdot m^{-3}$)
	$m = 0.0944$ ($mol \cdot kg^{-1}$)		$m = 0.2798$ ($mol \cdot kg^{-1}$)		$m = 0.6115$ ($mol \cdot kg^{-1}$)		$m = 0.8850$ ($mol \cdot kg^{-1}$)	
323.15	0.0123	996.54	0.0123	1013.00	0.0123	1041.04	0.0124	1062.39
348.15	0.0385	983.93	0.0385	1000.65	0.0386	1029.64	0.0389	1052.30
373.15	0.1013	967.71	0.1013	985.29	0.1019	1015.65	0.1029	1039.72
398.15	0.2322	948.65	0.2325	965.94	0.2337	996.15	0.2354	1020.46
423.15	0.4766	927.04	0.4779	945.57	0.4820	976.90	0.4870	1002.55
448.15	0.8942	902.73	0.8983	921.44	0.9092	952.56	0.9217	977.39
473.15	1.5592	874.72	1.5695	894.80	1.5948	926.70	1.6227	951.77
523.15	3.9953	809.55	4.0397	831.69	4.1410	866.74	4.2968	893.87
573.15	8.6432	725.02	8.7840	750.97	9.0939	789.90	9.4098	818.93

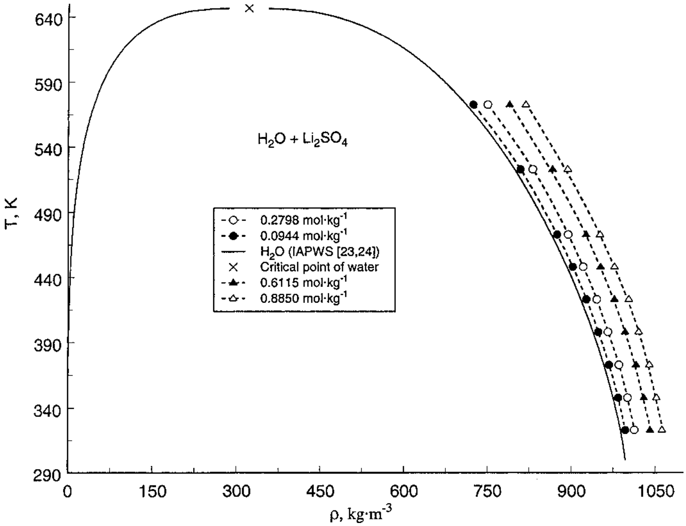

Fig. 8. Temperatures T and densities ρ of $H_2O + Li_2SO_4$ solutions at saturation derived from present measurements by extrapolation to vapor pressure curve together with coexistence curve for pure water calculated with IAPWS [23, 24] formulation.

ρ_{sol} to ϕ_V were calculated from the IAPWS [23, 24] formulation. Derived values of ϕ_V are given in Table V and in Figs. 9 to 12. These figures illustrate how ϕ_V changes with temperature, pressure, and concentration. Figure 9 shows that the apparent molar volume ϕ_V, plotted as a function of temperature, increases with temperature, passes through a maximum near 323 K, and decreases at higher temperatures. At temperatures of 423 K and above, depending on the pressure and composition, the values of ϕ_V become negative. At low temperatures ($T < 473$ K), the values of ϕ_V are little affected by the pressure or concentration (see Figs. 9 to 11). However, at temperatures above 473 K, the concentration and pressure have a significant influence on ϕ_V (see Figs. 9 and 10). The dependence of ϕ_V on temperature decreases significantly at $T > 500$ K (see Fig. 9).

The uncertainty in derived values of ϕ_V depends strongly on m, ρ_{sol}, and ρ_0. The maximum relative uncertainty $\delta\phi_V$ in the apparent molar volume ϕ_V determination can be estimated from following relation

$$\delta\phi_V = \left(1 - \frac{Mm}{1000}\right)\left(\frac{\rho_0}{\rho_0 - \rho_{\mathrm{sol}}}\right)\delta\rho_{\mathrm{sol}} + \left(\frac{\rho_{\mathrm{sol}}}{\rho_0 - \rho_{\mathrm{sol}}}\right)\delta\rho_0 + \delta m, \tag{9}$$

where $\delta\phi_V$, $\delta\rho_0 = 0.001\%$ (IAPWS standard), $\delta\rho_{\mathrm{sol}} = 0.06\%$, and $\delta m = 0.8\%$ (at low concentrations) and 0.08% (at high concentrations) are the relative uncertainties in the apparent molar volumes, pure water density, solution density, and concentration, respectively. At low concentration (dilute solutions), where differences between pure water and

Table V. Apparent Molar Volumes of Aqueous Li_2SO_4 Solutions

P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)
				$m = 0.0944\ \mathrm{mol \cdot kg^{-1}}$					
297.95 K		323.15 K		348.15 K		373.15 K		398.15 K	
36.24	25.5	39.04	22.9	36.73	18.6	38.06	17.9	36.40	10.6
30.26	24.0	31.93	21.8	30.75	16.8	30.89	15.8	30.84	8.6
20.94	20.6	20.43	19.9	21.12	14.0	20.93	13.7	21.04	4.5
11.23	21.9	10.49	19.6	11.23	12.2	10.33	10.2	11.47	2.3
4.94	18.7	5.20	18.8	4.97	11.7	5.30	8.70	5.250	2.2
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.95	4.2	37.65	−2.9	37.94	−4.9	37.61	−19.6	38.63	−40.5
30.85	1.7	31.57	−3.5	31.20	−7.0	31.69	−20.1	31.30	−43.0
20.84	−1.1	22.25	−4.5	22.10	−7.6	22.45	−23.5	22.10	−60.1
10.27	−2.8	12.00	−5.4	11.39	−12.0	12.33	−28.6	16.69	−70.0
5.63	−5.1	6.13	−11.9	5.92	−12.6	6.41	−32.5	12.11	−77.2

Table V. *(Continued)*

P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)	P (MPa)	ϕ_V ($cm^3 \cdot mol^{-1}$)
$m = 0.2798$ mol·kg^{-1}									
309.57 K		323.15 K		348.15 K		373.15 K		398.15 K	
35.98	23.2	38.74	22.0	35.10	20.1	38.05	15.7	35.49	13.3
30.10	22.1	30.84	21.0	29.77	18.9	30.97	14.6	30.26	11.5
20.21	20.7	20.94	20.4	20.70	17.5	20.67	13.1	21.02	9.7
10.74	19.3	10.42	20.0	10.90	16.1	10.84	11.5	11.47	8.8
4.76	18.0	5.04	19.4	5.01	15.7	5.21	10.6	4.76	7.9
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.05	7.9	37.87	1.8	36.77	−6.1	38.89	−23.0	39.65	−52.6
30.53	6.4	30.96	0.1	31.00	−7.5	31.73	−26.2	31.83	−58.9
20.68	4.2	22.41	−0.8	21.76	−9.3	21.96	−30.4	21.57	−74.2
10.42	1.5	12.25	−3.1	11.72	−12.5	12.53	−36.2	167.3	−80.0
4.89	0.1	5.74	−5.7	6.03	−13.4	6.33	−40.9	12.78	−92.2
$m = 0.6115$ mol·kg^{-1}									
306.68 K		323.15 K		348.15 K		373.15 K		398.15 K	
37.12	23.0	38.75	22.4	37.79	21.2	39.05	15.3	36.89	15.8
30.02	22.4	30.45	22.1	30.10	20.1	30.49	14.9	30.28	14.6
21.04	21.2	20.92	21.8	20.63	19.1	20.49	14.1	21.61	13.6
10.64	19.9	10.42	21.5	10.98	18.4	10.82	13.1	11.39	12.2
3.96	19.3	4.95	21.4	5.01	17.7	5.29	12.7	5.35	11.2
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.62	11.7	37.87	6.8	37.38	0.7	38.10	−15.8	38.51	−42.9
30.92	10.3	29.69	5.1	31.04	−0.7	31.49	−18.3	32.22	−47.6
20.84	8.3	21.76	3.8	21.43	−2.9	22.08	−22.3	22.59	−58.5
10.41	5.9	11.96	2.1	11.55	−5.6	11.96	−27.9	15.44	−70
5.39	4.6	5.43	0.4	5.62	−6.7	5.78	−31.2	11.35	−76.7
$m = 0.8850$ mol·kg^{-1}									
305.40 K		323.15 K		348.15 K		373.15 K		398.15 K	
38.20	24.1	38.95	24.7	35.00	22.2	38.95	18.8	36.39	17.3
30.51	23.5	30.65	24.4	25.94	21.4	30.85	17.9	30.35	16.5
21.04	22.6	20.64	24.0	16.06	20.5	20.83	16.7	20.78	15.5
11.23	21.5	10.83	23.7	9.84	20.0	10.39	15.2	10.74	13.8
4.86	20.9	5.39	23.6	5.09	19.6	5.46	14.4	5.43	13.4
423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
38.64	12.9	37.04	8.5	36.63	3.1	37.65	−11.6	38.28	−35.8
30.64	11.5	30.84	7.8	30.84	1.8	31.73	−13.3	30.88	−41.4
20.94	9.6	21.04	5.6	21.61	−0.1	22.45	−17.5	22.55	−50.1
10.82	7.3	11.58	4.2	12.29	−2.1	12.21	−22.1	154.3	−57.8
5.73	6.0	5.21	3.1	5.58	−3.9	6.45	−25.1	12.41	−63.4

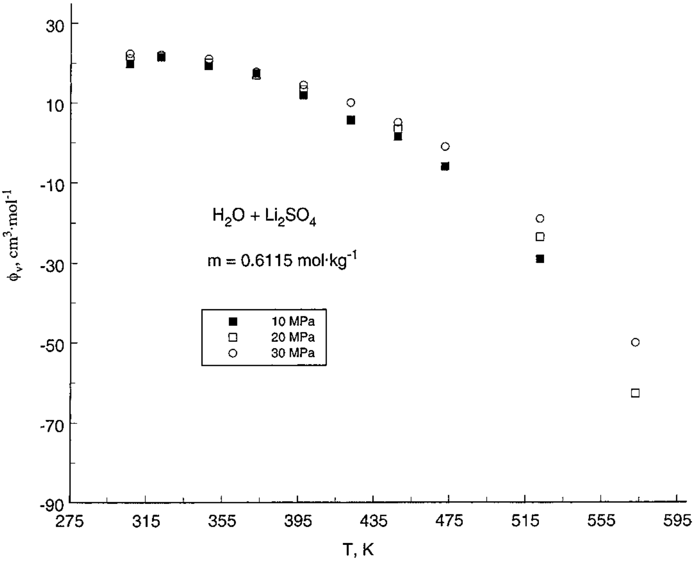

Fig. 9. Apparent molar volume ϕ_V for Li_2SO_4 as a function of temperature T at fixed composition of 0.6115 mol · kg^{-1} for selected pressures.

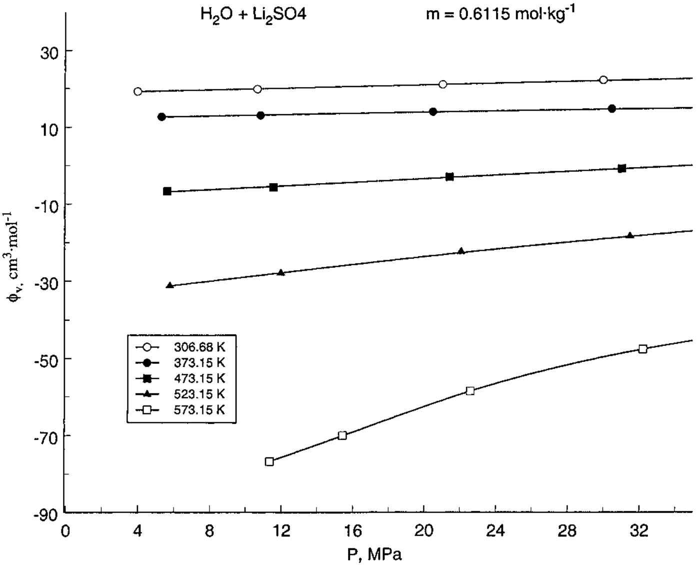

Fig. 10. Apparent molar volume ϕ_V for Li_2SO_4 as a function of pressure P at fixed composition of 0.6115 mol · kg^{-1} for selected temperatures.

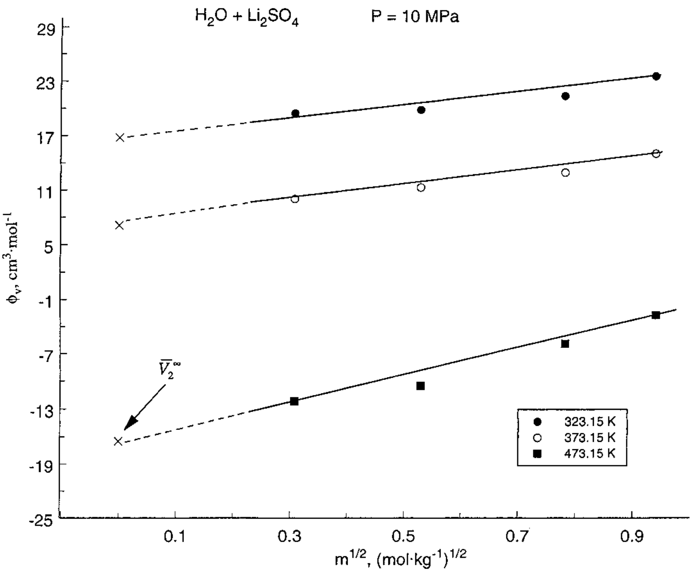

Fig. 11. Apparent molar volume ϕ_V for Li_2SO_4 against square root of molality $m^{1/2}$ at a pressure of 10 MPa for selected temperatures.

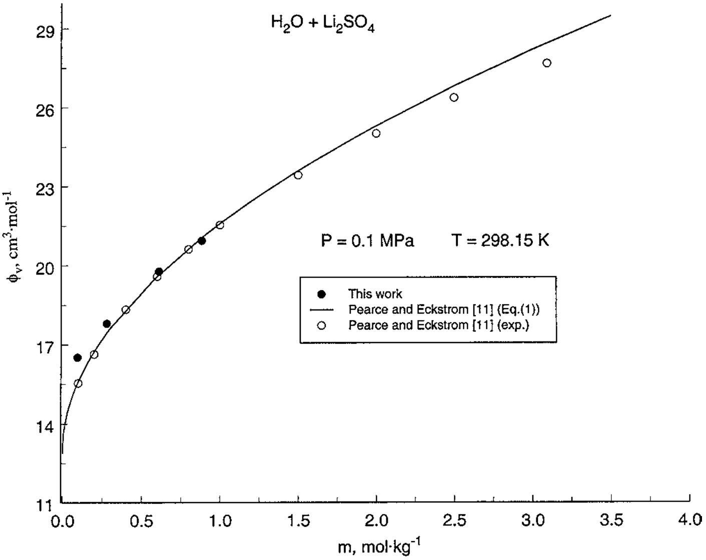

Fig. 12. Comparisons of present results for apparent molar volume ϕ_V for Li_2SO_4 with values reported by Pearce and Eckstrom [11] at a temperature of 298.15 K and atmospheric pressure.

solution are small, $(\rho_0 - \rho_{\text{sol}}) \to 0$, the uncertainty in apparent molar volumes calculated from Eq. (9) reached up to 40% and more, while at concentrations of about 0.5 $\text{mol} \cdot \text{kg}^{-1}$, the uncertainty in ϕ_V is about 4%. The values of ϕ_V calculated from Eq. (8) using the measured solution and pure water densities are very sensitive to the accuracy of the experimental values of ρ_{sol} and ρ_0. Even small variations in ρ_{sol} and ρ_0 within their experimental uncertainties cause significant changes (up to 40% and more) in derived values of ϕ_V, especially at low concentrations. For example, if we vary the values of solution density at concentration of 0.062 $\text{mol} \cdot \text{kg}^{-1}$ and temperature 573 K and pressure 11.23 MPa within 0.07%, the values of ϕ_V changed from 60.3 to 44.6 $\text{cm}^3 \cdot \text{mol}^{-1}$ (about 35%), while at a concentration of 0.529 and at the same temperature and pressure, the changes in density cause changes in ϕ_V from 48.0 to 46.2 $\text{cm}^3 \cdot \text{mol}^{-1}$ (about 4.3%).

Figure 12 compares the present results for ϕ_V with calculated values (Eq. (1)) and with those measured by Pearce and Eckstrom [11] at atmospheric pressure and 298.15 K. The present data, which are plotted in Fig. 12 together with the values reported by Pearce and Eckstrom [11], show good agreement (deviations of about 0.6%), except for one data point at a composition of 0.0944 $\text{mol} \cdot \text{kg}^{-1}$ for which the deviation is 1.1%.

Masson [34] found that the apparent molar volume can be represented over wide ranges by linear functions of the square root of the concentration $\sqrt{m}$,

$$\phi_V = \phi_V^0 + A_V \sqrt{m} \tag{10}$$

where ϕ_V^0 is the apparent molar volume of the electrolyte at infinite dilution or the partial molar volume $\bar{V}_2^\infty$ of the electrolyte at infinite dilution, and A_V is the experimental slope which varies with electrolyte type and charge. Equation (10) adequately represents the concentration dependence of ϕ_V over a wide temperature range (from 273 to 373 K). Redlich and Rosenfeld [35, 36] derived a linear square-root relation for the concentration dependence of ϕ_V from the theory of Debye and Hückel by differentiating the limiting law for activity coefficients with respect to pressure.

Roux et al. [37] reported an equation to accurately describe the apparent molar volume of dilute solutions of salt:

$$\phi_V = \bar{V}_2^\infty + A_V (d_1^0 m)^{1/2} + B_V m + C_V m^{1/2}. \tag{11}$$

The concentration dependence of ϕ_V at temperature of 298.15 K for the $H_2O + Li_2SO_4$ solutions was represented by Pearce and Eckstrom [11] as Eq. (1), where ϕ_V^0 or $\bar{V}_2^\infty$ is 12.91 $\text{cm}^3 \cdot \text{mol}^{-1}$.

Krumgalz et al. [38] reported the following equation for the apparent molar volumes:

$$\phi_V = \bar{V}_2^\infty + A_0 + A_1\beta_{MX}^{(0)V} + A_2\beta_{MX}^{(1)V} + A_3\beta_{MX}^{(2)V} + A_4 C_{MX}^V, \tag{12}$$

where A_i $(i = 0, 4)$ are the concentration-dependent parameters in the Pitzer's ion interaction model for volumetric properties. The values of parameters $\bar{V}_2^\infty$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V were calculated by least squares from the data reported in Refs. 9 to 12 for aqueous Li_2SO_4 solutions at 298.15 K. The derived value of $\bar{V}_2^\infty$ is 12.58 $cm^3 \cdot mol^{-1}$.

The standard experimental procedure of calculating $\bar{V}_2^\infty$ is by extrapolation of ϕ_V to infinite dilution, based on the Redlich–Mayer relation [39];

$$\phi_V = \bar{V}_2^\infty + A_V\sqrt{m} + bm, \tag{13}$$

where $A_V = kw^{3/2}$ and the terms w and k are expressed as

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

e is the electric charge, D is the dielectric constant of the solvent, N is Avogadro's number, v_i is the number of ions of species i formed from one mole of salt to which the electrolyte dissociates, Z_i is the valence of ionic species i, m is the solution molality, β is the compressibility of the solvent (water), and b is an empirical coefficient. The limiting slope depends only on temperature and the physical properties of the solvent (D, $\partial \ln D/\partial P$, and β). As a rule, the extrapolation by this relationship is carried out at fixed pressure P and temperature T. The infinite-dilution values of ϕ_V or $\bar{V}_2^\infty$ are obtained by extrapolation of Eq. (13) to zero concentration (to infinite dilution, $m \to 0$). The experimental values of the apparent molar volumes ϕ_V of the Li_2SO_4 vs. $m^{1/2}$ are shown in Fig. 11 for fixed pressures and temperatures. They are almost linear in the range of concentrations between 0 and 0.9 $mol \cdot kg^{-1}$. The applicability of Eq. (13) is limited to the concentration ranges where the Debye–Hückel theory holds. As Fig. 11 shows, the ϕ_V-$m^{1/2}$ dependence is linear. Treatment has been based on least-squares fits of all results using Eq. (13) up to terms in m from about $m = 0.1$ to $m = 0.885$ $mol \cdot kg^{-1}$. Derived values of $\bar{V}_2^\infty$ are summarized in Table VI for various T and P. The pressure and temperature dependences of the derived values of $\bar{V}_2^\infty$ are shown in Figs. 13 and 14 for selected isotherms and isobars. As one can see from these figures, the pressure dependence of $\bar{V}_2^\infty$ at low temperatures ($T < 498$ K) is small. Figure 13 indicates that at high temperatures ($T > 498$ K) the pressure has a significant effect on $\bar{V}_2^\infty$. The

Table VI. Infinite-Dilution Values of the Partial Molar Volume $\bar{V}_2^{\infty}$ ($cm^3 \cdot mol^{-1}$) of Li_2SO_4 in Water

	P (MPa)				
T (K)	5	10	20	30	40
298.15	15.4	15.3	15.1	15.1	15.2
323.15	16.1	16.1	16.1	16.4	16.8
348.15	12.0	13.6	16.6	19.4	21.9
373.15	4.80	6.90	10.9	14.3	17.2
398.15	−3.60	−1.50	2.40	5.80	8.70
423.15	−12.1	−10.5	−7.50	−4.70	−2.20
448.15	−20.8	−19.9	−17.9	−15.8	−13.5
473.15	−31.3	−30.7	−29.0	−27.0	−24.4
498.15	−47.5	−45.9	−42.4	−38.8	−35.1
523.15	−76.1	−71.0	−61.9	−54.2	−47.9
573.15	–	−191	−151	−122	−104

temperature dependence of $\bar{V}_2^{\infty}$ is shows a maximum near 323 K for each isobar. The location of the temperature maximum is slightly shifted to high temperatures with increasing pressure. At high temperatures (about 398 K) the values of $\bar{V}_2^{\infty}$ decrease and become negative. Comparisons between the present results for $\bar{V}_2^{\infty}$ and more accurate data reported by other authors in the literature at 298.15 K and at atmospheric pressure are given in Table VII. As one can see from Table VII, most calculated and measured data reported in the literature show good agreement within ± 0.7% (maximum deviation is 3.3% for the values by Krumgalz et al. [38]) with present results, except for the results calculated with the ion-solvent interaction model by Mukerjee [40]. Our values are very close (deviation of about 0.7%) to the values reported by Pearce and Eckstrom [11] and Millero [26, 41].

Table VII. Comparisons of the Values of $\bar{V}_2^{\infty}$ ($cm^3 \cdot mol^{-1}$) at 298.15 K and Atmospheric Pressure

This work (experiment)	13.00
Krumgalz et al. [38]	12.58
Pearce and Eckstrom [11]	12.91
Millero [26]	13.10
Mukerjee [40]	14.40[a]
This work (calculation)	12.68[b]

[a] Calculated from the model of ion-solvent interactions.

[b] Individual ion additive calculations from data [28, 41].

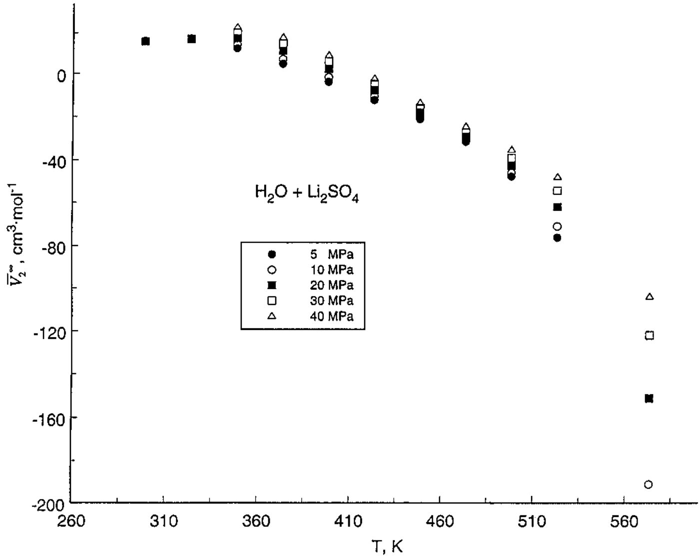

Fig. 13. Partial molar volume $\overline{V}_2^\infty$ of Li_2SO_4 at infinite dilution as a function of temperature T for selected pressures.

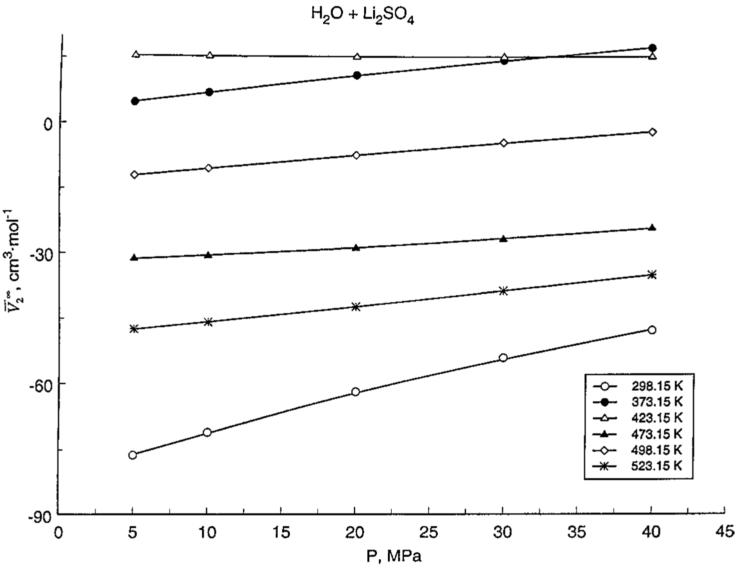

Fig. 14. Partial molar volume $\overline{V}_2^\infty$ of Li_2SO_4 at infinite dilution as a function of pressure P for selected temperatures.

4. CORRELATION

The results of $PVTx$ measurements for $H_2O + Li_2SO_4$ solutions were represented by the equation of state

$$V(P, t, m) = A + Bt + Ct^2 + Dt^7 \tag{14}$$

where V is the specific volume of the solution in $m^3 \cdot kg^{-1}$ and t is the temperature in °C. The pressure and concentration dependences of the specific volume V have been taken into account through coefficients $A(P, m)$, $B(P, m)$, $C(P, m)$, and $D(P, m)$ parameters as quadratic functions of concentration m (in $mol \cdot kg^{-1}$) and pressure (in MPa),

$$\begin{aligned} A &= \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} p^i m^j \qquad & B &= \sum_{i=0}^{2} \sum_{j=0}^{2} b_{ij} p^i m^j \\ C &= \sum_{i=0}^{2} \sum_{j=0}^{2} c_{ij} p^i m^j \qquad & D &= \sum_{i=0}^{2} \sum_{j=0}^{2} d_{ij} p^i m^j. \end{aligned} \tag{15}$$

Equation (14) represents the experimental densities with an AAD of 0.02% which is less than their experimental uncertainty (0.06%). Derived values of coefficients a_{ij}, b_{ij}, c_{ij}, and d_{ij} in Eq. (14) are given in Table VIII.

Table VIII. Values of the Coefficients of Eq. (14)

i	$j=0$	$j=1$	$j=2$
		$a_{i,j}$	
1	0.9971059×10^{0}	-9.888302×10^{-2}	1.847174×10^{-2}
2	-4.064421×10^{-5}	1.930827×10^{-5}	-7.134402×10^{-6}
3	-3.021962×10^{-9}	3.731894×10^{-9}	-6.581105×10^{-9}
		$b_{i,j}$	
1	1.607858×10^{-4}	1.204012×10^{-4}	-9.845169×10^{-5}
2	-1.108147×10^{-7}	7.155495×10^{-8}	-1.721349×10^{-8}
3	3.97276×10^{-10}	$-3.583128 \times 10^{-10}$	2.012300×10^{-10}
		$c_{i,j}$	
1	2.996893×10^{-6}	-1.499715×10^{-6}	-5.646814×10^{-7}
2	-2.40581×10^{-10}	$-7.739388 \times 10^{-10}$	6.076838×10^{-10}
3	$-2.072086 \times 10^{-12}$	2.938301×10^{-12}	$-1.757808 \times 10^{-12}$
		$d_{i,j}$	
1	5.810298×10^{-19}	-4.88875×10^{-19}	2.418292×10^{-19}
2	$-1.687343 \times 10^{-21}$	2.035891×10^{-21}	$-1.217391 \times 10^{-21}$
3	1.848694×10^{-24}	$-2.727159 \times 10^{-24}$	1.79105×10^{-24}

Equation (14) can be used to calculate the partial and apparent molar volumes and other derived thermodynamic properties of $H_2O + Li_2SO_4$ solutions over wide temperature (up to 600 K), pressure (up to 40 MPa), and concentration (up to $1\ \mathrm{mol \cdot kg^{-1}}$) ranges. Values of the partial molar volume $\bar{V}_2$ have been calculated from the following equation:

$$\bar{V}_2 = M_2 V + (1000 + m M_2)\left(\frac{\partial V}{\partial m}\right)_{PT}, \tag{16}$$

using experimental molar volumes $V(P, t, m)$ and the derivatives $(\frac{\partial V}{\partial m})_{PT}$ calculated from Eq. (14). The results are given in Table IX and in Figs. 15 to 18. The estimated uncertainty of the derived partial molar volumes from Eq. (16) is about 30% at low concentrations and 4% at high concentrations. As one can see from Figs. 15 and 16 at low temperatures ($T < 473$ K) and high concentrations ($m > 0.6\ \mathrm{mol \cdot kg^{-1}}$), the effect of

Table IX. Partial Molar Volumes ($\mathrm{cm^3 \cdot mol^{-1}}$) of Li_2SO_4 in Water

P (MPa)	T (K) 298.15	323.15	373.15	423.15	473.15	523.15	573.15
			$m = 0.0944\ \mathrm{mol \cdot kg^{-1}}$				
10	16.0	17.0	14.7	6.3	−10.1	−41.3	−105.1
20	17.4	18.3	15.9	7.6	−7.8	−34.3	−82.6
30	18.7	19.5	17.1	9.1	−5.3	−28.4	−67.1
40	20.0	20.6	18.2	10.8	−2.4	−23.6	−58.78
			$m = 0.2798\ \mathrm{mol \cdot kg^{-1}}$				
10	18.3	18.8	16.1	8.3	−6.2	−33.2	−87.2
20	19.5	19.9	17.2	9.6	−4.0	−27.2	−68.9
30	20.5	20.9	18.3	11.0	−1.7	−21.9	−55.8
40	21.5	21.8	19.3	12.5	0.9	−17.5	−47.9
			$m = 0.6115\ \mathrm{mol \cdot kg^{-1}}$				
10	23.3	22.8	19.4	12.8	2.0	−16.3	−51.0
20	24.0	23.5	20.4	14.1	4.0	−12.3	−41.2
30	24.5	24.1	21.2	15.3	6.0	−8.5	−32.7
40	24.9	24.6	21.9	16.5	8.0	−4.9	−25.7
			$m = 0.8850\ \mathrm{mol \cdot kg^{-1}}$				
10	28.2	26.8	22.9	17.5	10.2	−0.3	−17.2
20	28.5	27.3	23.7	18.8	12.0	1.9	−15.0
30	28.6	27.5	24.3	19.8	13.6	4.4	−10.9
40	28.6	27.6	24.7	20.6	15.0	7.2	−4.7

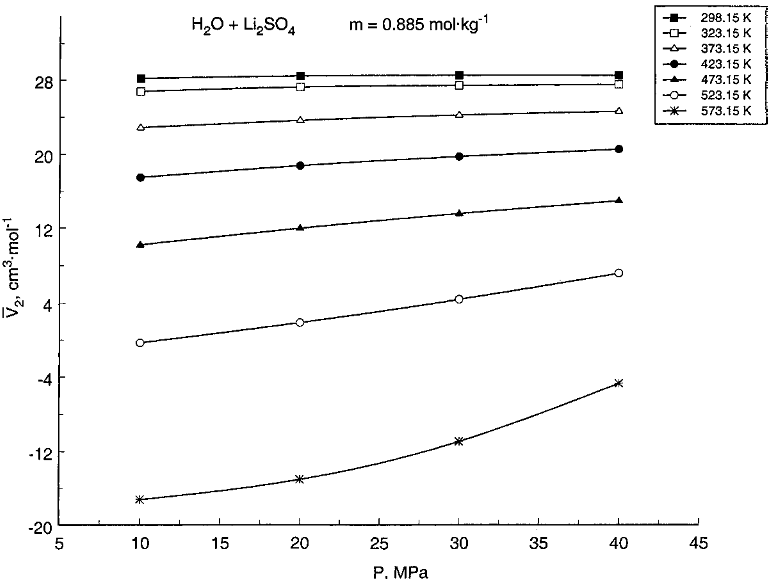

Fig. 15. Partial molar volume $\overline{V}_2$ of Li_2SO_4 as a function of pressure P at constant concentration of 0.885 mol · kg^{-1} for selected temperatures.

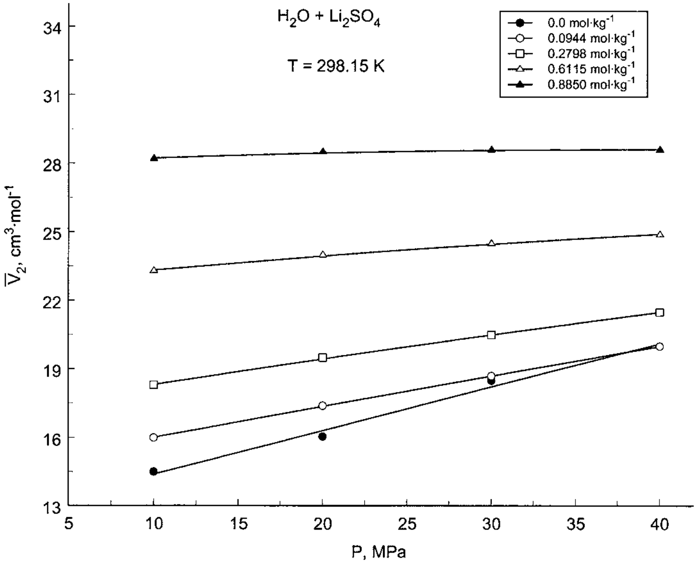

Fig. 16. Partial molar volume $\overline{V}_2$ of Li_2SO_4 as a function of pressure P at selected temperature of 298.15 for various compositions.

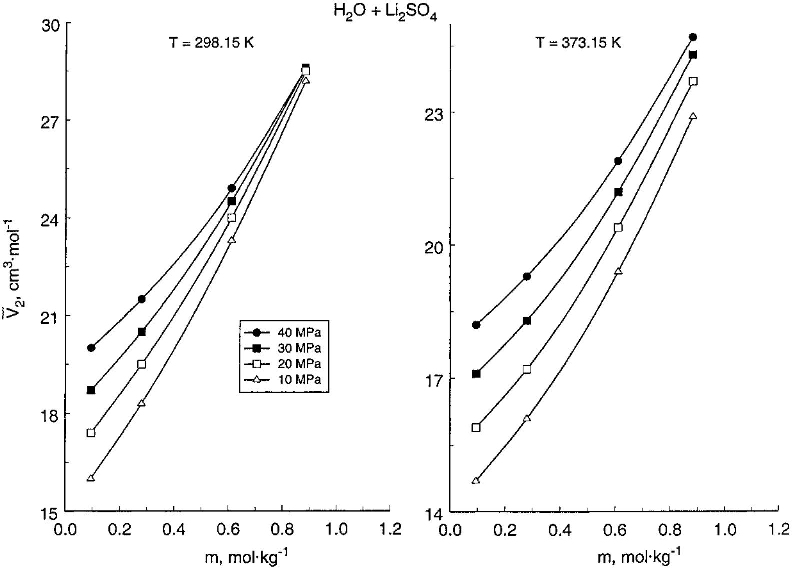

Fig. 17. Partial molar volume $\overline{V}_2$ of Li_2SO_4 as a function of concentration m at selected temperatures of 298.15 and 373.15 K for various pressures.

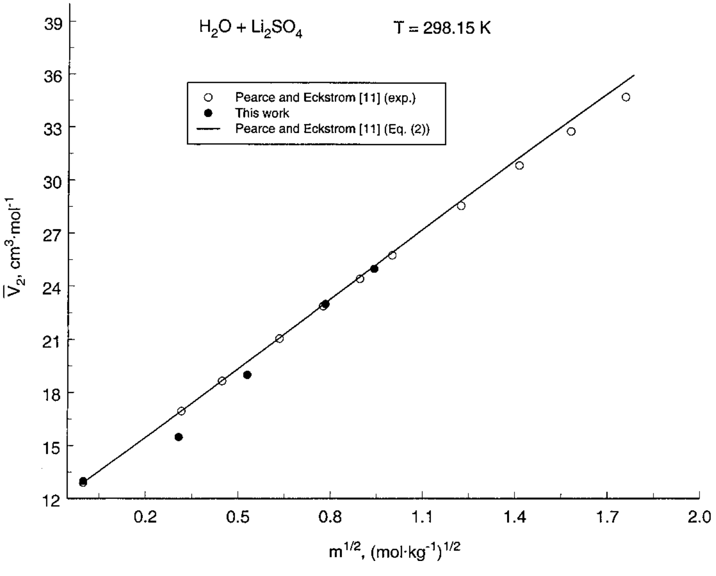

Fig. 18. Comparisons of present results for partial molar volume $\overline{V}_2$ against the square root of molality $m^{1/2}$ for Li_2SO_4 with values of Pearce and Eckstrom [11] at 298.15 K and atmospheric pressure.

pressure on the partial molar volumes is small, while at high temperatures ($T > 473$ K) and low concentrations ($m < 0.6\ \mathrm{mol \cdot kg^{-1}}$) the pressure effect is large. Figure 17 also shows that at low temperatures ($T < 373$ K) and high concentrations ($m \approx 0.9\ \mathrm{mol \cdot kg^{-1}}$) the partial molar volumes are almost independent of pressure. Comparisons between present partial molar volumes $\bar{V}_2$ and data reported by Pearce and Eckstrom [11] at atmospheric pressure and at 298.15 K are given in Fig. 18. As one can see from this figure, the agreement between the present data and the data reported by Pearce and Eckstrom [11] is good. Deviations are about 0.2 to 1% at high concentrations and are about 4 to 8% at low concentrations.

5. CONCLUSIONS

Accurate *PVTx* properties of four aqueous Li_2SO_4 solutions (0.0944, 0.2798, 0.6115, and $0.8850\ \mathrm{mol \cdot kg^{-1}}$ H_2O) were measured in the liquid phase with a constant-volume piezometer immersed in a precision liquid thermostat. The pressure range was from 3.9 to 40 MPa. Measurements were made for ten isotherms between 297 and 573 K. The total uncertainty of density, pressure, temperature, and concentration measurements were estimated to be less than 0.06%, 0.05%, 10 mK, and 0.014%, respectively. The accuracy of the method was confirmed by *PVT* measurements for pure water. The experimental values of density for pure water show excellent agreement with those calculated from the IAPWS formulation within the experimental uncertainties (AAD within 0.02 to 0.05%). Values of densities at saturation were determined by extrapolating experimental P-ρ data to the vapor-pressure curve at fixed temperature and composition using an interpolating equation. Values of the apparent ϕ_V and partial $\bar{V}_2$ molar volumes were derived using measured values of density for solutions and pure water. Values of partial molar volumes $\bar{V}_2^{\infty}$ at infinite dilution have been calculated using the Redlich–Mayer relation. The temperature, pressure, and concentration dependences of partial and apparent molar volumes were studied. A polynomial type of equation for specific volume was developed from the experimental data as a function of temperature, pressure, and composition by a least-squares method. The AAD between the measured densities and calculated values from this equation of state was 0.02%. Measured densities were also compared with data reported by other authors in the literature.

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