Conformations of polyelectrolyte macromolecules with different charge density in solutions of different ionic strengths

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Abstract. Studies of charged polymer chains are interesting in both fundamental and applied aspects. Especially, polyelectrolytes attract huge attention of researchers due to their ability to form interpolymer complexes with synthetic and biopolymers. The study was carried out on the fractions of hydrophilic copolymers of N-methyl-N-vinyl acetamide and N-methyl-N-vinyl amine hydrochloride of different degrees of polymerization and of different charge density using methods of molecular hydrodynamics. Hydrodynamic and conformational characteristics as well as molar masses of isolated molecules were estimated. In addition, the intrinsic viscosity of fractions was studied at the extreme ionic strengths – in distilled water (~10^{-6}M) and in 6M NaCl. Scaling relations for intrinsic viscosity, sedimentation and translational diffusion coefficients with molar mass were obtained. Conformational behavior of macromolecules with different linear charge density was compared.

1. Introduction
Polyelectrolytes are polymers which are able to dissociate in polar solvents. As a result, a charged polymer chains and mobile counterions appear [1, 2]. A recently new field of science is now developing – biomedical macromolecular systems. Many of such polymeric systems carry electric charges. The systematic studies of the relationship of chemical structure and biological activity of water-soluble neutral and charged polymers are carried out in the Institute of Macromolecular Compounds RAS in the laboratory of hydrophilic polymers (head corr. RAS, Prof. E.F. Panarin) [3]. A series of synthetic polymers exhibiting various types of biological activities have been synthesized. One of the important physical-chemical tasks in the investigation of these polymers is to determine the molar mass and to establish the Kuhn-Mark-Houwink relations (scaling relations) between the molar masses and the hydrodynamic characteristics.

In current research fractions of the hydrophilic copolymers of N-methyl-N-vinyl acetamide and N-methyl-N-vinyl amine hydrochloride (MVAA–MVAH) with average composition 95.6: 4.4% and 92:8 mol. % were studied using the methods of molecular hydrodynamic. The chemical structure of its recurrent units is shown below:
The homopolymer PMVAA and copolymers (MVAA–MVAH) with average composition 56: 44% were investigated earlier [4,5].

2. Experimental part

The hydrodynamic characteristics of charged macromolecules unambiguously correlate with the molecular characteristics only under the conditions when the polyelectrolyte effects are practically suppressed. This information was gained from the results of studying a homologous series of copolymers by methods of molecular hydrodynamics, namely, by studying viscous flow, translational diffusion, and velocity sedimentation of dilute solutions of the copolymers in 0.2 M aqueous NaCl.

The solution viscosity was measured in an Ostwald capillary viscometer under the conditions of negligible corrections for the kinetic energy and gradient dependence.

The translational diffusion was studied with a Tsvetkov polarizing diffusometer [6] in a metal cell with a Teflon centerpiece [7]. The optical path length was 3 cm. The diffusion coefficients D were determined from the slope of the linear dependences of the diffusion boundary dispersion $\sigma^2$ on time: 

$$D = \frac{l}{2} \frac{\partial \sigma^2}{\partial t}.$$ 

The velocity sedimentation was studied with a Beckman XLI analytical ultracentrifuge in a two sector cell with the optical path length of 12 mm at the rotor speed 40 000 rpm. The sedimentation interference scans were processed with Sedfit program [8] using the model of continuous distribution c(s) in which the solution of the general Lamm equation for velocity sedimentation of an ensemble of specifically noninteracting globular molecules, ensuring the best coincidence of the calculated and experimental profiles of the sedimentation boundary, is sought for. The Sedfit program allows obtaining the sample distribution with respect to sedimentation coefficients. The concentration dependence of the sedimentation coefficients was examined. The sedimentation coefficients at infinite dilution $s_0$ and the concentration coefficients $k_s$ characterizing the isolated macromolecules were determined from the linear approximations $s^{-1} = s_0^{-1}(1 + k_s c + \ldots)$ [9].

The set of the experimental hydrodynamic quantities ($[\eta]$, $D_0$, $s_0$, $k_s$) can be transformed into the matrix of hydrodynamic invariants and molar masses, which are calculated directly from the experimental quantities without using any model concepts [6, 10]. In so doing, the only assumption is that the translational friction coefficients and chain lengths in the transport methods used are assumed to be equivalent. The hydrodynamic invariant $A_0$ was calculated by the relationship 

$$A_0 = \frac{R[D][s][\eta]}{1 - \nu} = \frac{R[s]}{[D][s]}.$$ 

where $[s] = s_0\eta_0/(1 - \nu \eta_0)$ is the intrinsic sedimentation coefficient, $[D] = D_0\eta_0/T$ is the intrinsic diffusion coefficient, and $R$ is the gas constant. The intrinsic sedimentation and diffusion coefficients, like the intrinsic viscosity, are the quantities characterizing isolated macromolecules. Note that, for fractions of each polymer, the parameters $A_0$ vary insignificantly. This fact allows us to perform further interpretation of the hydrodynamic quantities. The hydrodynamic characteristics (intrinsic viscosity $[\eta]$, diffusion coefficient $D_0$, sedimentation coefficient at infinite dilution $s_0$, concentration sedimentation coefficient $k_s$), molar masses ($M_0$) and hydrodynamic invariants ($A_0$) for investigated copolymers MVAA–MVAH in 0.2M NaCl at 25 °C are presented in tables 1 and 2. Specific partial volume value: $\nu=0.828$ cm$^3$/g.
Table 1. The hydrodynamic characteristics, molar masses and hydrodynamic invariants for copolymers MVAA–MVAH 95:6: 4.4 mol% in 0.2M NaCl at 25 °C.

| [η]_s cm /g | D_0 10^1 cm^2 /s | s_0 10^{15} s | k_v cm^3/g | M^d 10^4 g/mol | A_0 10^10 erg/(mol·K) |
|-----------|------------------|--------------|----------|--------------|-----------------|
| ±1.4%     | ±1.5%            | ±5.3%        | ±19.1%   | ±6.8%        | ±1.5%           |
| 1         | 22               | 6.4          | 0.92     | -            | 21              | 3.26            |
| 2         | 37               | 4.81         | 1.19     | -            | 36              | 3.49            |
| 3         | 57               | 3.06         | 1.66     | 113          | 82              | 3.33            |
| 4         | 90               | 2.20         | 2.18     | 191          | 150             | 3.41            |
| 5         | 141              | 1.54         | 2.53     | 168          | 250             | 3.28            |
| 6         | 176              | 1.39         | 2.88     | 247          | 300             | 3.44            |
| 7         | 194              | 1.15         | 3.30     | 249          | 430             | 3.28            |
| 8         | 252              | 0.98         | 3.95     | 346          | 600             | 3.41            |

^a Average mean square deviations are given.

Table 2. The hydrodynamic characteristics, molar masses and hydrodynamic invariants for copolymers MVAA–MVAH 92:8 mol% in 0.2M NaCl at 25 °C.

| [η]_s cm /g | D_0 10^1 cm^2 /s | s_0 10^{15} s | k_v cm^3/g | M^d 10^4 g/mol | A_0 10^10 erg/(mol·K) |
|-----------|------------------|--------------|----------|--------------|-----------------|
| ±2.2%     | ±1.7%            | ±4.0%        | ±13.3%   | ±5.7%        | ±6.8%           |
| 1         | 34               | 3.94         | 1.19     | -            | 45              | 2.97            |
| 2         | 47               | 3.26         | 1.45     | 72           | 65              | 3.14            |
| 3         | 67               | 2.73         | 1.74     | 111          | 97              | 3.30            |
| 4         | 77               | 2.20         | 2.07     | 157          | 141             | 3.19            |
| 5         | 114              | 1.80         | 2.42     | 170          | 190             | 3.28            |
| 6         | 140              | 1.43         | 2.78     | 192          | 290             | 3.21            |
| 7         | 219              | 0.99         | 3.53     | 322          | 540             | 3.10            |
| 8         | 261              | 0.94         | 3.69     | 355          | 600             | 3.32            |

^a Average mean square deviations are given.

The intrinsic viscosity is a basic value of molecular physics of polymers, which is most frequently used to characterize linear polymers, especially synthetic. The classical Huggins (η_sp/c) = [η] + k′[η]^2 + ... and Kraemer (ln η/η_0 = [η] + k^′′[η]^2 + ...) plots are common method for the evaluation of intrinsic viscosity value ([η]), where c is the polymer concentration in the solution, η_sp = η_0 - 1 = η_0 - 1, η and η_0 are the dynamic viscosities of the solution and solvent, respectively. The Huggins and Kraemer relationships are mathematically equivalent when c → 0. Therefore, it is reasonable to consider Huggins and Kraemer plots together, like one twin plot. Such plots were used to obtain [η] values on 0.2M NaCl solutions, where polyelectrolyte effects are practically suppressed (tables 1,2). However, these plots become nonlinear in case of charged polymers and do not allow to determine the [η] value. But, these plots become the test for the presence of charges in linear chains. At the same time, a more "simple dependencies", namely: (η_sp vs. c) and (ln η vs. c) have similar shape both for the neutral and charged polymers. The initial slope of "simple plots" at c → 0 is regarded as estimate of the [η] value, characterizing the individual macromolecules of any kind [12,13]: [η] = lim (c→0)(η_sp/c) = lim (c→0)(ln η/c). Such plots for copolymers with 4.4 mol.% of charged monomers

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are presented below in figure 1. In both plots the initial slope increases with the increase of molar mass.

![Figure 1](image1.png)

**Figure 1.** Plots for copolymers MVAA–MVAH 4 mol % in distilled water (ionic strength ≈10^{-6}M)

The copolymers MVAA–MVAH of different charge density and homopolymer MVAA in different solutions were compared. The dependencies \( \lg [\eta]\cdot M_L \) vs \( \lg M/M_L \) (where \( M_L \) is the mass of the unit of length of the macromolecule) are presented below in Figure 2 (a, b).

![Figure 2](image2.png)

**Figure 2.** Comparison of copolymers MVAA–MVAH of different charge density and homopolymer MVAA in different solutions: a – 0.2M NaCl, b – distilled water (~10^{-6}M).

The conformational behavior of the macromolecules of different charged density in sodium chloride is practically the same. In the pure water solution (~10^{-6} M) there is sufficient difference. Firstly, the \([\eta]\cdot M_L\), i.e. the hydrodynamic volume per unit of length, increases with the increase of charge density. Secondly the slope increases, i.e. the rigidity of macromolecules increases.

### 3. Conclusions

Copolymers MVAA–MVAH were investigated and their hydrodynamic characteristics, molar masses and hydrodynamic invariants were obtained. The recent approach was applied to quantitative estimation of intrinsic viscosity at very low ionic strength (~10^{-6}M). It was demonstrated that this approach means to adequate evaluation of such crucial characteristic of linear macromolecules as the...
intrinsic viscosity. Copolymers of different charge density and different ionic strength of solution were compared. The charged macromolecules of MVAA-MVAH occupied much larger volume in pure water solutions (~10^{-6} M) than in NaCl (0.2 M) solutions where polyelectrolyte effects are practically suppressed.

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