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Studies on Cellulose Acetate Phthalate. 3. Osmotic Pressure Measurements

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ABSTRACT

Osmotic pressure measurements of aqueous solutions of cellulose acetate phthalate (CAP) were carried out with the help of a high-speed membrane osmometer. The value of the osmotic coefficient, g, for different concentrations of CAP, as well as at different degree of neutralization for various concentrations, were estimated. The effect of concentration and degree of neutralization on the value of g were investigated. The experimental results were also treated in the light of Oosawa's theory.

INTRODUCTION

Most chemical research in the field of polyelectrolytes has been directed toward an understanding of their behavior in aqueous solutions. In solution, they are ionized into polyvalent macroions (polyions) and small ions of opposite charge (counterions). The high charge of the macroions produces a strong electric field which attracts the counter-

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ions. In the absence of simple salt, the strong electrostatic field of the polyions more or less condenses a majority of the counterions. Thus the number of free counterions, which is a decisive factor for polyelectrolyte properties, can be determined by equilibrium techniques, viz., potentiometry and osmometry. Potentiometry is unsatisfactory, particularly in dilute solutions. In the present paper we have therefore used the most sensitive technique, high-speed membrane osmometry, for aqueous CAP solutions.

EXPERIMENTAL

Materials

Cellulose acetate phthalate (CAP) used in the present work was kindly supplied by Eastman Kodak Company. CAP was purified by repeated precipitation from dimethylformamide solution with n-butanol and dried in vacuum at ambient temperature. The acetyl and phthalate contents of CAP were determined, respectively, by microanalytical methods [1] and the method given by Malm [2]. The characteristics of the sample are given in Table 1. The polymer was dissolved in standard sodium hydroxide solution and passed through a regenerated cation exchanger (Amberlite IR 120) resin to transform it to the acid form. Partially neutralized (with aqueous sodium hydroxide solution) aqueous CAP solutions were used for osmotic pressure measurements. Conductivity water was used in the preparation of all solutions.

Osmotic Pressure Measurements

Osmotic pressure measurements of aqueous CAP solutions were carried out at 35°C on a high-speed membrane osmometer, Hewlett Packard Model-502. The method of conditioning the membranes and measuring the osmotic pressure was as described in our earlier publication [3].

TABLE 1. Characteristics of Cellulose Acetate Phthalate

Acetyl, %	Phthalate, %	$\overline{M}_w{}^a \times 10^{-4}$	$\overline{M}_n{}^b \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
11.2	26.0	1.78	1.41	1.26

[a] From light-scattering measurements.
[b] From osmotic pressure measurements.

RESULTS AND DISCUSSION

The osmotic coefficient, g, which is a fundamental property of a polyelectrolyte, is defined as

$$g = \Pi/\Pi_D, \tag{1}$$

where Π is the osmotic pressure of solution and Π_D (= nRT) is the Donnan osmotic pressure. (n is the concentration of ions, R is the gas constant, T is the absolute temperature.) Π_D is calculated by assuming complete dissociation of CAP to include the contribution of all counterions, the contribution of polyions to osmotic pressure being negligible. It can be seen from Table 2, as well as from Fig. 1, that the osmotic coefficient g decreases with increasing polymer concentration. Similar results have also been reported by Inoue [4]. An increase in the degree of neutralization increases the charge on the polyions, and hence g is found to increase with α at constant concentration of CAP (Table 3). These results are in good agreement with those reported by Takahashi and Kagawa [5].

The fraction of free ions f, which is the decisive factor for polyelectrolyte properties, is correlated with the osmotic coefficient as follows:

$$f = g/\alpha, \tag{2}$$

TABLE 2. Osmotic Pressure Results of Aqueous Cellulose Acetate Phthalate Solutions at 35°C (α = 0.58, $\overline{DS}$ = 0.45)

Concentration, meq/L	Solution Π_s, cm of H_2O	Solvent Π_0, cm of H_2O	$(\Pi_s - \Pi_0)$, cm of H_2O	g^a
0.42	18.20	15.49	2.71	0.245
0.84	19.60	15.52	4.08	0.185
1.26	21.10	15.49	5.61	0.169
1.67	21.80	15.48	6.32	0.144

[a] Calculated by Eq. (1) with RT = 2.63×10^4 L·cm·mol^{-1}.

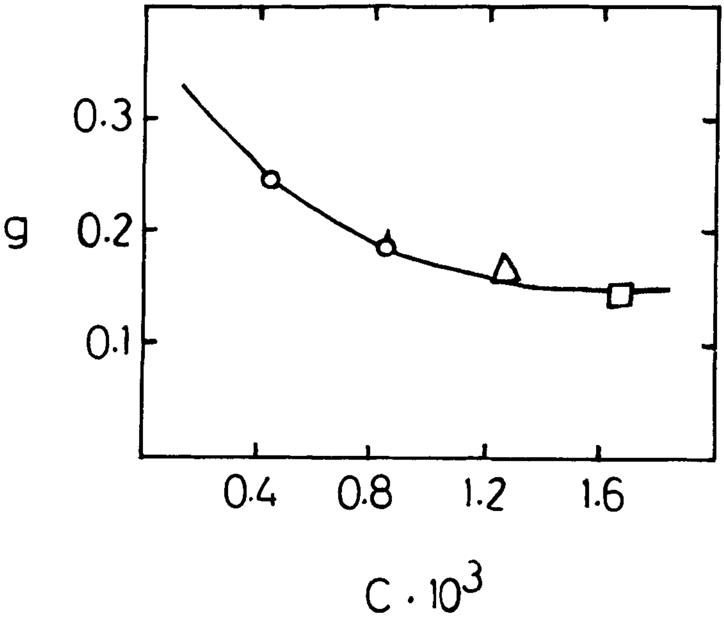

FIG. 1. The dependence of the osmotic coefficient, g, on the concentrations of CAP solutions at 58% neutralization: (○) 0.42×10^{-3} N, (ȯ) 0.84×10^{-3} N, (△) 1.26×10^{-3} N, and (□) 1.67×10^{-3} N.

TABLE 3. Osmotic Coefficients for Aqueous Cellulose Acetate Phthalate Solutions at 35°C

Degree of neutralization, α	g			
	Concentration, meq/L			
	0.42	0.84	1.26	1.67
0.19	0.14	0.10	0.08	-
0.38	-	0.12	0.12	0.11
0.58	0.25	0.18	0.17	0.14
0.77	0.30	0.21	0.17	0.15
0.98	-	0.21	0.19	0.16

[a] Calculated by Eq. (1) with $RT = 2.63 \times 10^4$ L·cm·mol^{-1}.

TABLE 4. Degree of Free Counterions, f, for Aqueous Cellulose Acetate Phthalate Solutions at 35°C

Degree of neutralization, α	f			
	Concentration, meq/L			
	0.42	0.84	1.26	1.67
0.19	0.70	0.52	0.44	-
0.38	-	0.32	0.31	0.29
0.58	0.43	0.318	0.29	0.24
0.77	0.39	0.27	0.22	0.20
0.98	-	0.21	0.19	0.16

where α is the degree of neutralization. The physical significance of Eq. (2) is that the Donnan term, which assumes complete dissociation of even partially neutralized CAP, is made more meaningful by considering the dissociation of only the neutralized groups. In other words, f counts the number of free counterions per unit charge (created by the neutralization process) on the polyion.

Table 4 shows that f decreases with increases in α at all concentrations. This behavior of f with α is also graphically represented in Fig. 2.

The results of the present investigation have been examined in light of the two-phase theory proposed by Oosawa [6] using a rodlike or cylindrical model of polyions. The two-phase distribution equilibrium between bound and free counterions may be written as

$$\ln\left(\frac{1 - f}{f}\right) = \ln\left(\frac{\phi}{1 - \phi}\right) + 2fQ \ln\left(\frac{1}{\phi}\right), \tag{3}$$

with

$$Q = e_0^2/\epsilon_0 kTd,$$

where ϕ is the apparent volume fraction of polyions in solution, Q is a parameter determining the intensity of the binding of counterions, ϵ_0 is the dielectric constant of the medium, e_0 is the protonic charge, k is the Boltzmann constant, T is the absolute temperature, and d is the average distance between the successive charges on the polyion.

The charge density parameter Q is the most important parameter

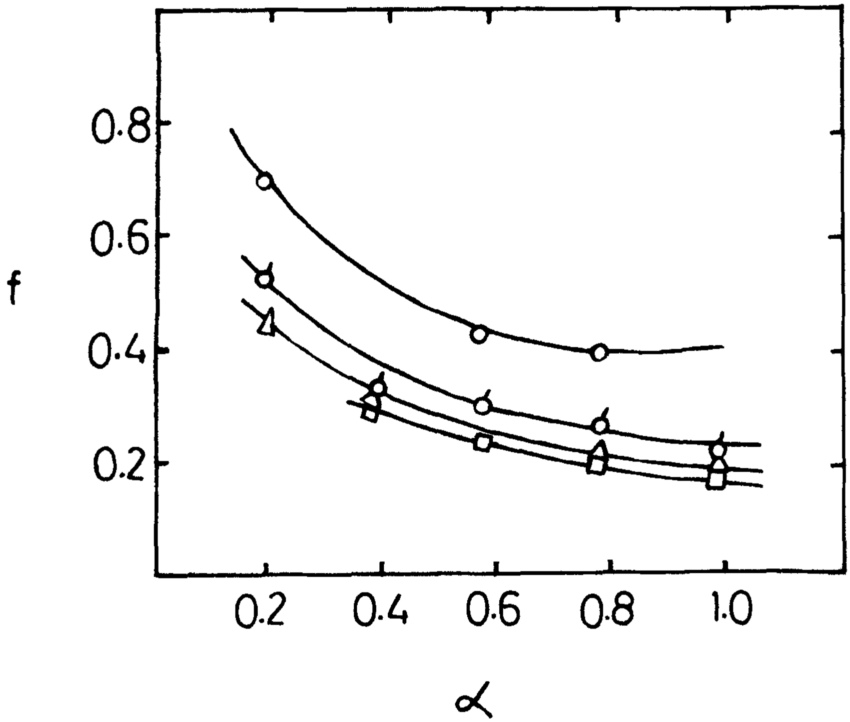

FIG. 2. The dependence of fraction of free ions, f, on the degree of neutralization, α, of CAP solutions: (○) 0.42 × 10^{-3} N, (ό) 0.84 × 10^{-3} N, (△) 1.26 × 10^{-3} N, and (□) 1.67 × 10^{-3} N.

for determining the intensity of binding of counterions, and its value is evaluated by substituting f and ϕ in Eq. (3). The value of ϕ is taken as the apparent volume fraction of CAP. The Oosawa plot [3, 4, 6] in Fig. 3 shows that the experimental results are in good agreement with the Oosawa theory. It is inferred, therefore, that CAP chains, even partially neutralized, behave like rigid rods in aqueous solutions. Thus the Oosawa theory, though quite simple, provides a good description of CAP polyions in solution. Hence it is concluded that the osmotic coefficient g and the fraction of free counterions f give useful information about the association of counterions in polyelectrolyte solutions.

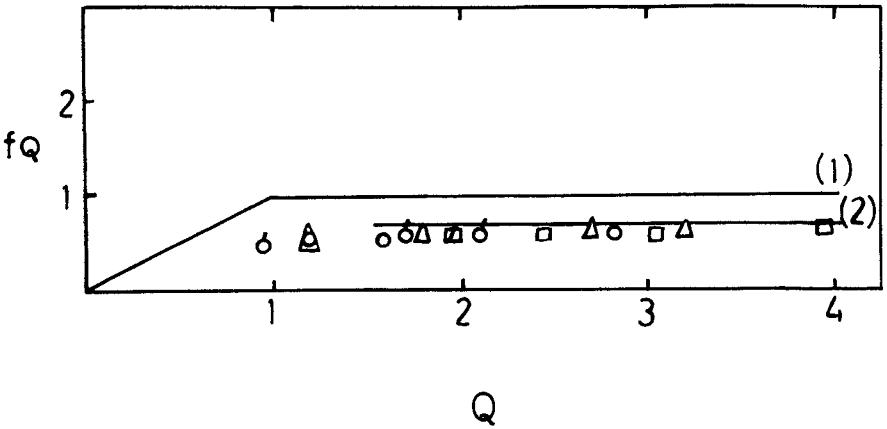

FIG. 3. Oosawa plot of number of free counterions fQ versus the charge density Q for CAP solutions. (1) In the limit of dilution; (2) the theoretical line calculated using the apparent volume concentration $\phi = 0.84 \times 10^{-3}$. (○) 0.42×10^{-3} N, (o̍) 0.84×10^{-3} N, (△) 1.26×10^{-3} N, and (□) 1.67×10^{-3} N.

REFERENCES

[1] A. Steyermark, Quantitative Organic Microanalysis, 2nd ed., Academic, New York, 1961, Chap. 17, p. 444.
[2] C. J. Malm, L. B. Genung, and K. William, Anal. Chem., 25, 245 (1953).
[3] H. C. Trivedi and R. D. Patel, J. Macromol. Sci.–Chem., A18, 555 (1982).
[4] T. Inoue, J. Chem. Soc. Jpn., 77, 826 (1956).
[5] A. Takahashi and I. Kagawa, Nippon Kagaku Zasshi, 83, 9 (1962).
[6] F. Oosawa, Polyelectrolytes, Dekker, New York, 1971, Chap. 2.

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