Macromol. Symp. ***126,*** *143–155 (1997)*

INTERPOLYELECTROLYTE COMPLEXES FORMATION IN DEPENDENCE ON THE NATURE OF POLYELECTROLYTES

Mariana Cristea*, Stela Dragan, Demetra Dragan

"Petru Poni" Institute of Macromolecular Chemistry, 6600 Iasi, Romania

Bogdan C. Simionescu

Department of Macromolecules, "Gh. Asachi" Technical University, 6600 Iasi, Romania

Abstract: Interpolyelectrolyte complexes (PECs) were obtained starting from polycations with (N,N-dimethyl-2-hydroxypropylenammonium chloride) units in the main chain and sodium salts of the poly(acrylic acid), on one hand, and poly (2-acrylamido-2-methylpropane sulfonic acid), on the other hand, as polyanions. The polycations were different as concerns both the content of the quaternary ammonium salt groups and the degree of branching. The polyanions were different both by their structure and molecular weight. The complex formation was followed through the variation of the reduced viscosity and of the conductivity of the reaction medium *vs.* the unit molar ratio polyanion/polycation in two ranges of concentration.

INTRODUCTION

The study of interpolymer complexes is still very attractive due to their numerous applications in both industrial (Refs. 1-5) and biological fields (Refs. 6-10). The formation of interpolymer complexes takes place by many types of interactions, such as electrostatic, hydrogen bonds, dipol-dipol or hydrophobic interactions and so on (Refs. 11-30). The coexisting interactions are directly determined by the complexity of the structure of the complementary polymers. The synthetic polyelectrolytes, by their large variety of structures and combination possibilities, offer a very useful field for the understanding of the multiple interactions that take place between biopolymers in the living cells. Also, as regards the structural characteristics of the

CCC 1022-1360/98/$ 10.00

complementary polymers (molecular weight, chain flexibility, type of ionic sites, charge density) and the synthesis conditions, synthetic interpolymer complexes find use as new polymeric materials (Refs. 10, 26).

The cationic polyelectrolytes of integral type, with quaternary ammonium salt groups in the main chain and pendent hydroxyl groups, could represent a complementary polymer in the synthesis of some less studied interpolyelectrolyte complexes. From the practical point of view these products could be useful in the improvement of the separation processes of some very fine suspensions or dyes frequently met in waste waters.

The aim of this paper is the study of the polyelectrolyte complexes (PECs), resulting from poly(N,N-dimethyl-2-hydroxypropylenammonium chloride)s with different branching degrees, as cationic component, and the sodium salts of poly(acrylic acid) or poly(2-acrylamido-2-methylpropane sulfonic acid) of different molecular weights, as anionic component. The stoichiometry of PECs depending on the unit molar ratio and its value at the endpoint, the release of the low molecular weight salt (NaCl) and the aspect of the PECs as concerns the structure and the concentration of the complementary polymers were followed.

EXPERIMENTAL

Poly(acrylic acid) was synthesized in aqueous solution, with $(NH_4)_2S_2O_8$ as radical initiator. The polymers were converted into sodium salts by use of aqueous sodium hydroxide. After two purifications with water/acetone system, the sodium salts were recovered from aqueous solutions by atomizing. The molecular weight of the sodium salts of poly(acrylic acid) (PANa) was determined by viscometry, in 2N NaOH aqueous solution, at 25°C and the following values were found: $PANa_2$ - 51,400 and $PANa_3$ - 217,600.

Homopolymers of the sodium salt of 2-acrylamido-2-methylpropansulfonic acid (PAMPSNa) with different molecular weights were prepared. The polymerization of the monomer (AMPSNa) was carried out in aqueous medium to high conversions, at 65-70 °C, under N_2, using ammonium persulfate (AP) - sodium metabisulfite (MB) as initiator-activator, and isopropyl alcohol (IA) as a chain transfer agent.

The polymers were purified by dialysis against distilled water, then concentrated and dried in vacuum at 50° C for several days. The average molecular weights were evaluated by viscometric measurements, in 1M NaCl aqueous solution, at 25° C. The Huggins parameter values, calculated according to equation (1), are included in Tab. 1.

$$\eta_{sp}/C = [\eta] + k_H[\eta]^2C \tag{1}$$

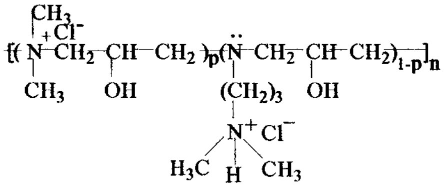
were η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, k_H is the Huggins parameter and C is polymer concentration. k_H is used extensively as a qualitative measure of branching in polymers, its value being afected by the bushy branching, i. e., the increase of the segmental density or of the coil volume (Refs. 31, 32).

The synthesis conditions and the molecular weights of PAMPSNa are summarized in Tab. 1.

Tab. 1. Synthesis conditions and some characteristics of PAMPSNa samples

Sample code	AP (wt-%)	MB (wt-%)	IA (vol-%)	Time (h)	$M_v x 10^{-5}$	k_H
I	0.15	0.06	20	4	0.73	0.85
VI	0.08	0.04	-	6	14.00	0.23
VII	0.04	0.02	-	6	26.00	0.38

The cationic polyelectrolytes with N,N-dimethyl-2-hydroxypropylenammonium chloride units in the main chain were synthesized by condensative polymerization of epichlorohydrin with dimethylamine and a polyfunctional amine such as N,N-dimethyl-1,3-diaminopropane, according to the method previously presented (Ref. 33). The theoretical structures of the cationic polyelectrolytes used in this work are presented in Scheme I:



p = 0.95, polycation PC_1; p = 0.80, polycation PC_2

Scheme I

In the above scheme the ideal structure unit was given; the used polyfunctional amine (DMDAP) has a functionality of 4 and consequently the branching can take place at the tertiary amine groups, this possibility being higher for a greater content of the amine. The polycation samples were carefully purified by dialysis against distilled water up to the absence of Cl^- ions in the external water; the presence of Cl^- ions in the external water was checked up with a 0.02N $AgNO_3$ aqueous solution. The diluted aqueous solutions were concentrated by gentle heating in vacuum and then recovered by atomizing. The cationic polymer samples were kept for days in vacuum on P_2O_5 at room temperature. The intrinsic viscosities were determined in 1M NaCl aqueous solution at 25°C and the following values were found: $[\eta]_{PC1} = 0.610$ and $[\eta]_{PC2} = 0.355$. Details on the characteristics of the polycation samples were presented elsewhere (Ref. 34).

Complex Formation. The aqueous solution of polyanion (or polycation), with a concentration of 10^{-2} or 10^{-3} unit mol/l, was slowly dropped into a 50 ml aqueous solution of polycation (or polyanion) having a concentration of 10^{-3}, respectively 10^{-4}, unit mol/l, under magnetic stirring at room temperature in a [PA]/[PC] unit molar ratio ranging from 0 to 3. The mixing was continued for 2 hours; the precipitates were removed by centrifugation at 600 g or by filtration when formed. The reaction between the two polyions was checked by comparison of the supernatant mixture characteristics (specific viscosity and conductivity) with those of a control sample prepared taking into account the composition expected for a stoichiometric reaction and a complete release of NaCl. Thus, on the left of the theoretical endpoint (1:1), the control samples included the polycation in excess and NaCl corresponding to the molar ratio at a given moment and on the right of the endpoint the control samples included NaCl calculated for a stoichiometric reaction at the theoretical endpoint (1:1) and the polyanion in excess.

The viscometric measurements were peformed with an Ubbelohde viscometer with internal dilution, at 25°C. The conductivities were measured in a specific cell with platinum/platinum electrodes (Radiometer Copenhagen, type CDM 2d).

RESULTS AND DISCUSSION

The interaction between two polyelectrolytes with opposite charges leads to the formation of interpolyelectrolyte complexes whose structure and properties depend mainly on their molecular weights, charge density, branching degree, on the concentration of both solutions, the mixing order and the unit molar ratio. The influence of the branching degree and of the charge density of the cationic polyelectrolytes on complex formation, for both weak and strong polyanions, was less studied. The cationic polyelectrolytes used in this paper are characterized by both different branching degrees and different types of charges (strong and weak) provided by the presence of the polyfunctional amine (Scheme I). They also have different chain conformations, as emphasized by their viscometric behaviour in aqueous solution (Ref. 34).

PANa and PAMPSNa were used as polyanions. They differ both by the charge strength and charge density.

Complex formation between PANa and polycations PC_1 and PC_2

First, the interaction between the weak polyanion (PANa) and the polycations of integral type (PC_1 and PC_2, Scheme 1) was analysed. The variation of the reduced viscosity *vs.* the PA/PC unit molar ratio (r) is presented in Fig. 1. Polymer concentration was calculated as a sum of the initial polycation content and of the polyanion content corresponding to the unit molar ratio. In this way the endpoint could be emphasized clearly. The decrease of the reduced viscosity with increasing the unit molar ratio between the two components before the endpoint is affected by a number of factors such as:

-the increase of the total polymer concentration in the mixture

-the release of the low molecular weight salt (NaCl)

-the decrease of the free ionic group number on the polycation chain.

The influence of the molecular weight of the PANa on complex formation with PC_1 is proved by the deviation of the endpoint from 1:1 unit molar ratio to 1.16:1 for $PANa_2$. In the case of $PANa_3$ the endpoint is close to a 1:1 unit molar ratio. The deviation of the endpoint from 1:1 is even higher when the complementary polymers were $PANa_2$ and PC_2. According to Scheme 1, PC_2 has a polyfunctional amine content higher than PC_1, i. e., a higher branching degree and also two types of cationic sites - quaternary ammonium and tertiary amine sites. The increase of the viscosity after the endpoint is induced by the excess of the polyanion, being dependent only on the molecular weight of the PANa and rather independent of the polycation. Since in all these systems the formation of the insoluble polysalts took place and these were removed from the medium, one may also assume that only the free polyelectrolyte could influence the specific viscosity of the reaction mixture.

The release of the low molecular weight salt was followed through the conductivity— unit molar ratio variation (Fig. 2). The conductivity values increase quite linearly with increasing of the PA/PC unit molar ratio up to the endpoint, when a break is evident, i.e., the end of complex formation; then the increase of the conductivity takes place mainly due to polyanion excess but also by the further release of microions caused by the rearrangements occuring inside the complex. The conductivity endpoint coincides with the endpoint found through viscosity measurements. As one can see from Fig. 2, the conductivity values are influenced before the endpoint mainly by the polycation and are rather independent on the polyanion

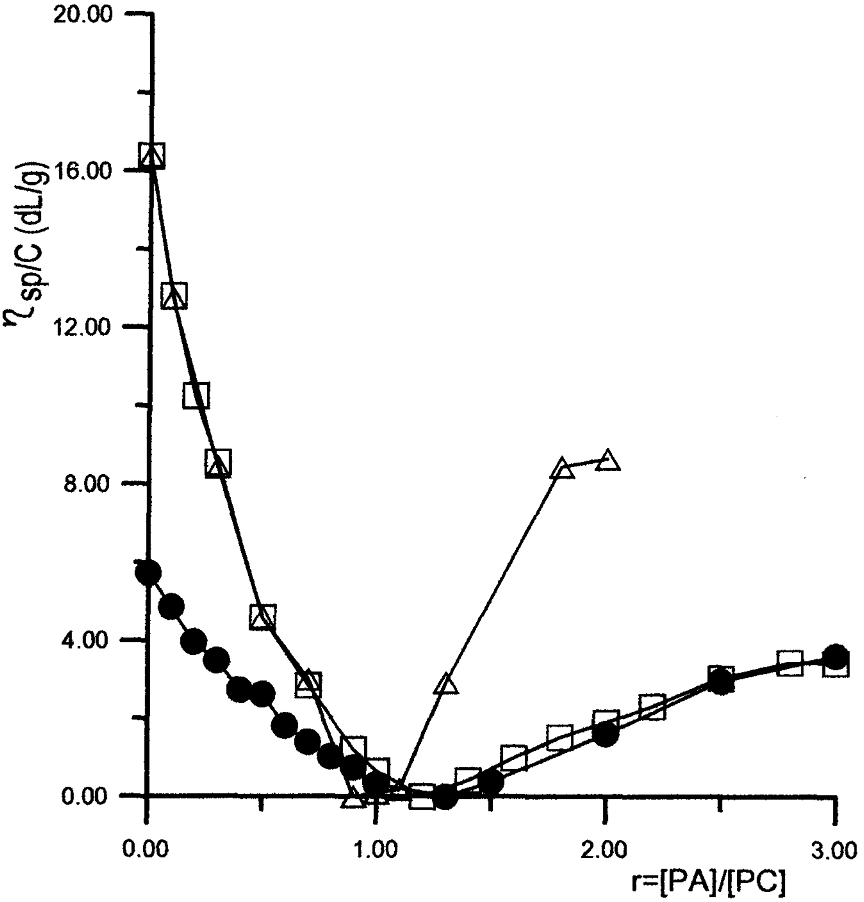


Fig. 1. Variation of the reduced viscosity in the system PANa/PC: □ - $PANa_2/PC_1$; Δ - $PANa_3/PC_1$; ● - $PANa_2/PC_2$

($PANa_2/PC_1$ and $PANa_3/PC_1$). The structural differences between the complementary polymers are much higher in the $PANa_2/PC_2$ system than in the $PANa_2/PC_1$ system and more restrictions in complex formation are to be expected. The presence of more branches makes difficult the compensation of the opposite charges, and conformational changes of the complementary polymers are required from the very begining of the process. This situation is reflected in the variation of the conductivity of the reaction medium *vs.* the PA/PC unit molar ratio: the increase of conductivity is slower in the $PANa_2/PC_2$ system than in the $PANa_2/PC_1$

one at unit molar ratios less than about 0.4. After reaching the endpoint the conductivity curves of all systems overlap, thus suggesting a further microion release in the case of the PANa$_2$/PC$_2$ system, due to the intracomplex rearrangements which result in the neutralization of more opposite charges standing on unfavourable positions. An argument for this process is also provided by the decrease of the difference between the experimental values and the control samples after the endpoint for this system. Another difference between PANa$_2$/PC$_1$ and PANa$_2$/PC$_2$ complexes consists in their physical aspect - a compact precipitate in the former case and a hydrophilic gel in the second one.

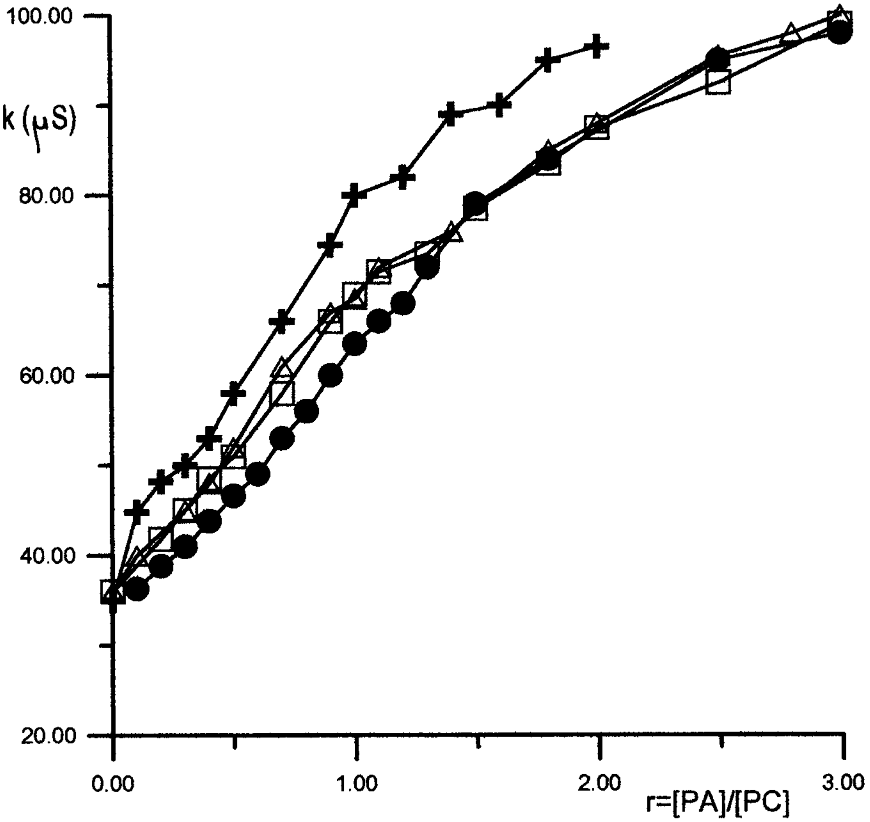


Fig. 2. Dependence of the conductivity on the PA/PC unit molar ratio for the systems: □ - PANa$_2$/PC$_1$; Δ - PANa$_3$/PC$_1$; ● - PANa$_2$/PC$_2$; ✚ - PANa$_2$/PC$_2$ - control samples

Complex formation between PAMPSNa and PC_I

The large range of the molecular weights of the PAMPSNa synthesized in this work and the different behaviour of this polyanion in the complexation with the polycation PC_I suggested the study of this system for different orders of mixing and at two concentrations. The variation of the reduced viscosity *vs.* the PA/PC or PC/PA unit molar ratio, when the concentration of the major polyelectrolyte was 10^{-3}M and that of the minor one was 10^{-2}M, is presented in Fig. 3.

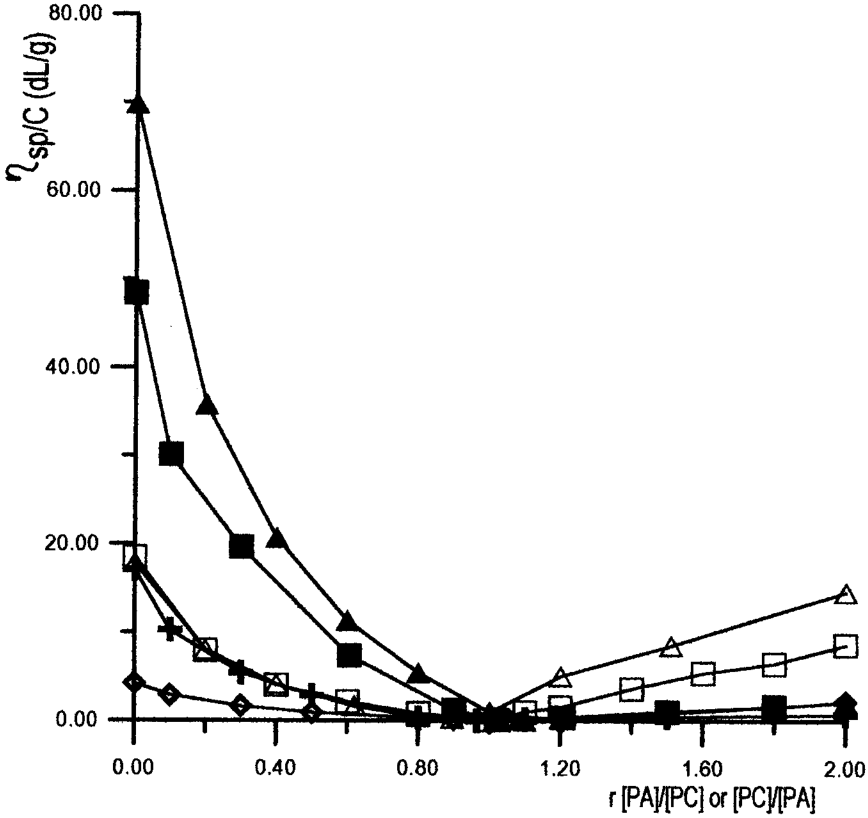


Fig. 3. Variation of the reduced viscosity *vs.* the unit molar ratio for the PAMPSNa/PC and PC/PAMPSNa systems: Δ - $PAMPSNa_{VII}/PC_I$; ▲ - $PC_I/PAMPSNa_{VII}$; □ - $PAMPSNa_{VI}/PC_I$; ■ - $PC_I/PAMPSNa_{VI}$; ✚ - $PAMPSNa_I/PC_I$; ◇ - $PC_I/PAMPSNa_I$

In the concentration range used in the above systems, the endpoint was evidenced at a 1:1 unit molar ratio, irrespective of the molecular weight of PAMPSNa and of the mixing order. The complexes resulted in all these systems looked like unstable coacervates. This could be a consequence of the important differences between the complementary polymers due to both the position of the ionic sites related to the backbone and the charge density. Huglin et al. reported the obtaining of only compact precipitates when PAMPSNa was used in combination with poly (4-vinylpyridinium chloride) as cationic component (Ref. 35).

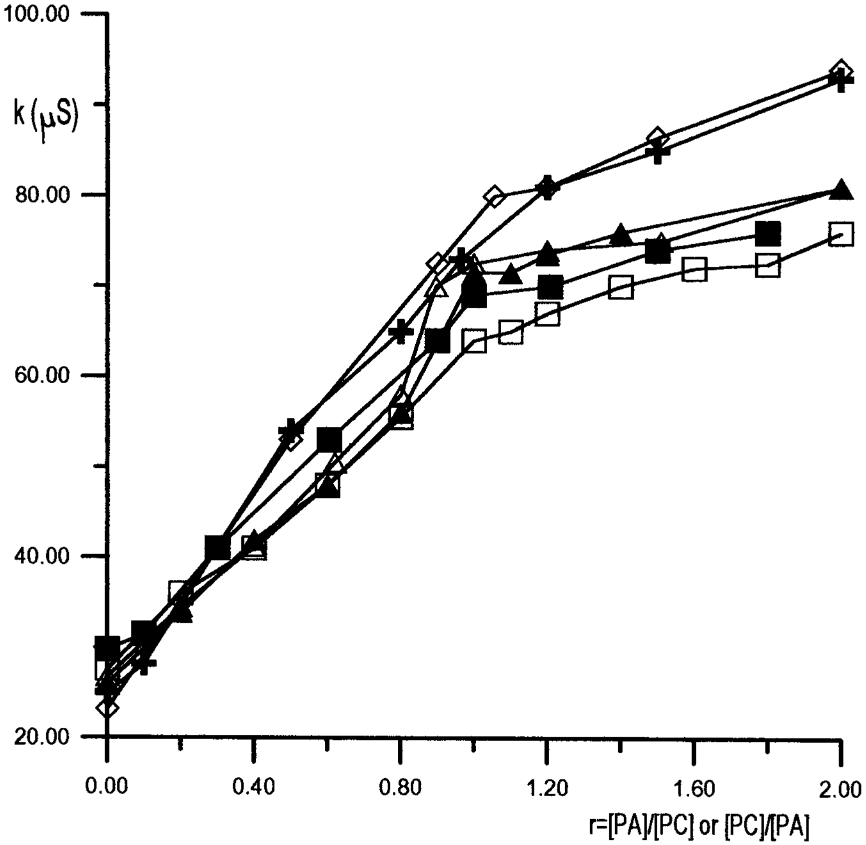


Fig. 4. Variation of the conductivity *vs.* the unit molar ratio for the PAMPSNa/PC and PC/PAMPSNa systems: ▲ - $PAMPSNa_{VII}/PC_{I}$; Δ - $PC_{I}/PAMPSNa_{VII}$; □ - $PAMPSNa_{VI}/PC_{I}$; ■ - $PC_{I}/PAMPSNa_{VI}$; ✚ - $PAMPSNa_{I}/PC_{I}$; ◇ - $PC_{I}/PAMPSNa_{I}$

The compensation of the opposite charges were also studied through the variation of the conductivity *vs.* the unit molar ratio (Fig. 4). The release of the low molecular weight salt is influenced more by the molecular weight of the polyanion than by the mixing order.

It is worth to remark that the release of NaCl, reflected in the increase of the conductivity, is faster and higher in the case of the polyanion with the lowest molecular weight ($PAMPSNa_I/PC_I$ system) than in the case of the polyanions with molecular weights much higher than that of the polycation. This behaviour was expected since the arrangement of the macromolecular chains proceeds easier when the molecular weights of the complementary polymers are comparable than when they are highly different. The sharp increase of the conductivity close to the endpoint proves the completion of the complexation process in the case of $PAMPSNa_{VII}$.

The important difference between the molecular weights of the complementary polymers allowed the study of these systems in a concentration range adequate for the obtaining of quasisoluble complexes. The variation of the reduced viscosity and of the conductivity *vs.* the unit molar ratio for the $PAMPSNa_{VII}/PC_I$ and $PC_I/PAMPSNa_{VII}$ systems, when the concentration of the major component was 10^{-4}M and that of the minor one was 10^{-3}M, were presented in Fig. 5. In this domain of concentration the endpoint is different as compared to the former concentration range. The stoichiometry of the complex was clearly dependent on the order of mixing, as made evident by both viscometric and conductometric measuremens. As in the case of the former range of concentrations, these systems are characterized by a strong increase of the conductivity just before the endpoint. The specific viscosity of the complex at the endpoint allowed the calculation of the density of the complex using the Einstein relation, which correlates the specific viscosity with the density for spherical stiff particles:

$$\eta_{sp} = 2.5 \cdot C/\rho \qquad (2)$$

where η_{sp} is the specific viscosity of the system at the endpoint, C is the total concentration of the polymers in the system and ρ is the density of the complex particles. The values thus obtained were $2.637 \cdot 10^{-2}$ g/cm^3 for the $PAMPSNa_{VII}/PC_I$ system and $3.16 \cdot 10^{-2}$ g/cm^3 for the $PC_I/PAMPSNa_{VII}$ system, respectively.

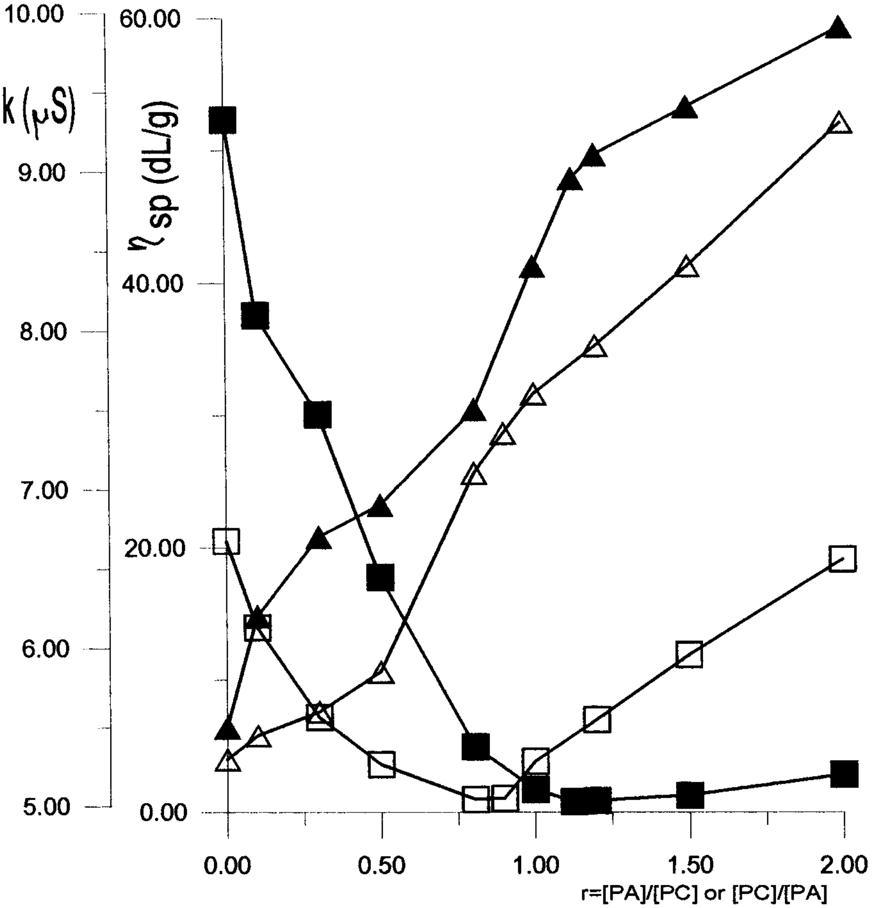


Fig. 5. Variation of the reduced viscosity and of the conductivity *vs.* the unit molar ratio for the PAMPSNa$_{VII}$/PC$_I$ (□, Δ) and PC$_I$/PAMPSNa$_{VII}$ (■, ▲) systems

CONCLUSIONS

In the complex formation between polycations of integral type as poly (N,N-dimethyl-2-hydroxypropylenammonium chloride) (PC1) and weak or strong polyanions, the structure of the polyanion was observed to determine the PEC properties - a compact precipitate in the case of PANa and a coacervate in the case of PAMPSNa, irrespective of polyanion molecular weight. In the 10^{-2}-10^{-3} M concentration domain, while the endpoint was more or less influenced by the molecular weight of PANa, for PAMPSNa the endpoint was 1:1, unaffected by the order of mixing or by the molecular weights. Otherwise, in the 10^{-3}-10^{-4}M concentration domain the order of mixing influenced the endpoint when PAMPSNa was the polyanion. This concentration domain also allowed the obtaining of quasisoluble complexes.

REFERENCES

(1) A. Rembaum, *J. Macromol. Sci. Chem.* **A3**, 87 (1969)

(2) H. H. Schwartz, K. Richau, D. Paul, *Polym. Bull.* **25**, 95 (1991)

(3) C. K. Trinh, W. Schnabel, *Angew. Makromol. Chem.* **212**, 167 (1993)

(4) Xiang Yu, P. Somasundaran, *Coll. Surf. A. Physicochem. Eng. Aspects* **81**, 17 (1993)

(5) J. Kötz, S. Kosmella, *J. Coll. Interf. Sci.* **168**, 505 (1994)

(6) Y. Kikuchi,T. Koda, *Bull. Soc. Chem. Jpn.* **52**, 880 (1979)

(7) K. Kataoka, T. Akaike, Y. Sakurai, T. Tsuruta, *Makromol. Chem.* **179**, 1121 (1978)

(8) K. Kataoka, T. Tsuruta, T. Akaike,Y. Sakurai, *Makromol. Chem.* **181**, 1363 (1980)

(9) V. A. Kabanov, *Makromol. Chem., Macromol. Symp.* **1**, 101 (1986)

(10) V. A. Kabanov, A. V. Kabanov, *Macromol. Symp.* **98**, 601 (1995)

(11) A.S. Michaels, R. G. Miekka, *J. Phys. Chem.* **65**, 1765 (1961)

(12) A. S. Michaels, L. Mir, N. S. Schneider, *J. Phys. Chem.* **69**, 1447 (1965)

(13) A. Nakajima, H. Sato, *Bull. Inst. Chem. Res. Kyoto Univ.* **47**, 177 (1969)

(14) E. Tsuchida, J. Osada, K. Sanada, *J. Polym. Sci., Polym. Chem. Ed.* **10**, 3397 (1972)

(15) E. Tsuchida, Y. Osada, K. Abe, *Makromol. Chem.* **175**, 583 (1974)

(16) K. Abe, H. Ohno, E. Tsuchida, *Makromol. Chem.* **178**, 2285 (1977)

(17) E. Tsuchida, Y. Osada, K. Abe, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 767 (1976)

(18) W. Jaeger, Lu Trong Hong, B. Philipp, G. Reinisch, Ch. Wandrey, *"Polymeric Amines and Ammonium Salts*", Ghent, Belgium, 1979, Edited by E. J. Goethals, Pergamon Press Oxford and New York, 1980, p. 155

(19) J. Kötz, B. Philipp, V. Sigitov, S. Kudaibergenov, E. A. Bekturov, *Coll. Polym. Sci.* **266**, 906 (1988)

(20) V. A. Kabanov, A. B. Zezin, M. I. Mustafaev, V. A. Kasaikin, *"Polymeric Amines and Ammonium Salts*", Ghent, Belgium, 1979, Edited by E. J. Goethals,

Pergamon Press Oxford and New York, 1980, p. 173

(21) S. K. Chatterjee, D. Zadav, S. Ghosh, A. M. Kham, *J. Polym. Sci., Polym. Chem. Ed.* **27**, 3855 (1989)

(22) B. Philipp, J. Kötz, K.-J. Linow, H. Dautzenberg, *Polym. News* **16**, 106 (1991)

(23) S. Ahmed, J. Xia, P. L. Dubin, *J. Macromol. Sci.- Pure. Appl. Chem.* **A31**, 17 (1994)

(24) V. A. Kabanov, A. B. Zezin, *Pure Appl. Chem.* **56**, 343 (1984)

(25) B. Philipp, H. Dautzenberg, K. J. Linow, J. Kötz, W. Dawydoff, *Progr. Polym. Sci.*, **14**, 91 (1989)

(26) E. Tsuchida, *J. Macromol. Sci.- Pure Appl. Chem.* **A31**, 1 (1994)

(27) T. Schindler, E. Nordmeier, *Polymer J.* **26**, 1124 (1994)

(28) V. V. Annenkov, V. A. Kruglova, N. L. Mazyar, *J. Polym. Sci. Part A: Polym. Chem.* **34** (1996)

(29) T. Tsuchida, S. Takeoka, *"Macromolecular Complexes in Chemistry and Biology"*, Eds. P. Dubin, J. Bock, R. Davis,D.N. Schulz,C.Thies, Springer-Verlag, Berlin, Heidelberg, 1994, p.183

(30) H. Dautzenberg, J. Hartmann, S. Grunewald, F. Brand, *Ber. Bunsenges. Phys. Chem.* **100**, 1024 (1996)

(31) T. Gillespie, *J. Polym. Sci. C* **3**, 31 (1963)

(32) L. H. Cragg, C. C. Bigelow, *J. Polym. Sci.* **15**, 177 (1955)

(33) S. Dragan, L. Ghimici, *Angew. Makromol. Chem.* **192**, 199 (1991)

(34) S. Dragan, M. Cristea, C. Luca, B. C. Simionescu, *J. Polym. Sci. Part A: Polym. Chem.* **34**, 3485 (1996)

(35) M. B. Huglin, L. Webster, Y. D. Robb, *Polymer* **37**, 1211 (1996)