I. Z. FISHER, A. M. ZAITSEVA

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. Z. FISHER, A. M. ZAITSEVA

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

(Presented by Academician I. I. Chernyaev on 5 VI 1963)

In the authors' work (^{1}), the influence of ion hydration in an aqueous solution on its shear viscosity was studied. In the present work the same problem is posed for the bulk viscosity of an electrolyte solution. Taking bulk viscosity into account is important for a correct understanding of the process of ultrasound absorption in a liquid medium. Therefore the question of the influence of ion hydration on the shear and bulk viscosity of solutions appears important in connection with ultrasonic methods for investigating electrolyte solutions.

As before, we shall proceed from the hydrodynamic theory of hydration (^{2}). We have obtained an estimate only for that part of the change in the bulk viscosity of a dilute electrolyte solution which is associated with the effect of ion hydration. The second part of the change in bulk viscosity, associated with the Coulomb interaction of ions, will not be considered here and should be the subject of an independent study.

The simplest exact solution of the equations of fluid motion describing the process of homogeneous stretching is, as is readily verified, the solution

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

where z^0 is the unit vector in the direction of the Oz axis, τ is an arbitrary constant, and ρ_0 is the value of the density at the moment $t = 0$. It may be assumed that the value of τ is chosen arbitrarily large and that the change of t is restricted to a small positive interval. Then solution (1) will not contradict the empirical fact of the very small compressibility of real liquids. Further, it is not difficult to obtain, according to the general theory (^{3}), that for the motion under consideration the dissipation of energy due to viscosity, referred to 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 shear and bulk viscosity, respectively.

We now place an ion at the point $x = y = z = 0$. As a result of its hydration, equations (1) will no longer correctly express the velocity of the liquid and its density near the ion. We shall therefore put

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

where Ψ is the self-consistent potential of the hydrate shell, $(\tau + t)^{-1}\varphi$ is the potential of the perturbation of the liquid flow near the ion, and σ is a correction function that takes into account the possible change in density in the hydrate shell as a consequence of the flow of the liquid (see ([1],[2])). It is assumed that the functions Ψ, φ, and σ rapidly vanish outside the hydrate shell.

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

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

where the terms describing viscosity have been omitted. Substituting (3) into (4), assuming the flow velocity within the hydration shell to be much smaller than the speed of sound c, and linearizing the equations in φ, we obtain the equations

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

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

For the potential $\Psi(r)$, as in [1, 2], we choose the following model expression:

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

Then the second equation (5) takes the form

$$\Delta\varphi - \chi\frac{\partial\varphi}{\partial r} = \chi r\cos^2\vartheta, \qquad r < R,$$

$$\Delta\varphi = 0, \qquad r > R, \tag{7}$$

where $\chi = \varepsilon/RkT$, and spherical coordinates with polar axis Oz have been introduced. The solution must be regular everywhere.

Equations (7) have the following solutions:

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

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

Here $P_2(\cos\vartheta)$ is the second Legendre polynomial and $A, B, \bar{A}, \bar{B}$ are constants, which must be determined from the continuity conditions for φ and $\partial\varphi/\partial r$ at $r = R$. Calculation gives

$$A = \frac{2}{x^2}\left(1 + x + \frac{1}{2}x^2 - \int_0^x \frac{e^y - 1}{y}\, dy\right),$$

$$B = \frac{20R^2 x^2}{9g},$$

$$\bar{A} = \frac{2}{x^2}\left(1 + x + \frac{1}{2}x^2 - \frac{1}{6}x^3 - e^x\right),$$

$$\bar{B} = \frac{90R^2 x^2}{9g}\left[e^x\left(1 - \frac{2}{5}x + \frac{1}{20}x^2\right) - \left(1 + \frac{3}{5}x + \frac{3}{20}x^2 + \frac{1}{60}x^3\right)\right], \tag{10}$$

where $x = \chi R = \varepsilon/RkT$ 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 completely absent. However, in [2, 4] it was shown that for low flow velocities $\varphi_{\text{visc}} \approx \varphi_{\text{id}}$, and therefore below we shall use the solution (3), (8), (9) also in the presence of viscosity.

We proceed to calculate the energy dissipation in the flow found. Subtracting from the total energy loss the part corresponding to the unperturbed flux (with the density according to equation (2)), we obtain [3]

Fig. 1

Figure 1: Fig. 1

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

where $\bar{\varphi}$ differs from φ by the inclusion in it of the unperturbed part of the motion (see (4)):

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

and we have supplied the values of the coefficients η and ζ for the pure solvent with zero subscripts. Using the solution found, after a cumbersome calculation we obtain 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 $\Phi_1(0)=\Phi_2(0)=1$ and close to unity for all $x \leqslant 1$. These functions were found by us in the form of series in powers of x; however, we shall not need them directly below, and we shall not present them here.

Fig. 1

The result (13) corresponds to the additional loss of energy in a liquid flow in the presence of one hydrated ion. If the solution contains several kinds of ions $\alpha = 1, 2, ...$, in amounts N_α, and if, instead of the radius of the hydration shell defined by (6), one introduces the effective volume of the hydration shell (2)

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

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 energy loss by a solution during its flow owing to the presence in it of hydrated ions. This result should, according to (2), be equated 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 viscosity coefficients of the solution and V is its total volume. The difference $\eta_s - \eta_0$ was calculated by us in work ⁽¹⁾:

$$\eta_s-\eta_0=\frac{8}{3}\sum_\alpha \frac{N_\alpha v_\alpha^*}{V}\left(\frac{\varepsilon_\alpha}{kT}\right)^2\left[\Phi_1^*\left(\frac{\varepsilon_\alpha}{kT}\right)\zeta_0+\frac{17}{105}\Phi_2^*\left(\frac{\varepsilon_\alpha}{kT}\right)\right]. \tag{17}$$

Substituting (17) into (16) and equating the result 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 $\Psi_2(x)$ are yet another pair of dimensionless functions, the behavior of which on the interval $0 \leqslant x \leqslant 1$ is shown in Fig. 1.

Let us turn to a discussion of the result. From comparison of expressions (17) and (18) it is seen that hydration of ions affects the bulk viscosity to a greater extent than the shear viscosity. At equal concentrations of ions and

At $(\varepsilon_a/kT) \sim 0.6$, the increase in ζ exceeds the increase in η by approximately a factor of 3-4. This result appears natural, since, from the viewpoint considered, the phenomenon of hydration itself is, first of all, a process of compression of the solvent in the vicinity of the ions. Therefore the flow of a liquid through the hydration shell of an ion is accompanied by compression—extension and the corresponding loss of energy due to bulk viscosity. The role of shear viscosity proves secondary in this case. It is interesting to note that $\zeta_s - \zeta_0$ is proportional to (ε_a/kT) to the first power, whereas $\eta_s - \eta_0$ is proportional to the square of this quantity.

It follows from (18) that the increase in bulk viscosity due to hydration of ions is proportional to the electrolyte concentration. In reality, apparently, by analogy with shear viscosity, one should expect the experimental result to have the form

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

where the first term arises from purely Coulomb effects, and the second from the combined influence of higher approximations of the Coulomb interaction and hydration effects. Our result (18) corresponds to the hydration contribution to the term Bc (see the analysis of an analogous situation in work (1)).

Belorussian State University
named after V. I. Lenin

Received
30 V 1963

CITED LITERATURE

1. I. Z. Fisher, A. M. Zaitseva, *ZhSKh*, **4**, No. 4 (1963).
2. A. M. Zaitseva, I. Z. Fisher, *ZhSKh*, **4**, No. 3 (1963).
3. L. D. Landau, E. M. Lifshitz, *Mechanics of Continuous Media*, Moscow, 1954.
4. A. M. Zaitseva, I. Z. Fisher, *ZhSKh*, **4**, 261 (1963).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.