https://doi.org/10.15407/ujpe64.3.230

#### V.M. MAKHLAICHUK

I.I. Mechnikov National University of Odesa (2, Dvoryans'ka Str., Odesa 65026, Ukraine; e-mail: interaktiv@ukr.net)

# SHEAR VISCOSITY OF AQUEOUS ELECTROLYTE SOLUTIONS

The kinematic shear viscosity of aqueous electrolyte solutions has been studied. The temperature dependence of this parameter is shown to be described by an exponential formula at  $T < T_d$  and a formula of the argon-like type at  $T > T_d$ , where  $T_d$  is the temperature of the dipole ordering, in the whole considered concentration interval. Main attention is focused on the peculiarities in the temperature and concentration dependences of the shear viscosity in the argon-like interval. It is shown that the root-like concentration dependence can appear, only if the Debye theory of dilute electrolyte solutions is applicable. Beyond its validity domain, the series expansion of the kinematic shear viscosity in the concentration parameter should have an analytical character. The latter behavior is inherent in the concentration dependence of the shear viscosity in the majority of experiments. The error of reproducing the experimental data did not exceed the experimental one, i.e. it was smaller than 4–5%.

Keywords: aqueous electrolyte solutions, kinematic shear viscosity, temperature dependence, concentration dependence.

#### 1. Introduction

Transport processes in aqueous electrolyte solutions attract the attention of scientists for a long time [1-4]. The majority of the works are based on the model of a hydration shell that arises around cations and anions in aqueous solutions [5-10]. The existence of hydration shells is considered to be the most important factor that directly affects the self-diffusion coefficients of ions. In particular, the self-diffusion coeffcient of neutral impurities in water can be described with a satisfactory accuracy, as a rule, by the wellknown Einstein formula [11, 12]. In this case, the radii of impurity molecules are in good agreement with the corresponding values estimated using the van der Waals radii of their constituent atoms. However, the application of the Einstein formula to the description of the self-diffusion coefficients of ions brings us to a conclusion that the effective radius of an ion substantially exceeds its van der Waals value [13]. This result is in a good agreement with the initial assumption about the role of hydration effects.

Hydrated complexes are also assumed to affect the shear viscosity of aqueous electrolyte solutions. This influence occurs identically as it takes place in dilute suspensions. In this case, the shear viscosity of a solution,  $\eta$ , is successfully described by the Einstein formula [11, 12]

$$\eta = \eta_0 \left( 1 + \frac{5}{2}\phi + \dots \right),\tag{1}$$

where  $\eta_0$  is the viscosity of water, and  $\phi$  is the relative volume occupied by the particles in the suspension. This dependence of the shear viscosity of weak electrolyte solutions on the relative volume of

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3

230

<sup>©</sup> V.M. MAKHLAICHUK, 2019

hydrated ions was obtained in the works by Falkenhagen [2,3], Fisher [4], and, later, some other authors [14, 15]. However, there is a discrepancy between the formulas obtained in the cited papers and the experimental data. Namely, according to works [1,3,4], the expansion of the shear viscosity in a series in the electrolyte concentration c, which is considered to be proportional to  $\phi$ , includes an additional root-like term:

$$\eta = \eta_0 (1 + A\sqrt{c} + Bc). \tag{2}$$

It should be noted that, at present, there is no consistent theory that would allow the coefficients in the root-like and linear terms to be reproduced selfconsistently and exactly.

A totally different approach to the calculation of the shear viscosity in liquids was developed in works [16–21]. The shear viscosity of molecular liquids was considered there as a result of the friction that occurs between the surfaces of molecular layers (Fig. 1). In those researches, it was shown that the normalized shear viscosity of a liquid  $\tilde{\nu} = \nu/\nu_{\rm tr}$ , where  $\nu_{\rm tr}$  is the kinematic shear viscosity at the triple point, is described by the formula

$$\tilde{\nu}(\tilde{v},t) \approx \frac{\zeta_0(t)}{(\tilde{v} - \tilde{v}_0^{(\mathrm{w})}(t))^{1/3}},\tag{3}$$

where  $t = T/T_{\rm tr}$  is the dimensionless temperature,  $T_{\rm tr}$  is the temperature at the triple point,  $\tilde{v} = v/v_{\rm tr}$  is the dimensionless specific volume, and  $v_{\rm tr}$  is the specific volume at the triple point. This formula successfully describes the shear viscosity for all those liquids, in which the averaged intermolecular potentials are similar to the Lennard-Jones potential in argon.

In work [17], it was shown that formula (3) reproduces the shear viscosity in such liquids as benzene, nitrobenzene, nitrogen, and liquid alkaline metals [22], as well as liquid transition metals [23], with a high accuracy. In work [20], it was shown that formula (3) also describes well the shear viscosity of water in a wide temperature interval 315 K < T < 620 K. The lower limit of this interval actually corresponds to the temperature of the crossover from the temperature interval inherent in normal water states, 273 K < T < 315 K, as well as supercooled ones, to the temperatures 315 K < T < 620 K [18]. The temperature dependence of the shear viscosity of water at T < 315 K has an exponential character, which corresponds to the jump-like character of the rotational

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3



Fig. 1. Schematic illustration of the motion of molecular layers with respect to one another

motion of molecules. At T > 315 K, the rotational motion of water molecules becomes quasifree [15], and the temperature dependence of the shear viscosity of water acquires an argon-like character.

There are no principal obstacles that would prohibit the generalization of formula (3) onto the case of aqueous electrolyte solutions. This is an issue that is dealt with in this work. On the basis of formulas obtained in this way for the shear viscosity, it will be shown that, at small concentrations, its series expansion in the concentration parameter is totally consistent with experimental results; i.e. it also includes the root-like term.

## 2. General Structure of the Shear Viscosity of Aqueous Electrolyte Solutions

In accordance with work [17], we adopt that the general structure of the kinematic shear viscosity in weak aqueous electrolyte solutions is described by the formula

$$\nu(\tilde{\nu}, x, t) = \nu_m(x) \begin{cases} \tilde{\nu}_0(x) \exp(\tilde{\varepsilon}(x)/t), & t < t_{\rm H}, \\ \tilde{\nu}_a(x) \frac{(1 - \tilde{\nu}_0(x))^{1/3}}{(\tilde{\nu} - \tilde{\nu}_0(x))^{1/3}}, & t > t_{\rm H}. \end{cases}$$
(4)

where  $t = T/T_m(x)$ ;  $T_m(x)$  is the melting point of the solution with the molar concentration  $x = \frac{N_s}{N_w + N_s}$ ;  $N_w$  and  $N_s$  are the total numbers of water and salt molecules, respectively;  $t_{\rm H} = T_{\rm H}/T_{\rm c}$ ; the characteristic temperature  $T_{\rm H}$  is the temperature of the crossover from the argon-like character of the molecular thermal motion in water to a regime, when the dipole correlations play an important role (as was shown in works [17, 18],  $T_{\rm H} \approx 315$  K); and  $T_{\rm c}$  is the critical temperature. The other parameters in formula (4) are  $\tilde{v}(x) = v/v_n(x)$ ;  $v = \frac{V}{N_w + N_s}$ ; V is the system volume;  $\tilde{v}_0(x) = v_0(x)/v_n(x)$ ;  $v_0(x)$  is the excluded solution

231

volume;

$$\upsilon_n(x) = (1-x)\upsilon_{\rm tr}^{(\rm w)} + x\upsilon_m^{\rm (s)} - \Delta\upsilon_m(x)$$

is the normalizing value of the specific volume;  $v_{\rm tr}^{(\rm w)}$ and  $v_m^{(\rm s)}$  are the specific volumes per molecule at the triple point in water and at the melting point in a salt, respectively; and  $\Delta v_m(x) \sim x(1-x)$  is the excess volume per particle, which arises due to the action of the electric field of ions. The excluded volume  $v_0(x)$ has an analogous structure,

$$v_0(x) = (1-x)v_0^{(w)} + xv_0^{(s)} - \Delta v_0(x,t),$$
(5)

where  $v_0^{(w)}$  and  $v_0^{(s)}$  are the excluded volumes for the shear viscosity in pure water and a molten salt, respectively; and  $\Delta v_0(x,t) \sim x(1-x)$ . It is reasonable to assume that  $\Delta v_0(x,t) \approx \Delta v_m(x)$  [17].

The excess volume  $\Delta v_m(x)$  can be determined independently, by analyzing the solution density:

$$\Delta v_m(x) = v_{\text{real}} - v_{\text{id}} = [m_1(1-x) + m_2 x] \times \left(\frac{1}{\rho_{\text{exp}}(x)} - \frac{1}{\rho_{\text{w}}(1-X) + \rho_{\text{s}} X}\right),\tag{6}$$

where  $v_{\text{real}}$  and  $v_{\text{id}}$  are the specific volumes per particle in the real and ideal solutions, respectively; x and x are, respectively, the molar and mass concentrations of the electrolyte solution;  $\rho_{\exp}(x)$  is the experimental value of the solution density;  $\rho_{w}(1-x) + \rho_{s}x$  is the density of the ideal solution;  $\rho_{w}$  is the water density near the triple point;  $\rho_{s}$  is the melt density near its melting point; and  $m_{1}$  and  $m_{2}$  are the masses of water and salt molecules, respectively. A direct calculation for the NaCl aqueous solution with the concentration x = 0.035 gives  $\Delta v_{m}(x) = 0.79$  A<sup>3</sup>, which is about 2.5% of the volume per one water molecule  $v_{w}(x,t) = 30$  A<sup>3</sup>.

Let us compare the value obtained for  $\Delta v_m(x)$  with that following from the Debye theory of electrolytes (see, e.g., works [5,24]). According to this theory, the thermodynamic potential of dilute electrolyte solutions looks like

$$\Phi = \Phi_p + \Phi_s,\tag{7}$$

where the first term corresponds to the pure solvent, and the second one is the contribution of strong electrolyte,

$$\Phi_{\rm s} = -\frac{k_{\rm B}T}{12\pi} \frac{v_{\rm w}}{r_{\rm D}^3},\tag{8}$$

232

where

$$r_{\rm D} = \left(\frac{4\pi n_i e^2}{\varepsilon_{\rm sr} k_{\rm B} T}\right)^{-1/2} = r_{\rm D}^{(0)} c^{-1/2} \tag{9}$$

is the Debye radius. In formula (9),

$$r_{\rm D}^{(0)} = \left(\frac{4\pi n_{\rm w} e^2}{\varepsilon_{\rm sr} k_{\rm B} T}\right)^{-1/2}$$

e is the elementary charge,  $\varepsilon_{\rm sr}$  the dielectric constant of water,  $n_i = n^+ + n^-$  is the total concentration of positive and negative ions, and

$$c = \frac{N_{\rm s}}{N_{\rm w}} = \frac{x}{1-x}$$

is the ratio between the numbers of the salt and water molecules.

The change in the specific volume per one water molecule is determined in the standard way:

$$\Delta \upsilon = -\frac{k_{\rm B}T}{12\pi r_{\rm D}^3} \left[ \frac{\partial \upsilon_{\rm w}}{\partial p} - 3\frac{\upsilon_{\rm w}}{r_{\rm D}} \frac{\partial r_{\rm D}}{\partial p} \right]$$

It is clear that

$$\frac{\partial v_{\rm w}}{\partial p} = -\frac{v_{\rm w}}{\rho_{\rm w} c_{\rm w}^2}.$$
  
Since  $n_i = 1/v_i$ , we have

$$\frac{\partial r_{\rm D}}{\partial p} = -\frac{1}{2} r_{\rm D} \beta_T^{\rm (I)},$$

where  $\beta_T^{(I)}$  is the isothermal compressibility of the "ionic gas", and  $c_w$  is the sound speed in water. In the ideal-gas approximation,

$$\beta_T^{(\mathrm{I})} = \frac{1}{n_i k_\mathrm{B} T} \Rightarrow \frac{\upsilon_\mathrm{w}}{c k_\mathrm{B} T}.$$

Using those estimates, we obtain

$$\Delta v = \frac{k_{\rm B}T}{12\pi} \frac{v_{\rm w}}{r_{\rm D}^3} \left[ \frac{1}{\rho_{\rm w} c_{\rm w}^2} - \frac{3}{2} \frac{v_{\rm w}}{ck_{\rm B}T} \right].$$
 (10)

It is easy to see that the second term in the brackets is 1/c times as large as the first one. Bearing this circumstance in mind and taking Eq. (9) into account, formula (10) reads

$$\Delta v = -\frac{k_{\rm B}T}{8\pi} \frac{v_{\rm w}}{\left(r_{\rm D}^{(0)}\right)^3} \left[\frac{v_{\rm w}}{k_{\rm B}T} - \frac{2c}{3\rho_{\rm w}c_{\rm w}^2}\right] c^{1/2} + \dots, \quad (11)$$

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3

i.e. the main contribution is proportional to the root of the concentration.

The applicability domain of the Debye theory of electrolytes is determined by the inequality

$$r_{\rm D}(c) > \frac{1}{(cn_{\rm w})^{1/3}}.$$
 (12)

At T = 338 K, the parameters are  $v_{\rm w} = 30.47$  Å<sup>3</sup>,  $n_{\rm w} = 0.033$  A<sup>-3</sup>, and  $r_{\rm D}^{(0)} = 0.62 \times 10^{-8}$  cm. Therefore, inequality (12) is equivalent to the inequality

$$c < 0.64 \times 10^{-4}.\tag{13}$$

Let us compare the values calculated according to estimate (11) with the corresponding values deter-

Table 1. Debye radius  $r_{\rm D}$  and excess volume

$\Delta v$ for various molar concentrations x at $T = 338$ K						
x	$r_{\rm D},$ Å	$\Delta v(x),  \mathrm{\AA}^3 (11)$	$\Delta v(x),  \mathrm{\AA}^3(6)$			
0.003 0.006 0.013 0.019 0.026 0.033 0.040 0.048	8.028 5.575 3.914 3.173 2.728 2.422 2.194 2.016	0.022 0.127	0.038 0.151 0.315 0.447 0.636 0.793 0.977 1.130			
$\begin{array}{c} 0.055\\ 0.063\\ 0.071\\ 0.080\\ 0.089\\ 0.098\end{array}$	$     1.872 \\     1.751 \\     1.648 \\     1.558 \\     1.480 \\     1.410 $		$     1.311 \\     1.517 \\     1.694 \\     1.897 \\     2.098 \\     2.299 $			

Table 2. Excess volumes  $v_0$ and  $v_m$  for various mass concentrations x

X	$v_0(X), \mathrm{\AA}^3$	$v_m(X), \mathrm{\AA}^3$	$v_m^{ m ap}$
0.02	30.139	30.144	29.647
0.04 0.06	30.101	30.107	29.680
	29.720	29.726	29.712
0.08	29.305	29.312	$29.745 \\ 29.778$
0.1	28.944	28.951	
0.12	28.441	28.451	$29.810 \\ 29.843$
0.14	28.079	28.090	
0.16	27.778	27.787	29.876
0.18	27.338	27.350	29.909
0.2	26.983	26.996	29.942
0.22	26.613	26.627	29.975
0.22	26.262	26.278	30.009

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3



Fig. 2. Dependences of the normalized kinematic shear viscosity on the normalized temperature at the concentration x = 0.14%: experimental data [25] (circles), at  $t < t_{\rm H}$  [Eq. (4), dashed curve], and at  $t > t_{\rm H}$  [Eq. (4), solid curve]

mined by formula (6) on the basis of experimental data for the solution, water, and melt densities (see Table 1). As one can see, the values of  $\Delta v(x)$  calculated from formulas (11) and (6) become closer to each other as the solution parameters approach the domain, where the Debye theory is valid. At concentrations that correspond to real experiments, the Debye theory have to be generalized, which will be done separately.

## 3. Temperature and Concentration Dependences of Shear Viscosity in Aqueous Electrolyte Solutions

### 3.1. Temperature dependence

The experimental temperature dependences of the shear viscosity in aqueous electrolyte solutions with various concentrations are similar to those shown in Fig. 2 (circles). The parameter dependences  $\tilde{\nu}_a(x)$ ,  $\tilde{\nu}_0(x)$ ,  $\tilde{\nu}_0(x)$ , and  $\tilde{\varepsilon}(x)$  were determined by fitting the experimental data for the kinematic shear viscosity of aqueous electrolyte solutions using formula (4) with the help of the least squares method. More specifically, the dependences of  $\tilde{\nu}^3 v$  on  $(\tilde{\nu}^3 - 1)$  were plotted. According to Eq. (4), they should be linear. The quantities  $v_0(x)$  and  $v_m(x)$  play the roles of the proportionality coefficient and the constant, respectively, in this dependence,

$$\tilde{\nu}^3 \upsilon = \upsilon_0 (\tilde{\nu}^3 - 1) + \upsilon_m$$

The values obtained for  $v_0(x)$  and  $v_m(x)$  in this way are quoted in Table 2.



mental data [25] (circles) and calculation by formula (4) (solid curve)

For comparison, the fourth column of Table 2 contains the values calculated for  $v_m(x)$  using the formula

$$v_m^{(\text{app})} = \frac{m_w(1-x) + m_{\text{NaCl}}x}{\rho_{\text{app}}(x)}$$

where  $\rho_{app}(x)$  is the solution density at the melting point. Since this parameter is known only for several concentrations, we used the linear interpolation and the extrapolation to determine  $\rho_{app}(x)$  at all other concentrations. Just this procedure seems to be re-

# Table 3. Values of parametersthat determine the kinematic shearviscosity in aqueous electrolyte solutions

Solution	$\tilde{\nu}_0(x) \times 10^5$	$\tilde{\varepsilon}(x)$	$\tilde{\nu}_a(x)$	$\tilde{v}_0(x)$	$\tilde{v}_0^{(\mathrm{s})}(x)$
NaCl $(x = 0.035)$	22.48	8.41	0.41	0.995	0.997
KCl $(x = 0.034)$	107.95	6.86	0.47	0.991	0.996
CaCl <sub>2</sub> $(x = 0.024)$	18.94	8.42	0.18	0.946	0.961

Table 4. Parameters  $\tilde{v}_0$ 

and  $\zeta = (1 - \tilde{v}_0)^{1/3}$  for various molten salts

Solution	$ ilde{v}_0$	ζ
NaCl	0.977	0.29
KCl	0.971	0.31
CaCl <sub>2</sub>	0.995	0.18

Table 5. Parameters	$ ilde{arepsilon}(x)$	) and $\tilde{\nu}_0(x)$	r) for NaCl
---------------------	-----------------------	--------------------------	-------------

x, NaCl	$ ilde{arepsilon}(x)$	$ ilde{ u}_0(x) imes 10^5$
0.035	8.41	22.48
0.048	8.37	21.24
0.089	8.35	20.41

sponsible for small discrepancies between the  $v_m(x)$ and  $v_m^{(\text{app})}$  values.

The activation energy for aqueous electrolyte solutions were determined for normal states that corresponded to the interval 1 < t < 1.12. In the case of supercooled pure water, its states corresponded to the interval 0.96 < t < 1.

The values of  $\tilde{v}_0^{(s)}$  were calculated according to formula (5), in which  $v_0^{(w)}$  and  $v_0^{(s)}$  were put equal to the corresponding values for pure liquid water and molten salt, respectively, whereas  $\Delta v_0(x,t)$  and  $\Delta v_m(x)$  were evaluated by formula (6). The values of  $v_0^{(s)}$  for the examined molten salts are presented in Table 4.

Small differences between the  $\tilde{v}_0(x)$  and  $\tilde{v}_0^{(s)}(x)$  values may be associated, probably, with a distortion of hydration shells around the ions owing to the relative displacement of molecular layers in the solution (see Fig. 1). As a result, the inequality  $\tilde{v}_0(x) < \tilde{v}_0^{(s)}(x)$  took place in all cases. This effect was especially pronounced for CaCl<sub>2</sub> aqueous solutions, where the size of a hydration shell is larger than that for single-charged electrolytes.

The values of  $\tilde{\varepsilon}(x)$  and  $\tilde{\nu}_0(x)$  calculated for NaCl aqueous solutions with various salt concentrations are quoted in Table 5. From this table, it follows that the activation energy is practically independent of the concentration. This fact can be easily explained under the assumption that the activation energy is associated with the rotational motion of water molecules. Different values of  $\tilde{\varepsilon}(x)$  and  $\tilde{\varepsilon}$  for pure water reflect the difference between the temperature intervals of their determination (the former quantity was determined from the experimental data for normal solution states, whereas the latter was calculated for supercooled water).

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3

#### 3.2. Concentration dependence

The concentration dependence of the shear viscosity was determined from the curves of its temperature dependence corresponding to various concentrations (Fig. 2). Here, we will consider only the temperatures T > 50 °C, for which the argon-like character of temperature dependences is observed. The behavior of the curves  $\tilde{\nu}(x) = \nu/\nu_{\rm tr}^{\rm (H_2O)}$  is shown in Fig. 3. The reproduction error of experimental data did not exceed 4%.

The concentration dependences of the parameters in formula (4) are given in Table 6. One can see that the  $v_0(x)$  values practically do not differ from the values for the specific volume per one molecule at the solution melting point,  $v_m(x)$ . At  $t < t_{\rm H}$ , the value of the parameter  $\tilde{\varepsilon}(x)$  in formula (4) changes approximately by 8%, as the concentration grows, whereas the factor  $\tilde{\nu}_0$  in front of the exponential function changes considerably.

Note that, for all concentrations, the transition from the exponential character of the temperature dependence of the shear viscosity to the argon-like one occurs in the temperature interval 30 °C < T < 50 °C ( $t \approx 1.2$ ), which coincides with the evaluation of the temperature  $t_d$  [17]. The reproduction error of experimental data did not exceed 5%.

Let us discuss the adequacy of formula (1). In accordance with Eq. (4), the shear viscosity of an electrolyte solution in the domain, where the argon-like approach is applicable, can be represented in the form

$$\nu(x) = \nu_{\rm id}(x) \left( 1 - \frac{\Delta v_m(x) - \Delta v_0(x)}{v_m^{\rm (id)} - v_0^{\rm (id)}(x)} \right)^{1/3} \times \left( 1 - \frac{\Delta v(x) - \Delta v_0(x)}{v_{\rm id}(x) - v_0^{\rm (id)}} \right)^{-1/3},$$

where  $\nu_{id}(x)$  is the shear viscosity of the ideal solution calculated by formula (4), in which all parameters correspond to the ideal solution. Surely, the series expansion of  $\nu_{id}(x)$  in the concentration contains only the contributions from terms with integer power exponents. At the same time, as follows from Eq. (11), the series for  $\Delta v_m(x)$  and  $\Delta v_0(x)$  also contain contributions with fractional power exponents. But they manifest themselves only at extremely low concentrations [see Eq. (13)]. Hence, at concentrations that are analyzed in most experiments, the expansion of the

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3



**Fig. 4.** Dependences of the ratio  $\nu(c)/\nu_{\rm w}$  on the molar concentration at T = 338 K: experimental data [25] (circles) and their least-squares fitting  $\nu(c)/\nu_{\rm w} = 1.01 + 1.14c + 53.64c^2 + ...$  (solid curve). The fitting confidence  $R^2 = 0.999$ 

kinematic shear viscosity in the power series in the parameter c has an analytical character,

 $\nu(c) = \nu_{\rm w} (1 + B \, c + K \, c^2 + \dots).$ 

This conclusion is completely confirmed by the experimental data exhibited in Fig. 4.

Concerning the dynamic shear viscosity, owing to the presence of contributions to the system density, which are root-like in the concentration, the concentration dependence of this parameter is also described by formula (1). Hence, formula (4) also reproduces the concentration dependence of the kinematic shear viscosity at temperatures  $t > t_{\rm H}$  rather satisfactorily.

Table 6. Parameters  $v_0$  and  $v_m(x)$ for aqueous electrolyte solutions at various mass concentrations x

Х	$v_0(X)$ (A <sup>3</sup> )	$v_m(X)$ (A <sup>3</sup> )	$\tilde{\varepsilon}(x)$	$\tilde{\nu}_0(x) \times 10^5$
$\begin{array}{c} 0.02\\ 0.04\\ 0.06\\ 0.08\\ 0.1\\ 0.12\\ 0.14\\ 0.16\\ 0.18\\ 0.2\\ \end{array}$	30.1393 30.1008 29.7195 29.3052 28.9435 28.4412 28.0789 27.7779 27.3381 26.9834	30.1443 30.1069 29.7259 29.3123 28.9506 28.4507 28.0890 27.7874 27.3497 26.9959	8.30 8.35 8.48 8.42 8.39 8.43 8.52 8.68 8.68 8.80	25.65 25.53 24.37 27.53 29.15 31.99 32.13 30.49 33.87 33.76
$0.22 \\ 0.24$	26.6132 26.2617	26.6271 26.2787	$9.01 \\ 8.97$	$31.56 \\ 37.04$

#### 4. Discussion of the Results Obtained

In this work, the shear viscosity of aqueous electrolyte solutions at temperatures higher than 315 K was considered analogously to the shear viscosity of molecular liquids. In other words, the quasifree rotational motion of water molecules results in the averaging of intermolecular (between water molecules) and ion-molecular interactions in the solutions. The system becomes similar to a solution of spherical particles with centrally symmetric interaction potentials. The Coulomb interaction between ions and water molecules only leads to an increase of the system density by no more than 2–3%. Actually, no assumptions were made in this work about the effective size of hydrated complexes.

At the same time, the change of a molecular volume induced by electrostatic forces is a certain function of the Debye radius. Therefore, in a sense, we may talk about hydrated complexes, whose size coincides with the Debye radius, and the number of hydrated molecules has to be evaluated as the difference between the number of molecules in a sphere with the Debye radius and the number of molecules in the same sphere, but in the case of uncompressed water. In the framework of this approach, the appearance of the root-like contribution to the shear viscosity can be explained rather plausibly, but only at extremely low concentrations.

To summarize, I would like to express my sincere gratitude to Academician Leonid Bulavin for his permanent interest in this work and the discussion of the results obtained. I am also grateful to Prof. Mykola Malomuzh for his useful advice when performing this work.

- L. Onsager, R.M. Fuoss. Irreversible processes in electrolytes. Diffusion, conductance and viscous flow in arbitrary mixtures of strong electrolytes. J. Phys. Chem. 36, 2689 (1932).
- H. Falkenhagen. Bemerkung zur inneren Reibung starker Electrolyte in sehr verdünnte Lösungen. *Phys. Z.* **32**, 745 (1931).
- H. Falkenhagen , E.L. Vernon. The viscosity of strong electrolyte solutions according to electrostatic theory. *Philos. Mag. J. Sci. Ser.* 7 14, No. 92, 537 (1932).
- I.Z. Fisher, A.M. Zaitseva. Influence of ion hydration on the viscosity of electrolyte solutions. *Zh. Strukt. Khim.* 4, 331 (1963) (in Russian).

- L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Part 1 (Pergamon Press, 1980).
- O.Ya. Samoilov. A new approach to the study of hydration of ions in aqueous solutions. *Discuss. Faraday Soc.* 24, 141 (1957).
- 7. O.Ya. Samoilov, Structure of Aqueous Electrolyte Solutions and the Hydration of Ions (Consultants Bureau, 1965).
- M.N. Rodnikova. Negative hydration of ions. Russ. J. Electrochem. 39, 192 (2003).
- M.N. Rodnikova, S.A. Zasypkin, G.G. Malenkov. On the mechanism of negative hydration. *Dokl. Akad. Nauk SSSR* 324, 368 (1992) (in Russian).
- M.N. Rodnikova, S.A. Zasypkin, G.G. Malenkov. Structural and dynamic studies of Na<sup>+</sup> and K<sup>+</sup> water clusters. *Zh. Strukt. Khim.* **34**, 96 (1993) (in Russian).
- A. Einstein. Eine neue Bestimmung der Moleküldimensionen. Ann. d. Phys. 19, 289 (1906).
- A. Einstein. A new determination of molecular dimensions. In *Investigation on the Theory of the Brownian Movement*. Edited by R. Fürth (Dover, 1956), p. 36.
- Molecular Dynamics Method in Physical Chemistry. Edited by Yu.K. Tovbin (Nauka, 1996) (in Russian).
- W. Peiming, A. Anderko. Modeling viscosity of aqueous and mixed-solvent electrolyte solutions. In *Proceedings of* the 14th International Conference on the Properties of Water and Steam (Kyoto, 2004), p. 116–121.
- G. Hefter, P.M. May, P. Sipos, A. Stanley. Viscosity of concentrated electrolyte solutions. J. Mol. Liq. 103–104, 261 (2003).
- N.P. Malomuzh, V.P. Oleinik. Nature of the kinematic shear viscosity of water. *Zh. Strukt. Khim.* 49, 1092 (2008) (in Russian).
- P.V. Makhlaichuk, V.N. Makhlaichuk, N.P. Malomuzh. Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type. J. Mol. Liq. 225, 577 (2017).
- L.A. Bulavin, N.P. Malomuzh. Upper temperature limit for the existence of living matter. J. Mol. Liq. 124, Iss. 1–3, 136 (2006).
- T.V. Lokotosh, N.P. Malomuzh, K.N. Pankratov. Thermal motion in water-electrolyte solutions according to quasielastic incoherent neutron scattering data. J. Chem. Eng. Data 55, 2021 (2010).
- L.A. Bulavin, A.I. Fisenko, N.P. Malomuzh. Surprising properties of the kinematic shear viscosity of water. *Chem. Phys. Lett.* **453**, 183 (2008).
- V.M. Makhlaichuk. Kinematic shear viscosity of water, aqueous solutions of electrolytes, and ethanol. Ukr. Fiz. Zh. 60, 855 (2015) (in Ukrainian).
- V.M. Makhlaichuk. Kinematic shear viscosity of liquid alkaline metals. Ukr. Fiz. Zh. 62, 672 (2017) (in Ukrainian).
- 23. V.Yu. Bardik, V.M. Makhlaichuk. Kinematic shear viscosity of pure liquid metals Sn, Bi, Pb and their binary melts. *Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky* No. 4, 179 (2017) (in Ukrainian).
- R.A. Robinson, R.H. Stokes. *Electrolyte Solutions* (Butterworth, 1959).

ISSN 2071-0194. Ukr. J. Phys. 2019. Vol. 64, No. 3

 $\mathbf{236}$ 

 I.D. Zaitsev, G.G. Aseev. Physicochemical Properties of Binary and Multicomponent Solutions of Inorganic Substances. A Handbook (Khimiya, 1988) (in Russian). Received 15.08.18.

Translated from Ukrainian by O.I. Voitenko

В.М. Махлайчук

ЗСУВНА В'ЯЗКІСТЬ ВОДНИХ РОЗЧИНІВ ЕЛЕКТРОЛІТІВ

Резюме

В роботі досліджується кінематична зсувна в'язкість водних розчинів електролітів. Показано, що при  $t < t_d$  її температурна залежність при усіх розглянутих концентраціях

має експоненціальний характер, а при  $t > t_d$  описується формулою аргоно-подібного типу (тут t позначає безрозмірну температуру:  $t = T/T_m$ , де  $T_m$  – температура плавлення розчину електроліту,  $t_d \approx 315$  К – температура дипольного впорядкування). Основна увага приділяється особливостям температурної і концентраційної залежностей зсувної в'язкості в аргоно-подібній області. Показано, що виникнення кореневої залежності від концентрації є можливим тільки в межах застосування Дебаєвської теорії розбавлених електролітів. За її межами розклад кінематичної зсувної в'язкості за степенями концентрації повинен мати аналітичний характер. Саме такою і є концентраційна залежність зсувної в'язкості згідно з більшістю експериментів. Похибка при відтворенні експериментальних даних не перевищує експериментальну похибку, тобто є меншою від (4–5)%.