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$$\int_0^h j_l(w)\,\mathrm{d}w = \frac{(2l+3)}{(l+1)} j_{l+1}(h) + \sum_{k=1}^{\infty} \frac{(2l+3+4k)}{(l+1+2k)} \left(\prod_{i=1}^{k} \frac{l+2i}{l+2i-1}\right) j_{l+1+2k}(h)$$

Effect of Cation Size on Heats of Dilution of Aqueous Solutions of Alkaline Poly(styrenesulfonates)

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ABSTRACT: Intermediate heats of dilution at 25 °C have been measured for salt-free aqueous solutions of poly(styrenesulfonic acid) and its alkaline salts and for *p*-toluenesulfonic acid and its lithium and rubidium salts in the moderate concentration range (up to 15% by weight). Dilution for all the monomers and the polyacid and its lithium salt is exothermic over the entire concentration range covered in this investigation. The other polymeric salts give endothermic heats of dilution at moderate concentration; as concentration decreases, dilution becomes exothermic. Results are discussed in terms of the Eigen and Wicke theory on moderately concentrated electrolyte solutions, underlying hydration phenomenon as a criterion to distinguish between site binding and ionic atmosphere binding. The chemical model describing ion hydration is used to explain some of the results obtained for the polymeric and monomeric salts.

Polyelectrolytes combine the many problems of ionic interactions in solution and all those of ordinary polymers. Many experimental techniques have been used in the physical chemistry of polyelectrolyte solutions and some of the problems have been partly solved.[1] Among those techniques, heats of dilution measurement is very useful since a large concentration range can be investigated and some interesting results have already been published.[2–8]

It has been shown[9,10] that poly(styrenesulfonic acid) is completely ionized in aqueous solution and it is believed that the same is true for all strong polyelectrolytes. However, their transport properties and the osmotic coefficient of the counterions indicate that only a small fraction of them are free to move in solution.[1] To explain these experimental facts, many authors[11,12] have suggested the existence of two types of binding as usually found in moderately concentrated simple strong electrolyte solutions. One type of interaction between the charged sites on the polyion and the counterions is due to electrostatic attraction between opposite charges; this type of interaction is sometimes called ionic atmosphere binding or physical association. The second type of ionic association is believed to be due to specific interaction between the counterions and the charged sites on the polyelectrolyte chain; this type of interaction is called "site binding" or chemical association and is described in terms of a chemical equilibrium and results in a simultaneous decrease of the actual charge born by the polyion and the concentration of free counterions. Manning's treatment[13] suggests that even for a very dilute polyelectrolyte solution many counterions will condense on the polyion and that the mobile ions may be treated in the Debye–Hückel approximation.

Positive evidence for site binding is based on many experimental grounds[12,14,15] and it seems that it is accompanied by the release of water molecules from the solvation shells of the participating species. So, dehydration would serve as a criterion to distinguish between site binding and ionic atmosphere binding since solvation shells are kept untouched in the second type of ion binding. Dehydration of large alkali metal ions such as Cs^+ and Rb^+ upon formation of site binding may be said to be almost complete but the site binding of smaller ions such as H^+ and Li^+ may occur without complete dehydration.

On the basis of what has been mentioned above, the dilution of a moderately concentrated aqueous solution of a strong polyelectrolyte may be accompanied by many phenomena. Dilution effects may be regarded under two different aspects which are intimately correlated, the ionic aspect and the molecular aspect of dilution. The first effect of dilution will be the release of site bound counterions and that will involve a great amount of energy. This endothermic effect will be immediately followed by hydration of charged species which is essentially an exothermic phenomenon. Enthalpy of hydration[16] of H^+ is -1092×10^3 J mol^{-1} and that of alkali metal ions ranges between -209×10^3 and -469×10^3 J mol^{-1} from Cs^+ to Li^+. However, if only large cations are believed to be almost completely dehydrated when site bound, freeing of partly dehydrated counterions such as H^+ and Li^+ will be less endothermic since they are loosely bound to the sites on the chain due to the screening effect of the water molecules still attached to cations and negative sites. Also, hydration upon freeing of large cations should be relatively more important than that of hydrogen and lithium ions.

Hydration is not as simple a phenomenon as it appears at first sight. Hydration mechanism is believed to differ from one group of ions to another and the change in molecular structure of water due to the presence of charges will then be different for each group of ions.[17–19] According to the chemical model, each ion is embodied in cospheres made of water molecules leading to hydration of the first and of the second kind. Small cations having negative second cosphere entropy values (K^+, Rb^+, Cs^+) are called structure-breaking ions and this effect on water structure surely contributes to the heat of dilution.

In the absence of added salt, intra- and intermolecular repulsions between charged sites set free by the diffusion of some counterions out of the immediate vicinity of the polyion are increasing as dilution of a concentrated solution increases. The dilution of repulsive charges (counterions and charged sites) leads to an exothermic effect.

Finally, dilution of a moderately concentrated polyelectrolyte solution will produce some changes in the conformation of the chains. At a given concentration, polyelectrolyte molecules are more or less coiled. Upon dilution, the chains will present a more extended conformation due to the repulsion between charged sites. Chain expansion should be an endothermic effect but the energy involved in chain expansion is probably very small as compared to the energy involved in the other effects discussed above.

The present work has been undertaken in order to see how the different phenomena discussed above may govern the behavior of polyelectrolytes in aqueous solutions.

Experimental Section

Chemicals. All the alkaline poly(styrenesulfonates) and the polyacid (HPSS) used in this work were derived from one single sample of sodium poly(styrenesulfonate) kindly supplied by Dow Chemical of Canada Ltd. It was a linear polymer completely sulfonated and having a viscosity average molecular weight of 525 000. First of all, the sodium salt was converted into acid form by passing through an ion-exchange column packed with Amberlite IR-120. The HPSS solution was freeze dried and then a 15% by weight solution of the polymer was prepared using bidistilled water as solvent. All other alkali salts were obtained by neutralizing a given volume of the stock solution of HPPS by a solution of the corresponding alkali hydroxyde. Lithium, sodium, and potassium hydroxydes were analytical reagents from Fisher Scientific Co. Ltd.; rubidium and cesium hydroxydes (99.8% pure) were from Chemical Procurement Laboratories, N.Y. The salts and the acid were precipated out from their aqueous solution by adding drop by drop the solution to a large quantity (1200 ml for a total volume of 200 ml of solution) of acetone (for lithium salt and acid) or absolute ethanol under stirring. The salts and the acids were then dried, redissolved, and reprecipitated using the same technique; they were finally dried over P_2O_5 under vacuum for 1 week. The *p*-toluenesulfonic acid (HTS) was also an analytical reagent from Fisher Scientific. Alkali salts of HTS were also obtained by neutralizing the acid solution by the corresponding alkali hydroxyde solution; the resulting solution was used as stock solution.

Calorimetry. Heat of dilution measurements were done according to a method described elsewhere.[7] Pyrex glass cells only were used in this work. It was not necessary to use glass beads to assure good stirring within the cell; it was found that rocking the microcalorimeter slowly for about 90 min produced sufficient stirring since no more heat effect was then detected and the final solution was homogeneous after that period of time.

Results and Discussion

The results obtained in this investigation are given in Tables I and II. The quantity n_1 is the number of moles of water in the solution before dilution and n_2 is either the number of base moles of polyelectrolyte or the number of moles of monomeric solute. Δn_1 is the number of moles of water added to the solution. The intermediate energy of dilution, ΔE_d, is expressed in joules.

The results are very similar to those of Skerjanc et al.[5,6] who have investigated the same poly(styrenesulfonates) using a different calorimeter. The polyacid and the lithium salt give exothermic heats of dilution over the entire concentration range as predicted in the introduction, i.e., H^+ and Li^+ are never completely dehydrated so that site binding is much less important due to the screening effect of solvation shells around these ions.

The results for the other salts of HPSS may be discussed in the light of Eigen and Wicke's treatment[20] of strong electrolytes at high concentration where the integral molal energy of infinite dilution at a given concentration is defined in terms of the degree of dissociation (α) of ions. At higher concentration, α being relatively small, dissociation (endothermic) takes place upon dilution and is immediately followed by hydration (exothermic); the larger the cation, the more important is the first phenomenon since the equilibrium constant K_α decreases as the size of counterion decreases. The second phenomenon being less important for large cations, the two energetically competitive phenomena will result in more endothermic energies of dilution over the entire concentration range as one goes from sodium to cesium ions as shown in Figure 1. Water structure changes induced by cation–water and charged site–water interactions following cation–site dissociation also contribute to energy of dilution.

Table I
Calorimetric Data for Poly(styrenesulfonates) at 25 °C

n_1	$n_2 \times 10^2$	Δn_1	$\Delta E_d \times 10^2$, J
		HPSS	
1.0953	0.9281	0.3904	−103.5
1.1212	0.7657	0.3903	−80.9
1.1588	0.4662	0.3986	−51.6
1.1685	0.3709	0.3952	−41.3
1.1655	0.2269	0.3925	−26.6
1.1691	0.1775	0.3969	−21.5
1.2074	0.1136	0.3915	−12.5
1.1978	0.0875	0.4049	−9.5
1.1564	0.0516	0.3962	−4.5
1.1729	0.0413	0.3975	−3.5
1.1770	0.0259	0.4002	0
		LiPSS	
1.0340	0.9969	0.4059	−48.5
1.1163	0.7764	0.4053	−36.9
1.1422	0.5823	0.4109	−27.1
1.1605	0.4131	0.4043	−15.4
1.1708	0.3092	0.3964	−9.8
1.1909	0.2108	0.4024	−4.7
1.1764	0.1569	0.3983	−2.4
1.2195	0.1123	0.3940	−1.4
1.2197	0.0819	0.3966	0
		NaPSS	
1.1078	1.0115	0.3893	14.2
1.1160	0.8416	0.3936	2.4
1.1172	0.7946	0.3842	0
1.3623	0.6576	0.3573	−4.6
1.1237	0.4359	0.3868	−5.0
1.1865	0.4373	0.3432	−5.2
1.1454	0.3078	0.4185	−6.3
1.1542	0.2401	0.4139	−5.3
1.1646	0.2279	0.3958	−4.4
1.1717	0.1295	0.3888	−0.7
1.1972	0.1184	0.3941	−1.2
1.1563	0.0864	0.3990	0
		KPSS	
1.1072	0.8161	0.3988	15.6
1.1515	0.6338	0.3969	4.5
1.1651	0.4456	0.3745	−1.4
1.1784	0.3394	0.3980	−2.3
1.1887	0.2295	0.4010	−2.7
1.1904	0.1848	0.4000	−2.0
1.2024	0.1153	0.3925	−0.7
1.1947	0.0923	0.3903	0
		RbPSS	
1.1209	0.9076	0.3919	35.2
1.1359	0.6745	0.3976	19.9
1.1585	0.4210	0.3897	0
1.1629	0.3180	0.3948	−1.1
1.1460	0.1963	0.4062	−1.7
1.1838	0.1535	0.3959	−0.6
1.2047	0.1014	0.3930	−0.3
1.2117	0.0759	0.3907	−0.3
1.1396	0.0464	0.3941	0
		CsPSS	
1.1190	0.8474	0.4072	42.9
1.1273	0.6150	0.4015	14.8
1.2407	0.3973	0.3303	3.4
1.1636	0.2977	0.3952	0
1.1927	0.1854	0.3988	−0.4
1.1774	0.1424	0.4135	−0.4
1.1881	0.0818	0.4013	−0.5
1.2173	0.0704	0.4002	0

Table II
Calorimetric Data for *p*-Toluene Sulfonates at 25 °C

n_1	$n_2 \times 10^2$	Δn_1	$\Delta E_d \times 10^2$, J
		HTS	
1.4788	1.2224	0.3967	−499.8
1.5018	0.6395	0.3912	−172.2
1.5604	0.4863	0.3973	−100.0
1.5708	0.3672	0.3909	−59.6
1.5650	0.2546	0.4009	−33.9
1.5759	0.1936	0.3850	−20.9
1.5811	0.1399	0.3962	−12.0
1.5759	0.1007	0.3967	−7.4
1.6044	0.0761	0.3937	−4.1
1.6059	0.0549	0.3960	−2.4
1.5985	0.0398	0.4032	−1.5
1.6138	0.0292	0.3966	0
		NaTS	
1.5034	1.1150	0.3967	−214.0
1.4935	0.8016	0.3890	−129.6
1.5438	0.5470	0.3912	−71.1
1.5594	0.4076	0.3979	−44.7
1.5679	0.2705	0.3886	−21.3
1.5735	0.2014	0.3886	−14.4
1.5806	0.1329	0.3987	−7.8
1.5951	0.0979	0.3899	−4.6
1.5922	0.0664	0.3981	−2.0
1.6102	0.0471	0.3998	−0.9
1.6042	0.0325	0.3973	−0.4
1.6027	0.0223	0.3923	0
		RbTS	
1.4336	1.3381	0.4059	−127.3
1.5448	0.9623	0.4055	−82.7
1.5483	0.6412	0.4003	−46.7
1.5465	0.4243	0.3991	−25.4
1.5944	0.3047	0.3954	−16.0
1.5700	0.2051	0.3928	−8.6
1.5816	0.1367	0.3955	−4.3
1.5972	0.1003	0.3970	−2.8
1.5788	0.0657	0.3913	−1.8
1.6103	0.0487	0.4011	−1.1
1.5873	0.0321	0.4046	0

If chain extension is considered, it should be less important the smaller the counterion since negative sites on the polymeric chain are "neutralized" to a lower degree by site binding in that case; this phenomenon would contribute to reduce the heat involved upon dilution when going from a small to a large cation.

A quantitative treatment taking into account all aspects of dilution of a polyelectrolyte solution as described above would be possible defining the integral heat of dilution as Skerjanc et al. did in their treatment following the cell model of Lifson and Katchalsky,[21] after having corrected for ionic radius of counterions which is not actually possible in LK theory, and adding a term for hydration energy that can be assumed to vary linearly with α. In fact, Skerjanc et al. have succeeded to explain the concentration dependence of energy of dilution very well in the case of HPSS and its lithium salt over a wide concentration range but their treatment failed in the case of other alkaline salts at higher concentration. They claimed that the failure for the salts is due partly to too low a value for the charging parameter corresponding to a less extended polymeric chain. Obviously, chain extension will increase as the counterions are released from the negative sites on the chain upon dilution. In order to obtain a better correlation between theory and experimental results, Skerjanc et al. have taken into account the temperature dependence of the distance between the axis of the macromolecular cylinder and its surface to which the center of counterions can approach.

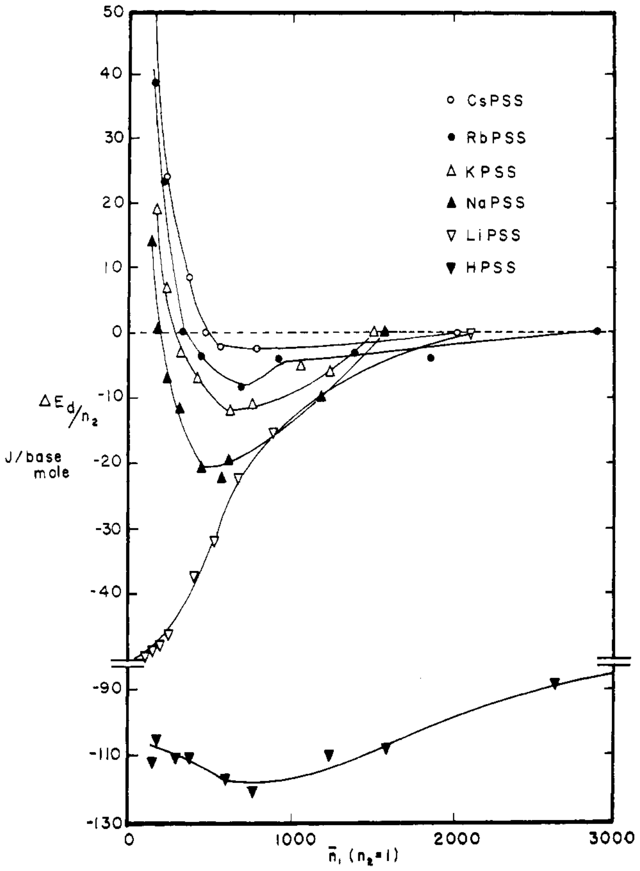

Figure 1. Variation of intermediate molal heats of dilution with the average number of moles of water for one basemole of polystyrenesulfonic acid and its alkaline salts at 25 °C.

Another relation for integral heat of dilution has been derived by Mita and Okubo[22] from Manning's limiting law.[13] The MO relation predicts that the intermediate heat of dilution will be endothermic when the charge density parameter becomes greater than unity because of a decrease in effective charges due to ion pairing. The present results confirm qualitatively this prediction. To summarize, the preceeding discussion of the results shown in Figure 1 seems to support the existence of site binding in strong polyelectrolyte solutions, a situation which has been proven right some time ago by using other experimental techniques.[23] The classification of counterions in terms of degree of site binding is obviously the following: $Ca^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+$.

Toluenesulfonic acid, being commercially available, was used as the molecular model for the monomeric unit of HPSS. The monoacid and its lithium salt behave very similarly to their polymeric counterparts, heats of dilution being much larger, however, as shown in Figure 2. The sodium and rubidium salts differ completely from NaPSS and even from their halides[20] as far as heats of dilution are concerned. The large *p*-toluenesulfonate anion interacts with water molecules as a water structure former like the *p*-ethylbenzenesulfonate anion[24] and the benzenesulfonic anion[25] and their effect on water appears to be similar to the fluoride.

In order to explain the different behavior between the monomeric and the polymeric sodium and rubidium salts, the nature of interactions between water molecules and organic groups must change going from the monomer to the polymer. In the case of the polymer, hydrophobic interactions take place mainly with benzene rings; in concentrated solution, the polymeric chain will adopt a compact conformation impermeable to water molecules, leading to a low degree of ionic

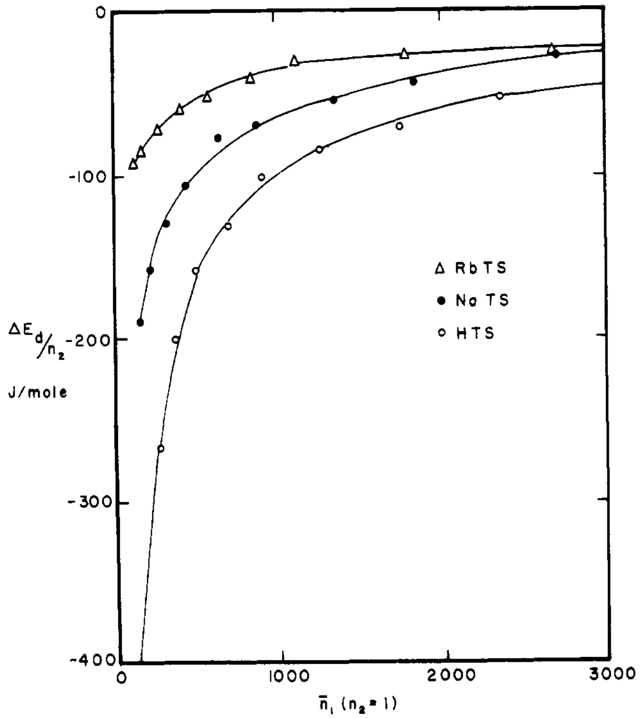

Figure 2. Variation of intermediate molal heats of dilution with the average number of moles of water for 1 mol of *p*-toluenesulfonic acid and its sodium and lithium salts at 25 °C.

dissociation. In the case of the monomer, the aliphatic group, which is less "soluble" than the aromatic group,[23] is exposed to water molecules inducing the formation of icebergs[24] which might extend over the entire anion. Hydration shells around *p*-toluenesulfonic anion are creating a screening effect, such as in the case of small cations, explaining the complete dissociation of all its alkaline salts over the concentration range covered here.

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Morphological Studies on the Viscous Crystalline Phase of Poly(diethylsiloxane) Including the Dynamics of Phase Formation and the Relationship of Viscous Crystalline Structure and Crystalline Structure

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ABSTRACT: A morphological study on the viscous crystalline phase of poly(diethylsiloxane) and its effects on the crystalline phase of the polymer has been done. It has been shown via optical microscopy and light scattering that formation of the phase, prior to crystallization, has a profound effect on the morphology of the crystalline phase. Normal spherulitic texture can be generated via quenching (elimination of the viscous crystalline phase) and an isotropically oriented birefringent structure can be obtained if the viscous crystalline phase is permitted to form (nonoriented rods?). The kinetics of formation of the viscous crystalline and crystalline phase have also been studied. Viscous crystal formation from the amorphous phase is Arrhenius activated with an energy of 47 kcal/mol. Kinetic studies of the crystalline formation have shown that the interaction parameter between the crystalline phase and surrounding material is small compared to normal semicrystalline polymer systems. These small interaction parameters are thought to be indicative of preordering of the crystal structure by the viscous crystalline phase.

Polymers are generally considered to exist in two phases: the amorphous and the crystalline.[1] The type of phase as well as the morphologies of the crystalline phase have been shown to be controlled by chemical composition, tacticity, and methods of crystallization. In addition, crystalline polymers contain amorphous and crystalline components and are called semicrystalline to denote the mixed state. Recently, two new ordered polymeric phases, which exhibit intermediate order