INFLUENCE OF HYDRATION OF IONS ON THE BULK VISCOSITY OF ELECTROLYTE SOLUTIONS

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The report of the authors [1] studied the influence of the hydration of ions in aqueous solution on its shearing viscosity. In this work, the same task was performed for the bulk viscosity of an electrolyte solution. A consideration of the bulk viscosity is important for a proper understanding of the process of absorption of ultrasound in liquid medium. Hence the question of the influence of hydration of ions on the shearing and bulk viscosity of solutions is important in connection with ultraacoustic methods of investigation in electrolyte solutions.

Just as before, we shall proceed from the hydrodynamic theory of hydration [2]. We obtained an estimate only for part of the variation of the bulk viscosity of a dilute solution of an electrolyte, related to the effect of hydration of the ions. The second part of the variation of the bulk viscosity, related to the Coulomb interaction of the ions, will not be considered here and should be the subject of an independent investigation.

The simplest accurate solution of the equations of liquid motion, describing the process of homogeneous stretching, as is easy to determine, is the solution

$$\mathbf{v} = \frac{z\mathbf{z}^0}{\tau + t}, \quad \rho = \frac{\rho_0 \tau}{\tau + t}, \tag{1}$$

where $\mathbf{z}^0$ is the unit vector in the direction of the axis Oz, τ is an arbitrary constant, and ρ_0 is the value of the density at the moment $t = 0$. We might assume that the value of τ is selected as large as convenient, and the variation of t is limited to a small positive interval. Then solution (1) will not contradict the empirical fact of the very small compressibility of real liquids. Then it is easy to obtain, according to the general theory [3], that in the motion under consideration, the energy displacement as a result of viscosity, related to a unit volume and unit time, is equal to

$$-\frac{\partial E}{\partial t} = \frac{4/3\eta + \zeta}{(\tau + t)^2}, \tag{2}$$

where η and ζ are the coefficients of the shearing and bulk viscosities, respectively.

Now let us place an ion at the point $x = y = z = 0$. As a result of its hydration, Eq. (1) will no longer correctly express the velocity of the liquid and its density close to the ion. Then let us assume

$$\mathbf{v} = \frac{1}{\tau + t}(z\mathbf{z}^0 + \vec{\nabla}\varphi), \quad \rho = \frac{\rho_0 \tau}{\tau + t} e^{-\Psi/kT + \sigma}, \tag{3}$$

where Ψ is the self-consistent potential of the hydrate shell, $(\tau + t)^{-1}\varphi$ is the potential of turbulization of the liquid flow close to the ion, and σ is a correction factor considering the possible variation of the density in the hydrate shell as a result of the liquid flow (see [1, 2]). It is assumed that the functions Ψ, φ, and σ disappear rapidly outside the hydrate shell.

Expressions (3) should be solutions of the equations of hydrodynamics in the presence of a hydrating ion [2]:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\vec{\nabla})\mathbf{v} = -c^2\vec{\nabla}\sigma, \quad \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho\mathbf{v}) = 0, \tag{4}$$

where the factors describing viscosity are omitted. Substituting (3) into (4), considering the rate of flow within the hydrate shell as much smaller than the velocity of sound c and linearizing the equation with respect to we obtain the equations

$$\sigma = 0, \quad \Delta\varphi - \frac{\Psi'(r)}{kT}\frac{\partial\varphi}{\partial r} = \frac{\Psi'(r)}{kT}\frac{z^2}{r}, \tag{5}$$

related to the analogous equations in [1]. Let us note that in the approximation considered, σ and φ do not depend on the time t.

Just as in [1, 2], let us take the following model expression for the potential $\Psi(r)$:

$$\Psi(r) = \frac{\varepsilon}{R}(r - R), \quad r < R; \qquad \Psi(r) = 0, \quad r > R. \tag{6}$$

Then the second equation (5) takes the form

$$\begin{aligned} &\Delta\varphi - \varkappa\frac{\partial\varphi}{\partial r} = \varkappa r\cos^2\vartheta, && r < R, \\ &\Delta\varphi = 0, && r > R, \end{aligned} \tag{7}$$

where $\varkappa = \varepsilon/RkT$, and spherical coordinates with a polar axis Oz are introduced. The solution should be regular everywhere.

Equation (7) has the following solutions:

$$\varphi(r, \vartheta) = A + \frac{2}{\varkappa^3 r}\left[1 - \frac{1}{2}\varkappa^2 r^2 - \frac{1}{12}\varkappa^3 r^3 - e^{\varkappa r} + \varkappa r\int_0^r \frac{e^{\varkappa r} - 1}{r}\,dr\right]$$
$$+\left\{\frac{B}{\varkappa^3 r^3}\left[e^{\varkappa r}\left(1 - \frac{1}{4}\varkappa r\right) - \left(1 + \frac{3}{4}\varkappa r + \frac{1}{4}\varkappa^2 r^2 + \frac{1}{24}\varkappa^3 r^3\right)\right] - \frac{r^2}{3}\right\} P_2(\cos\vartheta), \quad r < R. \tag{8}$$

$$\varphi(r, \vartheta) = \frac{1}{\varkappa r}\left[\overline{A} + \frac{\overline{B}}{\varkappa^2 r^2} P_2(\cos\vartheta)\right], \quad r > R. \tag{9}$$

Here $P_2(\cos\vartheta)$ is the second Legendre polynomial and A, B, $\overline{A}$, $\overline{B}$, are constants, which should be determined from the condition of continuity at φ and $\partial\varphi/\partial r$ when r = R. The calculation leads to the result:

$$\begin{aligned} A &= \frac{2}{\varkappa^2}\left(1 + x + \frac{1}{2}x^2 - \int_0^x \frac{e^y - 1}{y}\,dy\right), \\ B &= \frac{20R^2x^2}{9g}, \\ \overline{A} &= \frac{2}{\varkappa^2}\left(1 + x + \frac{1}{2}x^2 - \frac{1}{6}x^3 - e^x\right), \\ \overline{B} &= \frac{90R^2x^2}{9g}\left[e^x\left(1 - \frac{2}{5}x + \frac{1}{20}x^2\right) - \left(1 + \frac{3}{5}x + \frac{3}{20}x^2 + \frac{1}{60}x^3\right)\right], \end{aligned} \tag{10}$$

where $\varkappa = \varkappa R = \varepsilon/RkT$ and

$$g \equiv e^x\left(1 - \frac{1}{3}x\right) - \left(1 + \frac{2}{3}x + \frac{1}{6}x^2\right). \tag{10'}$$

The solution found corresponds to ideal flow, when viscosity is entirely absent. However, it was shown in [2, 4] that for small rates of flow $\varphi_{visc} \approx \varphi_{id}$, and hence we shall use the solution (3), (8), and (9) below in the presence of viscosity as well.

Let us turn to the calculation of the energy displacement in the flow found. Subtracting from the total energy loss the portion corresponding to nonturbulent flow [with density according to Eq. (2)], we obtain [3]:

$$-\frac{\partial(\Delta E)}{\partial t}=\frac{1}{(\tau+t)^2}\int\left\{2\eta_0\left(\frac{\partial^2\bar{\varphi}}{\partial x_i\partial x_k}\right)^2+\left(\zeta_0-\frac{2}{3}\eta_0\right)(\Delta\bar{\varphi})^2-\left(\frac{4}{3}\eta_0+\zeta_0\right)\right\}dV, \tag{11}$$

where $\bar{\varphi}$ differs from φ by the inclusion of the nonturbulent portion of the motion (see [4]):

$$\bar{\varphi}=\frac{1}{2}r^2\cos^2\vartheta+\varphi, \tag{12}$$

and we equipped the values of the coefficients η and ζ for the pure solvent with zero subscripts. Using the solution found, after a cumbersome calculation, we obtained the fact that

$$-\frac{\partial(\Delta E)}{\partial t}=\frac{4\pi R^3}{9(\tau+t)^2}\left(\frac{\varepsilon}{kT}\right)\left[\Phi_1\left(\frac{\varepsilon}{kT}\right)\eta_0+\frac{7}{4}\Phi_2\left(\frac{\varepsilon}{kT}\right)\left(\zeta_0-\frac{2}{3}\eta_0\right)\right]. \tag{13}$$

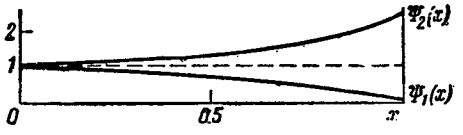
Here $\Phi_1(x)$ and $\Phi_2(x)$ are two dimensionless functions, possessing the property that $\Phi_1(0)=\Phi_2(x)=1$, and are close to one at all $x \leq 1$. We found these functions in the form of series with respect to the powers of $\underline{x}$; however, we do not use them directly below, and we shall not cite them here.

Result (13) corresponds to a supplementary loss of energy in the liquid flow in the presence of one hydrated ion. If there are several types of ions in the solution, $\alpha = 1,2,\ldots$ in amounts N_α, and if instead of the radius of the hydrate shell determined according to (6) we introduce the effective volume of the hydrate shell [2],

$$v^*=\frac{4\pi}{3}R^{*3},\quad R^*=-\frac{1}{\varkappa}\ln\frac{1-e^{-\varkappa R}}{2}, \tag{14}$$

then instead of (13) we obtain

$$-\frac{\partial(\Delta E)}{\partial t}=\frac{1}{(\tau+t)^2}\sum_\alpha\frac{8}{3}N_\alpha v_\alpha^*\left(\frac{\varepsilon_\alpha}{kT}\right)\left[\Phi_1^*\left(\frac{\varepsilon_\alpha}{kT}\right)\eta_0+\frac{7}{4}\Phi_2^*\left(\frac{\varepsilon_\alpha}{kT}\right)\left(\zeta_0-\frac{2}{3}\eta_0\right)\right], \tag{15}$$



where $\Phi_1^*(x)$ and $\Phi_2^*(x)$ are two new dimensionless functions, again possessing the property $\Phi_1^*(0)=\Phi_2^*(0)=1$.

Equation (15) expresses the increase in the loss of energy by the solution during its flow as a result of the presence of hydrated ions in it. This result, according to (2) should be set equal to the quantity

$$\frac{1}{(\tau+t)^2}\left[\frac{4}{3}(\eta_s-\eta_0)+\zeta_s-\zeta_0\right]V, \tag{16}$$

where η_s and ζ_s are the coefficients of viscosity of the solution and V is its total volume. We calculated the difference $\eta_s-\eta_0$ in [1]:

$$\eta_s-\eta_0=\frac{8}{3}\sum_\alpha\frac{N_\alpha v_\alpha^*}{V}\left(\frac{\varepsilon_\alpha}{kT}\right)^2\left[\overline{\Phi}_1^*\left(\frac{\varepsilon_\alpha}{kT}\right)\zeta_0+\frac{17}{105}\overline{\Phi}_2^*\left(\frac{\varepsilon_\alpha}{kT}\right)\right]. \tag{17}$$

Substituting (17) into (16) and setting the result equal to (15), we finally obtain

$$\zeta_s-\zeta_0=\frac{14}{3}\sum_\alpha\frac{N_\alpha v_\alpha^*}{V}\left(\frac{\varepsilon_\alpha}{kT}\right)\left[\Psi_1\left(\frac{\varepsilon_\alpha}{kT}\right)\zeta_0-\frac{2}{21}\Psi_2\left(\frac{\varepsilon_\alpha}{kT}\right)\eta_0\right]. \tag{18}$$

Here $\Psi_1(x)$ and $\Psi_2(x)$ represent one more pair of dimensionless functions, the powers of which on the segment $0 \leq x \leq 1$ is shown in Fig. 1.

Let us turn to a consideration of the result. From a comparison of expressions (17) and (18), we see that the hydration of ions has a greater influence on the bulk viscosity than on the shearing viscosity. At the same concentration of ions and $(\varepsilon_\alpha/kT) \sim 0.6$, the increase in ζ is approximately 3-4 times as great as the increase in η. This

result seems natural, since from the viewpoint considered, the very phenomenon of hydration is primarily a process of compression of the solution in the neighborhood of the ions. Hence, liquid flow through the hydrate shell of the ion is accompanied by compression-stretching and a corresponding loss of energy on account of the bulk viscosity. The role of the shearing viscosity in this case is secondary. It is of interest to mention that $\zeta_s - \zeta_0$ is proportional to (ε_α/kT) to the first degree, while $\eta_s - \eta_0$ is proportional to the square of this quantity.

We can see from (18) that the increase in the bulk viscosity as a result of hydration of the ions is proportional to the concentration of the electrolyte. Actually, apparently by analogy with the shearing viscosity, we should expect that the experimental results would have taken the form

$$\zeta_s - \zeta_0 = A\sqrt{c} + Bc, \tag{19}$$

where the first factor comes from purely Coulomb effects, while the second comes from the joint influence of the higher approximations of the Coulomb interaction and the effects of hydration. Our result (18) corresponds to the hydration contribution to the factor Bc (see analysis of the analogous situation in [1]).

LITERATURE CITED

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