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### Viscosities, densities, apparent and partial molar volumes of concentrated aqueous $\text{MgSO}_4$ solutions at high temperatures and high pressures

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## Viscosities, densities, apparent and partial molar volumes of concentrated aqueous MgSO<sub>4</sub> solutions at high temperatures and high pressures

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Density of two (2.224 and 2.535 mol kg<sup>-1</sup>) and viscosity of eight (0.085, 0.255, 0.437, 0.722, 0.923, 1.824, 2.291, and 2.623 mol kg<sup>-1</sup>) binary aqueous MgSO<sub>4</sub> solutions have been measured with a constant-volume piezometer immersed in a precision liquid thermostat and a capillary flow technique, respectively. Measurements were made at pressures up to 30 MPa. The range of temperature was 288 to 398 K for the density measurements and 298–448 K for the viscosity measurements. The total uncertainty of density, viscosity, pressure, temperature, and composition measurements were estimated to be <0.06%, 1.6%, 0.05%, 15 mK, and 0.02%, respectively. The effect of temperature, pressure, and concentration on density and viscosity of binary aqueous MgSO<sub>4</sub> solutions were studied. Apparent and partial molar volumes were derived using the measured values of density for the solutions. The viscosity data have been interpreted in terms of the extended Jones–Dole equation for strong electrolytes to accurately calculate the viscosity *A*- and *B*-coefficients as a function of temperature. The derived values of the viscosity *A*- and *B*-coefficients were compared with the results predicted by Falkenhagen–Dole theory of electrolyte solutions and calculated using the ionic *B*<sup>±</sup>-coefficient data. The hydrodynamic molar volumes *V*<sub>k</sub> were calculated using the present experimental viscosity data.

**Keywords:** Aqueous solution; Apparent molar volume; B-coefficient; Capillary viscometer; Constant volume piezometer; Density; Magnesium sulfate; Partial molar volume; Pressure; Viscosity; Water

### 1. Introduction

Volumetric (density, apparent and partial molar volumes) and transport (viscosity) properties of aqueous electrolyte solutions in a wide range of solute concentrations and solution temperatures and pressures are of fundamental importance for the

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understanding of various physico-chemical processes occurring in the chemical industry and in the natural environment, for example, separation process, crystallization, evaporation, desalination, waste water treatment, pollution control, oil recovery, heat and mass transfer, fluid flow, mineral transport and deposition, corrosion, etc. [1,2]. Knowledge of the volumetric and transport properties of sea water brines, which contain primarily NaCl, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>, is important in the development of an economic desalination process. MgSO<sub>4</sub> is one of the major components of sea salt and many natural waters. In order to understand the physical chemical properties of seawater and other natural waters, it is necessary to understand the ionic interactions occurring in multicomponent aqueous electrolyte solutions. The volumetric properties are needed also to calculate the pressure effects on the ionic activity coefficients, the osmotic coefficients, the mineral solubility, etc. in electrolyte solutions [3,4]. Apparent and partial molar volumes of electrolytes solutions are a very useful tool in understanding the structural interactions (ion–ion, ion–solvent, and solvent–solvent) occurring in solutions [3–6]. For example, the partial molar volumes of electrolytes at infinite dilution can be used to study ion–solvent and solvent–solvent interactions, while the concentration dependence of the apparent and partial molar volumes of electrolytes can be used to study ion–ion interactions. The partial molar volumes of electrolytes can also be used to calculate the effect of pressure on ionic equilibria for processes of engineering and oceanographic importance. The ion–solvent interaction in electrolyte solutions, which are a controlling factor in infinitely dilute solutions where ion–ion interactions are absent, are very important in developing a theory of electrolyte solutions. The limiting partial molar volume of a solute,  $\bar{V}_2^0$ , has proven to be a very useful value in examining the structural interactions in solutions [3,4,6]. In many applications (chemical engineering and geochemistry), these processes occur at high temperatures and high pressures. Surface and oceanic waters are near room temperature, similar aqueous solutions are present at high temperature and high pressure in deep geological formations. Aqueous systems also arise in steam-power generation, geothermal power plants, hydrothermal synthesis, seawater desalination processes, and other industrial operations at high temperatures and high pressures. The oceans and underground waters are the largest reservoirs of aqueous electrolyte solutions. Thus, there is great practical interest in the thermodynamic properties of aqueous salt solutions at these conditions.

Temperature and concentration dependences of viscosity of aqueous electrolytes solutions are crucial also for understanding ion–solvent interactions (long range electrostatic interactions) [7–14]. Precise viscosity data are needed to accurately calculate the physical meaning *A*- and *B*-coefficients in the limiting law of viscosity and extended Jones–Dole viscosity equation, respectively. The Jones–Dole viscosity *B*-coefficients are interest for the discussion of structure making and breaking ionic processes (solvation effects of cation and anion) [7–16]. The theory predicts only the values of the viscosity *A*-coefficient of electrolyte solutions at infinite dilution ( $m \rightarrow 0$ ) [17]. To accurately determine of the high degree viscosity coefficients (viscosity *B*- and *D*-coefficients, for example) in the extended Jones–Dole equation requires reliable viscosity data for electrolyte solutions at high concentration. Theoretical modeling [7–9,12,14,18–20] of the viscosity of H<sub>2</sub>O + MgSO<sub>4</sub> system will serve as an example for other ionic systems of 2:2 charge-type electrolytes.

## 2. Literature review

### 2.1. Volumetric measurements

A survey of the literature reveals the scarcity of reliable experimental volumetric and viscosity data at high temperatures and high pressures for  $MgSO_4(aq)$  solution. Most available experimental density data for  $MgSO_4(aq)$  cover a low temperature range (up to 323 K) and atmospheric pressure. Density measurements at high temperatures and high pressures are scarce. Few measurements [21–27] of density of the aqueous  $MgSO_4$  solutions have been performed at elevated pressure. Thus, one of the primary objectives of this work was to expand the existing volumetric database. The present density results considerably expand the temperature, pressure, and concentration ranges in which viscosities for aqueous  $MgSO_4$  solutions are available.

### 2.2. Viscosity measurements

Experimental viscosity data for  $MgSO_4(aq)$  solutions at high temperature and high pressure are also scarce. Most previous reported experimental data on the viscosity of  $MgSO_4(aq)$  cover near ambient temperatures (up to 333 K) and atmospheric pressure. A literature survey revealed that there are no viscosity data for  $MgSO_4(aq)$  solutions under pressure and at high temperatures, except the data reported by Lobkova and Pepinov [28]. Two techniques (capillary flow and Ostwald type viscometers) were used to measure viscosity of  $MgSO_4(aq)$ . Kaminsky [29] reported viscosity  $A$ -,  $B$ -, and  $D$ -coefficients for six values of temperature (288.15, 291.15, 298.15, 303.15, 308.15, and 315.5 K).

The main objective of the article is to provide new accurate experimental density and viscosity data for  $MgSO_4(aq)$  solutions at high temperatures (up to 448 K) and high pressures (up to 30 MPa) for compositions up to  $2.623 \text{ mol kg}^{-1}$  using a constant volume piezometer and capillary-flow techniques, respectively, which have been previously used for accurate measurements on other aqueous salt solutions at high temperatures and high pressures. This work is a part of a continuing program on the transport (thermal conductivity and viscosity) and volumetric (density, partial and apparent molar volumes) properties of electrolytes in aqueous solutions at high temperatures and high pressures. In our previous studies [30–61] we measured volumetric ( $PVT_x$ ) and transport properties (thermal conductivity and viscosity) of 45 aqueous salt solutions at high temperatures (up to 573.15 K) and high pressures (up to 100 MPa) using constant volume, coaxial cylinders, parallel-plate, and capillary-flow techniques.

## 3. Experimental

### 3.1. $PVT_x$ measurements

The  $PVT_x$  relationship of aqueous  $MgSO_4$  solutions was measured by a constant-volume method. The apparatus and experimental procedure described previously [21–23,30–39,59,60] was used without modification. Only a brief discussion will be given here. The main part of the apparatus consisted of a piezometer, separating

U-shape capillary tube with mercury, a liquid thermostat, heaters, a temperature regulator, and a  $10\ \Omega$  platinum resistance thermometer (PRT-10). The volume of the piezometer at 293 K and atmospheric pressure was  $V_{293} = 95.545 \pm 0.02\ \text{cm}^3$ . The value of  $V_{293}$  was previously calibrated from the known density of a standard fluid (pure water) with well-known  $PVT$  values (IAPWS standard) [62]. The piezometer was located vertically in the liquid thermostat with volume of  $0.02\ \text{m}^3$ . Three heaters were used to regulate the thermostat temperature. The thermostat temperature was controlled automatically to within 0.02 K by means of the high-precision temperature regulator. The temperature of the thermostat liquid was measured with PRT-10. The sample temperature was detected with a precision of  $\pm 15\ \text{mK}$ . The pressure of the solution was measured with a dead-weight pressure gauge (MP-600) with an uncertainty of 0.015% (maximum uncertainty was 0.05%).

The densities of the sample ( $\rho_i$ ) at a given temperature  $T$  and pressure  $P$  was obtained from measurements of the mass of the solution and volume of the piezometer as  $\rho_i = M_i/V_{PT}$ , where  $M_i$  ( $i = 1, N$ ) is the current mass of the sample in piezometer,  $N$  is the number of extractions,  $V_{PT} = V_{293} + \Delta V_T + \Delta V_P$  is the volume of the piezometer at a given temperature  $T$  and pressure  $P$ .

The temperature dependence of the piezometer volume  $\Delta V_T$  at fixed pressure was calculated by using the thermal expansion coefficient of the piezometer material. The pressure dependence of the piezometer volume  $\Delta V_P$  was calculated from the Love formula [63] for the cylinder. The uncertainty in piezometer volume  $V_{PT}$  at given temperature and pressure is  $< 0.038\%$ . The uncertainty of the mass  $m$  of solution can be estimated to be 0.007%. The experimental uncertainty in the concentration is estimated to be 0.02%. The total experimental uncertainty in density determination was 0.06%.

To test the apparatus and procedures, the density of pure water was measured at three selected isobars of 0.1, 5.55, and 29 MPa and compared with values calculated from IAPWS formulation [62]. The agreement between the IAPWS standard [62] and the present results along these isobars is 0.05, 0.048, and 0.040%, respectively. This excellent agreement confirms the reliability and accuracy of the present measurements for  $\text{MgSO}_4(\text{aq})$  solutions and corrects operation of the  $PVT$  apparatus.

### 3.2. Viscosity measurements

The apparatus and procedures used for the viscosity measurements of the  $\text{H}_2\text{O} + \text{MgSO}_4$  solutions has been described in detail in previous papers [21,32,35,40,44–46] and were used without modification. Only brief and essential information will be given here. The measurements were made using a capillary flow method which gives an uncertainty of 1.5% for the viscosity. The main parts of the apparatus consisted of a working capillary with an extension tube, a high temperature and high pressure autoclave, movable and unmovable cylinders, electrical heaters, and solid red copper block. The capillary together with the extension tube was located in the high temperature and high pressure autoclave. To generate and measure the pressure, the autoclave was connected with a dead-weight pressure gauge (MP-600) by means of separating vessel. The maximum uncertainty in pressure measurements was 0.05%.

The working equation for this method was derived from Poiseuille's law with corrections for the temperature effects on the capillary sizes and mercury and sample

densities at the experimental conditions ( $P, T$ ), and entrance effects (acceleration of a fluid at the inlet and outlet) on the fluid [32]. The time of fluid flowing through the capillary  $\tau$  was measured with a stop-watch with an uncertainty of  $<0.1$  s (0.5%). An electromagnetic device was used to start and stop the watch.

The accuracy of the viscosity measurements was assessed by analyzing the sensitivity of the working equation to the experimental uncertainties of the measured quantities [32]. At the maximum measured temperature (448 K), the value of the root-mean-square deviations in the viscosity measurements was  $\delta\eta = 2 \times 10^{-5} \text{ g cm}^{-1} \text{ s}^{-1}$ . Based on the detailed analysis of all sources of uncertainties likely to affect the determination of viscosity with the present apparatus, the combined maximum relative uncertainty  $\delta\eta/\eta$  in measuring the viscosity was 1.5% [32]. The Reynolds (Re) number occurring during all measurements was less than the critical values ( $\text{Re}_c = 300$ ).

As a check of the method and procedure of the measurements, the viscosity of pure water was measured from 299.76 to 574.54 K at three selected isobars (0.1, 10, and 30) MPa. These data were compared with values calculated from the IAPWS formulation [64]. The agreement between IAPWS [64] calculations and the present results along the isobars (0.1, 10, and 30) MPa is excellent (AAD = 0.52%, Bias = -0.13%, Std dev. = 0.61%, Std err. = 0.13%, and Max. dev. = 1.13%,  $N = 24$ ). This excellent agreement between the present data and IAPWS [64] calculations for pure water confirms the reliability and high accuracy of the measurements for  $\text{MgSO}_4(\text{aq})$  solutions and correct operation of the present instrument.

The  $\text{MgSO}_4(\text{aq})$  solutions were prepared from chemically pure  $\text{MgSO}_4$  (>99.5 mass %) and doubly distilled water.  $\text{MgSO}_4$  was carefully dried by heating under vacuum at progressively increasing temperatures up to 200°C. The solutions were prepared gravimetrically using an analytical balance having a precision of  $\pm 5 \times 10^{-8}$  kg. The solutions at the desired composition were prepared by mass. The composition was checked by comparison of the density of solution at 298.15 K and 0.1 MPa with reference data.

## 4. Results and discussion

### 4.1. Density, apparent and partial molar volumes

Measurements of the  $PVT_x$  relationship of the aqueous  $\text{MgSO}_4$  solutions were carried out at two compositions (2.224 and 2.535 mol  $\text{kg}^{-1}$ ) for temperatures between 288 and 398 K. The pressure ranged from 0.1 to 30 MPa. The experimental results are presented in tables 1 and 2. These tables also include apparent molar volumes, derived as discussed further. Some selected experimental results are shown in figures 1–3 as projections in the  $\rho$ - $m$ ,  $\rho$ - $P$ , and  $\rho$ - $T$  planes, together with values reported by other researchers.

The present results for density of  $\text{MgSO}_4(\text{aq})$  solutions at atmospheric pressure were compared with the experimental values reported by other authors and with the various correlation equations [65–67] (see figures 1 and 2). Figure 1 compares our density measurements at atmospheric pressure and temperature of 298.15 with the values calculated from correlation reported by Novotný and Söhnel [66] and Surdo *et al.* [67] and the measurements reported by various researchers. The values of density calculated with correlation by Novotný and Söhnel [66] and Surdo *et al.* [67] are deviate from



Table 1. Experimental values of density, temperature, concentration, and apparent molar volume of  $\text{MgSO}_4(\text{aq})$  solutions at atmospheric pressure.

$T$ (K)	$\rho$ ( $\text{kg m}^{-3}$ )	$\phi_V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$T$ (K)	$\rho$ ( $\text{kg m}^{-3}$ )	$\phi_V$ ( $\text{cm}^3 \text{mol}^{-1}$ )
$m = 0.084$ ( $\text{mol kg}^{-1}$ )			$m = 0.261$ ( $\text{mol kg}^{-1}$ )		
291.15	1008.8	-0.94	308.60	1024.48	2.38
323.15	998.05	-0.17	323.15	1018.30	2.61
348.15	984.50	2.68	348.15	1004.83	2.57
$m = 0.469$ ( $\text{mol kg}^{-1}$ )			$m = 0.841$ ( $\text{mol kg}^{-1}$ )		
303.03	1050.08	3.72	303.15	1090.98	6.04
323.15	1041.45	4.93	323.15	1082.67	6.13
348.15	1028.40	3.82	348.15	1069.05	5.26
$m = 2.224$ ( $\text{mol kg}^{-1}$ )			$m = 2.535$ ( $\text{mol kg}^{-1}$ )		
288.57	1235.34	11.36	288.57	1263.36	12.67
297.70	1231.87	11.81	297.70	1259.83	13.07
310.15	1226.56	12.08	310.15	1254.38	13.32
324.35	1219.96	11.92	324.35	1247.46	13.25
340.25	1211.60	11.38	340.25	1238.93	12.80
358.95	1200.88	10.22	358.95	1228.61	11.58

the present data within 0.02–0.15% at concentration of  $2.224 \text{ mol kg}^{-1}$  and at temperatures between 288 and 359 K. Excellent agreement within 0.002–0.080% is found between the present results and the data of Perry and Green [68] and Isono [69,70] at temperatures from 288 to 324 K and at atmospheric pressure. Good agreement within 0.05–0.50% is observed between the data reported by Ezrokhi [71] and the present values of density at temperatures up to 324 K and at 0.1 MPa. The AAD (average absolute deviations) between the present measurements and the data reported by other authors at temperatures 298.15 and 323.15 K and at 0.1 MPa is within 0.002–0.066%, except the data reported by Ezrokhi [71] at temperatures 298.15 and 323.15 K. The differences between the reported data (ours and those in the literature) are within their claimed uncertainties.

The data reported by Pepinov *et al.* [24,25] and Azizov and Akhundov [22] shows excellent agreement within 0.07% with the present measurements at pressure of 20 MPa and at temperatures of 323.15, 373.15, and 398.15 K. Extrapolation of our density results to zero concentration are in good agreement with pure water data (IAPWS standards) [62], deviation within 0.03%. Figure 2 demonstrate the pressure dependence of the present and our previous measurements (Azizov and Akhundov [22]) at constant concentration of  $0.084 \text{ mol kg}^{-1}$  and at 373.15 K. The agreement between various data sets [22,24–26] is excellent (deviations within 0.05%).

The present measured densities together with our previous density measurements results [22] were used to calculate apparent molar volumes  $\phi_V$  for each solution. The apparent molar volumes  $\phi_V$  were calculated from measured solution densities  $\rho_{\text{sol}}$  and pure water densities  $\rho_0$  by the following relationship

$$\phi_V = \frac{1000(\rho_0 - \rho_{\text{sol}})}{m\rho_{\text{sol}}\rho_0} + \frac{M}{\rho_{\text{sol}}}, \quad (1)$$

where  $M$  is the molecular weight of the salt,  $\rho_{\text{sol}}$  and  $\rho_0$  are the densities of solution and pure water, respectively, and  $m$  is the solution molality ( $\text{mol kg}^{-1}$ ). The derived values

Table 2. Experimental values of pressure, density, temperature, concentration, and apparent molar volume of  $MgSO_4(aq)$  solutions at high pressures.

$P$ (MPa)	$\rho$ ( $kg\ m^{-3}$ )	$\phi_V$ ( $cm^3\ mol^{-1}$ )	$P$ (MPa)	$\rho$ ( $kg\ m^{-3}$ )	$\phi_V$ ( $cm^3\ mol^{-1}$ )
$m = 2.5350$ ( $mol\ kg^{-1}$ )					
$T = 314.98$ K			$T = 348.13$ K		
2.157	1252.7	13.50	1.549	1235.1	12.47
8.159	1254.5	13.95	9.807	1237.7	13.09
15.69	1256.7	14.51	14.22	1238.9	13.47
25.91	1259.9	15.15	23.81	1241.9	14.13
29.80	1261.0	15.43	30.02	1243.8	14.54
$T = 373.22$ K			$T = 398.15$ K		
3.020	1220.3	10.85	5.810	1203.8	8.860
6.610	1221.6	11.11	11.10	1205.6	9.380
14.38	1224.1	11.76	21.70	1209.0	10.44
21.08	1226.1	12.34	29.40	1211.5	11.14
24.71	1227.4	12.57	–	–	–
29.80	1229.0	12.95	–	–	–
$m = 2.2242$ ( $mol\ kg^{-1}$ )					
$T = 299.67$ K			$T = 323.05$ K		
2.040	1231.7	12.04	2.197	1221.5	12.02
7.179	1233.3	12.47	10.12	1224.0	12.63
16.83	1236.3	13.24	19.85	1227.0	13.36
22.55	1238.2	13.63	26.30	1229.1	13.77
29.60	1240.3	14.18	30.50	1230.3	14.10
$T = 348.23$ K			$T = 373.24$ K		
2.118	1208.2	10.96	2.275	1192.8	9.18
8.002	1210.4	11.32	7.355	1194.5	9.64
14.71	1212.2	11.98	12.87	1196.4	10.11
25.30	1215.7	12.71	20.42	1198.9	10.74
30.02	1217.1	13.08	29.82	1201.7	11.61
$T = 398.19$ K					
2.452	1175.3	6.73	–	–	–
7.355	1177.2	7.19	–	–	–
12.08	1178.9	7.67	–	–	–
19.85	1181.7	8.42	–	–	–
26.22	1183.8	9.07	–	–	–

of  $\phi_V$  are given in tables 1 and 2 and are shown in figure 4 for the two selected isotherms (298.15 and 323.15 K) as an example of the present results. The uncertainty in derived values of  $\phi_V$  depends strongly on  $m$ ,  $T$ ,  $\rho_{sol}$  and  $\rho_0$  [31]. The accuracy of the derived values of  $\phi_V$  was assessed by analyzing the sensitivity of equation (1) to the experimental uncertainties of the measured quantities  $m$ ,  $T$ ,  $\rho_{sol}$ ,  $\rho_0$  (see Abdulagatov and Azizov [31]). The maximum relative uncertainty in the apparent molar volume determination is about 2% at low concentrations ( $m < 0.5\ mol\ kg^{-1}$ ) and 0.2%–0.5% at high concentrations [31] at low temperatures ( $< 323$  K). The uncertainty increases with temperature and the corresponding values for the same concentration ranges at 448 K are 3% and 1.0%, respectively. Figure 4 include also the data reported by other authors in the literature and calculated with various correlations. As figure 4 shows, the apparent molar volume  $\phi_V$  rapidly increases (changes by factor 2) with concentration  $m$  between 0 and  $0.5\ mol\ kg^{-1}$ . Good agreement within  $\pm 0.6\%$  is found with the



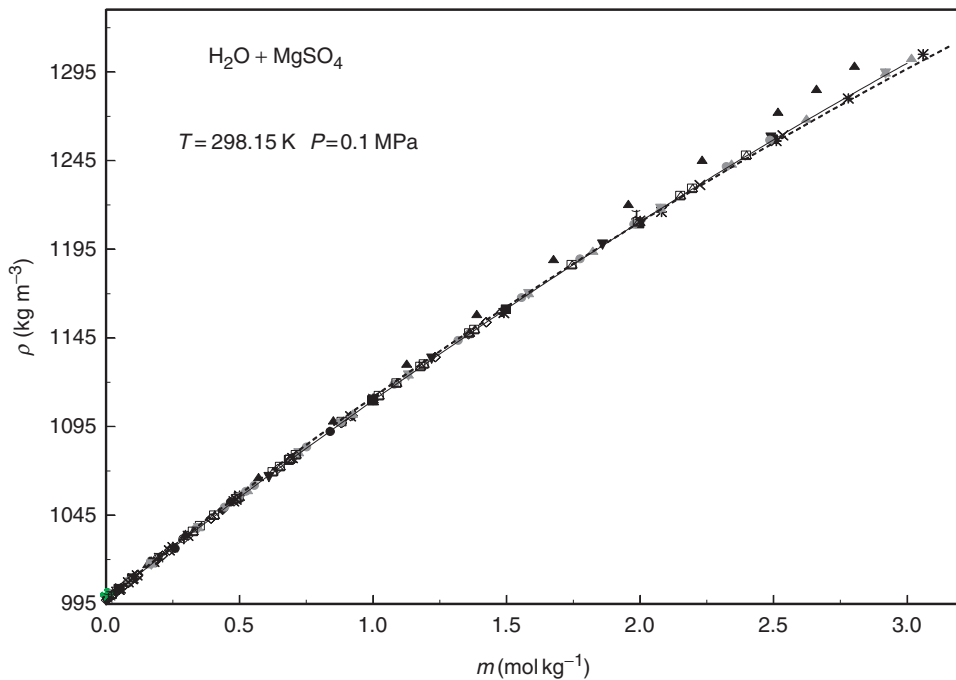


Figure 1. Density  $\rho$  of  $\text{MgSO}_4(\text{aq})$  solution as a function of composition  $m$  at atmospheric pressure for the selected isotherm of 298.15 K. (●), Azizov and Akhundov [21–23]; (○), Fabuss *et al.* [75,76]; (■), Isono [69,70]; (□), Korosi and Fabuss [92]; (Δ), Phutela and Pitzer [26]; (×), this work; (▲), Zaytseva and Ivanov [93]; (◆), Pepinov *et al.* [24,25]; (▼), Herz [95]; (▽), Kaminsky [29]; (◇), Chen *et al.* [27,74]; (⊞), Asmus [108,109]; (+), Perry and Green [68]; (\*), Ezrokhi [71]; (—), Surdo *et al.* [67]; (---), Novotný and Söhnel [66].

correlation equation of Surdo *et al.* [67] at high concentrations ( $m > 0.5 \text{ mol kg}^{-1}$ ) and  $\pm 10\%$  at low concentrations ( $m < 0.5 \text{ mol kg}^{-1}$ ). Acceptable agreement within  $\pm 7.0\%$  is found between the present apparent molar volumes and the data reported by Millero and Knox [72] and Emara and Farid [73] at low concentrations. The data reported by Chen *et al.* [27,74] and Fabus *et al.* [75,76] are higher (12%) than the present results at concentrations below  $0.5 \text{ mol kg}^{-1}$ .

The apparent molar volume  $\phi_V$  increases with temperature, passes through a maximum near 330 K, and then decreases at higher temperatures. At temperatures  $> 370 \text{ K}$   $\phi_V$  becomes negative. The dependence of  $\phi_V$  on temperature increases significantly above 370 K. The pressure dependence of  $\phi_V$  is almost linear. In the limit of infinite dilution, the apparent molar volume of the solute  $\phi_V(P, T, m)$  becomes equal to the partial molar volume ( $\lim_{m \rightarrow 0} \phi_V = \bar{V}_2^0$ ). The standard procedure for calculating  $\bar{V}_2^0$  is extrapolation of  $\phi_V$  to infinite dilution, based on the extended Redlich–Mayer relation [77–82]. In order to calculate values of  $\phi_V^0$  ( $\phi_V$  at infinite dilution,  $m \rightarrow 0$ ) or  $\bar{V}_2^0$  the data of the present study and those reported by other authors [26,27,67,72,73] were fitted, each isotherms separately to

$$\phi_V = \bar{V}_2^0 + A_V \sqrt{m} + bm + dm^{3/2}, \quad (2)$$

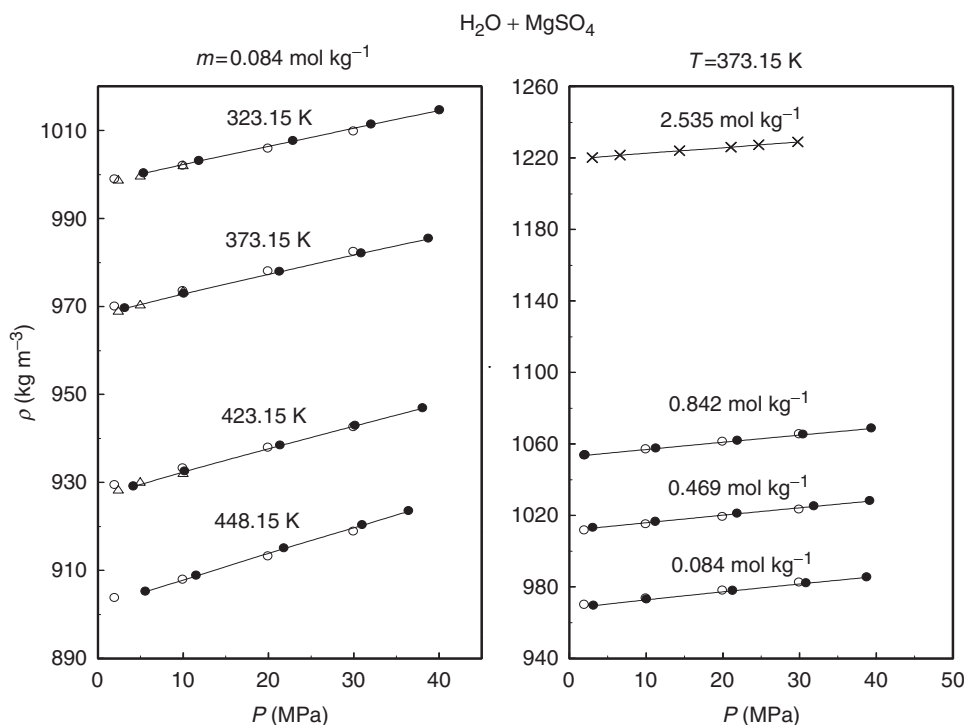


Figure 2. Density  $\rho$  of  $MgSO_4(aq)$  solution as a function of pressure  $P$  at selected temperatures and various constant concentrations. (○), Pepinov *et al.* [24,25]; (●), Azizov and Akhundov [21–23]; (×), This work; (Δ), Phutela and Pitzer [26].

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

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

$e$  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 molecule of dissociating salt,  $Z_i$  is the charge on species  $i$ ,  $m$  is the molality,  $\beta$  is the compressibility of the solvent,  $b$  and  $d$  are the empirical coefficients which take into account all deviations from the limiting law. The limiting slope  $A_V$  derived from the Debye–Hückel theory depends only on temperature and the physical properties (dielectric constant  $D$  and compressibility  $\beta$ ) of the solvent (pure water IAPWS standards [62,83]). As a rule, this relationship is applied at fixed pressure  $P$  and temperature  $T$ . The infinite-dilution values of  $\phi_V$  ( $\bar{V}_2^0$ ) are obtained by extrapolating (2) to zero concentration ( $m \rightarrow 0$ ). Our values for  $\phi_V$  at high concentration together with the data by other authors at low concentrations were fitted to the equation (2) for the fixed temperature of 298.15, 323.15, and 373.15 K and 0.1 MPa. The derived values of  $\bar{V}_2^0$  are presented in figure 5 as a function of temperature at 0.1 MPa. The results for 298.15 K are  $\bar{V}_2^0 = -7.285 \pm 0.12 \text{ cm}^3 \text{ mol}^{-1}$ ,  $A_V = 1.865 \text{ cm}^3 \text{ mol}^{-3/2} \text{ kg}^{1/2}$ ,  $b = -37.8612 \text{ cm}^3 \text{ mol}^{-2} \text{ kg}$ ,  $d = 16.9088 \text{ cm}^3 \text{ mol}^{-5/2} \text{ kg}^{3/2}$ . The experimental slope  $A_V = 1.865 \text{ cm}^3 \text{ mol}^{-3/2} \text{ kg}^{1/2}$  derived from our results at 298.15 K and 0.1 MPa is in excellent agreement with the

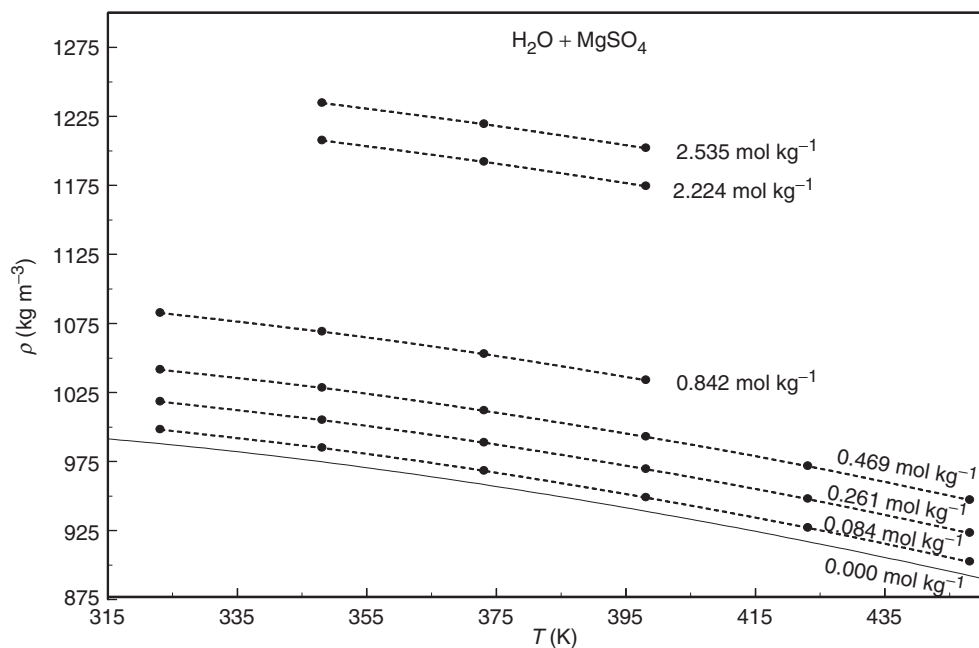


Figure 3. Density  $\rho$  of  $\text{MgSO}_4(\text{aq})$  solution as a function of temperature  $T$  at saturation for various concentrations.

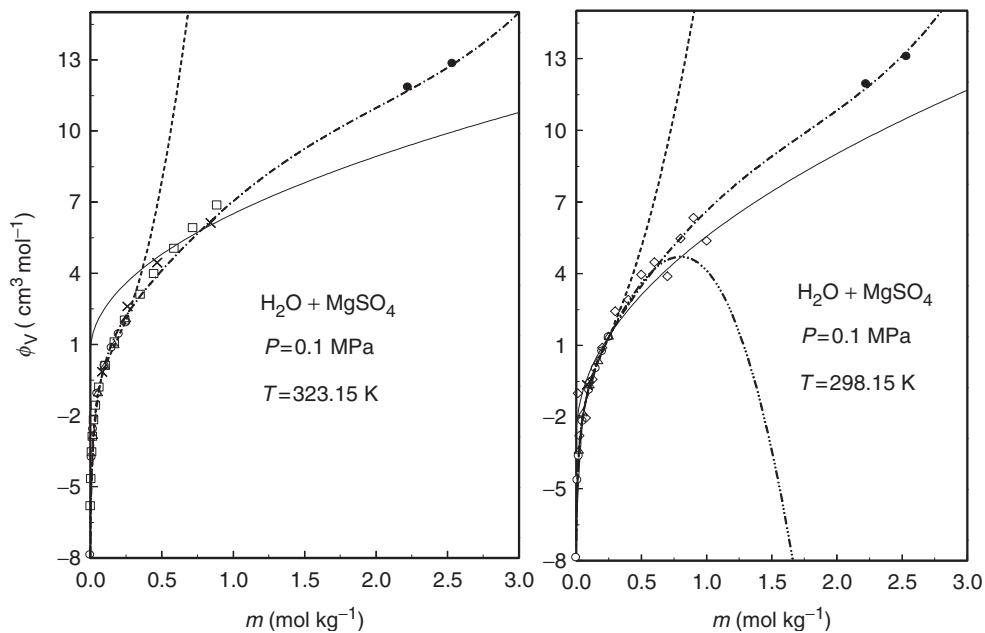


Figure 4. Apparent molar volume  $\phi_V$  for  $\text{MgSO}_4$  as a function of molality  $m$  at two selected temperatures 323.15 K and 298.15 K at atmospheric pressure. (●), This work (from the present density data); (×), This work (from Azizov and Akhundov [21–23]); (○), Phutela and Pitzer [26]; (□), Millero and Knox [72]; (Δ), Chen *et al.* [27,74]; (◇), Emara and Farid [73]; (—), Surdo *et al.* [67]; (---), Chen *et al.* [27,74]; (·····), Fabuss *et al.* [75]; (·····), Leyendekkers and Hunter [79].

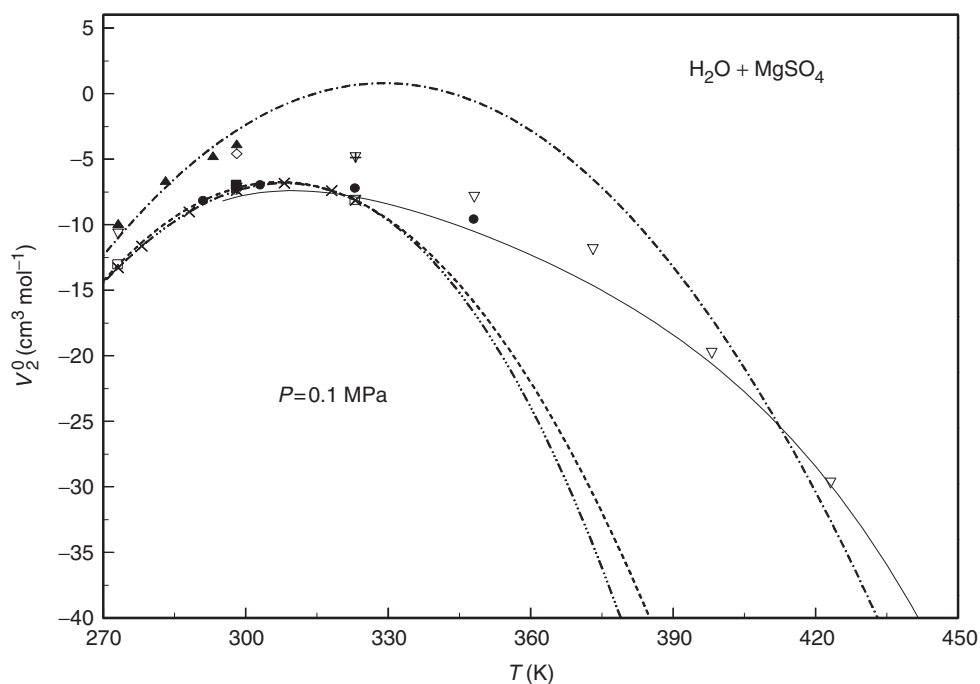


Figure 5. Partial molar volume at infinite dilution  $\bar{V}_2^0$  as a function of temperature at atmospheric pressure. (●), This work; (□), Millero and Knox [72]; (◇), Dücker [125]; (○), Krumgalz *et al.* [85]; (▽), Millero [3]; (+), Millero [4]; (▲), Zen [86]; (×), Surdo *et al.* [67]; (■), Emara and Farid [73]; (—), Phutela and Pitzer [26]; (---), Chen *et al.* [27]; (— · —), Fabuss *et al.* [75]; (· · · · ·), Surdo *et al.* [67].

theoretical coefficient  $1.870 \text{ cm}^3 \text{ mol}^{-1}$  derived from Debye–Hückel theory [84]. The values of  $\bar{V}_2^0$  were also calculated by using the Debye–Hückel plot,  $\phi_V$  versus  $m^{1/2}$  for the selected temperatures. The experimental value of  $\bar{V}_2^0 = -7.285 \pm 0.12 \text{ cm}^3 \text{ mol}^{-1}$  calculated from derived apparent molar volumes agrees well with the value  $-7.38 \text{ cm}^3 \text{ mol}^{-1}$  reported by Krumgalz *et al.* [85],  $-7.39 \text{ cm}^3 \text{ mol}^{-1}$  by Surdo *et al.* [67],  $-7.19 \text{ cm}^3 \text{ mol}^{-1}$  by Millero [4],  $-7.18 \text{ cm}^3 \text{ mol}^{-1}$  by Leyenndekkers and Hunter [79],  $-7.87 \text{ cm}^3 \text{ mol}^{-1}$  by Phutela and Pitzer [26], and  $-7.19 \text{ cm}^3 \text{ mol}^{-1}$  by Chen *et al.* [27]. These reported data show good agreement within  $\pm 0.69$ – $2.0\%$  with the present results. The maximum deviation  $7.9\%$  was found for the values by Phutela and Pitzer [26]. This is still acceptable because the uncertainty in  $\bar{V}_2^0$  (or  $\phi_V$  at infinite dilution) calculation is very high (about  $8$ – $10\%$  and more). As one can see from figure 5, the agreement between various data sets reported in the literature shows good agreement, except the data calculated using the additivity principle of the ionic partial molal volumes [3,4,86]). These data are systematically higher by  $20\%$  than the present and most published data sets (see figure 5). The agreement between the present  $\bar{V}_2^0$  results and the data reported by Phutela and Pitzer [26], Surdo *et al.* [67], and Chen *et al.* [27] is good (deviation within  $\pm 1.5$ – $2.0\%$ ) at temperatures up to  $335 \text{ K}$ . At high temperatures the present data shows satisfactory agreement with data by Phutela and Pitzer [26] and the values calculated from partial molal volumes of ions by Millero [3]. As figure 5 shows, the partial molar volume  $\bar{V}_2^0$  increases with temperature, passes through a maximum near  $315 \text{ K}$ , and then decreases at higher temperatures.

Table 3. Experimental values of viscosity, pressure, temperature, and concentration of  $\text{MgSO}_4(\text{aq})$  solutions.

$T$ (K)	0.1 MPa	10 MPa	30 MPa	$T$ (K)	0.1 MPa	10 MPa	30 MPa
$m = 0.085$ (mol kg <sup>-1</sup> )				$m = 0.255$ (mol kg <sup>-1</sup> )			
298.15	0.9407	0.9400	0.9415	298.15	1.0546	1.0540	1.0559
308.15	0.7610	0.7618	0.7645	308.15	0.8459	0.8466	0.8495
323.15	0.5785	0.5809	0.5856	323.15	0.6403	0.6431	0.6480
348.32	0.3976	0.4008	0.4066	348.25	0.4399	0.4432	0.4502
370.45	0.3053	0.3084	0.3144	372.40	0.3300	0.3336	0.3400
397.14	–	0.2381	0.2437	399.44	–	0.2566	0.2625
422.70	–	0.1945	0.1999	423.85	–	0.2113	0.2169
448.24	–	0.1643	0.1694	447.16	–	0.1798	0.1855
$m = 0.437$ (mol kg <sup>-1</sup> )				$m = 0.722$ (mol kg <sup>-1</sup> )			
298.15	1.1837	1.1840	1.1850	298.15	1.4420	1.443	1.445
308.15	0.9437	0.9460	0.9486	308.15	1.1510	1.153	1.156
323.15	0.7163	0.7198	0.7256	323.15	0.8612	0.8651	0.8714
348.15	0.491	0.4948	0.5024	348.36	0.5831	0.5875	0.5961
371.90	0.3654	0.3694	0.3766	370.45	0.4386	0.4433	0.4516
398.75	–	0.2834	0.2901	399.24	–	0.3306	0.3384
424.13	–	0.2300	0.2366	428.16	–	0.2597	0.2673
447.42	–	0.1966	0.2019	–	–	–	–
$m = 0.923$ (mol kg <sup>-1</sup> )				$m = 1.824$ (mol kg <sup>-1</sup> )			
298.15	1.6510	1.6530	1.6550	298.15	3.137	3.138	3.140
308.15	1.3048	1.3054	1.3092	308.15	2.415	2.418	2.422
323.15	0.9738	0.9781	0.9853	323.15	1.744	1.751	1.764
348.75	0.6495	0.6548	0.6642	348.20	1.127	1.135	1.151
370.40	0.4894	0.4945	0.5035	371.44	0.804	0.811	0.827
396.25	–	0.3770	0.3862	397.10	–	0.605	0.619
422.35	–	0.3000	0.3081	422.10	–	0.477	0.490
$m = 2.291$ (mol kg <sup>-1</sup> )				$m = 2.623$ (mol kg <sup>-1</sup> )			
298.15	4.414	4.415	4.417	298.15	5.789	5.790	5.792
308.15	3.374	3.376	3.348	308.15	4.352	4.355	4.364
323.15	2.373	2.382	2.400	323.15	2.997	3.009	3.031
348.15	1.503	1.514	1.536	348.35	1.849	1.863	1.889
370.10	1.068	1.078	1.099	370.75	1.295	1.308	1.333
398.70	–	0.774	0.792	394.16	–	0.9630	0.985

## 4.2. Viscosity

The viscosity measurements for eight (0.085, 0.255, 0.437, 0.722, 0.923, 1.824, 2.291, and 2.623 mol kg<sup>-1</sup>) binary aqueous  $\text{MgSO}_4$  solutions have been made in the temperature range from 298 to 448 K at pressures up to 30 MPa. All experimental viscosity data were obtained as a function of temperature at three isobars (0.1, 10, and 30 MPa). The experimental temperature, viscosity, pressure, and composition values for the aqueous  $\text{MgSO}_4$  solutions are presented in table 3. Some selected experimental viscosity data for  $\text{MgSO}_4(\text{aq})$  solutions as an example of the present results are shown in figures 6 and 7 in the  $\eta$ - $m$  and  $\eta$ - $T$  projections together with values reported by other authors. These figures include also the values of viscosity of  $\text{MgSO}_4(\text{aq})$  calculated with various correlations. Figure 6 demonstrates that the viscosity of  $\text{MgSO}_4(\text{aq})$  increases monotonically with the electrolyte concentration at fixed pressure and concentration. There are other types of electrolyte solutions, for example,  $\text{KNO}_3(\text{aq})$ ,  $\text{KBr}(\text{aq})$ ,  $\text{KCl}(\text{aq})$ ,  $\text{KI}(\text{aq})$ ,  $\text{RbCl}(\text{aq})$ , and  $\text{CsCl}(\text{aq})$  [87] for which the viscosity decreases with

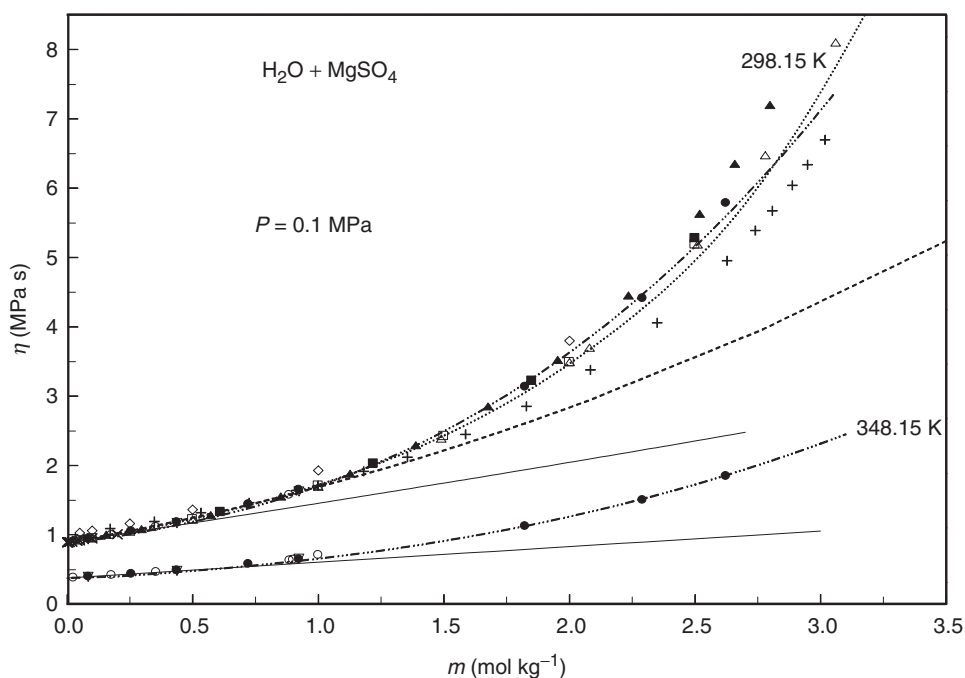


Figure 6. Measured values of viscosity  $\eta$  of  $\text{MgSO}_4(\text{aq})$  solutions as a function of molality  $m$  along various selected isotherms of 298.15 and 348.15 K and at pressure of 0.1 MPa. (●), This work; (○), Korosi and Fabuss [92]; (×), Kaminsky [29]; (□), Isono [69,70]; (■), Herz [95]; (▲), Ezrokhi [71]; (∇), Lobkova and Pepinov [28]; (◇), ITC [130]; (▲), Zaytseva and Ivanov [93]; (+), Urazov and Efimenko [137]; (—), Kaminsky [29]; (---), Zaytsev and Aseyev [94]; (·····), Leyenndekkers and Hunter [79]; (— · — · —), equation (10).

concentration at low electrolyte concentrations reaching a minimum value, then increasing monotonically for higher concentrations.

The viscosity of solution considerably decreases with temperature (see figure 7). For example, at constant pressures (0.1 and 10) MPa between temperatures 298 K and 435 K the viscosity of  $\text{MgSO}_4(\text{aq})$  solutions changes by a factor of 8. In concentration range  $m > 1 \text{ mol kg}^{-1}$ , the empirical equation of Andrade is valid for temperature dependence of viscosity. The Eyring's absolute rate theory enables a detailed description of the temperature dependence of viscosity [88,89] of concentrated aqueous electrolyte solutions. The temperature dependence of the viscosity of concentrated aqueous electrolyte solutions can be explained in terms of the temperature dependence of the  $E$  and  $V$  parameters of an equation developed by Goldsack and Franchetto [90] for the viscosity of solutions. Analysis of the  $E$  and  $V$  parameters of the alkali halide salts leads to absolute ionic hydration numbers [89]. The temperature dependence of these hydration numbers reveals two types of ionic behavior: structure making ions and structure breaking ions.

The viscosity is little affected (up to 3%) at high temperatures (448 K) and up to 0.12% at low temperatures (298 K) by pressure (at pressure changing between 0.1 and 30 MPa) along the isotherms. Grimes *et al.* [91] developed a correlation equation to describe the effect of pressure on the viscosity of  $\text{KCl}(\text{aq})$ . The values of experimental



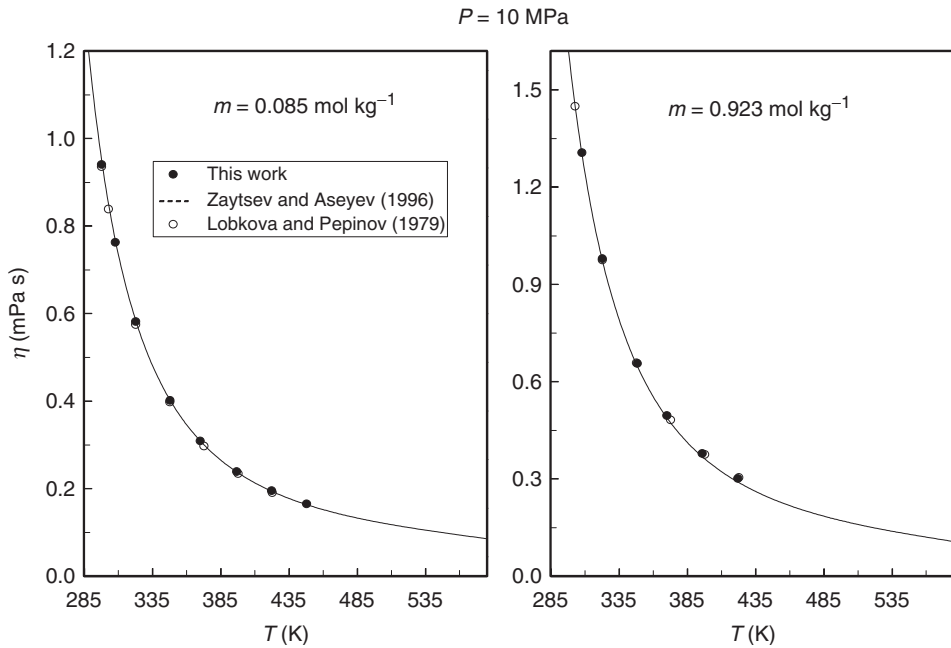


Figure 7. Measured values of viscosity  $\eta$  of  $\text{MgSO}_4(\text{aq})$  solutions as a function of temperature  $T$  at two selected concentrations of 0.085 and 0.923  $\text{mol kg}^{-1}$  and at pressures of 0.1 and 10 MPa.

viscosity along an isotherm were correlated as a function of pressure by means of a linear expression

$$\eta(T, c, P) = \eta_0(T, c)[1 + \beta(T, c)P], \quad (4)$$

where zero-pressure viscosity,  $\eta_0(T, c)$ , was correlated in terms of temperature and concentration. The effect of pressure on viscosity of the solution can be also calculated by TTG model [79] as

$$\frac{\eta_S^{(P)}}{\eta_S^{(1)}} = \frac{\eta_W^{(P_c+P)}}{\eta_W^{(P_c+1)}}, \quad (5)$$

where  $\eta_S^{(P)}$  is the solution viscosity at pressure  $P$ ,  $\eta_S^{(1)}$  is the solution viscosity at atmospheric pressure,  $\eta_W^{(P_c+P)}$  is the pure water viscosity at pressure  $P$ ,  $\eta_W^{(P_c+1)}$  is the pure water viscosity at atmospheric pressure, and  $P_c$  is the effective pressure due to the salt.

The present experimental values of the viscosity for  $\text{MgSO}_4(\text{aq})$  solutions were compared with the data reported by other authors in the literature. Figures 6 and 7 demonstrates the comparison of the present viscosity data for  $\text{MgSO}_4(\text{aq})$  solutions with those reported by various authors in the literature. As one can see from these figures, basically the agreement between various data sets is good, except scattering (within 10%) some data sets at high concentrations ( $m > 2 \text{ mol kg}^{-1}$ ). These figures illustrate that our data are consistent with most literature values at various pressures and temperatures. Most reported data at atmospheric pressure lie between  $\pm 0.4\%$  and  $2.0\%$  which is close to the experimental estimated uncertainty (1.6%). The excellent

agreement within  $\pm 0.8\%$  is found between the present measurements and the data reported by Isono [69,70] at temperatures of 298.15 and 323.15 K and at atmospheric pressure. The data of Korosi and Fabuss [92], Zaytseva and Ivanov [93], Lobkova and Pepinov [28], Ezrokhi [71], and Zaytsev and Aseyev [94] agree with the present viscosity data within 0.41, 1.5, 0.88, 1.43, and 0.95%, respectively, at atmospheric pressure and at temperatures from 298.15 to 348.15 K for compositions up to  $2.623 \text{ mol kg}^{-1}$ . Excellent agreement within 0.005% was found also between the present results and the data reported by Kaminsky [29] at 298.15 K, while the data by Herz [95] systematically deviate from the present results within 2.3%. The good agreement within  $\pm 1.03\%$  was found between the present viscosity data and the values reported by Lobkova and Pepinov [28] at high temperatures (to 423.15 K) and high pressures (up to 30 MPa). Although, Zaytsev and Aseyev [94] correlation initially was developed for atmospheric pressure and for the temperatures up to 373 K, as one can see from figure 7, this equation reproduces well (within  $\pm 0.22\%$  at low concentrations and  $\pm 1.10\%$  at concentrations to  $0.923 \text{ mol kg}^{-1}$ ) the temperature dependence of the viscosity data at high pressures and high temperatures for the composition up to  $0.9 \text{ mol kg}^{-1}$ , while the concentration dependence of this equation at  $m > 0.9 \text{ mol kg}^{-1}$  is incorrect (see figure 6). This good agreement between the present and published data confirms the reliability of the present measurements and its consistence with literature data. The present viscosity data at high pressures were compared with the values predicted by the TTM model [79] (equation (5)). The predicted values excellently (maximum deviation within 2.0%) agree with the present results.

The viscosity of  $MgSO_4(\text{aq})$  solutions is increasing monotonically with concentration without minimum. For these type electrolyte solutions the  $B$ -coefficient is positive. At a given concentration the  $B$ -coefficient can be interpreted in terms of a competition between specialized viscosity effects as (Coulombic interaction, size and shape of effects or Einstein effect, alignment or orientation of polar molecules by the ionic field, and distortion of the solvent structure). These effects are governing the viscosity behaviour of the aqueous electrolyte solutions. The values of viscosity  $B$ -coefficient is a highly specific property of the solute and can be determined by adding individual contributions of the solute constituents  $B = z^+ B^- + z^- B^+$ , where  $z^\pm$  and  $B^\pm$  refer to the ionic valence and ionic (cationic and anionic) viscosity  $B$ -coefficients (Marcus [5]; Cox and Wolfenden [96]). The values of  $B^\pm$  are constant at a given  $T$  for given ions in a specific solvent and describe solely the ion-solvent interactions. The values of  $B^\pm$  at different temperatures are available in the literature [15]. The values of viscosity  $A$ - and  $B$ -coefficients of an electrolyte provide information on the interaction between dissolved ions ( $Mg^{+2}, SO_4^{-2}$ ) and molecules of a solvent ( $H_2O$ ). For example, the  $A$ -coefficient of the Jones-Dole equation is determined by ion-atmosphere interaction and ionic mobilities and can be calculated from theory [97,98]. The value of the  $A$ -coefficient depends on the long-range Coulombic interactions between the ions and can be calculated from the ionic equivalent conductance, viscosity of the solvent  $\eta_0$ , its relative permittivity (dielectric constant)  $\epsilon_0$ , and the temperature  $T$  at infinite dilution [97,98] (see equations 7 and 8). The  $B$ - and  $D$ -coefficients are adjustable parameters and are related to the size and the shape of the ions and ion-solvent and ion-ion interactions, respectively. An extensive compilation of Jones-Dole  $A$ - and  $B$ -coefficients for the series aqueous electrolyte solutions has been reported by various authors [10,11,13,15,29,96,99-107]. Low concentration viscosity measurements for most aqueous electrolyte solutions show good agreement between experiment and

theory [29,96,99–102,105,110,111]. The values of the viscosity  $A$ -coefficient is always positive, but  $B$ -coefficient can be either positive or negative depending on the nature of the solute and the solvent. The sign of the  $B$ -coefficient depends on the degree of solvent structuring introduced by the ions. A positive value of the  $B$ -coefficient is associated with structure-making (ordering) ions, while a negative value of  $B$ -coefficient is associated with structure-breaking (disordering) ions. The temperature coefficient of  $B$ , ( $dB/dT > 0$ ), is positive in most cases. For example,  $dB/dT$  for  $Mg^{+2}$  and  $Li^+$  is negative, for  $Na^+$  it is almost zero, and for  $K^+$  it is positive. The viscosity  $B$ -coefficients for aqueous solutions shows strong temperature dependence, which can be attributed to ion-solvent interactions. However, measurements of the temperature dependence of the  $A$ - and  $B$ -coefficients have so far been limited to rather narrow ranges of temperature (up to 368 K) with less satisfactory accuracy. We examine the viscosity  $A$ - and  $B$ -coefficients values of aqueous  $MgSO_4$  solutions as a function of temperature in the temperature range from 298 K to 573 K. We also sufficiently extended the concentration range of the viscosity measurements to accurately determine high degree coefficient (viscosity  $D$ -coefficients) in the extended Jones–Dole equation.

Falkenhagen–Onsager–Fuoss [17,112] and Debye–Hückel–Onsager [113,114] theory predicts a square root concentration dependence of the viscosity of ionic solutions at infinite dilution,  $(\eta/\eta_0) \propto \sqrt{c}$ . This theory correctly explains the rise of viscosity with concentration in the limit of very low (dilute solutions) ion concentrations ( $c < 0.05 \text{ mol L}^{-1}$ ). This model was based on macroscopic consideration. Therefore, this model is inadequate when intermolecular correlation becomes important. Jones and Dole [115] proposed an empirical extension of the Falkenhagen and Dole [17] model to high concentrations as

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc, \quad (6)$$

for the viscosity of electrolyte solutions. In equation (6)  $\eta$  and  $\eta_0$  are the viscosities of an electrolyte solution and pure solvent (water), respectively,  $A$  is an always positive constant, and  $c$  is the electrolyte molarity concentration ( $\text{mol L}^{-1}$ ). This equation is valid only for concentrations below  $0.1 \text{ mol L}^{-1}$ , although theory cannot exactly predict the concentration range where equation (6) is valid. Usually, the values of parameters of the equation (6) are determined by using various fitting concentration ranges. The optimal concentration range also depends on temperature. Equation (6) provides a better description of the experimental viscosity data than  $(\eta/\eta_0) = 1 + A\sqrt{c}$ . Falkenhagen and Dole [17] gave a theoretical derivation of the  $A$ -coefficient. Its general form is [15]

$$A = \frac{A^*}{\eta_0(\epsilon_0 T)^{1/2}} f(\lambda_+^\infty, \lambda_-^\infty, z_+, z_-), \quad (7)$$

$$A^* = \frac{Fe^2 N_A^{1/2} (1 + \sqrt{2})}{12\pi(\epsilon^* k)^{1/2}}, \quad f = \frac{z^2(\lambda_+^\infty + \lambda_-^\infty)}{4(2 + \sqrt{2})(\lambda_+^\infty \lambda_-^\infty)} \left[ 1 - \frac{4(\lambda_+^\infty - \lambda_-^\infty)^2}{(1 + \sqrt{2})^2 (\lambda_+^\infty + \lambda_-^\infty)^2} \right], \quad (8)$$

where  $A^* = 1.113 \times 10^{-5} \text{ C}^2 (\text{mK mol}^{-3})^{1/2}$ ,  $f(\lambda_+^\infty, \lambda_-^\infty, z_+, z_-)$  is the function of the equivalent conductences  $\lambda_\pm^\infty$  at infinite dilution of the ions, and  $z_\pm$  are the charges. The value of the parameter  $A$  depends also on the viscosity of the solvent (pure water)  $\eta_0$ , its relative permittivity (dielectric constant)  $\epsilon_0$ , and the temperature  $T$ .

Jones and Talley [101], Kaminsky [29,100], Desnoyers and Perron [105], Feakins and Lawrence [116], Desnoyers *et al.* [117], and Robertson and Tyrrell [110], added a quadratic term  $Dc^2$  (extended Jones–Dole equation)

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2, \quad (9)$$

to extend the Jones–Dole equation for more concentrated electrolyte solutions ( $c < 0.1\text{--}0.2\text{ m}$ ). The new  $Dc^2$  term of (9) is including all solute–solvent and solute–solute structural interactions that were not accounted by the  $A\sqrt{c}$  and  $Bc$  terms at high concentrations such as [13,105]: high terms of the long-range Coulombic forces; high term hydrodynamic effect; and interactions arising from changes in solute–solvent interactions with concentration. The concentration range of the present viscosity measurements is large enough that the  $Bc$  and  $Dc^2$  terms in equation (9) are not sufficient. In the present study we included one more term  $Fc^{2.5}$  for application to higher concentration (up to  $3\text{ mol L}^{-1}$ )

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2 + Fc^{2.5}. \quad (10)$$

The present experimental data for the relative viscosity  $\eta/\eta_0$  for various temperatures together with data reported by other authors for  $\text{MgSO}_4(\text{aq})$  at low concentrations [29,69,70,92,108,109] were used to calculate  $A$ -,  $B$ -,  $D$ -, and  $F$ -coefficients in the extended Jones and Dole [115] equation (10). The results are presented in figure 8 as a function of temperature together with the values reported by other authors and calculated from the theory. As one can see from figure 8, the agreement between  $A$ - and  $B$ -coefficients derived in the present study and calculated with theory and ionic

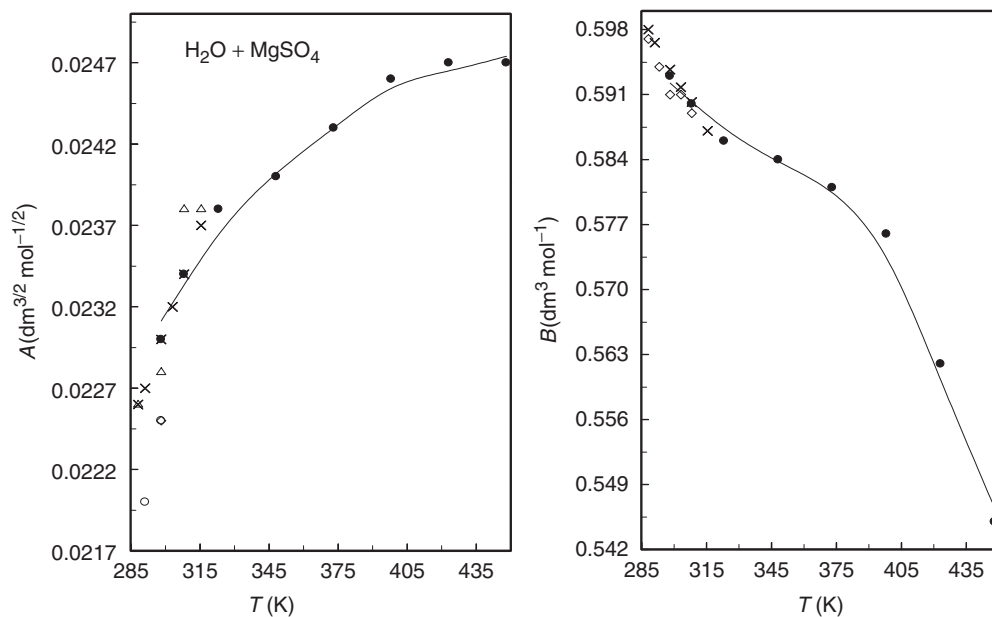


Figure 8. Experimental viscosity  $A$ - and  $B$ -coefficients of the  $\text{MgSO}_4(\text{aq})$  solutions as a function of temperature together with values reported by other authors. ( $\bullet$ ), This work; ( $\times$ ), Kaminsky [29]; ( $\Delta$ ), (theory, equation 7); ( $\diamond$ ), Jenkins and Marcus [15]; ( $\circ$ ), Asmus [108,109]. The solid curves are guides for the eye.

$B$ -coefficients data is good. Figure 8 demonstrates that viscosity  $A$ -coefficient monotonically increases with temperature and the derivative (temperature coefficient)  $dB/dT > 0$  is positive (structure-breaking ions). More typical large positive values of  $B$ -coefficient, found with ions which are strongly hydrated. At 298.15 K the  $B^+$ -coefficients values for  $Mg^{+2}$  is 0.385 and 0.206 for  $SO_4^{-2}$  (structure-ordering ions). The values of the  $B^+$  -coefficients for  $Mg^{+2}$  are decreasing with temperature ( $dB^+/dT < 0$ ), while for  $SO_4^{-2}$  become more positive as the temperature increases ( $dB^-/dT > 0$ ) (Jenkins and Marcus [15]).

According to the conventional technique of the viscosity coefficients determination, the  $B$ - and  $D$ -coefficients can be estimated also from experimental viscosity data by extrapolating the function

$$B + Dc = \frac{(\eta/\eta_0) - 1 - Ac^{1/2}}{c}, \quad (11)$$

to zero concentration ( $c \rightarrow 0$ ), using the theoretical value of  $A$ , or as slope of the dependence  $[(\eta/\eta_0) - 1]/c^{1/2}$  on  $c^{1/2}$  (Jones–Dole plot, see figure 9)

$$[(\eta/\eta_0) - 1]/c^{1/2} = A + Bc^{1/2}. \quad (12)$$

The present viscosity data for  $MgSO_4(aq)$  solutions together with data reported by other authors are presented in figure 9 in the Jones–Dole plot,  $[(\eta/\eta_0) - 1]/c^{1/2}$  versus  $c^{1/2}$ , for the two selected temperatures 298.15 and 348.15 K.

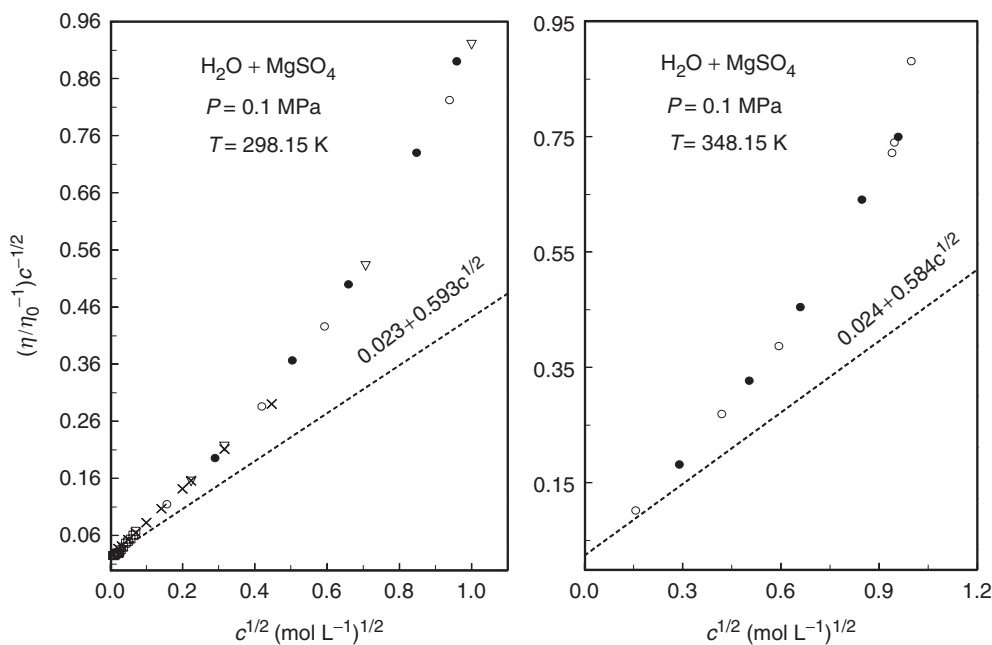


Figure 9. Jones–Dole plot,  $[(\eta/\eta_0) - 1]/c^{1/2}$  vs.  $c^{1/2}$  for  $MgSO_4(aq)$  solutions for selected isotherms of 298.15 and 348.15 K and at atmospheric pressure. (●), This work; (□), Asmus [108,109]; (×), Kaminsky [29]; (▽), Isono [69,70]; (○), Korosi and Fabuss [92].

Einstein [118] has calculated the size effect (hydrodynamic effect) for an infinitely dilute suspension of rigid spherical particles in a continuum and obtained following expression

$$\frac{\eta}{\eta_0} = 1 + k\phi, \quad (13)$$

where  $\phi$  is the volume fraction of the solute molecules ( $\phi = (4/3)\pi R^3 N_A c$ , where  $R$  is the effective solute ions radius). For solid spheres with large diameter compared to molecular dimensions, the value of  $k$  in equation (13) is commonly accepted to be 2.5, although values as large as 5.5 have been suggested by Happel [119]. If  $\phi$  is expressed in terms of concentration in  $\text{mol L}^{-1}$ , then equation (13) becomes

$$\frac{\eta}{\eta_0} = 1 + 2.5V_k c, \quad (14)$$

where  $V_k$  is the hydrodynamic molar volume in  $\text{cm}^3 \text{mol}^{-1}$ . If we relate the Einstein's equation (14) to Jones–Dole equation (12), the  $B$ -coefficient can then be related to molar volume  $V_k$  by  $B = 2.5 V_k$ . As discussed by Desnoyers and Perron [105]  $V_k$  should be given by the partial molar volume of the solute  $\bar{V}$ , although other authors (for example, Skinner and Fuoss [120]) considered  $V_k$  as apparent molar volume. Therefore, for such an ideal system the viscosities are predictable from densities and vice versa. Isono and Tamamushi [121] found the linear relation between the viscosity  $B$ -coefficient of electrolyte solution and the molal volume  $V_k$  of the hydrated salt,  $B = aV_k - b$ , where the values of parameter  $a$  are within 2.6–2.8 depending on temperature. As one can see, the values of  $a$  are very close to the Einstein value of 2.5.

Thomas [122] has extended the Einstein relation (13) for the hydrodynamic effect to high concentrations by showing that for suspensions the relative viscosity is given by the relation

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 10.05\phi^2 = 1 + 2.5V_k c + 10.05V_k^2 c^2. \quad (15)$$

As was shown by Breslau and Miller [123], this relation can be used to represent concentration dependence of the relative viscosity for concentrated electrolyte solutions if  $V_k$  is taken as an adjustable parameter (effective rigid molar volumes). In the present work we calculated the values of  $V_k$  for  $MgSO_4(\text{aq})$  solutions at temperature 348.15 K and at atmospheric pressure from viscosity data in the concentration range between 0.025 and 2.623 m. The derived values of  $V_k$  for  $MgSO_4(\text{aq})$  solutions is  $V_k = 0.1914 \text{ mol L}^{-1}$ . Moulik and Rakshit [124] also used equation (15) to correlate the concentration dependence of the viscosity of electrolyte solutions at high concentrations. Therefore, the relation (15) can be used to estimate the values of the hydrostatic volume by using experimental relative viscosity data.

## 5. Conclusions

Density of two (2.224 and  $2.535 \text{ mol kg}^{-1}$ ) and viscosity of eight (0.085, 0.255, 0.437, 0.722, 0.923, 1.824, 2.291, and  $2.623 \text{ mol kg}^{-1}$ ) binary aqueous  $MgSO_4$  solutions have been measured with a constant-volume piezometer immersed in a precision liquid thermostat and a capillary flow techniques, respectively. Measurements were made at



pressures up to 30 MPa. The range of temperature was 288–398 K for the density measurements and 298–448 K for the viscosity measurements. Good agreement (within 0.05–0.34% for the density and 0.75–1.46% for the viscosity) is found between the present measurements and the data sets reported by other authors in the literature. The effect of temperature, pressure, and concentration dependences on the density and viscosity are studied. The measured densities were used to calculate apparent and partial molar volumes for each solution. The values of the density  $A_V$ -coefficient (the limiting slope of the Debye–Hückel law) and viscosity  $A$ -,  $B$ -,  $D$ -, and  $F$ -coefficients of the extended Jones–Dole equation for the relative viscosity ( $\eta/\eta_0$ ) of aqueous  $\text{MgSO}_4$  solutions as a function of temperature are studied. The hydrodynamic molar volumes  $V_k$  were calculated using the present experimental viscosity data.

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