Studies on Polyelectrolytes XXXVIII. Polyion in Simple Salt Solution

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The study of electrical potential and counter ion distributions around a polyion in simple salt solution is one of the most important for clarifying the abnormal behavior of polyion. In this field, several interesting theories have so far been reported, including, Hermans and Overbeek's (H. O. theory)[1], Kimball, Cutler and Samelson's (K. C. S.)[2], Oosawa, Imai and Kagawa's (O. I. K.)[3], and Wall and Berkowitz's (W. B.)[4]. Although almost the same model of polyion was used in these theories, different potential distribution curves and free energies of the system were obtained because of the difference in procedure. Calculated from their expressions of the potential distribution and the free energy, therefore, the volume of polyion differs considerably, and, moreover, all volumes thus calculated as well as that calculated from assuming the balance between osmotic pressure and Kuhn entropy force by Flory[5] are much larger than the volume experimentally estimated[6-8]. The disagreement between observed and calculated volumes has sometimes been explained by presuming an association of counter ion with polyion and sometimes by pointing out the failure of the Debye-Hückel approximation for the exponentials in Poisson-Boltzmann equation.

The present paper is offered for the purpose of making a contribution toward the comprehension of the relationship among the theories so far published and an understanding of the cause of disagreement between theories and experiments. Taking into account the differences

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[1] J. J. Hermans and Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

[2] G. E. Kimball, M. Cutler and H. Samelson, *J. Phys. Chem.*, **56**, 57 (1952).

[3] F. Oosawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).

[4] F. T. Wall and J. Berkowitz, *J. Chem. Phys.*, **26**, 114 (1957).

[5] P. F. Flory and I. E. Osterheld, ibid., **58**, 653 (1954).

[6] N. S. Schneider and P. Doty, ibid., **58**, 762 (1954).

[7] H. J. L. Trap and J. J. Hermans, ibid., **58**, 757 (1954).

[8] H. Fujita, M. Mitsuhashi and T. Homma, *J. Colloid Sci.*, **9**, 466 (1954).

observed in several divisions of their theories, the authors' discussion is centered around the following three points: First, the relationship among the theories of H.O., K.C.S. and O.I.K. is compared and, based on the comparison, the authors introduce an analytical equation of potential distribution which is thought to be more reasonable in this category of polyelectrolyte theory. The characteristic features of the potential curve thus obtained are described in detail in relation to the Donnan membrane potential. Second, it is shown that when this potential distribution curve is used, the electrical free energy of the system can be easily calculated by simultaneously charging all ions in the solution from the non-charged state to the real state. The free energy thus obtained is compared with those of other theories[1,3,9]. Third, the polyion volume is calculated on the usual assumption that the electrical repulsive force is equal to the Kuhn entropy force. The volume obtained is still much larger than the volume estimated from the viscosity data, despite the fact that it must be the smallest of all theoretical volumes. Some comments are made on the cause of this.

The model of polyion employed here is a sphere having a uniform charge density throughout. It is assumed that the polyion is in an infinitely large volume of uni-uni valent simple electrolyte solution, and also that it has negatively charged groups and that the counter ion is the same univalent ion as the positive ion of the added electrolyte.

Potential and Ionic Distribution Around Polyion

Let us consider that R denotes the radius of polyion sphere and Ze the fixed charge of the polyion, then the density of fixed charge in the polyion ρ_0 is given by

$$\rho_0=Ze/\frac{4}{3}\pi R^3 \tag{1}$$

If it is assumed that we can express the relationship among this charge density (ρ_0), the concentration of the simple electrolyte in the solvent phase (n_c) and the concentration in the polyion sphere phase (n_c^P) by Donnan equilibrium, it follows that

$$n_c^P(\rho_0/e+n_c^P)=n_c^2 \tag{2}$$

and also that the potential difference between the polyion phase and the solvent phase (E_D) can be given by the following Donnan membrane potential equation:

$$E_D=-\frac{kT}{e}\ln\frac{\rho_0/e+n_c^P}{n_c}=-\frac{kT}{e}\ln\frac{n_c}{n_c^P} \tag{3}$$

Substitution of n_c^P calculated from Eq. (1) into Eq. (2) yields

$$E_D=-\frac{kT}{e}\ln\frac{1+\sqrt{1+\left(\frac{8\pi}{3}\frac{1}{Z}R^3n_c\right)^2}}{\left(\frac{8\pi}{3}\frac{1}{Z}R^3n_c\right)} \tag{4}$$

from which it follows that

$$E_D^\circ=-\frac{kT}{e}\frac{1}{\left(\frac{8\pi}{3}\frac{1}{Z}R^3n_c\right)}=\frac{kT}{e}\frac{\rho_0/e}{2n_c} \tag{5}$$

when $n_c\gg 2\rho_0/e$, i.e., $\frac{8\pi}{3}\frac{1}{Z}R^3n_c\gg 1$.

When E_D or E_D° is used, the potential distribution curves for a polyion at infinite dilution in H.O., K.C.S. and O.I.K. theory are simplified as follows:

H.O.,

$$\psi_1=E_D^\circ\left\{1-\mathrm{e}^{-\kappa R}(1+\kappa R)\frac{\sin\mathrm{h}(\kappa r)}{\kappa r}\right\} \qquad (r<R) \tag{6}$$

$$\psi_2=\frac{1}{2}E_D^\circ\{(1+\kappa R)\mathrm{e}^{-\kappa R}-(1-\kappa R)\mathrm{e}^{\kappa R}\}\frac{\mathrm{e}^{-\kappa r}}{\kappa r} \qquad (r>R) \tag{7}$$

K.C.S., (1) When Donnan approximation is applied:

$$\psi_1=\frac{kT}{e}\sin\mathrm{h}^{-1}\frac{e}{kT}E_D^\circ=E_D \tag{8}$$

$$\psi_2=0 \tag{9}$$

(2) When $\mathrm{e}\psi/kT\ll 1$:

Both ψ_1 and ψ_2 are the same as Eqs. (6) and (7).

O.I.K.,

$$\psi_1=E_D\left\{1-\frac{2}{\mathrm{e}^{\kappa R}+\mathrm{e}^{-\kappa R}}\frac{\sinh(\kappa r)}{\kappa r}\right\} \tag{10}$$

Here, in the theory of K.C.S. the equations for uniform distribution of fixed charge only are considered and in the theory of O.I.K. the equation at infinite dilution of polyion only is considered, κ being the reciprocal thickness of ionic atmosphere, i.e.,

$$\kappa^2=\frac{8\pi e^2}{DkT}n_c \tag{11}$$

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[9] S. Lifson and A. Katchalsky, *J. Polymer Sci.*, **13**, 43 (1954).

In all three theories it can be easily observed that the potential ψ_1 becomes E_D or E_D° and ψ_2 becomes zero when R is very large, that is

$$\left.\begin{array}{l}\text{H.O.,}\ \psi_1=E_D^\circ\\ \text{K.C.S.,}\\ \quad\text{(1) for Donnan approximation}\\ \qquad\qquad \psi_1=E_D\\ \quad\text{(2) for } e\psi/kT\ll1 \qquad \psi_1=E_D^\circ\\ \text{O.I.K.,}\ \psi_1=E_D\end{array}\right\} \quad (12)$$

This fact suggests a very close relationship among these three theories and the simple Donnan theory of ionic distribution, which is later discussed in more detail. (see p. 966)

The theory of Oosawa, Imai and Kagawa distingushes itself from the other theories in the feature that no Debye-Hückel approximation is used in its solution to the Poisson-Boltzmann equation. The fact that E_D, instead of E_D°, appears in the potential equation, Eq. (10) of this theory manifests this feature. Another difference observed between these three theories is the difference between the factors of the second term in the ψ_1 equations. This difference comes from the fact that in the O.I.K. theory the effect of the ionic distribution outside the polymer sphere upon the potential distribution inside is entirely neglected, while in the H.O. and the K.C.S. theory that effect is taken into account.

An inspection of the two differences among H.O., K.C.S. and O.I.K. theory may lead us to expect the following equations to be a better approximation in this category of the polyelectrolyte theory:

$$\psi_1=E_D\left\{1-\mathrm{e}^{-\kappa R}(1+\kappa R)\frac{\sinh(\kappa r)}{\kappa r}\right\} \qquad (r<R) \quad (13)$$

$$\psi_2=\frac{1}{2}E_D\{(1+\kappa R)\mathrm{e}^{-\kappa R}-(1-\kappa R)\mathrm{e}^{\kappa R}\}\frac{\mathrm{e}^{-\kappa R}}{\kappa r} \qquad (r>R) \quad (14)$$

This result can be easily verified through the following calculation: eqs. (13) and (14) can be easily calculated from the same fundamental equations as used by Hermans and Overbeek if the assumption $e(E_D-\psi_1)\ll1$ instead of $e\psi_1/kT\ll1$ is used. That is,

$$\Delta\psi_1=-\frac{4\pi}{D}[-\rho_0+n_ce\exp(-e\psi_1/kT) -n_ce\exp(e\psi_1/kT)] \quad (15)$$

$$\Delta\psi_2=-\frac{4\pi}{D}[n_ce\exp(-e\psi_2/kT) -n_ce\exp(e\psi_2/kT)] \quad (16)$$

As ψ_2 is in general smaller than kT/e, the Debye and Hückel approximation can be used for the exponentials in Eq. (16) and hence from that equation it follows that

$$\psi_2=A_2\frac{\mathrm{e}^{-\kappa r}}{r}+A'_2\frac{\mathrm{e}^{\kappa r}}{r} \quad (17)$$

where A_2 and A_2' are integral constants. However, ψ_1 may sometimes become considerably great, but even in such a case the difference between E_D and ψ_1, i.e., $\psi_1'=E_D-\psi_1$, may be so small that the linear approximation of the exponentials of $e\psi_1'/kT$ can be applied (see Fig. 1).

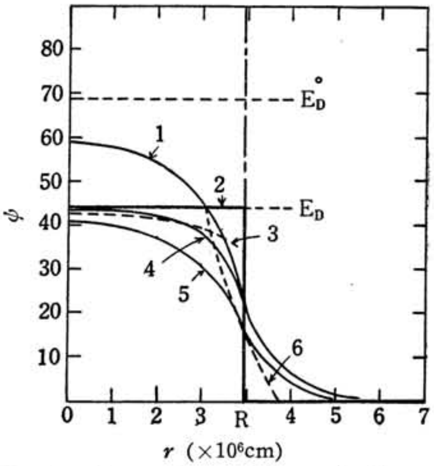

Fig. 1. Comparison of theoretical equations.
Sodium polyvinyl sulfate
$Z=1070$, $R=3.94\times10^{-6}$ cm
NaCl concn. $=1.31\times10^{-3}$ N
1. H.O.; 2. K.C.S.; 3. O.I.K.
4. Eqs. (13′) and (14′)
5. Eqs. (13) and (14)
6. Donnan-Helmholtz model

(Experimentally, ψ_1 is often greater than $kT/e=25.7$ mV at 25°C, but it is seldom greater than 2 kT/e even in considerably diluted solutions of simple salt. The assumption $e\psi_1'/kT<1$, therefore, may be true for a very wide range of simple salt solution.) When $\psi_1=E_D-\psi_1'$ is inserted in Eq. (15), the series expansion of exponentials of $e\psi_1'/kT$ are applied and higher terms are neglected, the equation becomes

$$\Delta\psi_1'=\kappa^2\cosh(eE_D/kT)\psi_1'=\kappa'^2\psi_1' \quad (18)$$

from which it follows that

$$\psi_1=E_D-\psi_1' =E_D-A_1\frac{\mathrm{e}^{-\kappa' r}}{r}-A_1'\frac{\mathrm{e}^{\kappa' R}}{r} \quad (19)$$

where A_1 and A_1' are integral constants and $\kappa'^2=\kappa^2\cosh(eE_D/kT)$.

Based on the boundary conditions that ψ is everywhere finite, is zero at infinity and is continuous on the surface of the sphere, all constants in Eqs. (17) and (19) can be determined. The final equations thus obtained are as follows:

$$\psi_1=E_D\left[1-\frac{1+\kappa R}{\kappa'\cosh(\kappa'R)+\kappa\sinh(\kappa R)}\cdot\frac{\sinh(\kappa'r)}{\kappa'r}\right] \qquad (13')^*$$

$$\psi_2=E_D\left[\frac{(1+\kappa'R)e^{-\kappa'R}-(1-\kappa'R)e^{\kappa'R}}{\kappa'(e^{-\kappa'R}+e^{\kappa'R})-\kappa(e^{-\kappa'R}-e^{\kappa'R})}\cdot e^{\kappa R}\right]\frac{e^{-\kappa r}}{r} \qquad (14')^*$$

If we assume $\kappa'=\kappa$ in Eqs. (13′) and (14′), we obtain Eqs. (13) and (14). As shown by Wall and Berkowitz in their numerical solution of Eqs. (15) and (16), the term E_D has a strong effect on ionic distribution, but the factor of the second term is less important. Therefore, to assume $\kappa'=\kappa$ in this stage, i.e., the assumption that E_D is not *very* large, scarecely lessens the applicability of the theoretical equations.

We have made a comparison between the results calculated from these theoretical equations for an experimental example in Fig. 1. It is observed that the values calculated from Eqs. (13) and (14) are the smallest of all calculated values. The difference between the values calculated from these equations and others grows smaller as the concentration of the simple salt solution increases.

The charge distribution around polyion can be calculated as follows. As the charge density ρ is given by the following equation,

$$4\pi r^2\cdot\rho=-\Delta\psi\cdot r^2D \qquad (20)$$

from this equation and Eqs. (13) and (14) it follows that

$$4\pi r^2\rho_1=D\cdot E_De^{-\kappa R}(1+\kappa R)\kappa r\cdot\sinh(\kappa r) \qquad (r<R) \quad (21)$$

$$4\pi r^2\rho_2=-\frac{DE_D}{2}\{(1+\kappa R)e^{-\kappa R}-(1-\kappa R)e^{\kappa R}\}(\kappa r)e^{-\kappa r} \qquad (r>R) \quad (22)$$

The total amount of the free charge inside and outside the polyion sphere ($[q]_1$ and $[q]_2$) can be calculated from the following integrations:

$$[q]_1=\int_0^R 4\pi r^2\rho_1 dr \qquad (23)$$

$$[q]_2=\int_R^\infty 4\pi r^2\rho_2 dr \qquad (24)$$

Hence, carrying out these integrations by using Eqs. (21) and (22), we have

$$[q]_1=-[q]_2=D\cdot\frac{E_D}{2\kappa}(1+\kappa R)e^{-\kappa R}[(1+\kappa R)e^{-\kappa R}-(1-\kappa R)e^{\kappa R}] \qquad (25)$$

In Fig. 2, the result calculated from Eqs. (21) and (22) for the same example as in Fig. 1 is shown.

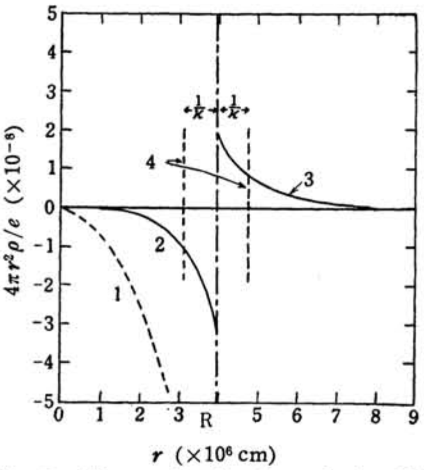

Fig. 2. Charge distribution calculated by Eqs. (21) and (22).

1. $4\pi r^2\rho_0$
2. $4\pi r^2\rho_1$
3. $4\pi r^2\rho_2$
4. Donnan-Helmholtz model

Calculation of the Electrical Free Energy

The electrical free energy discussed here means the difference between the free energy of systems at the real state and at the imaginary non-charged state, which causes the electrical repulsion of polyion sphere. That is, the electrical free energy is equal to the work which must be done when all ions in the solution are charged simultaneously from the imaginary non-charged state to the real state, keeping the interior and the exterior

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* These equations agree entirely with those independently derived by Lifson[16]. He pointed out that these equations are very close to the numerical solution of Wall and Berkowitz. Eqs. (13′) and (14′) have a little wider applicability to experiments than Eqs. (13) and (14), but to calculate the free energy using them is very difficult. The order of applicability of various theoretical equations is as follows:

H. O.<Eqs. (13), (14)<Eqs. (13′), (14′)<W. B.

In real experiments, however, experiments are rarely carried out in such a dilute simple salt solution as that in which the Hermans and Overbeek's theory does not hold, although Wall and Berkowitz have reported that H. O. theory gives far too high potential values.

16) S. Lifson, private communication.

of the polyion sphere at equilibrium. (This electrical free energy is not necessarily equal to that defined in the well-known theory of Debye and Hückel, where the work done while each ion is being charged against the electrical potential caused by the self-charge, must be subtracted from the electrical free energy defined here.)

The electrical free energy (F_e) of the system is given by the following integration:

$$\begin{aligned} F_e &= \int_0^\infty \int_0^1 \psi(\xi)\rho(\xi)/\xi 4\pi r^2 \cdot \mathrm{d}r \cdot \mathrm{d}\xi \\ &= \int_0^R \int_0^1 \psi_1(\xi)\rho_1(\xi)/\xi \cdot 4\pi r^2 \cdot \mathrm{d}r \cdot \mathrm{d}\xi \\ &+ \int_R^\infty \int_0^1 \psi_2(\xi)\rho_2(\xi)/\xi \cdot 4\pi r^2 \cdot \mathrm{d}r \cdot \mathrm{d}\xi \end{aligned} \tag{26}$$

where ξ denotes the fraction of final charges which the ions have at any stage of the integration. After some simple calculations using Eqs. (13), (14), (21) and (22), F_e becomes

$$\begin{aligned} F_e &= \frac{1}{2} D \frac{(\kappa R)^2}{2\kappa} E_D^2 \int_0^{\kappa R} f(x)\mathrm{d}x \\ &= \frac{1}{2} D \frac{(\kappa R)^2}{2\kappa} E_D^2 \sigma(\kappa R) \end{aligned} \tag{27}$$

where

$$f(x) = \frac{(3+6x+5x^2+2x^3)\mathrm{e}^{-2x}+(x^2-3)}{x^3} \tag{28}$$

$$\sigma(\kappa R) = \int_0^{\kappa R} f(x)\mathrm{d}x \tag{29}$$

and the values of $\sigma(\kappa R)$ can be easily obtained by graphical integration.

Calculated Dimension of Polyion Sphere and a Comparison of Calculated and Experimental Dimensions

The dimension of polyion sphere may be calculated from the condition that the total free energy of the system, that is, the sum of the electrical free energy and the Kuhn entropy, must have the minimum value. That is,

$$\frac{\mathrm{d}}{\mathrm{d}R}[F_e + TS_K] = 0 \tag{30}$$

Therefore,

$$\mathrm{d}F_e/\mathrm{d}R = -T\mathrm{d}S_K/\mathrm{d}R \tag{31}$$

The value of $\mathrm{d}F_e/\mathrm{d}R$ is given by differentiating Eq. (27) as follows:

$$\frac{\mathrm{d}F_e}{\mathrm{d}R} = \frac{1}{2} D(\kappa R) E_D \Big[E_D \Big\{ \sigma(\kappa R) + \frac{1}{2}(\kappa R)\frac{\mathrm{d}\sigma(\kappa R)}{\mathrm{d}(\kappa R)} \Big\} + R\frac{\mathrm{d}E_D}{\mathrm{d}R}\sigma(\kappa R) \Big] \tag{32}$$

Numerical values of $\sigma(\kappa R)$ and $\mathrm{d}\sigma(\kappa R)/\mathrm{d}R$ can be easily calculated by graphical method. In calculating the Kuhn entropy, we must express it as a function of R. Since such a calculation has already been performed by Hermans and Overbeek[1], we use their calculated result although it is a little different from the original Kuhn entropy; that is,

$$-T\frac{\mathrm{d}S_K}{\mathrm{d}R} = kT\Big[\frac{3}{R^2 - \frac{5}{36}NA^2} - \frac{108}{5}\frac{1}{NA^2}\Big] \cdot R \tag{33}$$

where A is the dimension of statistical segment and N the number of segments in a polyion.

Thus, when we know the polymerization degree and the charge density, we can graphically calculate the value of R from Eqs. (30)–(33) by assuming a value of A.

The experimental value of R can be calculated from the data of intrinsic viscosity; that is, the end-to-end distance of polymer is first calculated based on Flory's theory[11], and next is transformed into the radius of polyion sphere. According to Flory, the intrinsic viscosity of a polymer is expressed as follows:

$$[\eta] = \frac{\Phi(\sqrt{\bar{h}^2})^3}{M} \tag{34}$$

where M is the molecular weight of polymer and Φ is 2.1×10^{21} when $[\eta]$ is expressed by 100 c.c./g. The $\bar{h}$ is related to R by Hermans and Overbeek as follows:

$$R^2 = \frac{5}{36}NA^2\Big(1 + \frac{\bar{h}^2}{NA^2}\Big) \tag{35}$$

The calculated and the experimental values of R thus obtained for polyvinyl alcohol sulfate are shown as an example in Table I. In this Table, in addition, the values of $-T(\mathrm{d}S_K/\mathrm{d}R)$ and $(\mathrm{d}F_e/\mathrm{d}R)$ calculated by using the experimental values of R are shown. The value of A used for the calculation is 20–40 Å, which is thought to be reasonable for vinyl polymer[8].

It is observed that there is considerable disagreement between observed and calculated radii of polyion; values of the

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10) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 434 (1954).

11) P. F. Flory, "The Principles of Polymer Chemistry", Cornell University Press. p. 616 (1953).

TABLE
SODIUM POLYVINYL
Deg. of polym. = 1470,

NaCl concn. in solvent (N)	$A=20$ Å			
	R_η	$R_{\text{calcd.}}$	$\left(-T\frac{\mathrm{d}S_K}{\mathrm{d}R}\right)_{R,\text{obs.}}$	$\left(\frac{\mathrm{d}F_e}{\mathrm{d}R}\right)_{R,\text{obs.}}$
1.00	1.73×10^{-6}	1.75×10^{-6}	1.3×10^{-7}	1.6×10^{-7}
5.00×10^{-1}	1.89	2.07	1.7	2.8
1.00	2.25	2.83	2.3	9.6
5.02×10^{-2}	2.41	3.34	2.5	1.7×10^{-6}
2.01	2.76	4.14	3.0	2.3
1.00	2.99	4.65	3.3	2.9
5.04×10^{-3}	3.31	5.60	3.7	2.7
2.02	3.69	6.75	4.2	1.2
1.31	3.81	8.25	4.4	(2.0×10^{-7})
8.09×10^{-4}	3.92	—	4.5	(-1.1×10^{-6})
4.00	4.50	—	5.2	(−1,3)

former are much lower than those of the latter, that is to say, $(\mathrm{d}F_e/\mathrm{d}R)_{R,\text{obs.}}$ is much larger than $-T(\mathrm{d}S_K/\mathrm{d}R)_{R,\text{obs.}}$. If we arbitarily choose the dimension A, we can find better agreement, but here the value of A becomes so great that it can not be recognized as reasonable. These facts agree with those reported by Fujita[8] based on the theory of Hermans and Overbeek[1]. The results calculated using another sample of lower polymerisation degree are the same as those mentioned above.

TABLE II
SODIUM CARBOXYMETHYL CELLULOSE
(by Pals and Hermans[10])
Deg. of Polym. = 725, $Z=405$, $A=180$ Å

NaCl concn. in solvent (N)	R_η	$\left(-T\frac{\mathrm{d}S_K}{\mathrm{d}R}\right)_{R,\text{obs.}}$	$\left(\frac{\mathrm{d}F_e}{\mathrm{d}R}\right)_{R,\text{obs.}}$
∞	4.25×10^{-6}	0	0
0.192	4.31	1.3×10^{-9}	2.9×10^{-9}
0.096	4.39	6.1	9.0
0.048	4.53	1.3×10^{-8}	1.5×10^{-8}
0.024	4.66	1.7	4.5
0.012	4.83	2.4	6.5
0.006	5.07	3.1	2.0×10^{-7}
0.003	5.29	3.7	2.1
0.0015	5.57	4.5	3.5
0.00075	5.80	5.0	4.9
0.000375	6.11	5.6	4.5

In Table II, results calculated from data on carboxymethyl cellulose by Pals and Hermans[10] are given for reference. The value of A used for C.M.C. is 183 Å which is the same as used by Pals and Hermans. In this case also the calculated values are larger than the observed values. In section 2 it has been pointed out that the electrical potential ψ calculated from Eq. (13) is the smallest of all the calculated potentials. As shown later, not only the electrical potential ψ, but also the free energy equation used in this paper seem to give the smallest calculated values, and hence the values of R calculated from the present theory can be expected to be lower than those calculated from H.O. theory and others. Nevertheless, they are still much larger than the experimental values. Therefore, it is concluded that the improvement of Debye-Hückel linearization approximation is not sufficient to account for the discrepancy between calculated and experimental volumes of the polyion. The cause of the disagreement is discussed in the following section.

Discussion

a) **The relationship between the present theory and the Donnan approximation.**—From the discussion in section 2, it has been pointed out that theories based on the uniform sphere model have very close relationship with the Donnan theory. Here let us look over the details of the relationship. The survey may help us to understand the character of the theories.

At the Donnan membrane equilibrium, the potential difference between polyion sphere and outer solution E_D is expressed by Eq. (3). The existence of the potential difference means the existence of free charges at the boundary of two phases. In considering the charge distribution to be expressed by Helmholtz double layer model (see Fig. 3) and expressing the free charge by $[q]$ and the capacity of the double layer by K, there must be a relationship between $[q]$, K and E_D, as follows:

I

SULFATE

$Z=1070$

$A=40$ Å

R_η	$R_{\text{calcd.}}$	$\left(-T\frac{\mathrm{d}S_K}{\mathrm{d}R}\right)_{R,\text{obs.}}$	$\left(\frac{\mathrm{d}F_e}{\mathrm{d}R}\right)_{R,\text{obs.}}$
2.00×10^{-6}	2.15×10^{-6}	3.7×10^{-8}	8.0×10^{-8}
2.60	2.50	5.6	1.5×10^{-7}
2.46	3.40	9.3	5·6
2.61	3.85	1.1×10^{-7}	1.2×10^{-6}
2.94	4.75	1.4	1.9
3.17	5.30	1.6	2.5
3.46	6.35	1.8	2.7
3.81	7.65	2.1	1.4
3.94	—	2.2	4.6×10^{-7}
4.07	—	2.2	(-8.1×10^{-7})
4.60	—	2.6	(-1.3×10^{-6})

$$-[q]=KE_D \tag{36}$$

As these free charges constitute a sphere condenser, the electrical capacity K is expressed by

$$K=D\frac{R^2-\frac{\delta^2}{4}}{\delta}\fallingdotseq D\cdot\frac{R^2}{\delta} \tag{37}$$

where δ is the thickness of the double layer. When R is sufficiently great, δ can be assumed to be equal to $2/\kappa$. From Eqs. (36) and (37), it follows that

$$[q]\fallingdotseq -D\frac{(\kappa R)^2}{2\kappa}E_D \tag{38}$$

which agrees with Eq. (25) when κR is greater than unity, (If the effect of free charges in the solution phase be neglected that is, if it is assumed that $K=D\cdot R$, the surface charge of Oosawa, Imai and Kagawa can be obtained.)

From these considerations it is concluded that the Donnan model corresponds to the ion distribution which would have been obtained if the free ions distributed inside and outside the polymer according, respectively, to Eqs. (21) and (22) were rearranged to concentrate at the center of gravity of their respective distribution curves, as shown schematically in Fig. 2. The potential distribution corresponding to the model is shown in Fig. 1. When κ is sufficiently great, we can find no difference between the H. O. or the present theory and the Donnan theory. If not however, E_D does not equal E_D°, but even in that case the potential and the charge distribution of the present paper can completely agree with that by the Donnan theory when R is very great (see Fig. 1).

b) **Comparison between the electrical free energies described in the present paper and in others.**—If we assume the model shown in Fig. 3, we can easily calculate the electrical free energy of the system by the well-known theory of electrocapillarity[12]. That is,

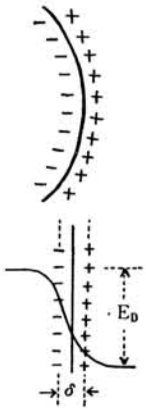

Fig. 3. Helmholtz double layer model.

$$\frac{\mathrm{d}F_e}{\mathrm{d}E}=-[q]=D\frac{(\kappa R)^2}{2\kappa}E_D \tag{39}$$

By integrating this equation at R=const., we have

$$F_e=\frac{1}{2}\cdot\frac{(\kappa R)^2}{2\kappa}E_D \tag{40}$$

By comparing this equation with Eq. (27), we can know that the charge distribution through the sphere results in the appearance of $\sigma(\kappa R)$.

In addition to these calculations, there are several others published on the electrical free energy: Hermans and Overbeek[1], Lifson and Katchalsky[9], and

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[12] J. Frenkel, "Kinetic Theory of Liquids", Oxford University press. p. 361 (1946).

Oosawa, Imai and Kagawa[3]. Hermans and Overbeek have given the following equation:

$$F_e(\text{H.O.})=\frac{1}{2}\int_0^\infty \rho_0\psi\cdot 4\pi r^2 \mathrm{d}r \qquad (41)$$

where

$$\rho_0=Ze/\frac{4}{3}\pi R^3 \qquad (42)$$

As can be understood from the physical meaning of this equation given by Hermans and Overbeek, their electrical free energy may equal the work done during the time when all charged groups of polyion are placed one-by-one on a non-charged skeleton of the polyion in simple salt solution, not taking into account the presence of counter ions. That is,

$$F_e(\text{H.O.})=\int_0^R\int_0^Z \frac{e\psi}{\frac{3}{4}\pi R^3}4\pi r^2\cdot \mathrm{d}Z\cdot \mathrm{d}r \qquad (43)$$

It can be proved that this integration give the same result as Eq. (41). Considering the features of Eqs. (26) and (43), therefore, we can see that

$$F_e(\text{H.O.})>F_e(\text{Eq.}(27))$$

According to Lifson and Katchalsky, the electrical free energy is given by the following equation:

$$F_e(\text{L.K.})=\int_0^1 \frac{U(\xi)}{\xi}\mathrm{d}\xi \qquad (44)$$

where

$$U=\frac{D}{8\pi}\int_V (\text{grad}\,\psi)^2\cdot \mathrm{d}V$$

Although it is too difficult to calculate this F_e using Eqs. (13) and (14), if the charge distribution be assumed to be expressed by the Donnan approximation, F_e can easily be calculated as follows:

$$\begin{aligned}F_e(\text{L.K.})&=\int_0^1 \frac{D}{8\pi}\frac{\kappa^2\cdot E_D^2}{4}4\pi R^2\frac{2}{\xi\kappa}\frac{1}{\xi}\mathrm{d}\xi\\&=\frac{1}{2}D\frac{(\kappa R)^2}{2\kappa}E_D^2\int_0^1\frac{1}{\xi^2}\mathrm{d}\xi \qquad (45)\end{aligned}$$

because

$$\text{grad.}\ \psi(\xi)\doteqdot\frac{E_D(\xi)}{\frac{2}{\kappa(\xi)}}=\frac{E_D\cdot\kappa}{2} \qquad (46)$$

Except for the difference between integral terms of Eqs. (45) and (40), both show the same result. (That the integral term of Eq. (45) becomes infinity at $\xi=0$ is because of the failure of the Donnan model.) We way now conclude that the electrical free energy of Eq. (26) may agree, at least qualitatively, with that of Lifson and Katchalsky.

The calculation of F_e used in the theory of Oosawa, Imai and Kagawa is not applicable to our system, in as much as the free volume is assumed in their theory. From numerical comparison, however, we can see that F_e of Eq. (27) may not have values higher than their free energy. As presumed by Flory[13], the osmotic pressure calculated from the number of simple ions gives almost the same value as our electrical repulsive force, but, strictly speaking, the former is a little higher than the latter. Thus, the electrical free energy calculated from Eq. (27) may be expected to be the smallest of all the calculated values.

c) **On the cause of discrepancy observed between calculated and observed values.**—When we consider the reason for the disagreement, we must first remember that the Donnan potential difference observed for macroscopic polyelectrolyte solution is usually much lower than the ideal value, Eq. (3)[14]. If the character of term E_D in Eqs. (13) and (14) be similar to that of the Donnan potential observed for macroscopic polyelectrolyte solution, the potential expressed by Eq. (13) may be much higher than the real potential, and hence the electrostatic repulsive force may have been overestimated in this paper. It is true that there is no reason why we should consider the ionic distribution around a polyion to be the same as that observed for the macroscopic system. Considering, however, the fact that the concentration of the counter ion within the polymer phase is almost the same as the concentration usually used for experiments of macroscopic Donnan equilibrium (for example, $8.19\times10^{-2}-4.35\times10^{-3}$N for sodium polyvinylsulfate in Table I), it seems to be also true that there is no reason why we should not consider the term E_D in Eqs. (13) and (14) to be of the same character as the macroscopic Donnan potential. (The result that the calculated values are comparatively close to the observed ones in concentrated solutions of sodium chloride, agrees with the behavior of macroscopic Donnan membrane equilibrium.) Although for a complete elucidation of this phenomenon there must be

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[13] P. F. Flory, ibid., p. 631.

[14] M. Nagasawa, H. Nakoji and I. Kagawa, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **57**, 9 (1954).

more intensive work, it seems certain that there are some important electrostatic effects other than those considered here. On further speculation we can name one of these effects which may be expressed in the following several ways:

(1) The association of the counter ion with polyion must be taken into account; this was pointed out by Flory and Osterheld[5].

(2) The "P" binding must occur in the polyion sphere, as reported by Oosawa, Imai and Kagawa[3].

(3) The activity coefficients of ions gathering within polyion sphere are very low compared with unity owing to their strong electrostatic interaction. In other words, the effect of the local ionic atmosphere around a simple ion must be taken into account.

(4) Schematically speaking, the fact that the polyion thread is enveloped by a double layer of cylindrical symmetry must be taken into account, as pointed out by Overbeek and Stigter (see Fig. 4)[15].

Fig. 4. Schematic picture of coiled polyelectrolyte chain.

It is to be noted that these expressions have the same meaning and give the same results of decrease in the value of the term E_D of potential distribution.

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[15] J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.*, **75**, 543 (1956).