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Viscosity for Aqueous Li_2SO_4 Solutions at Temperatures from 298 to 575 K and at Pressures up to 30 MPa

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Viscosities of four aqueous Li_2SO_4 solutions [(0.10, 0.28, 0.56, and 0.885) mol·kg^{-1}] have been measured in the liquid phase with a capillary flow technique. Measurements were made at four isobars [(0.1, 10, 20, and 30) MPa]. The range of temperatures was from (298 to 575) K. The total uncertainties of viscosity, pressure, temperature, and concentration measurements were estimated to be less than 1.5%, 0.05%, 10 mK, and 0.014%, respectively. The reliability and accuracy of the experimental method were confirmed with measurements on pure water for three isobars [(10, 20, and 30) MPa] and at temperatures between (298 and 575) K. The experimental and calculated values from the IAPWS (International Association for the Properties of Water and Steam) formulation for the viscosity of pure water show excellent agreement within their experimental uncertainty (AAD is about 0.51%). A correlation equation for viscosity was obtained as a function of temperature, pressure, and composition by a least-squares method from the experimental data. The AAD between measured and calculated values from this correlation equation for the viscosity was 0.7% for pure water and 0.74% for the solutions. The measured values of viscosity at atmospheric pressure were compared with the data reported in the literature by other authors.

Introduction

Transport properties of water + salt solutions are required in many industrial applications such as design calculation, heat and mass transfers, and fluid flow, developments and utilization of geothermal and ocean thermal energy, and so forth. Viscosity data are required also for calculating flow, heat transfer, and mass transfer rates in various pieces of industrial equipment. To understand and control those processes which use electrolyte solutions, it is necessary to know their thermodynamic and transport properties. However, the lack of reliable data over temperature, pressure, and concentration ranges makes it necessary to estimate the missing properties by empirical and semiempirical methods. For engineering uses, reliable methods for estimation of the viscosity of solutions over wide ranges of concentration, temperature, and pressure would be extremely valuable. Therefore, experimental data for the viscosity 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 which will be capable of reproducing the experimental viscosity data and will aid in the development of a new and more reliable prediction technique for viscosity behavior at high temperatures, high pressures, and high concentrations. However, measurements of the viscosity of aqueous salt solutions have so far been limited to rather narrow ranges of temperature, pressure, and concentration with less than satisfactory accuracy. Previous viscosity measurements by Puchkov and Sargaev[1] for aqueous Li_2SO_4 solutions were performed at atmospheric pressure and temperatures from (298 to 573) K and at concentrations between (0.486 and 2.274) mol·kg^{-1}. Measurements were made with the falling body method. The uncertainty in viscosity measurement is about 3%. Maksimova et al.[2] reported viscosity data for $H_2O + Li_2SO_4$ solutions in the temperature range from (293 to 363) K for compositions between (0.1 and 2.87) mol·kg^{-1} at atmospheric pressure. Measurements were performed by means of a capillary method with an uncertainty of 1%. Cartón et al.[3] reported the viscosities for aqueous solutions of lithium sulfate over the concentration range from (0.4 to 3.2) mol·kg^{-1}. The temperature ranged from (278 to 338) K. Measurements were made with a Hoppler-type BH falling sphere viscometer, using two different sphere diameters. The uncertainty of the viscosity results is ±1%. These authors[4] also reported the viscosity of saturated solutions of $H_2O + Li_2SO_4$ over the temperature range from 283 to 313 K. There are no viscosity data for aqueous Li_2SO_4 solutions as a function of pressure. Thus, the main objective of this work is to provide reliable experimental viscosity data for aqueous Li_2SO_4 solutions at high temperatures (up to 575 K) and high pressures (up to 30 MPa). In this work we continue our previous studies dealing with the systematic measurement of viscosity of aqueous systems.[5,6]

Experimental Apparatus and Procedures

The (η,P,T,m) relationships of aqueous Li_2SO_4 solutions were measured using a capillary flow method. The apparatus details were described in our previous publications.[5−7] The apparatus used in the present viscosity measurements is schematically shown in Figure 1.

The working capillary (1) with an i.d. of 0.3 mm and a length of 216 mm was made from stainless steel (1X18H9T,

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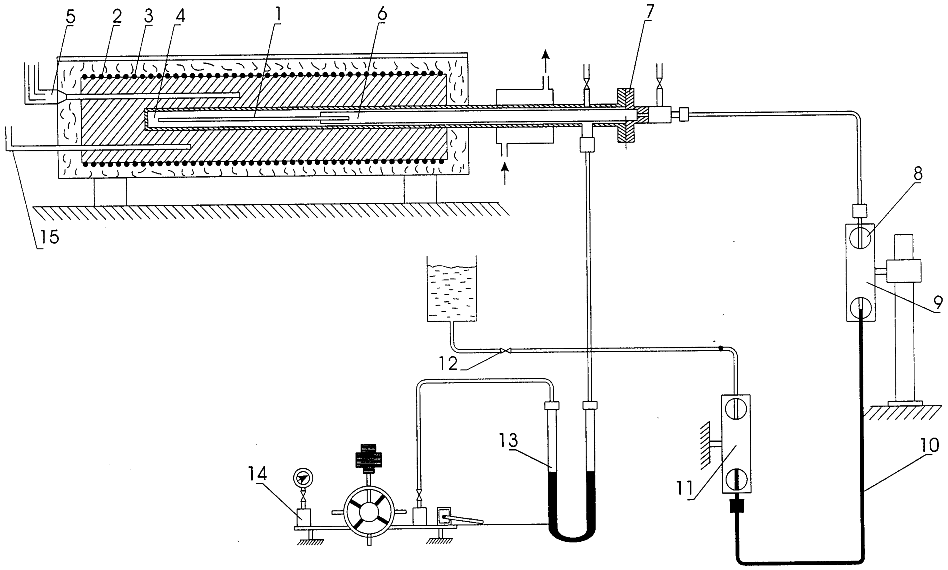

Figure 1. Schematic diagram of the experimental apparatus for measuring the viscosity of liquids and liquid mixtures at high temperatures and high pressures by the capillary method: 1, working capillary; 2, two electrical heaters; 3, solid (substantial) red copper block; 4, high-pressure autoclave; 5, thermocouple; 6, extension tube; 7, flange; 8, viewing windows; 9, movable cylinder; 10, flexible connecting tube; 11, unmovable (fixed) cylinder; 12, valve; 13, separating vessel; 14, dead-weight pressure gauge (MP-600); 15, PRT.

1 chrome-18 nickel-9 titanium). The capillary (1) is soldered to the extension tube (6). The fluid under study flows to a cold zone through the extension tube (6). The capillary (1) with the extension tube (6) was located in the high-temperature and high-pressure autoclave (4). The extension tube (6) was connected with a movable cylinder (9). The cylinder (9) was connected with an unmovable (fixed) cylinder (11) by means of a flexible connecting tube (10). Both cylinders (9 and 11) were supplied with identical expanded bottles. These bottles were used to stabilize the fluid efflux through the capillary. An unmovable cylinder was connected with a high-pressure autoclave (4). The input and output sections of the capillary had conical extensions. All parts of the experimental installation which have contact with the sample were made from stainless steel (1X18H10T). The Reynolds (*Re*) number occurring during all measurements was less than the critical values ($Re_c = 300$). The capillary tube (1) was filled with mercury. When the movable cylinder was moved vertically at constant speed, the fluid flowed through the capillary. Mercury flowed from the movable cylinder to the unmovable (fixed) cylinder and acted as a piston. Both cylinders were supplied with two viewing windows which were made with Plexiglass. The autoclave was placed in a solid red copper block. Two electrical heaters were wound around the surface of the copper block. The heaters were thermally insulated with asbestos covering-basalt cotton-wool and glass-wool. To create and measure the pressure, the autoclave was connected with a dead-weight pressure gauge (MP-600) by means of a separating vessel (13). The mercury was used as a separating liquid. The separating vessel was partly filled with mercury. The right arm of the separating vessel was connected with the sample filling unit. The rest of the volume of the separating vessel was filled with the fluid under study. The sample in the right arm of the separating vessel is located above the mercury. The left arm (bend) of the separating vessel was connected with a dead-weight pressure gauge (MP-600). The transformer oil in the left arm of the separating vessel is located above the mercury. Valve 12 was used to charge the viscosimeter with sample. The absolute values of the pressure in the autoclave were calculated as

$$P = P_m + P_b + \Delta h \rho_{mer} g + h_l \rho_l g + h_{oil} \rho_{oil} g \qquad (1)$$

where P_m is the pressure reading by the dead-weight pressure gauge (MP-600), P_b is the barometric pressure, Δh is the mercury level drop in the separating vessel, ρ_{mer} is the mercury density at room temperature and at experimental pressures, h_l is the height of the column of the fluid under study above the mercury, ρ_l is the fluid density under study at room temperature and experimental pressures, h_{oil} is the height of the column of oil below the mercury, ρ_{oil} is the oil density at room temperature and at experimental pressures, and g is the gravitational constant. The maximum uncertainty of the correction of mercury, sample, and oil levels was less than 5 mm. Therefore, the uncertainty in pressure measurements is 0.05%. The atmospheric pressure was measured with a standard barometer (aneroid) with an uncertainty of 1 mmHg.

Working Equation. The measurements of the viscosity are based on Poiseuille's law, which relates viscosity η to the rate v of fluid flow through a capillary tube

$$\eta = \frac{\pi R^4 \Delta P}{8 v L} \qquad (2)$$

where ΔP is the pressure drop ($\Delta P = P_{in} - P_{out}$, where P_{in} is the inlet pressure and P_{out} is the outlet pressure), R is the inner radius of the capillary, $v = dV/d\tau$ is the rate of fluid flow (V is the volume of the fluid flowing through the capillary for the time τ), L is the capillary tube length, and τ is the time of flow.

After corrections (which take into account the acceleration of a fluid at the inlet and outlet), the variation of the geometrical sizes of the capillary, and the mercury and sample densities at the experimental conditions were varied with temperature and pressure; the working equations for the viscosity can be written as

$$\eta = \frac{\pi R^4 \tau \Delta P}{8 L V}(1 + \alpha \Delta t)^3 - m\frac{\rho V}{8 \pi L \tau} \qquad (3)$$

where α is the linear expansion coefficient of the capillary material, Δt is the temperature difference between experimental temperature and room temperature, ρ is the density of fluid at capillary conditions, and $m = 1.12$ is a constant. The pressure drop is determined as

$$\Delta P = g\Delta H(\rho_{\mathrm{Hg}} - \rho) \tag{4}$$

where $\Delta H = \Delta H_0\rho_{0,\mathrm{Hg}}/\rho_{\mathrm{Hg}}$ is the average mercury level drop in the movable and unmovable cylinders at the beginning and ending of the measurements, ρ_{Hg} is the density of mercury at room temperature and experimental pressure, ρ is the density of the fluid under study, $\rho_{0,\mathrm{Hg}}$ is the density of mercury at room temperature and atmospheric pressure, and $\Delta H_0 = (H_1 - H_2)/\ln(H_1/H_2)$, where H_1 and H_2 are the mercury levels at the beginning and ending of the fluid flowing, respectively, at room temperature and atmospheric pressure. The mercury level in the cylinders was measured with a cathetometer (MK-8).

The volume V of the fluid flowing through a capillary tube at given temperature and pressure was determined as

$$V = V_{\mathrm{c}}\frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{exp}}} \tag{5}$$

where V_{c} is the volume of the unmovable (measuring) cylinder, ρ_{c} is the density of the fluid under study at room temperature and experimental pressure, and ρ_{exp} is the density of the fluid under study at the experimental conditions. The volume of the unmovable cylinder $V_{\mathrm{c}} = 1.2182\ \mathrm{cm}^3$ was determined using a weighing technique. By substituting eqs 4 and 5 into eq 3, the final working equation can be written as

$$\eta = A\tau\frac{\rho}{\rho_{\mathrm{c}}}\left(1 - \frac{\rho_{\mathrm{c}}}{\rho_{\mathrm{mer}}}\right)(1 + \alpha\Delta t)^3 - B\frac{\rho_{\mathrm{c}}}{\tau},$$
$$A = \frac{g\pi R^4\Delta H_0\rho_{0,\mathrm{mer}}}{8LV_{\mathrm{c}}}, \quad \text{and} \quad B = \frac{mV_{\mathrm{c}}}{8\pi L} \tag{6}$$

where the values of the parameters A and B can also be determined by means of a calibration technique.

Geometrical Sizes of the Capillary. Poiseuille's equation (eq 2) assumes steady laminar flow of the incompressible fluids in the capillary with smooth walls. This assumption is usually valid if the pressure drop ΔP is small. The inner surface of the capillary walls was perfectly polished with powders (MP-1 and MP-40) of successively smaller grain size (1 to 40 nm). For this method the correct determination of the geometrical size of the capillary is very important, because, for example, parameter A in eq 6 is proportional to R^4. The average capillary radius was measured using a weighing technique and by calibration (relative method) from the viscosity of a standard fluid (pure water) with well-known viscosity values (IAPWS[8] formulation). To determine the capillary radius R by a weighing method, the capillary was filled with mercury at room conditions. Then the mercury was discharged from the capillary and weighed with an analytical balance with an uncertainty of 0.1 mg. The empty capillary was weighed before and after each filling with mercury to make sure the entire amount of mercury was extracted from the capillary. The volume of the mercury was determined from the known density ρ_{Hg} of mercury and its mass m_{Hg} as

$$V_{\mathrm{Hg}} = \frac{m_{\mathrm{Hg}}}{\rho_{\mathrm{Hg}}} \tag{7}$$

Then the capillary radius can be calculated as

$$R = \sqrt{\frac{V_{\mathrm{Hg}}}{\pi l}} \tag{8}$$

where l is the total length of the capillary filled with mercury. The correction for capillary radius, due to the meniscus curvature (surface forces in a capillary), was made. The values of the capillary radius determined both with weighing and by calibration techniques are 0.15091 mm and 0.15048 mm, respectively. In this work we used the value 0.15091 mm. The length of the capillary l was measured with a microscope (UIM-21) with an uncertainty of ±0.001 mm. The final value of the capillary length is $l = 21.6534$ cm.

Flow Time Measurements. The measurements of the time of flow were made in the following way. Initially the movable cylinder was at a lower position. At this position the movable cylinder and its expanded vessel were filled with mercury. Then the movable cylinder was set up on the upper position. The pressure drop makes the mercury and the fluid flow: mercury, on flowing from the movable into the fixed (unmovable) cylinder, displaces the fluid there from via the capillary to the movable cylinder. When mercury passed by the marker on the lower viewing window, the stopwatch was started, and when mercury passed by the marker on the upper viewing window, the stopwatch was stopped. The time of fluid flowing through the capillary τ was measured with a stopwatch with an uncertainty of less than 0.1 s (0.5%). An electromagnetic device was used to start and stop the watch. All values of τ are averages of at least 5 to 10 measurements. At a temperature of 573 K, the minimal value of τ is 40 s.

Assessment of Uncertainties. Measurement uncertainties were associated with uncertainties that exist in the measured quantities contained in the working equation (eq 6) used to compute the viscosity from experimental data. The viscosity was obtained from the measured quantities R^4, ΔH_0, L, V_{c}, τ, ρ_{Hg}, ρ_{c}, T, P, and m. The accuracy of the viscosity measurements was assessed by analyzing the sensitivity of eq 6 to the experimental uncertainties of the measured quantities. The maximum relative root-mean-square deviations ($\delta\eta/\eta$) of viscosity measurements associated with R^4, ΔH_0, L, V_{c}, τ, ρ_{Hg}, ρ_{c}, T, P, and m measurements can be estimated from the equation

$$\frac{\delta\eta}{\eta} = \frac{1}{\eta}\sqrt{\left(\frac{\partial\eta}{\partial R^4}\right)^2 S_{R^4}{}^2 + \left(\frac{\partial\eta}{\partial\Delta H_0}\right)^2 S_{\Delta H_0}{}^2 + \ldots + \left(\frac{\partial\eta}{\partial m}\right)^2 S_m{}^2} \tag{9}$$

where $S_{R^4}{}^2$, $S_{\Delta H_0}{}^2$, ..., and $S_m{}^2$ are the root-mean-square deviations of R^4, ΔH_0, ..., and m, respectively. The systematic uncertainties of the viscosity measurements can be estimated from the equation

$$Q_\eta = \frac{1}{2}\left[\left(\frac{\partial^2\eta}{(\partial R^4)^2}\right)S_{R^4}{}^2 + \left(\frac{\partial^2\eta}{\partial(\Delta H_0)^2}\right)S_{\Delta H_0}{}^2 + \ldots + \left(\frac{\partial^2\eta}{\partial m^2}\right)S_m{}^2\right] \tag{10}$$

The mass of the mercury filling the capillary was determined as

$$G = \rho_{\mathrm{Hg}}V \tag{11}$$

where ρ_{Hg} is the mercury density at room conditions and V is the volume of mercury. The mercury in the capillary

Table 1. Experimental Viscosities, Pressures, Temperatures, and Concentrations of Water + Lithium Sulfate Solutions

		η/mPa·s		
m/mol·kg^{-1}	T/K	P/MPa = 10	P/MPa = 20	P/MPa = 30
0.1	298.35	0.9360	0.9361	0.9363
0.1	308.52	0.7647	0.7659	0.7682
0.1	313.67	0.6899	0.6927	0.6955
0.1	324.55	0.5660	0.5689	0.5716
0.1	331.86	0.5013	0.5035	0.5061
0.1	339.74	0.4463	0.4491	0.4520
0.1	347.05	0.4034	0.4061	0.4088
0.1	356.84	0.3566	0.3590	0.3621
0.1	365.04	0.3241	0.3265	0.3291
0.1	378.85	0.2812	0.2836	0.2862
0.1	389.16	0.2554	0.2577	0.2599
0.1	400.84	0.2306	0.2331	0.2360
0.1	410.95	0.2126	0.2150	0.2192
0.1	420.67	0.1980	0.2010	0.2031
0.1	431.72	0.1829	0.1849	0.1871
0.1	449.55	0.1630	0.1654	0.1680
0.1	459.89	0.1532	0.1553	0.1577
0.1	468.97	0.1454	0.1477	0.1500
0.1	473.25	0.1421	0.1467	0.1490
0.1	482.35	0.1352	0.1378	0.1404
0.1	490.35	0.1297	0.1322	0.1354
0.1	501.3	0.1228	0.1250	0.1275
0.1	510.93	0.1172	0.1199	0.1235
0.1	521.75	0.1115	0.1143	0.1170
0.1	530.53	0.1072	0.1097	0.1122
0.1	541.04	0.1024	0.1052	0.1087
0.1	547.35	0.0998	0.1027	0.1055
0.1	560.43	0.0948	0.0977	0.0999
0.1	569.15	0.0917	0.0945	0.0977
0.1	574.75	0.0897	0.0928	0.0957
0.280	298.25	0.1035	0.1035	0.1036
0.280	307.93	0.8517	0.8546	0.8570
0.280	312.27	0.7780	0.7812	0.7840
0.280	321.55	0.6508	0.6539	0.6569
0.280	329.44	0.5670	0.5700	0.5731
0.280	338.71	0.4914	0.4942	0.4979
0.280	343.35	0.4594	0.4623	0.4653
0.280	351.04	0.4150	0.4183	0.4215
0.280	362.74	0.3601	0.3630	0.3662
0.280	375.75	0.3127	0.3153	0.3181
0.280	383.06	0.2916	0.2942	0.2974
0.280	390.42	0.2721	0.2750	0.2784
0.280	399.95	0.2502	0.2528	0.2555
0.280	409.36	0.2314	0.2340	0.2369
0.280	417.42	0.2175	0.2199	0.2227
0.280	423.55	0.2080	0.2106	0.2133
0.280	430.73	0.1975	0.1999	0.2024
0.280	440.04	0.1858	0.1885	0.1910
0.280	449.35	0.1750	0.1776	0.1803
0.280	458.17	0.1658	0.1682	0.1704
0.280	462.13	0.1620	0.1649	0.1674
0.280	468.74	0.1558	0.1582	0.1612
0.280	475.55	0.1500	0.1528	0.1555
0.280	485.17	0.1424	0.1452	0.1475
0.280	495.14	0.1352	0.1377	0.1400
0.280	515.27	0.1224	0.1247	0.1271
0.280	525.95	0.1166	0.1196	0.1225
0.280	540.08	0.1096	0.1125	0.1156
0.280	560.12	0.1011	0.1040	0.1075
0.280	573.45	0.0962	0.0995	0.1025
0.560	298.15	1.1945	1.1945	1.1947
0.560	306.19	1.0130	1.0157	1.0179
0.560	311.24	0.9141	0.9168	0.9192
0.560	322.35	0.7352	0.7388	0.7422
0.560	331.27	0.6319	0.6354	0.6372
0.560	340.73	0.5456	0.5484	0.5514
0.560	349.55	0.4831	0.4864	0.4897
0.560	361.24	0.4168	0.4191	0.4222
0.560	372.13	0.3691	0.3721	0.3752
0.560	384.05	0.3274	0.3304	0.3335
0.560	390.35	0.3089	0.3124	0.3154
0.560	401.73	0.2797	0.2827	0.2855
0.560	411.05	0.2584	0.2613	0.2644
0.560	415.13	0.2502	0.2531	0.2564
0.560	418.18	0.2443	0.2469	0.2497
0.560	424.55	0.2330	0.2359	0.2390
0.560	431.83	0.2212	0.2231	0.2251
0.560	437.24	0.2130	0.2154	0.2185
0.560	446.35	0.2000	0.2030	0.2060
0.560	452.17	0.1927	0.1957	0.1984
0.560	459.12	0.1843	0.1878	0.1900
0.560	468.13	0.1750	0.1787	0.1813
0.560	479.55	0.1637	0.1668	0.1699
0.560	490.76	0.1538	0.1567	0.1595
0.560	510.12	0.1391	0.1420	0.1455
0.560	522.75	0.1308	0.1341	0.1373
0.560	532.85	0.1250	0.1281	0.1310
0.560	551.24	0.1151	0.1184	0.1214
0.560	560.72	0.1106	0.1132	0.1150
0.560	572.05	0.1056	0.1092	0.1126
0.885	298.45	1.4039	1.4042	1.4045
0.885	307.35	1.1698	1.1733	1.1764
0.885	314.12	1.0162	1.0194	1.0226
0.885	322.55	0.8649	0.8691	0.8731
0.885	330.24	0.7558	0.7598	0.7639
0.885	340.72	0.6414	0.6452	0.6494
0.885	348.95	0.5714	0.5753	0.5792
0.885	359.14	0.4999	0.5041	0.5080
0.885	369.72	0.4415	0.4452	0.4495
0.885	379.05	0.3993	0.4028	0.4065
0.885	384.27	0.3782	0.3820	0.3861
0.885	390.72	0.3550	0.3591	0.3633
0.885	397.35	0.3337	0.3371	0.3406
0.885	405.24	0.3115	0.3152	0.3194
0.885	415.76	0.2860	0.2901	0.2944
0.885	424.05	0.2687	0.2721	0.2756
0.885	430.26	0.2564	0.2601	0.2640
0.885	439.37	0.2402	0.2440	0.2479
0.885	449.15	0.2248	0.2283	0.2318
0.885	458.12	0.2109	0.2139	0.2179
0.885	466.79	0.2003	0.2038	0.2071
0.885	476.95	0.1885	0.1920	0.1956
0.885	485.13	0.1797	0.1835	0.1871
0.885	492.49	0.1725	0.1761	0.1790
0.885	500.43	0.1653	0.1688	0.1722
0.885	509.17	0.1580	0.1614	0.1649
0.885	517.75	0.1513	0.1550	0.1586
0.885	526.12	0.1453	0.1491	0.1527
0.885	538.24	0.1372	0.1408	0.1443
0.885	550.72	0.1297	0.1335	0.1372
0.885	560.18	0.1246	0.1282	0.1318
0.885	574.55	0.1176	0.1217	0.1255

has a cylindrical shape; therefore, the diameter of the capillary is

$$d^4 = \frac{4G}{\pi L \rho_{\mathrm{Hg}}} \tag{12}$$

The final uncertainty of the capillary length L measurements is ±0.005 mm: $L = (540.324 \pm 0.005)$ mm. The mass of the mercury column [$G = (0.5232 \pm 0.0001)$ g] was measured with an analytical balance with an uncertainty of ±0.1 mg. The density of the mercury at room temperature and atmospheric pressure is $\rho_{\mathrm{Hg}} = (13.5342 \pm 0.0001)$ g·cm^{-3}. Therefore, the value of d^4 is 82.989×10^{-8} cm^4. The final values of d^4 and the capillary radius R and their uncertainties are $(82.989 \pm 0.816) \times 10^{-8}$ cm^4 and 1.5091×10^{-2} cm, respectively. The relative root-mean-square deviation in the capillary diameter measurements $S_{\mathrm{d}}{}^4$ is $0.317\,57 \times 10^{-8}$ cm^4. At the maximum measured temperature (575 K), the value of the root-mean-square deviation in the viscosity measurements was $\delta\eta = 2 \times 10^{-5}$ g·cm^{-1}·c^{-1}. On the basis of the detailed analysis of all sources of uncertainties likely to affect the determination of viscosity

Table 2. Experimental Viscosities, Temperatures, and Concentrations of Water + Lithium Sulfate Solutions at Atmospheric Pressure

	η/mPa·s at the following values of m/mol·kg^{-1}			
T/K	0.1	0.28	0.56	0.885
298.15	0.939	1.037	1.195	1.411
303.15	0.862	0.951	1.096	1.294
313.15	0.707	0.778	0.891	1.054
323.15	0.578	0.630	0.722	0.853
333.15	0.490	0.532	0.610	0.718
343.15	0.429	0.462	0.530	0.624
348.15	0.401	0.433	0.495	0.582
358.15	0.355	0.381	0.437	0.511

Table 3. Experimental Viscosities, Pressures, and Temperatures of Pure Water

	η/mPa·s		
T/K	P/MPa = 10	P/MPa = 20	P/MPa = 30
297.88	0.8930	0.8933	0.8935
319.09	0.5912	0.5890	0.5978
340.98	0.4195	0.4232	0.4275
370.39	0.2947	0.2976	0.3012
408.77	0.2060	0.2107	0.2132
447.38	0.1576	0.1610	0.1637
483.66	0.1290	0.1314	0.1340
538.57	0.1005	0.1027	0.1058
574.32	0.0866	0.0903	0.0932

with the present apparatus, the combined maximum relative uncertainty $\delta\eta/\eta$ in measuring the viscosity was 1.5%. The relative systematic uncertainty Q_η/η was 0.001%. The experimental uncertainty in the concentration is estimated to be 0.014%. Chemically pure Li_2SO_4 and distilled water were used to prepare the solutions. The solutions at the desired concentration were prepared by the gravimetric method, and the concentration was checked using the density at 20 °C by means of pycnometers with reference data.

Results and Discussion

The viscosity measurements for aqueous Li_2SO_4 solutions have been made in the temperature range from (298 to 575) K at pressures up to 30 MPa for compositions from (0.1 to 0.885) mol·kg^{-1}. The experimental temperature, viscosity, pressure, and concentration values for the aqueous Li_2SO_4 solutions and pure water are presented in Tables 1−3. Some selected experimental results for H_2O + Li_2SO_4 solutions and pure water as an example of the present results are shown in Figures 2 and 3 as projections isopleth−isobar (constant concentration and constant pressure) and isobar−isotherm (constant pressure and constant temperature) in the $\eta-T$ and $\eta-m$ spaces together with values calculated from the IAPWS[8] formulation for pure water (m = 0) (see Figure 2). These are averaged values from the 5 to 10 measurements at the same temperature and the same pressure. The scattering of the experimental data is within ±0.3%. All experimental viscosity data were obtained as a function of temperature at four isobars [(0.1, 10, 20, and 30) MPa] and four compositions [(0.10, 0.28, 0.56, and 0.885) mol·kg^{-1}]. To check and confirm the accuracy of the method and procedure of the measurements, the viscosity measurements were made with pure water. Table 3 provides the present experimental viscosity data for pure water measured using the same experimental apparatus. These data were compared with values calculated from the IAPWS[8] formulation. The deviation plot is given in Figure 4. As one can see from the deviation plot (see Figure 4), the agreement between IAPWS[8] calculations and the present results along the isobars 10, 20, and 30 MPa is excellent. Deviation statistics for the present viscosity data for pure water and values calculated with IAPWS[8] formulation are as follows: AAD = 0.51%, bias = 0.59%, std dev = 0.52%, std err = 0.17%, and MaxDev = 1.07% (N = 27). The maximum deviation of 1.07% is found at the temperatures (319.09 and 408.77) K and at a pressure of 30 MPa. No systematic shape of the deviations was found for pure water (see Figure 4). This excellent

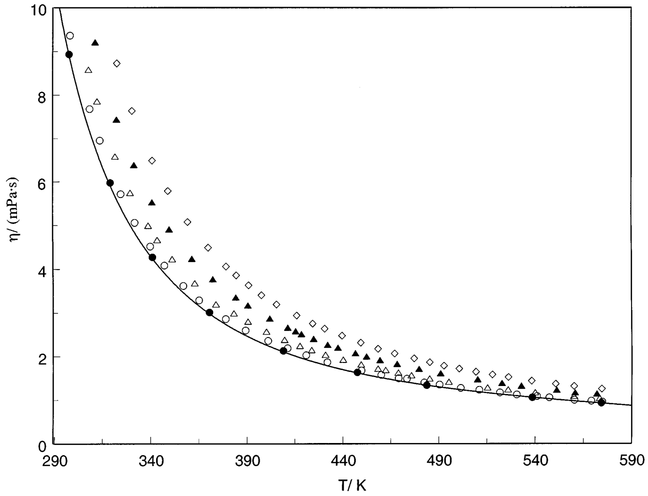

Figure 2. Measured values of viscosity of H_2O + Li_2SO_4 solutions as a function of temperature along the isobar 30 MPa for the various compositions together with values of viscosity for pure water calculated with the IAPWS[8] formulation: ●, pure water (this work); ○, 0.100 mol·kg^{-1}; △, 0.280 mol·kg^{-1}; ▲, 0.560 mol·kg^{-1}; ◇, 0.885 mol·kg^{-1}; —, calculated from the IAPWS[8] formulation.

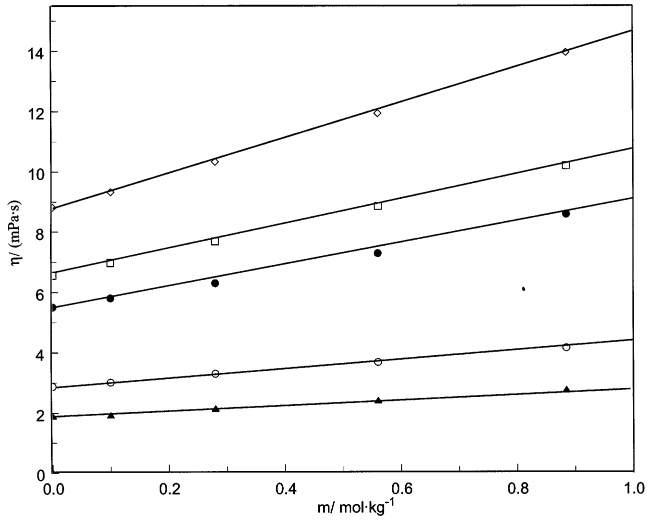

Figure 3. Measured values of viscosity of H_2O + Li_2SO_4 solutions as a function of concentration along various isotherms for a fixed pressure of 20 MPa: ◇, 298.15 K; □, 313.15 K; ●, 323.15 K; ○, 373.15 K; ▲, 423.15 K; —, calculated from eq 13.

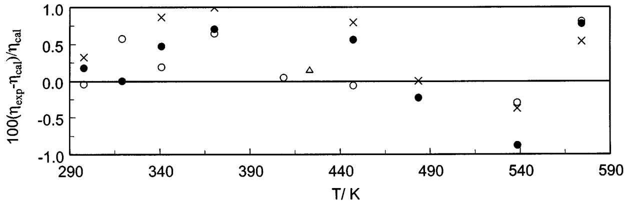

Figure 4. Percentage viscosity deviations, $\delta\eta = 100(\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}})/\eta_{\mathrm{cal}}$, of the experimental viscosities for pure water from the values calculated with the IAPWS[8] formulation: ○, 10 MPa; ●, 20 MPa; ×, 30 MPa.

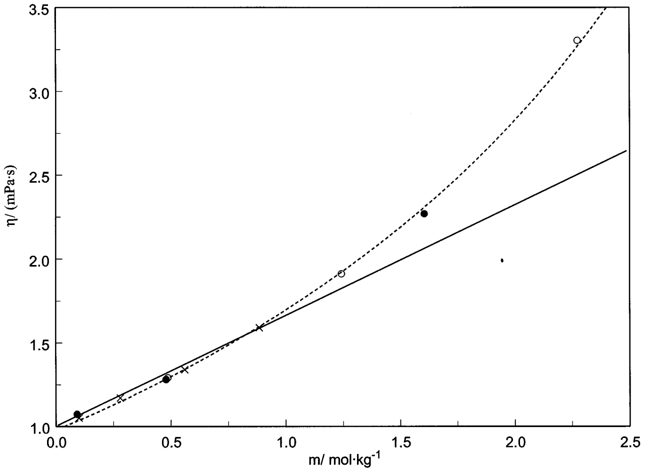

Figure 5. Comparison of the concentration dependence of the present viscosity results for $H_2O + Li_2SO_4$ solutions with the data reported in the literature at atmospheric pressure and at the selected temperature 298.15 K: ○, Phuchkov and Sargaev;[1] ●, Maksimova et al.;[2] × , this work (exp); —, this work (calculated from eq 13); - - -, calculated from correlation by Cartón et al.[3]

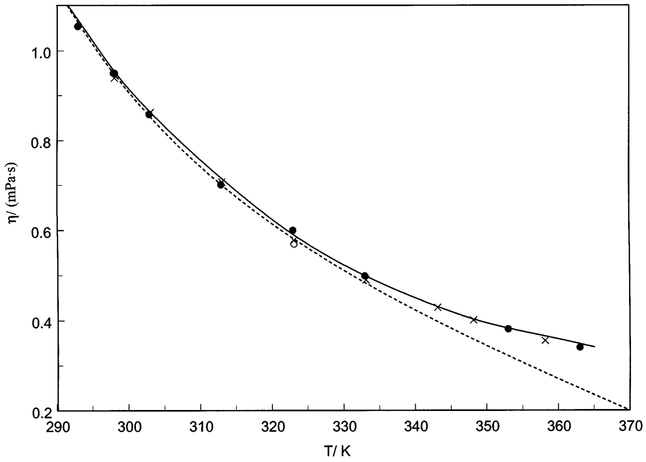

Figure 6. Comparison of the temperature dependence of the present viscosity results for $H_2O + Li_2SO_4$ solutions with the data reported in the literature at atmospheric pressure and the selected composition 0.1 mol·kg^{-1}: ○, Phuchkov and Sargaev;[1] ●, Maksimova et al.;[2] × , this work (exp); —, this work (calculated from eq 13); - - -, calculated from the correlation by Cartón et al.[3]

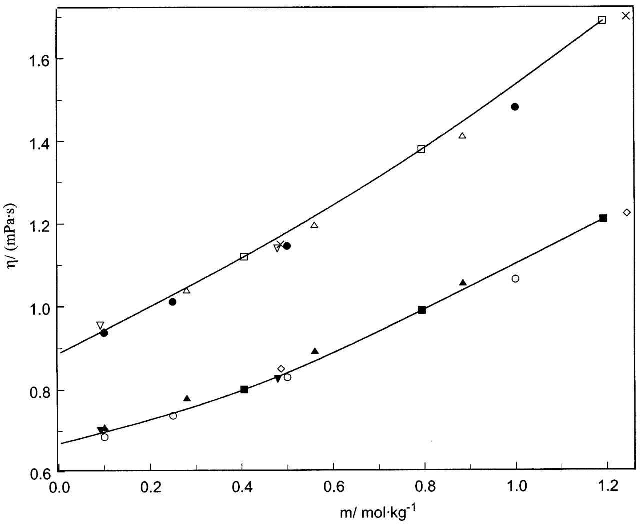

Figure 7. Comparison of the concentration dependence of the present viscosity results for $H_2O + Li_2SO_4$ solutions with the values reported by other authors from the literature and values calculated with the correlation equation reported by Cartón et al.[3] $T = 298.15$ K: ●, Bates and Baxter;[10] □, Cartón et al.;[3] × , Puchkov and Sargaev;[1] ▼, Maksimova et al.;[2] △, this work. $T = 313.15$ K: ○, Bates and Baxter;[10] ■, Cartón et al.;[3] ◇, Puchkov and Sargaev;[1] ▼, Maksimova et al.;[2] ▲, this work; —, Cartón et al.[3]

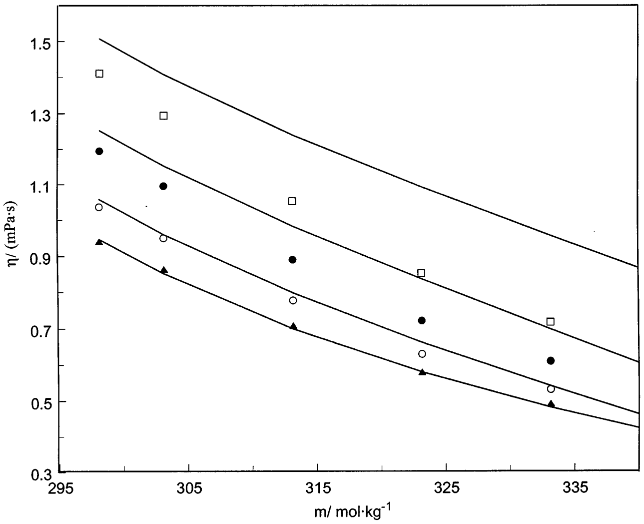

Figure 8. Comparison of the temperature dependence of the present viscosity results for $H_2O + Li_2SO_4$ solutions with the values calculated with the correlation equation reported by Cartón et al.:[3] ●, 0.56 mol·kg^{-1}; ○, 0.28 mol·kg^{-1}; ▲, 0.10 mol·kg^{-1}; □, 0.889 mol·kg^{-1}; —, Cartón et al.[3]

agreement between the present data and IAPWS[8] calculations for pure water confirms the reliability and high accuracy of the measurements for $H_2O + Li_2SO_4$ solutions and correct operation of the present instrument. This generally good agreement provides some confidence in the experimental values of Tables 1−3. The present results for the viscosity of $H_2O + Li_2SO_4$ solutions at atmospheric pressure (see Table 2) can be directly compared with experimental values reported in the literature. For example, Figures 5−7 contain the values of viscosity reported by Puchkov and Sargaev,[1] Maksimova et al.,[2] Cartón et al.,[3] and Bates and Baxter[10] together with the present results for selected isotherms [(298.15, 313.15, and 323.15) K] and for the isopleth of 0.1 mol·kg^{-1}. These figures include also the values of viscosity for $H_2O + Li_2SO_4$ solutions calculated with the correlation equation reported by Cartón et al.[3] As one can see from Figures 5−7, the agreement between various data sets is good (deviation is about 0.65%). As Figure 7 shows, the agreement between different data sets is good (within their experimental uncertainties). Figure 8 shows the comparison between the present viscosity results for $H_2O + Li_2SO_4$ solutions and the values of viscosities calculated from the correlation by Cartón et al.[3] As one can see from Figures 5−8, the agreement between the present data and calculated values with the correlation by Cartón et al.[3] for viscosity at low concentrations (up to 0.56 mol·kg^{-1}) is good (deviations within 1% for $m = 0.1$ mol·kg^{-1} and 2% for $m = 0.28$ mol·kg^{-1}) at temperatures up to 343 K, while at high concentrations the agreement is within 4 to 8%. Figures 5−8 illustrate that our data are consistent with literature values at atmospheric pressure. This agreement also confirms the reliability of the present measurements.

By extrapolation of $\eta - P$ curves to the vapor pressure point calculated with the correlation equation by Aseyev,[9] for each fixed temperature and composition, the values of viscosity at saturation were derived from the present

Table 4. Temperatures, Pressures, Densities, Compositions, and Viscosities at Saturation for Aqueous Li_2SO_4 Solutions

	m/mol·kg^{-1} = 0.1			m/mol·kg^{-1} = 0.28		
T_s/K	P_s/MPa	ρ_s/kg·m^{-3}	η/mPa·s	P_s/MPa	ρ_s/kg·m^{-3}	η/mPa·s
323.15	0.0123	996.54	0.5791	0.0123	1013.00	0.8510
373.15	0.1013	967.71	0.2964	0.1013	985.29	0.4221
423.15	0.4766	927.04	0.1858	0.4779	945.57	0.2673
473.15	1.5592	874.72	0.1397	1.5695	894.80	0.1899
523.15	3.9953	809.55	0.1092	4.0397	831.69	0.1453
573.15	8.6432	725.02	0.0899	8.7840	750.97	0.1181

Table 5. Parameters a_{ij}, b_{ij}, c_{ij}, and d_{ij} of Eq 13 for Pure Water

i	j	$10^{-2}a_{ij}$	$10b_{ij}$	$10^{-5}c_{ij}$	$10^{-7}d_{ij}$	P/MPa
0	0	−2.874 242	3.069 658	3.226 338	−1.163 827	10
0	0	−2.915 575	4.104 911	3.246 277	−1.188 281	20
0	0	−2.813 843	4.572 904	3.257 960	−1.206 117	30

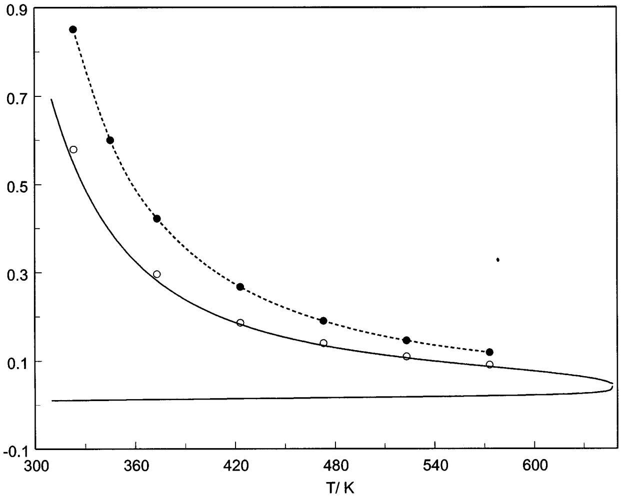

Figure 9. Derived values of viscosity of $H_2O + Li_2SO_4$ solutions and pure water at saturation as a function of temperature: ○, 0.100 mol·kg^{-1}; ●, 0.885 mol·kg^{-1}; —, pure water (calculated from the IAPWS^6 formulation); - - -, guide to the eye.

measurements. The results are presented in Table 4 and in Figure 9 together with values of viscosities at saturation for pure water calculated from the IAPWS^8 formulation. Because the experimental $\eta - P$ isotherms are almost linear, the extrapolation is reliable. The uncertainty in derived values of viscosity at saturation is less than 2%.

Correlation

The results of the (η,P,T,m) measurements for $H_2O + Li_2SO_4$ solutions were represented by the equation

$$\eta/\text{mPa·s} = A + B(t/°\text{C}) + \frac{C}{(t/°\text{C})} + \frac{D}{(t/°\text{C})^{2.5}} \quad (13)$$

where η is the viscosity of the solution in millipascal second and t is the temperature in degrees celcius. The pressure and concentration dependence of viscosity η has been taken into account through the A, B, C, and D parameters as a linear function of the pressure P (in MPa) and concentration m (in mol·kg^{-1})

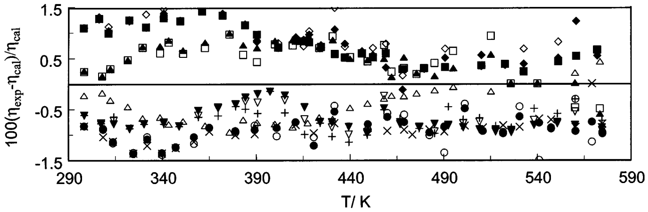

Figure 10. Percentage viscosity deviations, $\delta\eta = 100(\eta_{exp} - \eta_{cal})/\eta_{cal}$, of the experimental viscosities for $H_2O + Li_2SO_4$ solutions from the values calculated with eq 13. m = 0.100 mol·kg^{-1}: ×, 10 MPa; ●, 20 MPa; ○, 30 MPa. m = 0.280 mol·kg^{-1}: △, 10 MPa; ▲, 20 MPa; □, 30 MPa. m = 0.560 mol·kg^{-1}: ■, 10 MPa; ◆, 20 MPa; ◇, 30 MPa. m = 0.885 mol·kg^{-1}: ▼, 10 MPa; ▽, 20 MPa; +, 30 MPa.

$$A = \sum_{i=1}^{1}\sum_{j=0}^{1} a_{ij}P^i m^j, \quad B = \sum_{i=1}^{1}\sum_{j=0}^{1} b_{ij}P^i m^j$$

$$C = \sum_{i=1}^{1}\sum_{j=0}^{1} c_{ij}P^i m^j \quad D = \sum_{i=1}^{1}\sum_{j=0}^{1} d_{ij}P^i m^j \quad (14)$$

At high concentrations (m > 1 mol·kg^{-1}) nonlinear terms for the composition dependence in eq 14 have to be included. This equation previously (refs 5 and 6) was used to represent experimental viscosity data for aqueous $MgCl_2$ and $BaCl_2$ solutions. Equation 13 describes the viscosity of pure water and $H_2O + Li_2SO_4$ solutions with an accuracy which does not exceed their experimental uncertainty. The deviation plot between experimental and calculated values from eq 13 for the viscosity of $H_2O + Li_2SO_4$ solutions is given in Figure 10. The deviation statistics are as follows: AAD = 0.74%, bias = −0.16%, std dev = 0.8%, std err = 0.04%, MaxDev = 1.73%, and N = 366. Equation 13 also describes the viscosity of pure water with an accuracy of 0.70% in the temperature range from (293 to 575) K and at pressures up to 30 MPa. The coefficients of eq 13 have been exclusively determined in order to minimize the mean quadratic deviation of the fitted experimental viscosity values. The derived values of the coefficients a_{ij}, b_{ij}, c_{ij}, and d_{ij} in eq 14 for pure water and solution are given in Tables 5 and 6, respectively. Equation 13 is valid in the temperature range from (298 to 575) K, at pressures up to 30 MPa, and for concentrations up to 1 mol·kg^{-1}.

Conclusion

The viscosities of four aqueous Li_2SO_4 solutions [(0.10, 0.28, 0.56, and 0.885) mol·kg^{-1}] and pure water have been measured in the liquid phase with a capillary flow technique. Measurements for solutions were made at four isobars [(0.1, 10, 20, and 30) MPa]. The range of temperature was from (298 to 575) K. The total uncertainties of viscosity, pressure, temperature, and concentration measurements were estimated to be less than 1.5%, 0.05%, 10

Table 6. Parameters a_{ij}, b_{ij}, c_{ij}, and d_{ij} of Eq 13 for $H_2O + Li_2SO_4$ Solution

i	j	a_{ij}	b_{ij}	c_{ij}	d_{ij}
0	0	$-2.343\,145 \times 10^{2}$	$0.153\,986\,2 \times 10^{0}$	$3.084\,663 \times 10^{5}$	$-1.060\,490\,0 \times 10^{7}$
0	1	$-6.524\,586 \times 10^{2}$	$0.794\,480\,7 \times 10^{0}$	$2.273\,941 \times 10^{5}$	$0.768\,606\,5 \times 10^{7}$
1	0	$5.169\,833 \times 10^{-2}$	$5.687\,504 \times 10^{-4}$	$1.537\,555 \times 10^{1}$	$-0.211\,441\,3 \times 10^{4}$
1	1	$1.631\,061 \times 10^{-2}$	$3.050\,028 \times 10^{-4}$	$9.760\,994 \times 10^{0}$	$-1.272\,214\,0 \times 10^{3}$

mK, and 0.014%, respectively. The reliability and accuracy of the experimental method was confirmed with measurements on pure water for three isobars [(10, 20, and 30) MPa] and at temperatures between (298 and 575) K. The experimental and calculated values of viscosity for pure water from the IAPWS[8] formulation show excellent agreement within their experimental uncertainties (AAD within 0.51%). The values of viscosity at saturation were determined by extrapolating experimentally the $\eta - P$ curve to the vapor pressure along fixed temperature and composition using an interpolating equation. The correlation equation for viscosity was obtained as a function of temperature, pressure, and composition by a least-squares method from the experimental data. The AAD between measured and calculated values of viscosity for pure water and solution from this correlation equation were 0.7% and 0.74%, respectively. The measured viscosity values of solutions at atmospheric pressure were compared with the data reported in the literature by other authors. Good agreement (deviations within ±0.7%) is found between the present measurements and the data sets reported by other authors in the literature.

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Literature Cited

(1) Puchkov, L. V.; Sargaev, P. M. Viscosity of Aqueous Solutions of Li_2SO_4, Na_2SO_4, and K_2SO_4 at Temperatures up to 275 °C. *Russ. J. Appl. Chem.* **1974**, *1*, 96−109.

(2) Maksimova, I. N.; Pack, J. S.; Pravdin, N. N. *Electrolyte properties. A handbook;* Metallurgy Press: Moscow, 1987.

(3) Cartón, A.; Sobrón, F.; Bolado, S.; Gerbolés, J. I. Density, Viscosity, and Electrical Conductivity of Aqueous Solutions of Lithium Sulfate. *J. Chem. Eng. Data* **1995**, *40*, 987−991.

(4) Cartón, A.; Sobrón, F.; Bolado, S.; Gerbolés, J. I. Viscosity, Conductivity, and Refractive Index of Saturated Solutions of Lithium Sulfate + Water + Methanol. *J. Chem. Eng. Data* **1995**, *40*, 980−982.

(5) Azizov, N. D.; Akhundov, T. S. Viscosity of Aqueous $MgCl_2$ and $BaCl_2$ Solutions at Temperatures from (293 to 573) K. *Russ. J. Phys. Chem.* **1997**, *71*, 1955−1959.

(6) Azizov, N. D.; Akhundov, T. S. The Activation Parameters of the Viscous Flow in Aqueous Solutions of $MgCl_2$ and $BaCl_2$. *Russ. J. Phys. Chem.* **1999**, *73*, 1526−1528.

(7) Abdulagatov, I. M.; Rasulov, S. M. Viscosity of n-Pentane, n-Heptane and Their Mixtures Within the Temperature Range from 298 K up to Critical Points at the Saturation Vapor Pressure. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 148−154.

(8) Kestin, J.; Sengers, J. V.; Kamgar-Parsi, B.; Levelt Sengers, J. M. H. Thermophysical Properties of Fluid H_2O. *J. Phys. Chem. Ref. Data* **1984**, *13*, 175−189.

(9) Aseyev, G. G. *Electrolytes. Properties of Solutions. Methods for Calculation of Multicomponent Systems and Experimental Data on Thermal Conductivity and Surface Tension*; Begell-House Inc.: New York, 1998.

(10) Bates, S. J.; Baxter, W. P. Viscosity of Aqueous Solutions of Strong electrolytes. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill Book Co.: New York, 1929; Vol. V, pp 12−19.

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