

The effects of charge density and concentration on the composition of polyelectrolyte complexes

B. Vishalakshi*, S. Ghosh and V. Kalpagam*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

(Received 8 May 1992; revised 22 September 1992)

Polyelectrolyte complex formation involving carboxymethylcellulose and quaternized poly(vinylpyridine) as the polyions has been studied using viscosity and u.v. spectroscopic methods. The influence of charge density and molecular weight of two polycations on the composition of the complex has been investigated at two different concentrations. The charge density of the polycation is found to have different influences on the composition at different concentrations. The molecular weight of the polycation and the location of the ionic site on the polycation do not show any effect on the composition. A drastic increase in the viscosity of the polyion mixture containing quaternized poly(2-vinylpyridine) in the non-stoichiometric ratio shows evidence for the existence of the soluble polyelectrolyte complex. The results are analysed on the basis of the relative extension of the polyelectrolyte chains.

(Keywords: polyelectrolyte complex; carboxymethylcellulose; poly(vinylpyridine); charge density; chain extension; soluble polyelectrolyte complex)

INTRODUCTION

The polyelectrolyte complex (PEC) formation between two oppositely charged polymeric molecules in solution has been actively studied during the last three decades¹⁻³. The strong electrostatic interaction that exists between the polyions leads to precipitation of the PEC from the solution. The composition of the PEC precipitate, given by the molar ratio of the two oppositely charged polyions that it contains, is dependent on various structural parameters of the polyions, such as the molecular geometry, charge density, etc. It is also sensitive to the conditions under which complex formation is taking place, e.g. the nature of the solvent, ionic strength of the medium, concentration of the interacting molecules, etc.³. The nature of the complex can be varied easily by changing the composition of the complex. A knowledge of the composition is important as it affects the nature and properties of the complex^{4,5}.

PECs involving polysaccharide derivatives such as carboxymethylcellulose (CMC), cellulose sulfate, etc. are interesting due to their rigid, stereoregular backbone structure containing bulky pyranose rings. There are several reports in the literature on the stoichiometry of the PEC involving CMC as the polyanion component³. The molecular structure of the polycation is found to have an influence on the stoichiometry of these complexes. Stoichiometric complexes were obtained in the case of polyacrylamides³ and polyamines⁶ of linear structure whereas deviation from 1:1 stoichiometry was observed for highly branched cations like poly(ethylene imine) due to the inaccessibility of their charge sites⁷.

This paper reports studies on the complex formation between CMC and two flexible polycations, namely quaternized poly(2-vinylpyridine) and poly(4-vinylpyridine), which differ in the location of the ionic site. A systematic study of the effect of the charge density, molecular weight of the polycations and concentration of the polyions, on the stoichiometry of the complex is reported. The study is aimed at obtaining knowledge about the 'distance specific' interactions in polyelectrolytes. The distance between the ionic sites on the individual polyelectrolytes has been varied by changing the geometry and degree of substitution (*DS*) of the polycation and concentration of the polyions. The effect of the relative extension of the polyion chains on the composition of the PEC precipitates has been studied.

EXPERIMENTAL

Materials

The sodium salt of CMC (BDH, UK) and methyl iodide (Sisco, India) were used as received. 2-Vinylpyridine and 4-vinylpyridine (both from Merck) were distilled twice under reduced pressure before use. Standard methods were used to determine the *DS*⁸ and molecular weight (\bar{M}_w)⁹ of the CMC sample; they were found to be 0.73 and 4.3×10^5 , respectively.

Preparation of poly(vinylpyridine) samples

Poly(2-vinylpyridine)-low molecular weight (LMW) and poly(4-vinylpyridine)-LMW. 2-Vinylpyridine and 4-vinylpyridine were homopolymerized using AIBN as the

* To whom correspondence should be addressed

initiator. The polymerizations were carried out in methanol at 70°C under nitrogen atmosphere for 6 h¹⁰. Poly(2-vinylpyridine) was separated from the reaction mixture by precipitation in water. It was purified by reprecipitation from methanol in water. The \bar{M}_v of the sample, determined by the viscometric method¹¹ was 2.3×10^4 . The poly(4-vinylpyridine) was separated by precipitating in diethylether. It was purified by reprecipitation from methanol in diethylether and fractionated using the same solvent–non-solvent pair. The fraction with $\bar{M}_v = 8.0 \times 10^4$, determined by viscometry¹¹, was used in the experiments.

Poly(2-vinylpyridine)–high molecular weight (HMW). 2-Vinylpyridine was bulk polymerized¹² using AIBN (0.1 mol%) at 60°C for 2.5 h. The viscous mass was dissolved in benzene and precipitated in *n*-hexane. The product was fractionated using benzene and *n*-hexane. The fraction with $\bar{M}_v = 4.86 \times 10^5$ was used in the experiment.

Poly(4-vinylpyridine)–HMW. This polymer ($\bar{M}_v = 8.04 \times 10^5$) was a gift, the preparation of which is reported elsewhere¹³. It was purified by precipitating from methanol in water.

All the samples were characterized by ¹H n.m.r. recorded on a Bruker (200 MHz) spectrometer.

Preparation of quaternized poly(vinylpyridine) samples

Poly(2-vinyl-N-methylpyridinium iodide) with low DS (PC2-LDS). A mixture of poly(2-vinylpyridine) (1 g, 9.52 mmol) in methanol (20 ml) and methyl iodide (2 ml, 32 mmol) was stirred at room temperature for 24 h. The excess of the solvent and the halide were evaporated under vacuum. The pale yellow product was purified by precipitating from methanol in diethylether.

Poly(4-vinyl-N-methylpyridinium iodide) with low DS (PC4-LDS). Poly(4-vinylpyridine) (1 g, 9.52 mmol) in methanol (20 ml) and methyl iodide (0.86 ml, 13.7 mmol) were stirred at room temperature for 3.5 h. The product was purified as described above.

Poly(2-vinyl-N-methylpyridinium iodide) with high DS (PC2-HDS). Poly(2-vinylpyridine) (1 g, 9.52 mmol) in nitromethane (20 ml) and methyl iodide (4.0 ml, 64.1 mmol) were stirred at 50°C for 3 days¹³. The deep yellow precipitate was separated from the reagents by vacuum evaporation. It was purified by washing repeatedly with diethyl ether.

Poly(4-vinyl-N-methylpyridinium iodide) with high DS (PC4-HDS). Poly(4-vinylpyridine) (1 g, 9.5 mmol) in methanol (20 ml) and methyl iodide (2.1 ml, 33.6 mmol) were stirred at room temperature for 24 h. The product was washed with diethylether.

All the samples were dried at 50°C under vacuum. The appearance of a peak at $\delta = 4.1$ ppm in the ¹H n.m.r. of the quaternized products confirms the presence of $-N^+-CH_3$ group. The extent of quaternization of the products, i.e. the DS, was determined using Volhard's method of halide estimation. The various samples used in the experiment and the corresponding \bar{M}_v and DS values are listed in Table 1.

Table 1 Characteristics of the polyions used and the composition of the PEC formed at different concentrations

Polyion	$\bar{M}_v \times 10^{-4}$	DS	Composition (P^-/P^+) at the two concentrations, C (mol dm ⁻³)	
			8.2×10^{-3}	1.64×10^{-4}
CMC	43.0	0.73	–	–
PC2-LDS(LMW)	2.3	0.40	1.0	1.5
PC2-HDS(LMW)	2.3	0.71	0.67	1.0
PC2-LDS(HMW)	48.6	0.31	1.0	1.5
PC2-HDS(HMW)	48.6	0.71	0.67	1.0
PC4-LDS(LMW)	8.0	0.20	1.0 ^a	1.5
PC4-HDS(LMW)	8.0	0.82	0.67	1.0
PC4-LDS(HMW)	80.4	0.22	1.0 ^a	1.5
PC4-HDS(HMW)	80.4	0.73	0.67	1.0

^a $C = 7.13 \times 10^{-3}$ mol dm⁻³

Complex formation and measurements

The method reported in the literature¹⁴ has been followed to study the complex formation. The aqueous solution of the polycation (PC) was added to the polyanion (PA) solution of the same concentration, expressed in terms of the number of moles of ionic groups per cubic decimetre. A series of mixtures containing varying amounts of CMC and PC2 or PC4 were made. The total volume of the mixture was maintained constant. The solutions were shaken well after the addition and left overnight. The precipitated PEC was centrifuged out from the solution. The viscosity of the supernatant liquid relative to water (η_r) was measured at 26°C with an Ubbelohde viscometer. The amount of the PC component in the supernatant solution was also measured using a u.v. spectrophotometer (Hitachi U3400). The absorbance (*A*) of the solution was recorded at 263 and 258 nm for PC2 and PC4, respectively.

For each reaction mixture, a control solution was made containing the polyelectrolyte added in excess and NaI which would be released from the precipitate upon complete ionic interaction between the polyelectrolytes. The η_r and *A* values of these solutions were also measured for comparison with those of the reaction mixtures.

Scanning electron microscopy (SEM) was used to study the morphology of the PEC precipitates. Samples were prepared by coating the dry PEC precipitate with gold under vacuum. The micrographs were recorded on a scanning electron microscope (Stereoscan-120) at 10 kV.

RESULTS

The complex formation was carried out at two different concentrations. When the polyions were mixed at high concentration ($C = 8.2 \times 10^{-3}$ mol dm⁻³) the mixture consisted of the PEC precipitate and a turbid supernatant solution. At a particular mixing ratio of the polyions (P^-/P^+) the resulting PEC completely flocculated and centrifugation yielded a clear solution. The reaction mixture shows a minimum in the relative viscosity (η_r) and absorbance (*A*) values for this composition. The results of the experiment are shown in Figures 1–4.

Complex formation at high concentration

Effect of DS of PC. Figures 1a and b show the η_r and *A* of the mixtures containing CMC and HMW PC2, at the two concentrations studied. At high concentration,

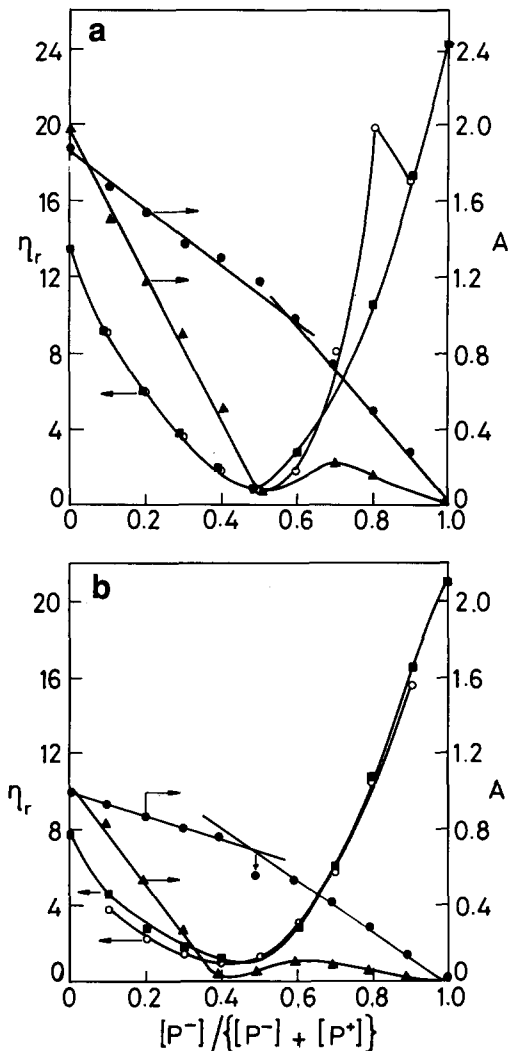


Figure 1 Relative viscosity (η_r) and absorbance (A) versus composition of the reaction mixtures of CMC and the following PCs: (a) PC2-LDS(HMW), (b) PC2-HDS(HMW). \bullet , $C = 1.64 \times 10^{-4} \text{ mol dm}^{-3}$; \blacktriangle , \blacksquare and \circ , $C = 8.2 \times 10^{-3} \text{ mol dm}^{-3}$; \blacksquare , control solution

with PC2-LDS (Figure 1a), the minima in η_r and A values occur at $P^-/(P^- + P^+) = 0.5$, which corresponds to 1:1 stoichiometry. However, deviation from the stoichiometric ratio was observed with PC2-HDS (Figure 1b) given by the minimum at 0.4 corresponding to $P^-/P^+ = 0.67$.

Effect of molecular weight. Figure 2 shows the effect of the charge content on the stoichiometry when LMW PC2 was used. Comparison of Figures 1 and 2 shows that values of $P^-/P^+ = 0.67$ and 1.0 are obtained with PC2 of higher and lower charge content, respectively, independent of the molecular weight of the PC.

Effect of location of charge site. Figures 3 and 4 represent similar data for the complex with PC4 of two different molecular weights and DS. PC4 is observed to behave similarly to PC2 in spite of their difference in geometry. In all the cases, when $P^-/P^+ = 0.67$, the deviation from 1:1 stoichiometry is reflected in the difference in the η_r values of the reaction mixtures and control solutions. The effect is clearly visible for HMW PCs (Figures 1b and 3b). Excellent agreement between the η_r values of the control and the reaction mixture is observed when $P^-/P^+ = 1.0$.

Complex formation at low concentration

At low concentration of the polyions, the complex formation is followed by measuring only the absorbance of the solution, as it is highly sensitive to the concentration compared to the viscosity method. The complex formation was indicated by the turbid nature of the mixture. The minimum value in the absorbance was shown by the solution having maximum turbidity. The point of coagulation of the precipitate is indicated by the vertical arrow in the figures.

Effect of DS. Figures 1b, 2b, 3b and 4b show that both PC2 and PC4 maintain 1:1 stoichiometry with CMC when the charge content is higher. However, Figures 1a, 2a, 3a and 4a show the deviation from 1:1 to a value of $P^-/P^+ = 1.5$ for PCs of low DS.

The differences in geometry and molecular weight of the PCs do not show any effect on the stoichiometry, even at low concentration. The P^-/P^+ values for the various systems studied are tabulated in Table 1.

DISCUSSION

The process of complexation is governed by a two-step mechanism: the approach of the oppositely charged species, which is a diffusion-controlled process, followed

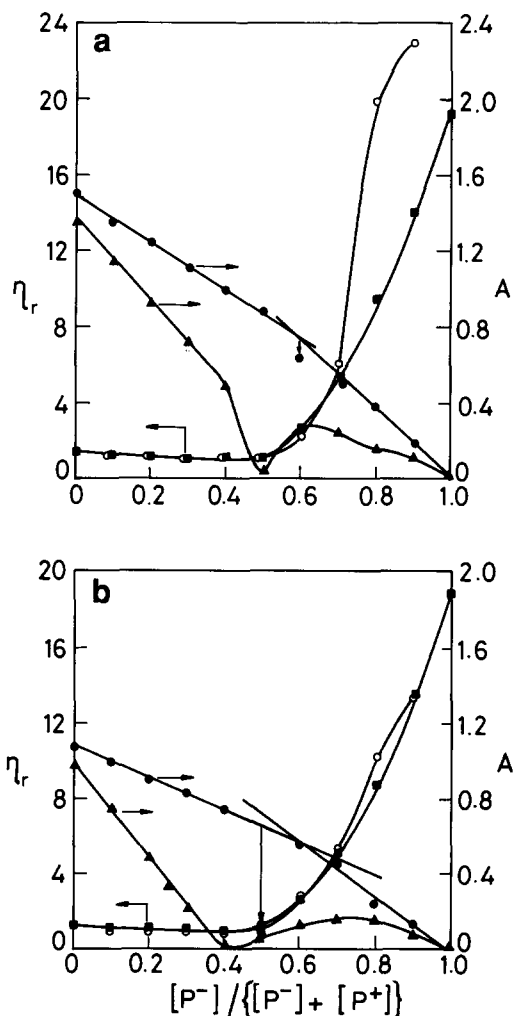


Figure 2 Relative viscosity (η_r) and absorbance (A) versus composition of the reaction mixtures of CMC and the following PCs: (a) PC2-LDS(LMW), (b) PC2-HDS(LMW). Symbols are the same as in Figure 1

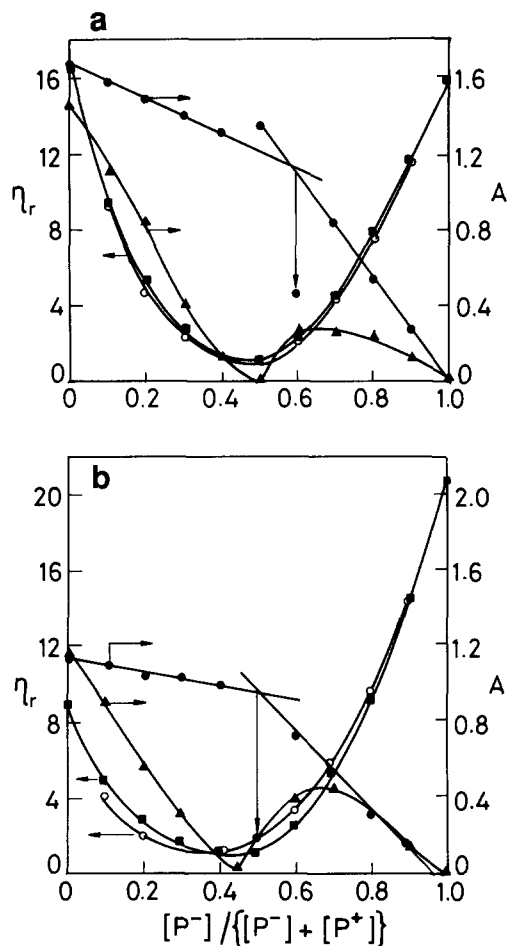


Figure 3 Relative viscosity (η_r) and absorbance (A) versus composition of the reaction mixtures of CMC and the following PCs: (a) PC4-LDS(HMW), (b) PC4-HDS(HMW). \bullet , $C = 1.64 \times 10^{-4} \text{ mol dm}^{-3}$; \blacktriangle , \blacksquare and \circ , $C = 7.13 \times 10^{-3} \text{ mol dm}^{-3}$ for (a) and $8.2 \times 10^{-3} \text{ mol dm}^{-3}$ for (b); \blacksquare , control solution

by the neutralization of the charges on the interacting chains. The rate of the latter step is dependent on the structure of the molecule, the charge density and the mobility of the micro-ions diffusing out of the polyions on complexation. A faster second step will leave some of the charges on the polyions trapped, and these remain unneutralized in the complexation process¹⁵.

In the present study, CMC, an inherently stiff polysaccharide molecule, has been selected as the PA to complex with vinylic-type PCs which take up relatively flexible conformations. It is known that, at low ionic strength (high dilution) and when the charge density is high, expansion of the polyelectrolyte chains takes place due to the electrostatic repulsion. As the 'monomer length' for a vinylic-type polymer is considered to be 0.25 nm and 0.44 nm for a polysaccharide¹⁶, the number of charges per unit length of the chain is higher for the PCs considered here than the PA of same DS. Due to the higher charge content and flexibility, the size of the PC has a stronger dependence on the ionic strength of the medium. This is clear from the relation between the radius of gyration (R_g) and the concentration (C) for the two types of polyelectrolytes; $R_g \propto C^{-0.07}$ for CMC¹⁷, and $R_g \propto C^{-0.3}$ and $C^{-0.1}$ for a vinylic-type PC of high and low DS respectively¹⁸. The difference in the relative extension of the two types of polyions of opposite charges under the different conditions of complexation is reflected in the composition of the PEC.

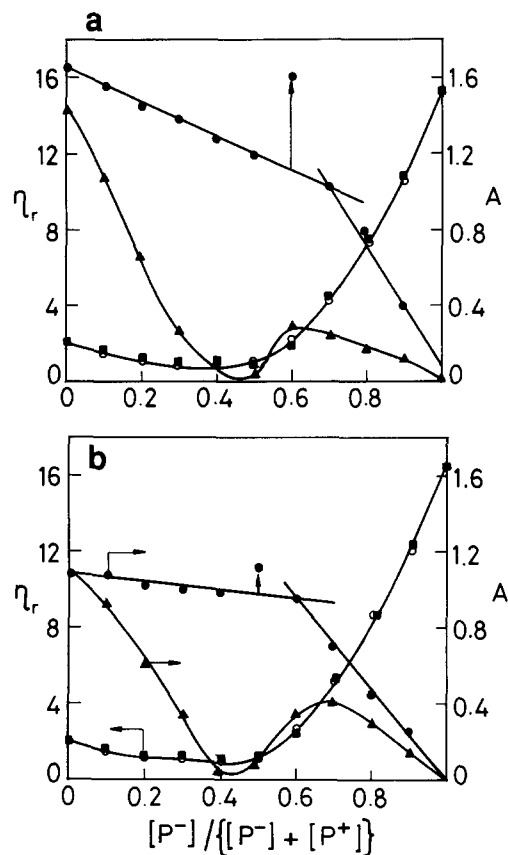


Figure 4 Relative viscosity (η_r) and absorbance (A) versus composition of the reaction mixtures of CMC and the following PCs: (a) PC4-LDS(LMW), (b) PC4-HDS(LMW). Symbols are the same as in Figure 3

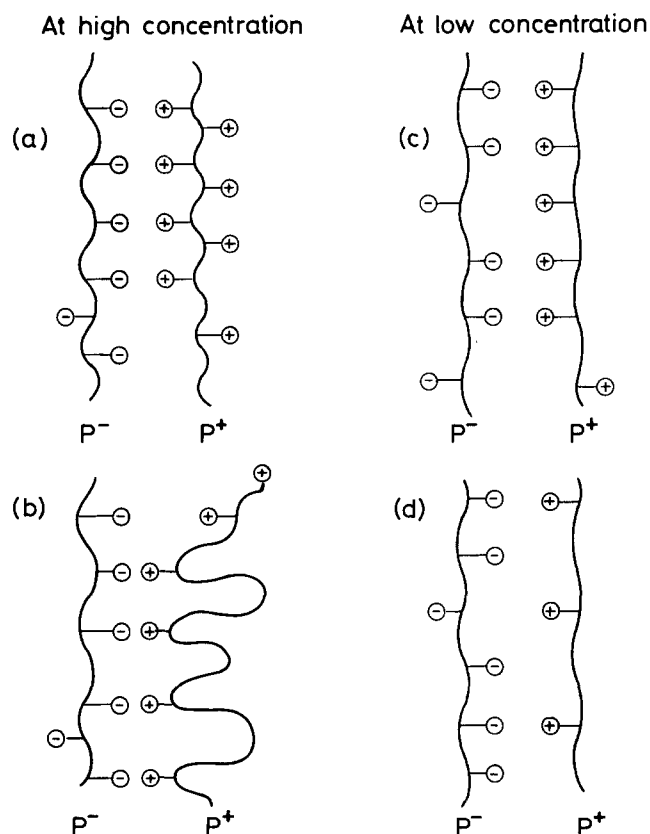


Figure 5 Schematic representation of the effect of charge content on the expansion of the PA (P^-) and the following PC (P^+) chains at two different concentrations and PEC formation: (a) and (c) PC-HDS; (b) and (d) PC-LDS

The process of complexation under the different conditions studied is represented schematically in *Figure 5*. (Here, charge neutralization between two individual chains has been considered for simplicity and is not an ideal representation of the system where several chains may be involved.) At high concentration, when the PC chains are less extended and the density of the fixed positive charges is greater than the negative charges, complexation leads to the entrapment of some of the positive charges of the PC (*Figure 5a*). This results in the composition $P^-/P^+ = 0.67$ for the complex, i.e. there is an excess of PCs over PAs. The entrapped PCs remain neutralized by the negative micro-ions. Under the same condition, when PC of low *DS* is used, 1:1 stoichiometry is maintained in the complex, as expected from the lowering of positive charge density on the PC (*Figure 5b*).

At the low concentration studied ($C = 1.64 \times 10^{-4}$ mol dm^{-3}), polyions assume a rod-like conformation due to the increased coulombic repulsion¹⁹. Under this condition the charge density of the PC decreases appreciably due to the higher stretching of the PC chain compared to the PA (*Figure 5c*). The complexation between the polyions in this extended open conformation results in the composition of $P^-/P^+ = 1.0$. When the PC of low *DS* is used, the density of the fixed positive charges decreases further, resulting in entrapment of the negative charges giving a composition of $P^-/P^+ = 1.5$ (*Figure 5d*).

Hence, the resulting complex has a higher PA content.

The above interpretation of the result is confirmed by studying the effect of the ionic strength on the composition of the complex. Complexation carried out in low concentration in the presence of NaCl (0.016 M) is found to shift the composition of the complex from $P^-/P^+ = 1.0$ to 0.67 in the case of PEC involving PC of high *DS*. This is due to the greater contraction of the PC chains than the PA chains in the presence of NaCl, leading to entrapment of the positive charges.

The concentration-dependent influence of the *DS* was not observed for the PEC made with CMC of varying *DS* and different PCs, reported in the literature⁶. This could be due to the different methods used to study the complex formation. In our study, the composition of the reaction mixture was changed at a constant ionic strength, an important factor which affects the conformation of the polyions.

The effect of the composition of the PEC on the morphology of the precipitate can be observed in the scanning electron micrographs in *Figure 6*. The PECs containing PC of low *DS* show smooth surface features compared to the PECs made of PC of high *DS*.

Another important observation of the present study is the drastic increase in the solution viscosity when the polyions are mixed in particular ratios. This was observed for the mixtures containing PC2 in the ratio

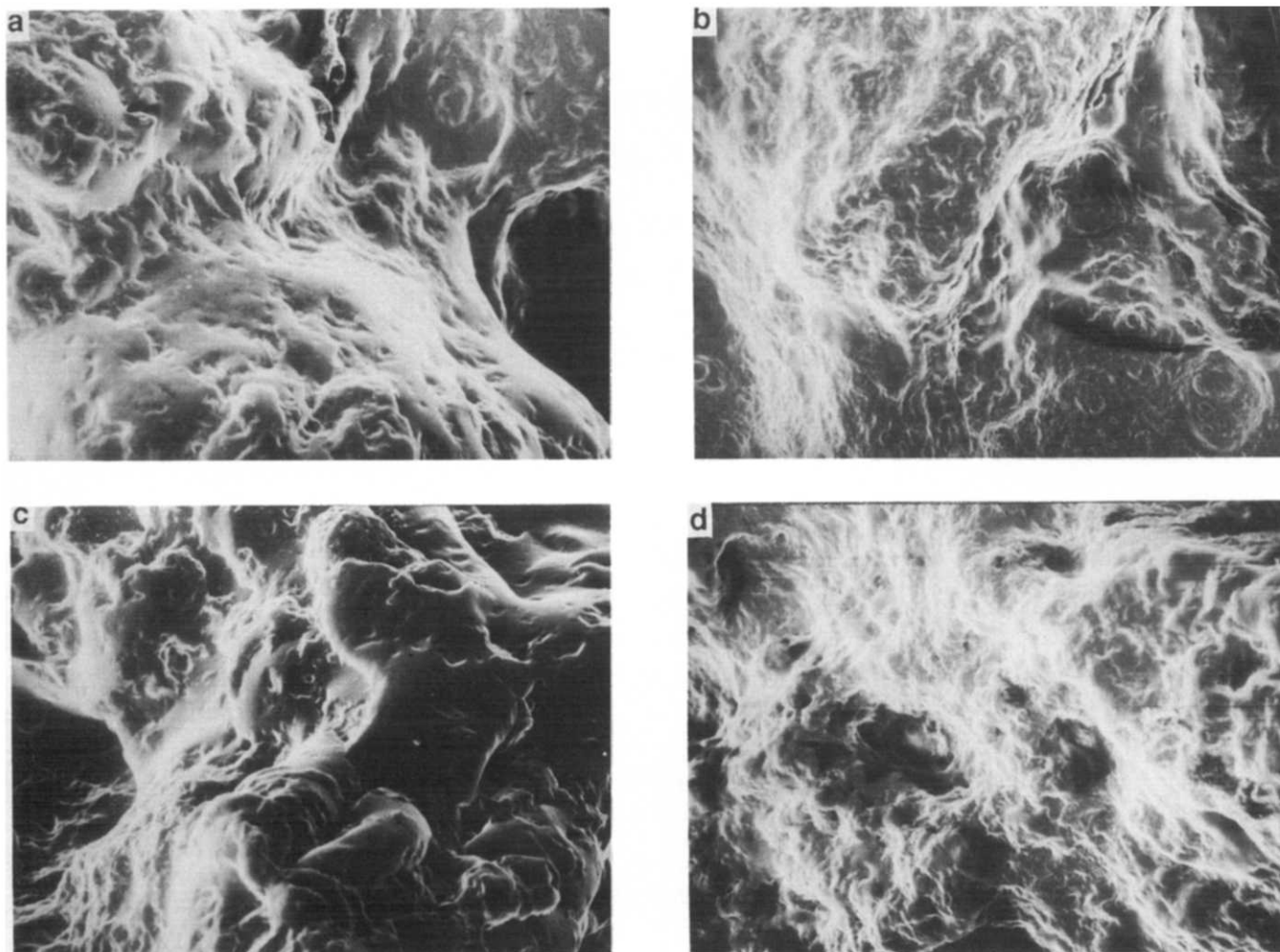


Figure 6 Scanning electron micrographs of PEC precipitates of CMC and the following PCs (500 ×): (a) PC2-LDS(LMW); (b) PC2-HDS(HMW); (c) PC4-LDS(LMW); (d) PC4-HDS(HMW)

$P^-/(P^+ + P^-) = 0.8$ and 0.9 (Figures 1a, 2a and 2b). The unexpected increase in the viscosity over the control solution could only be due to the presence of soluble PEC. This effect is dependent on the molecular weight and *DS* of the PC. It is found to be highest for the LMW PC2-LDS (Figure 2a) and relatively small for the HMW PC2-LDS (Figure 1a). It reduces considerably for the LMW PC2-HDS (Figure 2b) and is totally absent when HMW PC2-HDS was used (Figure 1b). The presence of soluble PEC was not observed for PC4. It could be due to the more coiled nature of PC4 compared to PC2²⁰, which favours the involvement of more oppositely charged chains in the complexation process resulting in a more compact structure of the PEC. More detailed studies need to be carried out to confirm the above inference.

CONCLUSIONS

The charge content of the flexible cations used in this study is found to have an influence on the composition of the PEC precipitates. This effect on the composition is found to depend on the concentration of the polyions involved in the complexation. The relative change in the conformations of the two kinds of complexing polyions, governed by the above factors, is thought to be the cause of variations in the composition. PEC particles formed from the PC of high *DS* differ from the PC of low *DS* in morphology and the amount and type of excess charge. This is expected to be reflected in the properties exhibited by the PEC such as the capacity for water and electrolyte absorption, permeability etc. The molecular weight and geometry of the PC used in this study do not have any influence on the chemical composition of the precipitate. However, the formation of soluble complex is observed

only for PC2. The rigidity of PC2 compared to PC4 seems to favour the formation of soluble PEC.

ACKNOWLEDGEMENT

The generous gift of the poly(4-vinylpyridine)-HMW sample by Professor M. Chanda is gratefully acknowledged.

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