The Second Virial Coefficient of Sodium Carboxymethyl Amylose

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The second virial coefficients determined by the light scattering technique and the intrinsic viscosity of sodium carboxymethyl amylose fractions in water were studied using 1-1 valence electrolyte as the extraneous salt. The results are analysed in light of the different theories of second virial coefficient.

THE second virial coefficient of polyelectrolyte solutions is extremely non-ideal because of the fact that polyelectrolytes possess the combined properties of both non-ionic polymers and simple electrolytes, and hence there exists a chain character of polyion as well as electrostatic interaction between charges. A high concentration of added salt screens the polymeric charges and decreases the electrostatic forces between them. At a low concentration of added salt, the polyelectrolyte expands tremendously, and electrostatic interaction as well as the excluded volume of polyelectrolytes increases greatly. These phenomena greatly affect the second virial coefficient of polyelectrolytes and hence their values are found to be larger than those for non-ionic polymers.

Recently Nagasawa *et al.*[1] analysed the second virial coefficient of sodium polystyrene sulphonate (NaPSS) and found that electrostatic interaction, defined as Γ_2 (α), i.e. h (z), decreases with decrease in added salt concentration, which contrasts with the results obtained by many workers[2,3]. In the present work the second virial coefficient of sodium carboxymethyl amylose (NaCMA) has been studied and discussed in the light of all the theories of the second virial coefficient.

EXPERIMENTAL

Samples

NaCMA used in this work was prepared and separated into fractions in the molecular weight ranges as described previously[4]. The degree of substitution (DS) was found to be 0·8 by Wilson's[5] method. The sodium chloride (NaCl) included in each fraction was removed by dialysing it against distilled water for four days. The pH of the final solutions lay between 6·9 and 7·1. Each fraction thus purified was collected by a rotary evaporator under vacuum at 45°C. The samples were dried in a vacuum at 50°C for one day. The sample solutions were prepared by dissolving NaCMA in the known concentrations of aqueous NaCl solutions and were dialysed against the corresponding aqueous NaCl solutions. The same solvent was used for dilution.

Viscosity

Viscosity measurements were made with a suspended level Ubbelohde viscometer. The shear had little effect on the intrinsic viscosity $[\eta]$ even at a low salt concentration and with a high molecular weight sample; hence no correction was applied. Measurements at four concentrations chosen to yield relative viscosities in the range 1 to 2 were extrapolated to infinite dilution in the customary manner. The kinetic energy correction was negligible.

Light scattering

Light scattering measurements were carried out with a Brice-Phoenix light scattering photometer at 436 nm. The photometer was calibrated with a Cornell standard polystyrene sample which had excess turbidity of $3{\cdot}2 \times 10^{-3}$ cm^{-1} in toluene (0·5 per cent solution). The original solutions and solvents were cleaned by centrifuging them at 17 000 rev/min for two hours and filtering them through a G-5 sintered glass filtering funnel. The scattered intensities were measured at various angles from 30° to 135° for four different concentrations from 0·4 to 0·06 g/100 ml.

The refractive index increment for NaCMA in different salt solutions at $\lambda = 436$ nm were determined using a Brice–Phoenix differential refractometer. The calibration of the differential refractometer was made by taking different potassium chloride solutions as standard.

RESULTS

In *Table 1* are given the experimentally observed values of refractive index increment dn/dc for each of the polyelectrolyte systems investigated. The measurements recorded were made at 30° ±0·5°C. The values observed appear to be independent of both the molecular weight and the ionic strength at low ionic strengths of the salt, while at high ionic strengths these values were found to be independent of molecular weight and dependent on ionic strength.

Table 1. Refractive index increments of NaCMA (30°C)

C_s^0, *mole/l.*	0·0065	0·01	0·03	0·35	1·0	2·5
dn/dc, cm^3/g	0·138	0·138	0·138	0·134	0·124	0·103

Figure 1 shows the logarithmic plots of intrinsic viscosity $[\eta]$ in salt solutions of different ionic strengths as a function of molecular weight. The values of ν calculated from the slope are listed in *Table 2*.

Table 2. Value of ν of NaCMA

C_s^0, *mole/l.*	0·35	0·65	0·85	1·5
ν	0·64	0·5	0·5	0·5

However, in polyelectrolyte systems investigated in 0·65, 0·85 and 1·5 M NaCl concentrations, it is found that the exponent ν remains constant. From this it is concluded that to attain exact theta conditions is difficult with polyelectrolytes. Light scattering measurements are performed at low polymer concentration because of the high expansion of the polyion which

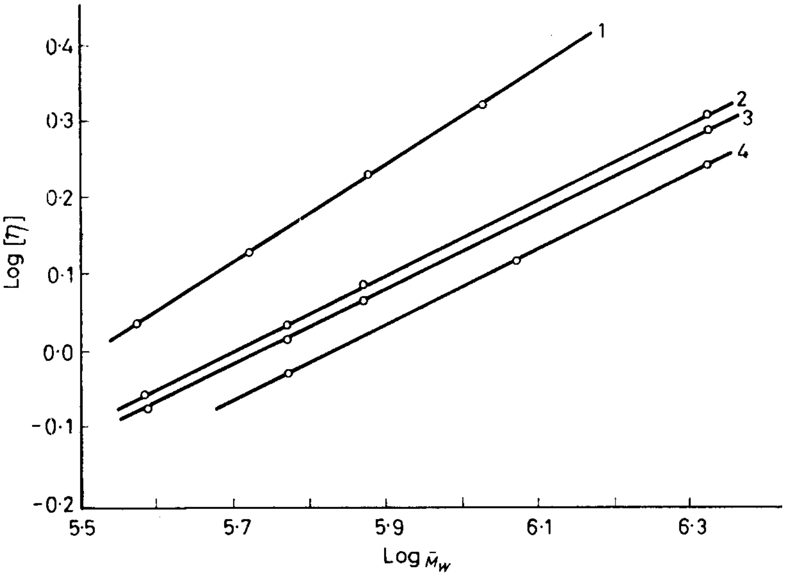

Figure 1—Relation between intrinsic viscosity and molecular weight at 30°C in (1) 0·35, (2) 0·65, (3) 0·85 and (4) 1·5 M NaCl solutions

will reduce the tendency to ordering of molecules or segments in solutions. Such intermolecular interference causes the diminution of scattering per molecule and the reduction of dissymmetry at high concentrations as pointed out by Doty and Steiner[6].

Figures 2 and *3* show typical Zimm plots of $(C/\tau)_{\theta=0}$ versus C and $(C/\tau)_{C=0}$ versus $\sin^2 \frac{1}{2}\theta$ respectively for sample No. 2. Values of $\bar{M}_w$, A_2 and $\langle S^2 \rangle$ have been calculated and are recorded in *Table 3*. The dependence of A_2 on molecular weight is shown in *Figure 4* for 0·35 M aqueous NaCl (solvent) at 30°C.

Table 3. Light scattering data of NaCMA at 30°C

C_s^0 (*mole/l.*)	$\bar{M}_w$ $\times 10^{-5}$	A_2 $\times 10^4$	[η]	$\langle S^2 \rangle$ $\times 10^{10}$	$h(z)$	Φ' $\times 10^{-22}$	α
2·5	7·5	—	1·08	—	—	—	0·98
1·0	7·5	1·03	1·3	0·213	0·96	1·01	1·04
0·35	10·8	1·9	2·16	—	—	—	—
0·35	7·5	2·2	1·68	0·212	0·69	1·3	1·15
0·35	5·25	2·52	1·35	—	—	—	—
0·35	3·75	2·65	1·10	—	—	—	—
0·03	7·5	10·7	3·82	0·367	0·85	1·02	1·5
0·01	7·5	22·9	6·07	0·526	1·04	1·19	1·76
0·0065	7·5	28·2	7·5	0·580	1·12	1·28	1·88

DISCUSSION

The plot of log A_2 versus log C_s^0 for sample No. 2 (*Figure 5*) is linear with a slope of $-2/3$. This agrees well with the results obtained by Trap and

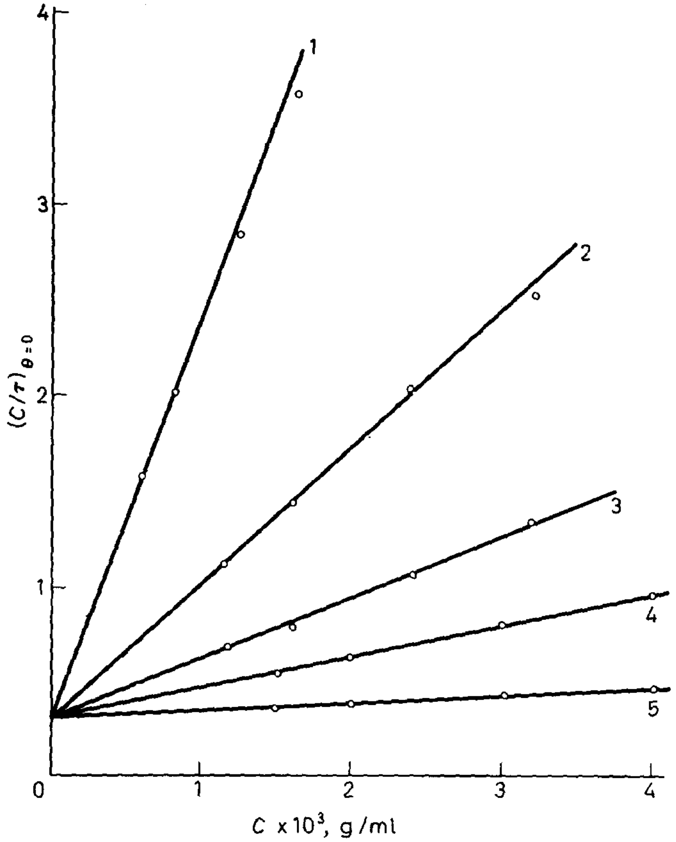

Figure 2—Plot of $(C/\tau)_{\theta=0}$ versus C in (1) 0·0065, (2) 0·01, (3) 0·03, (4) 0·35 and (5) 1·0 M NaCl solutions

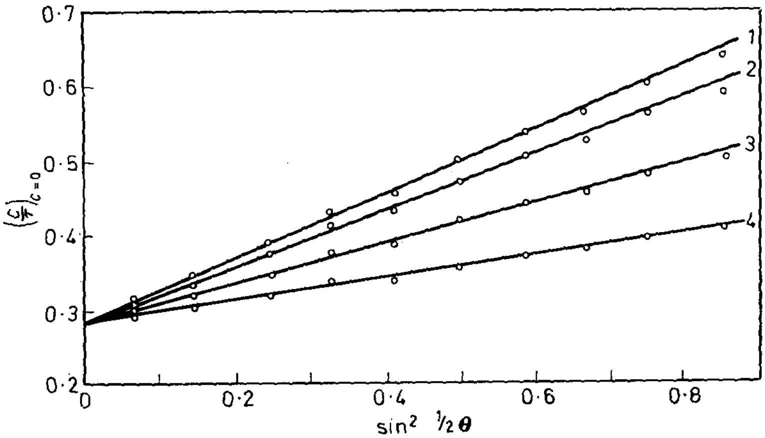

Figure 3—Typical plot of $(C/\tau)_{C=0}$ versus $\sin^2 \frac{1}{2}\theta$ in (1) 0·0065, (2) 0·01, (3) 0·03 and (4) 0·35 M NaCl solutions

Hermans[7] for sodium carboxymethyl cellulose. Thus the second virial coefficient determined by light scattering measurements is proportional to $(1/C_s^0)^{2/3}$ while the second virial coefficient determined by the Donnan osmotic pressure measurements was usually found to be proportional to $1/C_s^0$. The discrepancy between the two results may be due to (1) the difference between the concentrations of polymer used in both types of measurements (Nagasawa *et al.*[1]) or (2) because, in the Donnan membrane equilibrium theory for polyelectrolytes, activity coefficients which have varying effects in NaCl of different concentrations are neglected.

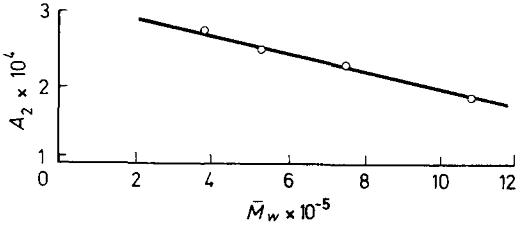

Figure 4—Dependence of A_2 on molecular weight in 0·35 M NaCl solution

In general all theories of the second virial coefficient of a linear polymer derived from various theories of excluded volume can be represented by a general expression

$$A_2 = \{4N_A\pi^{3/2}\langle S^2\rangle^{3/2}/M^2\}\,\bar{z}\,h(\bar{z}) \qquad (1)$$

where $\bar{z} = z/\alpha^3$, N_A is Avogadro's number, M and $\langle S^2\rangle$ are the molecular weight and square of the radius of gyration of the polymer respectively. The values of $\bar{z}$ have been calculated by using the equation $\alpha^3 - 1 = 1{\cdot}55\ z$ which has proved most satisfactory for intrinsic viscosity data of the polyion[2,10,11].

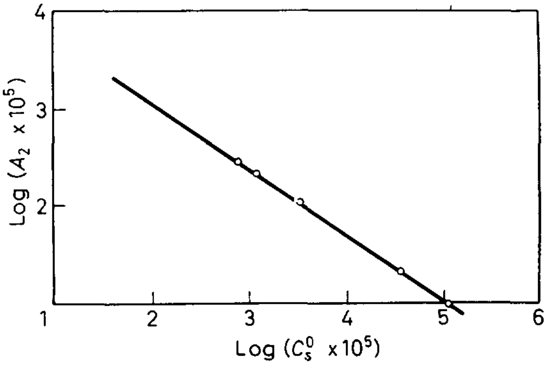

Figure 5—Relation between A_2 and C_s^0

The values of the linear expansion factor α have been calculated by using $K = 1{\cdot}32 \times 10^{-3}$, which is obtained from the Fixman[12] plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$. Thus by use of the above equations the values of $h(\bar{z})$ obtained experimentally are plotted (*Figure 6*) against $(\alpha^2 - 1)$ along with $h(\bar{z})$

calculated from the theories put forward by Flory and co-workers[13,14], Ptitsyn[15], Fixman[12], Kurata[16] and Casassa and Markovitz[17] and others. It is interesting to note that particularly at low expansion of polyions, i.e. in moderately concentrated NaCl solutions all theories of second virial coefficient (except Flory's), which are put forward for non-ionic polymers are applicable to polyelectrolytes. However, at high expansion of polyions no theory is applicable. This may be due to the increase of electrostatic interaction with decrease of NaCl concentrations, and will have small value at moderate NaCl concentrations, where polyions behave almost like non-ionic polymers due to the screening of charges on polyions by byions. A second complication is caused by the excluded volume of the polyions, which must make a separate contribution to A_2. This contribution also increases rapidly with decrease of NaCl concentration.

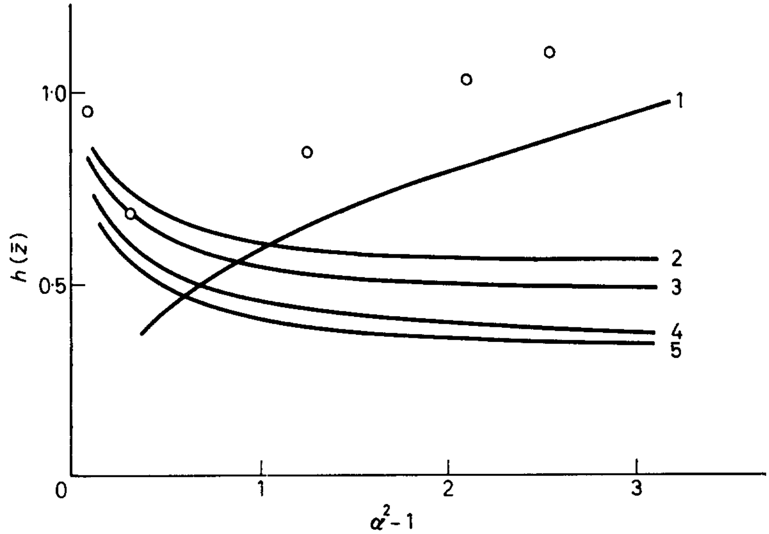

Figure 6—Dependence of $h(\bar{z})$ on α^2-1: (1) FKO, (2) Ptitsyn, (3) modified FKO, (4) Kurata, (5) Casassa and Markovitz theories. ○ Experimental points

Nagasawa *et al.*[18], and Alexandrowicz[19] proposed the following equation

$$A_2 = A_2^0 (\gamma_C^0)^2 / \gamma_s^0 \tag{2}$$

where γ_s^0 is the activity coefficient of added salt without polyelectrolyte and γ_C^0 is the activity coefficient of counterions in the salt-free polyelectrolyte solution. The values of A_2^0 have been calculated using

$$A_2^0 = 10^3 z_p^2 / 4M^2 C_s^0 \tag{3}$$

where z_p is the number of charges present on the macroion. The values of γ_s^0 have been taken directly from the literature. The values of γ_C^0 obtained by applying equation (2) are listed in *Table 4*.

Table 4. Calculated values of activity coefficient ($\gamma_C{}^0$)

(*mole/l*) $C_s{}^0$	$A_2/A_2{}^0 \times 10^2$	$\gamma_s{}^0$	$\gamma_C{}^0$
1·0	2·12	0·655	0·117
0·35	1·36	0·702	0·098
0·35	1·58	0·702	0·105
0·35	1·8	0·702	0·112
0·35	1·9	0·702	0·115
0·03	0·66	0·850	0·075
0·01	0·47	0·898	0·065
0·0065	0·38	0·913	0·060

From *Table 4* it is seen that γ_C^0 values are small, which can reasonably be accepted for linear polyelectrolytes. However, it is seen that the values of γ_C^0 are dependent on both molecular weight and ionic strength. The value of γ_C^0 decreases with decrease of salt concentration and increases with decrease of molecular weight.

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