

ENTHALPIES OF DILUTION OF AQUEOUS IONENE SOLUTIONS[#]**Katja Arh and Ciril Pohar ****Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI – 1000 Ljubljana, Slovenia*

[#]This paper is dedicated to Professor Davorin Dolar on the occasion of his 80th birthday

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Abstract

The enthalpies of dilution ($\Delta H_D, c \rightarrow 0.002 \text{ mol/dm}^{-3}$) of aqueous solutions of 3,3- 4,5- 6,6- and 6,9- ionenes with Br⁻ and Cl⁻ counterions, respectively, have been measured over a broad concentration range at 25°C. The enthalpies of dilution show rather big dependence on the kind of the counterion, as well as large dependence on the charge density of ionenes. For 3,3- and 4,5- types dilution effects are endothermic, while for 6,6- and 6,9- ionenes are exothermic in the low concentration range and become endothermic in more concentrated solutions. The concentration dependence of the enthalpy of dilution of ionene solutions were compared with predictions of electrostatic cell theory. An agreement between theory and experiment was found only if the effects of specific interactions were included in the calculations.

Introduction

During last decades the thermodynamic and transport properties of polyelectrolytes, have been extensively investigated. The reason for this interest lies in important role that polyelectrolytes play in natural and technological processes. For example, polyelectrolytes are now used in industry for the flocculation of a wide range of aqueous suspensions, colloids, and solutions.¹ Solutions containing charged macroions display large deviations from the thermodynamic ideality, and very low values of the activity and osmotic coefficients of counterions are observed even in dilute solutions. These nonidealities are a consequence of different interactions between species in a solution. The main influence is as generally recognized ascribed to large electrostatic interaction between highly charged macroion and small counterions. Because of this interaction counterions become trapped in the vicinity of polyions and significantly lose their identity as independent mobile species.²

To date several theories, which model physicochemical properties of polyelectrolyte solutions on the basis of electrostatic interactions among charged species have been developed. For example, the popular rodlike model,³⁻⁵ or the line charge model,⁶ have gained considerable success in explaining various experimental results. However, numerous disagreements between theory and experiment, have also been observed.^{3-5,7-12} Measurement of heats of dilution, ΔH_D , of poly(styrenesulfonates) show that there is a strong temperature dependence of ΔH_D . In addition the effect is strongly dependent on the nature of the counterions. Agreement between the electrostatic cell model and experiment is less good for lower temperatures and more concentrated solutions. The reasons for this marked discrepancy are not yet clear. Among the parameters which have a direct influence on the electrostatic interaction between charged entities, and thus on the behavior of a charged macromolecule in solution, are certainly an amount and spatial arrangement of charged groups on a macromolecule. Within the frame of the electrostatic theories of polyelectrolyte solutions these effects are approximated by the charge density parameter λ , which is defined as

$$\lambda = \frac{e^2}{4\pi\epsilon_0\epsilon kTb} \quad (1)$$

where e is the protonic charge, ϵ_0 the permittivity, ϵ the dielectric constant of water ($\epsilon = 78.5$ at 25°C), k the Boltzmann constant, T the absolute temperature, and b the average linear charge spacing on the polyion.

The aim of this study is to extend measurements of the enthalpy of dilution to the system of synthetic polyelectrolytes named ionenes, which are characterized with different linear charge densities λ . Ionenes are strongly charged cationic polyelectrolytes whose charged groups are located on the polymer main chain.¹³ The aliphatic x,y-ionene¹⁴ is a compound which consists of specimens with different numbers (x,y) of methyl groups between the quaternized nitrogen atoms. The charge densities of these compounds can be varied in the synthesis by using appropriate reagents.¹⁵ Thus the ionenes by different charge densities were used to examine the enthalpy of dilution, a property, which is considered to be a very rigorous test of any electrostatic theory. The

experimental results are discussed in light of the extended cell model of polyelectrolyte solutions.

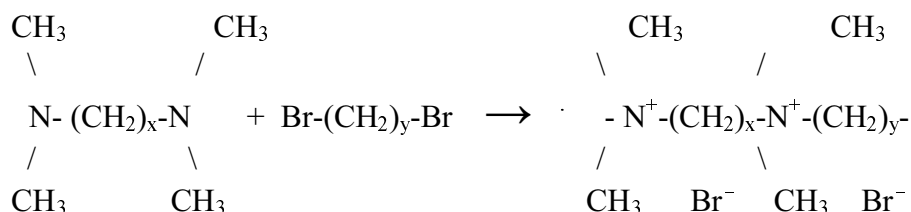
It is interesting to note that a vast amount of the experimental and theoretical studies of the enthalpy of dilution have been devoted to anionic polyelectrolytes,^{8-12, 16-22} while for cationic polyelectrolytes only few articles have been found in the literature.^{23,24}

Experimental

Materials

All investigated polyelectrolyte ionene salts were synthesized in our laboratory following the procedure described by A. Rembaum et al.²⁵⁻²⁷

Bromide salts of aliphatic x, y ionenes (3,3- 4,5-, 6,6- and 6,9-ionene-Br) were prepared in DMF by using appropriate reagents. A solution of a N,N,N',N' - tetramethyl-1,x – diaminoalkane was mixed with a solution of a 1,y – dibromoalkane at the molar ratio of the both reagents 1:1 and the mixture was stirred at room temperature about 22°C under argon atmosphere. The following reaction takes place



After 48 hours, the precipitated polymer ionenes were filtered by using teflon filters, washed with large amount of acetone and dried under vacuum at 40°C. The sample solutions were dialysed for three weeks in cellulose bags (SIGMA; MWCO = 12.000) and concentrated by vacuum evaporation before use. Chloride salts were prepared from hydroxides by the neutralization reaction with HCl. Hydroxides were obtained from bromides by ion exchange. Because of the instability of the basic form, the ion-exchange was carried out just before the preparation of the chloride form. The structure

and purity of the polymeric products were checked by NMR analysis, which showed the absence of the monomer reactants in all final products.

Apparatus

Calorimetric measurements were performed at 25°C in an LKB 10700-1 Flow microcalorimeter using the flow-mix method. The solution and distilled water were pumped simultaneously by means of two peristaltic pumps with equal flow rates into the calorimetric cell where the incoming flows mixed. The initial concentration of solution for each calorimetric measurement was prepared to match the concentration obtained in a previous dilution experiment. By summing up the heat effects accompanying successive dilutions, ΔH_D over a large concentration range was obtained.

Results and discussion

The experimental enthalpies of dilution, ΔH_D , of aqueous ionene solutions are presented in Figures 1-2.

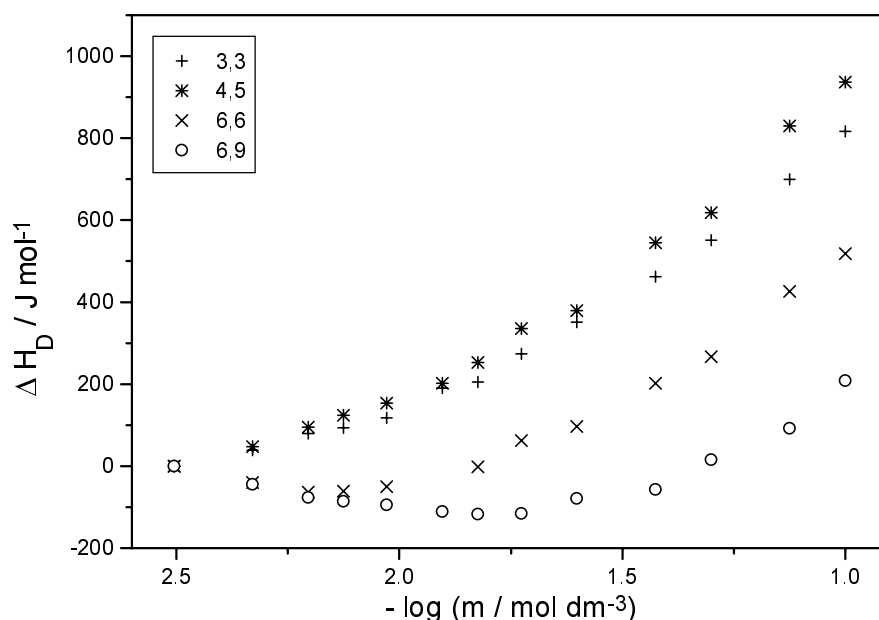


Figure 1: Enthalpies of dilution of aqueous solutions of x,y-ionene-Br at 25°C

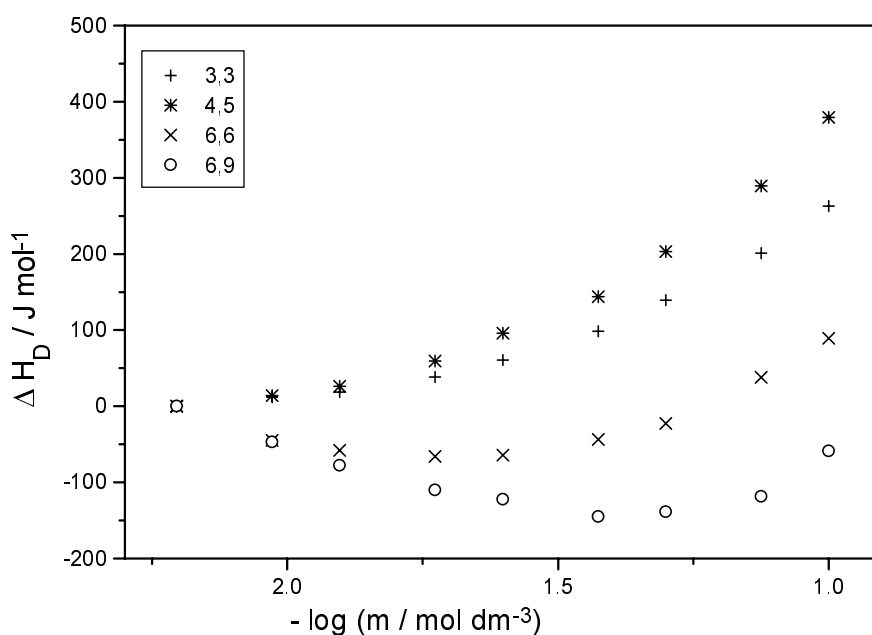


Figure 2: Enthalpies of dilution of aqueous solutions of x,y-ionene-Cl at 25°C

The experimental data indicate strong dependence of the enthalpies of dilution on the kind of counterions. A comparison of the absolute values of the enthalpies of dilution presented in Figures 1 and 2 shows that the values for bromide salts exceeds the values for chlorides by a factor almost two. This characteristics resembles solutions of anionic polyelectrolytes, where also a strong dependence of the enthalpy of dilution on the nature of counterions has been observed.^{9,16,17}

Next important result is a strong dependence of ΔH_D on the linear charge density of ionenes. The enthalpies of dilution increase with the increasing charge density parameter (decreasing spacing between charges on a backbone of the macroion). The experimental values can be compared with predictions of appropriate polyelectrolyte theories. For solutions containing no simple electrolyte, two theories, based on the cylindrical cell and infinite line charge models are very popular. In the cell model,^{3,4} the polyions are treated as very long cylinders, each placed in the center of its own cell of cylindrical symmetry. The equivalent number of counterions which maintain electroneutrality are distributed within the cell according to the Poisson-Boltzmann

equation. In this theory the molecular nature of the solvent is ignored, as are all other than Coulombic interactions. According to the cell theory the electrostatic enthalpy of a polyelectrolyte solution is given by the expression¹⁶

$$H_e = \frac{z_1 RT}{z_2 \lambda} \left[(1 + \beta^2) \gamma + \ln \frac{(1 - \lambda)^2 - \beta^2}{1 - \beta^2} + \lambda \right] \left(1 + \frac{d \ln \epsilon}{d \ln T} \right) + \frac{z_1 RT}{2 z_2 \lambda} \left[1 - \beta^2 - \frac{2 \lambda e^{2\gamma}}{e^{2\gamma} - 1} \right] \left(\frac{d \ln V}{d \ln T} - \frac{2 d \ln a}{d \ln T} \right) \quad (2)$$

This quantity may be in the first approximation related to the observed enthalpy of dilution $\Delta H_{D(m_1 \rightarrow m_2)}$, defined as the enthalpy change which accompanies dilution from concentration m_1 to m_2 calculated per monomole of solute. It may be formally divided into two parts:

$$\Delta H_{D(m_1 \rightarrow m_2)} = \Delta H_{(m_1 \rightarrow m_2)}^0 + \Delta H_{e(m_1 \rightarrow m_2)} \quad (3)$$

where ΔH^0 is the nonelectrostatic and ΔH_e the electrostatic contribution. It was assumed that ΔH^0 is much smaller than ΔH_e and therefore can be neglected. In Eq. (2) z_1 is the charge carried by the ionic group on the polyion and z_2 is the charge on the counterion, R is the gas constant, a is the radius of the polyion, γ is a concentration parameter proportional to $-\ln c$, β is a constant related to γ and λ by the equation:

$$\lambda = \frac{1 - \beta^2}{1 + \beta \coth \beta \gamma} \quad (4)$$

The $\frac{2 d \ln a}{d \ln T}$ term in Eq. 2 was introduced arbitrarily in order to include possible specific interactions in the most simple way into the theory.

To confront the experimental and theoretical results we used the parameters presented in Table I. In the table included also the values of the empirical terms

$d\ln a/d\ln T$, which helped to bring the theory into a reasonable agreement with the observed data.

Table I. The structural properties of ionenes.

Ionene	3,3-	4,5-	6,6-	6,9-
a/nm	0.5	0.5	0.5	0.5
b/nm	0.498	0.685	0.879	1.063
λ (Eq. 1)	1.43	1.04	0.81	0.67
$d\ln a/d\ln T(\text{Cl})$	-	3.3	2.3	-
$d\ln a/d\ln T(\text{Br})$	-	5	2.7	-

For the other parameters needed in calculations, the following values were used: $T=298.15$ K, $d\ln \epsilon/d\ln T = -1.372$, and $d\ln V/d\ln T = 0.0767$.

The comparison of the experimental enthalpies of dilution of x,y -ionene Br and x,y - ionene Cl solutions with those predicted by the electrostatic cell theory is shown in Figures 3 and 4, respectively. From the curves which represent pure electrostatic theory and are designated by the value of the parameter $d\ln a/d\ln T = 0$, it is seen that the theory fails to account for the experimental results. The reason for this discrepancy may be sought in the intrinsic deficiencies of the cell model to treat other than Coulombic interactions.^{28,29} Ionenes consist of a fairly long nonpolar main chain which causes hydrophobic interaction between the polyion and counterions. The more hydrophobic or less hydrated ion interacts with the polyion more strongly.³⁰⁻³² Another possible explanation for the discrepancy may exhibit a considerably lower dielectric constant in the vicinity of the macroion than in the bulk water what lead to a stronger interaction of the macroion with the counterions than is predicted.²⁴

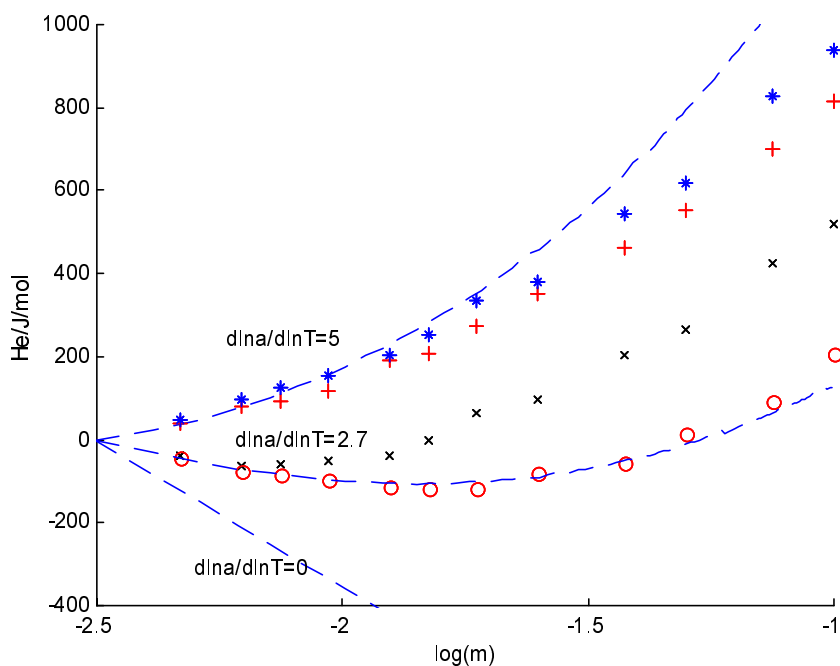


Figure 3: Comparison of the experimental enthalpies of dilution of solutions of x,y-ionene-Br with the theory (dashed lines).

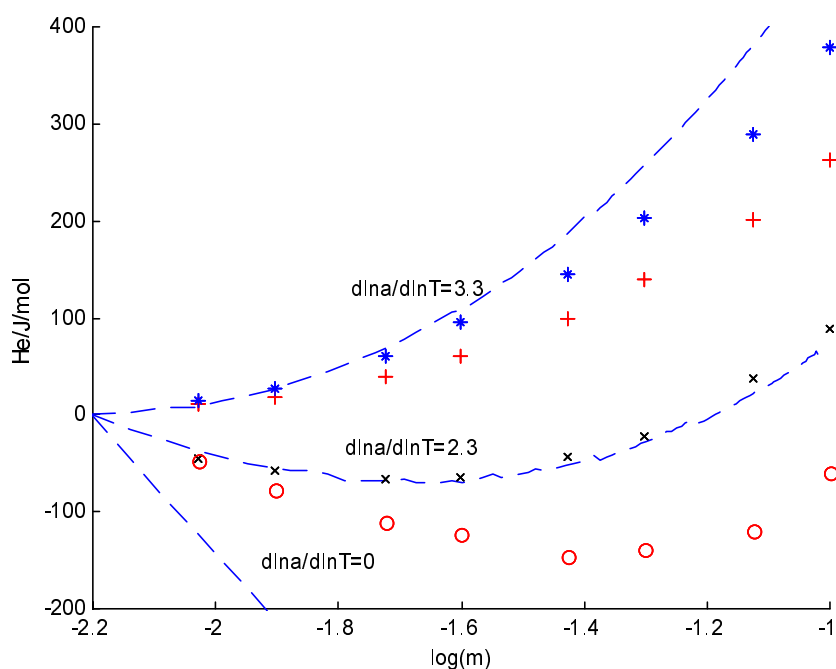


Figure 4: Theoretical enthalpies of dilution of aqueous solutions of x,y-ionene-Cl (dashed lines) at 25°C.

In order to gain some more quantitative information of the intensity of the specific interactions in aqueous solutions of ionenes, we include them in the calculations through the $dlna/dlnT$ term in the way as done before.^{9-11,16,17} In Figures 3 and 4 the used values of the $dlna/dlnT$ term with the corresponding theoretical curves are presented for 4,5- and 6,6- ionene bromide and chloride solutions, respectively. The adjustable coefficients are bigger for Br than for Cl salts, and are of the same order of magnitude as those which took into agreement theory and experiment for the dilution enthalpies of cesium polystyrenesulfonate solution at 0 °C.⁹

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Povzetek

Izmerili smo razredčilne entalpije ($\Delta H_D, c \rightarrow 0.002 \text{ mol/dm}^{-3}$) vodnih raztopin 3,3- 4,5- 6,6- in 6,9- ionenov z Br^- in Cl^- protiioni v širokem koncentracijskem območju in pri temperaturi 25 °C. Razredčilne entalpije so zelo odvisne od vrste protiiona ($\text{Br}^- \gg \text{Cl}^-$), kakor tudi od vrste ionena. Pri 3,3 in 4,5- ionenih so efekti endotermni, medtem ko imajo krivulje 6,6- in 6,9- ionenov minimum. Koncentracijsko odvisnost razredčilnih entalpij raztopin ionenov, zadovoljivo opiše le razširjena celična teorija.