



Heat effects measured in aqueous solutions of salts of poly(anethole sulfonic acid) upon mixing with alkali-, alkaline-earth-, and tetraalkylammonium chlorides



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ABSTRACT

Experimental and theoretical results for the enthalpies of mixing, $\Delta_{\text{mix}}H$, for aqueous solutions of selected salts of poly(anethole sulfonic acid) with some low-molecular-mass salts are presented. The enthalpies of mixing for aqueous solutions of alkali (Li^+ , Cs^+) and tetraalkylammonium (Me_4N^+ , Bu_4N^+) polyanethole sulfonates (PAS^-) with alkali-metal chlorides (LiCl , KCl , CsCl) and tetraalkylammonium chlorides (Me_4NCl , Et_4NCl , Pr_4NCl , Bu_4NCl) were measured with an isothermal titration calorimeter at 298.15 K. The first two polysalts (LiPAS , CsPAS) were also titrated with MgCl_2 and SrCl_2 solutions. Manning's theory was used to predict the electrostatic contribution to the enthalpy of mixing for polyelectrolyte and simple electrolyte solutions. The observed differences between the experimental and calculated values were ascribed to the ion-specific interactions. The cumulative heat effects obtained from the titration of the poly(anethole sulfonic) salts with the alkali chlorides, including Me_4NCl , for a molar ratio $r = 4.6$, decreased with the hydration enthalpy, $\Delta_{\text{hyd}}H$, of the added counterions. In contrast to this, the enthalpies of mixing for poly(anethole sulfonic) salts with tetraalkylammonium chlorides increased with the length of the alkyl chain in the added counterion. The results show a strong dependence of the enthalpy of mixing on the difference in the nature of the counterions in the mixture. Additionally, the results allow us to classify the counterions as either hydrophilic or hydrophobic based on the heat effects provoked by their introduction into a polyelectrolyte solution.

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1. Introduction

Polyelectrolytes (PEs) are polymers having ionisable groups, which, in appropriate solvents, dissociate into charged polymer chains (macroions) and small counterions. Well-known examples of such systems are proteins, nucleic acids and synthetic systems, such as polystyrene sulfonic acid or polyacrylic acid, together with their salts. Because of their fundamental importance for biology and biochemistry, ionisable polymers have been the subject of continued interest since the early days of polymer science (see, e.g., [1,2] and references therein). It is, however, widely acknowledged [3] that they are still among the least understood systems in macromolecular science.

One of representatives of synthetic PEs is polyanethole sulfonate, a compound with multiple biological functions. It was originally developed as an anticoagulant and is used *in vitro* to inhibit blood coagulation. It is also an inhibitor of complement and lysozymes and, as such, it lowers the bactericidal action of the blood. For this latter purpose it is used as a diagnostic reagent that encourages the growth of pathogens

in the blood. It plays an active role in a process for the stabilization of biologically active substances immobilized on solid phases [4–6].

In our previous paper [7] we presented experimental and theoretical results for the osmotic pressure and enthalpy of dilution for polyanethole sulfonic acid and its lithium, sodium, and cesium salts in an aqueous solution at 298.15 K. The results were compared with previously published data for a polyelectrolyte with a similar structure, namely, polystyrene sulfonic acid and its alkali salts. From the osmotic pressure measurements it was concluded that the polystyrene sulfonate ion (PSS^-) binds the counterions more strongly than the polyanethole sulfonic ion (PAS^-). Consistent with this finding, the enthalpies of dilution reveal that more heat is released upon the dilution of polyanethole sulfonates (stronger exothermic effect) than with the corresponding solutions of polystyrene sulfonic acid and its alkali salts. Solutions of different alkali salts of polyanethole sulfonic acid have weaker ion-specific effects than alkali PSS^- solutions. This finding was attributed to the structural differences between the two polyions. A detailed investigation of the origin of the differences between the physicochemical properties of PAS^- and PSS^- salt solutions has not yet been carried out.

In several recent studies of the properties of different PE solutions [8–16] the basis of the experimental data were extended to measurements of the heat of mixing for PE solutions with low-molecular-mass

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electrolyte solutions. This method yields results that complement the heat-of-dilution data, and are capable of revealing small differences between the properties of the different ions. However, in spite of the fact that calorimetric data provide valuable information about the interactions in polyelectrolyte solutions, they may not always be easy to interpret theoretically.

Numerous experimental results show that short-range (salt-specific) interactions play an important role, even in strong PE solutions where the long-range Coulombic effect should be dominant. The unexplained temperature dependence of the enthalpies of dilution for PSS⁻ solutions and the endothermic effects upon the dilution of cationic PEs are two such examples. Nevertheless, synthetic PEs are considered to be relatively simple vis-a-vis biological PEs where non-Coulombic effects play an even more important role than in synthetic ones. The short-range interactions are mediated by water and, obviously, any progress in understanding these solutions is possible only through an increased understanding of the ion–water and water–water interactions. In PE solutions, in addition to charged, also uncharged, hydrophobic groups are often present. The presence of uncharged hydrophobic groups gives rise to hydrophobic interactions that are manifested by the release of heat upon dilution of the solution [3]. In some cases ion-specific heat effects prevail over electrostatic contributions, even changing the sign of the heat effect [15–18,24,28].

Since both long- and short-range interactions are intertwined in PE solutions, it is obvious that the interpretation of the experimental data of different PE systems requires a complex approach. The conclusions drawn from various computer-simulation methods (MC, MD) can be successfully applied in the interpretation of the experimental results [13]. In addition, the experimental data obtained using contemporary methods, such as for instance, NMR, XLS, NLS and SAXS, which reveal specific ion effects from other perspectives, may help to elucidate the issues [19–23].

An additional hydrophobicity can be brought into the investigated system by selecting the counterions that have hydrophobic characters. An example of counterions having such characteristics are tetraalkylammonium ($N(C_nH_{2n+1})_4^+$), frequently denoted as TAA⁺ counterions. The hydrophobic character of TAA⁺ ions is considered to be tunable via the length of the four alkyl chains attached to the central nitrogen atom. The first four members of the TAA⁺ series, referred to subsequently as Me₄N⁺ (tetramethyl-), Et₄N⁺ (tetraethyl-), Pr₄N⁺ (*n*-tetrapropyl-), and Bu₄N⁺ (*n*-tetra-butyl-), have been the most intensively studied. These compounds have been good models for studying hydrophobic effects (for a review, see ref. [25–27]). The specific interactions dramatically influence the properties of PE solutions and may overshadow the electrostatic interactions. It is expected that a study of TAAPAS solutions would contribute to clarifying the role of the ion-specific interactions in the investigated systems.

Despite the efforts put into this research area, our basic understanding of the role of solute–solute interactions, where the solute contains both polar and non-polar regions, is far from being complete. Assuming that the experimental data of thermodynamic quantities such as $\Delta_{dil}H$ and $\Delta_{mix}H$ reflect the specific ion effects in PE solutions [12–16], it seemed justifiable to extend our measurements to the enthalpy of mixing for different PAS⁻ salts with various low-molecular-mass electrolytes. From the analysis of the experimental results we expect to obtain information about specific interactions and their influence on the physical properties of PE solutions. The main enthalpy changes that accompany the substitution of counterions in a mixing experiment are supposed to be (i) the electrostatic (Manning's) contribution, (ii) the enthalpy of dilution of the electrolyte used as a titrant, (iii) the enthalpy changes arising from a decrease or increase in the overlap of the hydration sheaths (dehydration and hydration) for all the participating ions, and (iv) possible interactions between the hydrophobic parts of the polymer chain and the TAA⁺ counterions [16,29,30]. In the present investigation we were focused on these effects, which are responsible for the deviations from predictions of the electrostatic theories.

2. Experimental part

2.1. Sample preparation

Aqueous solutions of polyanethole sulfonates were prepared from the commercially available sodium salt of polyanethole sulfonic acid (NaPAS), viscosity average molar mass, M_v , 9–11 kDa (Aldrich, SKU 444464). We converted the sodium salt into an acidic form by ion-exchange during dialysis. The dialysis tubes (Sigma, MWCO = 8 kDa) were filled with ~0.02-M NaPAS while ~0.05-M HCl was used as an exchanging solution. After three weeks of intense dialysis, a negative flame test showed the complete removal of the Na⁺ ions. Further dialysis against deionized water was performed until the conductivity of the exchanging water solution fell below 2 $\mu\text{S}/\text{cm}$.

Polysalt solutions were prepared with a neutralizing titration of polyanethole sulfonic acid using the corresponding metal carbonate or tetraalkylammonium hydroxide until the pH was about 5 [31]. During the titration, N₂ was introduced into the solution in order to remove any CO₂ that was present and so prepare a CO₂-free solution. The concentrations of polysalts were determined spectrophotometrically at 284.4 nm by diluting the sample solution with a known excess of 5% KCl solution. The monomolar extinction coefficient in 5% KCl was obtained from a calibration with a polyanethole sulfonic acid solution of a known concentration. The concentrations of low-molecular-mass salts (LiCl, KCl, CsCl, MgCl₂, SrCl₂, Me₄NCl, Et₄NCl, Pr₄NCl and Bu₄NCl) were determined by using a 736 GP Titrimo automatic titrator (Metrohm, Switzerland). A standard AgNO₃ solution was used as a titrant, a Metrohm chloride-sensitive electrode (6.0502.120) was used as an indicator electrode, and a mercury (I) sulfate electrode was used as a reference. All chemicals used in this research were of p.a. grade.

2.2. Isothermal titration calorimetry measurements

The enthalpies of mixing for LiPAS, CsPAS, Me₄NPAS and Bu₄NPAS solutions with the low-molecular-weight salts LiCl, KCl, CsCl, Me₄NCl, Et₄NCl, Pr₄NCl, Bu₄NCl, MgCl₂, and SrCl₂ were measured with a VP-ITC isothermal titration calorimeter (Microcal Inc., Northampton, MA, USA). Isothermal titration calorimetry (ITC) experiments were performed at 298.15 K by adding a titrant (low-molecular-mass salt) to a measuring cell with a volume equal to 1.3862 cm³, containing a degassed aqueous solution of HPAS salt. The area under the peak following each injection of titrant, obtained by integrating the raw signal, was expressed per mole of the added titrant per injection, to give the corresponding enthalpy changes. By subtraction of the enthalpy change resulting from titration in the absence of PAS⁻ (pure water), we obtained the enthalpy corresponding to the PAS⁻ - salt interaction. In all the reported ITC experiments the concentrations of the solutions of PAS⁻ with different counterions, c_m , was 0.005 mol dm⁻³ (given per mole of the charged groups on the polyion) and the concentration of the titrant was 0.1 for the monovalent and 0.07 mol dm⁻³ for the divalent counterions. The total volume of titrant added to PE solution was 280 μL . The dilution of the PE solution due to the addition of the titrant was neglected.

3. Theoretical part

A theory to evaluate the Coulombic contribution to the properties of PE solutions was proposed by Manning [29,30]. According to his approach, the polyion is pictured as an infinitely long, rigid charged line, while the counterions are treated as point charges immersed in a dielectric continuum (solvent). The counterions can condense onto the polyions until the charge density between neighboring monomer charges along the polyion chain is reduced below a critical value. The uncondensed mobile ions in the ionic atmosphere surrounding the polyion are treated within the Debye–Hückel approximation. The theory

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