

# Viscosities of aqueous LiI solutions at 293–525 K and 0.1–40 MPa

I.M. Abdulagatov<sup>a,\*</sup>, N.D. Azizov<sup>b</sup>

<sup>a</sup> *Institute for Geothermal Problems of the Dagestan Scientific Center of the Russian Academy of Sciences, 367003 Makhachkala, Shamilya Str. 39-A, Dagestan, Russia*

<sup>b</sup> *Azerbaijan State Oil Academy, Baku 370601, Azerbaijan*

Received 15 July 2005; received in revised form 24 August 2005; accepted 30 August 2005

Available online 7 October 2005

## Abstract

The effects of temperature, pressure, and concentration on viscosity of aqueous LiI solutions were determined with a capillary-flow technique and compared with literature data and correlations. The data are interpreted with the extended Jones–Dole equation for strong electrolytes to calculate the viscosity  $A$ -,  $B$ -, and  $D$ -coefficients. Good agreement was found between derived values of the viscosity  $A$ - and  $B$ -coefficients and the results predicted by Falkenhagen–Dole theory of electrolyte solutions and calculated with the ionic  $B$ -coefficient data. It was found that the temperature coefficient,  $dB/dT > 0$ , for LiI(aq) is positive (structure-breaking ions). Physical meaning parameters  $V$  and  $E$  in the absolute-rate theory of viscosity and hydrodynamic molar volume  $V_k$  were calculated using present experimental viscosity data. The values of parameter  $E$  almost independent on temperature (around 11.1), while the values of parameter  $V$  monotonically decreasing as temperature increases. The Arrhenius–Andrade parameters ( $A$  and  $E_a/R$ ) were calculated from measured viscosity data. The predicted capability and validity of the various theoretical models for the viscosity of electrolyte solutions were tested.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Aqueous solution;  $B$ -coefficient; Capillary viscometer; Lithium iodide; Viscosity; Water

## 1. Introduction

Thermodynamic and transport properties of aqueous electrolyte solutions in a wide range of solute concentrations and solution temperatures and pressures are of fundamental importance for the understanding of various physico-chemical processes occurring in the chemical industry and in the environment. In many applications, these processes occur at high temperatures and pressures. Viscosity is one of the key transport properties. Temperature and concentration dependences of viscosity of aqueous electrolytes solutions are crucial for understanding ion–solvent interactions. The solvational properties are reflected in the viscosity  $B$ -coefficients of ions which are specific property of the solute and can be determined by adding individual contributions of the solute constituent  $B = z^+ B^- + z^- B^+$ , where

$z^\pm$  and  $B^\pm$  refer to the ionic valence and ionic viscosity  $B$ -coefficient [1–3]. The Falkenhagen–Dole theory predicts only the values of the viscosity  $A$ -coefficient of electrolyte solutions at infinite dilution [4–10]. Determination of the  $B$ - and  $D$ -coefficients in the extended Jones–Dole equation for  $(\eta/\eta_0)$  requires reliable viscosity data for electrolyte solutions at high concentrations.

Viscosity data for LiI(aq) solutions are scarce, especially under high pressure and at high temperatures and with less than satisfactory accuracy. Theoretical modeling [11–18] of the viscosity of LiI(aq) can serve as an example for other 1:1 electrolytes. The main aim of the present paper is to measure the viscosity of LiI(aq) solutions at 293–525 K, at pressures up to 40 MPa, and at molalities up to 3 mol kg<sup>-1</sup>, to calculate the viscosity  $A$ - and  $B$ -coefficients, effective hydrodynamic molar volume  $V_k$  in the extended Einstein relation for the relative viscosity  $(\eta/\eta_0)$ , and the parameters  $V$  and  $E$  in the absolute-rate theory of viscosity. The present results considerably expand the temperature, pressure, and concentration ranges in which viscosity for aqueous LiI solutions are available. Most reported experimental data on the viscosity of LiI(aq) are at near ambient temperatures (298–323 K) and atmospheric pressure [2,19–21].

\* Corresponding author. Present address: Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA. Tel.: +1 303 497 4027; fax: +1 303 497 5224.

E-mail addresses: [mangur@datacom.ru](mailto:mangur@datacom.ru), [ilmutdin@boulder.nist.gov](mailto:ilmutdin@boulder.nist.gov) (I.M. Abdulagatov), [Nazim\\_Azizov@yahoo.com](mailto:Nazim_Azizov@yahoo.com) (N.D. Azizov).

<sup>1</sup> Tel.: +7 8722 62 66 23; fax: +7 8722 62 70 79.

Only two sources of data on LiI(aq) solutions under pressure are available in the literature [22,23], up to 573 K and pressures up to 40 MPa at concentration from 0.4 to 5 mol kg<sup>-1</sup>. Mashovets et al. [21] measured the viscosity of LiI(aq) at atmospheric pressure and at 273.15–363.15 K between 0.097 and 9.17 mol kg<sup>-1</sup>. Several compilations of the volumetric and transport properties of LiI(aq) at atmospheric pressure exist in the literature [24,25]. However, new data have appeared since Lobo and Quaresma [24] and Aseyev [25] reported a comprehensive review of all the LiI(aq) viscosity measurements which were made between 1908 and 1994, except some missing works.

## 2. Experimental

The details of the experimental method, the description of the apparatus and procedures used for the viscosity measurements of the LiI(aq) solutions have been described in previous papers [26–33]. 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%. The capillary viscometer is the most frequently used instrument for the measurement of viscosity of aqueous electrolyte solutions at high temperatures and high pressures (see for example [34–37]). The technique is based on the Poiseuille's law, which relates viscosity to the rate of fluid flow through a capillary tube. 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 a solid red copper block. The capillary together with an extension tube were located in the high-temperature and high-pressure autoclave. When the movable cylinder was moved vertically at constant speed, the fluid flowed through the capillary. The autoclave was placed in a solid red copper block. To create and measure the pressure, the autoclave was connected with a dead-weight pressure gauge (MP-600) by means of a separating vessel. The maximum uncertainty in the pressure measurements was 0.05%.

Poiseuille's law assumes adherence to the same conditions during flow through the capillary (see Ref. [38]). After taken into account all corrections the final working equations for this method are [26]:

$$\eta = U\tau \left( \frac{\rho}{\rho_r} \right) \left( \frac{1 - \rho_r}{\rho_{\text{Hg}}} \right) (1 + \alpha \Delta t)^3 - W \left( \frac{\rho_r}{\tau} \right), \quad (1)$$

$$U = \frac{g\pi R^4 \Delta H_0 \rho_{0,\text{Hg}}}{8LV_{\text{cyl}}}, \quad W = \frac{nV_{\text{cyl}}}{8\pi L},$$

where  $R = 0.15091 \pm 0.005$  mm is the inner radius of the capillary,  $L = 540.324 \pm 0.005$  mm the capillary tube length,  $\tau$  the time of flow,  $\alpha$  the linear expansion coefficient of the capillary material,  $\Delta t$  the difference between experimental temperature and room temperature,  $n = 1.12$  a constant (kinetic-energy correction factor [39]),  $\rho(P, T)$  the density of the fluid under study at the experimental conditions  $(P, T)$ ,  $V_{\text{cyl}} = 1.2182$  cm<sup>3</sup> the volume of the unmovable (measuring) cylinder,  $\rho_r$  the density of the fluid

under study at room temperature and experimental pressure,  $\Delta H_0 = (H_1 - H_2)/\ln(H_1/H_2)$ , where  $H_1$  and  $H_2$  are the mercury levels at the beginning and end of the flowing fluid, respectively, at room temperature and atmospheric pressure,  $\rho_{\text{Hg}}$  is the density of mercury at room temperature and experimental pressure, and  $\rho_{0,\text{Hg}}$  is the density of mercury at room temperature and atmospheric pressure.

The values of the parameters  $U$  and  $W$  can also be determined by means of a calibration technique. The time of fluid flow through the capillary  $\tau$  was measured with a stop-watch with an uncertainty of less than 0.1 s (0.5%). An electromagnetic device was used to start and stop the watch.

In this method, the measurement of the following basic quantities are needed:  $R^4$ ,  $\Delta H_0$ ,  $L$ ,  $V_{\text{cyl}}$ ,  $\tau$ ,  $\rho_{\text{Hg}}$ ,  $\rho_r$ ,  $T$ , and  $P$ . The uncertainty of the viscosity measurements was assessed by analyzing the sensitivity of Eq. (1) to the experimental uncertainties of the measured quantities [26]. At the maximum measured temperature (525 K), the values of the root-mean-square deviations in the viscosity measurements was  $\delta\eta = 1.91 \times 10^{-5}$  g cm<sup>-1</sup> s<sup>-1</sup>. Based on a 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 less than 1.5% [26]. The Reynolds ( $Re$ ) number occurring during all measurements was (about 300) considerably less than the critical values ( $Re_c = 2000$ ).

As one can see from Eq. (1), to calculate the dynamic viscosity from measured quantities, the values of the density of the solution under study at room temperature and experimental pressure  $\rho_r$ , and the density at the experimental conditions  $\rho(P, T)$  are needed. For this purpose, we used the density data reported in our previous publication [40] for aqueous LiI solutions at high temperatures (up to 600 K) and high pressures (up to 40 MPa) for concentration up to 3 mol kg<sup>-1</sup>.

As a check of the method and procedure of the measurements, before engaging in measurements on aqueous LiI solutions, we have measured the viscosity of triple-distilled water along three selected isobars 0.1, 10, and 40 MPa and over the range of temperature from 284 to 436 K. These data were compared with values calculated from the IAPWS formulation [41]. The agreement between both sets of data (IAPWS [41] formulation and the present results) along the isobars (0.1, 10, and 40 MPa) is excellent (average absolute deviation, AAD = 0.64%; see Table 1). This excellent agreement between the present data and IAPWS [41] calculations for pure water confirms the reliability and high accuracy of the measurements for LiI(aq) and gives us an assurance that our instrument is functioning correctly.

The LiI(aq) solutions were prepared from chemically pure LiI (Merck GR, >99.5 mass%) and triple-distilled water. The solutions were prepared gravimetrically with an analytical balance having a precision of  $\pm 5 \times 10^{-8}$  kg. The solutions at the desired composition were prepared by mass by carefully weighing. To check the accuracy, we determined the density of each solution at room temperature (298.15 K) and atmospheric pressure with the aid of a pycnometer accurate to 0.005% and compared it with the reference data.

Table 1  
Test measurements of the viscosity (mPa s) of pure water

<i>T</i> (K)	0.1 MPa		10 MPa		40 MPa	
	This work	IAPWS [41]	This work	IAPWS [41]	This work	IAPWS [41]
284.56	1.2570	1.2550	1.2490	1.2460	1.2310	1.2250
304.83	0.7654	0.7697	0.7725	0.7692	0.7745	0.7701
335.46	0.4482	0.4506	0.4504	0.4529	0.4635	0.4604
368.64	0.2938	0.2957	0.2966	0.2983	0.3086	0.3064
397.56	–	–	0.2278	0.2258	0.2358	0.2334
435.61	–	–	0.1679	0.1690	0.1745	0.1770
Deviation statistics	AAD (%) = 0.632; bias = 0.012; S.D. = 0.718; S.E. = 0.179; max. dev. = 1.433; <i>N</i> = 16; confidential interval (%) = 95					

### 3. Results and discussion

Viscosity measurements have been made for seven (0.0800, 0.1600, 0.2832, 0.6621, 1.6046, 2.1603, and 3.0886 mol kg<sup>-1</sup>) LiI(aq) solutions in the temperature range from 284 to 525 K at pressures up to 40 MPa. All experimental viscosity data were obtained as a function of temperature on three isobars (0.1, 10, and 40 MPa) at fixed concentrations. The experimental temperature, viscosity, pressure, and composition values for the LiI(aq) solutions are presented in Table 2. Some of selected experimental viscosity data for LiI(aq) solutions, as an example of the present results, are shown in Figs. 1–3 in the  $\eta$ -*m*,  $\eta$ -*T*, and  $\eta$ -*P* projections, together with values reported by other authors. These figures also include the values of viscosity of LiI(aq) calculated with correlations by Goldsack and Franchetto [42,43] and Zaytsev and Aseyev [44].

Fig. 4(left) demonstrates the concentration dependence of the viscosity of a series of aqueous solutions with the same anion (negative ion I<sup>-</sup>) and various cations (positive ions Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, NH<sup>+</sup>, and Cs<sup>+</sup>). This figure demonstrates the effect of nature of NO<sub>3</sub><sup>-</sup> various cations on the values and concentration dependence of the viscosity of salt solutions (iodides). As one can see from Fig. 4(left) the CdI<sub>2</sub>(aq) solution observed highest values of the viscosity among most other aqueous iodide solutions (CsI, LiI, KI, NaI, and BaI<sub>2</sub>) at the same thermodynamic (*P*, *T*, *m*) conditions. Fig. 4(right) shows also the concentration dependence of the viscosity of a series of aqueous solutions with the same cation (positive ion Li<sup>+</sup>) and various anions (negative ions SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>). As Fig. 4 (right) shows the LiSO<sub>4</sub>(aq) observed highest values of the viscosity compared to other aqueous (LiCl, LiBr, LiNO<sub>3</sub>, and LiI) solutions, while the viscosity of LiI(aq) showed lowest values. Fig. 4 demonstrates also how the concentration dependence of the viscosity of solutions depends on the nature of the solute ions.

#### 3.1. Temperature dependence of the viscosity of LiI(aq) solutions

Some selected experimental viscosity data for LiI(aq) solutions as a function of temperature are shown in Fig. 2(a and b) in the  $\eta$ -*T* projection together with values reported by other authors. The viscosity of solution is considerably decreases with temperature (see Fig. 2(a and b)). For example, at pressures from

0.1 to 40 MPa and between temperatures 293 and 525 K the viscosity of LiI(aq) solutions changes by a factor of 8–10. In the concentration range  $m > 1$  mol kg<sup>-1</sup>, the empirical equation of Arrhenius–Andrade is valid for the temperature dependence of viscosity [45–47]:

$$\eta = A \exp\left(\frac{b}{T}\right), \quad (2)$$

where *A* and  $b = E_a/R$  ( $E_a$  is the flow activation energy) are function of concentration. The values of these parameters for LiI(aq) solution calculated with present measurements at atmospheric pressure are given in Table 3. This equation represents present viscosity data within 0.8–1.0% in the temperature range from 293 to 373 K. However, Eq. (2) failed to represent present data over the complete temperature range at high pressures. As one can see from Table 3, the values of activation energy  $E_a$  for the flow are monotonically decreasing with concentration of LiI.

The Eyring's absolute-rate theory (Glasstone et al. [45]) enables a detailed description of the temperature dependence of viscosity of concentrated aqueous electrolyte solutions as:

$$\eta = \left(\frac{hN}{V}\right) \exp\left(\frac{\Delta G^+}{RT}\right) \quad \text{or} \quad \eta = A \exp\left(\frac{\Delta H^+}{RT}\right), \quad (3)$$

where  $\Delta G^+$  and  $\Delta H^+$  are the free enthalpy of activation and enthalpy of activation, *h* the Planck's constant, *N* the Avogadro's constant, *R* the gas constant, and *V* is the molar volume of the hole in the liquid. The enthalpy of activation  $\Delta H^+$  can be calculated from the slope of the curve by the ln  $\eta$  function of 1/*T* (Arrhenius plot; see Fig. 5). In simplified form for a 1:1 electrolyte, Eq. (3) can be given by the relation [42,43]:

$$\eta = \eta_0 \exp \frac{xE}{1 + xV}, \quad (4)$$

where  $\eta$  is the viscosity of the electrolyte solution at a concentration *m* and temperature *T*,  $\eta_0$  the viscosity of the solvent (pure water) at temperature *T*, *x* the mole fraction of the cation or anion in the solution, and the parameters *E* and *V* are defined as:

$$E = \frac{\Delta G_c^* + \Delta G_a^* - 2 \Delta G_0^*}{RT} \quad \text{and} \quad V = \frac{V_c + V_a}{V_0 - 2}, \quad (5)$$

where  $V_+$  is the molar volume of the cation particle,  $V_-$  the molar volume of the anion particle,  $V_0$  the molar volume of the solvent particle (pure water),  $\Delta G_+^*$  the molar free energy of

Table 2  
Experimental values of viscosity, pressure, temperature, and concentration of H<sub>2</sub>O + LiI solutions

<i>T</i> (K)	0.1 MPa	10 MPa	40 MPa	<i>T</i> (K)	0.1 MPa	10 MPa	40 MPa
<i>m</i> = 0.0800 (mol kg <sup>-1</sup> )				<i>m</i> = 0.1600 (mol kg <sup>-1</sup> )			
293.15	1.0085	1.0046	0.9978	293.15	1.0151	1.0118	1.0041
298.15	0.8961	0.8946	0.8920	298.15	0.9025	0.9012	0.8979
304.77	0.7764	0.7770	0.7779	308.74	0.7215	0.7221	0.7256
324.62	0.5385	0.5407	0.5475	323.74	0.5504	0.5527	0.5599
341.69	0.4164	0.4192	0.4252	344.06	0.4065	0.4093	0.4177
369.35	0.2968	0.2996	0.3079	368.79	0.3014	0.3044	0.3128
396.70	–	0.2301	0.2381	397.82	–	0.2304	0.2385
422.12	–	0.1885	0.1959	424.49	–	0.1874	0.1947
449.02	–	0.1581	0.1648	448.75	–	0.1602	0.1674
472.45	–	0.1387	0.1452	473.46	–	0.1397	0.1467
523.72	–	0.1089	0.1163	522.70	–	0.1109	0.1182
<i>m</i> = 0.2832 (mol kg <sup>-1</sup> )				<i>m</i> = 0.6621 (mol kg <sup>-1</sup> )			
293.15	1.0246	1.0205	1.0135	293.15	1.0497	1.0466	1.0393
298.15	0.9114	0.9098	0.9070	298.15	0.9363	0.9351	0.9225
310.64	0.7028	0.7047	0.7074	304.75	0.8141	0.8149	0.8164
322.51	0.5682	0.5704	0.5768	324.23	0.5733	0.5758	0.5829
347.42	0.3940	0.3976	0.4052	343.64	0.4337	0.4368	0.4458
367.05	0.3119	0.3142	0.3227	369.49	0.3189	0.3222	0.3313
398.32	–	0.2331	0.2414	399.03	–	0.2447	0.2534
424.14	–	0.1913	0.1988	421.45	–	0.2060	0.2139
449.71	–	0.1622	0.1696	449.06	–	0.1725	0.1802
472.92	–	0.1429	0.1501	474.98	–	0.1497	0.1572
524.07	–	0.1123	0.1199	525.42	–	0.1185	0.1266
<i>m</i> = 1.6046 (mol kg <sup>-1</sup> )				<i>m</i> = 2.1603 (mol kg <sup>-1</sup> )			
293.15	1.1218	1.1184	1.1115	293.15	1.1578	1.1543	1.1472
298.15	1.0021	1.0008	0.9979	298.15	1.0395	1.0385	1.0355
311.74	0.7684	0.7700	0.7748	312.45	0.7939	0.7957	0.8016
323.45	0.6301	0.6327	0.6406	324.02	0.6554	0.6584	0.6666
344.66	0.4673	0.4708	0.4804	345.43	0.4884	0.4912	0.5015
368.75	0.3544	0.3580	0.3678	364.95	0.3905	0.3944	0.4048
398.94	–	0.2713	0.2809	397.72	–	0.2921	0.3023
422.47	–	0.2275	0.2363	424.41	–	0.2400	0.2494
447.94	–	0.1945	0.2029	444.25	–	0.2119	0.2206
473.06	–	0.1699	0.1784	473.07	–	0.1815	0.1900
524.86	–	0.1344	0.1433	525.49	–	0.1435	0.1531
<i>m</i> = 3.0886 (mol kg <sup>-1</sup> )							
293.15	1.2270	1.2237	1.2150				
298.15	1.1078	1.1009	1.0975				
307.45	0.9235	0.9250	0.9291				
325.64	0.6865	0.6896	0.6986				
348.24	0.5101	0.5144	0.5255				
363.94	0.4275	0.4317	0.4435				
398.72	–	0.3165	0.3278				
422.41	–	0.2666	0.2770				
447.54	–	0.2284	0.2383				
473.71	–	0.1992	0.2091				
523.42	–	0.1603	0.1711				

activation for viscous flow of the cation particle,  $\Delta G^*$  the molar free energy of activation for viscous flow of the anion particle,  $\Delta G_0^*$  the molar free energy of activation for viscous flow of the solvent particle, and  $x = m/(55.5 + 2m)$ , where  $m$  is the molality of the salt. The individual ionic components of the parameter  $V$  are related to ionic solvation numbers, and the individual ionic free energy of activation components of the  $E$  are related to a surface free energy for formation of a hole in the liquid.

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 Eq. (4) for the viscosity of solutions. Analysis of the  $V$  parameter of the electrolytes leads to absolute ionic hydration numbers [42,43]. The temperature dependence of these hydration numbers reveals two types of ionic behavior: structure-making ions and structure-breaking ions. The results of the application of Eq. (4) to the present viscosity measurements for LiI(aq) are presented in Table 4 as a function of temperature. As one can see from Table 4, the values of parameter  $E$  almost independent on temperature (around 11.1), while the

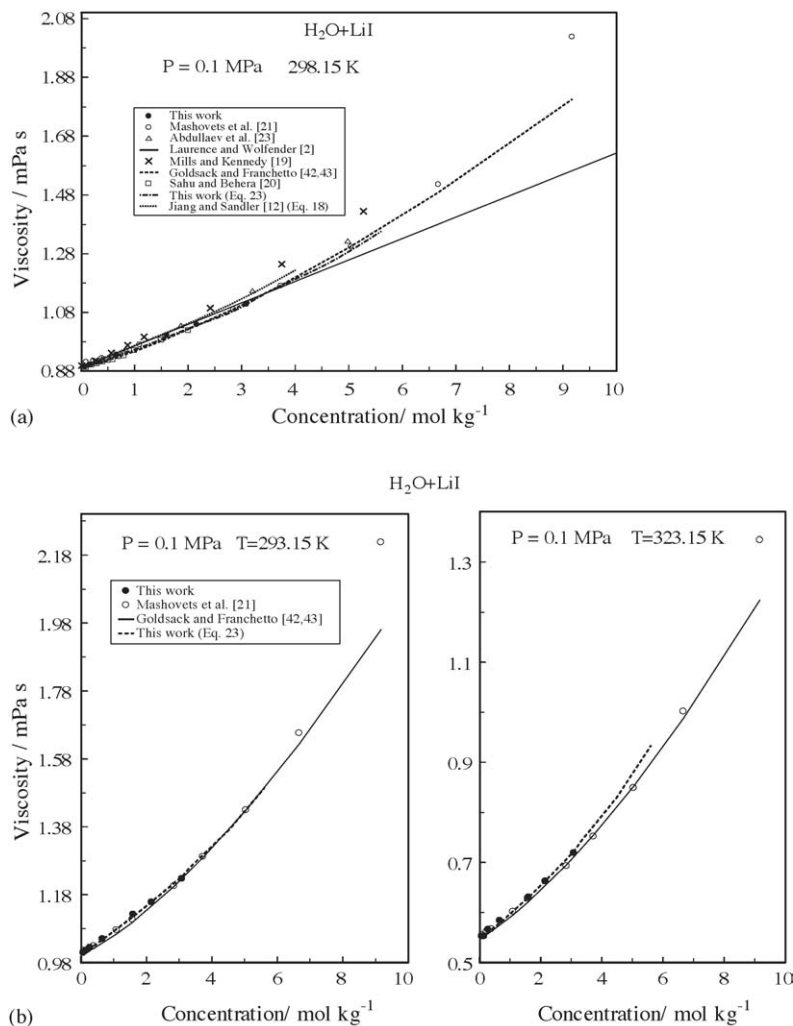


Fig. 1. (a and b) Measured values of viscosity  $\eta$  of LiI(aq) solutions as a function of molality  $m$  along various selected isotherms of 293.15, 298.15, and 323.15 K and at atmospheric pressure together with published data.

Table 3

The values of parameters  $\ln A$  and  $b$  (Eq. (2)) for LiI(aq) as a function of composition at atmospheric pressure

$m$ (mol kg <sup>-1</sup> )	$\ln A$ (mPa s)	$b = E_a/R$ (K)
0.0800	-5.9551	1741.18
0.1600	-5.9346	1736.77
0.2832	-5.9038	1730.54
0.6621	-5.7453	1691.68
1.6046	-5.5306	1647.77
2.1603	-5.4018	1620.67
3.0886	-5.2323	1588.74

Table 4

The values of parameters  $V$  and  $E$  (Eq. (4)) for LiI(aq) as a function of temperature

$T$ (K)	$V$	$E$	$B$ (dm <sup>3</sup> mol <sup>-1</sup> ) Eq. (17)
293.15	7.90	10.9	0.0541
298.15	7.70	11.1	0.0613
303.15	7.53	11.1	0.0649
323.15	6.45	11.1	0.0837
333.15	6.04	11.1	0.0911
353.15	5.41	11.1	0.1025

values of parameter  $V$  monotonically decreasing as temperature increases.

### 3.2. Pressure dependence of the viscosity of LiI(aq) solutions

The viscosity is little affected (up to 3–4%) at high temperatures (367 K) and high concentrations (3 mol kg<sup>-1</sup>) and up to 1.0% at low temperatures (298 K) by pressure (for pressures between 0.1 and 40 MPa) along the isotherms–isopleths (see Fig. 3). The pressure dependence of the experimental viscosities for LiI(aq) in the range from 0.1 to 40 MPa is almost linear (see Fig. 3). Leyendekkers [48] and Leyendekkers and Hunter [49] have applied the Tammann–Tait–Gibson (TTM) model to the calculation of viscosity of the aqueous electrolyte solutions at high pressures. According TTM model the viscosity equation can be present as:

$$\eta_s = \eta_{wis} \exp[f(m)], \quad (6)$$

$$f(m) = a_1 m + a_2 m^2 + \dots, \quad (7)$$

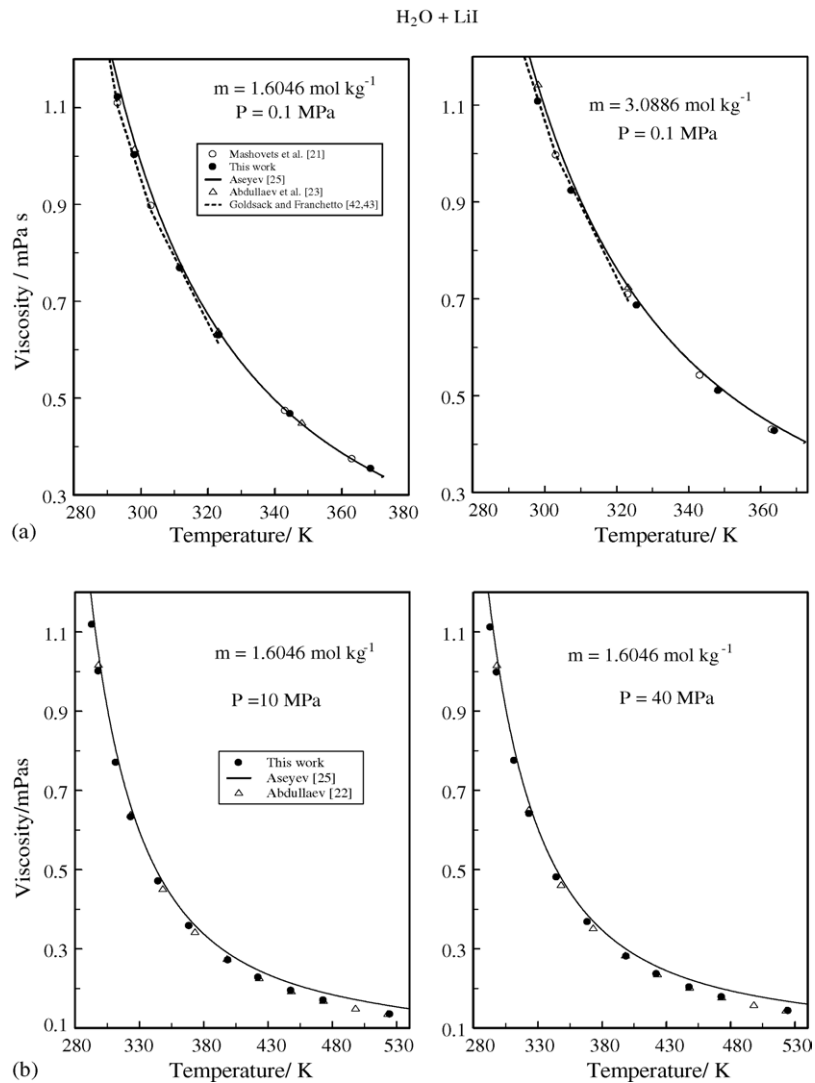


Fig. 2. (a and b) Measured values of viscosity  $\eta$  of LiI(aq) solutions as a function of temperature  $T$  at selected concentrations of 1.6046 and 3.0886 mol kg<sup>-1</sup> and at pressures of 0.1, 10, and 40 MPa together with reported data.

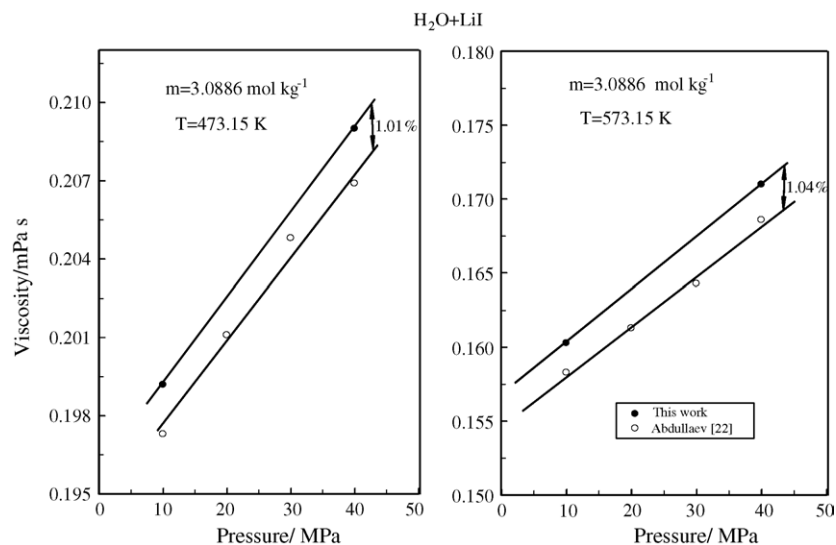


Fig. 3. Measured values of viscosity  $\eta$  of LiI(aq) solutions as a function of pressure  $P$  at two selected temperatures 473.15 and 573.15 K and at concentration of 3.0886 mol kg<sup>-1</sup>. The solid lines are guides for the eye.

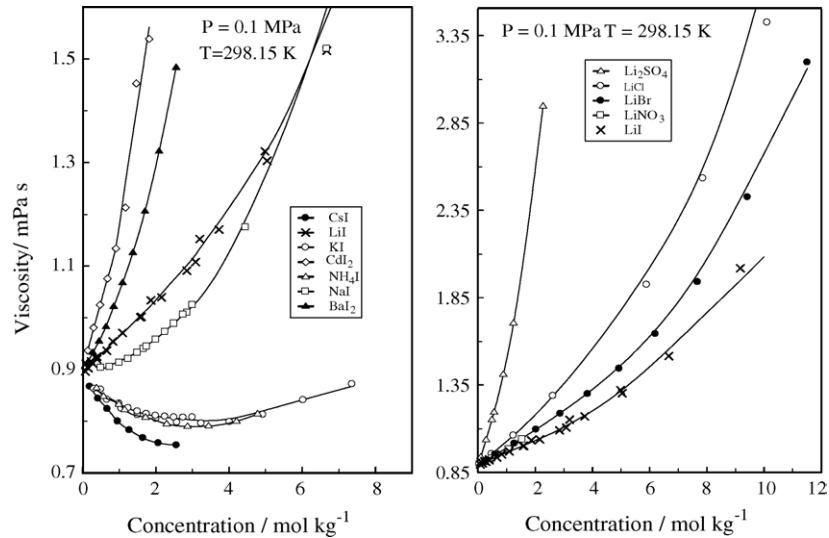


Fig. 4. Viscosity of a series of aqueous solutions as a function of composition at a selected temperature 298.15 K and a pressure of 0.1 MPa reported by various authors (this work and [44,87–89,91]).

where  $\eta_S$  and  $\eta_{wis}$  are the viscosities of the solution and water in solution, respectively, and  $m$  is the concentration in molality. This model predicts the viscosity of the solution at pressure  $P$  as:

$$\frac{\eta_S^{(P)}}{\eta_S^{(1)}} = \frac{\eta_W^{(P_e+P)}}{\eta_W^{(P_e+1)}}, \quad (8)$$

where  $\eta_w$  is the viscosity of pure water,  $P$  the external pressure, and  $P_e$  is the effective pressure due to the salt (function of concentration):

$$P_e = h_0 + h_1x + h_2x^2 + h_3x^3, \quad (9)$$

where  $x$  is the concentration of the solute in grams per gram of solution and  $h_i$  parameters are functions of temperature only. The lack of the  $P_e$  data as a function of temperature precluded

the testing of Eq. (8) for LiI(aq) solution. We used this technique to predict the pressure dependence of the viscosity of NaBr(aq) and CaCl<sub>2</sub>(aq) solutions for which there are the  $P_e$  data. The difference between predicted and measured values of viscosity for these solutions is about 0.5–1.0%.

### 3.3. Concentration dependence of the viscosity of LiI(aq) solutions

For some electrolyte solutions such as H<sub>2</sub>O + NaCl, H<sub>2</sub>O + LiCl, H<sub>2</sub>O + LiBr, H<sub>2</sub>O + LiI, H<sub>2</sub>O + NaF, H<sub>2</sub>O + KF, H<sub>2</sub>O + RbF, and H<sub>2</sub>O + CsF the viscosity increases monotonically with the electrolyte concentration, while for other types of electrolyte solutions such as H<sub>2</sub>O + KCl, H<sub>2</sub>O + RbCl, H<sub>2</sub>O + CsCl, H<sub>2</sub>O + KI, and H<sub>2</sub>O + KBr, the viscosity decreases with concentration at low electrolyte concentrations reaching a

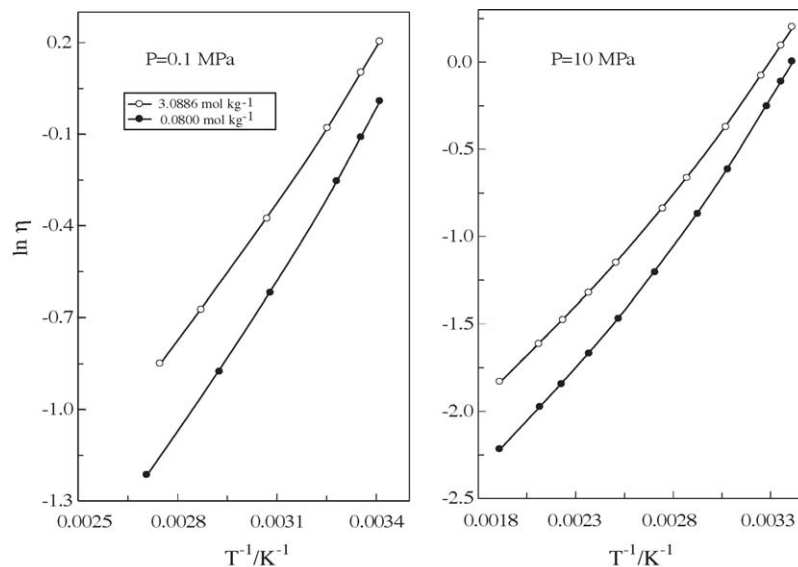


Fig. 5. Measured values of  $\ln \eta$  as a function of  $T^{-1}$  (Arrhenius plot) at two selected concentrations 0.0800 and 3.0886 mol kg<sup>-1</sup> and at pressures 0.1 and 10 MPa.

minimum value, then increasing monotonically for higher concentrations (see, for example, Fig. 4). As one can see from Fig. 1(a and b), the viscosity of LiI(aq) solutions monotonically increases with the electrolyte concentration without minimum.

The existing theoretical result, which describes the concentration dependence of the viscosity of ionic solutions, is valid only at very dilution. Falkenhagen–Onsager–Fuoss [9,10,50] and Debye–Hückel–Onsager [51,52] theories predict a square-root concentration,  $(\eta/\eta_0) \propto \sqrt{c}$ , dependence of the viscosity of ionic solutions at infinite dilution ( $c \rightarrow 0$ ). 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 considerations. Therefore, this model is inadequate when intermolecular correlations become important. Jones and Dole [53] proposed an empirical extension of the Falkenhagen [4–8] model to high concentrations as:

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc, \quad (10)$$

for the viscosity of electrolyte solutions. In Eq. (10),  $\eta$  and  $\eta_0$  are the viscosities of an electrolyte solution and pure solvent (water), respectively,  $A$  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 the theory cannot exactly predict the concentration range where Eq. (10) is valid. Usually, the values of the parameters of Eq. (10) are determined by fitting over various concentration ranges. The optimal concentration range also depends on the temperature. The values of  $B$ -coefficient strongly depend on the fitting concentration range. This is one of the reasons of the discrepancies between reported by various authors' the values of the  $B$ -coefficients. Eq. (10) provides a better description of the experimental viscosity data than limiting law,  $(\eta/\eta_0) = 1 + A\sqrt{c}$ . Falkenhagen and Dole [9,10] gave a theoretical derivation of the  $A$ -coefficient. Its general form is [54]:

$$A = \frac{A^*}{\eta_0(\varepsilon_0 T)^{1/2}} f(\lambda_+^\infty, \lambda_-^\infty, z_+, z_-), \quad (11)$$

$$A^* = \frac{\text{Fe}^2 N_A^{1/2} (1 + \sqrt{2})}{12\pi(\varepsilon^* k)^{1/2}},$$

$$f = \frac{z^2(\lambda_+^\infty + \lambda_-^\infty)}{4(2 + \sqrt{2})(\lambda_+^\infty \lambda_-^\infty)} \left[ 1 - \frac{4(\lambda_+^\infty - \lambda_-^\infty)^2}{(1 + \sqrt{2})^2 (\lambda_+^\infty + \lambda_-^\infty)^2} \right], \quad (12)$$

where  $A^* = 1.113 \times 10^{-5} \text{ }^\circ\text{C}^2 \text{ (m K mol}^{-3}\text{)}^{1/2}$ ,  $f(\lambda_+^\infty, \lambda_-^\infty, z_+, z_-)$  is a function of the equivalent conductences  $\lambda_\pm^\infty$  at infinite dilution of the ions, and  $z_\pm$  is the charges. The value of parameter  $A$  depends also on the viscosity of the pure solvent (water)  $\eta_0$  (IAPWS [41]), its relative permittivity (dielectric constant)  $\varepsilon_0$  (IAPWS [90]), and the temperature  $T$ . 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 behavior of the aqueous electrolyte solutions. The values of ionic  $B^\pm$ -coefficients are constant at a given  $T$  for given ions in a specific solvent and describe solely the ion–solvent interactions. The values of  $B^\pm$ -coefficients for various ions at different temperatures are available in the literature (see, for example Jenkins and Marcus [54]). The behavior of the concentration dependence of the viscosity of solutions depends on the nature of the solute ions. The values of  $A$ - and  $B$ -coefficients of an electrolyte provide information on the interaction between dissolved ions ( $\text{Li}^{1+}$ ,  $\text{I}^{1-}$ ) and molecules of a solvent ( $\text{H}_2\text{O}$ ). For example, the  $A$ -coefficient of the Jones–Dole equation is determined by ion–atmosphere interaction (long-range coulombic interactions) and ionic mobilities of solute ions. The  $B$ - and  $D$ -coefficients are adjustable parameters and related to the size and shape of the ions and the ion–solvent and ion–ion interactions, respectively. Therefore, the viscosity  $A$ - and  $B$ -coefficients of electrolyte solutions are useful tools in study structural interactions (ion–ion, ion–solvent, and solvent–solvent) in solutions. An extensive compilation of Jones–Dole  $A$ - and  $B$ -coefficients for a series aqueous electrolyte solutions is reported by various authors [1,46,54–68]. Low concentration viscosity measurements for most aqueous electrolyte solutions show good agreement between experiment and theory [57–61,69–72]. The values of the  $A$ -coefficient are 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 the  $B$ -coefficient is associated with structure-breaking (disordering) ions. The temperature coefficient of  $B$  ( $\text{dB}/\text{dT} > 0$ ), is positive in most case. For example,  $\text{dB}/\text{dT} < 0$  for  $\text{Mg}^{2+}$  and  $\text{Li}^+$  is negative, for  $\text{Na}^+$  it is almost zero, and for  $\text{K}^+$  it is positive. The values of  $B$ -coefficients for  $\text{Li}^+$  are decreasing with temperature ( $\text{dB}/\text{dT} < 0$ ), while for  $\text{I}^-$  are increasing with temperature ( $\text{dB}/\text{dT} > 0$ ) (Jenkins and Marcus [54]). The viscosity  $B$ -coefficient 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 values of  $A$ - and  $B$ -coefficients for aqueous LiI solutions as a function of temperature in the range from 298 to 523 K.

Some authors [57–60,67,73–75] added a quadratic term  $Dc^2$  (extended Jones–Dole equation):

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2, \quad (13)$$

to extend the Jones–Dole equation for more concentrated electrolyte solutions ( $c < 0.1\text{--}0.2m$ ). The new  $Dc^2$  term of Eq. (13) 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 [46,67,74]: high terms of the long-range coulombic forces; high term hydrodynamic effect; and interactions arising from changes in solute–solvent interactions with concentration. The range of the concentration in present study



Table 5

The viscosity  $A$ -,  $B$ -, and  $D$ -coefficients (Eq. (13)) of aqueous LiI(aq) as a function of temperature

$T$ (K)	$A$ (dm <sup>3/2</sup> mol <sup>-1/2</sup> )	$B$ (dm <sup>3</sup> mol <sup>-1</sup> )	$D$ (dm <sup>6</sup> mol <sup>-2</sup> )
298.15 <sup>a</sup>	0.0042	0.073	0.005
323.15 <sup>a</sup>	0.0056	0.085	0.010
373.15 <sup>a</sup>	0.0080	0.116	0.011
423.15 <sup>b</sup>	0.0100	0.135	0.012
473.15 <sup>b</sup>	0.0140	0.145	0.014
523.15 <sup>b</sup>	0.0160	0.160	0.021

<sup>a</sup> At pressure of  $P=0.1$  MPa.

<sup>b</sup> At pressure of  $P=10$  MPa.

is overlaps range where  $Bc$  and  $Dc^2$  terms are essential. In our previous publications (Abdulagatov et al. [30–33]), we included one more term,  $Fc^{2.5}$ , for applications to higher concentrations:

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2 + Fc^{2.5}. \quad (14)$$

Including a term containing the  $Fc^{2.5}$ , the concentration range of the validity of Eq. (14) can be sufficiently extended to higher concentrations. The present experimental data for the relative viscosity ( $\eta/\eta_0$ ) for various temperatures, together with data reported by other authors for LiI(aq) at low concentrations were used to calculate  $A$ -,  $B$ -, and  $D$ -coefficients in the extended Jones and Dole Eq. (13) in the concentration range up to 3 mol kg<sup>-1</sup>. The results are summarized in Table 5 and presented in Fig. 6 as a function of temperature, together with values reported by other authors and those calculated from theory. As one can see from Fig. 6, the agreement between the  $A$ - and  $B$ -coefficients derived in present study and those calculated with theory and the ionic  $B$ -coefficient data, is good. Fig. 6 also demonstrates that the  $A$ -coefficient monotonically increasing (almost linearly) with temperature and the derivative (temperature coefficient)  $dB/dT > 0$  is positive (structure-breaking ions).

According to a conventional technique of determining the viscosity coefficient, the  $B$ - and  $D$ -coefficients can be estimated

also from experimental viscosity data by extrapolating the function:

$$B + Dc = \frac{(\eta/\eta_0) - 1 - Ac^{1/2}}{c}, \quad (15)$$

to zero concentration ( $c \rightarrow 0$ ), using theoretical value of  $A$  (Eqs. (11) and (12)), or the slope of the experimental dependence  $[(\eta/\eta_0) - 1]/c^{1/2}$  on  $c^{1/2}$  (Jones–Dole plot; see Fig. 7):

$$\frac{(\eta/\eta_0) - 1}{c^{1/2}} = A + Bc^{1/2}. \quad (16)$$

The experimental values of the  $A$ - and  $B$ -coefficients are determined by plotting the left side of the Eq. (16),  $[(\eta/\eta_0) - 1]/c^{1/2}$ , against  $c^{1/2}$ . Fig. 7 illustrate such plots for a LiI(aq) solutions for the selected temperature of 298.15 K. The intercept and slope of the linear plot are viscosity  $A$ - and  $B$ -coefficients, respectively. Unfortunately, there are no experimental viscosity data for LiI(aq) at dilute to accurate determination of the intercepts and slopes of the Jones–Dole plot. Therefore, the estimated uncertainty in derived values of the  $A$ - and  $B$ -coefficients from Eq. (13) is about 0.001–0.0021 mol<sup>-1</sup>.

The Jones–Dole viscosity  $B$ -coefficient is related to the parameters  $V$  and  $E$  in Eq. (4) by the relation:

$$B = \frac{E - V}{55.51}. \quad (17)$$

The values of viscosity  $B$ -coefficients calculated with Eq. (17) using the values of  $V$  and  $E$  parameters for LiI(aq) are given in Table 4 and shown in Fig. 6 together with data reported in the literature. The agreement between these data and the values derived by other authors is acceptable (4–5%).

Jiang and Sandler [12] proposed a new statistical mechanics-based equation to describe the concentration dependence of the viscosity of various types electrolyte solutions. This model based on the combination of liquid-state theory and absolute-rate theory. The adjustable parameters in the model ( $\sigma_1^+$ ,  $\varepsilon_1$ ,  $b$ ) have physical meaning and are related with the degree of ion

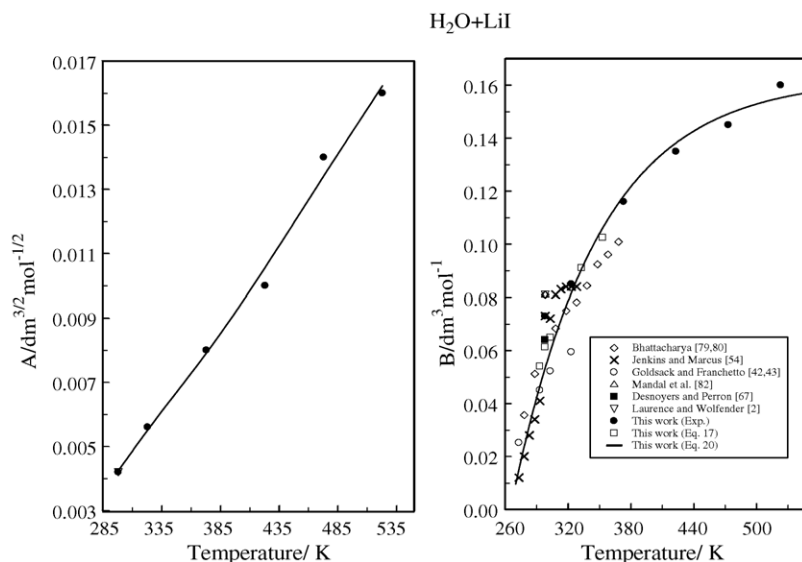


Fig. 6. Experimental viscosity  $A$ - and  $B$ -coefficients of the LiI(aq) solutions as a function of temperature together with values reported by other authors.

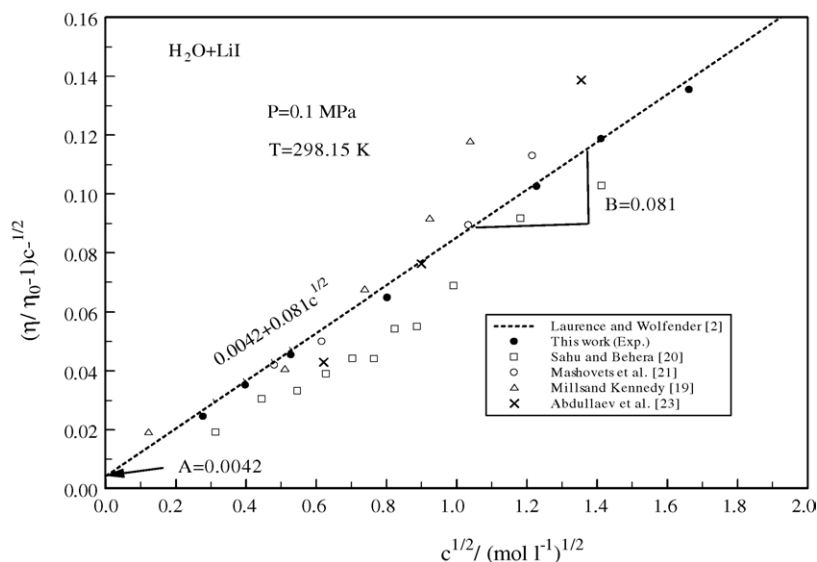


Fig. 7. Jones–Dole plot  $[(\eta/\eta_0) - 1]/c^{1/2}$  vs.  $c^{1/2}$  for LiI(aq) solutions for selected isotherms of 298.15 K at atmospheric pressure.

hydration. According to the model, the reduced viscosity of the electrolyte solution is:

$$\eta = \eta_0(1 + a\sqrt{x} + bx) \exp\left(\frac{f_{\text{EX}}}{RT}\right), \quad (18)$$

where  $f_{\text{EX}}$  is the excess contribution of the activation Helmholtz energy of the solution with the pure solvent. Jiang and Sandler [12] provided the analytical expression for hard-sphere and electrostatic contributions,  $f_{\text{EX}} = f_{\text{HS}} + f_{\text{EL}}$ . This model was applied to LiI(aq) solution to describe the concentration dependence of viscosity (up to  $4.4 \text{ mol l}^{-1}$ ) at 298.15 K and atmospheric pressure. Fig. 1 shows the comparison of the model with present experimental data. The agreement is within 0.3–0.5%.

Lencka et al. [13] developed a comprehensive model for calculating the viscosity of aqueous electrolyte solutions ranging from dilute to very concentrated. The model includes a long-range electrostatic interactions term,  $\eta_r^{\text{LR}}$  (Onsager–Fuss theory), contributions of individual ions,  $\eta_r^{\text{S}}$  (Jones–Dole  $B$ -coefficients), and a contribution of specific interactions between ions or neutral species,  $\eta_r^{\text{S-S}}$  (for the concentrated solutions, function of the ionic strength):

$$\frac{\eta}{\eta_0} = 1 + \eta_r^{\text{LR}} + \eta_r^{\text{S}} + \eta_r^{\text{S-S}}, \quad (19)$$

where analytical expression for  $\eta_r^{\text{LR}}$ ,  $\eta_r^{\text{S}}$ , and  $\eta_r^{\text{S-S}}$  are given in Ref. [13]. A technique for predicting the temperature dependence of the viscosity  $B$ -coefficients has been developed using the concept of structure-breaking and structure-making ions [13]:

$$B = B_E + B_S \exp[-K(T - 273.15)], \quad (20)$$

where  $K=0.012$  is the constant;  $B_E=0.16261 \text{ mol}^{-1}$  the Einstein contribution (hydrodynamic, intrinsic term); and  $B_S = -0.14731 \text{ mol}^{-1}$  were calculated using the present values of  $B$ -coefficients for LiI(aq). The model reproduces the viscosity of aqueous systems ranging from dilute to concentrated solu-

tions ( $30m$ ) at temperatures up to 573 K. The comparisons the values of  $B$ -coefficients calculated from Eq. (20) with the values reported in the literature are given in Fig. 6. As one can see, this model excellent represent present and published data for LiI(aq) at temperatures up to 523 K.

Einstein [76] has calculated the size effect (hydrodynamic effect) for an infinitely dilute suspension of rigid spherical particles in a continuum and obtained following expression:

$$\frac{\eta}{\eta_0} = 1 + k\phi, \quad (21)$$

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 or hydrodynamic radius of the ions, and  $c$  is the salt concentration). For solid spheres with a diameter large compared to molecular dimensions, the value of  $k$  in Eq. (21) is commonly accepted to be 2.5, although values as large as 5.5 have been suggested by Happel [77]. If  $\phi$  is expressed in terms of the concentration in  $\text{mol l}^{-1}$ , then Eq. (21) becomes:

$$\frac{\eta}{\eta_0} = 1 + 2.5 V_k c, \quad (22)$$

where  $V_k$  is the hydrodynamic molar volume in  $\text{cm}^3 \text{ mol}^{-1}$ . If Einstein's Eq. (21) is related to the Jones–Dole Eq. (10), the

Table 6  
The values of  $V_k$  (Eq. (23)) for LiI(aq) as a function of temperature at atmospheric pressure

$T$ (K)	$V_k$ ( $\text{l mol}^{-1}$ )
293.15	0.0258
298.15	0.0271
303.15	0.0286
313.15	0.0312
323.15	0.0337
333.15	0.0357
343.15	0.0375
353.15	0.0389

$B$ -coefficient can then be related to the molar volume  $V_k$  by  $B = 2.5V_k$ . As discussed by Desnoyers and Perro [67],  $V_k$  should be given by the partial molar volume of the solute  $\bar{V}$ , although other authors (for example, Skinner and Fuoss [78]) considered  $V_k$  as the apparent molar volume. General empirical expressions have been proposed by several authors [79–81] for the  $B$ -coefficient  $B = a\bar{V}^\infty + b$ . Other authors prefer to use the

volumes of hydrated ions ( $V_h$ ) instead of  $\bar{V}^\infty$ , with the coefficient  $a$  nearer to 5 or 6 (Mandal et al. [82]). Therefore, for such an ideal system the viscosities are predictable from densities and vice versa. Isono and Tamamushi [83] 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

Table 7

Deviations,  $\delta\eta = 100(\eta_{\text{exp}} - \eta_{\text{rep}})/\eta_{\text{exp}}$ , of present experimental values of viscosity from those reported by various authors from the literature

$m$ (mol kg <sup>-1</sup> )	Abdullaev et al. [23] (at high pressures)						
	298.15 K	323.15 K	373.15 K	423.15 K	473.15 K	523.15 K	
0.6621	-0.6	-0.3	0.3	-0.1	1.9	0.4	
1.6046	-0.9	-0.5	0.5	0.6	1.6	0.4	
2.1603	-1.9	-0.6	0.9	1.7	1.8	0.5	
3.0886	-3.7	-1.2	0.6	1.4	2.3	1.4	
Deviation statistics	AAD = 1.2; bias = 0.27; S.D. = 1.51; S.E. = 0.36; maximum deviation = 3.7						
$m$ (mol kg <sup>-1</sup> )	Mashovets et al. [21] (at atmospheric pressure)			Goldsack and Franchetto [42,43] (at atmospheric pressure)			
	293.15 K	298.15 K	323.15 K	293.15 K	298.15 K	323.15 K	
0.0800	-	-	-	-0.34	0.19	0.25	
0.1600	0.83	1.26	0.92	-0.55	0.25	0.00	
0.2832	-0.23	0.82	-0.55	-0.87	-0.71	-1.48	
0.6621	-0.25	0.68	-0.59	-1.13	-0.91	-1.57	
1.6046	-1.31	0.11	-0.19	-1.50	-1.13	-1.60	
2.1603	-0.52	0.25	-0.73	-0.94	0.78	-1.19	
3.0886	0.13	0.43	-1.40	0.03	0.51	-1.06	
Deviation statistics	AAD = 0.62; bias = -0.019; S.D. = 0.76; S.E. = 0.18; maximum deviation = 1.4			AAD = 0.81; bias = -0.62; S.D. = 0.74; S.E. = 0.16; maximum deviation = 1.6			
$m$ (mol kg <sup>-1</sup> )	Zaytsev and Aseyev [44]						
	293.15 K	298.15 K	304.77 K	324.62 K	341.64 K	369.35 K	
0.0800	0.11	0.11	0.07	0.06	0.04	-0.02	
0.1600	0.13	0.09	0.09	0.07	-0.01	-0.05	
0.2832	0.55	0.40	0.40	0.41	0.32	0.00	
0.6621	2.04	1.83	1.71	1.45	0.98	1.35	
1.6046	3.1	2.9	1.9	0.9	0.15	-0.39	
3.0886	4.1	3.2	2.4	2.1	2.1	2.7	
Deviation statistics (at $m < 0.6621$ )	AAD = 0.16; bias = 0.16; S.D. = 0.17; S.E. = 0.04; maximum deviation = 0.55						
Deviation statistics (at $m > 0.6621$ )	AAD = 1.9; bias = 1.9; S.D. = 1.1; S.E. = 0.3; maximum deviation = 4.1						
Mills and Kennedy [19]							
$m$ (mol kg <sup>-1</sup> )	298.15 K						
0.0800	0.82						
0.1600	0.71						
0.2832	0.68						
0.6621	1.45						
1.6046	2.80						
2.1603	3.35						
3.0886	5.58						
Deviation statistics	AAD = 2.2; bias = 2.2; S.D. = 1.8; S.E. = 0.7; maximum deviation = 5.6						

on temperature. As one can see, the values of  $a$  very close to the Einstein value of 2.5.

Thomas [84] has extended the Einstein relation (21) for the hydrodynamic effect to high concentrations by showing that for suspensions the relative viscosity is given by the relation:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 10.05\phi^2 = 1 + 2.5V_k c + 10.05V_k^2 c^2. \quad (23)$$

As was shown by Breslau and Miller [85], this relation can be used to represent the concentration dependence of the relative viscosity for concentrated electrolyte solutions if  $V_k$  is taken as an adjustable parameter. We determined the values of  $V_k$  as a function of temperatures for LiI(aq) in Eq. (23). The derived values of the  $V_k$  for LiI(aq) are given in Table 5. The value of  $V_k = 0.02711 \text{ mol}^{-1}$  at 298.15 K is satisfactory and agree with the value  $0.03201 \text{ mol}^{-1}$  reported by Sahu and Behera [20]. Therefore, the relation (23) can be used to estimate the values of the hydrodynamic volume  $V_k$  using experimental relative viscosity data. Moulik and Rakshit [86] also used Eq. (23) to correlate the concentration dependence of the viscosity of 72 different type electrolyte solutions at high concentrations. As Fig. 1 shows, calculated values of the relative viscosity for LiI(aq) with Eq. (23) are good represent present experimental viscosities in the concentration range up to  $3 \text{ mol kg}^{-1}$ . A least-squares fit of the correlation between viscosity  $B$ -coefficients and the hydrostatic volumes  $V_k$  for LiI(aq) results in the following correlation  $B = 3.46V_k - 0.0334$ . Breslau and Miller [85] correlation for the aqueous electrolyte solutions is  $B = 2.90V_k - 0.018$ . Sahu and Behera [20] also represented experimental relative viscosity of electrolyte solutions by extending the limiting Einstein equation as (Table 6):

$$\frac{\eta}{\eta_0} = 1 + 2.5\bar{V}c + k_1\bar{V}^2c^2 + k_2\bar{V}^3c^3 + k_3\bar{V}^4c^4, \quad (24)$$

where  $\bar{V}$  is the molar volume of electrolyte in solution ( $\text{dm}^3 \text{ mol}^{-1}$ ) and  $c$  is the concentration in  $\text{mol dm}^{-3}$ . The values of correlating coefficients  $k_i$  ( $i = 1, 3$ ) for series electrolyte solutions were derived from experimental viscosity data at  $25^\circ\text{C}$ .

### 3.4. Comparison with other data and correlation

The present experimental values of the viscosity for LiI(aq) solutions were compared with data reported by other authors in the literature. Figs. 1–3 demonstrates the direct comparison between present viscosity data for LiI(aq) solutions and the values reported by various authors from the literature. As one can see from these figures, basically the agreement between various data sets is good, except scattering (up to 10%) some data sets at high concentrations ( $m > 3 \text{ mol kg}^{-1}$ ). These figures illustrate that our data are consistent well with most literature values at various pressures, temperatures, and concentrations. The relative percentage deviations between present viscosity data for LiI(aq) solutions and the data reported by other researchers are given in Table 7 together with their deviation statistics. Most reported data at atmospheric pressure lie between 0.6 and 2.0%, which close to their experimental estimated uncertainty (1.5%). Excellent agreement within 0.6–0.8% is observed

between present measurements and data reported by Mashovets et al. [21] and Goldsack and Franchetto [42,43] at temperatures between 298.15 and 323.15 K and at atmospheric pressure. The data of Abdullaev [22] and Abdullaev et al. [23] agree with present results within  $\pm 1.2\%$  at high pressures and at high temperatures (from 298.15 to 523 K). These data are generally within 0.6–0.7% of the present results at concentration below  $2.1603 \text{ mol kg}^{-1}$  and at atmospheric pressure, while at high concentrations and high pressures the deviations are within  $\pm 1.6\%$  (see Fig. 3), the maximum deviation is 3.7%. Differences up to 0.16% are found for the viscosities calculated with Aseyev [25] correlation at low concentrations ( $m < 0.6621 \text{ mol kg}^{-1}$ ) and up to 1.9% at high concentrations ( $m > 0.6621 \text{ mol kg}^{-1}$ ). The data reported by Mills and Kennedy [19] are consistently 2.2% higher than present data at 298 K and atmospheric pressure. Maximum deviation up to 5–6% is found for the data by Mills and Kennedy [19] at high concentrations (around  $3.0 \text{ mol kg}^{-1}$ ).

## 4. Conclusions

Viscosities of seven (0.0800, 0.1600, 0.2832, 0.6621, 1.6046, 2.1603, and  $3.0886 \text{ mol kg}^{-1}$ ) aqueous LiI solutions have been measured with a capillary-flow technique. Measurements were made at pressures up to 40 MPa. The temperature range was 293–525 K. The reliability and accuracy of the experimental method and the reported values of viscosities for LiI(aq) were confirmed with measurements on pure water. The experimental and calculated values of viscosity for pure water from the IAPWS [41] formulation show excellent agreement with our results, within their experimental uncertainty (AAD = 0.63%). Good agreement (within 0.6–2.0%) is found between the present measurements and the most data sets reported by other authors in the literature. The temperature, pressure, and concentration dependencies of the viscosity were studied. The values of the viscosity  $A$ -,  $B$ -, and  $D$ -coefficients of the extended Jones–Dole equation were obtained for the relative viscosity ( $\eta/\eta_0$ ) of aqueous LiI solutions as a function of temperature. It was found that the temperature coefficient,  $dB/dT > 0$ , for LiI(aq) is positive (structure-breaking ions). Physical meaning parameters  $V$  and  $E$  in the absolute-rate theory of viscosity and hydrodynamic molar volume  $V_k$  were calculated using present experimental viscosity data. The Arrhenius–Andrade parameters ( $A$  and  $E_a/R$ ) were calculated from the measured values of viscosity. The predicted capability and validity of the various theoretical models for the viscosity of LiI(aq) solutions were tested.

## Acknowledgement

Abdulagatov I.M. thanks the Physical and Chemical Properties Division at the National Institute of Standards and Technology for the opportunity to work as a Guest Researcher at NIST during the course of this research.

## References

- [1] W.M. Cox, J.H. Wolfenden, Proc. R. Soc. A (Lond.) 145 (1934) 475.
- [2] V.D. Laurence, J.H. Wolfender, J. Chem. Soc. (1934) 1144.

- [3] Y. Marcus, *Ion Solvation*, John Wiley & Sons Inc., NY, 1985.
- [4] H. Falkenhagen, E.L. Vernon, *Phys. Z.* 33 (1932) 140.
- [5] H. Falkenhagen, *Nature* 127 (1931) 439.
- [6] H. Falkenhagen, *Theorie der Elektrolyte*, S. Hirzel, Leipzig, 1971.
- [7] H. Falkenhagen, *Z. Phys.* 32 (1931) 745.
- [8] H. Falkenhagen, *Z. Physik. Chem. B* 6 (1931) 159.
- [9] H. Falkenhagen, M. Dole, *Phys. Z.* 30 (1929) 611.
- [10] H. Falkenhagen, M. Dole, *Z. Phys. Chem. B6* (1929) 159.
- [11] P. Wang, A. Anderko, R.D. Young, *Fluid Phase Equilib.* 226 (2004) 71.
- [12] J. Jiang, S.I. Sandler, *Ind. Eng. Chem. Res.* 42 (2003) 6267.
- [13] M.M. Lencka, A. Anderko, S.J. Sanders, R.D. Young, *Int. J. Thermophys.* 19 (1998) 367.
- [14] M.J.C. Esteves, J.E. de M. Cardoso, O.E. Barcia, *Ind. Eng. Chem. Res.* 40 (2001) 5021.
- [15] A. Chandra, B. Bagchi, *J. Chem. Phys.* 113 (2000) 3226.
- [16] A. Chandra, B. Bagchi, *J. Phys. Chem.* 104 (2000) 9067.
- [17] A. Anderko, P. Wang, M. Rafal, *Fluid Phase Equilib.* 194–197 (2002) 123.
- [18] Yu. Hu, *Chem. Eng. Sci.* 59 (2004) 2457.
- [19] F.R. Mills, J.W. Kennedy, *J. Am. Chem. Soc.* 75 (1953) 5696.
- [20] B. Sahu, B. Behera, *Ind. J. Chem. A* 19 (1980) 1153.
- [21] V.P. Mashovets, N.M. Baron, M.U. Sherba, *Russ. J. Appl. Chem.* 9 (1971) 1981.
- [22] A.A. Abdullaev, Ph.D. Thesis, Azer. Institute of Oil and Gas, Baku, Azerbaijan, 1991.
- [23] A.A. Abdullaev, A.I. Iskenderov, T.S. Akhundov, *Aqueous solutions of LiCl, LiBr, and LiI. Density, vapor pressures, and dynamic viscosity*, in: *Recommended Values, GSSSD, Moscow*, 1991.
- [24] V.M.M. Lobo, J.L. Quaresma, *Electrolyte Solutions*, vol. II, University of Coimbra, Coimbra, Portugal, 1981.
- [25] G.G. Aseyev, *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.
- [26] I.M. Abdulagatov, N.D. Azizov, *J. Chem. Eng. Data* 48 (2003) 1549.
- [27] I.M. Abdulagatov, N.D. Azizov, *Ind. Eng. Chem. Res.* 44 (2005) 416.
- [28] I.M. Abdulagatov, N.D. Azizov, *Int. J. Thermophys.* 26 (2005) 593.
- [29] I.M. Abdulagatov, A.A. Zeinalova, N.D. Azizov, *Fluid Phase Equilib.* 227 (2005) 57.
- [30] I.M. Abdulagatov, A.A. Zeinalova, N.D. Azizov, *J. Chem. Eng. Data* 49 (2004) 1444.
- [31] I.M. Abdulagatov, N.D. Azizov, *J. Sol. Chem.* 34 (2005) 645.
- [32] I.M. Abdulagatov, A.A. Zeinalova, N.D. Azizov, *J. Chem. Thermodyn.*, in press.
- [33] I.M. Abdulagatov, A.A. Zeinalova, N.D. Azizov, *J. Mol. Liquids*, in press.
- [34] S.L. Rivkin, E.A. Kremenevskaya, S.N. Romashin, O.M. Tractuev, in: V.V. Sytchev, A.A. Aleksandrov (Eds.), *Proc. 10th Int. Conf. Prop. Steam*, v.2, Mir Publ., Moscow, 1984, p. 289.
- [35] L.V. Puchkov, P.M. Sargaev, *Russ. J. Appl. Chem.* 46 (1973) 2637.
- [36] R.J. Lee, R.M. DiGuilio, S.M. Jeter, A.S. Teja, *ASHRAE Trans.* 96 (1990) 709.
- [37] R.I. Pepinov, N.V. Lobkova, I.A. Panakhov, *Russ. High Temp.* 27 (1989) 1086.
- [38] W.A. Wakeham, A. Nagashima, J.V. Sengers (Eds.), *Measurements of the Transport Properties of Fluids*, vol. III, Blackwell Scientific Publications, Oxford, 1991.
- [39] J.F. Swindells, J.R. Coe Jr., T.B. Godfrey, *J. Res. NBS* 48 (1952) 1.
- [40] I.M. Abdulagatov, N.D. Azizov, *J. Chem. Thermodyn.* 36 (2004) 829.
- [41] J. Kestin, J.V. Sengers, B. Kamgar-Parsi, J.M.H. Levelt Sengers, *J. Phys. Chem. Ref. Data* 13 (1984) 175.
- [42] D.E. Goldsack, R.C. Franchetto, *Can. J. Chem. Rev. Can. Chim.* 56 (1978) 1442.
- [43] D.E. Goldsack, R.C. Franchetto, *Can. J. Chem. Rev. Can. Chim.* 55 (1977) 1062.
- [44] I.D. Zaytsev, M.A. Aseyev, *Properties of Aqueous Solutions of Electrolyte*, CRC Press, Boca Raton, 1992.
- [45] S. Glasstone, K. Laidler, E. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
- [46] R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon Press, Inc., New York, 1965.
- [47] T. Erday-Grúz, *Transport Phenomena in Aqueous Solutions*, John Wiley & Sons Inc., NY, 1974.
- [48] J.V. Leyenndekkers, *J. Sol. Chem.* 8 (1979) 853.
- [49] J.V. Leyenndekkers, R.J. Hunter, *J. Chem. Eng. Data* 22 (1977) 427.
- [50] L. Onsager, R.M. Fuoss, *J. Phys. Chem.* 36 (1932) 2689.
- [51] P. Debye, H. Hückel, *Z. Phys.* 25 (1924) 49.
- [52] L. Onsager, *Z. Phys.* 27 (1926) 388.
- [53] G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [54] H.D.B. Jenkins, Y. Marcus, *Chem. Rev.* 95 (1995) 2695.
- [55] A.L. Horvath, *Handbook of Aqueous Electrolyte Solutions: Physical Properties, Estimation Methods and Correlation Methods*, Ellis Horwood, West Sussex, England, 1985.
- [56] R.A. Horne (Ed.), *Water and Aqueous Solutions, Structure, Thermodynamics, and Transport Properties*, Wiley Interscience, New York, NY, 1972.
- [57] M. Kaminsky, *Z. Phys. Chem.* 5 (1955) 154.
- [58] M. Kaminsky, *Z. Phys. Chem.* 12 (1957) 206.
- [59] M. Kaminsky, *Z. Phys. Chem. (N.F.)* 8 (1956) 173.
- [60] G. Jones, S.K. Talley, *J. Am. Chem. Soc.* 55 (1933) 4124.
- [61] E. Hückel, H. Schaaf, *Z. Phys. Chem. N.F.* 21 (1959) 326.
- [62] R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, second ed., Butterworths Scientific Pub., London, 1959.
- [63] R. Dordick, L. Korson, W. Drost-Hansen, *J. Colloid. Inter. Sci.* 72 (1979) 206.
- [64] R.S. Dordick, W. Drost-Hansen, *J. Phys. Chem.* 85 (1981) 1086.
- [65] R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* 70 (1966) 2336.
- [66] Y.C. Wu, *J. Phys. Chem.* 72 (1968) 2663.
- [67] J.E. Desnoyers, G. Perron, *J. Sol. Chem.* 1 (1972) 199.
- [68] R. Palepu, G. Worth, G. Marangoni, *Thermochim. Acta* 136 (1988) 119.
- [69] E. Asmus, *Z. Phys.* 108 (1938) 491.
- [70] E. Asmus, *Ann. Der. Phys.* 35 (1939) 1.
- [71] D.J.P. Out, J.M. Los, *J. Sol. Chem.* 9 (1980) 19.
- [72] P.K. Mandal, D.K. Chatterjee, B.K. Seal, A.S. Basu, *J. Sol. Chem.* 7 (1978) 57.
- [73] D. Feakins, D.G. Lawrence, *Chem. Soc. A* (1966) 212.
- [74] J.E. Desnoyers, M. Arel, P.A. Leduc, *Can. J. Chem.* 47 (1969) 547.
- [75] C.T. Robertson, H.J.U. Tyrrell, *J. Chem. Soc. A* (1969) 1938.
- [76] A. Einstein, *Ann. Phys.* 34 (1911) 591.
- [77] J. Happel, *J. Appl. Phys.* 28 (1957) 1288.
- [78] J.F. Skinner, R.M. Fuoss, *J. Phys. Chem.* 67 (1964) 2998.
- [79] M.M. Bhattacharya, *Can. J. Chem.* 67 (1989) 1324.
- [80] M.M. Bhattacharya, *Bull. Chem. Soc. Jpn.* 65 (1992) 1170.
- [81] B.S. Krungal, *J. Chem. Soc. Faraday Trans. I* 78 (1982) 437.
- [82] P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem. (N.F.)* (Frankfurt) 87 (1973) 295.
- [83] T. Isono, R. Tamamushi, *Electrochim. Acta* 12 (1967) 1479.
- [84] D.G. Thomas, *J. Colloid. Sci.* 20 (1965) 267.
- [85] B.R. Breslau, I.F. Millero, *J. Phys. Chem.* 74 (1970) 1056.
- [86] S.P. Moulik, A.K. Rakshit, *J. Ind. Chem. Soc.* 52 (1975) 450.
- [87] D.T. Burns, *Electrochim. Acta* 10 (1965) 985.
- [88] T. Isono, *Rikagaku Kenkyusho Hokoku* 61 (1985) 53.
- [89] M. Afzal, M. Saleem, M. Tarlq Mahmood, *J. Chem. Eng. Data* 34 (1989) 339.
- [90] D.P. Fernandez, A.R.H. Goodwin, E.W. Lemmon, J.M.H. Levelt Sengers, R.C.A. Williams, *J. Phys. Chem. Ref. Data* 26 (1997) 1125.
- [91] M. Wimby, T. Berntsson, *J. Chem. Eng. Data* 39 (1994) 68.