

# Solution Properties of Some Cationic Polyelectrolytes

LUMINITA GHIMICI\*, MARIA BERCEA, ECATERINA STELA DRAGAN

“Petru Poni” Institute of Macromolecular Chemistry, 41A Aleea Grigore Ghica Voda, 700487, Iasi, Romania

The solution properties of some cationic polyelectrolytes with ammonium quaternary centers either attached to an acrylic macromolecular chain (polycation PDMAEMQ type) or in the backbone (polycation PCA type) have been measured in order to identify how charge density, polyelectrolyte concentration, solvent polarity as well as temperature influence their behavior in solution by viscometric, conductometric and rheological methods. The viscometric data revealed that all copolymers PDMAEMQ exhibit a polyelectrolyte behaviour in water and methanol and were plotted in the terms of Rao equation. Straight lines were obtained in all cases, allowing the calculation of intrinsic viscosity,  $[\eta]$ . Data from the conductometric study emphasized for PDMAEMQ<sub>50</sub> and PCA<sub>5</sub> an increase of the equivalent conductivity values,  $\Lambda$ , with decreasing concentration over the whole concentration range in water, methanol and their mixture (1:1). The comparison between the complex viscosity values  $\eta^*$ , at the same polymer concentration,  $c_p = 4\%$ , for PCA<sub>5</sub>D<sub>1</sub> and PCA<sub>5</sub> shows higher values in the whole interval of temperatures under study ( $T = 10-60\text{ }^\circ\text{C}$ ) and a pseudoplastic behaviour at temperatures higher than  $50\text{ }^\circ\text{C}$  for the former system.

Keywords: polyelectrolyte, viscosity, electrolytic conductivity, rheology

Polyelectrolytes are macromolecules bearing repeating charged or chargeable groups that can dissociate in suitable solvents into charges bound to the chain and an equivalent number of counterions free in solution. Both the attractive and repulsive electrostatic interactions between these charged species represent dominant factors influencing the properties of polyelectrolytes in solution. Moreover, if ionic polymers contain hydrophobic structural components, then these polymers, called amphiphilic polyelectrolytes, exhibit solution properties resulting from the competition between the hydrophobic and electrostatic interactions. Besides the theoretical interest, both the electrostatic and hydrophobic interactions play an important role in biological systems as well as in technological and environmental applications, such as: paper processing, film coating, flocculants, biomedical devices and drug formulations, membranes, and so on [1]. These interactions are strongly sensitive to some parameters, like: the chain length, the charge density, the polyelectrolyte concentration, the counterion type, the ionic strength, the solvent polarity, the length and content of hydrophobic groups, etc. [2-7].

In this study, we address the issue of polyion-counterion interactions under different experimental conditions (charge density, polyelectrolyte concentration and solvent polarity) for some cationic polyelectrolytes, which possess the ammonium quaternary centers either attached to an acrylic macromolecular chain (N-benzyl-N,N-dimethylammonium chloride - polycation PDMAEMQ type) or located in the backbone (N,N-dimethyl-2-hydroxypropylammonium chloride - polycation PCA type) by viscometric and conductometric methods. In addition, the rheological behaviour of polyocations of type PCA has been investigated as a function of polyelectrolyte concentration and temperature.

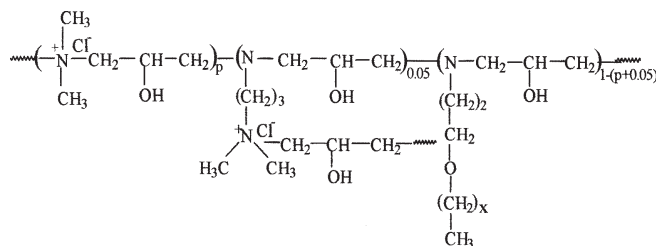
## Experimental part

### Materials

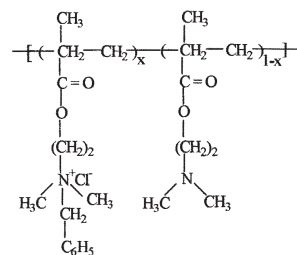
The cationic polyelectrolytes PCA<sub>5</sub> and PCA<sub>5</sub>D<sub>1</sub> were synthesized by condensation polymerization of

\* email: lghimici@icmpp.ro

epichlorohydrin (ECH) with dimethylamine (DMA), N,N-dimethyl-1,3-diaminopropane (DMDAP) – polymer PCA<sub>5</sub>, and primary amine with nonpolar chain, decyloxypropylamine - polymer PCA<sub>5</sub>D<sub>1</sub>, according to the method presented in detail elsewhere [8, 9]. Their general structure is presented in scheme 1.



$p = 0.95$ , polycation PCA<sub>5</sub>;  $p = 0.94$ ,  $x = 9$ , polycation PCA<sub>5</sub>D<sub>1</sub>



$x = 0.5$ , polycation PDMAEMQ<sub>50</sub>,  $x = 0.75$ , polycation PDMAEMQ<sub>75</sub>,

$x = 0.85$ , polycation PDMAEMQ<sub>85</sub>

Scheme 1

The definitions of the abbreviations of these polyocations are the followings: PC - polycation; A - asymmetrical diamine; D – the hydrophobic amine; the first number means mole percent of the polyfunctional amine and the last one means mole percent of the hydrophobic amine. Polyelectrolytes were purified by ultrafiltration (Hollow-Fiber Concentrator CH2A,

**Table 1**  
SEVERAL PROPERTIES OF THE QUATERNIZED PDMAEM SAMPLE

Sample	Cl <sub>i</sub> , %	mol% quaternary amino group	b <sup>a</sup> , nm	ξ
PDMAEMQ <sub>50</sub>	8	50	0.504	1.4
PDMAEMQ <sub>75</sub>	10.57	75	0.33	2.15
PDMAEMQ <sub>85</sub>	11.45	85	0.292	2.43

<sup>a</sup>) b = the average spacing between two vicinal ionized groups on the polyion; based on a spacing of 0.25 nm for vinyl groups

ξ = the charge density parameter, calculated according to references [11,12].

$$\xi = e^2 / \epsilon k T b, \quad (1)$$

e = the elemental charge, ε = the dielectric constant of the solvent, k = the Boltzmann constant and T = the temperature in ° K.

Amicon). Solids were obtained by vacuum freeze-drying (Beta 1-16, Christ, Germany). Polycations were characterized by the content in ionic chlorine (determined by potentiometric titration with 0.02 N aqueous AgNO<sub>3</sub> solution) (Cl<sub>i</sub>), total chlorine (determined by the combustion method – Schöniger technique) (Cl<sub>t</sub>) and intrinsic viscosity in 0.1M NaCl aqueous solution: Cl<sub>i</sub> 21.67%, Cl<sub>t</sub> 22.56%,  $[\eta]_{0.1M NaCl} = 108.31$  mL/g for PCA<sub>5</sub>; Cl<sub>i</sub> 21.32%, Cl<sub>t</sub> 22.11%,  $[\eta]_{0.1M NaCl} = 120.86$  mL/g for PCA<sub>5</sub>D<sub>1</sub>.

Copolymers with quaternary ammonium salt groups in the side chain, PDMAEMQ, were synthesized by the quaternization reaction of poly (N,N-dimethylaminoethyl methacrylate) (PDMAEM) with benzyl chloride (BC). PDMAEM has been synthesized, purified and characterized as previously described [10]. Starting from a polymer with average molar mass  $M_w$  42338 g.mol<sup>-1</sup> and  $M_w/M_n = 1.984$  (average contour length of  $L = 67.5$ nm) three polymers possessing different charge densities were obtained. Their general structure is also presented in scheme 1. Table 1 lists several properties of the quaternized PDMAEM samples.

All polyelectrolytes were dissolved in highly purified deionized water from a Milli-Q PF (Millipore, Switzerland). The concentrations of the stock solutions of the polycations were determined by potentiometric determination of the chloride counterion using a 736 GP Titrino, Metrohm, Switzerland) and from the solid content of these polycations.

#### Methods

The PDMAEM molar mass was determined by GPC with a Chromatograph PL-EMD 950 Evaporative Mass Detector type.

Viscometric measurements of the polyelectrolyte solutions were carried out at 25°C with a Viscologic TI 1 type viscometer .

Conductivity measurements were performed with a model 712 conductometer (Metrohm, Herisau, Switzerland) using a conductivity cell with platinized electrode. All measurements were carried out at 20°C under nitrogen atmosphere. The specific conductance of the highly purified water in the measuring vessel was always in the range  $2 \cdot 10^{-7}$  to  $4 \cdot 10^{-7}$  S.cm<sup>-1</sup>.

The rheological measurements were performed by using a CVO50 Rheometer with parallel plate geometry

(60 mm diameter) and thermal control by Peltier effect. Dynamic shear oscillation measurements have been carried out in the frequency range of 0.01 – 100 rad/s under a shear stress  $\sigma = 1$  Pa. The oscillatory shear measurements were conducted within the linear viscoelastic regime of the samples under frequencies and strains for which the storage ( $G'$ ) and loss ( $G''$ ) moduli as well as the loss angle ( $\delta$ ) are independent of the strain amplitude.

## Results and discussion

### Viscosity and conductivity measurements

The investigation of transport properties, such as viscosity and conductivity, is very useful in the study of polyion-counterion interactions depending on some experimental variables. Perhaps the most significant parameter affecting the solution properties of a polyelectrolyte is the linear charge density whose importance has been promoted by Manning in his counterion condensation theory [11,12]. The reduced viscosity ( $\eta_{sp}/c_p$ ) – polymer concentration ( $c_p$ ) profiles in water and methanol for the copolymers PDMAEMQ are illustrated in figures 1a and 1b.

Some behaviours may be identified: *a*) all copolymers had a polyelectrolyte behaviour in water, that is, a typical upturn of the  $\eta_{sp}/c_p = f(c_p)$  variations at low concentration arising from intra- and intermolecular repulsive electrostatic interactions (fig. 1a); *b*) the reduced viscosity values, at the same polymer concentration, increased in the order PDMAEMQ<sub>50</sub> < PDMAEMQ<sub>75</sub> < PDMAEMQ<sub>85</sub>, that means with the increasing charge density; a higher content of the quaternized units in the copolymer, at constant degree of polymerization, brought about an increase of the dimension of the coil; *c*) a polyelectrolyte behaviour of PDMAEMQs in methanol was also observed (fig.1b), due to the capacity of the ionizable groups along the chain to dissociate in this polar solvent. At the same time, for the same copolymer, the reduced viscosity value at a given concentration was lower in methanol than in water. This means that the lower dielectric constant of methanol ( $\epsilon = 32.70$ ) in comparison with H<sub>2</sub>O ( $\epsilon = 78.39$ ) led to a decrease of the dissociation of the ionizable groups and consequently, of the free charges of the polycation which resulted in less extended coils.

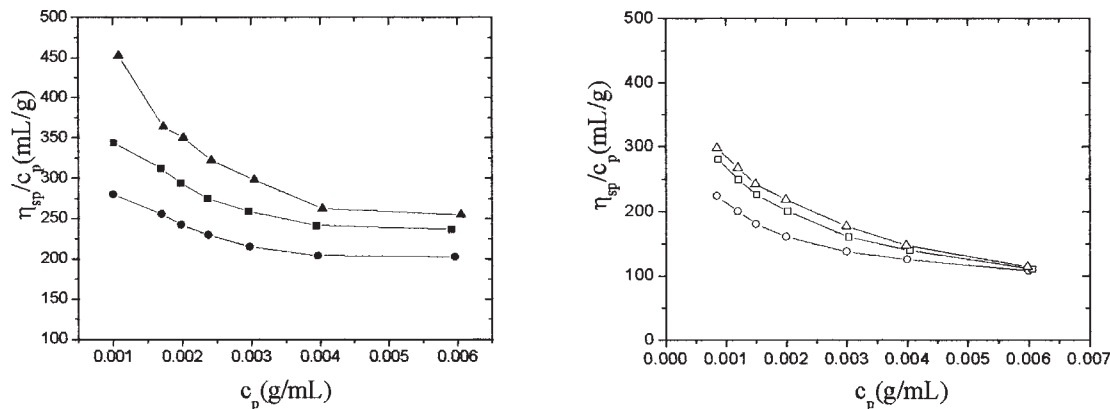


Fig. 1. Variation of the reduced viscosity ( $\eta_{sp}/C$ ) versus the concentration of the copolymers PDMAEMQ, at 25°C: a) (in H<sub>2</sub>O) (●) PDMAEMQ<sub>50</sub>, (■) PDMAEMQ<sub>75</sub>, (▲) PDMAEMQ<sub>85</sub>; b) (in methanol) (○) PDMAEMQ<sub>50</sub>, (□) PDMAEMQ<sub>75</sub>, (△) PDMAEMQ<sub>85</sub>.

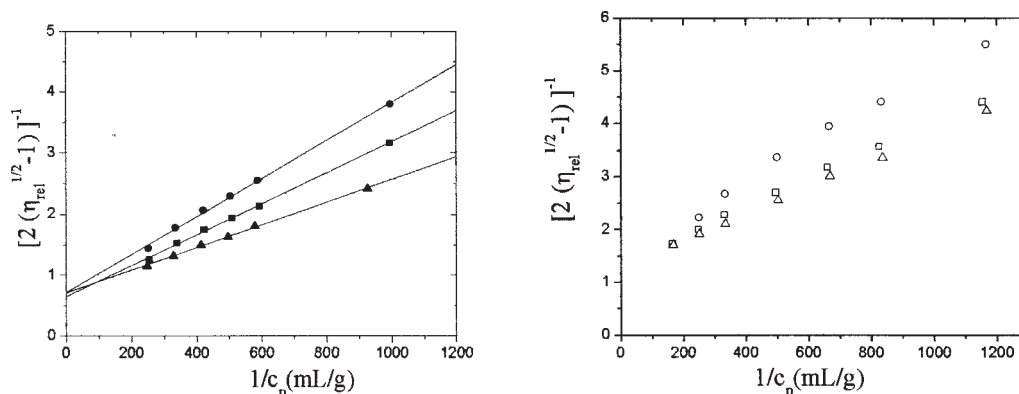


Fig. 2: Representation of the Rao equation for PDMAEMQs: a) (in H<sub>2</sub>O) (●) PDMAEMQ<sub>50</sub>, (■) PDMAEMQ<sub>75</sub>, (▲) PDMAEMQ<sub>85</sub>; b) (in methanol) (○) PDMAEMQ<sub>50</sub>, (□) PDMAEMQ<sub>75</sub>, (△) PDMAEMQ<sub>85</sub>.

Obviously, it was not possible to extrapolate the reduced viscosity to zero concentration in order to determine the intrinsic viscosity  $[\eta]$ . This problem is usually solved either by addition of low-molar-mass electrolyte or by means of empirical equations, like Fuoss equation [13], Rao [14] applicable for describing the viscosity of diluted to moderately concentrated neutral polymer solution and  $\eta_r$  values from 1 to about 100. As  $\eta_r$  values for all samples under study lied in this range, the curves shown in figures 1a and 1b were linearized applying Rao equation (2):

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta] c} - \frac{a-1}{2.5} \quad (2)$$

where  $\eta_r$  = the relative viscosity and  $a$  is a constant for a given polymer-solvent system. As can be observed in figures 2a and 2b straight lines were obtained for all polyelectrolytes, both in water and methanol, showing that the Rao equation is suitable to describe the viscometric behaviour of these samples and to estimate the  $[\eta]$  values in salt-free solutions. The applicability of the Rao equation to describe the viscosity of the polymer solution was also found in the case of other polyelectrolytes [2, 3, 7].

The calculated values for the intrinsic viscosity,  $[\eta]$ , are summarized in table 2. The lower  $[\eta]$  values of the copolymers in methanol confirmed the reduction of the hydrodynamic dimension of the polyion coils in methanol.

**Table 2**  
INTRINSIC VISCOSITY ( $[\eta]_0$ ) AND OVERLAP CONCENTRATION ( $c^*$ ) FOR PDMAEMQ COPOLYMERS IN WATER AND METHANOL

Sample	Water		Methanol	
	$[\eta]$ ml/g	$c^* = 1/[\eta]$ g/ml (mol.L <sup>-1</sup> )	$[\eta]$ ml/g	$c^* = 1/[\eta]$ g/ml (mol.L <sup>-1</sup> )
PDMAEMQ <sub>50</sub>	322.58	$3.1 \times 10^{-3}$ ( $1.41 \times 10^{-2}$ )	286.53	$3.65 \times 10^{-3}$ ( $1.66 \times 10^{-2}$ )
PDMAEMQ <sub>75</sub>	400.00	$2.5 \times 10^{-3}$ ( $9.92 \times 10^{-3}$ )	374.53	$2.67 \times 10^{-3}$ ( $1.05 \times 10^{-2}$ )
PDMAEMQ <sub>85</sub>	537.25	$1.86 \times 10^{-3}$ ( $7 \times 10^{-3}$ )	396.82	$2.52 \times 10^{-3}$ ( $9.49 \times 10^{-3}$ )

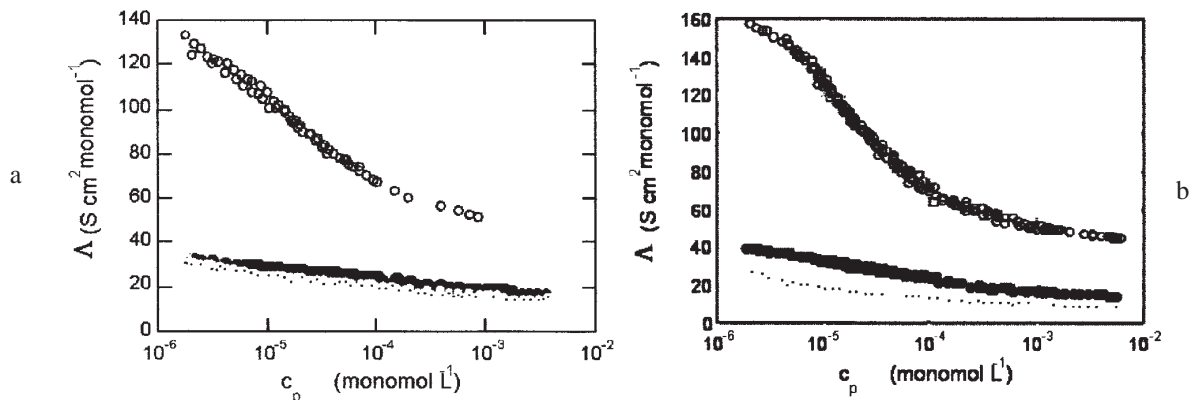


Fig. 3: Equivalent conductivity,  $\Lambda$ , as a function of concentration for polycations in various solvents for: a) PDMAEMQ<sub>50</sub>, b) PCA<sub>5</sub>  
 (○) water, (●) water/methanol 1:1, (⊙) methanol. T = 20°C.

It is a well-known fact that polyelectrolyte molecules are highly expanded in salt free solutions, and consequently, the overlap concentration,  $c^*$ , which is the limit between dilute and semidilute regim, is very low in polyelectrolyte solutions. We have determined  $c^*$  values by means of the equation (3) [15]:

$$c^* = 1/[\eta] \quad (3)$$

where  $[\eta]$  = intrinsic viscosity.  $c^*$  values of the PDMAEMQ copolymers are also summarized in table 2. As it was expected the overlap concentration decreased as the ionic content of the copolymer increased.

The effect of the polyelectrolyte concentration and dielectric constant of the solvent on the electrolytic conductivity of PDMAEMQ<sub>50</sub> and PCA<sub>5</sub> solutions were analyzed and interpreted in terms of the Manning's theory. The conductivity investigations were performed by measuring the specific conductance ( $\kappa$ ) as a function of the polymer concentration ( $c_p$ ). Specific conductance, defined by Fuoss [16], includes the contributions of counterions, co-ions and polyions at the current transport and depend both on the number of ions per unit volume and on their mobility. We have used the values of  $\kappa$  to obtain the experimental equivalent conductivity of polyelectrolyte solution [17]. The equivalent conductivity of polyelectrolyte was calculated with the equation (4)

$$\Lambda = (\kappa - \kappa_0) / c_p \quad (4)$$

where:

- $\kappa$  is the electrolyte conductivity of solution;
- $\kappa_0$  is the electrolyte conductivity of the solvent;
- $c_p$  is the equivalent concentration of the polyelectrolyte in mol.L<sup>-1</sup>.

Figures 3a and 3b show the equivalent conductivity dependence on the polymer concentration in water, methanol and mixture of water/methanol 1:1 for polycations PDMAEMQ<sub>50</sub> and PCA<sub>5</sub>.

The conductivity has been measured in a wide polyion concentration range (from  $1 \cdot 10^{-6}$  up to about  $5 \cdot 10^{-3}$  mol.L<sup>-1</sup>) to cover the whole dilute region.

The equivalent conductivity increased with decreasing concentration for both polycations in water, methanol and the mixture of both. Polycations under study are highly charged polyions having the charge density parameter  $\xi > 1$ . In this case, Manning's counterion condensation theory predicts that a fraction of counterions condenses onto the polyion to make the effective charge density equal to unity. The condensed counterions do not participate to the electrical conduction

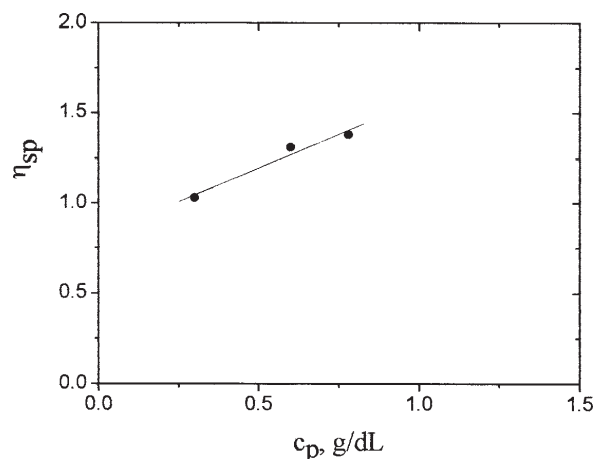


Fig. 4. Variation of the specific viscosity ( $\eta_{sp}$ ) versus the concentration ( $c_p$ ) for PCA<sub>5</sub>D<sub>1</sub>.

whereas the free counterions behave as in a simple salt solution. On dilution, more counterions are far away from the polyion increasing the equivalent conductivity. At the same time, the equivalent conductivity value of a given concentration decreases with decreasing dielectric constant. The addition of methanol, a less polar solvent, into water decreased the medium polarity which brought about the weakening of the dissociation along the polyion backbone; the number of free ions decreased and consequently, the equivalent conductivity values decreased, too.

#### Rheological measurements

Rheological measurements can be fruitfully employed to probe the delicate balance between the factors that contribute to the behavior of these polyelectrolytes in solution including hydrophobic and electrostatic interactions.

The experimental rheological data in figure 4 for the polycation PCA<sub>5</sub>D<sub>1</sub> in salt-free aqueous solution emphasize the influence of the concentration on the complex viscosity ( $\eta^*$ ) of polycation solutions in the frequency range investigated at 20°C.

Thus, at constant temperature, the PCA<sub>5</sub>D<sub>1</sub> aqueous solutions had a Newtonian behavior, that is, the viscosity was independent upon the frequency value, irrespective of the polymer concentration. Furthermore, the shapes of the curves were quite similar and, for a given frequency, the  $\eta^*$  values increased with increasing polymer concentration. The specific viscosity,  $\eta_{sp}$ ,

defined as  $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ , where  $\eta_0$  is the zero shear viscosity and  $\eta_s$  is the solvent viscosity, varied as a function of  $c_p$  as  $\eta_{sp} \sim c_p^{0.75}$ , as shown in figure 5.

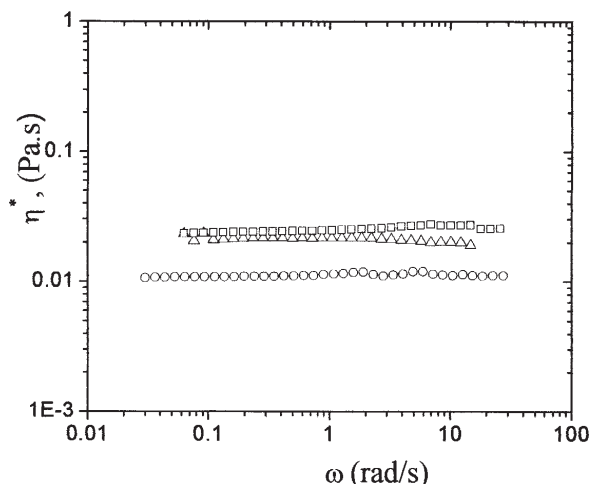


Fig. 5. Dynamic complex viscosity  $\eta^*$  ( $\omega$ ) as a function of frequency ( $\omega$ ) for  $\text{PCA}_5\text{D}_1$  in water at  $T = 20^\circ\text{C}$ ,  $\text{H}_2\text{O}$  at  $c_p$ : (○) 2%; (Δ) 4%; (□) 6%

The exponent of the dependence of  $\eta_{sp}$  on  $c_p$  (0.75) is not far from what is theoretically predicted for polyelectrolytes in the semidilute unentangled regime ( $\eta_{sp} \sim c_p^{0.5}$ ) [18]. Hence, one can assume that, at these concentrations, the polycation  $\text{PCA}_5\text{D}_1$  was situated in the semidilute unentangled regime, where the intermolecular interactions prevail over the intramolecular ones. Thus, the increase of  $\eta^*$  was attributed to an enhanced number of interchain hydrophobic associations as the polycation concentration increased.

The temperature effect on the behavior of polyelectrolyte solutions is complex and by no means

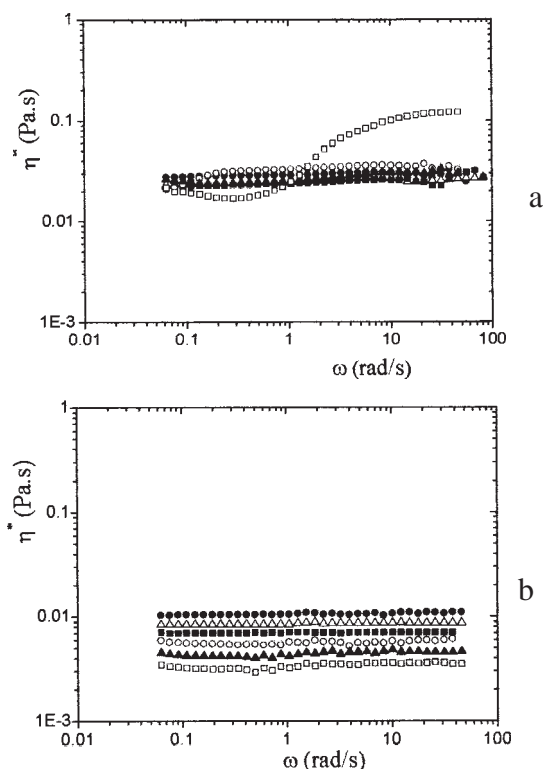


Fig. 6. Complex viscosity ( $\eta^*$ ) as a function of the frequency ( $\omega$ ) for (a)  $\text{PCA}_5\text{D}_1$  and (b)  $\text{PCA}_5$ : (●) 10 °C; (Δ) 20 °C; (■) 30 °C; (○) 40 °C; (▲) 50 °C; (□) 60 °C;  $c_p = 4\%$ .

easy to elucidate. In fact, the influence of temperature may be strongly dependent on the nature of polymer and of the solvent quality. In the case of  $\text{PCA}$  polycation solutions with  $c_p$  of 4%, the variation of the complex viscosity as a function of frequency at various temperatures ranging from 10 to 60 °C is shown in figures 6a and 6b.

The complex viscosity values slightly decreased for temperatures between 10 and 40 °C followed by an increase for higher temperatures. The decrease in coil dimensions suggested a loss of the interchain interactions with increasing temperature. On the other hand, the pronounced viscosity increase observed at 50 °C reflected an increase in hydrophobic associations being well known that hydrophobe-hydrophobe interaction is an endothermic process so, favored at higher temperatures. This rise in viscosity with temperature was also observed in the case of other associating polymers [19,20]. Another aspect was that at  $T = 60^\circ\text{C}$  the rheological behaviour of 4%  $\text{PCA}_5\text{D}_1$  solution has been similar with that classically observed for semi-dilute polymer solutions: a Newtonian plateau at frequency up to about  $\omega = 1$  and a slight shear-thinning effect at higher frequency attributed to the disruption of intermolecular hydrophobic association under shear. The solution rheological behaviour of the polyelectrolyte without nonpolar side chains,  $\text{PCA}_5$ , with  $c_p$  of 4%, was investigated for comparison. As it is obvious from figure 6b, the Newtonian plateau was kept over the entire range of frequency and temperatures. For  $\text{PCA}_5$  the temperature effect has been qualitatively different from that observed for the solution of  $\text{PCA}_5\text{D}_1$ , at the same concentration, i.e., the  $\eta^*$  values decreased with increasing temperature in all temperature interval under investigation. Comparing the complex viscosity at the same value of frequency and temperature for  $\text{PCA}_5\text{D}_1$  and  $\text{PCA}_5$  solutions of  $c_p = 4\%$ , higher values were observed in the case of the former polycation, which was an indication of an increased number of hydrophobic associations.

## Conclusions

Copolymers PDMAEMQs had a polyelectrolyte behaviour both in water and methanol; the reduced viscosity values, at the same polymer concentration, increased with increasing charge density.

The equivalent conductivity values of  $\text{PCA}_5$  and PDMAEMQ<sub>50</sub> polycations solutions increased with dilution and the dielectric constant of the solvent.

At constant temperature,  $T = 20^\circ\text{C}$ , the  $\text{PCA}_5\text{D}_1$  aqueous solutions had a Newtonian behaviour and the  $\eta^*$  increased with increasing concentration in the entire frequency range under study.

For  $\text{PCA}_5\text{D}_1$  and  $\text{PCA}_5$  solutions of  $c_p = 4\%$ , higher values of the complex viscosity were observed in the case of the former polycation, at the same value of frequency and temperature, which is an indication of an increased number of hydrophobic associations.

## References

1. WANDREY, C., HUNKELER, D. Handbook of Polyelectrolytes and Their Applications, Tripathy, S.K., Kumar, J., Nalwa, H.S. (Eds.), American Scientific Publisher USA; 2002, 2, Chapter 5, p 147
2. GHIMICI, L., DRAGAN, S., Env. Eng. Manag. J., 1, 2002, p. 333
3. DRAGAN, S., MIHAI, M., GHIMICI, L., Eur. Polym. J., 39, 2003, p. 1847

4. NAGY, M., Colloids Surf., **250**, 2004, p.467
5. DRAGAN, S., GHIMICI, L., WANDREY, C., Macromol. Symp. **211**, 2004, p. 107
6. BORDI, F., CAMETTI, C., GILI, T., SENNATO, S., ZUZZI, S., DOU, S., COLBY, R.H., J. Chem. Phys. **122**, 2005, p. 234906
7. GHIMICI, L., NICHIFOR, M., J. Colloid Interface Sci., **302**, 2006, p. 589
8. DRAGAN, S., GHIMICI, L., Angew. Makromol. Chem., **192**, 1991, p. 199
9. DRAGAN, S., GHIMICI, L., Bull. Inst. Pol. Iasi **XLIV**, 1998, p. 109
10. DRAGAN, S., PETRARIU, I., DIMA, M., J. Polym. Sci. Polym. Chem. Ed., **19**, 1981, p. 2881
11. MANNING, G.S., J. Chem. Phys., **51**, 1969, p. 924
12. MANNING, G.S., J. Phys. Chem., **79**, 1975, p. 262
13. FEDORS, R.F., Polymer, **20**, 1979, p. 225
14. RAO, M.V.S., Polymer, **34**, 1993, p. 592
15. FRISH, H.L., SIMHA, R. The viscosity of colloidal suspension and macromolecular solution, Academic Press, New York, 1956
16. MAC FARLANE, R., FUOSS, R.M., J. Polym. Sci., **34**, 1957, p. 13
17. VINK, H., J. Chem. Soc., Faraday Trans. 1 **77**, 1981, p. 2439
18. RUBINSTEIN, M., COLBY, R.H., DOBRYNIN, A.V., Phys. Rev. Lett., **73**, 1994, p. 2776
19. BIGGS, S., SELB, J., CANDAU, F., Polymer, **34**, 1993, p. 580
20. HWANG, F.S., HOGEN-ESCH, T.E., Macromolecules, **28**, 1995, p. 3328

---

Manuscript received: 10.06.2008