Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies on Carboxymethylcellulose: Osmotic Pressure Measurements. II

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To cite this Article Trivedi, H. C. and Patel, R. D.(1982) 'Studies on Carboxymethylcellulose: Osmotic Pressure Measurements. II', Journal of Macromolecular Science, Part A, 18: 4, 555 — 563

To link to this Article: DOI: 10.1080/00222338208082068

URL: http://dx.doi.org/10.1080/00222338208082068

J. MACROMOL. SCI.–CHEM., A18(4), pp. 555-563 (1982)

Studies on Carboxymethylcellulose: Osmotic Pressure Measurements. II

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ABSTRACT

The osmotic coefficient g* is calculated for sodium carboxymethylcellulose (NaCMC) samples of different degrees of substitution. The dependence of g* on $\overline{\text{DS}}$, concentration of NaCMC, and added NaCl has been investigated for all samples. The true osmotic coefficient ϕ_p has also been calculated for all the samples by applying Donnan's equilibrium concept. ϕ_p is found to be independent of the amount of extraneous salt accounting for Donnan's membrane equilibrium. The dependence of ϕ_p on the charge density of polyions can be explained quantitatively by Oosawa's and Katchalsky's theories.

INTRODUCTION

In a previous paper [1] the behavior of different samples of NaCMC in NaCl solutions of various ionic strengths has been studied by using a high-speed membrane osmometer. In the present study the osmotic pressure results of all NaCMC samples [1] are used to calculate the osmotic coefficient (g*) and the osmotic coefficient of counterions in

TABLE 1. Characteristic Parameters of NaCMC Samples[a]

$\overline{DS}$	$(\pi/C)_0$ (L·cm/g)	$\overline{M}_n \times 10^{-4}$ g/mol	Q_{struct}	Q_{adj}	Monomer weight M_0 (g/mol)
0.80	0.36	7.20	1.10	2.75	226.0
1.08	0.89	2.90	1.49	3.72	248.2
1.35	0.42	6.15	1.84	4.60	271.6
1.70	0.38	6.80	2.33	5.82	298.0

[a] $RT = 2.592 \times 10^4$ L·cm/mol at 33°C.

the NaCMC solution (ϕ_p). The results obtained are also treated in light of Oosawa's and Katchalsky's theories.

EXPERIMENTAL

Materials

The methods of preparation, purification of all NaCMC samples, and their measurements of degree of substitution were the same as in our earlier publication [1].

The NaCMC samples used in the present work are characterized in Table 1. The average degree of substitution, number-average molecular weight, the charge density, structural and adjusted values, and the monomer weights for each sample are shown in the table.

Sodium chloride 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 in the manner described in our earlier publication [1].

RESULTS AND DISCUSSION

In analogy to the osmotic coefficient in salt-free polyelectrolyte solutions, one can define an osmotic coefficient in a polyelectrolyte-salt solution as

$$g^* = \pi/\pi_D \tag{1}$$

where π is the observed osmotic pressure and π_D is that calculated from the Donnan expression at the same concentrations of the polyions and the added salt. Experimentally, the reduced osmotic pressure and the calculated Donnan π/C are used to calculate g*. The Donnan term is calculated as

$$\left(\frac{\pi}{C}\right)_D = \frac{RTr^2C}{4X} + \left(\frac{\pi}{C}\right)_0 \tag{2}$$

The first term in Eq. (2) depends on the concentrations of the polyelectrolyte and the added salt. The second term is experimentally obtained as an intercept on the ordinate in the plot of π/C versus c. It is observed that the contribution of the second term is negligible in the presence of low salt content, while it makes a significant contribution to g* at high salt content. Thus g* is calculated for NaCMC samples of different degrees of substitution by using Eqs. (1) and (2) from the osmotic pressure data given in Figs. 1-4 of our previous publication [1].

Figure 1 shows the typical behavior of g* with concentrations of NaCMC and added NaCl in the case of NaCMC with $\overline{DS} = 1.35$. It is seen that g* decreases with polymer concentration and increases with salt concentration (X). Moreover, g* tends to unity when c approaches zero. The osmotic coefficient g* may be considered to represent the state of association of simple ions with the polyions since π_D is calculated on the assumption that NaCMC is completely dissociated.

It has been pointed out by Inagaki et al. [2] that different curves of g* versus C at several values of X are superposed on a single curve when g* is plotted against Y or Y^{-1}, where the parameter Y is defined as

$$Y = (rC + X)/rC \tag{3}$$

according to Howard and Jordan [3]. This parameter Y was originally introduced by them in their treatment for diffusion and sedimentation coefficients of a polyelectrolyte in simple salt solutions.

The behavior of g* with 1/Y is shown in Fig. 2 for NaCMC of $\overline{DS} = 1.35$ and in Fig. 3 for NaCMC of $\overline{DS} = 1.70$. In each case a single curve is observed, hence g* may be considered as a unique function of 1/Y. Again, g* tends to unity as 1/Y approaches zero. This condition is achieved either with a very low polyelectrolyte concentration or with a high salt content in the polyelectrolyte

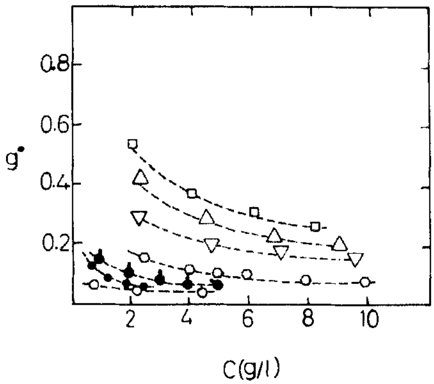

FIG. 1. The dependence of the osmotic coefficient g* on the concentration of NaCMC ($\overline{DS}$ = 1.35) solution at several ionic strengths. NaCl concentrations: 0.91 × 10^{-2} $\underline{N}$ (○), 2.5 × 10^{-2} $\underline{N}$ (●), 5.0 × 10^{-2} $\underline{N}$ (♠), 10.0 × 10^{-2} $\underline{N}$ (o), 28.57 × 10^{-2} $\underline{N}$ (▽), 45.5 × 10^{-2} $\underline{N}$ (△), and 75.0 × 10^{-2} $\underline{N}$ (□).

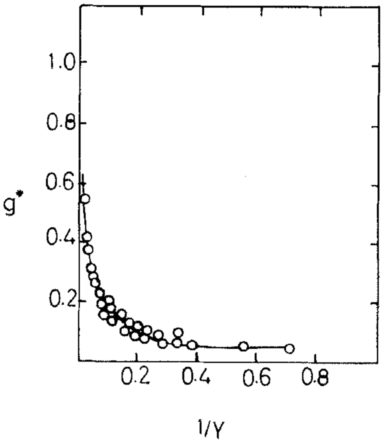

FIG. 2. The relation between the osmotic coefficient g* and parameter Y at all the concentrations of NaCl and NaCMC ($\overline{DS}$ = 1.35) indicated in Fig. 1.

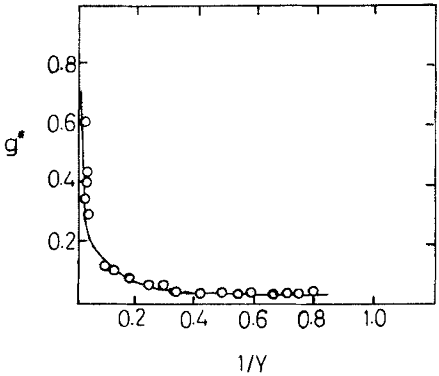

FIG. 3. The relation between the osmotic coefficient g* and parameter Y for NaCMC ($\overline{DS}$ = 1.7) solution.

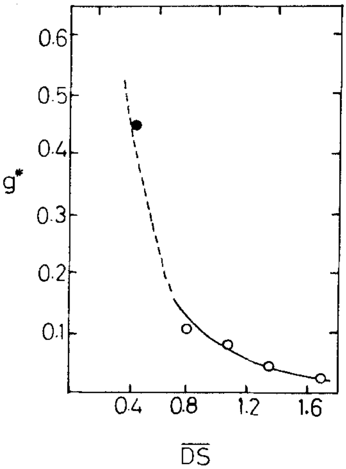

FIG. 4. The dependence of g* on $\overline{DS}$ of NaCMC samples. (○) Present data on NaCMC. (●) Data on NaCMC reported by Inagaki et al. [2].

solution. The observed value of g* is around 0.6 at high salt concentration (X) in all NaCMC samples.

It is interesting to see the behavior of g* at low salt and high polymer concentrations. The asymptotic values of g* are obtained from plots of the type given in Fig. 2 for all the NaCMC samples studied. The dependence of g* on $\overline{DS}$ is shown in Fig. 4. The osmotic coefficient g* decreases with increasing $\overline{DS}$ of NaCMC sample. The osmotic coefficient g* tends to unity as the charge density approaches zero. The osmotic coefficient of NaCMC ($\overline{DS}$ = 0.45) reported by Inagaki et al. [2] has been included in the figure. The value of g* reported for NaCMC ($\overline{DS}$ = 0.45) seems to be higher than the general trend indicated by the present data.

It has been pointed out by Katchalsky et al. [4] that to a first approximation the values of ϕ_p (the true osmotic coefficient) derived from the straight lines of π/C versus C of polymer-salt systems correspond closely to that obtained by the direct study of salt-free polyelectrolyte solutions. Hence the estimation of ϕ_p was done from the osmotic pressure measurements. The osmotic coefficient of counterions in the solution, ϕ_p, is defined by

$$\phi_p^2 = (A_2/A_2^0)\phi_S \qquad (4)$$

where

$$A_2^0 = r^2/4X \qquad (5)$$

The osmotic coefficient ϕ_p for NaCMC samples is evaluated from osmotic pressure measurements using Eq. (4). A_2^0 was obtained from Eq. (5), and the activity coefficient of salt, ϕ_S, was computed from the literature [5]. Table 2 shows the osmometry data on NaCMC samples including the values of osmotic coefficients at several ionic strengths. It is seen from Eq. (4) that ϕ_p should be independent of the ionic strength; however, some experimental scatter in ϕ_p values is observed in each of the NaCMC sample as shown in Table 2. In the last column of the table, therefore, an average value of ϕ_p is shown for each NaCMC sample. It is revealed that the higher the $\overline{DS}$ of NaCMC, the lower is the value of ϕ_p and vice versa.

The osmotic coefficient was examined in light of the theories of rodlike polyions. In Oosawa's theory [6] the degree of free counterions f is replaced by the osmotic coefficient ϕ_p. The value of Q (the charge density) was calculated by assuming the volume concentration of the NaCMC solution to be 0.01 for all NaCMC samples. The experimental values of ϕ_p could be fitted satisfactorily with the theoretical ϕ_p values with $Q_{adj} = 2.5Q_{struct}$.

Figure 5 shows a plot of $\phi_p Q$ versus Q due to Oosawa. The

TABLE 2. The Osmotic Coefficient Data of NaCMC Samples in Salt-Added Solutions

$\overline{DS}$	Concentration of NaCl $\times 10^2$	ϕ_S[a]	$(A_2/A_2^0) \times 10^2$	ϕ_p	Average ϕ_p
1.70	0.50	0.930	2.25	0.14	0.16
	1.00	0.902	2.13	0.14	
	4.55	0.835	3.72	0.18	
	9.09	0.785	3.46	0.17	
1.35	0.91	0.905	4.23	0.20	0.20
	2.50	0.865	3.72	0.18	
	5.00	0.830	4.13	0.19	
	10.00	0.777	5.59	0.21	
1.08	1.00	0.902	5.93	0.23	0.24
	2.50	0.865	7.27	0.25	
	5.00	0.830	7.22	0.25	
	9.09	0.785	7.11	0.24	
0.80	2.50	0.865	8.52	0.27	0.30
	4.55	0.835	10.56	0.30	
	9.09	0.785	14.50	0.34	

[a] See Ref. 5.

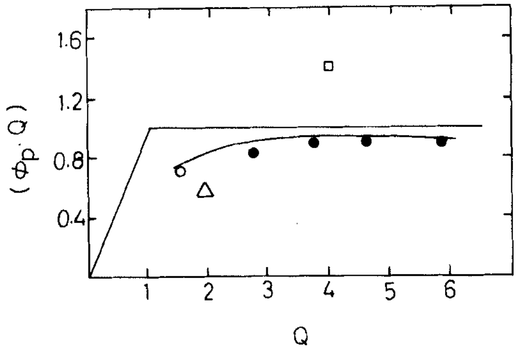

FIG. 5. The Oosawa plot of numbers of free counterions $\phi_p Q$ versus the charge density Q for NaCMC of varying $\overline{DS}$. The curve is due to Oosawa theory for $Q_{adj} = 2.5Q_{struct}$. (●) Present data on NaCMC. (○) Data on NaCMC reported by Inagaki et al. [2]. (□) Data on NaCMC reported by Pals and Hermans [7]. (△) Data on NaCMC reported by Doty and Schneider [8].

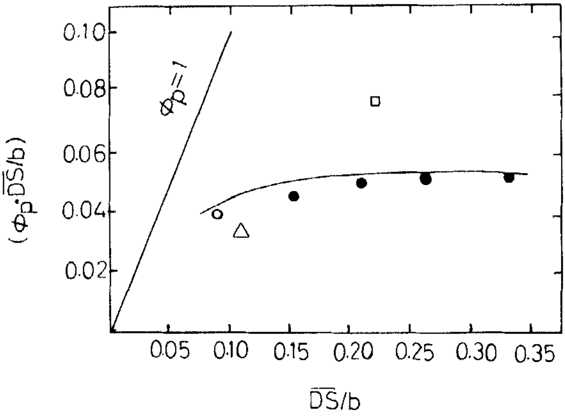

FIG. 6. The Katchalsky plot of number of free counterions per unit monomer length $\phi_p \cdot \overline{DS}/b$ versus the charge per unit length $\overline{DS}/b$. $\phi_p = 1$ line is the ideal case and the curve is due to Katchalsky's theory for $Q_{adj} = 2.5\ Q_{struct}$. The points have the identities shown in Fig. 5.

experimental points of all four NaCMC samples are quite close to the theoretical line with $Q_{adj} = 2.5\ Q_{struct}$. Some of the literature data on NaCMC are also included in the figure. The data reported by Inagaki et al. [2] are quite consistent with the present data on NaCMC. The experimental ϕ_p value of NaCMC from the data of Pals and Hermans [7] lies below the present data and that reported by Doty and Schneider [8] lies above the present data. This may be due to the inherent difficulties in osmometry and light scattering as applied to polyelectrolyte solutions.

The analysis of ϕ_p by Katchalsky's theory is also shown in Fig. 6 where $\phi_p \overline{DS}/b$ versus $\overline{DS}/b$ is plotted. The present experimental points are best explained by the theoretical line corresponding to $Q_{adj} = 2.5\ Q_{struct}$. The data on CMC of $\overline{DS} = 0.45$ (Inagaki et al. [2]) are again in good agreement with the present data. Other literature data deviate from the present data as before.

Two important points are made clear from the above analysis. First, the osmotic pressure measurements of all the NaCMC samples are internally consistent so that all ϕ_p can be explained by a single theoretical line. Second, the true osmotic coefficient ϕ_p and the degree of free counterions f give information about the association of counterions in polyelectrolyte solutions.

ACKNOWLEDGMENTS

The authors' sincere thanks are due to Prof Dr K. C. Patel and Prof Dr C. K. Patel for valuable suggestions and constant inspiration throughout the work.

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Accepted by editor August 27, 1981
Received for publication September 6, 1981