however, it was possible to make a more detailed study of the particle trajectories during barrier crossings. It was found that for both cases (isotropic and highly anisotropic viscosity tensor) barrier crossings occurred over a saddle point with energy equal to one barrier height. In the isotropic case the average path followed was one of steepest descent on the energy surface and corresponded to uncorrelated barrier crossing. In the anisotropic case, however, the average path followed through the saddle point was a constant-energy path and corresponded to correlated motion of the two "dihedral angles" but with a phase lag between them. These average paths help make understandable the insensitivity of the activation energy for the two-dimensional model. It remains for future work to determine the extent to which these ideas are applicable to long-chain molecules.

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(34) Units used are dimensionless. They correspond to a system where the mass of a carbon atom, the length l of a C–C bond, and k_BT_{ref}, where T_{ref} = 600 K, are all unity. A δt of 1 corresponds to 7.51×10^{-14} s and a value of the coefficient η of 1 corresponds to 2.67×10^{-10} dyn/(cm s^{-1}) in cgs units. Note that this coefficient η, which multiplies atom velocity in the Langevin equation to yield the frictional force acting upon it, is not the solvent viscosity μ; it is obtained from the latter by a relation such as Stokes' law, $\eta = 6\pi a\mu$, where a is an effective atomic radius.
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Influence of Counterion Exchange on the Induced Dipole Moment and Its Relaxation for a Rodlike Polyion

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ABSTRACT: The influence of the exchange between associated and free counterions on the distribution of the former along a uniformly charged, one-dimensional rod in the presence of a vanishingly small electric field has been investigated. The *two-phase model* has been used together with simplifying boundary conditions, and counterion–counterion as well as polyion–polyion interactions have been neglected. Expressions for the induced dipole moment in the associated phase and its relaxation time have been evaluated. Therein appears a characteristic length Z representing the ratio of the diffusion coefficient of the associated counterions in the axial direction along the rod to the rate of exchange. For a rod of length L these expressions reduce to those obtained from an analogous model in which exchange is neglected if $Z \gg L$. The induced dipole moment and its relaxation time are then proportional to L^3 and L^2, respectively. In the opposite case where $Z \ll L$ the value of the induced dipole moment is strongly reduced and proportional to L whereas the relaxation time is determined solely by the rate of exchange and is independent of L. It is thus demonstrated that such an exchange should have a considerable influence on the dielectric properties of polyelectrolyte solutions.

Introduction

Several theories have already been proposed to explain the contribution of linear polyelectrolytes in the ionized state to the electric polarization of their aqueous solutions. Many of them were based on a simplified model (the so-called two-phase model of Oosawa[1]) and the polarization

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contribution was ascribed to an induced dipole moment arising from the perturbation by the electric field of the bound (or associated) counterions along the charged macromolecular chain. Although the use of the two-phase model itself may be questioned, it leads to analytical expressions with, in principle, no adjustable parameters. Many features observed experimentally could be explained qualitatively or even semiquantitatively by it. Nevertheless the problem of the dielectric properties of a polyelectrolyte solution has not yet been solved in a completely satisfactory way and further theoretical investigation is necessary.

Up to now in the two-phase model the exchange of counterions between the two phases has not been taken into account or only insofar as its influence on the dielectric relaxation is concerned.[2,3] In the present paper we extend the two-phase model treatment for a rodlike charged macromolecule, introducing explicitly such an exchange. It may serve to represent in a simplified way the occurrence of fluctuations in the radial distribution of counterions and thus also in the number of induced dipole moment determining counterions, provided the time scale considered is long enough. As we are only interested to see whether counterion exchange between the two phases may have any influence on the induced electric dipole moment and dielectric relaxation time, interaction effects have been neglected in a first approximation. As will be shown below the influence of the exchange on the two electric quantities may be considerable indeed.

The Model

The macromolecule will be represented by a one-dimensional, uniformly charged, rod with counterions distributed over two phases, the bound phase and the free phase. End effects, counterion interactions in the longitudinal direction along a macromolecular chain, and interactions between polyions will be neglected as in previous work. The two-phase approximation implies that every counterion must be in either of the two phases. The concentration of the counterions in the free phase is assumed to be time independent, uniform, and undisturbed by an external electric field. These counterions are supposed not to contribute significantly to the polarization of the polyelectrolyte solution. The distribution of the associated counterions of the bound phase along the rod is assumed to be uniform in the absence of an external electric field and characterized by the linear counterion density ϕ_0.

In the presence of a small external field this distribution will be perturbed and the counterion density $\phi(x)$ will become a function of the position x along the chain. It will be found as a solution of the von Smoluchowski diffusion equation with an additional term to account for the exchange of counterions between the free and bound phases. This exchange tends to restore the equilibrium condition for the distribution of the counterions which has been perturbed by the change of ϕ with respect to ϕ_0. The flux from or to the bound phase will be represented by a scalar quantity (sink or source) in order to maintain the unidimensionality of the problem. As only small deviations from the equilibrium distribution in the absence of an external field will be considered, this flux will be expanded in a power series of $\Delta\phi \equiv \phi - \phi_0$ up to the linear term. The net counterion flux per unit length F from the free to the bound phase will therefore be represented by

$$F(x) = -K\Delta\phi + O(\Delta\phi^2) \tag{1}$$

where K is the rate constant for the exchange. The modified von Smoluchowski equation for the change with time t of the counterion density then reads

$$\frac{\partial\phi}{\partial t} = uk_BT\frac{\partial^2\phi}{\partial x^2} + zeuE\frac{\partial\phi}{\partial x} - K\phi + K\phi_0 \tag{2}$$

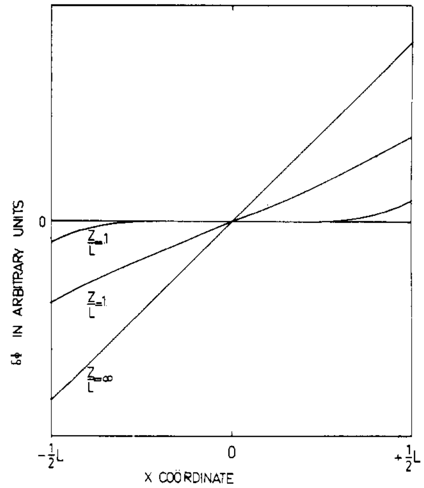

Figure 1. $\Delta\phi$ in arbitrary units as function of x for different values of Z/L.

Here u is the counterion mobility along the chain, k_B the Boltzmann constant, T the temperature, z the valency of the counterion, e the elementary charge, and E the time-independent electric field along the rod, assumed to be uniform.

Electric Dipole Moment

In the stationary state defined by

$$\partial\phi/\partial t = 0 \tag{3}$$

the general solution of (2) can be represented by

$$\phi = c_+e^{s_+x} + c_-e^{s_-x} + \phi_0 \tag{4}$$

in which

$$s_\pm = 2uk_BT\{-zeuE \pm [(zeuE)^2 - 4Kuk_BT]^{1/2}\} \tag{5}$$

To evaluate the integration constants c_+ and c_- we need two boundary conditions, which can be found by assuming that at the end of the polyelectrolyte rod no flux in the x direction exists. This yields the two conditions

$$\left[zeuE + uk_BT\frac{\partial\phi}{\partial x} = 0\right]_{x=\pm L/2} \tag{6}$$

where L is the length of the rod and the origin of the x axis has been taken in the center of macromolecule. These conditions are consistent with the conservation of the number of bound counterions up to the first order in E. Up to this order the solution can be written as

$$\phi = \phi_0\left[1 + \frac{zeZ}{2k_BT}\frac{\sinh(x/Z)}{\cosh(L/2Z)}E\right] + O(E^2) \tag{7}$$

where Z is defined by

$$Z = (uk_BT/K)^{1/2} \tag{8}$$

and turns out to be a characteristic length in our treatment. In Figure 1 ϕ is represented as a function of x for three different values of the ratio Z/L.

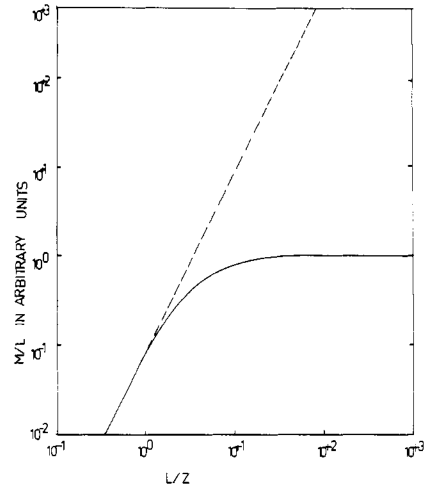

Figure 2. M/L in arbitrary units as function of L/Z: (—) according to formula 9; (---) according to formula 10.

The electric dipole moment due to the field-dependent counterion density ϕ is given up to the first order in E by

$$M = ez\int_{-L/2}^{+L/2} x\phi \, dx = \frac{\phi_0(ze)^2LZ^2E}{k_BT}\left[1 - \frac{2Z}{L}\tanh\frac{L}{2Z}\right] \tag{9}$$

where (7) has been used to derive the last member. This result is represented in Figure 2.

There are two limiting cases which may be interesting to consider. The first is when $Z/L \gg 1$ (or $D \equiv uk_BT \gg KL^2$, where D is the diffusion coefficient of the associated counterions along the macromolecular chain). In this limit the dipole moment reduces to

$$(M)_{Z/L\gg 1} = \phi_0(ze)^2L^3E/12k_BT \tag{10}$$

This result is identical with the one found previously under the same assumptions but neglecting the exchange of counterions between the bound and free phases. The polarizability is proportional to L^3, as ϕ_0 is independent of the length of the rod under conditions where the fraction of associated counterions is independent of L.

The other limiting case occurs for $Z/L \ll 1$ (or $D \ll KL^2$). Here the polarizability becomes proportional to L

$$(M)_{Z/L\ll 1} = \phi_0(ze)^2Z^2LE/k_BT \tag{11}$$

and is strongly reduced (by a factor $12(Z/L)^2$) with respect to the value expected if no exchange could take place.

Relaxation Time

In order to evaluate the relaxation time characteristic for the dipole moment established in the preceding paragraph, we shall start from the Fourier-analyzed form of the stationary perturbation in the uniform counterion distribution according to (7) and consistent with the boundary condition (6).

$$\Delta\phi = \sum_{n=1}^{\infty} A_n^{\,0} \sin\,[(2n-1)\pi x/L] \tag{12}$$

Here $A_n^{\,0}$ represents the amplitude of the nth mode and is given by

$$A_n^{\,0} = \frac{(-1)^{n+1}C^0}{1 + [(2n-1)\pi(Z/L)]^2} \tag{13}$$

where C^0 is a constant. The decay of $\Delta\phi$ will be characterized by time-dependent amplitudes $A_n(t)$, which may be found from the modified von Smoluchowski equation (2) for $E = 0$

$$\frac{\partial\Delta\phi}{\partial t} = ukT\frac{\partial^2\Delta\phi}{\partial x^2} - K\Delta\phi \tag{14}$$

This yields the following expression for the decay of the fluctuation

$$\Delta\phi(t) = \sum_{n=1}^{\infty} A_n^{\,0}e^{-t/\tau_n}\sin\frac{(2n-1)\pi x}{L} \tag{15}$$

where τ_n represents the nth-mode relaxation time given by

$$\tau_n = (ukT)^{-1}\left[\frac{(2n-1)^2\pi^2}{L^2} + \frac{1}{Z^2}\right]^{-1} \tag{16}$$

For $Z/L \gg 1$ the amplitude $A_n^{\,0}$ decreases rapidly with increasing n and practically only the first mode is needed to describe the relaxation process. Therefore

$$\tau_{Z/L\gg 1} \simeq \tau_1 \simeq L^2/\pi^2ukT \tag{17}$$

In the opposite limit, when $Z/L \ll 1$, only those modes will contribute significantly for which $(2n-1)\pi Z/L < 1$. Consequently (16) reduces to

$$\tau_{Z/L\ll 1} \simeq (ukT)^{-1}Z^2 = K^{-1} \tag{18}$$

where use has been made of (8). In the former case the characteristic relaxation time increases with L^2, as found previously for the model in which exchange has been neglected; in the latter the relaxation time is independent of the length of the rod and solely determined by the inverse of the rate constant of the exchange.

Discussion

It is clear that within the framework of the simplified model used counterion exchange between the bound and the free phases may have a considerable influence on both the amplitude and the relaxation of the electric dipole moment due to the pertubation of the associated counterion distribution along the polyelectrolyte chain. It is the ratio of the characteristic length Z, which is entirely defined by the diffusion coefficient of the associated counterions along the chain and the rate constant for the exchange with the free phase, and the linear dimension of the polyelectrolyte which determines the dependence of the polarizability and the relaxation time on L. If Z is much larger than the length of the macromolecular rod, the exchange has no influence on these quantities. In the other extreme, the relatively fast exchange considerably limits the extent of the stationary perturbation in the counterion distribution, thus reducing the polarizability of the polyelectrolyte. Concomitantly the relaxation mechanism is completely dominated by the rate of the exchange, which is independent of the macromolecular dimension.

It still remains necessary to estimate a value for the rate constant for counterion exchange K in order to evaluate the characteristic length Z. Recently, the relaxation time for the disappearance of a perturbation in the counterion density near the rod by a radial diffusion mechanism has been estimated.[5] Although this calculation was not based on a two-phase model but on a continuous distribution of counterions perpendicular to the rod, the reciprocal of this concentration-dependent relaxation time may be considered as a reasonable approximation for K. In Figure 3 both K and the corresponding Z (using for u the mobility of Na^+ in an infinitely diluted electrolyte solution, i.e., $u = 3.1 \times 10^{11}$ m s^{-1} N^{-1}) are plotted as a function of concentration. From this figure it may be concluded that for a concentration of 10^{-3} monomol L^{-1} a change in the molar mass dependence of polarizability and relaxation time can be

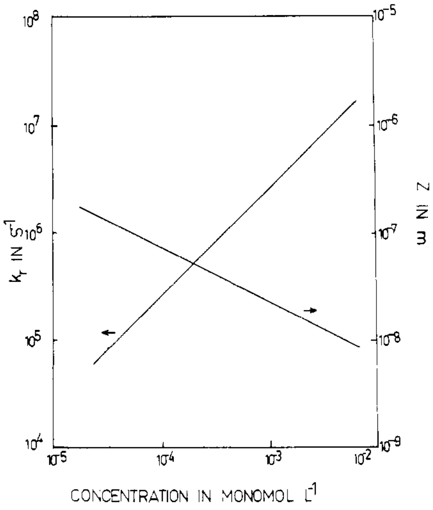

Figure 3. Values of K as calculated in ref 5 (left scale) and the corresponding values of Z (right scale) as function of monomolar concentration.

expected if the contour length of the polyelectrolyte increases above 100 nm, provided the charged macromolecule remains rodlike.

It thus seems that counterion exchange may be an important phenomenon for understanding the dielectric properties of polyelectrolytes in solution. The importance of this conclusion may strongly depend, however, on the validity of the model used to reach it. As indicated above, the two-phase model is a highly simplified approach which in the case of the electric polarizability leads to the neglect of the contribution of a certain fraction of the counterions to the dielectric properties of the solution and implies the neglect of the influence of concentration gradients on the dipole moment. The least that one can conclude from the present calculation, however, is that the two-phase model, without considering counterion exchange between the two phases, may be limited, for rodlike polyelectrolytes, to molecules not exceeding a certain length, depending on Z. Above this critical contour length the simple description without counterion exchange breaks down, thus eventually affecting the L dependence of both the polarizability and relaxation time of the induced electric moment. In a recent paper[6] Fixman, starting from a different and more general model, has derived an expression for the dipole moment of a cylindrical polyion which has a functional dependence on L comparable to our eq 9, although the quantity Z in his theory is defined quite differently.

At present there are no experimental data available on systems that fulfill the necessary conditions to test this more general conclusion or those of the preceding section. To satisfy the assumptions underlying the model, the charged macromolecule should at least be rodlike in a wide range of molar masses and at concentrations where the dielectric effects still can be measured. For most polyelectrolytes this cannot be realized simultaneously. Moreover, in order to reduce the influence of concentration gradients in the free phase and of intermolecular interactions, addition of low molecular salt might be necessary, but this in turn may not be without effect on the average conformation of the macromolecule and on the sensitivity of the dielectric measurements. Therefore although in principle an experimental verification of the theoretical prediction seems to be possible, in practice many experimental problems may still have to be overcome. Hopefully in the near future new experiments will be designed which will give a decisive answer to the question whether the approach used in the present work is useful or not.

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Critical Evaluation of Electron Microscopy of Ionomers

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ABSTRACT: Electron microscopy has been used to examine the morphology of four ionomers. The transfer theory of imaging, which has been overlooked in previous ionomer studies, has been used to interpret the images of both solvent-cast and microtomed thin films. Solvent casting was found to produce a number of interesting artifacts but no useful information about ionic domains. Microtomed sections of a copolymer of ethylene and methacrylic acid, sulfonated polypentenamer, and sulfonated polystyrene contained no preparative artifacts but showed no distinct domain structure even in the ionomers neutralized with cesium, probably because of film thickness problems. Microtomed sections of sulfonated EPDM, however, contain 300-nm phase-separated regions. Osmium tetraoxide staining of these EPDM sections showed domains averaging less than 3 nm in size primarily inside these regions. Unfortunately, the section thickness prohibits an accurate determination of the size distribution or the detailed shape of these domains and hence the selection of the most appropriate model of domain structure.

Introduction

Ionomers have gained commercial importance in recent years due to the beneficial change in mechanical and ion transport properties obtained by adding a small number of ionic groups to a nonionic polymer. The copolymerization of ethylene with less than 10 mol % of methacrylic acid (E–MAA) and then neutralization with a metal cation inhibit spherulite formation, producing a material which behaves as if cross-linked at room temperature but is melt processable.[1] Incorporation of neutralized sulfonate groups into rubbers such as polypentenamer or EPDM also yields polymers with thermally

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