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Volumetric and calorimetric properties of aqueous ionene solutions

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ABSTRACT

The volumetric (partial and apparent molar volumes) and calorimetric properties (apparent heat capacities) of aqueous cationic polyelectrolyte solutions – ionenes – were studied using the oscillating tube densitometer and differential scanning calorimeter. The polyion's charge density and the counterion properties were considered as variables. The special attention was put to evaluate the contribution of electrostatic and hydrophobic effects to the properties studied. The contribution of the CH₂ group of the polyion's backbone to molar volumes and heat capacities was estimated. Synergistic effect between polyion and counterions was found.

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1. Introduction

Over the bygone decades, vast research work has been performed in the field of physical chemistry of charged macromolecules in solutions. Besides academic motivation, interest in polyelectrolytes lies in the fact that these substances possess an indispensable role in a great variety of technological and industrial applications and are the key life driving molecules in living organisms [1–3]. Mechanisms of hydration of polar or ionic (hydrophilic) and non-polar (hydrophobic) solutes or solute's residues on molecular level is inevitable for all natural sciences dealing with physical, chemical or biological aspects of (bio)macromolecules. Studies of micelle or lipid membrane formation, protein folding or aggregation, molecular recognition etc. are only few examples of the biochemical processes for which knowledge of thermodynamics of hydration is crucial. Physico-chemical properties of synthetic and natural ionic macromolecules in solution (usually water) show complex interdependence of two basic characteristics of polyelectrolytes: *i*) the distribution of charges on the macroion, and *ii*) the chemical nature of the counterions (ions dissociated from the polyion) [4–7]. For linear type polyions usually the so-called linear charge density parameter, $\xi = \lambda_B/b$, is used to characterize the effect of charged groups; $\lambda_B = e_0^2/4\pi\epsilon_0\epsilon k_B T$ is the Bjerrum's length (e_0 the elementary charge, ϵ_0 and ϵ the permittivity of vacuum and of solvent, respectively, k_B the Boltzmann constant,

and T the absolute temperature) and b denotes the average length in-between two charged sites of the polyion. The larger the ξ the more charged (less hydrophobic) is the macroion. A methodical research of the two effects (charges plus ion-specificity) on thermodynamic and transport properties is of general interest.

Our laboratory has paid much attention to aqueous solutions of ionenes precisely because of the fact that these compounds enable one a *systematic* investigation of the two above-mentioned effects [8–15]. From chemical point of view, ionenes are synthetic polyelectrolytes with the repeating unit shown on Fig. 1 [16]. The number of methylene groups (x and y) in-between charged nitrogens can be varied almost at will, preparing in this way analogues with varying charge density (hydrophobicity). Besides changing the structure of the polyion, ionenes with different counterions can be synthesized.

Thermodynamic and transport properties of ionenes have been investigated by our group both experimentally (osmotic and activity coefficients, heats of dilution, conductivity and transport numbers etc.) and theoretically [8–15,18,19]. It has been demonstrated that effects of charges and of the nature of the corresponding counterions are complex and interdependent. For analogues with counterions of the XVII. group of the periodic table (F⁻, Cl⁻, Br⁻, I⁻) the most striking differences are revealed in heats of dilution. For ionene fluorides they are exothermic (as predicted by well established electrostatic theories), while for chlorides and bromides they can be exo- or endothermic (depending on charge density and/or concentration), and for ionene iodides the values are endothermic for all investigated samples [8,12]. The thermodynamic and transport properties, such

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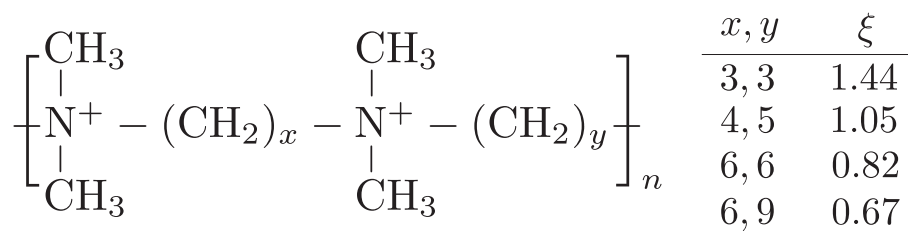


Fig. 1. Repeating unit of x, y -ionene and the structural values of the linear charge density parameter ξ for selected x and y [17]. Corresponding counterion(s) are not shown.

as osmotic coefficients, heats of dilution, transport numbers, and conductivity, show strong dependence on the charge density of the polyelectrolyte's backbone as well. Interestingly, the spectroscopic methods, such as dielectric relaxation spectroscopy [18,19], neutron scattering data and NMR [20–22], and ultrafast optical Kerr effect [23], suggest that the ionenes studied, in spite their relatively low backbone charge density (linear charge density parameter ξ varying between 1.44 and 0.67; see Fig. 1) show surprisingly hydrophilic character, an exception being 12,12-ionenes with $\xi = 0.43$ [20].

Two thermodynamic properties that are particularly sensitive to hydrophobic interactions are partial molar volumes [24–27] and heat capacities [28–32]. Both of these thermodynamic properties are helpful in the identification of solute-solvent, as well as the solvent-solvent interactions. In this paper we present and discuss the partial and apparent molar volumes and apparent molar heat capacities of aqueous x, y -ionene solutions as a function of the ionene's backbone charge density, as well as of the counterion type. Considering previous results on thermodynamic properties of these solutions described above, we focused only on ionene fluorides and bromides; it is known that these two ions have different hydration [33]: while fluoride ion interacts strongly with surrounding water molecules (kosmotrope), bromide ion does not (chaotrope). By applying the cell-model electrostatic theory, we wish to show that thermodynamic properties cannot be described by arguments of electrostatics alone.

The article is organized as follows: after the Introduction, we define all three quantities (partial and apparent molar volume, and apparent molar heat capacity). Next, we give Experimental details and proceed with Results and discussion section. Relevant observations are summarized in the Conclusions.

2. Definitions

2.1. Partial and apparent molar volumes

One of the thermodynamic quantities that is used to study the hydration of the polyion is the volume (density) of the solution, or more precisely the information on the partial, \bar{V}_2 , or apparent molar volume, Φ_V , of the solute [24]. \bar{V}_2 is defined as the change in the volume of the solution (V) per unit of moles upon addition of an infinitesimal amount of the solute (n_2) at constant temperature, pressure, and composition, i. e. $\bar{V}_2 = (\partial V / \partial n_2)_{T, p, n_1}$. On the other hand, Φ_V represents the formal contribution of the solute to the total volume of the solute-solvent system. For a solution of n_2 moles of the solute in n_1 moles of the solvent, the total volume of the solution can be expressed as $V = n_1 \bar{V}_1 + n_2 \bar{V}_2 = n_1 V_1^* + n_2 \Phi_V$, where \bar{V}_1 and V_1^* denote the partial molar volume of the solvent and molar volume of the pure solvent, respectively.

The partial molar volumes of solutes contain contributions of both the intrinsic volume and volumetric effects due to solute-solvent interactions (hydration). The water molecules around the

polyion rearrange under the influence of charged and hydrophobic groups. The charged groups strongly attract (electrostrict) the neighbouring water molecules, increasing the local density of the solvent, leading to the reduction in partial molar volumes of the polyelectrolyte [34,35]. The electrostriction of water by the counterions should also be taken into account [25,26]. Hydrophobic hydration usually leads to an increase in the partial molar volume of the solute [34]. Although Durchschlag and Zipper [36] or Gianni and Lepori [37] have used empirical procedures to account for partial molar volumes (all these authors give additivity rules to calculate partial molar volumes of solutes at infinite dilution), up to date, no theory of partial (apparent) molar volumes of polyelectrolyte solutions, capable of considering all types of interactions, exists.

2.2. Apparent molar heat capacity

Heat capacity is a thermodynamic property which depends directly on the chemical and physical structure of the solution under investigation. At constant pressure it is defined as $C_p = (\partial H / \partial T)_p$, where H denotes the enthalpy of the solution. For a particular binary solution, C_p can be written as a sum of the heat capacity contribution of the solvent and of the solute, i. e. $C_p = n_1 \bar{C}_{p1} + n_2 \bar{C}_{p2}$, where n_i is the number of moles of species i , and \bar{C}_{pi} is the partial molar heat capacity of the species i in the solution [38]. Indices 1 and 2 stand for the solvent and the solute, respectively. Assuming the ideal behaviour of the solvent, i. e. $\bar{C}_{p1} = C_{p1}^*$ (molar heat capacity of pure solvent), we can write $C_p = n_1 C_{p1}^* + n_2 C_{p,\phi}$, where $C_{p,\phi}$ denotes the apparent molar heat capacity of the solute and represents a formal contribution of the solute to the total heat capacity of the solute-solvent system [38,39].

The $C_{p,\phi}$ measurements have been widely applied in the studies of aqueous solutions of simple solutes [40] and systems containing biopolymers [41]. Namely, hydrophobic interactions and changes in hydration cause large changes in the molar heat capacity of the solute. The heat capacity of hydration is positive for hydrophobic solvents and negative for hydrophilic ones [28,30]. This is because the strong solute-water electrostatic interactions induce the distortion of the water structure around the solute and break hydrogen bonds, while the presence of a non-polar solute orders the hydration water [31,42,43]. Such picture is consistent with the results for the polyelectrolytes where $C_{p,\phi}$ decreases with the increasing degree of ionization (increasing charge density) of polyacids [34,38,39]. Another classification was proposed by Makhatadze and Privalov [29] who classified the amino acid side chains as hydrophobic or hydrophilic according to the sign of the temperature derivative of the apparent molar heat capacity (for hydrophobic amino acids, $\partial C_{p,\phi} / \partial T < 0$, and for hydrophilic $\partial C_{p,\phi} / \partial T > 0$).

Polyelectrolytes consist of a backbone with discrete charges and hydrophobic parts in-between. It is therefore convenient to split the apparent molar heat capacity into the electrostatic, $C_{p,\phi}^e$, and non-electrostatic, $C_{p,\phi}^n$, contribution [38], i. e. $C_{p,\phi} = C_{p,\phi}^e + C_{p,\phi}^n$. While

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