

**Theory of the Electroviscous Effect  
in Polymer Solutions**

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**J. J. HERMANS and J. Th. G. OVERBÈEK** (Groningen and Utrecht)

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## Theory of the Electroviscous Effect in Polymer Solutions (\*)

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J. J. HERMANS and J. Th. G. OVERBEEK (Groningen and Utrecht)

**SUMMARY.** — The statistical form of a long chain molecule is modified if the macromolecule contains charged spots, e.g. by dissociation of carboxylic groups. The coil formed by the large molecule is less dense as a consequence of the repulsive force between different charged spots. This repulsion and therefore the inflation of the coil will be less pronounced if electrolyte is present which, by the formation of ionic atmospheres around the charged spots, diminishes the interaction.

A quantitative theory of the average dimensions of the coil is developed based on the statistics of coil molecules and on the free energy of the electric charges on the coil.

Application of the theory to the viscosity of solutions of charged polymers results in a natural explanation of the so-called electroviscous effect.

The limits of applicability of the theory due to certain approximations in the statistical theory and to the use of the Debye-Hückel approximation in evaluating the free energy of the charges is discussed.

**RÉSUMÉ.** — La forme moyenne d'une macromolécule à longue chaîne se modifie quand la macromolécule acquiert des charges électriques, par exemple par dissociation des groupes carboxyliques. La pelote formée par la grosse molécule devient moins dense à cause de la répulsion entre les charges. Cette répulsion et l'expansion de la pelote qui en résulte sont moins prononcées en présence d'électrolytes, qui en formant des nuages d'ions autour des charges, diminuent leur interaction.

Nous avons développé une théorie quantitative sur les dimensions moyennes de la pelote, en employant la statistique des molécules en chaîne et en calculant l'énergie libre des charges électriques de la macromolécule.

De l'application de la théorie précédente à la viscosité des solutions des macromolécules chargées découle une explication simple de l'effet électro-visqueux.

Nous avons discuté les limites en dehors desquelles la théorie cesse d'être applicable. Ces limites sont déterminées par certaines approximations dans la théorie statistique et par l'utilisation de l'approximation de Debye et Hückel dans l'évaluation de l'énergie libre.

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It is a well-known fact that the viscosity of many colloidal solutions is higher, the higher the electric charge of the particles. The problem has been treated by von Smoluchowski <sup>(1)</sup> as early as 1916. This treatment assumes rigid spheres surrounded by an electric double layer. Some objections have been raised to von Smoluchowski's treatment, but at present we are not concerned with this problem. We are concerned, rather,

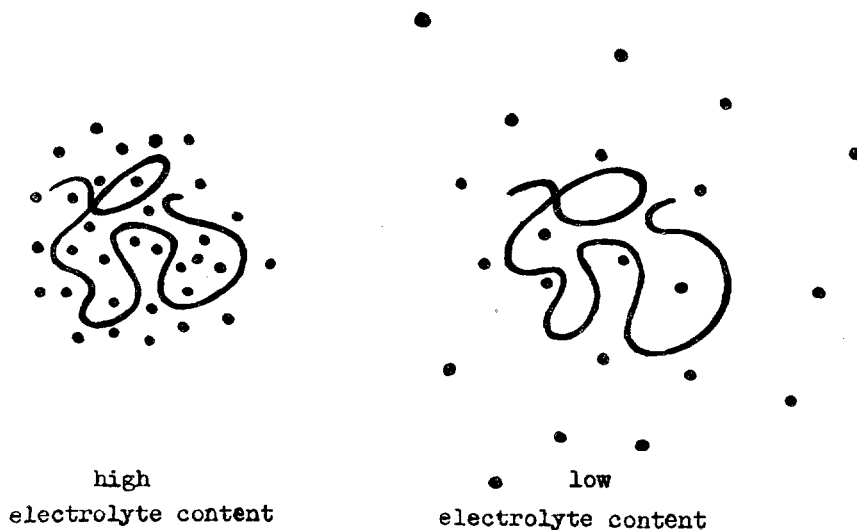


FIG. 1.

with long chain molecules which adopt the shape of a random coil. It would certainly represent a very drastic extrapolation to apply von Smoluchowski's treatment to structures of this kind. The treatment which we propose is, briefly, the following.

We consider the polymer as a random coil whose statistics are changed by the presence of charges. High charges have the effect of *inflating* the molecule. This effect will depend to a large extent on the concentration of electrolytes present. In fact, the charges on the polymer molecule are compensated by a diffuse cloud of gegenions in the electrolytic solution. With low electrolyte content this cloud extends over large distances, distances in fact which may be much larger than the size of the polymer coil (fig. 1b). In this case the inflation of the

<sup>(1)</sup> M. VON SMOLUCHOWSKI, *Kolloid-Z.*, **48**, 194 (1916).

polymer molecule may be said to result from the electrostatic repulsion between the constituent parts of the chain. As the electrolyte content is increased, however, the Debye-Hückel cloud becomes more dense (fig. 1a); every charge on the polymer chain becomes more and more *compensated separately* by a double layer; the electrostatic repulsion between the charges on the chain is reduced considerably or even annulled altogether. The distribution of ions in this limiting case becomes very similar to that found in a Donnan equilibrium: the «outer surface» of the polymer coil may be considered as impermeable to the ions fixed on to the chain. In as far as a residual inflation of the polymer coil remains, it can be visualised as a result of the osmotic pressure within this coil. In the following we give a brief account of the theory of this effect. Mathematical details will be given elsewhere.

The statistics of the random coil have been worked out by Kuhn <sup>(2)</sup>. We follow his method in that we introduce the so-called statistical chain elements of length  $A$ . Each element contains a certain number of monomer units, and must be chosen in such a manner that the statistics of the molecule can be described by assuming that the orientations of the statistical chain elements are completely random. If there are  $N$  statistical chain elements per molecule, the average square of the distance,  $h$ , between the two end points of the molecule is

$$\overline{h^2} = NA^2. \quad (1)$$

The number of molecules with distance between  $h$  and  $h + dh$  between the ends is proportional to

$$dh h^2 \exp\left(-\frac{3h^2}{2NA^2}\right). \quad (2)$$

On an average, the statistical chain elements fill a spherical space. The density within this sphere is not uniform; it is highest in the centre of gravity and gradually drops to zero if the distance from this centre is increased. In the following calculations we shall need an effective radius, which is representative for the properties of the random coil. Now, it was shown by Debye <sup>(3)</sup>, that the quantity which is determinative for viscosity is a radius  $R$  defined as follows:

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

<sup>(2)</sup> W. KUHN, *Kolloid-Z.*, **68**, 2 (1934).

<sup>(3)</sup> P. DEBYE, *J. Chem. Phys.*, **14**, 636 (1946); *International Congress of Pure and Applied Chemistry*, London, July 1947.

In this equation  $r_k$  is the distance between the  $k$ 'th statistical chain element and the centre of gravity; the bar denotes the statistical average.

In an uncharged random coil, where the equations (1) and (2) apply, one has

$$R^2 = \frac{5}{18} NA^2. \quad (4)$$

The physical meaning of this equivalent radius is as follows. If the packing of the chain elements in the sphere is so tight, that the sphere behaves as a rigid particle (all liquid within the sphere being practically immobilised), the contribution of a molecule to the specific viscosity,  $\frac{\eta - \eta_0}{\eta_0}$ , is given by Einstein's expression:  $5/2 \cdot 4/3 \cdot \pi R^3$ . In the other extreme case, where the liquid flows freely through the meshes of the coil (free-drained molecule), the viscosity contribution becomes

$$\frac{3\pi}{10} ANR^2$$

Since we are dealing with viscosity effects, it is consistent to take the quantity defined by equation (3) as effective radius. The equations (1), (2) and (4), however, are no longer valid if the polymer molecule is charged. For, in that case the molecule has a tendency to assume the largest possible volume. This is counterbalanced by the tendency of the distance  $h$  to be small, and the result of these opposing tendencies is some new distribution of  $h$ -values and a new average  $h^2$ .

The new distribution of  $h$ -values will be obtained by multiplying the distribution (2) by a Boltzmann factor. It would be wrong, however, to use the total electric energy (field energy) of the charged coil with its gegenions in the exponent of the Boltzmann term. This would include the potential energy of the ions and consequently also the entropy of the ions would have to be included in the distribution function. Fixing our attention exclusively on the distribution of the coil, the correct procedure is to use the free energy of the electric charges on the polymer molecule in the Boltzmann function. This free energy will be defined later on. (eq. (11) and (16-18)).

The new distribution of  $h$ -values will then be of the form

$$dh h^2 \exp\left(-\frac{3 h^2}{2 NA^2} - \frac{F}{kT}\right) \quad (5)$$

and the average square of  $h$  becomes

$$\bar{h}^2 = \frac{\int_0^\infty dh h^4 \exp\left(-\frac{3h^2}{2NA^2} - \frac{F}{kT}\right)}{\int_0^\infty dh h^2 \exp\left(-\frac{3h^2}{2NA^2} - \frac{F}{kT}\right)} \quad (6)$$

The problem is thus reduced to that of finding the electrical free energy of the charged system as a function of  $h$ . What we shall calculate instead is the free energy as a function of the volume of the coil, i.e. the effective radius,  $R$ . We shall therefore need, in addition, the relation between  $h$  and  $R$ . Now, this latter problem is one of simple statistics. We shall not go into the details of these statistics and only mention the result, which is of the following simple form

$$R^2 = \frac{5}{36} NA^2 \left(1 + \frac{h^2}{NA^2}\right). \quad (7)$$

This relation assumes that the distance,  $h$ , between the ends is small compared with the maximum extension,  $NA$ , of the polymer molecule. It will therefore fail to give accurate results if the inflation of the polymer coil becomes very pronounced.

Now, all we have to do is to calculate the electrical free energy,  $F$ , as a function of  $R$ . Substituting in equation (6) and using (7), we obtain the average square of  $h$  and of  $R$ . In this method no account is taken of the fluctuation in  $R^2$  for a given value of  $h$ . For large values of the molecular weight the error involved will be small.

To calculate the electrical free energy, we treat the charges fixed on the polymer molecule as a continuous charge of density  $\rho$ . As a result of this charge density there will exist a certain electric potential,  $\psi$ .

Let us first consider a polymer molecule carrying electric charges in an extremely dilute electrolytic solution, in which case the diffuse double layer extends over distances which are large compared with the radius  $R$  of the coil. In this limit (zero electrolyte content) the electric potential,  $\psi$ , conforms to the followings requirements

$$\left\{ \begin{array}{l} \text{inside the coil } \Delta\psi = -\frac{4\pi\rho}{\epsilon} \\ \text{outside the coil } \Delta\psi = 0 \end{array} \right. \quad (8)$$

$\psi$  is finite everywhere,  $\psi = 0$  at infinity,  $\psi$  and  $\frac{d\psi}{dr}$  are continuous at the surface of the coil;  $\epsilon =$  dielectric constant<sup>(4)</sup>,  $\rho =$  charge density inside the coil. To begin with, let us assume that this charge density may be considered as constant; we shall show that even serious departures from this assumption involve only very slight variations in the free energy. With constant charge density the total charge on the polymer is

$$e = \frac{4}{3} \pi R^3 \rho. \quad (9)$$

The solution of the electrical problem is as follows:

$$\left\{ \begin{array}{l} \text{inside the coil } \psi = \frac{2}{3} \pi \frac{\rho}{\epsilon} (3R^2 - r^2) \\ \text{outside the coil } \psi = \frac{e}{\epsilon r}. \end{array} \right. \quad (10)$$

The electrical free energy is found by integrating  $\frac{1}{2} \rho \psi$  over the entire sphere, which gives

$$F = \frac{3}{5} \frac{e^2}{\epsilon R}. \quad (11)$$

From this expression one can calculate the dimensions of the polymer molecule by using equations (6) and (7). To show that the assumption of constant charge density is immaterial, we considered the following distribution of charges within the coil

$$\rho = ce^{-b^2 r^2}, \quad (12)$$

$b$  being a constant, chosen in such a manner that  $\sum_k r_k^2$  has the correct value required by equation (3). The Gaussian distribution (12) is doubtless a quite close approximation to the actual distribution of the chain elements within the coil. Computing the electric free energy on the basis of equation (12) we found, instead of (11),

$$F = 0,63 \frac{e^2}{\epsilon R}. \quad (13)$$

<sup>(4)</sup> When the coil is not very compact, the mean dielectric constant in the coil may, without appreciable error, be put equal to the dielectric constant of the dispersion medium.

We now turn to the much more interesting case, in which the electrolyte content plays a decisive part. This case can be treated in a similar manner if we assume that Debye and Hückel's approximation is permissible. Instead of equations (8) we get

$$\left\{ \begin{array}{l} \text{inside the coil } \Delta\psi - \kappa^2\psi = -\frac{4\pi\rho}{\varepsilon} \\ \text{outside the coil } \Delta\psi - \kappa^2\psi = 0, \end{array} \right. \quad (14)$$

where  $\kappa$  is the well-known reciprocal length from Debye and Hückel's theory :

$$\kappa^2 = \frac{4\pi \sum_i e_i^2 n_i}{\varepsilon kT} \quad (15)$$

The final expression for the electrical free energy is somewhat more complicated than formerly. It can be shown that this free energy once again has practically the same value, irrespective of whether we take the charge density  $\rho$  to be constant or otherwise. With constant charge density,  $\rho$ , one finds the following expression for the electrical free energy

$$F = \frac{3}{5} \frac{e^2}{\varepsilon R} \left\{ \frac{5}{2\kappa^2 R^2} - \frac{15}{4} \frac{\kappa^2 R^2 - 1 + (1 + \kappa R)^2 \exp(-2\kappa R)}{\kappa^5 R^5} \right\}, \quad (16)$$

whereas with a charge density of the form (12),

$$F = 0,63 \frac{e^2}{\varepsilon R} \left\{ 1 - \sqrt{\frac{\pi}{5}} \kappa R e^{\frac{\kappa^2 R^2}{5}} \left( 1 - \sqrt{\frac{2}{\pi}} \int_0^{\kappa R} \sqrt{\frac{2}{5}} dw e^{-\frac{w^2}{2}} \right) \right\} \quad (17)$$

Both the expressions (16) and (17) can be represented quite accurately by the following simple interpolation formula :

$$F = \frac{3}{5} \frac{e^2}{\varepsilon R} (1 + 0,6 \kappa R + 0,4 \kappa^2 R^2)^{-1} \quad (18)$$

which was used to compute the statistical average of  $h^2$  according to equation (6). The result is shown in figure 2. When comparing this result with experimental data it should be borne in mind that the charge,  $e$ , for a given type of polymer in a given solution, is proportional to the number,  $N$ , of



statistical chain elements, i.e. to the degree of polymerization. The parameter  $\lambda$  in fig. 2 is, therefore, proportional to  $N^{3/2}$ .

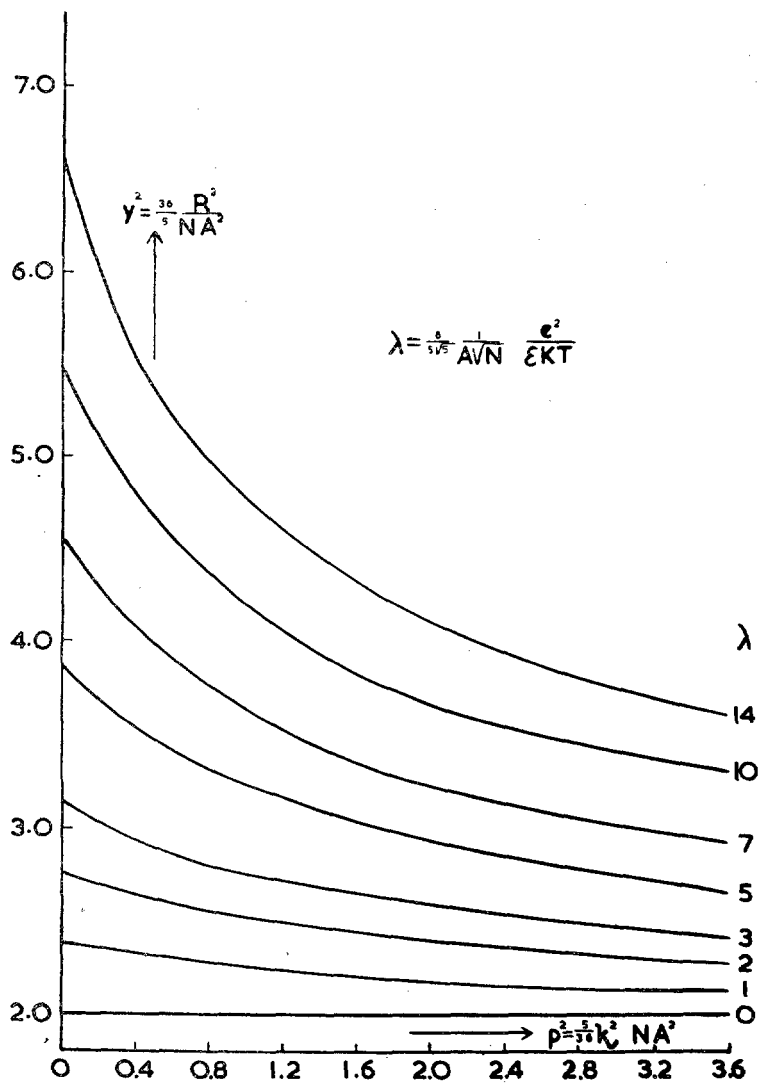


Fig. 2. — Dimensions of polymer coil as a function of electrolytic concentration for various values of polymer charge,  $e$ .

To conclude, we wish to point out that two approximations restrict the applicability of our theory. The first is the assumption that the distance between the ends of the molecule

is small compared with the maximum length. A highly charged molecule in a dilute electrolytic solution may become stretched to such an extent, that this approximation becomes noticeable. The statistical treatment of this limiting case will always remain very approximate, but it will doubtless be possible to find a solution for this case which is better than ours.

The second restriction is imposed by the Debye-Hückel approximation, which excludes high values of the electric potential in those cases where the electrolyte plays an important part in the phenomenon. Accordingly, if the polymer molecule is highly charged, the influence of the valency of the gegenions (rule of Schulze and Hardy) is only approximately accounted for.

UNIVERSITY OF GRONINGEN,  
*Laboratory of inorganic and physical chemistry.*

UNIVERSITY OF UTRECHT,  
*van 't Hoff Laboratory.*