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THE DIMENSIONS OF CHARGED LONG CHAIN MOLECULES IN SOLUTIONS CONTAINING ELECTROLYTES ¹⁾

BY

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If a long chain molecule in a solution carries electric charges, the statistical coil is inflated, and the average square of the distance between the ends of the chain is larger than in the uncharged state. For a number of properties the determining factor is the value of $\sum_k (r_k^2)_{av}$, where r_k is the distance between the k 'th link in the molecule and the centre of gravity. This quantity is proportional to the square of the effective radius and is related to the square of the distance between the ends by a simple formula (section 2), provided the radius of the coil is small compared with the length of the extended chain.

In section 3 the electrical free energy of the molecule is derived as a function of effective radius on the assumption that no electrolytes are present. This free energy determines in its turn the average dimensions of the coil.

In section 4 a similar theory is developed for charged polymer molecules in the presence of electrolytes. The change of the effective radius with the charge on the polymer and the concentration of the electrolytes is calculated. In the limit of high electrolyte content the equilibrium between the interior and the exterior of the polymer coil may be considered as a *Donnan* equilibrium.

§ 1. Introduction.

In the interpretation of many properties of solutions of long chain molecules, the extension of the statistical coil is a very fundamental factor. When the large molecule is electrically charged by ionization or by adsorption of ions, the charges will drive the constituent parts of the chain apart, thus causing an inflation of the coil. As a variety of synthetic and natural high polymers (e.g. poly-acrylic and poly-methacrylic acid, polyvinylpyridonium-salts ²⁾, gum arabic, agar, oxidized starch, nucleic acids, proteins) contain ionizable groups, a

¹⁾ A preliminary account of the theory developed in this paper was presented at the colloquium on large molecules held in Liège in April 1948, and has been published in *Bull. soc. chim. Belges* **57**, 154 (1948).

theoretical investigation of the above mentioned inflation seems worth while.

Besides the total charge of the chain (or its degree of dissociation) and the distance between the charges on one chain, the electrolyte content will be an important factor, as the formation of ionic atmospheres around the charged spots will diminish the interaction. Given the typical long range character of the electrostatic interaction it may be expected, that a treatment in which the charges are assumed to be smeared out over the whole coil will be satisfactory. A treatment based on a pairwise interaction of the charged spots (each surrounded by its own ionic atmosphere) seems less promising, as usually the thickness of the ionic atmosphere is much larger than the distance between neighbouring charged spots and in many cases even larger than the dimensions of the whole coil. Only in the case of very high concentrations of electrolyte the picture of interaction of separate charged spots might be preferable but in those circumstances the whole effect of inflation is negligible.

The description of the effect may then be divided into two parts, *viz.*

- A. The calculation of the free energy (F) of the system of charges for a given configuration of the coil (§ 3, § 4).
- B. The determination of the most probable form of the coil, by taking both the *a priori* probability and the free energy F into account (§ 2).

Thermodynamic properties like the solubility of the macromolecular substance or the dissociation of its charged groups will be governed especially by the free energy of the molecules. On the other hand all dynamic properties like viscosity, sedimentation velocity, double refraction of flow, or electrophoresis will be strongly dependent upon the modified form of the coil.

In this paper special attention will be directed to the viscosity of solutions of charged long chain molecules. A discussion³⁾ of the dissociative properties of these systems has been presented at the colloquium on large molecules held in Liège in April 1948.

The treatment of the viscosity seemed especially promising, because the influence of electrolytes on the viscosity of large molecules has already been investigated and is known under the name "electroviscous, or quasi-viscous effect"⁴⁾.

²⁾ R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.* **3**, 246 (1948).

³⁾ J. Th. G. Overbeek, *Bull. soc. chim. Belges*, **57**, 252 (1948).

⁴⁾ H. R. Kruyt and H. G. Bungenberg de Jong, *Z. physik. Chem.* **100**, 250 (1922); *Kolloid Beihefte* **28**, 1 (1928); H. R. Kruyt, *Colloids*, 2nd ed. p. 183, Wiley, New York 1930.

The electroviscous effect consists in a decrease of the viscosity by addition of relatively small amounts of electrolytes which has been established by *Kruyt, Bungenberg de Jong* and their coworkers for a large number of hydrophilic colloids, e.g. gum arabic, agar-agar, starch, and many others. Fig. 1 shows how the viscosity of a solution

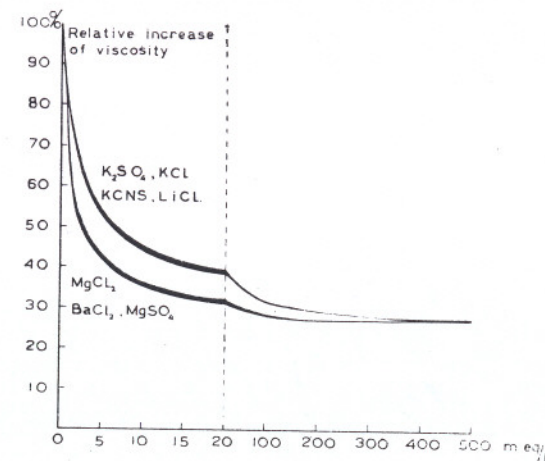


Fig. 1. Electroviscous effect of gum arabic. The relative increase of the viscosity, $(\eta_s - \eta_0)/\eta_0$ for the pure sol is arbitrarily taken as 100%.

of gum arabic is decreased by electrolytes⁵⁾. The influence of different electrolytes is mainly determined by their valency, the ions of larger positive valency having a stronger effect in low concentrations, whereas the viscosity reached at high concentrations is practically independent of the individual properties of the electrolyte used.

This effect has been generally explained on the basis of a theory given by *von Smoluchowski*⁶⁾ according to whom the viscosity of a suspension of massive spherical particles is increased by the presence of an electrical double layer around the particles. *Von Smoluchowski* derived the following equation,

$$\frac{\eta_s - \eta_0}{\eta_0} = \frac{5}{2} \Phi \left[1 + \frac{1}{\lambda \eta_0 R^2} \left(\frac{\zeta \epsilon}{2 \pi} \right)^2 \right] \dots \dots \dots (1)$$

in which η_s is the viscosity of the suspension, η_0 that of the dispersion medium, Φ the concentration by volume, λ the conductivity, ϵ the

⁵⁾ H. R. Kruyt and H. J. Edelman, *Kolloid-Beihefte* **36**, 350 (1932).

⁶⁾ M. von Smoluchowski, *Kolloid.-Z.* **18**, 190 (1916); c.f. also W. Krasny-Ergen, *Kolloid.-Z.* **74**, 172 (1936); F. Booth, *Nature* **161**, 83 (1948).

dielectric constant of the medium, R the radius of the particles, and ξ their electrokinetic potential.

The electroviscous effect was then explained by the decrease of the ξ -potential and the increase of the conductivity accompanying the addition of electrolytes.

It is however very doubtful whether the hydrophilic sols mentioned above contain massive spherical particles. A much more probable structure, more in accord with the high intrinsic viscosity of these sols, is a randomly kinked long chain which may or may not contain ramifications. In that case the theory of *von Smoluchowski* cannot be applied and the electroviscous effect may be explained by a diminution of the interaction between the charged spots on account of the screening effect of the ionic atmospheres which entails a more dense form of the kinked chains. In the following sections a quantitative description of this image will be developed.

§ 2. Statistics of the polymer coil.

Consider a chain in which $N + 1$ equal mass points or "beads" numbered $0, 1, \dots, N$ are connected by N links of length A , the k 'th link connecting the $(k - 1)$ th with the k 'th bead. These links are assumed to be of the nature of the so-called statistical chain elements introduced by *Kuhn*⁷⁾, i. e., the orientation of any of the links in space may be considered as being practically independent of that of the others. Let r_k be the distance of the k 'th mass point from the centre of gravity. Then, by definition,

$$\sum_{k=0}^N \vec{r}_k = 0 \quad \dots \quad (2)$$

We shall consider the value of $\sum_k (r_k^2)_{av}$, where *av* denotes the statistical mean. This quantity is determinative for various properties of the polymer coil. *Debije*⁸⁾ has shown, for instance, that the intrinsic viscosity can be described in terms of a radius R defined as follows

$$R^2 = \frac{5}{3N} \sum_k (r_k^2)_{av} \quad \dots \quad (3)$$

This is true⁹⁾ irrespective of whether the coil is free-drained¹⁰⁾ or otherwise. The birefringence of flow has so far been developed only

⁷⁾ *W. Kuhn*, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936).

⁸⁾ *P. Debije*, *J. chem. Phys.* **14**, 636 (1946); see also *Kramers*, reference 11.

⁹⁾ *P. Debije* and *A. M. Bucche*, *J. chem. Phys.* **16**, 573 (1948); *Internat. Congress of Pure and Applied Chemistry*, London, July 1947.

¹⁰⁾ *W. Kuhn* and *H. Kuhn*, *Helv. Chim. Acta* **26**, 1394 (1943).

for free-drained molecules^{10) 11)}, where it is proportional to R^2 . A further property in which $\sum_k (r_k^2)_{av}$ plays a decisive part is the dissymmetry of light scattering¹²⁾. We shall therefore focus our attention on this quantity and use *Debije's* definition (3) for the effective radius of the coil.

In a random uncharged coil the probability of finding a distance h between the ends is proportional to

$$dh h^2 \exp(-3h^2/2NA^2) \quad \dots \quad (4)$$

The average square of this distance is

$$(h^2)_{av} = NA^2, \quad \dots \quad (5)$$

and the value of R^2 is found to be⁸⁾

$$R^2 = \frac{5}{18} NA^2 \quad \dots \quad (6)$$

We need not derive this formula for R because it will follow at once from a more general formula given below. If the polymer coil carries electric charges, it tends to become inflated, which means that larger values of h are somewhat more frequent. The new distribution of h -values is given by the expression

$$dh h^2 \exp\left(-\frac{3h^2}{2NA^2} - \frac{F}{kT}\right), \quad \dots \quad (7)$$

where F is the electrical free energy of the molecule. Consequently we shall find the average square of h from the equation

$$(h^2)_{av} = \frac{\int_0^\infty dh h^4 \exp\left(-\frac{3h^2}{2NA^2} - \frac{F}{kT}\right)}{\int_0^\infty dh h^2 \exp\left(-\frac{3h^2}{2NA^2} - \frac{F}{kT}\right)} \quad \dots \quad (8)$$

The appearance of the free energy instead of the energy in the *Boltzmann* exponent is explained by the fact that we are to account for the effect of the charges on both the energy and the entropy of the system. The factor $\exp(-3h^2/2NA^2)$, being proportional to the number of configurations for a given h -value, determines the configurational entropy of the polymer molecule irrespective of its charge. When taking account of the potential energy of the ionic

¹¹⁾ *H. A. Kramers*, *Physica* **11**, 1 (1944); *J. Chem. Phys.* **14**, 415 (1946); *J. J. Hermans*, *Physica* **10**, 777 (1943); *Rec. trav. chim.* **63**, 25 (1944).

¹²⁾ *B. H. Zimm*, *R. S. Stein* and *P. Doty*, *Polymer. Bull.* **1**, 90 (1945).

charges we must therefore add the entropy factor which takes care of the probability of finding the charge distribution required.

In sections 3 and 4 the electrical free energy will be calculated in terms of the radius, R , of the coil. To evaluate the equation (8) we shall need the relation between h and R . This can be found from statistical considerations as follows. Consider an assembly of polymer molecules whose one end is at distance h from the other end, and let X, Y, Z be the components of h , so that $X^2 + Y^2 + Z^2 = h^2$. We assume that $h \ll NA$. If N is large, this holds good for the majority of molecules. In fact, X^2, Y^2 and Z^2 will almost always be of the order NA^2 and hence small compared with N^2A^2 .

Let α_k be the cosine of the angle between the k 'th link and the x -axis. The values of the α 's may be considered as the result of a lottery in which the sum X/A is distributed statistically between N members. Consequently the distribution of α -values is a simple canonical distribution¹³⁾

$$dx f(\alpha) = dx c \exp(g\alpha),$$

where g is determined by the requirement

$$(\alpha)_{av} = X/NA \dots \dots \dots (9)$$

Since we assume that $X \ll NA$, we find $g = 3X/NA$. Further, according to a well-known formula¹⁴⁾ we have

$$(x^2)_{av} - (\alpha)^2_{av} = d(\alpha)_{av}/dg$$

In the present case this becomes $1/3$, and consequently

$$(x^2)_{av} = \frac{1}{3} + O\left(\frac{1}{N}\right) \dots \dots \dots (10)$$

where O signifies "order of magnitude". We shall need, further, an expression for the average value of $\alpha\alpha'$, where α and α' are the direction cosines of any two links in the chain with respect to the x -axis. This can be found by first determining the average $[\alpha']_m$ of the second link if it is known that the cosine of the first is α , and then averaging the product $\alpha[\alpha']_m$ over all possible α -values. In other words,

$$(\alpha\alpha')_{av} = (\alpha[\alpha']_m)_{av}$$

However, $[\alpha']_m$ is nothing but the average value of the cosine found in an assembly of $N - 1$ links with the condition that the sum is $X/A - \alpha$. Or also, $[\alpha']_m = (N - 1)^{-1} \cdot (X/A - \alpha)$, which gives

¹³⁾ W. Kuhn and F. Gr \ddot{u} n, Kolloid-Z. 101, 248 (1942).
¹⁴⁾ See, for example, E. Schr \ddot{o} dinger, Statistical thermodynamics, p. 25, (Cambridge University Press 1948).

$$(\alpha\alpha')_{av} = \frac{1}{N-1} \left[\frac{X}{A} (\alpha)_{av} - (x^2)_{av} \right] = \frac{X^2}{N^2A^2} - \frac{1}{3N} + O\left(\frac{1}{N^2}\right) \dots \dots (11)$$

Now let us first calculate the average square of the distance between the center of gravity and one of the ends of the molecule. Taking bead number 0 in the origin, let $\xi_k \eta_k \zeta_k$ be the coordinates of the k 'th bead. Clearly,

$$\xi_k = A \sum_{j=1}^k \alpha_j \dots \dots \dots (12)$$

The coordinates $\xi_z \eta_z \zeta_z$ of the centre of gravity are given by equations of the form

$$\xi_z = (N + 1)^{-1} \sum_{k=0}^N \xi_k = (N + 1)^{-1} A \sum_{j=0}^{N-1} (N-j) \alpha_{j+1}$$

The average square of this quantity is

$$A^2 (N + 1)^{-2} \{ (\alpha^2)_{av} \sum_j (N-j)^2 + (\alpha\alpha')_{av} \sum_k \sum_l (N-j)(N-k) \}$$

Taking account of the equations (10) and (11) and carrying out the summation we obtain

$$(\xi_z^2)_{av} = NA^2 \left\{ \frac{1}{9} + \frac{1}{4} \left(\frac{X^2}{NA^2} - \frac{1}{3} \right) + O\left(\frac{1}{N}\right) \right\} \dots \dots (13)$$

We now proceed to calculate the average square of the distance between the beads and the centre of gravity. If $x_k y_k z_k$ are the coordinates of the k 'th bead, taking the centre of gravity as origin, we have $x_k = \xi_k - \xi_z$, and $\sum_k \xi_k = (N + 1) \xi_z$ because of equation (2). Consequently,

$$\sum_k x_k^2 = \sum_k \xi_k^2 - (N + 1) \xi_z^2$$

From equation (12) it follows that

$$(\xi_k^2)_{av} = A^2 k (\alpha^2)_{av} + A^2 k (k-1) (\alpha\alpha')_{av}$$

or, in view of equations (10) and (11),

$$(\xi_k^2)_{av} = \frac{1}{3} A^2 k + A^2 \frac{k(k-1)}{N} \left(\frac{X^2}{NA^2} - \frac{1}{3} \right)$$

Summing, and using the formula (13) for $(\xi_z^2)_{av}$ we obtain

$$\sum_k (x^2_k)_{av} = \frac{1}{18} N^2 A^2 + \frac{1}{12} N^2 A^2 \left(\frac{X^2}{NA^2} - \frac{1}{3} \right)$$

It is obvious that similar results apply to $\sum_k (y^2_k)_{av}$ and $\sum_k (z^2_k)_{av}$, giving as a final result

$$\sum_k (r^2_k)_{av} = \frac{1}{6} N^2 A^2 + \frac{1}{12} N^2 A^2 \left(\frac{h^2}{NA^2} - 1 \right) = \frac{1}{12} N^2 A^2 \left(1 + \frac{h^2}{NA^2} \right)$$

In view of the definition (3) this means that

$$R^2 = \frac{5}{36} NA^2 \left(1 + \frac{h^2}{NA^2} \right) \dots \dots \dots (14)$$

This, then, is the relation between R and h . When averaging over all values of h we find, for uncharged random coils where $(h^2)_{av} = NA^2$, Debye's value (6) for R^2 , as it should be.

§ 3. Electrical free energy and average dimensions of charged coil in the absence of electrolytes.

Suppose the polymer is dissolved in a solution containing electrolytes. Then the charges fixed on the polymer molecule will be surrounded by an electric double layer. This double layer is very diffuse if the electrolytic solution is dilute, in which case it may extend over distances which are large compared with the dimensions of the coil. We shall first consider this limiting case, because it allows of the simplest mathematical treatment and therefore serves to bring out most clearly the nature of our method.

We treat the charges inside the coil as a continuous charge of density ρ and consider two models. The first model assumes that the shape of the coil may be approximated by a sphere of radius R and that ρ is constant throughout this sphere. In this case the total charge of the molecule is

$$Ze = 4/3 \pi R^3 \rho \dots \dots \dots (15)$$

In the second model we assume a charge density of the form

$$\rho = a \exp(-b^2 r^2) \dots \dots \dots (16)$$

where a and b are constants. The constant b is chosen in such a manner that the average value of r^2 satisfies the equation (3), according to which it must be equal to $3R^2/5$. This requires that

$$b^2 = \frac{5}{2R^2} \dots \dots \dots (17)$$

To ensure that the total charge is Ze , we must have

$$a = Ze b^3 / \pi^{3/2} \dots \dots \dots (18)$$

The actual charge distribution in the coil can probably be approximated quite closely by a Gaussian form of the type (16), but for our purpose this is not very important because we shall show that

*) In the following treatment the total charge of the coil is supposed to be constant, which implies, that complete dissociation of the charge bearing groups is assumed. Incomplete dissociation would imply a dependence of the charge on the dimensions of the coil and on the electrolyte content (c.f. footnote 3) and would complicate the treatment of the electroviscous effect, without adding fundamentally new points of view.

the electrical free energy calculated on this assumption is practically the same as that found on the basis of a constant charge density.

Let us first consider this case of constant ρ , and let ϵ be the dielectric constant in the interior of the coil. If the coil is not too dense, ϵ may be identified with the dielectric constant of the surrounding solution. The electric potential, ψ , will satisfy the following differential equation:

$\Delta\psi = -4\pi\rho/\epsilon$ inside, and zero outside the sphere, while the boundary conditions are: ψ is everywhere finite and zero at infinity; ψ and $d\psi/dr$ are continuous at the surface of the sphere. This problem has the following solution

$$\psi = \frac{Ze}{2\epsilon R^3} (3R^2 - r^2) \text{ inside the sphere}$$

$$\psi = \frac{Ze}{\epsilon r} \text{ outside the sphere.}$$

We find the electrical free energy by integrating $1/2 \cdot \rho\psi$ over the entire volume of the sphere, giving

$$F = \frac{3}{5} \frac{Z^2 e^2}{\epsilon R} \dots \dots \dots (19)$$

In our second model, where ρ satisfies equation (16), we have $\Delta\psi = -4\pi\rho/\epsilon$ everywhere, which gives, considering that ψ must be finite in the centre of the coil and zero at infinity,

$$\psi = \frac{2\pi a}{\epsilon b^2} \frac{1}{r} \int_0^r du e^{-b^2 u^2}$$

$$F = \frac{1}{2} \int_0^\infty dr 4\pi r^2 \rho\psi = \left(\frac{\pi}{2}\right)^{1/2} \frac{\pi^2 a^2}{\epsilon b^5} = \left(\frac{5}{4\pi}\right)^{1/2} \frac{Z^2 e^2}{\epsilon R}$$

As $(5/4\pi)^{1/2} = 0.63$, the difference between this result and the formula (19) is very slight, showing that the value of F calculated is not very sensitive to the charge distribution assumed. When applying the result (19) to evaluate $(h^2)_{av}$ in equation (8), we are confronted with the integrals

$$\int_0^\infty dh h^4 \exp\left(-\frac{3h^2}{2NA^2} - \frac{3}{5} \frac{Z^2 e^2}{\epsilon RkT}\right)$$

and $\int_0^\infty dh h^2 \exp\left(-\frac{3h^2}{2NA^2} - \frac{3}{5} \frac{Z^2 e^2}{\epsilon RkT}\right),$

where R is related to h by equation (14). Let us introduce the auxiliary dimensionless quantities x and y according to

$$x^2 = \frac{h^2}{NA^2}; y^2 = \frac{36}{5} \frac{R^2}{NA^2} = 1 + x^2 \quad \dots \quad (20)$$

Then $\frac{1}{2} (y^2)_{av}$ represents the square of the radius of the charged coil divided by that of the uncharged coil, and the average value of x^2 is given by the ratio of the following integrals

$$P = \int_0^\infty dx x^4 \exp\left(-\frac{3}{2} x^2 - \frac{\beta}{y}\right); Q = \int_0^\infty dx x^2 \exp\left(-\frac{3}{2} x^2 - \frac{\beta}{y}\right), \quad (21)$$

provided

$$\beta = \frac{18}{5\sqrt{5}} \frac{1}{A\sqrt{N}} \frac{Ze^2}{\epsilon kT} \quad \dots \quad (22)$$

This quantity, β is also dimensionless. The integrals P and Q can be evaluated graphically, but it was found that the ratio P/Q is given within a few per cent by the square of the value of x for which the function

$$x^3 \exp\left(-\frac{3}{2} x^2 - \frac{\beta}{y}\right)$$

has its maximum value *).

This maximum value determines y as the solution of the equation

$$y^3 \frac{y^2 - 2}{y^2 - 1} = \frac{\beta}{3} \quad \dots \quad (23)$$

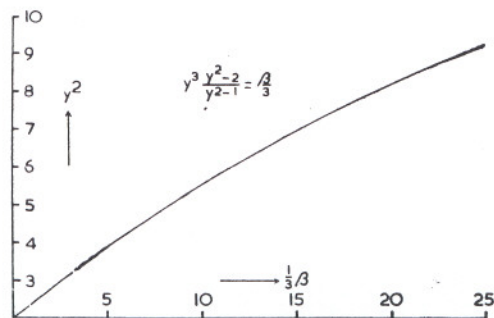


Fig. 2. y^2 as determined by equation (23).

* For example, with $\beta = 6.9$, a graphical integration gave $(y^2)_{av} = 2.80$, whereas the solution of equation (23) gives $y^2 = 2.85$. With $\beta = 30$ the result of the graphical integration was $(y^2)_{av} = 5.57$ and the solution of equation (23) gives $y^2 = 5.60$.

which is represented in fig. 2 as a function of β . Thus, all we have to do is to solve (23), i.e. to read y^2 from fig. 2; the value found is practically identical with $(y^2)_{av}$. In the limit of large β -values one finds

$$(y^2)_{av} = (\beta/3)^{2/3} \quad \dots \quad (24)$$

Since for a given polymer in a given solution the charge, Ze , is proportional ** to the chain length, N , the quantity β in equation (22) is proportional to $N^{3/2}$ and thus, in the limit of high β -values, $(y^2)_{av}$ becomes proportional to N . The validity of the results obtained in this section is restricted only by the assumption made in section 2, according to which $h \ll NA$. If the charge becomes so high that the coil is straightened out to a large extent, our approach to the problem becomes inadequate.

§ 4. Electrical free energy and average dimensions of charged coils in electrolytic solutions.

A similar theory can be developed if electrolytes are present. Here again we shall consider two models, one with constant density of charges fixed on the polymer and one with a charge distribution given by equation (16). If n_i is the number of ions of charge e_i in unit volume, and c_i the average number at a large distance from the polymer molecule, we may write, for both models

$$n_i = c_i \exp(-e_i\psi/kT) \quad \dots \quad (25)$$

Let ρ , as before, represent the charge density due to the charges fixed on the polymer. Then $\rho + \sum_i e_i n_i$ is the total charge density, and

$$\Delta\psi = -\frac{4\pi}{\epsilon} (\rho + \sum_i e_i n_i) \quad \dots \quad (26)$$

Henceforward we shall use the *Debye* and *Hückel* approximation for the exponentials in (25). Introducing the well-known reciprocal characteristic length, κ , of the *Debye* and *Hückel* theory,

$$\kappa^2 = \frac{4\pi \sum_i c_i e_i^2}{\epsilon kT} \quad \dots \quad (27)$$

$$\Delta\psi - \kappa^2\psi = -4\pi\rho/\epsilon \quad \dots \quad (28)$$

In our first model, where ρ is constant for $r < R$ and zero for $r > R$, while the boundary conditions are the same as those mentioned in the previous section, we find

** This is only exact if the charge is due to strongly dissociated groups. If the dissociation is incomplete, it will depend among other things upon the chain length, so that the proportionality between N and Ze is lost. See reference 3.

$$r < R, \psi = \frac{4 \pi Q}{\epsilon \kappa^2} - \frac{2 \pi Q}{\epsilon \kappa^3} e^{-\kappa R} (1 + \kappa R) \frac{e^{\kappa r} - e^{-\kappa r}}{r}$$

$$r > R, \psi = \frac{2 \pi Q}{\epsilon \kappa^3} \left\{ (1 + \kappa R) e^{-\kappa r} - (1 - \kappa R) e^{\kappa R} \right\} \frac{e^{-\kappa r}}{r}$$

The electrical free energy of the system is equal to the work done when charging the polymer molecule while equilibrium with the electrolytic solution is maintained. Here again this is found by integrating $\frac{1}{2} Q\psi$ over the interior of the sphere.

One might conceive that the spatial rearrangement of the electrolytic ions, which accompanies the charging process, would also contribute to the free energy. This rearrangement, however, takes place automatically, which means that it does not change the free energy. To express this more explicitly¹⁵⁾ we remark that an ion of type *i* needs an energy $U = e_i \psi$ to penetrate into a region of potential ψ , but at the same time the entropy is changed by an amount $S = -k \ln n_i/c_i = -e_i \psi/T$, because the concentration in this region is $c_i \exp(-e_i \psi/kT)$. Consequently the free energy $U - TS$ is not affected by this process.

For the present problem, replacing $4/3 \pi R^3 Q$ by the total charge, Ze , of the polymer molecule, and abbreviating

$$\kappa R = p \dots \dots \dots (29)$$

we find

$$F = \frac{3 Z^2 e^2}{5 \epsilon R} \left\{ \frac{5}{2 p^2} - \frac{15 p^2 - 1 + (1 + p)^2 e^{-2p}}{4 p^5} \right\} \dots \dots (30)$$

Next, let us consider the second model, where Q is given by equation (16). Here we shall make use of a short-cut by calculating the free energy directly without evaluating the electric potential ψ . The mathematical details are given in the appendix II, where it is shown that the free energy becomes

$$F = \left(\frac{5}{4 \pi} \right)^{1/2} \frac{Z^2 e^2}{\epsilon R} \left\{ 1 - \frac{2 p}{\sqrt{5}} \exp \left(\frac{p^2}{5} \right) \int_0^\infty d\omega e^{-\omega^2} \right\} \dots \dots (31)$$

Both the results (30) and (31) are rather complicated, but it is obvious from table I that they are almost equal numerically and can be represented quite accurately by the simple interpolation formula

$$F = \frac{3 Z^2 e^2}{\epsilon R} (1 + 0.6 p + 0.4 p^2)^{-1} \dots \dots \dots (32)$$

¹⁵⁾ E. J. W. Verwey and J. Th. G. Overbeek, Theory of the stability of lyophobic colloids, p. 54, Elsevier, Amsterdam 1948.

Table I.
Values of $\frac{5}{3} \frac{\epsilon R}{Z^2 e^2} F$ according to equations 30, 31 and 32.

| $p = \kappa R$ | 0 | 0.5 | 1 | 2 | 3 | 4 | ∞ |
|----------------|------|------|------|------|------|------|-----------|
| eq. 30 | 1 | 0.67 | 0.47 | 0.25 | 0.15 | 0.10 | $2.5/p^2$ |
| " 31 | 1.05 | 0.72 | 0.51 | 0.28 | 0.17 | 0.11 | $2.6/p^2$ |
| " 32 | 1 | 0.70 | 0.50 | 0.27 | 0.16 | 0.10 | $2.5/p^2$ |

This proves that here again the spatial distribution of the charges fixed on the polymer is not very important for the result of the calculation. We shall use the interpolation formula (32) to compute the average value of h^2 (and thus of R^2) from equation (8). Using the quantities x , y and β defined by the equations (20) and (22), and abbreviating

$$G = -\frac{3}{2} x^2 - \frac{\beta}{y} (1 + 0.6 p + 0.4 p^2)^{-1} \dots \dots (33)$$

we find $(x^2)_{av}$ as the ratio of the following two integrals

$$U = \int_0^\infty dx x^4 \exp G; \quad W = \int_0^\infty dx x^2 \exp G.$$

In these integrals $p = \kappa R$ and thus, according to the equations (20),

$$p^2 = \frac{5}{36} N A^2 \kappa^2 y^2 = \frac{5}{36} N A^2 \kappa^2 (1 + x^2) \dots \dots (34)$$

The integrals U and W were evaluated graphically for a few typical values of β and p/y and it was found that here again the ratio U/W is given with surprising accuracy by the square of the value of x , for which the function $x^3 \exp G$ reaches its maximum value. Taking into account the relations (20) and (34) between x , y and p , this means that $(y^2)_{av}$ is determined by the solution of the following equation

$$y^3 \frac{y^2 - 2}{y^2 - 1} \frac{(1 + 0.6 p + 0.4 p^2)^2}{1 + 1.2 p + 1.2 p^2} = \frac{\beta}{3} \dots \dots (35)$$

Fig. 3 gives y as a function of p/y for a number of β -values. The points inserted in this figure represent the exact results, $(y^2)_{av}^{1/2}$, of a graphical evaluation of the integrals U and W ; (a) with $\beta = 30$ and $p/y = 1$, (b) with $\beta = 15$ and $p/y = 0.2$; (c) with $\beta = 15$ and $p/y = 2$. It is seen that the graphical integration leads to practically the same result as the solution of equation (35). Finally, fig. 4. represents y^2 as a function of p^2/y^2 .

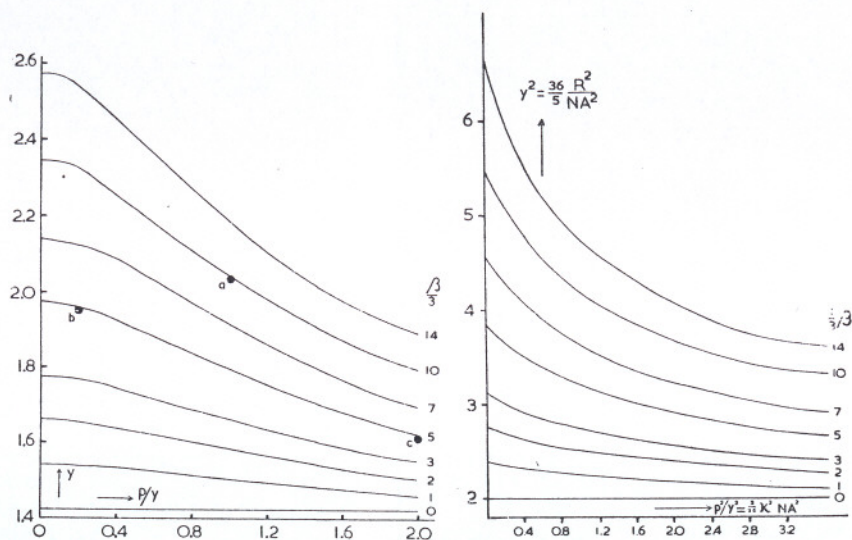


Fig. 3. y as a function of p/y for various values of β .

Fig. 4. y^2 as a function of p^2/y^2 for various values of β .

In view of the relation (34), the quantity p^2/y^2 , for a given polymer, is proportional to κ^2 , i.e. proportional to the electrolytic concentration. As is obvious from the relation (35), the dimensions of the polymer coil become normal ($y^2 = 2$) if the electrolyte content is sufficiently high (p^2 very large), but fig. 4 shows that this normal value of y^2 is approached very slowly. It is further to be remembered that y is the factor by which the effective radius of the polymer coil is increased by the influence of the charges. For example, in the case of a completely free-drained polymer molecule, where the intrinsic viscosity is proportional to R^2 , the value of y^2 represents the ratio between the intrinsic viscosity of the charged molecule to that of the uncharged one, or also, the ratio of the intrinsic viscosity of the charged molecule in the electrolyte considered to that of the same molecule in the limit of very high electrolyte content. In the case of a molecule which is not completely free-drained one would have to take into account the change in the density of the coil as a result of the change in dimensions¹⁶⁾.

There is no doubt that the general character of fig. 4 is the same as that of the experimental curves in fig. 1. A quantitative comparison will be possible if the charge and the molecular weight of the polymer

¹⁶⁾ See *Debye's* theory, reference 9.

are known. For the present we confine ourselves to observing that two restrictions must be made. As mentioned at the end of § 3, the linear dimensions of the polymer coil must remain small compared with the maximum extension NA ; in the present case, however, where the electrolytic ions play a part in the phenomenon, the validity of our results is restricted by one further condition: the *Debye* and *Hückel* approximation must remain valid, i.e., ψ should not be too large.

Appendix I.

Donnan equilibrium in the limit of high electrolyte content.

Consider the limiting case in which $p(=\kappa R)$ is large compared with unity. This means that the electric double layer is thin compared with the radius of the sphere; in other words, the electric potential is zero if $r > R$ and the distribution of ions outside the sphere is uniform. In this limit we may consider the equilibrium between the interior and the exterior of the sphere as a simple Donnan equilibrium; the "surface" of the sphere acts as a membrane which is impermeable to the charges fixed on the polymer. This concept implies that the charge density in the interior of the coil is uniform, but we know already that this makes no difference to the result anyhow. From equation (30) it is seen that F approaches the value

$$F = \frac{3}{5} \frac{(Ze)^2}{\epsilon R} \frac{5}{2p^2} = \frac{3}{2} \frac{(Ze)^2}{\epsilon \kappa^2 R^3} = \frac{2\pi(Ze)^2}{\epsilon \kappa^2 V} \cdot \left(V = \frac{4}{3} \pi R^3 \right) \dots (36)$$

This result is in conformity with the requirements of the Donnan equilibrium. In fact, if ψ is the electric potential and n_i the concentration of ions i inside the sphere,

$$n_i = c_i \exp\left(\frac{e_i \psi}{kT}\right) = c_i - c_i e_i \frac{\psi}{kT} + \frac{1}{2} c_i e_i^2 \left(\frac{\psi}{kT}\right)^2$$

$$\rho + \sum_i n_i e_i = 0 \quad P = kT \sum_i (n_i - c_i),$$

where P denotes the osmotic pressure. In conformity with our previous calculations we consider $e_i \psi/kT$ as a small quantity and thus find to a first approximation

$$P = \frac{kT}{\sum_i c_i e_i^2} \frac{\rho^2}{2} = \frac{2\pi Z^2 e^2}{\epsilon \kappa^2 V^2}$$

This is in agreement with the result (36), because $P = -\partial F/\partial V$. As regards the dimensions of the polymer molecule, it follows from equation (35), that in this limiting case

$$y^3 \frac{y^2 - 2}{y^2 - 1} = \frac{5\beta}{2p^2}$$

Considering the relations (22) and (34) this means that

$$y^5 \frac{y^2 - 2}{y^2 - 1} = \frac{3}{2} \left(\frac{36}{5 A^2 N} \right)^{3/2} \frac{Z^2 e^2}{\kappa^2 \epsilon kT} = \lambda, \text{ say.}$$

If the effect of the charge Ze is large, the solution of this equation approaches the form $y^2 = \lambda^{2/5}$ which, since Ze is proportional to N , means that y^2 becomes proportional to $N^{1/5}$.

Appendix II.

Derivation of equation 31.

If the charge density, ρ , conforms to equation (16), the electrical free energy of the polymer molecule in the electrolytic solution is

$$F = 2 \pi a \int_0^{\infty} dr r^2 \psi' \exp(-b^2 r^2) \dots \dots \dots (37)$$

where ψ' is the solution of the differential equation

$$\Delta \psi' - \kappa^2 \psi' = -4 \pi a / \epsilon \cdot \exp(-b^2 r^2) \dots \dots \dots (38)$$

To compute F , let us consider the function

$$E(t) = \int_0^{\infty} dr \psi' r^2 \exp(-tr^2), \dots \dots \dots (39)$$

where t is a variable and ψ' still conforms to equation (38). Then, clearly, $F = 2 \pi a E(b^2)$. Now differentiating $E(t)$ with respect to t , we find by partial integration of the result obtained

$$\frac{dE}{dt} = - \int_0^{\infty} dr r^4 \psi' \exp(-tr^2) = - \frac{3E}{2t} - \frac{1}{2t} \int_0^{\infty} dr r^3 \frac{d\psi'}{dr} \exp(-tr^2).$$

On further partial integration,

$$\frac{dE}{dt} = - \frac{3E}{2t} - \frac{1}{4t^2} \int_0^{\infty} dr r^2 \Delta \psi' \exp(-tr^2).$$

Using the differential equation (38) this reduces to

$$\frac{dE}{dt} = - \left(\frac{3}{2t} + \frac{\kappa^2}{4t^2} \right) E + \frac{a}{4\epsilon t^2} \left(\frac{\kappa}{t + b^2} \right)^{3/2} \dots \dots \dots (40)$$

From the definition of $E(t)$, taking into account the properties of the potential ψ , it follows that $E(0)$ is finite. This condition suffices to determine the solution of the differential equation (40) which runs

$$E(t) = \frac{a}{4\epsilon} \left(\frac{\kappa}{t} \right)^{3/2} \exp\left(\frac{\kappa^2}{4t}\right) \int_0^t \frac{du \exp(-\kappa^2/4u)}{\sqrt{u} (u + b^2)^{3/2}}$$

Substituting $\sqrt{u} = \kappa/2\lambda$ and putting $t = b^2$, we find

$$E(b^2) = \frac{\kappa a}{4\epsilon} \frac{\kappa^{3/2}}{b^6} \exp\left(\frac{\kappa^2}{4b^2}\right) \int_{\kappa/2b}^{\infty} \frac{d\lambda \lambda \exp(-\lambda^2)}{(\lambda^2 + \kappa^2/4b^2)^{3/2}}$$

Finally, we substitute $\omega^2 = \lambda^2 + \kappa^2/4b^2$ under the integral sign and insert the values of a and b which follow from the relations (17) and (18), remembering that $\kappa R = p$. This gives, after partial integration,

$$F = 2 \pi a E(b^2) = 1/2 \frac{Z^2 e^2}{\epsilon R} \left(\frac{5}{\pi} \right)^{1/2} \left\{ 1 - \frac{2p}{\sqrt{5}} \exp\left(\frac{p^2}{5}\right) \int_{p/\sqrt{5}}^{\infty} d\omega e^{-\omega^2} \right\},$$

which is the result (31).

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