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Studies on Carboxymethylcellulose: Osmotic Pressure Measurements. I

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Studies on Carboxymethylcellulose: Osmotic Pressure Measurements. I

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ABSTRACT

A high-speed membrane osmometer has been used to study the behavior of different samples of sodium carboxymethylcellulose (NaCMC) in NaCl solutions of varying ionic strengths. The large magnitude of second virial coefficient (A_2) and the change in A_2 with salt concentration have been reported.

INTRODUCTION

It is clear from their chemical structures that polyelectrolytes must show the features of both electrolytes and linear polymers when they are dissolved in water. Because of the combination of both features, polyelectrolytes show a characteristic thermodynamic behavior which looks quite different from that of either nonionic polymers or simple electrolytes. The osmometry of such polyelectrolyte solutions [1-3] has proved that, in the presence of simple salts, the reduced osmotic pressure is a linear function of polyelectrolyte concentration with the second virial coefficient which increases linearly with the reciprocal of added salt content. The second virial coefficient of linear polyelectrolytes is extremely nonideal because of the electrostatic interaction between charges of ions as well as because of the polymeric character of polyions.

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Light-scattering measurements on sodium poly(styrene sulfonate) [4], however, showed the linearity between A_2 and $1/X$ only at low ionic strengths, whereas at high ionic strengths A_2 depends on the molecular weight of the polyelectrolyte and is linear with respect to $1/\sqrt{X}$. Takahashi et al. [4], Orofino and Flory [5], and Eisenberg [6] have reported that the second virial coefficient of linear polyelectrolytes in the salt-added system is determined not only by the electrostatic interactions between ions, but also by the intermolecular interactions of polyion coils. Takahashi et al. [7], have shown by careful estimation of osmotic second virial coefficient that A_2 is linearly related with $1/X$ at low ionic strengths and with $1/\sqrt{X}$ at high ionic strengths.

In this paper, second virial coefficients of NaCMC samples of different degree of substitutions were determined by osmometry in solutions of different ionic strengths.

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EXPERIMENTAL

Materials

The methods of preparation, purification of all NaCMC samples, and their measurement of degree of substitution were followed as mentioned in our earlier publication [8]. The average degrees of substitution ($\overline{DS}$) of all NaCMC samples were found to be 0.8, 1.08, 1.35, and 1.70, respectively.

Sodium chloride used was of A.R. grade.

Osmotic Pressure Measurements

The osmotic pressure measurements of all samples of NaCMC in NaCl solutions of varying ionic strength were carried out at 33°C on a high-speed membrane osmometer, Hewlett Packard Model-502. The cellulose membranes used for the measurements were conditioned in the usual way prior to use and were stored under refrigeration in a closed container filled with the deionized water.

After each measurement on the solutions, the solution cell compartment was thoroughly washed with the corresponding NaCl solution to avoid uncertainty in measurements due to diffusion of small polyions into the solvent compartment, if any. The osmotic pressures reported are the average of at least two measurements on each sample solution.

RESULTS AND DISCUSSION

The experimental results of osmotic pressure measurements on NaCMC solutions in the presence of an extraneous salt, NaCl, are shown

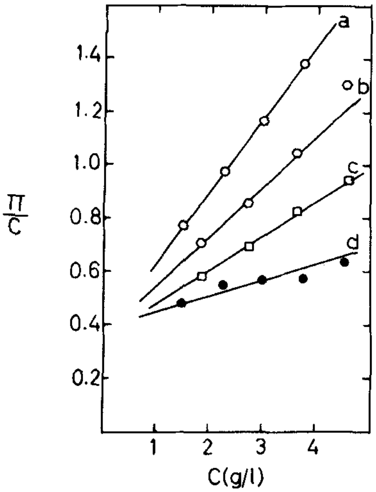

FIG. 1. π/C (L·cm/g) versus C (g/L) for NaCMC ($\overline{DS}$ = 0.8) in different ionic strengths of NaCl: (a) 0.025 N, (b) 0.04545 N, (c) 0.091 N, and (d) 0.5 N.

in Figs. 1-4, respectively, for $\overline{DS}$ of NaCMC 0.8, 1.08, 1.35, and 1.70. The osmotic pressure measurements have been carried out at several concentrations of NaCl solutions as indicated in the figures to see the effect of ionic strength on the colligative properties of NaCMC solutions. In each of these figures, reduced osmotic pressure, π/C (L·cm/g) is plotted versus polymer concentration C (g/L). The plots are generally linear as expected from the following equation for a polyelectrolyte solution in the presence of extraneous salt:

$$\frac{\pi}{C} = RT\left[\frac{1}{M} + A_2C\right] \qquad (1)$$

where

$$A_2 = \left(\frac{\overline{DS}}{m_0}\right)^2 \frac{\phi_P^{\,2}}{4X}$$

$$= r^2 \frac{\phi_P^{\,2}}{4X}$$

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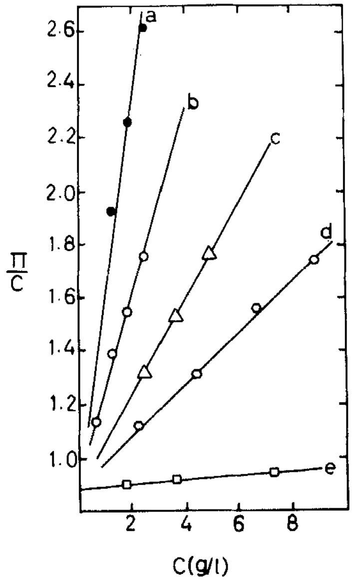

FIG. 2. π/C (L·cm/g) versus C (g/L) for NaCMC ($\overline{DS}$ = 1.08) in different ionic strengths of NaCl: (a) 0.01 N, (b) 0.025 N, (c) 0.05 N, (d) 0.091 N, and (e) 0.5 N.

Here r is expressed in number equivalents per gram of a polyelectrolyte. If we introduce the activity of a salt, the expression of the second virial coefficient, A_2, may take the form

$$A_2 = \frac{r^2}{4X}\,\frac{\phi_P{}^2}{\phi_S} \qquad (2)$$

The slope of a π/C versus C line increases with decreasing concentration of the added salt in all NaCMC samples, which is in accordance with Eq. (2). It is evident, therefore, that the extrapolation of π/C versus C lines to zero polymer concentration is difficult in the presence of a small amount (low concentration) of NaCl. The molecular weight determination of the samples is therefore based on the osmotic pressure measurements in the presence of a large excess of extraneous salt.

It is known that in the absence of salts the osmotic pressure is determined by the concentration of free counterions, while in the limit of high concentrations of salts it is determined by the concentration of polyions. Between these two limits the salt concentration greatly

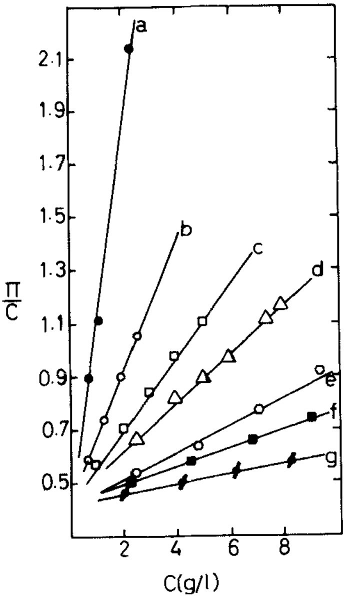

FIG. 3. π/C (L·cm/g) versus C (g/L) for NaCMC ($\overline{\text{DS}}$ = 1.35) in different ionic strengths of NaCl: (a) 0.0091 N, (b) 0.025 N, (c) 0.05 N, (d) 0.1 N, (e) 0.286 N, (f) 0.4545 N, and (g) 0.75 N.

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changes the osmotic pressure. This has been demonstrated in Fig. 5 which shows the dependence of reduced osmotic pressure, π/C, versus NaCl concentration, X, at a constant polyion concentration. The data of Fig. 5 are obtained from Fig. 3 (NaCMC, $\overline{\text{DS}}$ = 1.35) by interpolation at the polymer concentration C = 2.0 g/L. The degree of free counterions is high at low salt concentration, consequently the polyions interact strongly, resulting into high osmotic pressure. With the addition of more salt, the charge on the polyion is decreased (by lowering the degree of free counterions) and the osmotic pressure decreases.

The second virial coefficient, A_2, has been determined from the slopes of the lines ($\pi/C \rightarrow C$) by

$$A_2 = \text{slope}/RT \tag{3}$$

for quantitative understanding of A_2. The values of A_2 obtained for various NaCMC samples in different ionic strengths are given in Table 1. The positive value of A_2 is the result of the repulsive forces between polyions. The repulsive forces decrease by the addition of salts and consequently A_2 decreases.

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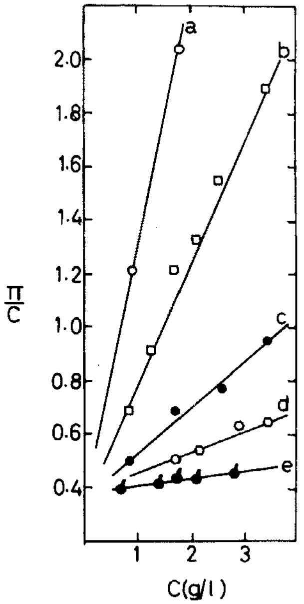

FIG. 4. π/C (L·cm/g) versus C (g/L) for NaCMC ($\overline{DS}$ = 1.7) in different ionic strengths of NaCl: (a) 0.005 N, (b) 0.01 N, (c) 0.04545 N, (d) 0.091 N, and (e) 0.5 N.

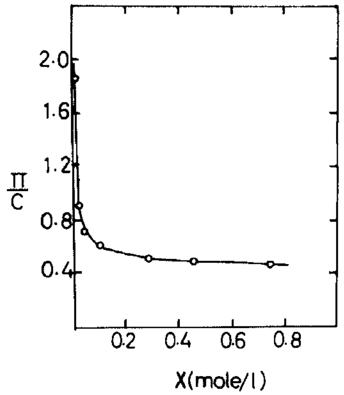

FIG. 5. The relation between the osmotic pressure of NaCMC ($\overline{DS}$ = 1.35) solution and the concentration of NaCl at a constant NaCMC concentration C = 2.0 (g/L) from the data of Fig. 3.

TABLE 1. Second Virial Coefficients of NaCMC Solutions in the Presence of NaCl at 33° C

NaCMC ($\overline{DS}$)	Concentration of NaCl × 10^2	Slope (S)	A_2[a] × 10^4 (cc·mol/g^2)
0.80	2.50	0.277	106.8
	4.55	0.188	72.6
	9.09	0.130	50.0
	50.00	0.062	23.8
1.08	1.0	0.727	280.6
	2.5	0.357	137.7
	5.0	0.177	68.4
	9.1	0.096	37.0
	50.0	0.008	2.9
1.35	0.9	0.765	295.0
	2.5	0.245	94.6
	5.0	0.136	52.4
	10.0	0.092	35.7
	28.6	0.051	19.5
	45.5	0.035	13.4
	75.0	0.018	7.0
1.70	0.50	0.943	364
	1.00	0.447	172
	4.55	0.172	66.4
	9.10	0.080	30.7
	50.00	0.028	10.7

[a] A_2 = S/RT, where RT is in L·cm/mol.

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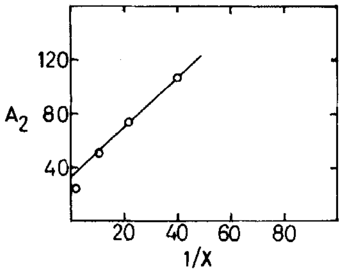

FIG. 6. The variation of second virial coefficient, A_2 (cc•mol/g^2), with the reciprocal of NaCl concentration for NaCMC ($\overline{DS}$ = 0.80) from the data of Fig. 1.

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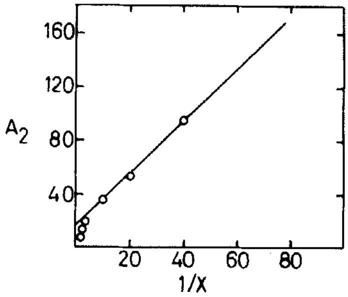

FIG. 7. The variation of second virial coefficient, A_2 (cc•mol/g^2), with the reciprocal of NaCl concentration for NaCMC ($\overline{DS}$ = 1.35) from the data of Fig. 3.

Two features of A_2 are noticeable from Table 1: The magnitude of A_2 and the change in A_2 with salt concentration. For example, the value of A_2 for NaCMC ($\overline{DS}$ = 1.7) in 0.5 N NaCl solution is 10.7×10^{-4} cc•mol/g^2 and it increases to 364×10^{-4} cc•mol/g^2 in 0.005 N NaCl solution. Such high value of A_2 and large variation in A_2 with solvent power have never been observed in the case of neutral polymers [9]. The electrostatic interactions [10] that prevail in polyelectrolyte-salt solution are responsible for the above-mentioned anomalous behavior of polyelectrolyte solutions.

It is indicated by Eq. (1) that A_2 is proportional to the square of the charge on the polyion and inversly proportional to the added salt concentration. In Figs. 6 and 7, the dependences of A_2 on 1/X, for example, for NaCMC (DS = 0.8) and NaCMC (DS = 1.35), are shown, respectively.

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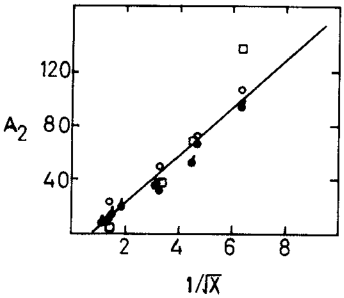

FIG. 8. The relation between the second virial coefficient, A_2, and the reciprocal of the square root of ionic strength $1/\sqrt{X}$ for NaCMC solutions: NaCMC with $\overline{DS}$ = 0.8 (○), 1.08 (□), 1.35 (●), and 1.7 (●).

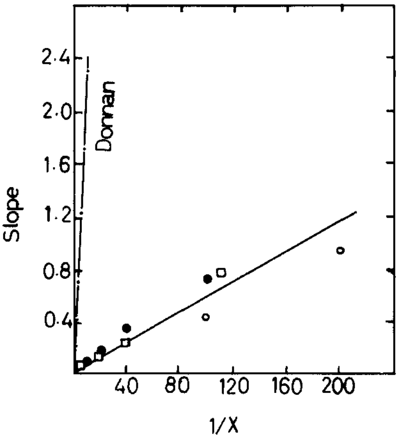

FIG. 9. The relation between the slope of π/C versus C plots and the reciprocal ionic strength for NaCMC solutions: NaCMC with $\overline{DS}$ = 1.08 (●), 1.35 (□), and 1.70 (○). (- ·) corresponds to the Donnan term.

It is observed in both figures that the linearity of A_2 with respect to 1/X holds over a wide range of ionic strengths, but at high ionic strengths the experimental data deviate from the linear relationship. The line does not pass through the origin as predicted by Eq. (1). The theory of Donnan equilibrium is therefore only qualitatively satisfied. The deviation from the linear plot of A_2 vs 1/X at high ionic strengths arises from the intermolecular interaction between coils. If the concentration of added salt is low, the expansion of the polyion coil is so high that the effect of intermolecular interaction on A_2 becomes practically independent of added-salt concentration, consequently A_2 appears to be linear with respect to the reciprocal salt concentration.

The experimental data of the present investigation on NaCMC are shown in Fig. 8, where A_2 is plotted versus $1/\sqrt{X}$ for all four NaCMC samples. A linear behavior at low ionic strength is not observed, but it is observed at high ionic strength. This type of dependence of A_2 on $1/\sqrt{X}$ was also observed by Takahashi et al. [7].

Figure 9 shows a plot of S (slope) versus 1/X for all NaCMC samples studied in a wide range of concentration of NaCl. A scatter of experimental points is observed. However, the points may be explained by the single line shown in the figure. The slope of this line is very small compared to that of the Donnan equilibrium theory as seen in the figure.

The Donnan line is obtained by assuming that the polyelectrolyte ionizes completely and the osmotic coefficient of the salt is unity. Then

$$\text{Slope} = RTA_2^\circ = RTr^2/4X \tag{4}$$

The slope of the Donnan line is about 30 times the experimental one. Such a discrepancy in the slope is often reported in the literature [10].

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REFERENCES

[1] H. R. Kruyt, Colloid Science, Vol. I, Elsevier, 1952, p. 188; D. T. F. Pals and J. J. Hermans, Rec. Trav. Chim. Pays-Bas, 71, 458 (1952).
[2] M. Nagasawa, H. Nagoji, and I. Kagawa; J. Chem. Soc. Jpn. (Ind. Chem. Sec.), 57, 9 (1954).
[3] H. Ingaki and T. Oda, Makromol. Chem., 21, 1 (1956).
[4] A. Takahashi, T. Kato, and M. Nagasawa, J. Phys. Chem., 71, 2001 (1967).
[5] T. A. Orofino and P. J. Flory, Ibid., 63, 283 (1959).
[6] H. Eisenberg, J. Chem. Phys., 44, 137 (1966).

[7] A. Takahashi, N. Kato, and M. Nagasawa, J. Phys. Chem., 74, 944 (1970).
[8] H. C. Trivedi, C. K. Patel, and R. D. Patel, Angew. Makromol. Chem., 70, 39 (1978).
[9] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.
[10] S. A. Rice and M. Nagasawa, Polyelectrolyte Solutions, Academic, New York, 1961.

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