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SURFACE POTENTIAL OF A CYLINDRICAL POLYMER MACROMOLECULE IN ELECTROLYTE SOLUTION

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The distribution of potential on the surface of cylindrical macromolecules in a solution not containing an ordinary electrolyte has been calculated¹. The calculations concerned a system of parallel equidistant macromolecules surrounded by counterions. In this case it is possible to obtain an exact solution of the Poisson-Boltzmann equation for any potential. In the calculations no allowance was made for the interaction between different macromolecules, which in the absence of an external electrolyte is quite important. In fact, as shown by Onsager², a parallel distribution of cylindrical macromolecules minimises the free energy of the system when the forces of electrostatic repulsion between the macromolecules are fairly high. The present paper describes the determination of the potential difference between a solution of an ordinary electrolyte surrounding a macroion and the surface of the latter. Here the external non-polymeric electrolyte acts as a screen to the forces of electrostatic repulsion between the macroions when the concentration of the latter is not too high. At high concentrations of the non-polymeric electrolyte the cylindrical macromolecule may undergo twisting in a sense opposite to the original as a result of the screening of the charges on neighbouring units of the polymer chain.

However, at large values (0.8–1) of α at certain concentrations of the non-polymeric electrolyte the radius of the double layer surrounding the individual charges may prove to be greater than the mean distance between the

charges which with $\alpha = 0.8-1$ is equal to the length of a single chain unit $b = 5.1 \times 10^{-8}$ cm. In this case the effect of screening is small and the cylindrical form of the macroion remains virtually unchanged. It can be readily shown that this state of affairs holds right up to 0.1 M concentration of the external electrolyte, such as NaCl and KCl, up to polymer concentrations equivalent to a 0.1–0.5 M solution of the monomer. In fact, in this case the radius of the diffuse double layer is a minimum, of the order of $10^{-7}-10^{-8}$ cm, i.e. equal to b or greater by a power of 10. A knowledge of the distribution of potential around the individual cylindrical macroions is necessary both in an investigation of equilibrium thermodynamic properties and in an examination of kinetic phenomena in electrolyte solutions.

Calculation of Potential Distribution

Consider a cylindrical polymer macromolecule of length $h = zb$ and radius a . We shall assume that $h \gg a$. In this case the molecule may be regarded as infinitely long and the problem has cylindrical symmetry. The cylinder contains on its entire surface ν charges with the average density

$$|\sigma| = \frac{\nu e}{2\pi a h}, \quad (1)$$

where $e = 4.8 \times 10^{-10}$ CGSE, and a is the radius of the cylinder. A distribution of potential in the region surrounding the cylinder satisfies the Poisson-Boltzmann equation:

$$\Delta \Psi = -\frac{4\pi}{D} \rho, \quad (2)$$

where D is the dielectric constant of the solution. The potential Ψ varies only in the plane perpendicular to the axis of the cylinder, in a direction perpendicular to the surface of the cylinder, its absolute value decreasing with distance from the surface. It is to be expected that the decrease is fairly rapid because of the strong screening of the charge on the surface by the counterions of the double layer surrounding the macroion. The counterions and the ions of the ordinary electrolyte will be regarded as univalent in order to simplify the calculations. We shall divide the region surrounding the macroion into two parts in relation to r . In the region $a \leq r \leq R$ the potential is assumed to be so large that $|e\Psi/kT| \gg 1$. In the second region where $R < r < \infty$ the potential Ψ satisfies the relation $|e\Psi/kT| \ll 1$. The system as a whole, containing the macroion, the counterions, and the ordinary electrolyte, is electrically neutral. Therefore the overall charge of the free ions in solution is numerically equal, but of opposite sign, to the charge on the surface of the macroion.

The charge density ρ in Eqn. (2) may be put in the following form:

$$\rho = \sum_i n_i e_i \exp\left(-\frac{e_i \Psi}{kT}\right), \quad (3)$$

where n_i is the number of ions of a given kind per unit volume of the solution and e_i is the ionic charge. ρ does not include the macroions. In the case of a uni-univalent electrolyte and univalent counterions ρ becomes

$$\rho = n_1 e_1 \exp\left(-\frac{e_1 \Psi}{kT}\right) + n_2 e_2 \exp\left(-\frac{e_2 \Psi}{kT}\right), \quad (4)$$

where n_1 is the total number of counterions and the ordinary electrolyte ions of the same sign as the former and n_2 the number of ordinary electrolyte ions having a charge of the

same sign as that on the surface of the macroion, both per unit volume at $\Psi = 0$. Then, evidently, $e_1 = -e_2$ and $|e_1| = e$. Further, it is obvious that

$$-e_1\Psi/kT > 0,$$

and

$$-e_2\Psi/kT < 0. \quad (5)$$

Strictly speaking, the application of the full Poisson-Boltzmann equation [Eqn. (2)] with ρ on the right-hand side defined by Eqn. (4) is not entirely legitimate. This is because the exponent of the exponential function contains the mean value of the potential whereas in actual fact it should contain the potential associated with the mean force acting on the given ion with charge e_i at point r , i.e. allowance is not made for the small change in the distribution of all the ions of the system when an ion is transferred from infinity to another ion, which is ultimately reflected in the value of work performed in this process. However, this change is very small, because in the electrical double layer surrounding the given macroion there is such an enormous number of the electrolyte microions that a change in their number by unity by introducing or removing a single ion from the system has virtually no effect on the average charge distribution so that the mean potential remains unchanged. When finding the potential in the region $a \leq r < R$ Eqn. (4) may be simplified by rejecting the second term on the right-hand side, since it is small by comparison with the first. This means that near the macroion, ions of the opposite sign, i.e. ions of the first kind, predominate. In this region Eqn. (2) has the form

$$\Delta\Psi_1 = -\frac{4\pi}{D}n_1e_1\exp(-e_1\Psi_1/kT). \quad (6)$$

The exact solution of this equation is well known for the case of cylindrical symmetry. In our case this solution must be made consistent at the boundary of the region where $r = R_0 + a$ with the solution for small potentials. However, the resulting transcendental equations, containing integration constants and the unknown quantity R_0 , are exceptionally cumbersome and not susceptible to satisfactory solution. In order to simplify the calculations, we can use the fact that the width of the region in which $|e\Psi_1/kT| \gg 1$ is small by comparison with the radius of the cylinder. Then Eqn. (6) can be solved on the assumption that the surface of the macromolecule is planar:

$$d^2\Psi/dx^2 = -(4\pi/D)n_1e_1\exp(-e_1\Psi_1/kT). \quad (7)$$

The solution takes the form

$$\Psi_1 = kT/e_1 \left\{ \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2(\beta x - \delta) \right] \right\}. \quad (8)$$

The constants β and δ can be either real or imaginary, depending on the concentration of the polymer and electrolyte. The coordinate x has its origin on the surface of the macromolecule, and at the boundary of the two regions

$$x = R - a = R_0. \quad (9)$$

The quantity κ_1^2 is given by

$$\kappa_1^2 = \frac{4\pi n_1 e_1^2}{DkT}. \quad (10)$$

In the region where $|e\Psi_2/kT| \ll 1$ Eqn. (2) may be linearised. Then, retaining only terms of second order with respect to $e\Psi_2/kT$, we have

$$\Delta\Psi_2 = -\frac{4\pi}{D}(n_1e_1 + n_2e_2) + \frac{4\pi}{D}(n_1e_1^2 + n_2e_2^2)(\Psi_2/kT). \quad (11)$$

Using the relation $e_1^2 = e_2^2$ and $e_1 = -e_2 = e$, and making the substitution

$$\kappa_2^2 = \frac{4\pi e^2(n_1 + n_2)}{DkT}, \quad (12)$$

we obtain

$$\Delta\Psi_2 = -\frac{4\pi}{D}e_1(n_1 - n_2) + \kappa_2^2\Psi_2. \quad (13)$$

The solution of the resulting inhomogeneous equation consists of two additive parts: the general solution of the homogeneous and a special solution of the inhomogeneous equation of the type of Eqn. (13):

$$\Psi_2 = \Psi_{20} + \Psi_{21}, \quad (14)$$

where $\Psi_{20} = [4\pi e_1(n_1 - n_2)/D\kappa_2^2]$ is a special solution of the inhomogeneous equation and

$$\Psi_{21} = CK_0(\kappa_2 r) + BI_0(\kappa_2 r) \quad (15)$$

is the general solution of the homogeneous equation. Since the solution is bounded at infinity, we have $B = 0$. Then

$$\Psi_2 = \frac{4\pi e_1(n_1 - n_2)}{D\kappa_2^2} + CK_0(\kappa_2 r) \quad (16)$$

where

$$K_0(\kappa_2 r) = \int_0^\infty \exp(-\kappa_2 r \cosh \eta) d\eta. \quad (17)$$

In order to determine the constants C , β , δ , and R_0 we can use the following relations: the conditions of electro-neutrality of the system consisting of a macromolecule and a surrounding electrolyte,

$$ve = 2\pi ah \int_0^{R_1} \rho_1 dx + 2\pi h \int_{R=R_0+a}^\infty \rho_2 r dr; \quad (18)$$

the continuity of the potential and field strength at the point where the solutions are to be matched, i.e. when $x = R_0$ or $r = R_0 + a$:

$$\Psi|_{x=R_0} = \Psi_1|_{r=R_0+a}, \quad \frac{d\Psi_1}{dx}|_{x=R_0} = \frac{d\Psi_2}{dr}|_{r=R_0+a}. \quad (19)$$

However, the number of relations is one less than the number of constants to be determined. In order to obtain a fourth relation between the constants, we can use the fairly obvious fact that the value of $|e\Psi/kT|$ at the point where the solutions are to be matched should be of the order of unity. The solution Ψ_1 may be extended with fair accuracy right up to the point where $|e\Psi_1/kT| \sim 1$. Indeed the second term in Eqn. (4) is then about ten times smaller than the first and can be neglected, so that the solution Ψ_1 remains valid. The solution Ψ_2 in the region where $|e\Psi_2/kT| \sim 1$ is not valid. However, the width of this region is slight when Ψ_2 changes rapidly. In order to estimate it accurately, it is necessary to know the concentration of the polymer and the ordinary electrolyte in solution. However, even without this we can estimate approximately how rapidly the potential varies at the point where the two solutions are to be matched, by extrapolating it from the region of low potentials by means of the function Ψ_2 . The extent of the change in Ψ_2 is determined by the function $K_0(\kappa_2 r)$. At the point where the solutions are to be matched $\kappa_2 r = \kappa_2(R_0 + a)$. Over a wide range of concentrations of the polymer and electrolyte, from $c_p = 0.1$ mole of monomer per litre and $c_{el} = 0.1$ M to $c_p = 0.01$ mole of monomer per litre and $c_{el} = 0.01$ M, κ_2 changes slightly, remaining of the order of 10^7 cm⁻¹. It has been established experimentally that the radius of the macromolecules a varies within the limits

$$5 \times 10^{-8} \text{ cm} < a < 10^{-7} \text{ cm}, \quad (20)$$

when $\alpha = 0.6-0.8$. Then $\kappa_2(R_0 + a) > \kappa_2 a \sim 1$. The function $K_0(\kappa_2 r)$ can then be represented by its asymptotic form when $\kappa_2 r \gg 1$, since even when $\kappa_2 r \sim 1$, the deviation of $K_0(\kappa_2 r)$ from the asymptote at large values of the argument $\sqrt{\pi/\kappa_2 r} \exp(-\kappa_2 r)$ is small. Thus, over a wide range of polymer and electrolyte concentrations, Ψ_2 varies exponentially even in the region where the solutions are to be matched and its value varies rapidly over a narrow range of values of r . Hence we can write with fair accuracy the following expression for the fourth relation required to determine the constants:

$$e\Psi_1/kT = 1. \quad (21)$$

After substituting in Eqns. (18), (19), and (21) explicit expressions for ρ_1 and ρ_2 in terms of Ψ_1 and Ψ_2 , as well as $d\Psi_1/dx$ and $d\Psi_2/dr$, we obtain

$$\left. \begin{aligned} \frac{2ve}{Dh} &= -\left[a \frac{2kT}{e_1} \beta \coth \delta - R_0 C \kappa_1 K_1(\kappa_1(R_0 + a)) \right], \\ \frac{kT}{e_1} \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2(\beta R_0 - \delta) \right] &= \left(\frac{n_1 - n_2}{n_1 + n_2} \right) \frac{kT}{e_1} + CK_0[\kappa_1(R_0 + a)], \\ \frac{2kT}{e_1} \beta \coth(\beta R_0 - \delta) &= -\kappa_2 CK_1[\kappa_2(R_0 + a)], \\ \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2(\beta R_0 - \delta) \right] &= -1. \end{aligned} \right\} \quad (22)$$

The resulting system of transcendental equations is extremely cumbersome. It can be simplified by making a reasonable estimate of R_0 , the distance from the surface of the cylinder to the point where the solutions are to be matched. The value of R_0 depends on the concentrations of the polymer and electrolyte. With increase in concentration, R_0 decreases, remaining smaller than $1/\kappa_2$. However, R_0 and $1/\kappa_2$ are of similar order of magnitude. Since in our case this is also true of $1/\kappa_2$ and a , we may expect that $R_0 \sim a$. In the case of colloids a may be considerably greater than $1/\kappa_2$. Then also $R_0 \ll a$.

In the case of a long cylindrical macromolecule a satisfies Eqn. (18) and it is quite reasonable to put $R_0 \approx a$. The system of equations (22) then greatly simplifies, and it is then easy to estimate the integration constant. Naturally, the solution of the problem is more exact in the case where $R_0 \ll a$, because then the planar-surface approximation becomes valid right up to the point where the potentials derived from the two solutions must coincide.

When $R_0 \approx a$, the difference between the planar and symmetrical cylindrical cases becomes significant in the region where $r \sim R_0 + a$. However since the potential in both cases is described by fairly similar logarithmic functions, this discrepancy has little effect on the total potential difference between the bulk of the solution and the surface of the macromolecule.

We shall now replace in Eqn. (22) R_0 by a in those cases where it results in substantial simplification of the expressions. R_0 would be retained in the functions $\coth(\beta R_0 - \delta)$ and $\sinh^2(\beta R_0 - \delta)$ and then evaluated in order to check the validity of its replacement by a . Eqns. (22) then assume the form

$$\frac{2ve}{Dh} = -\frac{2kT}{e_1} \beta \coth \delta - C \kappa_1 K_1(2\kappa_1 a), \quad (23)$$

$$\frac{kT}{e_1} \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2(\beta R_0 - \delta) \right] = \left(\frac{n_1 - n_2}{n_1 + n_2} \right) \frac{kT}{e_1} + CK_0(2\kappa_1 a), \quad (24)$$

$$\frac{2kT}{e_1} \beta \coth(\beta R_0 - \delta) = -\kappa_2 CK_1(2\kappa_1 a), \quad (25)$$

$$\ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2(\beta R_0 - \delta) \right] = -1. \quad (26)$$

We now introduce the auxiliary function

$$f = K_1(2\kappa_1 a) / K_0(2\kappa_1 a). \quad (27)$$

Using Eqn. (26), we obtain from Eqn. (24)

$$C = -\frac{2kT}{e_1} \left(\frac{n_1}{n_1 + n_2} \right) \left[(1/K_0(2\kappa_1 a)) \right]. \quad (28)$$

Eqns. (24)–(26) readily yield

$$\beta^2 = \kappa_2^2 \left(\frac{n_1}{n_1 + n_2} \right)^2 f^2(2\kappa_1 a) - \frac{\kappa_1^2 \times 2.71}{2}. \quad (29)$$

β^2 may be either positive or negative, depending on the relative magnitudes of the first and second terms on the right-hand side of Eqn. (29). If β is known, we can obtain δ from Eqn. (23):

$$\coth \delta = -\frac{ve^2}{kT D h a \beta} - \left(\frac{n_1}{n_1 + n_2} \right) \kappa_2 \frac{f(2\kappa_1 a)}{\beta}. \quad (30)$$

We can express Eqns. (29) and (30) in terms of the concentrations of the polymer and electrolyte (c_p and c_{el}) and the degree of ionisation α . In fact

$$\frac{n_1}{n_2} = \frac{\alpha c_p + c_{el}}{\alpha c_p + 2c_{el}}. \quad (31)$$

We have the relation

$$\frac{v}{h} = \frac{v}{zb} = \frac{\alpha}{b}. \quad (32)$$

R_0 can be calculated from the expression

$$\coth(\beta R_0 - \delta) \approx \sqrt{\frac{1.35 \kappa_1^2}{\beta^2} + 1}. \quad (33)$$

On solving for R_0 , we obtain

$$R_0 \approx \frac{\delta}{\beta} + \frac{1}{\beta} \coth^{-1} \sqrt{\frac{1.35 \kappa_1^2}{\beta^2} + 1}. \quad (34)$$

The potential difference between the surface of the molecule and the solution is

$$\Delta\Psi = \frac{kT}{e_1} \left\{ \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2 \delta \right] - \frac{n_1 - n_2}{n_1 + n_2} \right\} \quad (35)$$

or

$$\frac{e_1 \Delta\Psi}{kT} = \ln \left[\frac{\kappa_1^2}{2\beta^2} \sinh^2 \delta \right] - \frac{\alpha c_p}{\alpha c_p + 2c_{el}}. \quad (36)$$

The second term in Eqn. (36) is very small if the amount of excess ions in solution is small. In our case it cannot be neglected.

Comparison with Experiment

The values of $\Delta\Psi$ obtained may be compared with the experimental data for $\alpha = 0.8$ (see Table). The following expressions are then used for κ_1^2 and κ_2^2 :

$$\begin{aligned} \kappa_1^2 &= \frac{4\pi e^2 N}{kT D \times 10^8} (\alpha c_p + c_{el}), \\ \kappa_2^2 &= \frac{4\pi e^2 N}{kT D \times 10^8} (\alpha c_p + 2c_{el}), \end{aligned} \quad (37)$$

where N is the Avogadro number, c_p the concentration of the polymer in moles of the monomer per litre, and c_{el} the molar concentration of the electrolyte. Polymethacrylic acid in sodium chloride solutions of various ionic strengths was investigated. The results of the calculations by Eqn. (36) and experimental data are collected in the Table, which also gives the values of R_0 calculated from Eqn. (34) and of κ_1^2 and κ_2^2 calculated from Eqn. (37). The values

TABLE.

Concentration	$10^{34}\kappa_2^2$ cm ⁻²	$10^{34}\kappa_2^2$ cm ⁻²	$10^6 R_0$, cm	$\frac{e\Delta\Psi}{kT}$ exp	$\frac{e\Delta\Psi}{kT}$ theor
$c_p = 0.1 M^*$ $c_{el} = 0.1 M$	1.45	1.03	≈ 5.7	≈ 2.7	≈ 3.3
$c_p = 0.05 M^*$ $c_{el} = 0.04 M$	0.62	0.42	≈ 9.0	≈ 4.2	≈ 5.6
$c_p = 0.02 M^*$ $c_{el} = 0.01 M$	0.188	0.136	≈ 9.8	≈ 6	≈ 8.8

* Mole of monomer per litre.

$a \approx b \approx 5 \times 10^{-8}$ are based on the experimental data for a large class of polymers.

It is readily evident that at small values of c_p and c_{el} the discrepancies with experimental data become appreciable as a result of an increase in the diffuseness of the double layer when $1/\kappa_2$ becomes appreciably greater than a and the condition $R_0 \sim a$ is valid only as regards the order of magnitude. However, when a is of the order of 10^{-7} cm and above (large cylindrical colloids), it is to be expected that the calculation will be accurate at lower concentrations.

SUMMARY

1. An equation has been derived for the distribution of potential on the surface of a cylindrical polymer macromolecule in an electrolyte solution for the case of a large potential.
2. A theoretical calculation has been made of the total potential difference between the surface of a polymeric molecule and the bulk of the electrolyte solution, which is in satisfactory agreement with experimental data.

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THE ELECTROCHEMICAL MECHANISM OF THE CORROSION OF METALS UNDER THE INFLUENCE OF ALTERNATING CURRENT. II. DISSOLUTION OF LEAD

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The electrochemical and corrosion behaviour of lead in various electrolytes has been extensively investigated. Lead has a high rate of ionisation and discharge of its ions^{1,2}. Oxygen depolarisation and discharge of hydrogen

ions proceed on lead with high overvoltage³⁻⁸. For this reason, the dissolution rate of lead in many electrolytes is controlled by the rate of the cathodic process. In neutral solutions stable protective films form on lead which slow down the rate of corrosion^{9,10}. However, no published data are available on the corrosion behaviour of lead under the action of alternating current, which is of theoretical and practical interest.

Appraisal of the corrosion hazards due to the action of alternating current on lead is very important because the proposed wide application of alternating current in the electrification of railways and in other power installations will increase the density of stray alternating currents¹¹ which will aggravate the possibility of corrosion damage to underground installations and cables.

This work deals with the mechanism of dissolution of lead in various solutions on polarisation of the electrodes by sinusoidal and rectangular alternating currents of frequencies 50 and 5 c/s.

EXPERIMENTAL

The electrodes investigated were cylinders 5 mm in diameter and 70 mm long, prepared from commercial lead. The auxiliary electrode for polarisation consisted of a lead cylinder 5 cm in diameter. In order to reduce the internal resistance of the cell, no partition was employed between the test and auxiliary electrodes. In the polarisation of the electrode by alternating current the amplitudes of the current densities were measured separately in the cathodic and anodic half-cycles. The amplitudes of the electrode potentials were also measured in the two half-cycles. The apparatus and procedure have been previously described¹². The electrode investigated was rotated at 2500 rev. min⁻¹. The experiments were made at room temperature.

The cathodic and anodic polarisation curves for lead in 0.5 N NaCl under the action of 50 c/s sinusoidal alternating current are plotted in Fig. 1†. The amplitude of the lead electrode potential in the anodic half-cycle changes very little with the density of polarising current (curve 1), implying that the rate of anodic ionisation of lead is high. The discharge of lead ions on the electrode surface takes place in the subsequent cathodic half-cycle. The relatively small phase angle between the electrode potential and the polarising current (curve 3) shows that the contribution of the capacitive component of the current to the total polarising current is small‡.

It follows from Fig. 1 that retardation of the process is very much greater in the cathodic than in the anodic half-cycle. Regions of low and high overvoltage of the cathodic reaction are observed on the rising part of the electrode potential-time curve in the cathodic half-cycle. At the beginning of the cathodic half-cycle there is an arrest in the tendency of the electrode potential to become less noble (this region corresponds to the unimpeded discharge of lead ions). Then the electrode potential shifts abruptly

† In all the figures the electrode potentials are referred to the standard hydrogen electrode.

‡ Curve 3 in Fig. 1 shows the phase angle between the amplitudes of the anodic electrode potential and the anodic current. It has not been possible to measure the phase angle for lead in the cathodic half-cycle, because the current and potential curves are very distorted.