

HEATS OF MIXING OF MIXED SOLVENT SOLUTIONS OF ALKALI METAL SALTS OF SUBSTITUTED BENZENESULFONIC ACIDS

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Abstract

The enthalpy change on mixing solutions of methyl-substituted benzenesulfonic acids and their salts, with salts having a common cation or anion, at constant ionic strength in mixtures of 1,4-dioxane with water, were measured at 25°C. The heat effects of mixing solutions having a common anion increase almost linearly with the reciprocal value of the dielectric constant of the solvent. The heat effects of mixing solutions having a common cation, which are all negative in water-rich solutions, become endothermic after a certain value of the dielectric constant is passed. The results are discussed in terms of the solute–solvent structural properties.

Keywords: alkali metal benzenesulfonates, enthalpy of mixing, dioxane–water mixtures

Introduction

During recent decades the thermodynamic and transport properties of electrolytes and polyelectrolytes have been extensively investigated [1]. It has been widely demonstrated that these properties depend not only on electrostatic, but also on specific ion interactions in solution [2]. Important information about specific interactions in solution may be obtained by studying the heats of mixing. When measurements are made at constant ionic strength and with a common ion, effects of the ionic atmosphere and oppositely charged ion pairs cancel for charge-symmetrical mixtures. Therefore, the pair and triplet interactions of like-charged ions may be sensed [3, 4].

Recent studies in this laboratory investigated the heats of mixing of aqueous solutions of poly(styrenesulfonic acid) [5, 6] and methylsubstituted benzenesulfonic acids and their alkali metal salts [7]. In this work it was found that cation-common anion heat effects follow the empirical sign rule of Young *et al.* [8]. In contrast with this, the anion-common cation mixing heat effects are only exothermic and increase with increasing difference in the size of the participating ions. This behaviour suggests the conclusion that specific interactions involving anions and solvent exceed the Coulombic contribution to the heats of mixing.

In order to gain additional information about the nature of these interactions, we have now extended measurements of the heats of mixing of alkali metal salts of sub-

stituted benzenesulfonic acids to various dioxane–water mixtures at 25°C. This medium allows continuous variation of the solvent polarity over a large range [9]. Since dioxane–water mixtures have electric permittivities, D , lower than water, the Coulombic contribution to the heats of mixing is expected to increase.

Various alkyl substituted benzenesulfonates (BS) may act as low molecular-mass analogues for polyelectrolyte solutions [10, 11]. They are also effective hydrotropes, i.e. they can solubilize substantial quantities of hydrocarbons in water [12].

Experimental

Benzenesulfonic acid (HBS), *p*-toluenesulfonic acid (HTS), 2,5-dimethylbenzenesulfonic acid or xylenesulfonic acid (HXS), and 2,4,6-trimethylbenzenesulfonic acid or mesitylenesulfonic acid (HMS) were used as starting materials for preparation of alkali benzenesulfonates. All salts were prepared by neutralisation of an acid solution by the corresponding metal hydroxide or carbonate until a pH of about 7 was obtained. The solutions were then lyophilized. Solutions of salts of substituted benzenesulfonic acids in mixed solvents were prepared from the dry salts, distilled water and 1,4-dioxane by weighing. 1,4-dioxane and all other reagents were ‘pro-analysis’ grade from Merck and were used without further purification. Calorimetric measurements were performed at 25°C in an LKB 10700-2 Batch microcalorimeter with gold reaction cells. The detailed experimental procedure was given elsewhere [7].

Results and discussion

The heats of mixing, ΔH_m , in the present study were obtained in experiments in which two solutions of alkali metal salts of substituted benzenesulfonic acids, A and B, of the same concentration were mixed. By mixing appropriate amounts of solutions A and B the dependence of ΔH_m on the mole fraction X_A , was obtained. A typical calorimetric result is shown in Fig. 1.

Figure 1 shows the heat of mixing of LiBS and LiMS in a 50 mass% dioxane as a function of the mole fraction X_A at the total salt concentration of 0.5 mol kg⁻¹. The curves obtained for other mixing pairs (not shown here), having either a maximum or minimum, are also symmetrical with respect to the mole fraction. Because of the regular parabolic shape of the curves, such as the one shown in Fig. 1, only the extreme values of ΔH_m obtained at the mole fraction of the mixture $X_A=0.5$, are examined in further discussion.

In the next section, the results of the measurement of the heat of mixing of alkali salts of substituted benzenesulfonic acid having common anions and common cations in 50% dioxane at 25°C are presented.

Cation-common anion mixing effects in dioxane–water mixtures at 25°C

In Fig. 2, the heats of mixing of Li–Na and Li–Cs salts of HBS, HTS, HXS, and HMS at the same total concentration of 0.5 mol kg⁻¹ in 50% dioxane are compared. For ref-

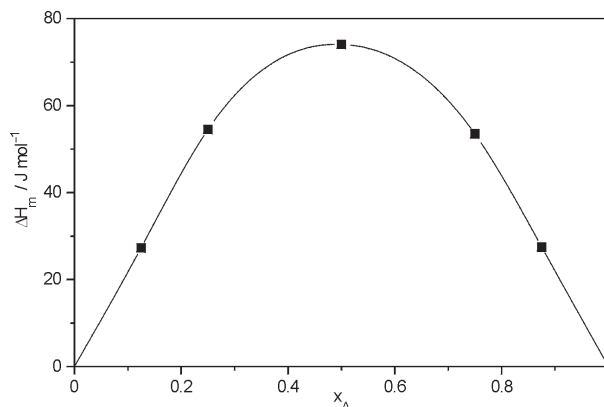


Fig. 1 Heat of mixing of LiBS and LiMS in 50% dioxane as a function of the mole fraction x_A . Salt concentration is 0.5 mol kg^{-1}

erence, also the curves for the same mixtures in water, obtained in our previous work, are included [7]. Li, Na and Cs salts were chosen for investigation because of the different influence of these cations on the structure of water. In aqueous solutions Li^+ and Na^+ ions act as those that enhance the structure of water, whereas Cs^+ ion degrades it [13]. These ion properties are, according to Young, Wu and Krawetz [8] used to predict the sign of the heats of mixing of inorganic salts with a common ion. The mixing of two structure makers or two structure breakers gave an endothermic heat of mixing, while a structure maker combined with a structure breaker gave an exothermic heat of mixing.

Our data are in accordance with the above classification of ions, because mixing Li^+ with Na^+ salts gave endothermic heat effects, and mixing Li^+ and Cs^+ salts gave exothermic heat effects. However, in contrast to aqueous solutions, a small but distinct dependence of the mixing effect on the kind of anion was found. From Fig. 2 it is also evident that in 50% dioxane the absolute values of the mixing effects exceed those in water. From these results one can conclude that the cation interactions change only in degree rather than in kind in the investigated solvent composition range. This conclusion seems to be supported by the findings presented in Fig. 3. In Fig. 3 results of the measurements of cation-common anion mixing heat effects as a function of the solvent composition, expressed by the reciprocal value of the solvent permittivity, $1/D$, at 25°C is shown.

The absolute values of heats of mixing of both two structures making Li and Na ions, and structure making Li and structure breaking Cs ions increase linearly with the reciprocal value of the dielectric constant of the solvent. On the basis of these findings, it may be reasonable to assume that the contribution of the short range cation-solvent interactions to the heat of mixing also originates from the electric charge of the cations.

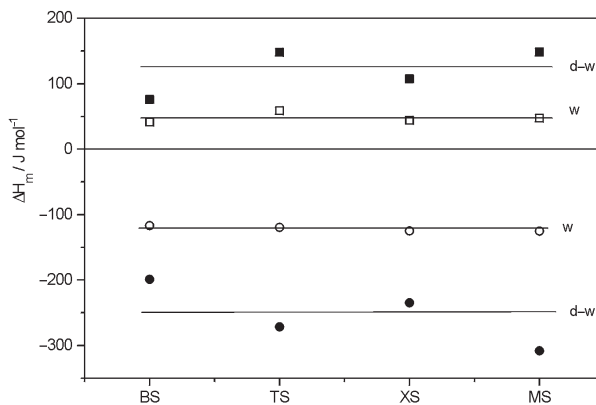


Fig. 2 Heats of mixing of benzenesulfonates having a common anion in 50% dioxane, (d-w), and in water, (w), at 25°C and $X_A=0.5$. Salt concentration is 0.5 mol kg^{-1} , \square – Li–Na, \circ – Li–Cs, \blacksquare – Li–Na, \bullet – Li–Cs

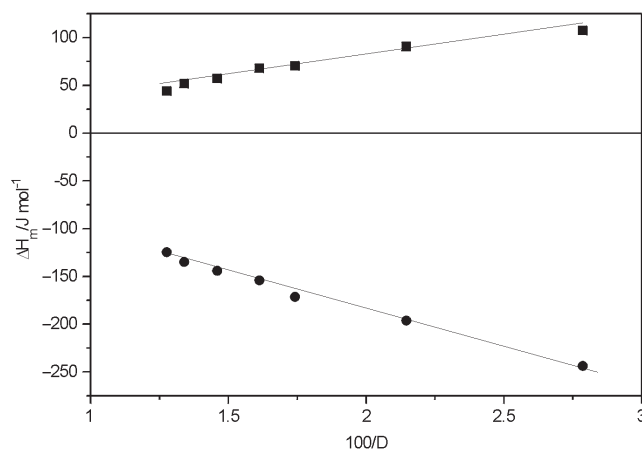


Fig. 3 Heats of mixing of benzenesulfonates having a common anion as a function of the reciprocal dielectric constant of the solvent at 25°C and $X_A=0.5$. Salt concentration is 0.5 mol kg^{-1} , \blacksquare – LiXS–NaXS, \bullet – LiXS–CsXS

Anion-common cation mixing effects in dioxane–water mixtures at 25°C

The mixing heat effects of some representative salt pairs having a common Li or Cs ion are given in Table 1. The anions chosen were such that a distinction in size difference in the number of substituted $-\text{CH}_3$ groups, Δ , on the benzene ring, could be made. These are, for instance, mixtures LiXS–LiMS which differ in one $-\text{CH}_3$ group, and LiBS–LiMS, which differ in three $-\text{CH}_3$ groups.

Table 1 Anion–common cation heats of mixing of benzenesulfonates in 50 mass% dioxane at 25°C. $c=0.5 \text{ mol kg}^{-1}$, $X_A=0.5$

Electrolyte pair	$\Delta (-\text{CH}_3)$	$\Delta H_m/\text{J mol}^{-1}$
LiXS–LiMS	1	4.0
LiTS–LiXS	1	4.8
LiBS–LiTS	1	5.1
CsTS–CsXS	1	13.4
LiBS–LiXS	2	28.0
LiTS–LiMS	2	29.4
CsTS–CsMS	2	24.5
LiBS–LiMS	3	74.1
CsBS–CsMS	3	74.0

An examination of Table 1 shows that all the heat effects in 50% dioxane are endothermic. The values of the heat effects strongly increase with increasing difference in the size of the participating anions. It should be noted that the heat effects of all the above mixtures are exothermic in water [7]. This means that the kind of interaction experiences a dramatic change when going from water to 50% dioxane (Fig. 4). In Fig. 4 anion–common cation mixing effects as a function of the reciprocal value of the solvent electric permittivity at 25°C are shown. Three Li salt mixtures, which differ in one, two or three substituted methyl groups on the benzene sulfonate anion, were chosen. All mixing heat effects, which are negative in a water-rich solution, first strongly increase, become endothermic, and increase only slightly after a certain value of the reciprocal dielectric constant is passed.

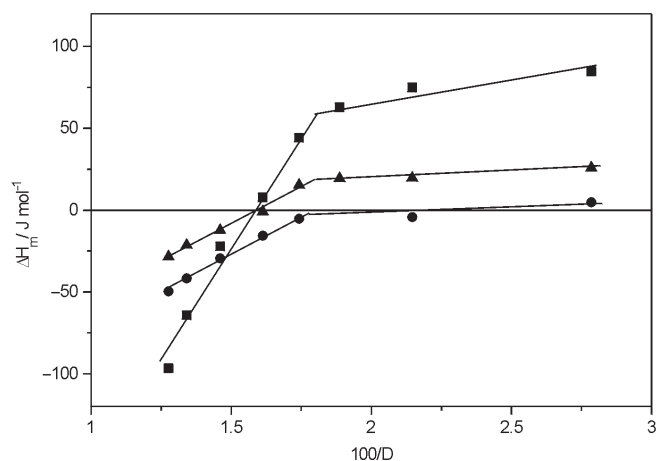


Fig. 4 Dependence of the heat of mixing of benzenesulfonates having a common cation on the reciprocal dielectric constant of the solvent, ■ – LiBS–LiMS, ● – LiXS–LiMS, ▲ – LiBS–LiXS

Exothermic mixing heat effects in water-rich solutions may be attributed to the reduction in the overlap of the hydration shells [14] of the large organic anions (the apparent molal volume at infinite dilution, Φ_v° of LiMS at 25°C is equal to 150 ml mol⁻¹), when the ion is mixed with another smaller ion (e.g. LiBS: Φ_v° = 103 ml mol⁻¹, LiXS: Φ_v° =132 ml mol⁻¹ [15]). On mixing (diluting the larger ions) more structure is formed per ion, and heat is evolved [4, 16]. On the other hand, endothermic mixing heat effects for a dielectric constant of the solvent below ca 55, may be explained by the loss of water structure in the mixed solvent [17].

Conclusions

The present results indicate that the heat of mixing of alkali salts of substituted benzenesulfonic acid may be qualitatively explained by invoking the solvent structural properties of the ions. A well pronounced difference between the mixing effects of solutions having common cations and solutions having common anions as a function of dioxane–water composition suggests that the solvation pattern of the alkali cations is much less sensitive to changes in the solvent structure than that of large organic anions.

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