Effect of Cation Size and of the Presence of Hydrophobic Groups on Heats of Dilution of Aqueous Solutions of Alkali Metal and Tetramethylammonium Salts of the Polyacrylic Series

Hubert Daoust* and Marc-André Chabot

Department of Chemistry, Université de Montréal, Québec, Canada H3C 3V1.

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ABSTRACT: Intermediate heats of dilution at 25 °C have been measured for aqueous solutions of alkali metal and tetramethylammonium (TMA) salts of poly(acrylic, methacrylic, and ethacrylic acids) in the absence of added salt. The concentrations ranged from 0.01 to 15% by weight in polymer. Results show that the cation size and the presence of hydrophobic groups on the chain or on the cations affect notably the heats of dilution. For instance, in the concentrated range, intermediate heats of dilution are endothermic for the sodium salt and exothermic for the cesium salt of the first two polyacids; TMA salts give only exothermic heats of dilution in that range. The presence of hydrophobic groups on the chain seems to create a competition between hydrophobic hydration and electrostatic hydration. In the dilute range, when hydrophobic groups are present, dilution becomes endothermic and this cannot be explained by hydrolysis alone. The notably high endothermic heats of dilution may be caused by the dehydration of the hydrophobic groups on the chain or/and on the TMA ions. This phenomenon is probably due to the strong electrostatic field produced by the charged species in dilute solution.

When only electrostatic forces are implied, the thermodynamic properties of strong polyelectrolytes in dilute aqueous solutions can be described by well-known theories.[1-4] Poly(styrenesulfonic acid) (HPSS) and its alkali metal salts are typical strong polyelectrolytes whose behavior in dilute aqueous solutions can be rather well predicted by the above-mentioned theories.[5] However, no theory yet can predict the thermodynamic properties of solutions of polyelectrolytes when strong gegenion-charged site interactions and hydrophobic interactions both exist such as in the case of many biopolymers in dilute and moderately concentrated systems. In order to obtain a somewhat clearer picture of those interactions, different experimental techniques have to be used and measurements on different monomeric and polymeric model compounds have to be done. Microcalorimetry is one of those techniques, and its application to biological systems has been recently reviewed.[6]

In the very dilute region and when only electrostatic forces are taken into account, a very simple expression for enthalpy of dilution can be derived from Lifson and Katchalsky's or Manning's expression for the electrostatic free energy. In salt-free dilute solution, the integral heat of dilution from an initial molality m_i to a reference very low final molality m^* is given by [5,7]

$$\Delta H_d(m_i \rightarrow m^*) = \frac{NkT}{2z^2\xi}\left(1 + \frac{d \ln D}{d \ln T}\right) \ln \left(\frac{m_i}{m^*}\right) \quad (1)$$

with the charge density parameter ξ ($>z^{-1}$) defined by

$$\xi = e_0^2/DkTb \quad (2)$$

where N is the Avogadro number, k the Boltzmann constant, T the temperature, z the charge number of counterions, D the dielectric constant of solvent, e_0 the unit charge, and b the distance between neighboring ionic groups taken along the axis of the fully extended macroion. A more complicated expression has been derived allowing us to take into account the nature of the cation through the temperature dependence of the polyionic radius.[5]

The mechanism of dilution of moderately concentrated strong polyelectrolyte solutions has already been described elsewhere.[8] The dissociation of ionic species (endothermic) is followed by hydration of charges set free (exothermic) and the electrostatic interaction between free ionic species is exothermic in pure water according to eq 1 since $(1 + d \ln D/d \ln T)$ is negative in that case. As far as hydrophobic interactions are concerned, the sign of their contribution to the enthalpy of dilution depends on temperature.[6,9] It has been shown that heats of dilution of polyacrylic acid (HPA) in aqueous solutions are endothermic[10] whereas aqueous solutions of poly(methacrylic acid) (HPMA) produce exothermic heats of dilution. Figure 1 shows the variation of the integral heat of dilution with initial molality for the two weak polyacids which are not dissociated in the concentration range investigated. The broken line gives the variation with concentration of the net exothermic effect on dilution due to the presence of a methyl group on α-C of the HPMA chain. Another contribution to the heat of dilution of strong polyelectrolyte solutions may come from interactions between macroions through the intermediary of gegenions.[7] This contribution should be endothermic since dilution produces a "swelling" of the lattice-like regular distribution of macroions.

In this paper results are reported on measurements of heats of dilution of aqueous solutions of tetramethylammonium (TMA) and alkali metal salts of HPA, HPMA, and poly(ethacrylic acid) (HPEA) in the dilute and moderately concentrated ranges. These polymers may be used as model compounds for some biopolymers having hydrophobic groups and carboxylate ionic groups along their backbone.

Experimental Section

Chemicals. HPA and HPMA have been obtained by polymerization of their corresponding monomeric acid according to a technique described elsewhere.[12] The viscosity average molecular weight determined in 0.2 N HCl is 230 000 for HPA and 165 000 for HPMA. The HPEA sample has been prepared by emulsion polymerization in water at 50 °C of ethacrylic acid in the presence of a redox system (1% by weight, on monomer basis, of potassium persulfate and 0.25% of sodium bisulfite); potassium laurate was used as an emulsifier. The monomer has been prepared from dimethyl malonate.[13] HPEA is very slightly soluble in water but very soluble in basic aqueous solutions. So, the molecular weight of its sodium salt has been determined by the Archibald method in 1 M NaCl; it has been found to be 60 500. Reagent grade chemicals were used in the preparation of polymers.

The alkali metal and TMA salts of the three polyacids have been prepared by potentiometric titration with the corresponding hydroxide. A slight excess of hydroxide was added each time and the resulting solution was dialyzed against deionized water replaced every 12 h over a period of 1 week; then the solution was

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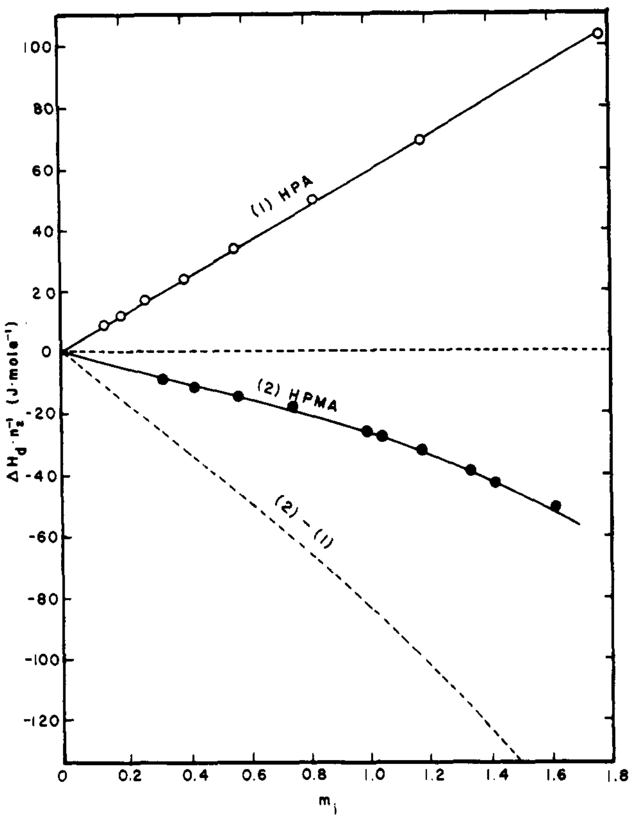

Figure 1. Integral heat of dilution as a function of initial molality: (○) HPA (calculated from ref 10); (●) HPMA (calculated from ref 11). The net effect of methyl side groups is shown by the broken line (25 °C). n_2 is the number of base moles of polymer.

evaporated and the salt freeze-dried. Each salt has been analyzed by thermogravimetry for water content before its use.

Stock solutions for calorimetric measurements have been prepared with the use of deionized water having a conductivity less than 1.5×10^{-6} mho cm^{-1}.

Calorimetry. Heats of dilution at 25 °C have been obtained by mixing equal volumes of solution and water in a Tian-Calvet microcalorimeter (equipped with 50 and 100 cm^3 cells) according to a technique already described.[8] The initial concentrations ranged from 15 to 0.01% by weight and dilutions were carried out by mixing 6.5 or 15 cm^3 of solution with an equal amount of water. The values of intermediate heats of dilution ranged from 750 to 0.001 J, the lowest reliable value for any heat effect to be measured with the experimental setup used.

Results and Discussion

Since the precision on the value of the integral heat of dilution at a given initial molality depends greatly on the values obtained at very low concentrations where precision is lost, it is preferable to express the results in terms of intermediate heats of dilution which can be defined in the very low concentration range by

$$\Delta h_d(m_i \rightarrow m_f) = \frac{NkT}{2z^2\xi}\left(1 + \frac{d \ln D}{d \ln T}\right) \ln\left(\frac{m_i}{m_f}\right) \qquad (3)$$

where m_f is the molality after dilution. Then by definition

$$\Delta H_d(m_i \rightarrow m^*) = \sum_{m^*}^{m_i} \Delta h_d(m_i \rightarrow m_f) \qquad (4)$$

However, for the results to be significant, the ratio (m_i/m_f) should be made close to a constant value for all dilutions. Thus, according to eq 3, Δh_d should be constant for $m_f \geq m^*$.

All the results obtained in the present work are given in Figures 2–4. The two extremes of the concentration range seem to present the greatest interest.

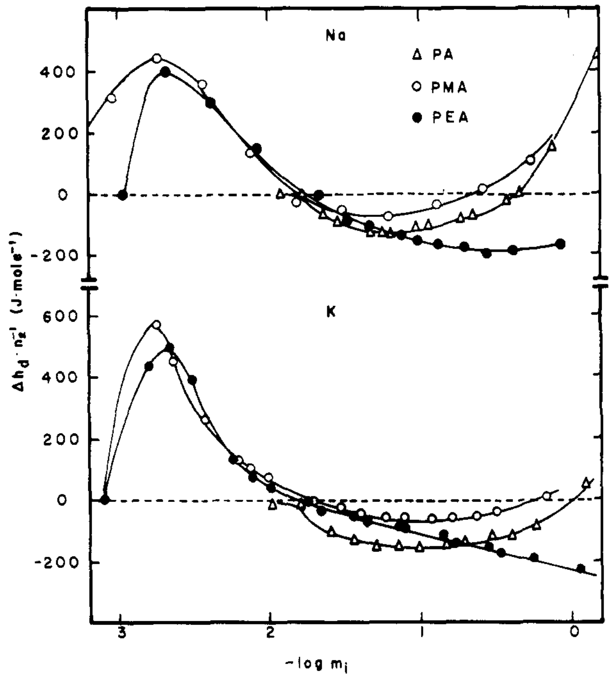

Figure 2. Intermediate heat of dilution as a function of initial molality for 1:1 dilution: upper curves, for sodium salts; lower curves, for potassium salts (25 °C). n_2 is the number of base moles of polymer.

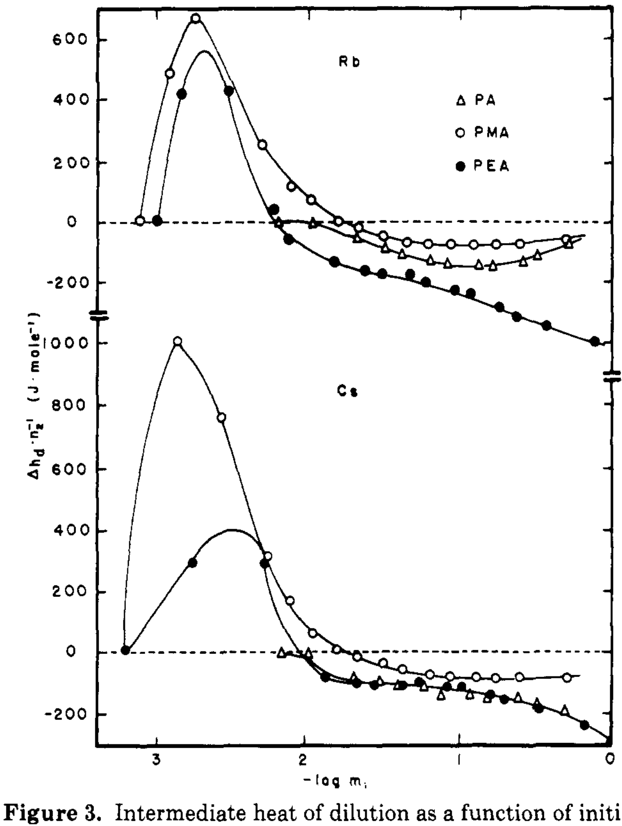

Figure 3. Intermediate heat of dilution as a function of initial molality for 1:1 dilution: upper curves, for rubidium salts; lower curves, for cesium salts (25 °C). n_2 is the number of base moles of polymer.

Concentrated Range. Effect of Cation Size. In this range where dilution produces ionic dissociation followed by hydration of the charged species set free, Δh_d values become more and more endothermic as the size of the alkali metal cation decreases, except for Li$^+$, for the three series of salts. From these results, the classification of

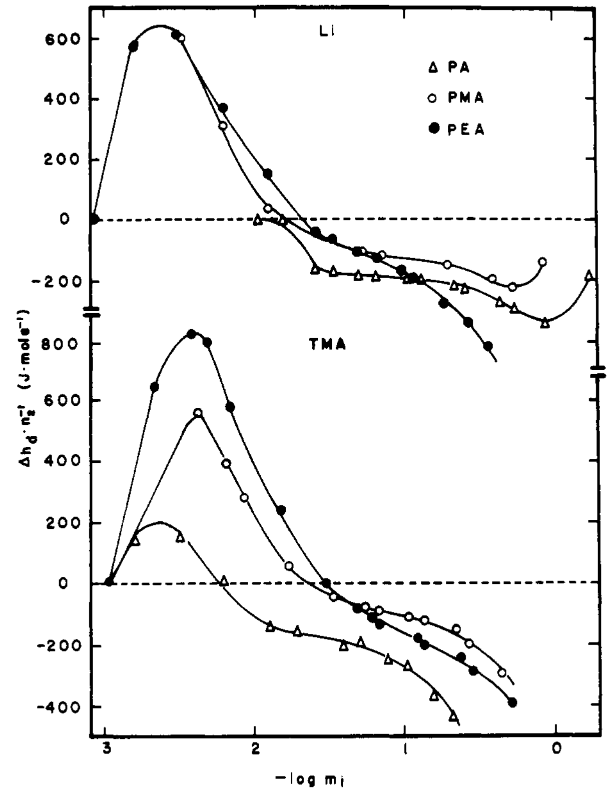

Figure 4. Intermediate heat of dilution as a function of initial molality for 1:1 dilution: upper curves, lithium salts; lower curves, tetramethylammonium salts (25 °C). n_2 is the number of base moles of polymer.

counterions in terms of degree of ionic association is the following: $Na^+ > K^+ > Rb^+ > Cs^+$. This classification is in opposition to that found for alkali metal salts of HPSS[5,8,14] whose behavior is very similar to that of simple alkali chlorides or bromides[15] as far as heat of dilution is concerned. We believe the explanation to be given by the specific character of the carboxylate anion which interacts very strongly with water and which is known as a strong water structure former.[16] The phenylsulfonate anion is also believed to be a water structure maker[17] but at a much lower degree since the structure-forming effect of the phenyl group on water molecules is partly counterbalanced by the slight structure-breaking effect of the sulfonate anion.[16] It has been shown that when both cation and anion are strong water structure formers such as Li^+ and OH^-, or both water structure breakers such as Cs^+ and Br^- or Cl^-, they interact very strongly and show a low value for the activity coefficient in moderately concentrated aqueous solutions.[16] However, when a structure-former ionic species is in the presence of a structure-breaker one such as in the case of LiBr or CsOH, the ionic association is less important and the values for activity coefficients are relatively higher.[16] Furthermore, it has been shown that the degree of association of Na^+ to the polyacrylic chain in dilute aqueous solution is larger (about 50%) than that of Cs^+ (about 20%),[18] and this is supported by the present results. Obviously water molecules play a major role in the ionic interactions discussed above[19] and more particularly when a low atomic weight alkali metal cation such as Li^+ and Na^+ interacts with an anionic group containing a strongly negative oxygen atom such as in COO^-. This type of interaction has been called hydrolytic binding by Harned and it is believed that hydrogen-bound water molecules act as ligands between the two ionic species.[20] In the present case, Li^+ ions might be so strongly bound to the carboxylate groups on the chain that only very little ionic dissociation occurs upon dilution; furthermore completion of hydration of dissociated Li^+ ions is highly exothermic as compared to that of the other alkali metal cations.[21] These two factors combined together might explain the exothermicity of dilution of all solutions of Li^+ salts in the more concentrated range as shown in Figure 4, where the contribution to Δh_d from interactions between free ions probably dominates.

As mentioned above, interaction between macroions may contribute to the net value of Δh_d. When gegenions strongly interact with macroions, formation of intra- and interchain ion triplets surely occurs in the concentrated range. If one excepts Li^+ cations, this contribution to Δh_d, which is due to the swelling of the lattice-like system, should be more endothermic when the size of the gegenions decreases, in the present case. There is a net evidence for this conclusion when results are compared for Na^+ and Cs^+ salts in the more concentrated range.

Effect of Hydrophobic Side Groups. As shown in Figure 1, at zero degree of neutralization when only dipole–dipole interactions are present between water molecules and carboxylic groups and between water molecules themselves in the formation of icebergs around hydrophobic groups, the net effect of the methyl groups on the dilution of HPMA aqueous solutions is exothermic. So, the dilution of aqueous solutions of salts of HPMA should be more exothermic than that for the corresponding salts of HPA, but the results show the opposite. To explain this apparent anomaly, one has to recall Ikegami's views on hydration of a completely neutralized polyacrylic chain.[22] In that case, chain hydration results mostly from strong ion–dipole interactions and complete hydration of the chain is produced by the cooperative action of two or more charged groups on the polyion. The hydrated chain may be compared to a uniformly "frosted" string. When hydrophobic side groups are added to the fully neutralized chain as in the case of salts of HPMA, the strong electrostatic field created by the charged sites on the chain and the cations might interfere with the dipole–dipole interactions between water molecules implicated in hydrophobic hydration lowering the importance of the contribution from this type of hydration to the net value of Δh_d. So, this competition between hydrophobic hydration and electrostatic hydration probably breaks the cooperativity of neighboring charged sites in the hydration mechanism of the chain. This might decrease the degree of hydration of the carboxylate groups which in turn might retain more strongly the cations due to a decrease in the screening effect of the water molecules around the negative charged sites leading to a more endothermic contribution from ionic dissociation upon dilution. Another explanation is that the presence of methyl side groups may lower the local dielectric constant, thus increasing the electrostatic forces between ionic species of opposite charges. This effect of alkyl side groups has been mentioned by Strauss and Schlesinger.[23]

The net exothermic effect of the hydrophobic hydration is more pronounced for the ethyl side groups as shown by the results obtained for the salts of HPEA as compared to those of HPMA. The high exothermic values for Δh_d for the three TMA salts at high concentration come from the hydrophobic hydration of the methyl groups of TMA^+ ions.

Dilute Range. The alkali metal salts of HPA give exothermic values for Δh_d in this concentration range. Exothermic heats of dilution have been reported in the literature for NaPA.[10,24,25] But dilute solutions of TMAPA as well as TMAPMA and TMAPEA show endothermic

Δh_d values. Ise et al.[25] have also obtained endothermic heats of dilution in the dilute range for aqueous solutions of R_4NPA salts. According to eq 3, for 1:1 dilutions of a fully extended vinylic chain in water at 25 °C (where $\xi = 2.85$ and $d \ln D/d \ln T = -1.372$), Δh_d should have a constant value of -112 J mol^{-1} in the dilute range. Positive and varying values for Δh_d in the dilute range reported in this work when hydrophobic groups are present either on the chain or on the cation might be explained in a way similar to that reported by Ise et al. They proposed that some of the iceberg structure around the hydrophobic groups of the R_4N^+ ions "is lost with dilution and in extremely dilute solutions, the effect of hydrophobic bonds almost disappears and only the electrostatic interactions are important". The same thing can be said about the methyl or ethyl side groups on the chain. The dehydration of the hydrophobic groups may be due to the effect of the increasing electrostatic field around the charged sites and the gegenions, which are separated upon dilution, on the dipole–dipole interaction between water molecules involved in the iceberg structure around the hydrophobic groups which are very close to the charges on the chain or on the TMA^+ ions. Obviously, when the dilution reaches the point where no more gegenion can escape from the immediate vicinity of the polyion, no more dehydration occurs.

The strong electrostatic field produced by charges carried by polyions and gegenions surely interferes with the dipole–dipole interaction between the water molecules implicated in iceberg formation around hydrophobic groups. This explanation is very similar to that given above on hydration of the PMA chain when both hydrophobic and electrostatic hydrations are present on the same chain.

Hydrolysis should be taken into account in the case of dilute aqueous solutions of salts of weak acids. Since the apparent dissociation constant of a weak polyacid decreases as the degree of dissociation increases, the apparent hydrolysis constant for an alkali metal salt of that polyacid should increase as the concentration decreases. Consequently, the pH of the salt solution should go through a maximum value as dilution progresses. This has been supported in the case of aqueous solutions of sodium salt of each of the three polyacids for $0.001 \leq m_i \leq 0.1$ ($9.5 \geq \text{pH} \geq 8.4$), the concentration range where hydrolysis contributes notably to the heat measured for a 1:1 dilution. The change in enthalpy (ΔH_h) for the total hydrolysis reaction can be estimated at 59.6 kJ mol^{-1}, including the enthalpy change for the dissociation of water into its ions (55.6 kJ mol^{-1}) and for the formation of the COOH group ($\sim$4 kJ mol^{-1}).[26] Obviously, the actual value for ΔH_h, which depends on the degree of hydrolysis, will increase very sharply as concentration goes below 0.01 m and approximate calculations indicate that, for 1:1 dilutions, the contribution from hydrolysis to the heat of dilution reaches a maximum value which varies between 275 and 400 J mol^{-1} at $m_i = 0.01$ for the three salts. The net value for the heat of dilution is the result of many heat effects and the contribution from hydrolysis is partly or completely counterbalanced by that from electrostatic interactions (-112 J mol^{-1}). If hydrolysis was the only endothermic heat effect measured in the dilute range in the present work, endothermic heats of dilution should have been obtained also for NaPA and for all other alkali metal polyacrylate solutions. But, further dilutions beyond 0.01 m gave no detectable heat effects contrary to the works of Klein and Scholz[27] and of Skerjanc[28] where endothermic heats of dilution have been reported for NaPA aqueous solutions (containing CO_2 as in the present work) for concentrations below 0.1 m. On the other hand, as mentioned above, Ise et al. reported exothermic heats of dilution in the same concentration range. It is difficult even to know about the sign of the intermediate heats of dilution of NaPA aqueous solutions from previous works. There is no doubt that hydrolysis is one of the reasons why (contrary to sodium poly(styrene sulfonate)) NaPA dilute aqueous solutions do not follow too well the predictions of Manning's limiting law as far as heat of dilution is concerned.[7,25,29] So, an unknown exothermic heat effect, in addition to the electrostatic forces effect, counteracts the hydrolysis effect to give athermal dilutions in the dilute range in the case of NaPA.

The TMA salts are hydrolyzed to a greater extent and the endothermic Δh_D values reported for TMAPA are probably due in great part to hydrolysis. But once again, ΔH_h should be a comparable value for TMA salts of the three polyacids and for all their alkali metal salts.

In summary, the explanation given above for the endothermic heats of dilution measured in the dilute range for HPMA and HPEA salts is maintained.

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