Abstract

Experimental and theoretical results for the enthalpies of mixing, the enthalpies of dilution, conductance and transference numbers of alkali, alkaline earth and tetraalkylammonium polyanetholesulfonates in aqueous solutions are presented. Measurements were performed in the concentration range of c_p = 0,001 to 0,2 monomol/L and temperature range of $T = 5\ ^oC$ to $40\ ^oC$. The results were compared with the theoretical ones calculated by Manning's theory. The differences between experimental and calculated values were ascribed to the ion specific interactions.

The enthalpies of mixing of the polyelectrolyte solutions of alkali and earth alkaline metal chlorides (taken at r = 4,6), decreased with the $\Delta_{hyd}H$ of the added counterions. Contrary to this, the $\Delta_{mix}H$ of PAS^- salts and TAACl solutions increased with the hydration enthalpy of TAA^+ ions. This means that the substitution mechanisms of hydrophilic and hydrophobic counterions may be different. Furthermore Me_4N^+ ion does not show such a strong hydrophobic character than other ions of the TAA^+ homologue series and to its substitution abilities it may be placed together with other members of the alkali metal ion series.

The results show that the $\Delta_{mix}H^{nc}$ is closely related to the apparent size of the hydrated hydrophilic and hydrophobic counterions. More precisely, when larger ions replace smaller ones in the close vicinity of the polyion, the heat is consumed and inversely. This rule is valid for hydrophilic and hydrophobic counterions and also for different kind of polyelectrolytes. A linear dependence of the $\Delta_{mix}H$ on the $\Delta_{hyd}H$ of the hydrophilic counterions leads to the conclusion, that the $\Delta_{mix}H^{nc}$ or enthalpy of dilution may emanate from changes of the hydration structure around the substituted counterions. When mixing polyelectrolyte and electrolyte solutions containing the hydrophobic counterions, the dominant contribution to the enthalpy of mixing may cause changes of the hydration structure around the alkyl chains of the TAA^+ counterions.

The enthalpies of dilution of earth alkaline PAS^- are lower than that of alkali PAS^- solutions and are almost independent on the nature of the counterions and temperature. $\Delta_{dil}H$ of tetraalkylammonium PAS^- solutions decrease with the length of the alkyl chain in the added counterion and show rather strong temperature dependence.

The results of the electrical conductivity and transference number measurements of LiPAS and CsPAS solutions were used to calculate the fraction of free counterions as a function of the concentration. Fractions of free Li^+ and Cs^+ ions are higher in polyanetholesulfonate than in polystyrenesulfonate solutions. These findings can be explained in terms of the structural differences between the two polyions.

From the experimental results of the thermochemical and the transport properties of polyanetholesulfonate solutions, new and mutually consistent information was obtained.

The most important recognition of the present dissertation is that different behavior of the polyelectrolyte solutions with different counterions is most likely induced by the changes in the water structure around polyion and counterions.