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Charge Density, Solvent Polarity and Counterion Nature Effects on the Solution Properties of Some Polycations

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Summary: The electrolytic conductivity and solution viscosity of some strong polycations, which possess the 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 counterion nature influence the ultimate solution properties. The investigations reveal for all polycations an increase of the equivalent conductivity with decreasing concentration. The onset of the strong increase shifts to lower concentration if the charge density augments. Polyelectrolyte behavior was observed for PCA_5D_1 in the mixture of water/methanol for all solvent compositions employed and in the mixture of water/acetone up to 60 vol % of acetone content. At all experimental concentrations the reduced viscosity decreases with the dielectric constant of the mixed solvent. Furthermore, the specific interaction between several mono- and divalent counterions with some of these polycations was clearly proved by conductometric measurements.

Keywords: electrolytic conductivity; polycations; polyelectrolytes; polyion-counterion interactions

Introduction

Polyelectrolytes are increasingly important as advanced polymers in many fields including environmental technologies, biotechnology, and medicine.[1-2] However, their solution behavior and structure-properties interdependencies are far from being fully understood. Both intramolecular and intermolecular electrostatic interactions represent dominant factors influencing the properties of polyelectrolytes in solution.[3-5] The significance of intermolecular interactions has been suggested by Ise et al.[6,7] as well as Priel et al.[8] and was recently demonstrated and approved by viscometric experimental studies employing polyelectrolyte-surfactant complexes[9], stiff-chain polyelectrolytes[10], branched polyelectrolytes[11], as well as spherical architectures[12-14] as model systems. Viscosity studies are limited in their precision if the polymer concentration decreases, in particular, if the molar masses are

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not very high. On the other hand, electrolytic conductivity studies in aqueous solution, if carefully performed, can be extended up to concentrations far below the critical overlap concentration[5, 15] of low and medium molar mass polyelectrolytes only limited by the purity of the solvent and the onset of its self-dissociation. Therefore, electrolytic conductivity measurements are a powerful tool to study the polyion - counterion interactions dependent on the polyion's chemical structure, concentration, and the medium properties.[5, 16-18] It is well recognized that in solvents without added salt the electrostatic interaction between polyions and their counterions primarily depends on the polyion charge density,[19-21] though the influence of the chemical structure has been reported, too.[22]

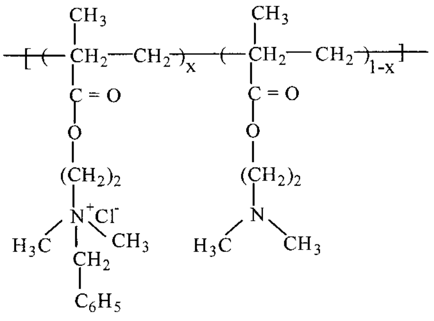
In this study, the effect of charge density, polyelectrolyte concentration, as well as dielectric constant of the solvent on the viscometric behavior and the electrolytic conductivity of some polycations which possess the ammonium quaternary centers either attached to an acrylic macromolecular chain (polycation PDMAEMQ type) or in the backbone (polycation PCA type), have been analyzed in aqueous solution and aqueous mixtures. Reports on the electrolytic conductivity of polyelectrolytes in non-aqueous solution or in mixed solvents are relatively scarce, though can provide important information about electrostatic interactions.[23-26] In addition, specific interactions between some polycations of the PCA type and various counterions have been examined and will be discussed.

Experimental

Materials

Copolymers of the PDMAEMQ type with quaternary ammonium salt groups in the side chain, and with controlled quaternization degrees were synthesized by quaternization of poly(N,N-dimethylaminoethyl methacrylate) (PDMAEM) (M_w = 42340 g/mol and M_w/M_n = 1.98) with benzyl chloride (BC).[27] Their general structure is presented in Scheme 1.

Table 1 lists some characteristics of the copolymers. The charge density parameter in Table 1 is defined as $\xi = l_B/b =$, with b the average charge distance, $l_B = e^2/4\pi\varepsilon kT$ the Bjerrum length containing e the elemental charge, ε the dielectric constant of the solvent, k the Boltzmann constant, and T the temperature in K.[28,29]



x = 0.5, polycation $PDMAEMQ_{50}$, x = 0.75, polycation $PDMAEMQ_{75}$,
x = 0.85, polycation $PDMAEMQ_{85}$

Scheme 1. Chemical structure of the PDMAEMQ type polyelectrolytes

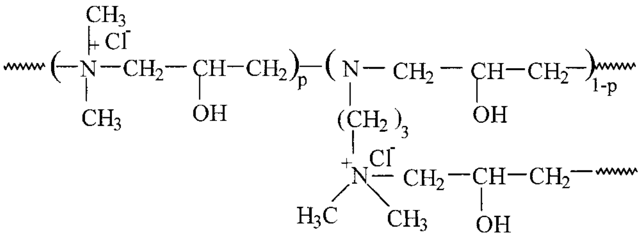
Table 1. Characteristics of the quaternized PDMAEM samples.

Sample	Cl_i	Quaternization degree[a)]	$b^{b)}$	ξ
	%	mol.-%	nm	
$PDMAEMQ_{50}$	8	50	0.50	1.42
$PDMAEMQ_{75}$	10.57	75	0.33	2.15
$PDMAEMQ_{85}$	11.45	85	0.29	2.43

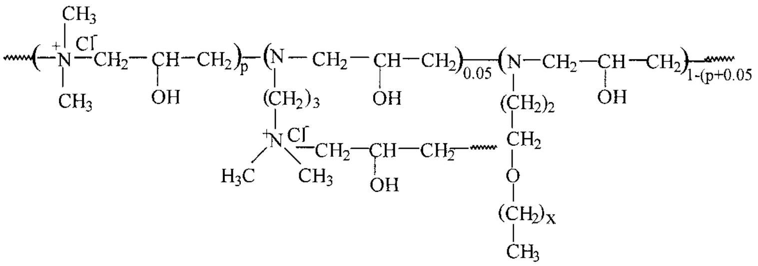
[a)] calculated on the basis of the ionic chlorine content;

[b)] based on 0.25 nm for vinylic polymers.

The cationic polyelectrolytes of the PCA type were synthesized by polycondensation of epichlorohydrin (ECH) with dimethylamine (DMA) and N,N-dimethyl-1,3-diaminopropane (DMDAP) – polymer PCA_5, and primary amines with non-polar chains (hexyloxypropylamine - polycation PCA_5H_1 and decyloxypropylamine - polycation PCA_5D_1, according to the method presented in detail elsewhere.[30,31] Their general structures are presented in Scheme 2.



$p = 0.95$, polycation PCA_5



$p = 0.94$, $x=5$, polycation PCA_5H_1; $p = 0.94$, $x=9$, polycation PCA_5D_1

Scheme 2. Chemical structure of the PCA type polyelectrolytes

The definitions of the acronyms of these polycations are the followings: PC – polycation; A – asymmetrical amine; H, D – hydrophobic amine, the first index number designates mole percent of the polyfunctional amine whereas the last one stands for mole percent of the hydrophobic amine. All polycations were purified by ultrafiltration (Hollow-Fiber Concentrator CH2A, Amicon, USA) and solid polymers were obtained after vacuum freeze-drying (Beta 1-16, Christ, Germany).

Cationic polyelectrolytes of the PCA type were characterized by the content in ionic chlorine (determined by potentiometric titration with 0.02 N aqueous $AgNO_3$ solution) (Cl_i), total chlorine (determined by the combustion method – Schöniger technique) (Cl_t) and intrinsic viscosity, $[\eta]$, in 1 M NaCl aqueous solution: $Cl_i = 21.67\%$, $Cl_t = 22.56\%$, $[\eta]_{1M\ NaCl} = 56.6$ ml/g at 25 °C for PCA_5; $Cl_i = 19.82\%$, $Cl_t = 19.79\%$, $[\eta]_{1M\ NaCl} = 39.5$ ml/g for PCA_5H_1; $Cl_i = 20.66\%$, $Cl_t = 21.03\%$, $[\eta]_{1M\ NaCl} = 45.0$ ml/g for PCA_5D_1.

Methods

Viscometric measurements of the polyelectrolyte dissolved in water, methanol, mixtures of water/methanol, or water/acetone were carried out at 25 ± 0.03 °C using an Ubbelohde type viscometer with automatic internal dilution (Viscologic TI1, SEMATech, France). All aqueous polymer solutions were prepared in double-distilled water before diluting with the organic solvent.

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 ± 0.03 °C under nitrogen atmosphere. The polyelectrolyte was dissolved in highly purified deionized water from a Milli-Q PF (Millipore, Switzerland). The specific conductance of the water in the measuring vessel was always in the range 2×10^{-7} to 4×10^{-7} S cm^{-1}.

Results and discussion

Charge Density Effects

The reduced viscosity (η_{red}) – polymer concentration (c_p) profiles in water for the copolymers PDMAEMQ are illustrated in Figure 1. All copolymers exhibit polyelectrolyte behavior in water, that is, a typical upturn of the $\eta_{red} = f(c)$ plots at low concentration. The reduced viscosity values, at the same polymer concentration, are seen to increase in the order PDMAEMQ$_{50}$ < PDMAEMQ$_{75}$ < PDMAEMQ$_{85,}$ that means with increasing charge density.

As the polymer concentration decreases the Debye length, $l_D = (4\pi N_A l_B \xi^{-1} c_p)^{-1/2}$ for polyelectrolyte solutions without added salt, increases resulting in an enhanced contribution of intermolecular repulsive interactions and, consequently, η_{red} increases. In terms of l_D, it also increases if the charge distance b decreases.

A more detailed discussion of the viscosity results can be performed on the basis of equation (1)[11], modified for $c_s \rightarrow 0$,

$$\eta_{red} = [\eta]_0 + k_H [\eta]_0^2 c_p + \frac{1}{160} \eta_H \left(\frac{4 \pi e^2 N_A}{M_p \varepsilon \varepsilon_0 k T} \right)^{1/2} \frac{Z_{eff}^{5/2}}{c_p^{1/2}} \qquad (1)$$

where the first two terms represent the Huggins equation. The third term considers polyelectrolyte behavior. Z_{eff} is the effective charge number per polymer, which was found to increase with decreasing ionic strength.[11]

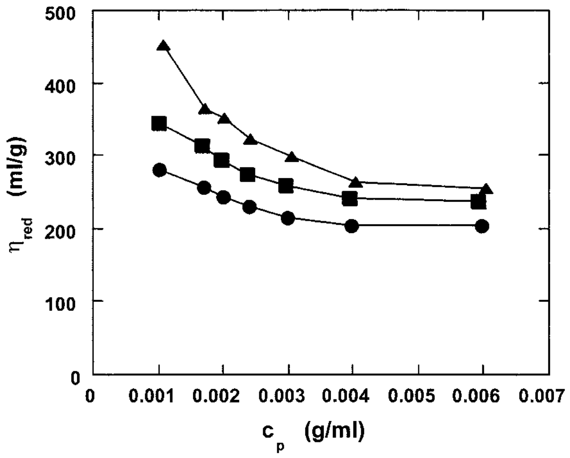


Figure 1. Reduced viscosity, η_{sp}/c, as a function of the concentration for polyelectrolytes with various charge distances in water: ▲Q85, ■ Q75, ● Q50,T = 25 °C

The Odijk theory predicts for the critical overlap concentration c* independence of the charge density for highly charged polyelectrolytes, if the highly dilute concentration regime is reached.[32] The calculation according to $c^* = (N_A L^2 a)^{-1}$ yields 5.75×10^{-3} monomol/L (contour length L = 34 nm calculated from the molar mass of PDMAEM; monomer unit length a = 0.25 nm), or 1.52×10^{-3} g/ml, 1.45×10^{-3} g/ml, and 1.2×10^{-3} g/ml for $PDMAEMQ_{85}$, $PDMAEMQ_{75}$, and $PDMAEMQ_{50}$, respectively. Comparison of these values with the experimental data of Figure 1 identifies the experimental range to be above c* where no change of the counterion activity is expected.[22]

The conductivity investigations were performed by measuring the specific conductivity, κ, as a function of the polymer concentration, c_p, where c_p is the equivalent concentration of the polyelectrolyte in monomol/L. The specific conductivity considers the contribution of counterions and polyions to the current transport and depends on both the number of ions per unit volume and on their mobility. The equivalent conductivity, Λ, of the polyelectrolyte was calculated from equation 2:[16, 33-36]

$$\Lambda = \frac{\kappa - \kappa_0}{c_p} = f_c\left(\lambda_c^0 + \lambda_p\right) \qquad (2)$$

where κ is the specific conductivity of the solution, and κ_0 is the specific conductivity of the solvent.

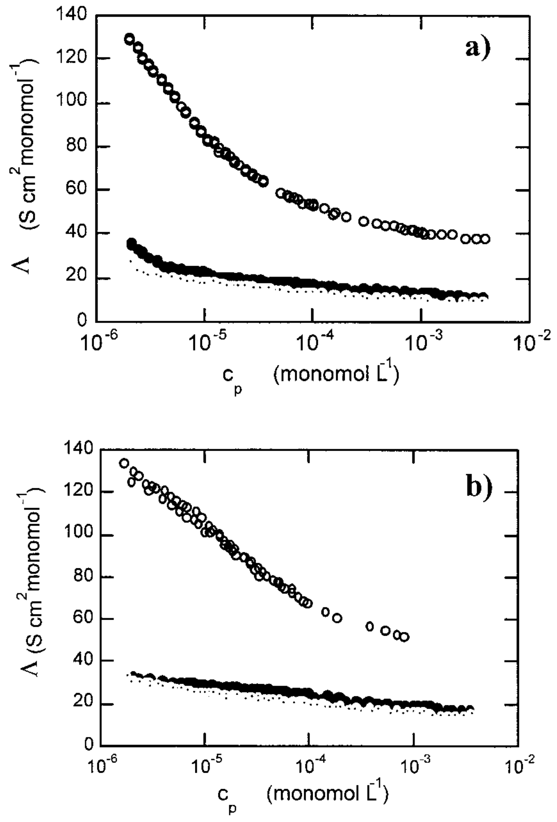


Figure 2. Equivalent conductivity, Λ, as a function of concentration for polycations of various charge density in various solvents: a) Q_{85}, b) Q_{50}; (○) water, (●) water/methanol 1:1, (•) methanol. T = 20 °C.

Figure 2a and Figure 2b show the concentration dependence of the equivalent conductivity in water for the two copolymers PDMAEMQ_{85} and PDMAEMQ_{50}. The conductivity has been measured over three orders of magnitude of the polyion concentration, from 2 x 10^{-6} up to about 5 x 10^{-3} monomol/L.

The equivalent conductivity increases with decreasing concentration for all polycations and solvents. It seems that the onset of the strong increase in water is shifted to a lower concentration for a higher charge density. Furthermore, the equivalent conductivity was determined to be higher for the lower charge density, over the whole concentration range. This is expected according to Equation (2) with f_c higher for the lower charge density sample

$PDMAEMQ_{50}$ if the equivalent conductivity is plotted vs. the equivalent concentration in monomol/L. No theory can explain the strong increase below a certain concentration quantitatively. However, an empirical model based on experimental findings has been proposed to explain this behavior.[15]

Solvent Polarity Effects

The environment that is the solution ionic strength and the solvent polarity also affects the electrostatic interaction between charged groups of the polyions and counterions. Extensive experimental data are available exploring the ionic strength influence. By comparison, reports on the electrolytic conductivity and viscometric behavior of polyelectrolytes in non-aqueous solution or in mixed solvents are relatively scarce,[23,26,37,38] though can provide important information about electrostatic interactions useful for practical activities. Therefore, the conductometric behavior of the PDMAEMQ polyelectrolytes was studied in methanol and solvent mixtures of water/methanol. The results presented in Figure 2a ($PDMAEMQ_{85}$) and Figure 2b ($PDMAEMQ_{50}$) clearly show differences by modifying the solvent quality; the equivalent conductivity decreases with the dielectric constant. To explain the solvent influence on the equivalent conductivity the change of the dielectric constant with its effects on the Bjerum length, l_B, and the Manning parameter, ξ, have to be considered. Both l_B and ξ increase if the dielectric constant of the solvent decreases yielding a lower f_c in Equation (2). As a consequence, less ions will participate in the current transport.

Also the viscosity of a polyelectrolyte solution depends on the solvent polarity, which affects the electrostatic interactions Varying the dielectric constant in the range of 78.5 to 33.3 the reduced viscosity, as a function of the polymer concentration, is shown for the polycation PCA_5D_1 dissolved in mixtures of water/methanol and water/acetone in Figure 3. The plots reveal that the reduced viscosity values increase with decreasing polymer concentration for all mixed solvents. This typical polyelectrolyte behavior, which is usually observed in salt-free aqueous solutions, occurs because the quaternary ammonium salt groups along the backbone can ionize in these polar solvent mixtures.

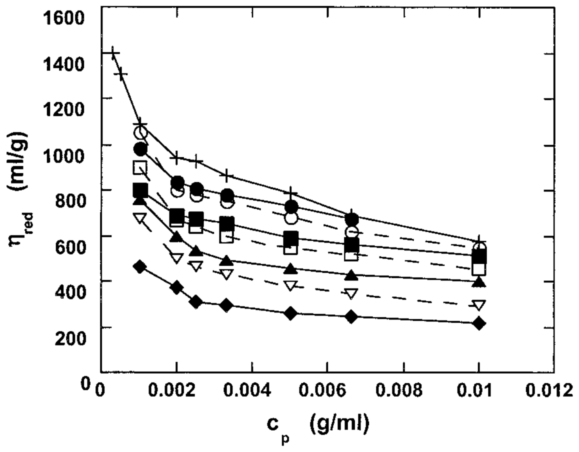


Figure 3. Influence of the dielectric constant on the reduced viscosity of PCA_5D_l in water/methanol: (+) 100/0; (●) 75/25; (■) 50/50; (▲) 25/75; (◆) and water/acetone: (O) 75/25; (□) 50/50; (V) 40/60.

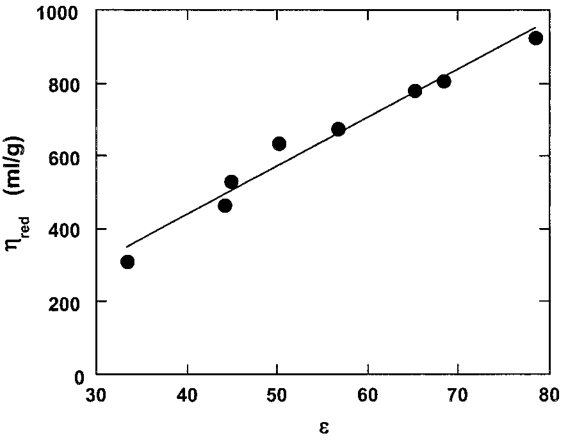


Figure 4. Reduced viscosity as a function of the dielectric constant, $c_p = 2.5\times10^{-3}$ g/mL.

For acetone, being a non-solvent for this polymer, the measurements also served to determine the acetone concentration above which the polyelectrolyte precipitates. Polyelectrolyte behavior of PCA_5D_l was observed in water/acetone mixtures with acetone contents up to 60 vol %, whereas, polymer precipitation occurred at higher acetone concentration.

It has been demonstrated that both Z_{eff} and the hydrodynamic radius r_H in Equation (1) increase with the dielectric constant[9]. This is in accordance with this study and is supported by plotting η_{red} vs. ε as it is illustrated in Figure 4 for $c_p = 2.5 \times 10^{-3}$ g/mL. Appropriate dependencies exist for the other concentrations. The overall contribution of the dielectric constant is more complicated since it affects according to Equation (1) the hydrodynamic radius, and Z_{eff} directly but has, additionally, a reciprocal influence.

Specific Interactions between Polyions and Counterions

This study was stimulated on the one hand by the fact that the most studies of counterion-polyion interactions were carried out in systems containing anionic polyelectrolytes and counterions; by comparison studies on cationic polyelectrolytes are relatively rare.[19,39-43] On the other hand the polyelectrolytes of the PCA type have proved efficiency in fields such as water purification,[44] formation of interpolyelectrolyte complexes,[45-47] or surface modification.[48,49] Since in these application areas low molar mass electrolytes can be present it was interesting to address this problem. Herein, selected conductometric results are presented. It is known that the electrical transport properties of polyelectrolyte solutions vary with the counterion type if low molar mass salts are added. Different strength of the interactions between these polymers and counterions was suggested. The theory predicts that the counterions associated with the polyion do not,[33] or only partially,[50] contribute to the conductivity whereas the free counterions behave as in a simple salt solution. Pursuing the variation of the molar conductivity of the polyelectrolyte (Λ_m) in different aqueous salt solutions as a function of the polyelectrolyte concentration for three polycations of the PCA type, the results plotted in Figure 5 and Figure 6 were obtained.

For polycations PCA_5 and PCA_5D_1, Figure 5 shows that the molar conductivity increases slowly with decreasing c_p in presence of univalent low molar mass salts. In the case of the SO_4^{2-} counterion, the curves exhibit a minimum between 1×10^{-3} unit mol/L and 3×10^{-3} unit mol/L. The minimum could be explained by the increase of the counterion-polyion interactions due to the capacity of the divalent anion to bind two cationic groups by intra- or interchain bridges. One may also observe that at the same polymer concentration, Λ_m decreases in the following sequence: $Cl^- > Br^- > I^- > SO_4^{2-}$, concluding the counterion binding increases in the same order. This sequence is similar to that found by other authors for different polycations.[39-43]

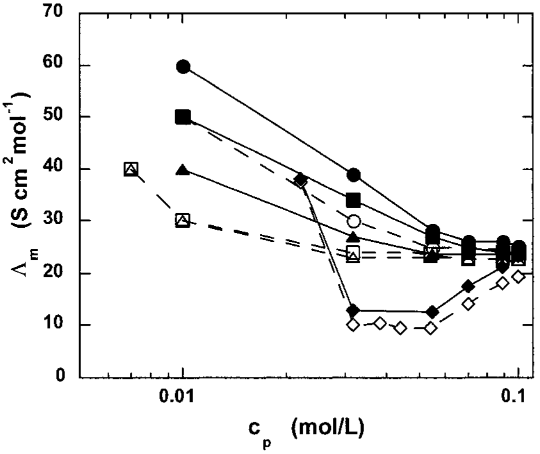


Figure 5. Influence of the counterion type on the concentration dependence of the molar conductivity (Λ_m) for PCA_5 (open symbols) and PCA_5D_I (filled symbols) in: (○) and (●) NaCl; (□) and (■) NaBr; (△) and (▲) NaI; (◇) and (◆) Na_2SO_4.

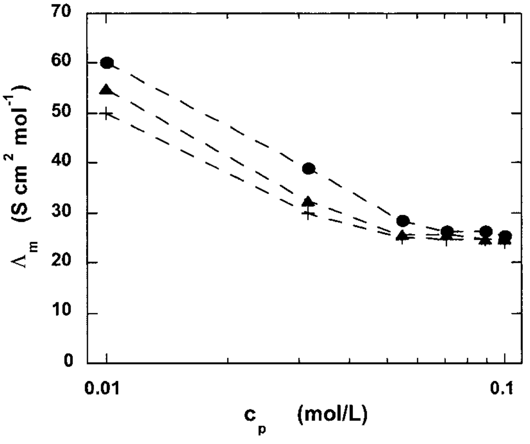


Figure 6. Influence of the polycation structure on the molar conductivity (Λ_m) in NaCl 10^{-3} M aqueous solution: (●) PCA_5D_I; (▲) PCA_5H_I; (+) PCA_5.

The increase of the polyion-counterion interactions for Cl^- compared with I^-, i. e. with the decrease of the radius of the hydrated counterion, indicates that the counterion binding is not accompanied by appreciable dehydration and suggests, as assumed by other authors,[51] that the counterion binding in the halide series is non-specific. The counterion condensation phenomenon is specific for polyelectrolytes depending on their charge density[28, 29] and persists in the presence of low molar mass salts even at salt concentration up to 1 M.[52]

To gain information about the influence of the polycation structure on the counterion binding, the interaction between NaCl and three cationic polyelectrolytes differing by both their content of (N,N-dimethyl-2-hydroxypropyleneammonium) chloride units in the main chain and the length of the non-polar side chain was monitored, (Figure 6).

For comparable polyelectrolyte concentrations, the Λ_m values decrease in the order: $PCA_5D_1 > PCA_5H_1 > PCA_5$, i. e. with decreasing of the non-polar chain length and increasing the charge density. This might be taken as an indication that the presence of a non-polar side chain in the polyelectrolyte repeat unit causes the decrease of the polyion-counterion interactions.

Conclusions

Flexible highly charged cationic quaternary ammonium polyelectrolytes soluble not only in water but also in solvents and solvent mixtures with dielectric constant up to 30 have been synthesized. The study of both molecular and medium influences on the electrolytic conductivity and the reduced viscosity reveal interesting dependencies, which have not been reported before. Excluding the influence of molar mass the effect of the charge density has been approved on the reduced viscosity in water and the electrolytic conductivity in water, methanol, and mixtures thereof. A linear dependency of the reduced viscosity on the dielectric constant has been estimated for these flexible polyelectrolytes though this could not be quantified with the existing theoretical approaches yet.

The description of the electrolytic conductivity behavior remains very complex. Existing theoretical approaches need reconsideration concerning the significance of intermolecular interactions for the charge transport. Furthermore, the concentration, structure, and medium dependent changes of the polyion-counterion interaction need to be incorporated. Appropriate and more detailed investigations are in progress. The experimental results presented herein are seen to be useful to contribute to such approaches.

Acknowledgement

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[1] S. K. Tripathy, J. Kumar, H. S. Nalwa, Eds., “*Handbook ofpolyelectrolytes and their applications", Vol. 1-3*, Am. Scientific Publishers, 2002.

[2] H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel, D. Stscherbina, “*Polyelectrolytes: Formation, Characterization, Application"*, Carl Hanser, München 1994.

[3] M. Mandel in *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds., New York 1988, Vol. 11, p 739.

[4] K. S. Schmitz, “*Macroions in Solution and Colloidal suspension"*, VCH, New York 1993.

[5] C. Wandrey, D. Hunkeler, in “*Handbook ofpolyelectrolytes and their applications",* S. K. Tripathy, J. Kumar, H. S. Nalwa, Eds., Am. Scientific Publishers, 2002, Vol. 2, p. 147-172.

[6] J. Yamanaka, H. Matsuoka, H. Kitano, M. Hasegawa, N. Ise, *J. Am. Chem. Soc.* **1990**, *112,* 587.

[7] J. Yamanaka, H. Araie, H. Matsuoka, H. Kitano, N. Ise, T, Yamaguchi, S. Saeki, M Tsubokawa, *Macromolecules* **1991**, *24*, 6156.

[8] J. Cohen, Z. Priel, *J. Chem. Phys.* **1990**, *93*, 9062.

[9] M. Antonietti, S. Förster, M Zisenis, J. Conrad, *Macromolecules* **1995**, *28*, 2270.

[10] G. Brodowski, A. Horvath, A. Ballauff, M. Rehahn, *Macromolecules* **1996**, *29*, 6962.

[11] M. Antonietti, A. Briel, S. Förster, *Macromolecules* **1997**, *30*, 2700.

[12] M. Antonietti, A. Briel, S. Förster, *J. Chem. Phys.* **1996**, *105*, 7795.

[13] F. Gröhn, M. Antonietti, *Macromolecules* **2000**, *33*, 5938.

[14] M. Antonietti, A. Briel, F. Gröhn, *Macromolecules* **2000**, *33*, 5950.

[15] C. Wandrey, *Langmuir* **1999,** *15*, 4069.

[16] P. van Leeuven, R. F. M. Cleven, P. Valenta, *Pure Appl. Chem.* **1991**, *63*, 1251.

[17] O. V. Davydova, A. N. Zelikin, S. I. Kargov, V. A. Izumrudov, *Macromol. Chem. Phys.* **2001**, *202*, 1361.

[18] O. V. Davydova, A. N. Zelikin, S. I. Kargov, V. A. Izumrudov, *Macromol. Chem. Phys.* **2001**, *202*, 1368.

[19] B. Boussouira, A. Ricard, R. Audebert, *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 649.

[20] W. F. Reed, S. Ghosh, G. Medjahdi, J. Francois, *Macromolecules* **1991**, *24*, 6189.

[21] A. N. Zelikin, N. I. Akritskaya, V. A. Izumrudov, *Macromol. Chem. Phys.* **2001**, *202*, 3018.

[22] C. Wandrey, D. Hunkeler, U. Wendler, W. Jaeger, *Macromolecules* **2000**, *33*, 7136.

[23] M. Hara, Ed. “*Polyelectrolytes. Science and Technology",* Marcel Dekker, New York 1993.

[24] S. Dragan, L. Ghimici, *Polymer* **2001**, *42*, 2887.

[25] L. Ghimici, S. Dragan, *Colloid Polym. Sci.* **2002**, *280*, 130.

[26] Y. Nishiyama, M. Satoh, *Macromol. Rapid Commun.* **2000**, *21*, 174.

[27] S. Dragan, I. Petrariu, M. Dima, *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2881.

[28] G. S. Manning, *J. Chem Phys.* **1969**, *51*, 924.

[29] G. S. Manning, *Ann. Rev. Phys. Chem.* **1972**, *23*, 117.

[30] S. Dragan, L. Ghimici, *Angew. Makromol. Chem.* **1991**, *192*, 199.

[31] S. Dragan, L. Ghimici, *Bull. Inst. Pol. Iasi* **1998**, *44*, 109.

[32] T. Odijk, *Macromolecules* **1979**, *12*, 688.

[33] G. S. Manning, *Biopolymers* **1970**, *9*, 1543.

[34] J. R. Huzienga, P. F. Grieger, F. T. Wall, *J. Am. Chem. Soc.,* **1950**, *72*, 2636.

[35] H. Eisenberg, *J. Polym. Sci.* **1958**, *30*, 47.

[36] T. Kuruczev, B. J. Steel, *Pure Appl. Chem.*, **1967**, *17*, 149.

[37] V. O. Aseyev, S. I. Klenin, H. Tenhu, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1107.

[38] G. R. Barraza, L. M. Pena, and H. E. Rios, *Polymer Internat.* **1997**, *42*, 112.

[39] E. Prokopova, J. Stejskal, *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1537.

[40] M. Satoh, M. Hayashi, J. Komiyama, T. Iijima, *Polymer* **1990**, *31*, 501.

[41] H. E. Rios, L. N. Sepulveda, C. I. Gamboa, *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 505.

[42] H. E. Rios, C. Gamboa, G. Ternero, *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 805.

[43] J. Nagaya, A. Minakata, A. Tanioka, *Langmuir* **1999**, *15*,4129.

[44] S. Dragan, A. Maftuleac, I. Dranca, L. Ghimici, T. Lupascu, *J. Appl. Polym. Sci.* **2002**, *84*, 871.

[45] S. Dragan, D. Dragan, M. Cristea, A. Airinei, L. Ghimici, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 409.

[46] S. Dragan, M. Cristea, *Eur. Polym. J.* **2001**, *37*, 1571.

[47] S. Dragan, M. Cristea, *Polymer* **2002**, *43*, 55.

[48] S. Dragan, S. Schwarz, K.-J. Eichhorn, K. Lunkwitz, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2001**, *195*, 243.

[49] S. Dragan, S. Schwarz, *Progr. Colloid Polym. Sci.* **2003**, *122*, 8.

[50] N. J. Yoshida, *Chem. Phys., Lett.*, **1982**, *90*, 207.

[51] M. Satoh, T. Kawashima, J. Komiyama, T. Iijima, *Polym. J.* **1987**, *19*, 1191.

[52] G. S. Manning, *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 909.