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Influence of dielectric friction and near-surface increase of viscosity on rotational Brownian motion of charged biopolymers in solutions

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Abstract

Influence of surface charges of biopolymer macromolecule on its rotational Brownian dynamics in solutions is considered in terms of dielectric friction and electrovisocosity. A mean spherical approximation for electric field of macromolecule is used. It is shown that for irregular surface charges distribution the rotational diffusion coefficient D_R depends only on two variables: on the total charge of macromolecule and on the "partial" ionic strength of the solution associated with surface charges. The pH dependence of D_R for lyzozyme is calculated and compared with available experimental data. The experimental data agree much better with our theory which has no fitting parameters, than with the ordinary Stokes–Einstein–Debye theory.

Keywords: Rotational Brownian motion; Charged biopolymers; Dielectric friction

1. Introduction

It is well known that the surface of biopolymer macromolecules always is charged and that the electrostatic interaction between the polar solvent and charged groups on the biopolymer surface is strong enough [1]. A change of the surface charge causes a change of solvent–macromolecule interactions and hence of the Brownian dynamics of the macromolecule. In this paper we present a theory that describes the influence of the biopolymer–solvent electrical interactions on the macromolecule's rotational Brownian motion. The influence of the electrical interactions on the rotational Brownian dynamics is twofold. Firstly, the dielectric friction in a polar solvent decrease the molecular mobility. Secondly, the extremely strong electrical field in the vicinity of a macromolecule causes pressure enhancement and hence a local modification of the solvent viscosity. Both these effects may be described in a framework of continuum approach to the solvent with microscopical expressions for molecular variables, such as Debye relaxation time of the solvent molecules [2].

Since the electric field in the vicinity of a macromolecule is very complicated, one has to use a model field obtained from the actual one by averaging it over the angular variables. We calculate the rotational diffusion coefficient D_R for this model field and show that if the surface charges distribution is irregular, only two variables, the total charge Q and the partial ionic strength of the solution associated with the

biopolymer charges I_b, determine the value of D_R.

The present theory has no fitting parameters, such as the volume of the hydration shell of biopolymer, so a direct comparison of the theory with experimental data is possible.

The outline of the paper is as follows. In the next section we briefly discuss the results of the continuum theory in which the solute–solvent interactions are considered in terms of the dielectric friction and electroviscosity. In Section 3 we introduce charge distribution coefficients and calculate them for the case of irregular surface charges distribution. In Section 4 we present the results of our calculations for the rotational diffusion coefficient D_R and compare our theory with the available experimental data to lyzozyme. In the last section, Section 5, we summarize our findings.

2. Continuum theory of rotational Brownian motion of charged particles

In the continuum theory the biopolymer–solvent electrostatic interactions are regarded in terms of electroviscosity and dielectric friction. The first mechanism is caused by electrostriction, which leads to enhancement of the hydrostatic pressure in the vicinity of a charged particle. Properties of the compressed solvent surrounding the Brownian particle may be sufficiently different from those of the bulk. For example, the solvent viscosity in the vicinity of a charged particle is noticeably modified by the electrostriction [3] (the so-called electroviscosity effect), therefore, the local viscosity can be regarded as a function of a distance from the Brownian particle, i.e. $\eta = \eta(r)$ [4,5]. The modified Stokes relations for translational and rotational friction coefficients for the fluid with inhomogeneous viscosity were derived in [6]. The influence of the electroviscosity effect on the translational friction coefficient of charged particles was studied in Refs. [7,8]. As it follows from [7,8], for atomic or small polyatomic ions in aqueous solution the electroviscosity effect should be taken into account. A similar situation appears for a biopolymer with charges located on its surface. Actually, the electric field in the vicinity of the surface charge is the same as for the atomic ion in solution and is of the order 10^7–10^9 V/m (depending on whether or not the dielectric saturation of the solvent is taken into account). The corresponding pressure enhancement in aqueous solutions is more than 10^8–10^9 Pa and the local change in viscosity is significant (the local viscosity may be twice the bulk one). When the number of surface charges is large, modification of the solvent viscosity occurs throughout the near-surface region. Therefore, the electroviscosity effect should be important too for biopolymers having a large number of surface charges.

The second mechanism is associated with an additional stress that appears in a dielectrical continuum when it moves in the electric field of the brownian particle. This additional stress, caused by dielectric relaxation of the solvent molecules in the electric field, decreases the particle mobility and thus is called "dielectric friction" (see e.g. [9,10]). The latter mechanism plays an important role in rotational and translational motion of atomic and small polyatomic ions (for a review see [11,12] and references therein). As it was pointed out by Felderhof [13], the dielectric friction may be also important in the rotational motion of a macroion with a large surface charge. However, it was shown in Ref. [14] that the dielectric friction for macroions is significant, even if a total surface charge is low, provided that it is a sum of a large number of positive and negative charges.

The theory of the rotational Brownian motion of charged particles in which both electroviscosity and dielectric friction effects are taken into account has been developed recently [2]. For a spherical Brownian particle of radius R, with a spherically symmetrical radial electric field $E_r(r)$ the following expression for the rotational diffusion coefficient has been obtained [2]:

$$D_R = \frac{3R^2 D_{RS}}{1 + BE_r^2(R)} \int_R^\infty \frac{dr}{r^3 \eta(r)/\eta_0} \times \exp\left[-\int_R^r \left\{ \frac{1 + E_r r'^2 \, d(E_r B/r')/dr'}{1 + BE_r^2} \right\} \frac{dr'}{r'} \right] \quad (1)$$

where $B = \pi a^3 \chi / kT$. Note, that eq. (1) is a rigor-

ous result of continuum electrohydrodynamics. Here $D_{RS} = kT/8\pi R^3\eta_0$ is the Stokes–Debye–Einstein value for the rotational diffusion coefficient, η_0 is the viscosity of a pure solvent, a the radius of a solvent molecules, χ is a polarisability coefficient of the solvent, k Boltzmann's constant, T is an absolute temperature. The $\eta(r)$ in eq. (1) is a distance-dependent viscosity, r is the distance from the Brownian particle. In derivation of eq. (1) the stick hydrodynamic boundary conditions on the biopolymer surface and Debye expression for the orientational relaxation time for the solvent molecules, $\tau_D = 4\pi a^3/kT$ were used [2]. Note that the value τ_D specifies the orientational molecular dynamics of a pure solvent.

The question arises why the rotation of a particle with a spherically symmetrical charge distribution gives rise to any dielectric friction, while the electric field of the charged particle does not change during rotation. The physical reason of the additional torque exerted on the rotating particle, which causes in this case the dielectric friction is the so-called "electrohydrodynamic coupling", discussed in Ref. [13]: the molecular dipoles of the solvent tend to orient along the radial electric field, and when dielectric medium flows around the rotating charged particle the molecular dipoles move from one point with some direction of the electric field to another point with other direction. Therefore reorientation of the molecular dipoles occurs, which gives rise to the additional dissipation (dielectric friction).

It should be noted that in eq. (1) the effect of the electrolyte in the solvent is not taken into account, since it is negligible. Actually, the effect of the counterion friction associated with the ionic atmosphere of the Brownian particle reduces the particle translational diffusion coefficient, but this reduction is quite small (5–10%) [15,16]. Since the counterion friction arise due to deformation of the ionic atmosphere and since for the translation motion of the macroion this deformation is much more pronounced than for the rotational motion, we conclude that the effect of the counterion friction for the rotational motion is negligibly small.

Now we turn to the distance-dependent viscosity $\eta(r)$. It may be calculated, if the pressure dependence of the viscosity, $\eta = \eta(p)$, is known. The thermodynamic approach to the electrostriction gives [2,17]:

$$p(r) = p_0 + \tfrac{1}{2}E^2(r)\rho_0 \left.\frac{\partial\chi}{\partial\rho}\right|_{\rho_0} \tag{2}$$

Here p_0 and ρ_0 are the bulk values of pressure and of the solvent density, $E(r)$ is the electric field at point r. The value of $\partial\chi/\partial\rho$ may be calculated by using the Onsager–Kirkwood relation for the dielectrical permittivity, $\epsilon = 1 + 4\pi\chi$, [18]:

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \frac{4\pi}{9}\left(\frac{\rho}{m}\right)\left(\frac{\mu^2}{kT}\right)g_k \tag{3}$$

where ϵ_∞ is the high-frequency value of ϵ, μ and m are the dipole moment and mass of the solvent molecules, g_k is the Kirkwood g-factor. Differentiating eq. (3) with respect to ρ one can find $\partial\epsilon/\partial\rho$ and thus, $\partial\chi/\partial\rho = (4\pi)^{-1}(\partial\epsilon/\partial\rho)$. Using once again eq. (3), assuming that $\rho\partial\epsilon_\infty/\partial\rho = \epsilon_\infty$ and omitting the term $\rho\partial \ln g_k/\partial\rho$ one obtains after simple manipulation for the distance-dependent viscosity:

$$\eta(r) = \eta(p(r)) \tag{4}$$

where

$$p(r) = p_0 + \frac{1}{8\pi}E^2(r)\frac{\epsilon(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{(2\epsilon^2 + \epsilon_\infty^2)}F \tag{5a}$$

$$F = \frac{\epsilon}{\epsilon - \epsilon_\infty} + \frac{2\epsilon_\infty}{\epsilon_\infty + 2} - \frac{\epsilon_\infty}{2\epsilon + \epsilon_\infty} \tag{5b}$$

To calculate the rotational diffusion coefficient, one should know the electric field $E(r)$ around the biopolymer, which depends on the charge distribution in macromolecule.

Note that according to the eqs. (1)–(5) the influence of the electric field on the rotational Brownian dynamics is twofold. First, it changes the solvent viscosity in the vicinity of the biopolymer and, secondly, it causes the additional stress, associated with the electrical field. The second

effect is accounted for by the explicit dependence of the rotational diffusion coefficient D_R on the electrical field $E_r(r)$ in eq. (1).

If only the first mechanism is taken into account, then the direction of electrical field $E(r)$ may be arbitrary. However, the second mechanism may be rigorously accounted for only when the electrical field is radial.

The real electrical field in the vicinity of biopolymer, is produced by a number of charged groups on the biopolymer surface and is very complicated. Therefore, one had to use some simplified models of the real electrical field in calculations. In the next section we discuss how the model electrical field may be defined and how it is related to the charges distribution in macromolecule.

3. Charges distribution coefficients and a model electric field

Now we shall consider the electrical field in the vicinity of charged biopolymer surface. Let the macromolecule have N charged groups with charges q_i ($i = 1,2,\cdots,N$), located at points with spherical coordinates r_i, θ_i, ϕ_i. Here we regard the charged groups as point charges, located at depth $d_i = R - r_i$ from the surface of macromolecule, where d_i is a radius of ith charged group. For the spherical components of the electric field $E(r)$ around the biopolymer at point $r = \{r, \theta, \phi\}$ one obtains by solving the electrostatic equations for the sphere with permittivity ϵ_b embedded into dielectric continuum with permittivity ϵ:

$$E_r(r,\theta,\phi) = -\sum_{i=1}^{N}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1} \times \frac{(2l+1)(l+1)}{(l+1)\epsilon + l\epsilon_b}\frac{r_i^l q_i}{r^{l+2}} \times Y_{lm}^*(\theta_i,\phi_i)Y_{lm}(\theta,\phi) \quad (6a)$$

$$E_\theta(r,\theta,\phi) = -\sum_{i=1}^{N}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1} \times \frac{(2l+1)(l+1)}{(l+1)\epsilon + l\epsilon_b}\frac{r_i^l q_i}{r^{l+2}} \times Y_{lm}^*(\theta_i,\phi_i)\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi) \quad (6b)$$

$$E_\phi(r,\theta,\phi) = -\sum_{i=1}^{N}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1} \times \frac{(2l+1)(1+1)}{(l+1)\epsilon + l\epsilon_b}\frac{r_i^l q_i}{r^{l+2}} \times \frac{Y_{lm}^*(\theta_i,\phi_i)}{\sin\theta}\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) \quad (6c)$$

Here $Y_{lm}(\theta,\phi)$ are spherical harmonics of rank l. As it follows from eqs. (6), the real electric field in the vicinity of macromolecule is very complicated; so one needs simplified models to use in calculations. If the distribution of the surface charges is approximately uniform it seems reasonable to use spherically averaged values. Although this approach is not rigorous, we believe that such model electric field mimics the most important properties of the real field, when the rotational diffusion coefficient is considered (actually, D_R characterizes an ensemble of rotating particles with uniform angular distribution of their rotational axes, so the angular averaging is assumed).

Thus, instead, of the actual, perhaps non-radial, electric field we shall use the model electric field with radial symmetry, performing an averaging over the angular variables $\{\theta, \phi\}$. For example, we shall use the following average value for $E_r^2(r,\theta,\phi)$:

$$E_r^2(r,\theta,\phi) \to \overline{E_r^2}(r) = \frac{1}{4\pi}\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \times E_r^2(r,\theta,\phi) \quad (7)$$

with the analogous expressions for the other val-

ues. Using eqs. (6) and performing integration over the angular variables we obtain:

$$\overline{E_r^2}(r) = \sum_{l=0}^{\infty} \frac{H_l}{r^{2l+4}} \frac{(2l+1)(l+1)^2}{\left[(l+1)\epsilon + l\epsilon_b\right]^2} \tag{8}$$

$$\overline{E^2}(r) = \overline{E_r^2}(r) + \overline{E_\theta^2}(r) + \overline{E_\phi^2}(r)$$

$$= \sum_{l=0}^{\infty} \frac{H_l}{r^{2l+4}} \frac{(2l+1)^2(l+1)}{\left[(l+1)\epsilon + l\epsilon_b\right]^2} \tag{9}$$

$$\overline{E_r(r) r^2 (\partial/\partial r)\left(E_r(r)/r\right)}$$

$$= \sum_{l=0}^{\infty} \frac{H_l}{r^{2l+4}} \frac{(2l+1)(l+1)(l+3)}{\left[(l+1)\epsilon + l\epsilon_b\right]^2} \tag{10}$$

Here H_l are the charges distribution coefficients. They are defined by the relations:

$$H_l = \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j r_i^l r_j^l P_l(\cos\theta_{ij}) \tag{11}$$

Here $P_l \cos\theta_{ij}$ is a Legendre polynomial of rank l, θ_{ij} is an angle between vectors $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$, directed from the center of the macromolecule to the point charges q_i and q_j. In deriving eqs. (8)–(11), we have used the properties of the spherical harmonics.

Note that q_i in eq. (11) are statistical variables, so one should treat them in terms of probabilities $P(q_i)$. Namely, if the ith charged group may be at s different charge states $e_1, e_2, \cdots, e_s$, with corresponding energies $E_1, E_2, \cdots, E_s$, then we have for the probability of the ith charged group to have a charge e_α:

$$P(q_i = e_\alpha;\, pH) = \frac{\exp(-E_\alpha/kT)}{\sum_{\alpha=1}^{s} \exp(-E_\alpha/kT)},$$

$$\alpha = 1,2,\ldots,s \tag{12}$$

Here, we have stressed that these probabilities depend on the pH of the solvent. Taking into account the statistical nature of the surface charges q_i one should write eq. (11) in the following form:

$$H_l = \langle \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j r_i^l r_j^l P_l \cos\theta_{ij} \rangle \tag{13}$$

Here the angular brackets $\langle\ \rangle$ denote the equilibrium average, i.e., the value averaged with the use of the distribution (12).

Note that it follows from the previous considerations that the charge distribution influences the rotational Brownian dynamics of macromolecule through the charge distribution coefficients H_l. When the pH of the solvent varies, it causes the variation of charges q_i at points $\boldsymbol{r}_i$ and, hence, the variation of coefficient H_l. To perform calculations of H_l one should know the details of the charge distribution.

Usually, the biopolymers (proteins) have approximately 10^2 to 10^3 charged groups distributed over its surface. At the same time, the total charge of the biopolymer, $Q = Ze$ (e is the electron charge), is of the order of $1e$ to $10e$. So, in a wide region of parameters (such as temperature, pH, etc.), the number of positively and negatively charged groups on the biopolymer surface is approximately equal.

Let us rewrite eq. (13) for the charge distribution coefficients H_l in the following form:

$$H_0 = \langle \sum_{i=1}^{N} q_i \sum_{j=1}^{N} q_j \rangle = \overline{Q^2},\ l = 0 \tag{14}$$

$$H_l = H_{ls} + H_{ld},\ l \geqslant 1 \tag{15}$$

Here we extract the coefficient H_0, which is equal to the average square of the total charge of the macromolecule. The coefficients H_l with $l \neq 0$ we express as a sum of a "self" part ($i = j$) and a "distinct" part ($i \neq j$):

$$H_{ls} = \langle \sum_{i=1}^{N} q_i^2 (R - d_i)^{2l} \rangle \tag{16}$$

$$H_{ld} = \langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} q_i q_j P_l(\cos\theta_{ij}) (R - d_i)^l (R - d_j)^l \rangle \tag{17}$$

In eqs. (14) and (16) we use the identity $P_l(1) = 1$.

One can see, that the "distinct part" H_{ld} (eq. (17)) is a sum of approximately 10^4 to 10^6 terms which are products of the P_l ($\cos\theta_{ij}$) (the latter either may be negative or positive depending on the mutual location of the charged groups) and

$q_i q_j$. As it was pointed out, the number of the positively and negatively charged groups are approximately equal, so one can conclude that if the surface charge distribution is irregular, we have approximately equal numbers of positive and negative terms in eq. (17) which cancel out by summation. Therefore it is reasonable to assume that the "self" part of the coefficients H_l which is the sum of about 10^2 positive terms exceeds significantly its "distinct" part, i.e. $H_{ls} \gg H_{ld}$. If we neglect the distinct part and assume that $d_i = d$ for all $i = 1, \cdots, N$, we obtain:

$$H_l = \overline{Q^2}\delta_{l0} + (1 - \delta_{l0})(R - d)^{2l} J_b \tag{18}$$

$$J_b = \sum_{i=1}^{N} \langle q_i^2 \rangle \tag{19}$$

Therefore, one can see that the charge distribution coefficients depend on two variables only, viz. on the average square of the total charge, $\overline{Q^2}$, and on the sum of the average squares of surface charges, J_b. The latter may be related to the partial ionic strength I_b, associated with charged groups of macromolecules:

$$I_b = \tfrac{1}{2} n \sum_{i=1}^{N} \langle q_i^2 \rangle = \tfrac{1}{2} n \sum_{\beta=1}^{p} N_\beta \overline{q_\beta^2} = \tfrac{1}{2} \sum_{\beta=1}^{p} n_\beta \overline{q_\beta^2} \tag{20}$$

Here n is a number concentration of biopolymer macromolecules in solution, i.e. $n = MN_a$, where M is the molar concentration of the biopolymer, N_a Avogradro's number, N_β is the number of charged groups of sort β per macromolecule, and $\overline{q_\beta^2}$ is the square average charge of this group, $n_\beta = nN_\beta$ is total number concentration of charged groups of sort β in the solution (here $\beta = 1,2,\cdots, p$, and $N_1 + N_2 + N_3 + \cdots N_p = N$). Therefore, from eqs. (19) and (20), we obtain:

$$J_b = 2I_b/n \tag{21}$$

Substituting eqs. (18) and (21) into eqs. (8)–(10), one can obtain the explicit expressions for $\overline{E^2(r)}$, $\overline{E_r^2(r)}$ and $\overline{E_r(r) r^2 \partial/\partial r (E_r(r)/r)}$ for the following cases: $\epsilon = \epsilon_b$, $\epsilon \ll \epsilon_b$, and $\epsilon \gg \epsilon_b$. If the dielectrical permittivity ϵ of the solvent is much higher than that of the biopolymer (the case which is relevant for aqueous solutions when $\epsilon = 78.3$), i.e., if $\epsilon \gg \epsilon_b$ one has:

$$\overline{E^2}(r) = \frac{\overline{Q^2}}{\epsilon^2 r^4} + \frac{(2I_b/n)}{\epsilon^2 r^4} u_0\left(\frac{R-d}{r}\right) \tag{22}$$

$$\overline{E_r^2}(r) = \frac{\overline{Q^2}}{\epsilon^2 r^4} + \frac{(2I_b/n)}{\epsilon^2 r^4} u_1\left(\frac{R-d}{r}\right) \tag{23}$$

$$\overline{E_r r(\partial/\partial r)(E_r/r)} = -\frac{3\overline{Q^2}}{\epsilon^2 r^4} - \frac{(2I_b/n)}{\epsilon^2 r^4} \times u_2\left(\frac{R-d}{r}\right) \tag{24}$$

Here the functions u_0, u_1, u_2 are defined by the relations ($\epsilon \gg \epsilon_b$):

$$u_0(x) = \left[\frac{2x}{1-x^2}\right]^2 - \frac{1}{x^2} \ln|1 - x^2| - 1 \tag{25}$$

$$u_1(x) = x^2 \frac{3 - x^2}{(1-x^2)^2} \tag{26}$$

$$u_2(x) = \frac{3 + 3x^2 - 2x^4}{(1-x^2)^2} - 3 \tag{27}$$

Substituting eqs. (22) and (25) into eqs. (4) and (5), one can calculate $\eta(r)$. Substituting $\eta(r)$ and eqs. (23), (24) and (26), (27) into eq. (1) and performing integration, one obtains the rotational diffusion coefficient as a function of the total charge of biopolymer $\overline{Q^2}$ and the "partial ionic strength" I_b. It should be noted that $\overline{Q^2}$ and (I_b/n) are comparable in magnitude, moreover (I_b/n) often exceeds $\overline{Q^2}$.

The charged groups commonly have only two charged states. For example, the most important groups such as COOH and NH_2 have the charge states $(0, -e)$ for $(COOH, COO^-)$ and $(0, +e)$ for (NH_2, NH_3^+). Thus, for a square average charge $\overline{q_\beta^2}$ of this groups one has:

$$\overline{q_\pm^2} = 0^2 P(0) + (\pm e)^2 P(\pm e) = 0 + (\pm e)^2 \frac{e^{-E_\pm/kT}}{e^{-E_0/kT} + e^{-E_\pm/kT}} \tag{28}$$

Here the positive sign is used for NH_3^+ groups and the negative sign for COO^- groups. At the

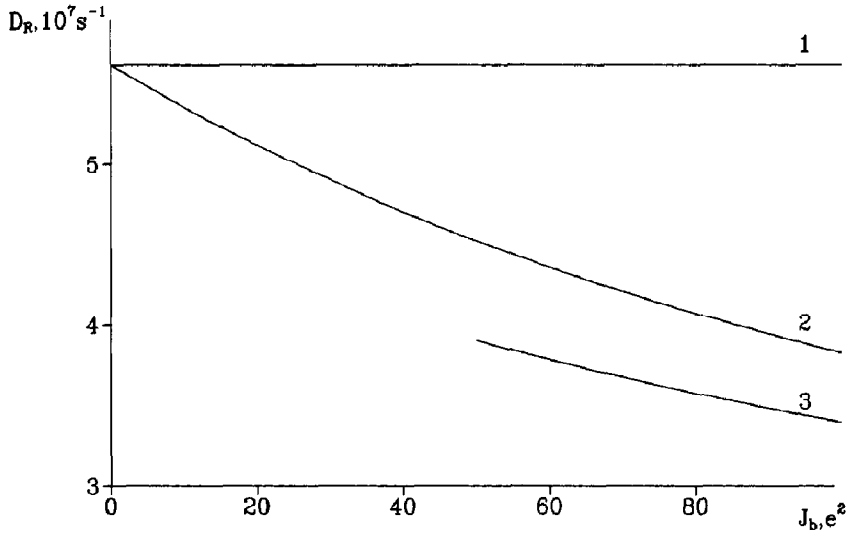

Fig. 1. Rotational diffusion coefficient D_R versus partial ionic strength $J_b = \Sigma_i q_i^2$, ($J_b = 2I_b/n$) for model particle with different total charges (Charges are given in electron units, e). 1 – the SED-theory, 2–$Q = 0$, and 3 – $Q = 50e$.

same time, the corresponding average charges $\bar{q}_+$ or $\bar{q}_-$ for these groups may be expressed as follows:

$$\bar{q}_\pm = 0P(0) + (\pm e)P(\pm e) = 0 + (\pm e)\frac{e^{-E_\pm/kT}}{e^{-E_0/kT} + e^{-E_\pm/kT}} \quad (29)$$

From eqs. (28) and (29) it follows that:

$$\overline{q_\pm^2} = e|\bar{q}_\pm| \quad (30)$$

Thus to calculate the square average charge for these charged groups, one only needs to know their average charges. The calculation of the latter values is straightforward.

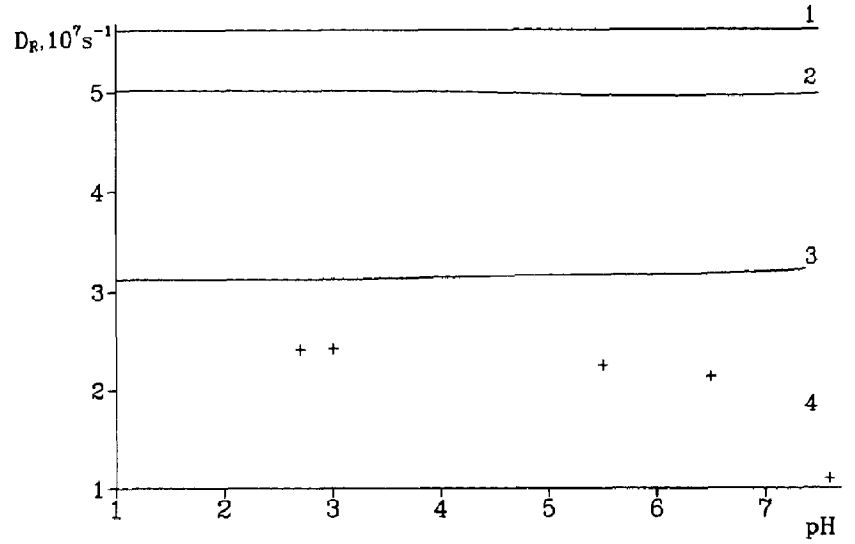

Fig. 2. Rotational diffusion coefficient D_R versus pH of the solvent for lysozyme ($R = 15$ Å). 1 – the SED-theory, 2 – calculations for $\epsilon = 78.3$, 3 – calculations for the model of the total dielectrical saturation of the solvent $\epsilon = \epsilon_b = \epsilon_\infty = 5.2$, and 4 – (+) experimental data [6,7].

4. Numerical results for model macromolecule and for lyzozyme

Using eqs. (1), (4), (5) and (21)–(27), we calculate the rotational diffusion coefficient as a function of the total charge Q and the partial ionic strength (I_b/n). The results for $R = 15$ Å, and $d = 1.43$ Å (the latter value corresponds to the radius of NH_4^+-group [19]) are presented in Fig. 1. One can see that the rotational diffusion coefficient decrease significantly with increasing partial ionic strength I_b.

We also perform calculations for the pH dependence of the D_R for lyzozyme which is nearly spherically shaped [1] (we use the value of 15 Å for its radius [1]). The total charge and the partial ionic strength I_b was calculated using the dissociation constants for the charged groups on the biopolymer surface from Ref. [20]. The results of these calculations are shown in Fig. 2. The available experimental data for D_R [21,22] and the corresponding values of D_{RS} from the ordinary Stokes–Einstein–Debye (SED) theory are also shown in Fig. 2.

One can see from Fig. 2 that the experimental data differs significantly from the predictions of the ordinary SED-theory. It is well known that the ordinary SED-theory overestimates the values of D_R. It gives the values 1.5–2 times higher than the experimental values for various proteins if the "net"protein radius is used. The agreement with the SED-theory may be achieved if one uses the so-called "hydrodynamic" radius, which includes the hydration shell radius of 3.5 Å (see e.g. [23] and references therein). The latter is a fitting parameter. Moreover, there is no physical reason for the whole hydration shell to follow rigidly the macromolecule in its rotational motion, so we use the "net" radius in our theory.

It should be noted that the effect of the dielectric saturation of the solvent has not been taken into account in our calculations where we have used the low-field value of the dielectrical permittivity: $\epsilon = 78.3$. The electric field in the vicinity of the biopolymer surface, however, is so strong that this effect may not be neglected. Unfortunately, the electrostatic problem with the locally inhomogeneous dielectrical permittivity is analytically unsoluble, but simple estimates show that the solvent saturation near the biopolymer surface is total. So, the local value of ϵ is close to that of the biopolymer, ϵ_b. Therefore we assume that the saturation effect may be taken into account if we consider the case $\epsilon = \epsilon_\infty = \epsilon_b$, which is analytically soluble (ϵ_∞ is saturated value of the solvent permittivity). The corresponding expressions for the values $E^2(r)$, $\overline{E_r^2(r)}$ and $\overline{E_r(r)r^2\partial/\partial r(E_r(r)/r)}$ in the case $\epsilon = \epsilon_\infty = \epsilon_b$

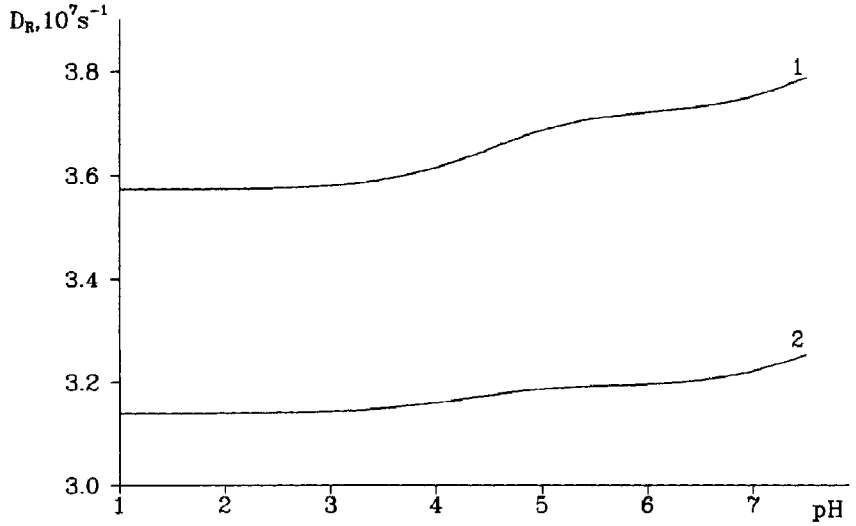

Fig. 3. Rotational diffusion coefficient D_R versus pH of the solvent for lysozyme ($R = 15$ Å), calculated with and without account of the electroviscosity effect. 1 – The electroviscosity effect is not taken into account, and 2 – the electroviscosity effect is taken into account.

are just the same as in eqs. (22)–(24) but with new functions u_0, u_1, u_2 defined now by the following relations ($\epsilon = \epsilon_\infty = \epsilon_b$):

$$u_0 = \frac{1+3x^2}{(1-x^2)^3} - 1 \tag{31}$$

$$u_1(x) = \frac{1}{8x}\ln\left(\frac{1+x}{1-x}\right) - \frac{1-7x^2+4x^4}{4(1-x^2)^2} \tag{32}$$

$$u_2(x) = \frac{5}{16x}\ln\left(\frac{1+x}{1-x}\right) + \frac{1+8x^2-x^4}{8(1-x^2)^3} - \frac{3}{4}\frac{1-7x^2+4x^4}{(1-x^2)^2} \tag{33}$$

Using the value of $\epsilon_\infty = 5.2$ for water [19] we calculate the pH dependence of the rotational diffusion coefficient for the model of totally saturated solvent. The results are also shown in Fig. 2. One can see that the pH dependence of D_R for this model is in quite satisfactory agreement with experimental data [21,22]. Once more we note that we use the "net" radius in our calculations, and do not use any fitting parameters. Therefore we conclude that our theory agrees with the experiment if the effect of the dielectrical saturation is included in the theory. The assumption $\epsilon - \epsilon_\infty = \epsilon_b$ is not very crude because it holds true in the most important solvent region just in the vicinity of the biopolymer surface.

For the model of totally saturated solvent the importance of the electroviscosity effect was investigated. In Fig. 3 the pH dependence of the rotational diffusion coefficient of lysozyme, calculated with and without account for the electroviscosity effect are compared. One can see that electroviscosity reduces the value of D_R approximately by 15%, so the influence of the dielectric friction on the rotational Brownian motion is much more pronounced than that of the electroviscosity.

5. Discussion

Influence of surface charges of biopolymer macromolecule on its rotational Brownian dynamics in solutions is considered in terms of dielectric friction and electroviscosity. A mean spherical approximation for electric field of macromolecule is used. The charge distribution coefficients are introduced and evaluated for irregular surface charges distribution. It is shown that for the latter case the rotational diffusion coefficient D_R depends only on two variables: on the total charge of macromolecule and on the "partial" ionic strength of the solution associated with the surface charges of the biopolymer.

We calculate the rotational diffusion coefficient, D_R, as a function of the total charge and of the partial ionic strength for model particles in aqueous solutions and show that the rotational diffusion coefficient decrease significantly with increasing total charge and partial ionic strength of the particles. The pH dependence of D_R for lyzozyme at low ionic strength is calculated and compared with available experimental data which differ significantly from predictions of the ordinary Stokes–Einstein–Debye theory. Our theory is in good agreement with experimental data if the model of the total dielectric saturation of the solvent is used. The theory agrees quite satisfactorily with experiment, although it has no fitting parameters.

For the model of the total dielectric saturation of the solvent the relative significance of the electroviscosity and dielectric friction effects is studied. It is shown that whereas the dielectric friction reduces the rotational diffusion coefficient approximately by a factor of two, compared to its SED value, the additional reduction of D_R due to the electroviscosity is no more than 15%. Thus the dielectric friction is the main mechanism reducing the molecular mobility of charged biopolymers in aqueous solutions.

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