

Conformation of Polyelectrolyte Chains in Dilute Aqueous Solutions Investigated by Conductometry. 4.[†] Influence of Molecular Mass and Charge Density of the Chains on Conformation of Symmetrical Aliphatic Ionene Bromides

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Samples of 3,3-, 4,4-, 6,6-, and 10,10-ionene bromides of different degree of polymerization (DP) were synthesized, fractionated, and characterized. Salt-free dilute aqueous solutions of the samples were investigated by means of conductometry. On the basis of Manning's polyelectrolyte theory, the mean charge spacing b of the polyion chains was calculated from these data. The calculated b values were used for the estimation of the conformational changes of the polyions. The decrease in the chain length of 3,3-ionene bromide to DP \approx 50 was followed by a growth of b indicating a transition from coillike to rodlike regimes. Once this DP was attained, further shortening of the chain did not affect the parameter b suggesting the persistence length (P) of approximately 50 monomer units. This value proves to be significantly higher than P estimated by the same approach for 2,4-ionene bromide having the same mean charge density. This implies that the distribution of charges along the ionene chain (symmetrical or nonsymmetrical) could noticeably affect the flexibility of the chain. For 3,3-ionene bromide and poly(*N*-ethyl-4-vinylpyridinium) bromide, a linear correlation between the determined P value and the corresponding Debye screening lengths, κ^{-1} , was established. P values estimated from the calculated κ^{-1} values on the basis of this correlation successively decreased in the series 3,3- > 4,4- > 6,6- > 10,10-ionene bromides and were in good agreement with the trends of the corresponding b vs DP curves. The obtained data suggest that for all studied ionene samples including the least charged 10,10-ionene bromide, the chain conformation is determined primarily by the electrostatic repulsion of the quaternized nitrogen atoms in the ionene backbone.

Introduction

In the first paper¹ of this series, we studied conductivity of salt-free aqueous solutions of synthetic polyanions poly(sodium styrenesulfonate) (PSS) and poly(sodium acrylate) of different degree of polymerization (DP). The same experiments were performed with samples of native DNA differing by the number of base pairs in the double helices. On the basis of Manning's polyelectrolyte theory, the mean charge spacing b of the polyion chains were calculated from these data according to the approach developed previously.⁴ The calculated b values increased with the decrease in DP of all studied polyanions. Although the numerical values of b could not be considered as "accurate",¹ their increase upon the shortening of the charged chain indicated a transition from coillike to rodlike regimes. It is particularly remarkable that both determined DP regions proved to be in a good accordance with the data on the persistence lengths of the polyanions obtained by small-angle neutron scattering of dilute aqueous PSS and DNA solutions.⁵ This finding suggests that the developed conductometric approach adequately describes, at least qualitatively, the state of polyions in solution and allows conclusions to be drawn about the chain conformation.

In the second paper,² we demonstrated the advantages of the developed approach while studying salt-free dilute aqueous

solutions of poly(*N*-alkyl-4-vinylpyridinium) cations exhaustively alkylated by various alkyl bromides. The obtained data implied that the persistence length of poly(*N*-ethyl-4-vinylpyridinium) bromide (PEVP) corresponds to 100 monomer units. It is significant that even PEVP chains with DP \leq 100 did not adopt their fully stretched rod conformation at room temperature, since the heating of their solutions resulted in the increase of b . The important role of the hydrophobic interactions in the stabilization of chain conformation was revealed with the use of poly(*N*-alkyl-4-vinylpyridinium) cations having different *N*-alkyl substituents. The values of b decreased proportionally with the increase in hydrophobicity of the substituent, indicating the transition from rather stretched rodlike chain to the coils.

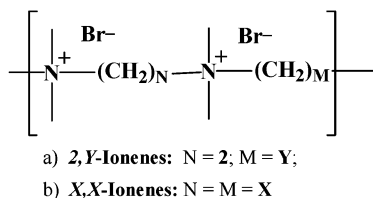
In the third paper,³ the developed approach was used to reveal the impact of the charge density of the chains on their conformation in salt-free aqueous solutions. The greater part of the work was carried out using partly alkylated poly(*N*-ethyl-4-vinylpyridinium) bromides, PEVP- β , with various degrees of alkylation, β . Samples of relatively short 2,*Y*-ionene bromides (Scheme 1a) with *Y* values of 4, 8, and 10 were prepared and studied for comparison. The obtained results suggested folding of the chains upon decrease in their charge density, irrespective of whether PEVP- β with a random distribution of the charges along the chains or 2,*Y*-ionenes with the regular charge distribution were under consideration.

Strictly regular alternation of charged moieties in the ionenes results from their synthesis by Menshutkin polyaddition reaction. The distance between the charges is predetermined by the

[†] For parts 1, 2, and 3, see refs 1, 2, and 3, respectively.

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SCHEME 1



number X of methylene groups in N,N,N',N' -tetramethyldiaminoalkanes and the number Y of methylene groups in α,ω -dibromoalkanes that were used in the ionene synthesis. Contrary to nonsymmetrical X,Y-ionenes (Scheme 1a), symmetrical X,X-ionenes (Scheme 1b) are prepared from the starting reagents with the same number X of the methylene groups. The perfect regularity in distribution of the charges along the chains makes X,X-ionenes the most appropriate polyelectrolytes to establish correlation between charge density of the chains and their conformation.

The goal of the present work was to ascertain conformation of symmetrical ionenes of different DPs and charge density in salt-free dilute aqueous solutions. To verify whether symmetrical charge distribution affects the conformational changes, the conductivity approach was used for studying ionenes with the same mean charge density but different (symmetrical and nonsymmetrical) regularity in the charge distribution.

To eliminate the problem of polydispersity of the ionene samples, preparation of well-defined ionene fractions was carried out according to the previously described method.⁶ This procedure was also used for synthesis of 2,Y-ionene bromides studied in the previous paper.³ The wide range of X values and molecular mass of the fractions of X,X-ionene bromides allowed us to reveal the influence of DP and charge density of the symmetrical ionenes on conformation of their chains in salt-free dilute aqueous solutions.

Experimental Part

Reagents. Aliphatic X,X-ionene bromides ($X = 3, 4, 6$, and 10) were synthesized from corresponding N,N,N',N' -tetramethyldiamines and α,ω -dibromoalkanes, subsequently fractionated and characterized as described in detail elsewhere.⁶ In brief, polydisperse samples of the aliphatic ionenes, modified on both termini with nitrobenzene moieties, were fractionated using ion-exchange chromatography in a gradient of NaCl concentration with UV detection. The number-average degree of polymerization of each fraction was established by combination of UV-spectroscopy (determining the concentration of terminal groups, that is, twice the concentration of chains) and turbidimetric titration with sodium salt of poly(styrenesulfonate) (estimating the concentration of the charged groups). According to this procedure, fractions of X,X-ionenes in DP range 23–217 were obtained.

Methods. Conductivities of polyelectrolyte solutions were measured using precision conductivity measuring equipment from LKB (Sweden)—the thermostatic bath 7601 A, the temperature controller 7602 A, the flow conductivity cell 5311 with a cell constant of 0.73 cm^{-1} at 25°C , and Conductolyzer 5300 B with the bridge frequency 2 kHz.

In all experiments, doubly distilled water, additionally purified by Millipore Milli-Q water system (USA), was used. The water had the conductivity no higher than $1 \times 10^{-6} \Omega^{-1}\cdot\text{cm}^{-1}$. The concentration of polyelectrolyte monomer units was varied in the range $(1\text{--}4) \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

According to Manning's polyelectrolyte theory, the conductivity K of a salt-free polyelectrolyte solution can be expressed by the following equation:⁷

$$K = K_0 + (0.866 \times 10^{-3})\xi^{-1} \times C_P \left\{ \lambda_c^0 + \frac{0.866FA|0.5 \ln(C_P\xi^{-3}) + B|}{10^4 + 0.134FA(\lambda_c^0)^{-1}|0.5 \ln(C_P\xi^{-3}) + B|} \right\} \quad (1)$$

where K_0 is the conductivity of the solvent (water) in the absence of the polyion, C_P is the polyion concentration, λ_c^0 is the limiting mobility of the counterion, T is the absolute temperature, F is the Faraday constant, $A = 4\epsilon_0\epsilon kT/(3\eta e)$, ϵ is the solvent dielectric constant, η is the solvent viscosity, e is the elementary charge, k is the Boltzmann constant, $B = \ln(e^3 N_A^{0.5}/(4\pi)) + 1.5 \ln(10/(\epsilon_0\epsilon kT))$, N_A is Avogadro's constant, and ξ is the linear charge density parameter of the polyion, which is inversely proportional to the mean charge spacing b on the polyion,

$$\xi = L_b/b \quad (2)$$

where $L_b = e^2/(4\pi\epsilon_0\epsilon kT)$ is the Bjerrum length.

Different numeric coefficients (in comparison with Manning's original expressions) are because, while traditional units for conductivities and limiting mobilities ($\Omega^{-1}\cdot\text{cm}^{-1}$ and $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively) were retained, all other units were converted to the SI system.

The experimental values of K , K_0 , C_P , and T for every data point were substituted into eq 1, the equation was solved numerically by an iterative method with respect to ξ , and the corresponding b values were obtained by eq 2.

All calculations were made on a personal computer with the use of programs developed by the authors.

Molecular modeling and computations were performed with the CS ChemBats3D Pro version 6.0 (CambridgeSoft Corporation) computer program using the molecular mechanical MM2 method. The ionic charges on the polyions and the counterions were taken into account in the computer simulations.

Results and Discussion

Figure 1a shows the typical curves of the conductivity of aqueous solutions of relatively long (DP ≈ 100) X,X-ionene bromides with different X as a function of their concentration. The concentration dependencies of the mean charge spacing b , derived from these data according to Manning's theory (see Experimental Part), are depicted in Figure 1b. Analogous dependencies for 3,3-ionene bromides with different DP obtained from the conductivity curves of Figure 2a are presented in Figure 2b.

It is seen that the conductivity K of the solutions increases linearly with concentration of the ionene, whereas the b values remain practically unchanged. The same effect was observed during the conductometric investigation of all studied ionenes. The increase in K can be readily explained by a growth in the number of charge carriers (the charged chains and Br^- counterions) in the solution due to the successive addition of the ionene bromide. The fact that b values are scarcely affected by the concentration suggests the absence of noticeable conformational changes of the chains at fixed DP in the studied region of the ionene concentration $1.2 \times 10^{-3} \leq [\text{ionene bromide}] \leq 4.0 \times 10^{-3} \text{ M}$. This finding evidences insignificant, if any, influence of the chains on each other. Rather slight negative slope of the curves in Figure 2 implies that in the studied

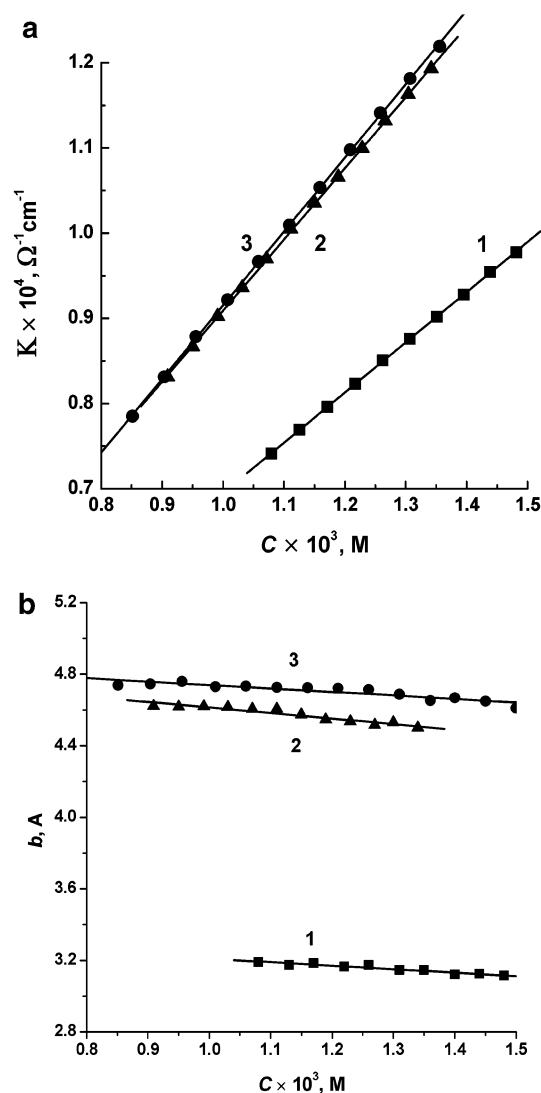


Figure 1. Concentration dependencies of (a) the conductivity of dilute aqueous solutions of 3,3- (1), 6,6- (2), and 10,10- (3) ionenes with DP = 100 and (b) mean charge spacing b for 3,3- (1), 6,6- (2), and 10,10- (3) ionenes with DP = 100.

concentration range the polyelectrolyte swelling effect is negligible and can be ruled out.

The b values obtained from the conductivity measurements at the fixed concentration $4.0 \times 10^{-3} \text{ M}$ of 3,3-ionene bromide are depicted in Figure 3 as a function of DP. It can be seen that for relatively highly polymerized samples, the decrease in the ionene length is accompanied by a progressive growth of b indicating unfolding of the chains. Such behavior is common to all polyions studied by us earlier and was discussed in our previous papers of this series.¹⁻³ The most pronounced growth of b occurs in the range of DP = 80–50, whereas further decrease in the ionene length does not result in a noticeable change of b . These findings suggest that the persistence length of 3,3-ionene bromide in $4.0 \times 10^{-3} \text{ M}$ aqueous solution is about 50 monomer units.

This value is distinctly higher than the persistence length of 2,4-ionene bromide. The curve for 2,4-ionene bromide obtained under the same conditions³ is depicted in Figure 3 by the dotted line. While the mean charge spacing calculated for the fully stretched chains of these two ionenes is the same, the observed change in b is different. The curve for 2,4-ionene bromide is shifted to substantially lower values of DP, and the growth of b occurs in the whole studied range of DP = 29–13 without a

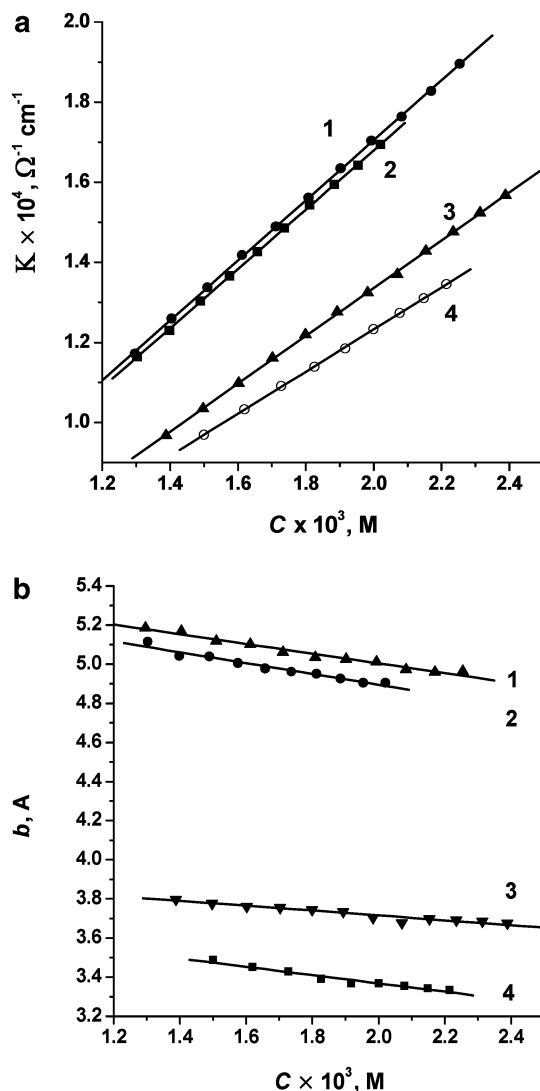


Figure 2. Concentration dependencies of (a) the conductivity of dilute aqueous solutions of 3,3-ionene with DP = 24 (1), 50 (2), 65 (3), and 149 (4) and (b) mean charge spacing b for 3,3-ionenes with DP = 24 (1), 50 (2), 65 (3), and 149 (4).

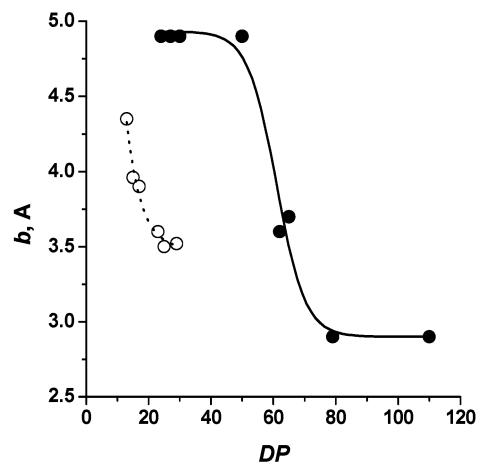


Figure 3. Dependence of the mean charge spacing b on DP of 3,3-ionene (1) and 2,4-ionene (2).

noticeable tendency to saturation in the range of the shortest chains. This implies that the persistence length of 2,4-ionene bromide does not exceed 13 monomer units (the shortest studied sample).

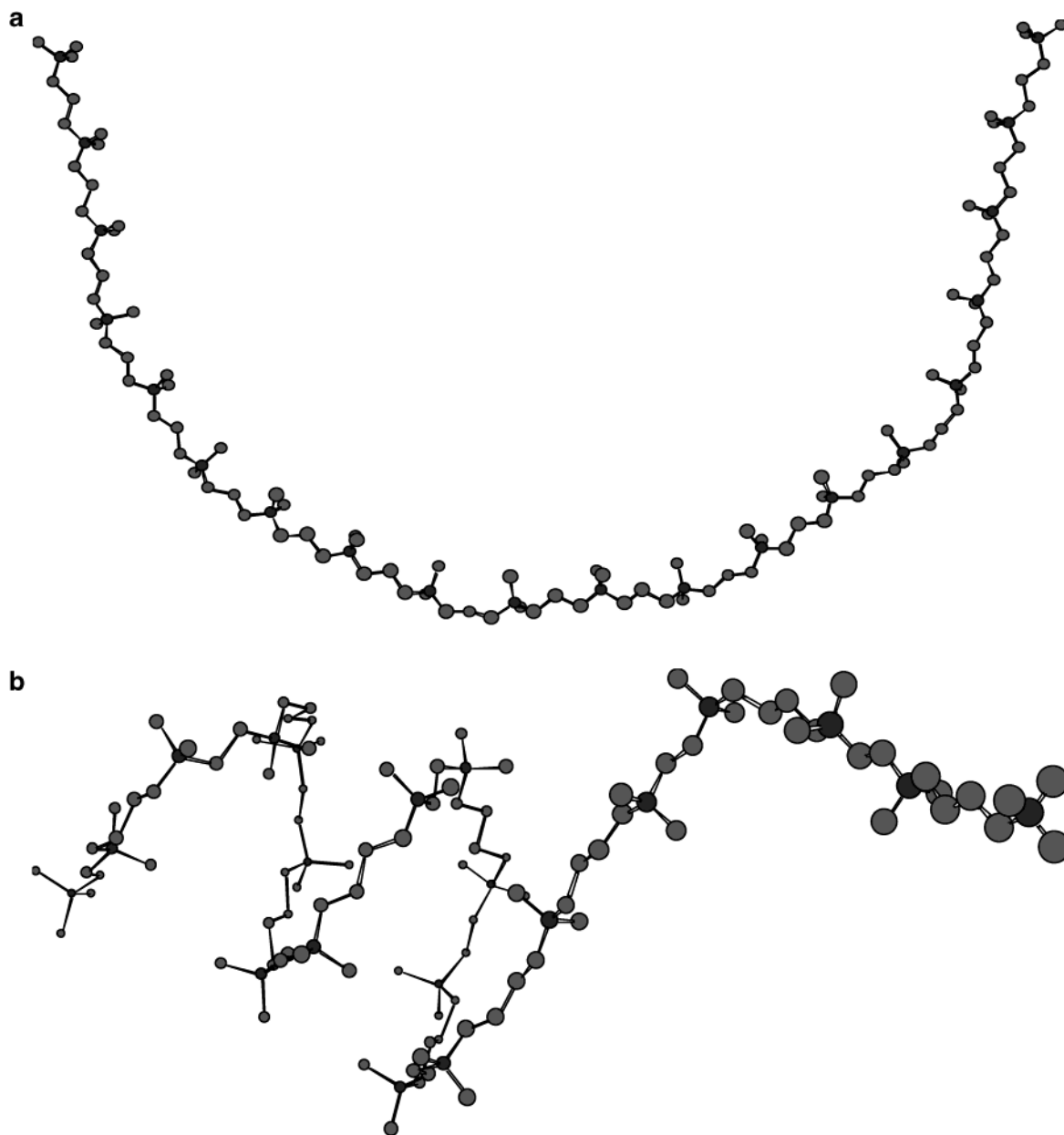


Figure 4. Image of MM2 modeling of 20-mer of (a) 3,3-ionene and (b) 2,4-ionene.

The revealed significant difference in persistence lengths of the above ionenes is intriguing. Nevertheless, it must be considered a real possibility. The experimental observations are supported by computer simulations for the 20-mers of 2,4- and 3,3-ionene bromides (Figure 4, the hydrogen atoms and the counterions are not shown for the sake of clarity). Even though the used molecular mechanical MM2 method takes into account only electrostatic interactions between the charges on the polyion and the counterions, but not polymer–solvent and hydrophobic interactions, the images clearly indicate a rather stretched chain of 3,3-ionene (Figure 4a) and a more folded chain of 2,4-ionene (Figure 4b). Thus, despite the images presenting only a rough estimation of the chain conformation, they reinforce the statement that rigidity of 3,3-ionene is noticeably higher.

One of the plausible reasons of higher flexibility of 2,4-ionene compared with 3,3-ionene is the presence of closely positioned charges on its chain, that is, two charged nitrogen atoms spaced by only two methylene groups. According to Manning's theory, the fraction of counterions "condensed" onto the polyion with

charge density ξ is given by the following expression:

$$f = 1 - 1/\xi \quad (3)$$

While the mean charge density parameter ξ for 2,4- and 3,3-ionenes is the same, $\xi = 1.44$ ($f = 0.3$), the modes of distribution of the charges and the condensed counterions along the polyion backbone are distinctly different. For symmetrical 3,3-ionene, the distribution is uniform and no particular region of counterion condensation can be discriminated. This obviously is not the case for 2,4-ionene. The mean charge density parameter calculated for two charged nitrogen atoms spaced with two methylene groups equals 1.93 resulting in $f = 0.48$. This implies condensation of one Br^- into this region reducing the effective charge from two to one. Thus 2,4-ionene bromide can be considered as a polycation with a repeat unit that consists of one positively charged nitrogen, six methylene groups, and the quaternized nitrogen atom effectively neutralized by Br^- . In this case, the effective repeat unit of 2,4-ionene is similar to the

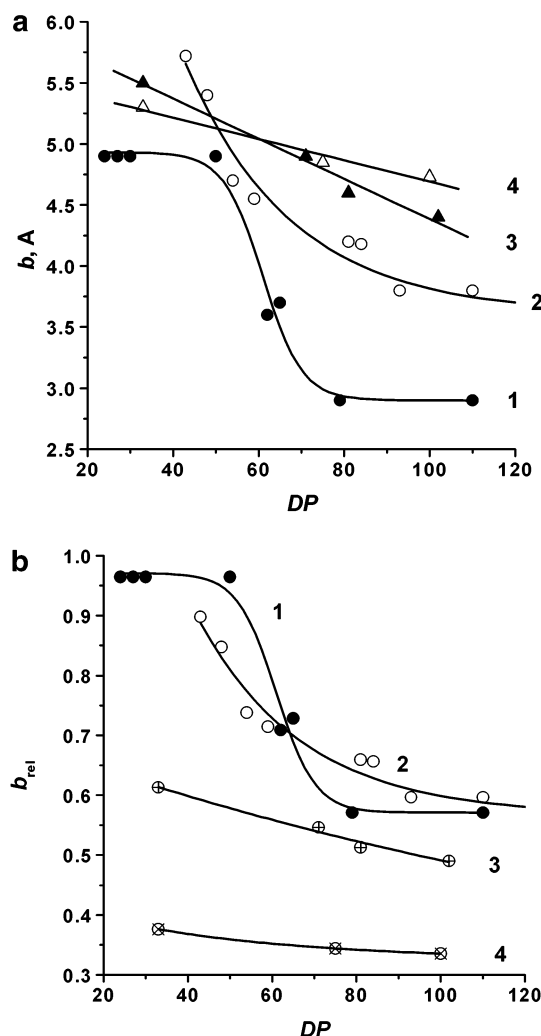


Figure 5. Dependence of (a) mean charge spacing b and (b) relative mean charge spacing $b_{rel} = b/b_{calc}$ (b is experimentally obtained mean charge spacing; b_{calc} is calculated for the fully stretched chain) on DP of 3,3- (1), 4,4- (2), 6,6- (3), and 10,10- (4) ionenes.

repeat unit of 6,6-ionene. As will be shown below, the persistence length of 6,6-ionene bromide under the chosen experimental conditions is expected to be almost an order of magnitude lower as compared to 3,3-ionene bromide.

This conclusion agrees with the data on the flexibility of 2-, 10- and 6,6-ionenes obtained by means of viscosimetry.⁸ Although the mean charge densities of these two ionenes are the same, 2,10-ionene was found to be more flexible compared to 6,6-ionene.

The b values for various X,X -ionene bromides ($X = 3, 4, 6$, and 10) of different DPs were determined from the conductivity of the ionene solutions by the same procedure. The data obtained at fixed concentration of the ionenes, $C = 4.0 \times 10^{-3}$ M, are presented in Figure 5a. Figure 5b shows these data as a dependence of the relative charge spacing $b_{rel} = b/b_{calc}$ on DP, where b_{calc} is the value calculated for the fully stretched conformation of the ionene. The run of the curve 2 corresponding to 4,4-ionene bromide follows the above-discussed trend for 3,3-ionene bromide (curve 1) with DP decrease. The lack of samples with DP lower than 40 did not allow us to reach the point where b values become DP-independent and hence to determine the value of the persistence length of 4,4-ionene bromide. Nevertheless, it is evident that this value is noticeably lower than the persistence length of 3,3-ionene bromide. For 6,6-ionene bromide (curve 3) and 10,10-ionene bromide (curve

TABLE 1: Properties of X,X -ionenes ($C_p = 4 \times 10^{-3}$ M) and PEVP ($C_p = 5 \times 10^{-3}$ M)

| polymer | b_{calc} , nm | ξ | κ^{-1} , nm | κ^{-1} , monomer units | P , monomer units | P/κ^{-1} |
|--------------|-----------------|-------|--------------------|-------------------------------|---------------------|-----------------|
| 3,3-ionene | 0.495 | 1.44 | 10.3 | 17 | ~ 50 | ~ 3.0 |
| 4,4-ionene | 0.621 | 1.15 | 9.2 | 12 | | |
| 6,6-ionene | 0.873 | 0.82 | 7.8 | 7 | | |
| 10,10-ionene | 1.376 | 0.52 | 6.2 | 4 | | |
| PEVP | 0.25 | 2.85 | 10.3 | 41 | ~ 100 | ~ 2.5 |

4), b_{rel} values remain almost constant and correspond to a rather folded conformation of the chains in the whole range of DPs.

These findings are in a good agreement with reported values of effective charge densities ξ determined by monitoring the counterion activity coefficients for polydisperse samples of different ionene bromides,⁹ which suggest an extended conformation of 3,3-ionene and more folded conformations of the other ionenes with the folding more pronounced for ionenes with a higher calculated charge spacing value.

The persistence length P of a polyelectrolyte is assumed to be the sum of the steric (P_0) and the electrostatic (P_{el}) components.¹⁰ While the determined herein value of the persistence length of 3,3-ionene bromide corresponds to approximately 50 monomer units (about 25 nm), the reported P_0 value for the aliphatic ionenes corresponds to 1.4 nm irrespective of the charge spacing of the ionene.¹⁰ For poly(*N*-ethyl-4-vinylpyridinium) bromide having persistence length of approximately 100 monomer units,² P_0 has a value of the same magnitude (2.0 nm). Thus, for both polycations the P_{el} value is substantially higher than P_0 . This means that the electrostatic factor by far dominates over the steric factor and determines relatively high rigidity of these polycations in salt-free aqueous solutions.

The P_{el} value is known¹¹ to correlate with the Debye screening length, κ^{-1} . In a salt-free polyelectrolyte solution, κ^{-1} value is expressed as¹²

$$\kappa^{-1} = \left(4\pi N_A L_b C_p \frac{1}{\xi} \right)^{-0.5} \quad (4)$$

The κ^{-1} values calculated with the formula 4 for fully extended X,X -ionenes are listed in Table 1, along with the data for PEVP. The ratio of the determined persistence length to corresponding κ^{-1} value (expressed in the number of monomer units) is ~ 3.0 for 3,3-ionene and ~ 2.5 for PEVP. This observation suggests linear correlation between P_{el} and κ^{-1} , which is characteristic for the flexible chain polyelectrolytes.¹¹

Thus, for the polycations under study the P_{el} value is expected to be a multiple of κ^{-1} with a coefficient ~ 2.5 – 3 . This correlation allows us to estimate the values of persistence lengths of X,X -ionenes and compare them with the experimental observations. The κ^{-1} value for 4,4-ionene corresponds to ~ 12 monomer units (Table 1) suggesting the persistence length of about 30 monomer units that was not achieved in the experiments (Figure 5). The corresponding κ^{-1} values for 6,6- and 10,10-ionenes are even lower (7 and 4 monomer units, respectively), which explains the observed folded conformation of these ionenes in the whole studied DP range (Figure 5b).

The data of Table 1 also suggest that even for the least charged 10,10-ionene bromide, P_{el} dominates over P_0 , that is, for all ionene samples under study the main factor determining rigidity of the chain is the electrostatic repulsion of the charged nitrogen atoms in the ionene backbone.

Finally, one more conclusion follows from the dependencies of the obtained b values for X,X -ionene bromides on the charge

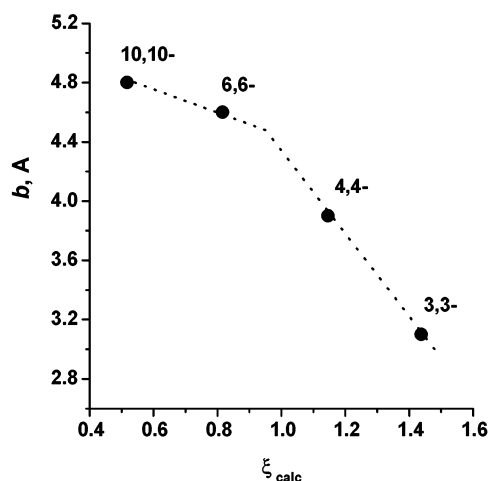


Figure 6. Dependence of the mean charge spacing b on linear charge density ξ_{calc} of the fully extended chains of the X,X -ionenes with DP = 100.

density parameter ξ_{calc} calculated for their fully extended conformation. The data are plotted in Figure 6 for the ionenes with DP = 100 as a dependence of b on ξ_{calc} . The plot in Figure 6 consists of two linear parts with the inflection point at ξ close to unity (shown by the dotted line). In contrast to a significant increase in b with ξ decrease at $\xi \geq 1$, further decrease in ξ results in a minor change of b . The probable reason for this finding stems from the balance of two factors that act in the opposite directions: electrostatic repulsion of the charged groups and the entropically driven tendency of the chain to fold. These two factors are equal at the distance between the two unit charges equal to the Bjerrum length, $L_b = 7.1 \text{ \AA}$ (at 25 °C), corresponding to $\xi = 1$. At $\xi > 1$, the electrostatics dominates and the polyelectrolyte chain tends to stretch; otherwise the chain folds.

Concluding Remarks

The results described above and reported in the previous works of this series^{1–3} demonstrate that the approach based on conductivity measurements provides valuable information on conformation of polyions in salt-free dilute aqueous solutions that correlate well with the data obtained by other methods. The preparing of well-defined samples of aliphatic ionenes of different DP allowed us to perform the detailed systematic investigation of conformational changes of these polycations upon variation of their chain length. The revealed pronounced influence of this parameter on conductivity of the ionene solutions suggests that for the correct interpretation of experimental data the use of fractionated samples is required. The procedure recently developed by us⁶ for obtaining fractions of ionenes with a predefined set of the macromolecular charac-

teristics allows solving of this problem. Our results also show that both symmetrical and nonsymmetrical ionenes are valuable polycations to reveal the effect of mean charge density and the charge distribution of the chains on their properties. The presented herein data imply that aliphatic ionenes are highly perspective objects for verification and further development of polyelectrolyte theories.^{7,13–15}

Finally, it is worth noting that studying of conformation of the ionenes in aqueous solutions is not only of fundamental importance. Applications of the ionenes as components of polyelectrolyte complexes is intriguing as well.^{16–19} Our recent report²⁰ evidenced that the conformation and conformational changes of aliphatic ionenes preceding the dissociation of their DNA-containing polyelectrolyte complexes control the stability of the complexes to the action of salt. In turn, the stability of the complexes in water–salt solutions correlates well with their ability to deliver gene material in the cell.²¹ Thus well-defined fractions of aliphatic ionenes prove to be unique objects for investigation of the properties of polyelectrolytes and polyelectrolyte complexes in solutions.

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