Note on the Donnan Membrane Equilibrium in Polymer Salt Solutions with Extraneous Salts

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Introduction

It has been reported that the osmotic behavior of polymer salts in aqueous salt solutions is in qualitative agreement with that predicted from the theory of the Donnan equilibrium, which is expressed by the following equation[1,2],

$$\pi/C_p=RT\{1/M+[\beta+(r^2/4X)]C_p\}, \qquad (1)$$

where π is the osmotic pressure, C_p is the polymer concentration, R and T are, respectively, the gas constant and the absolute temperature, M is the molecular weight of the polymer salt, β is the interaction parameter between the polymeric ions, X is the salt content, and r is the number of equivalents per gram of the polymer salt.

It was found, however, that the calculation in terms of Equation (1) gives too great a value for the second virial coefficient in comparison with observed data. This difference has been interpreted in several ways[2-4]. In the membrane equilibrium, if a certain fraction of the added simple ions is bound or fixed in or on the molecular domain of the polymeric ion, the number of the permeant (free) ions, which coexist with the polymeric ions, will decrease in comparison with a case where the association does not occur. This, in turn, results in a decrease in the osmotic pressure contributed by the permeant ions.

The present work deals theoretically with the osmotic equilibrium on the basis of the Donnan method, by taking *formally* the simple ion association into account. It is shown that the expression for the osmotic pressure is identical in form with Equation (1) derived by previous investigators[1,5] for the electrolyte-ideal solution, provided that the value of r is replaced by a parametric factor r^*, which is smaller than r. The ratio r^*/r, which is evaluated from the observed data, is discussed in terms of the Oosawa-Imai-Kagawa theory for the simple ion association[6].

THEORETICAL

Derivation of the Osmotic Pressure Equation

On one side (phase I) of a semipermeant membrane we have an aqueous solution of a uni-univalent electrolyte, the concentration of which is C_0 (molecules/cc.). On the other side (phase II) of the membrane, impermeant anionic polymeric ions are present together with the electrolyte.

The concentrations of the electrolyte in phase II may be written in the form:

$$C_+=J_+/(V-Nv) \quad \text{and}$$
$$C_-=J_-(V-Nv), \qquad (2)$$

where J_+ and J_- are, respectively, the numbers of *free* positive and negative ions, V is the total volume of phase II, and N and v are, respectively, the total number and the molecular volume of the polymeric ion. C_+ and C_- may be regarded as the actural concentrations of simple ions which may contribute to the osmotic pressure of the solution.

The requirement for the Donnan equilibrium can thus be given by

$$C_+C_-=C_0^2, \qquad (3)$$

subject to the condition for neutrality

$$C_+=C_-+NZ^*/V', \qquad (4)$$

where $V'=V-N_v$.

Here Z^* is the effective charge of the polymeric ion and given by the equation:

$$Z^*=Z-n_++n_-, \qquad (5)$$

where Z is the stoichiometric valence of the polymeric ion, and n_+ and n_- are, respectively, the numbers of positive and

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1) D T. F. Pals and J. J. Hermans, *Rec. trav. chim., Bay-Bas*, **71**, 458 (1952).

2) H. Inagaki and T. Oda, "Makromolekulare Chemie", **21**, 1 (1956).

3) H. J. L. Trap and J. J. Hermans, *J. Phys. Chem.*, **58**, 757 (1954).

4) N S. Schneider and P. Doty. ibid., **58**, 762 (1954).

5) H. R. Kruyt, "Colloid Science", Vol. I, Elsevier Publ. Co., Amsterdam (1952), p. 188.

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

negative ions bound in the molecular domain of the polymeric ion. It follows that the total concentrations of positive and negative ions present in phase II are given, respectively, by $(J_{+}+Nn_{+})/V$ and $(J_{-}+Nn_{-})/V$. It should be noticed that activity coefficient is formally introduced in Equation (3) for the interaction between the polymeric ions and the simple ions but not for those between simple ions themselves.

Substituting Fquation (4) for C_{+} in Equation (3), we obtain,

$$C_{-}=-\frac{1}{2}(Z^{*}N/V')+\frac{1}{2}\sqrt{(Z^{*}N/V')^{2}+4C_{0}}. \tag{6}$$

If the term $Z^{*}N/V'$ is small compared with C_0, expansion of Equation (6) yields

$$C_{-}=-\frac{1}{2}(Z^{*}N/V')+C_{0}$$
$$+(1/8)(Z^{*2}/8C_{0})(M/V')^{2}+\cdots\cdots, \tag{7}$$

so that concentration C_{+} can be written

$$C_{+}=\frac{1}{2}(Z^{*}N/V')+C_{0}$$
$$+(1/8)(Z^{*2}/8C_{0})(N/V')^{2}+\cdots\cdots. \tag{8}$$

We shall now assume that the observed osmotic pressure π is formally the sum of pressures, π_1 and π_2, which are, respectively, the contributions from the permeant ions and from the polymeric ions. Thus the osmotic pressure π_1 is given approximately by

$$\pi_{1}=kT(C_{+}+C_{-}-2C_{0}), \tag{9}$$

which may be put with the aid of Equations (7) and (8) in the form:

$$\pi_{1}=kT\frac{Z^{*2}}{4C_{0}}\left(\frac{N}{V}\right)^{2}. \tag{10}$$

The term $(Z^{*2}/4C_0)$ in Equation (10) is the Donnan term.

If the osmotic pressure π_2 is assumed to be identical with the osmotic pressure in dilute solutions of neutral polymers and if the unit of concentration in Equation (10) is converted into the usual one, we have

$$\pi/C_{p}=RT\{1/M+[\beta+r^{*2}/4X)]C_{p}\}, \tag{11}$$

where r^{*} is the parametric factor related with the Z^{*}-value, and the other notations are the same as those used in Equation (1). Equation (11) becomes identical with Equation (1) derived for the electrolyte-ideal solution[1,5], if r^{*} is replaced by r. Thus the ratio r^{*}/r, which is equated to Z^{*}/Z, may be considered to be the degree of electrolytic dissociation of the polymer salt, and will now be interpreted in terms of the theory developed by Oosawa, Imai and Kagawa[6].

Short Summary of the Oosawa-Imai-Kagawa Theory

As for the association of simple ions with a polymeric ion, we may refer to the theoretical work made by Oosawa, Imai and Kagawa[6]. They solved the Poisson-Boltzmann equation for the coiled polymeric ion in salt solutions without introducing the Debye-Hückel approximation. In so doing, they assumed that the fixed electric charges on the polymeric chain are continuously distributed in a volume v occupied by the polymeric ion ($v=(4/3)\times\pi a^{3}$, where a is the apparent radius of the polymeric ion) and that the dissociation of the polymeric ion is sufficiently suppressed by the simple ion association that $\langle\lambda\rangle\ll1$, where $\langle\lambda\rangle$ is the degree of dissociation averaged over the volume v.

In accordance with the theory, the theoretical value of Z^{*} is given by an equation of the form:

$$Z^{*}=Z\langle\lambda\rangle=\frac{DkTa}{e_{0}^{2}}\ln\left(\frac{Z}{v}\frac{V_{+}}{ZN+J}\frac{1+\sqrt{1+\delta^{2}}}{2}\right), \tag{12}$$

where

$$\delta^{2}=\frac{v^{2}}{Z^{2}}\frac{J}{V_{-}}\frac{ZN+J}{V_{+}}, \tag{12'}$$

and D is the dielectric constant in the volume v, e_0 is the unit charge, J is the total number of molecules of added salt and the other notations are the same as those used in the foregoing section. Further notations V_{+} and V_{-} are the normalization factors of the Boltzmann relation for the distribution of charges.

Experimental Results and Discussion

The experimental details of osmometry and viscometry for the present data have been described in a previous paper[2]; only the results, which are necessary for the present discussion, are shown below. The molecular weight of sodium carboxymethyl cellulose used as the sample was osmometrically found to be 8.3×10^{4}. The slopes of the osmotic pressure plot for the system sodium carboxymethyl cellulose and sodium chloride are collected in Table I, wherein those calculated in accordance with Equation (1) are also recorded. The fourth column in the table gives the ratio of the observed slope against the theoretical one, S_0/S_t; the square root of this ratio is equal to r^*/r if β is neglected (see Equations (1) and (11)), and will be discussed in terms of the degree of dissociation.

TABLE I

SLOPES OF OSMOTIC PRESSURE PLOT.

Added Salt Concentration X(mole/cc.) $\times 10^3$	Observed Slope $S_0 \times 10^{-7}$	$10^{-7}RT\times$ $(r^2/4X)$ (S_t)	S_0/S_t	r^*/r*
0.1	13.7	44	0.31	0.55
0.05	25	88	0.28	0.52
0.03	42	146	0.29	0.53
0.02	60	220	0.27	0.51
0.01	120	440	0.27	0.51

* The r-value for the sample polymer salt is 2.7×10^{-3}.

TABLE II

INTRINSIC VISCOSITIES AS A FUNCTION OF ADDED NaCl CONTENTS

Added Salt Concentration (mole/l.)	$[\eta]$
0.004	11.29
0.010	9.20
0.020	7.48
0.040	6.40
0.100	5.41
$\to\infty$	$[\eta]_\infty = 4.69$

Table II gives the intrinsic viscosity obtained for the same system as a function of the salt content. The value of intrinsic viscosity is plotted against $x^{-1/2}$ (x is the salt content) according to Pals and Hermans' treatment⁷⁾, and the extrapolation of the plot to $x\to\infty$ enables us to evaluate the intrinsic viscosity $[\eta]_\infty$ for the polymer salt discharged completely.

To compare experimental data with the theory, we shall first estimate the apparent radius of the polymeric ion, a, which appears in Equation (12). As was suggested by Fujita et al.⁸⁾ and by Inagaki et al.⁹⁾, an approximate dimension of the polymeric ion may be estimated from the value of $[\eta]_\infty$ with the aid of the Flory-Fox viscosity equation¹⁰⁾:

$$\sqrt{\langle h^2\rangle}=([\eta]M/\Phi)^{1/3}, \qquad (13)$$

where $\langle h^2\rangle$ is the mean square end-to-end distance of the polymer, M is the molecular weight and Φ is the Flory universal constant of the order of 2.1×10^{-21}. Putting $[\eta]=4.7$, $\Phi=2.1\times 10^{-21}$ and $M=8.3\times 10^4$ into Equation (13), we have 1200 Å for $\sqrt{\langle h^2\rangle}$. Conversion of this into the mean square distance from the center of gravity $\langle s^2\rangle$ in the terms of the following equation¹¹⁾:

$$a=\sqrt{\langle s^2\rangle}=\sqrt{\langle h^2\rangle}/6 \qquad (14)$$

gives 500 Å.

Now we shall assume $V_+=V_-=V$ in Equation (12). Let us take $C=2$ g./l., $Z=230$ and $X=0.1$ mole/l. as a typical example. We then obtain

$$ZN/V\approx 3\times 10^{18}\ \text{molecules/cm}^3,$$

and

$$J/V\approx 6\times 10^{19}\ \text{molecules/cm}^8.$$

Putting the values obtained above into Equation (12), the $\langle\lambda\rangle$-value is found to be 0.006 for the condition assumed here.

It is seen from Table I that, although the $\langle\lambda\rangle$-value changes with the polymer- and salt-concentrations in accordance with Equation (12), the observed ratios r^*/r are practically independent of these factors and are much higher than the $\langle\lambda\rangle$-value. This discrepancy between experimental and theoretical values may be due to the fact that the Oosawa-Imai-Kagawa theory is only applicable to solutions of high dilution: In the solutions studied in the present work, the free volume of the polymeric ion is so small that the effect of neighbouring polymeric ions can not be neglected on the distribution of the permeant ions. In order to obtain agreement between experiment and theory, one should extended the theory to solutions of higher concentrations of polymer.

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10) P. J. Flory and T. G. Fox, *J. Polymer Sci.*, **5**, 745 (1950).

11) See for example, P. J. Flory, "Principles of Polymer Chemistry", Chap. X. lb. cornell Univ. Press (1955).