

Studies on Cellulose Acetatephthalate II, Polarographic Studies of Ion Binding-Cadmium Cellulose Acetate Phthalate

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The polarographic method of analysis was applied to study cadmium ion binding in cellulose acetate phthalate (CAP) solutions. It has been observed that the degree of free ions virtually remains constant in wide range of concentrations of CAP solutions and decreases with degree of neutralization. The results are interpreted according to Oosawa's two phase model of polyelectrolytes.

INTRODUCTION

The ion binding phenomenon which is a characteristic property of polyelectrolytes has been studied by several equilibrium-nonequilibrium techniques, *e.g.* viscosity potentiometry, conductometry and polarography. The polarographic method¹⁻⁶ has been proved to be relatively simple, rapid and reliable than the other methods. In the present investigation, therefore, this method has been applied to study Cd⁺² ion binding on cellulose acetate phthalate (CAP) in solution.

EXPERIMENTAL

Cellulose acetate phthalate (CAP) used in the present work was kindly supplied by Eastman Kodak Company. The purification method for cellulose acetate phthalate was followed as described earlier⁷. The characteristics of cellulose acetate phthalate sample are reported elsewhere⁷. The polymer was dissolved in standard sodium hydroxide solution and passed through the cation exchange resin column to get acid form (CAP) of it. The cadmium salt of the polymer was obtained by treating CAP solution with CdO with continuous agitation.

Polarographic measurements were made at 30°C. A Devis Southern Cathode Ray Polarograph (A-1670) was used. Mercury pool was used as a reference electrode. Dissolved oxygen was removed from all solutions by bubbling nitrogen gas, and no maximum suppressor was used. High sweep speed of voltage and absence of drop wave make the technique more rapid and sensitive than the conventional polarography. Typical polarograms are shown in Fig. 1 for 5.2×10^{-3} N CdCAP solution with (B) and without (A) supporting electrolytes. The peak height is propor-

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tional to the concentration in the same way as the diffusion current in conventional polarography.

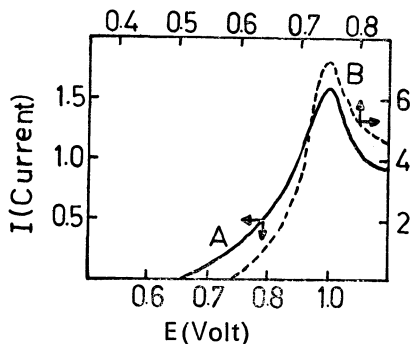


Fig. 1. Typical current voltage curves in 5.2×10^{-3} N CdCAP solution, B. with and A. without supporting electrolyte.

In the present work the following three different types of experiments were carried out:

- (i) Polarograms were run of CdCAP solutions with and without supporting electrolyte solution.
- (ii) Polarographic measurements of CdCAP solutions of different concentrations were carried out, and
- (iii) Ion binding of CdCAP solutions was studied at different degrees of neutralization and this was done by mixing CdCAP solution with CAP solution of the same concentration in different proportions. Similar procedure was reported by Katchalsky *et al.*⁸ for polymethacrylic acid neutralization.

Volume correction was applied to the observed polarographic current.

RESULTS AND DISCUSSION

The degree of free ions, f , which is a decisive factor for polyelectrolyte properties may be written as:

$$f = \frac{I_d^0}{I_d} \quad (1)$$

where I_d^0 and I_d have their usual meanings¹. The transference number of Cd^{+2} ion in ordinary electrolyte is 0.4. The same value of t_+ was assumed in the calculation of the degree of free ions¹ from Eq. (1), since independent measurements of transference number of polyions were not carried out. The results thus obtained are tabulated in Table 1. It is seen from this table that the values of f remain almost constant in the wide range of concentrations. The concentration dependence of degree of free ions

TABLE 1
POLAROGRAPHIC DATA ON CdCAP ($\overline{DS} = 0.45$) IN AQUEOUS
SOLUTION AT 30°C

Concentration		Polarographic currents (arbitrary units)			Degree of free ions f
Equiv./l $C = 10^3$	Volume fraction* $\phi \times 10^3$	I_t	I_{d^0}	I_d	
5.20	5.20	21.4	12.84	37.0	0.35
2.60	2.60	11.6	9.96	18.5	0.38
1.30	1.30	6.25	3.75	9.25	0.405
0.650	0.65	3.15	1.89	4.62	0.41
0.325	0.325	1.58	0.95	2.31	0.41
0.163	0.163	0.78	0.47	1.16	0.405
0.081	0.081	0.39	0.235	0.58	0.405
0.041	0.041	0.196	0.118	0.29	0.41

* $\phi = 0.45 C/\overline{DS}$; \overline{DS} = Degree of Substitution.

for CdCAP is shown in Fig. 2. It is seen from this figure that the degree of free ions, f , is independent of the CAP concentration. Such depen-

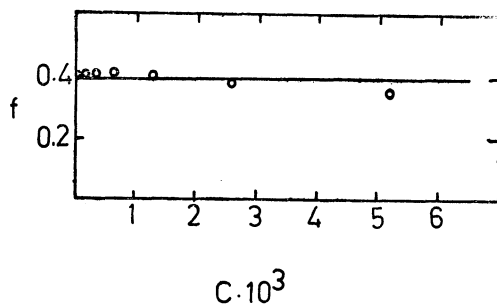


Fig. 2. Dependence of degree of free ions, f , on the concentration (equiv./l) of CdCAP solutions.

dency has also been already verified for sodium cellulose acetate phthalate (NaCAP) by employing viscosity method⁹, an entirely different technique.

The results of the variation of f with degree of neutralization are tabulated in Table 2 and are also shown graphically in Fig. 3. The results

TABLE 2
 POLAROGRAPHIC DATA ON CdCAP ($\overline{DS} = 0.45$)
 IN AQUEOUS SOLUTIONS AT SEVERAL
 DEGREES OF NEUTRALIZATION

Degree of neutralization 100α	Polarographic currents		Degree of free ions f
	I_d^0	I_d	
9.1	3.1	3.36	0.560
16.7	5.25	6.15	0.510
23.1	7.00	8.55	0.490
28.6	8.5	10.55	0.484
37.5	10.8	13.85	0.468
44.4	12.4	16.40	0.454
55.6	15.0	20.56	0.438
62.5	16.8	23.13	0.436
71.4	18.3	26.43	0.415
76.9	19.2	28.46	0.405
83.3	20.4	30.83	0.397
90.0	21.6	33.64	0.385
100.0	23.4	37.00	0.380

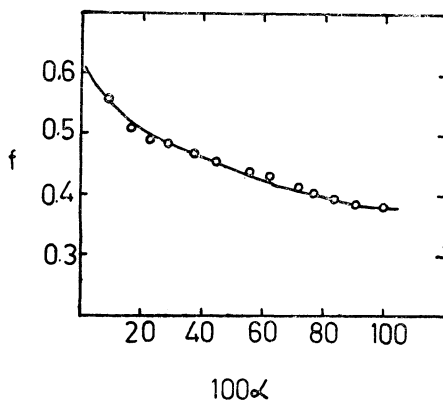


Fig. 3 Dependence of the degree of free ions, f , on the degree of neutralization, α , of CdCAP solutions.

indicate that f decreases with increasing degree of neutralization implying that more and more counterions associate with the polyions of increasing charge density.

We have examined the results of the present investigation in light of the two phase theory proposed by Oosawa¹⁰ using a rodlike or cylindrical model of polyions. The two-phase distribution equilibrium between bound and free bivalent counter ions may be written as:

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

with
$$Q = \frac{e_0^2}{\epsilon_0 kTd}$$

where ϕ is the apparent volume fraction of polyions in solution, Q a parameter determining the intensity of the binding of counterions, ϵ_0 the dielectric constant of the medium, e_0 the protonic charge, k the Boltzmann constant, T the absolute temperature and d the average distance between the successive charges on the polyion. The charge density parameter Q determined from the structure of CdCAP according to Eq. (2) comes out to 0.608 and is denoted by $Q_{\text{structure}}$.

Equation (2), when substituted with the experimental values of ϕ and f yields the charge density parameter $Q_{\text{adj}} = 1.34$. With this value of Q_{adj} f is in turn evaluated from Eq. (2) and theoretical curves of f versus C have been calculated and are shown in Fig. 2 as the solid line. It can be seen from this figure that the experimental data are in good agreement with the Oosawa theory. The degree of free counterions virtually remains constant indicating the condensation phenomenon of counterions. This phenomenon of counterion condensation has been reported for several polyelectrolytes^{1-6, 9, 10}, irrespective of the charge of the counterions. In Table 3 the observed value of $f(f_{\text{obs}})$, for CdCAP sample, corresponds to that of in the wide range of concentration while the value of f_{theo} is obtained theoretically, for CdCAP sample, in the limit of dilution *i.e.* at infinite dilution. According to the limiting law given by Oosawa¹⁰ f tends to $1/ZQ$ at infinite dilution. The limiting value of f thus obtained is labelled as f_{theo} and listed in Table 3 for its comparison with the experimental

TABLE 3
COMPARISON OF EXPERIMENTAL AND
THEORETICAL VALUES OF f FOR Cd^{+2}
COUNTERIONS IN CAP SOLUTIONS

Sample	CdCAP		
	Q_{adj}	f_{theo}^*	f_{obs}
CdCAP	1.34	0.373	0.397

*Calculated from the limiting law: $f = \frac{1}{ZQ_{\text{adj}}}$

one. It can be seen that a good agreement is observed between f_{theo} , and f_{obs} , for CdCAP sample. It is implied, therefore, that concentration of the polymer solution has a little effect on f . As a result, the fact that the polyelectrolyte molecules do not dissociate completely at infinite dilution is also supported by the present experimental data.

At infinite dilution, the degree of free ions, the osmotic coefficient and the activity coefficient of counterions are identical. If we assume that the same identity holds in moderately dilute polyelectrolyte solutions, the effective degree of ionization¹¹ may be written as:

$$i = \alpha \cdot f \tag{3}$$

where α is the degree of neutralization of the polyacid. The dependence of i on α , for CdCAP sample, is derived from the data of Figure 3. The Alexandrowicz-Katchalsky plot¹² of charge density per unit length, $\alpha f \overline{DS}/b$ (cellulose monomer unit length $b = 5.15\text{\AA}$), versus reciprocal intercharge distance $\alpha \overline{DS}/b$ is constructed and shown in Fig 4. The solid curve is the

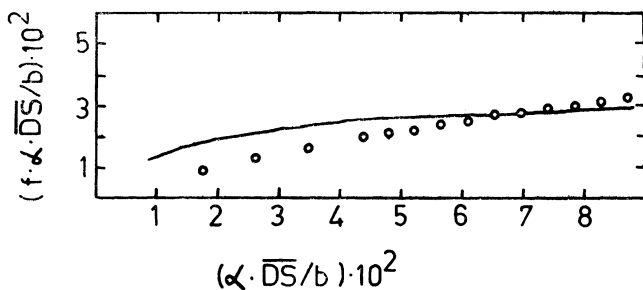


Fig. 4. Alexandrowicz-Katchalsky plot of charge density per Angstrom, $f\alpha\overline{DS}/b$, versus reciprocal intercharge distance, $\alpha\overline{DS}/b$ for CdCAP example :

- (o) : CdCHP
- (a) — Q_{adj} . — $4Q_{\text{struct}}$.

theoretical line for $Q_{\text{adj}} = 4Q_{\text{struct}}$. The curve fits with the experimental data at higher degree of neutralization, but at low degree of neutralization the experimental points deviate from the theoretical line. The results of the present investigation indicate that the theoretical model of polyelectrolytes is inadequate in extremely dilute solutions and in the case of polyelectrolytes with very low charge density as was pointed out by Oman and Dolar¹³.

CONCLUSIONS

It can be concluded from the above results that

- (i) the degree of free ions, f , is independent of CAP concentration and it decreases with increasing degree of neutralization,

- (ii) the Oosawa theory of cylindrical polyelectrolytes is found to be quite satisfactory to explain the behaviour of CAP except in the extremely dilute solutions.

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