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ENTHALPIES OF SOLUTION OF $SrCl_2$ AND $BaCl_2$ IN AQUEOUS MIXTURES OF METHANOL AND ETHANOL AT 298.15 K

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ABSTRACT

Enthalpies of solution of alkaline earth metal chlorides have been determined in water and aqueous mixtures of methanol and ethanol, and the enthalpies of transfer obtained. Plots of standard enthalpy of solution $\Delta H_m^{\ominus}$ vs. binary solvent composition are discussed and compared with the corresponding curve for water–methanol solutions of $CaCl_2$.

INTRODUCTION

The thermochemical properties of water–alcohol mixtures have been arousing wide interest for years [1,2]. There have been many studies of solutions of salts of 1 : 1 valence type [3–5]; but the alkaline earth metal salts have been the topic of very few investigations so far [6–9].

In an earlier paper [7] we noted a number of differences between the behaviour of $CaCl_2$ and that of the previously investigated electrolytes of 1 : 1 valence type in water–methanol mixtures. In the water-rich region, the plot of standard solution enthalpy of $CaCl_2$ vs. mol% of methanol was found to be flat rather than showing an expected maximum. It seemed interesting to test whether the same difference is to be observed for other alkaline earth metal chlorides. In the present paper we report enthalpies of solution ΔH_m determined for selected electrolytes ($SrCl_2$ and $BaCl_2$) in water–methanol and water–ethanol mixtures at 298.15 K.

EXPERIMENTAL

The $SrCl_2$ and $BaCl_2$ salts used for the investigations were crystallized from water and dried at 450 K under vacuum. Methanol and ethanol produced by POCH (Gliwice, Poland) were purified by standard methods [10]. The water–alcohol mixtures were prepared by weight. All the calori-

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metric measurements were performed using an isoperibol calorimeter, as described in a previous work [7].

RESULTS AND DISCUSSION

Measurements of the heats of solution of strontium chloride and barium chloride in aqueous mixtures of methanol and ethanol were carried out across a range of electrolyte concentrations from ca. 10^{-3} up to 2×10^{-2} mol kg^{-1} at 298.15 K. The standard enthalpies of solution of the salts $\Delta H_m^\ominus$ in water and in the mixtures were extrapolated to infinite dilution using the method proposed by Criss and Cobble [11] (Table 1). Electric permittivities and densities for the water–alcohol mixtures were taken from the literature [12,13].

A well known feature common to all the water–alcohol solutions of 1 : 1 type electrolytes that have been investigated so far is the appearance of a maximum in the water-rich region of the curve of standard solution enthalpy of the electrolyte $\Delta H_m^\ominus$ [2–7]. Many authors [16,17] have attributed this extremum to the stabilizing effect of a small amount of alcohol on the three-dimensional structure of water.

As can be seen from Table 1, the values of the calculated function $\Delta H_m^\ominus$ obtained for $SrCl_2$ and $BaCl_2$ reached maxima in both the solvents investi-

TABLE 1

Standard enthalpies of solution $\Delta H_m^\ominus$ of $SrCl_2$ and $BaCl_2$ in water + alcohol mixtures at 298.15 K

X_2 [a]	Water + methanol		Water + ethanol	
	$-\Delta H_m^\ominus$ [$SrCl_2$] (kJ mol^{-1})	$-\Delta H_m^\ominus$ [$BaCl_2$] (kJ mol^{-1})	$-\Delta H_m^\ominus$ [$SrCl_2$] (kJ mol^{-1})	$-\Delta H_m^\ominus$ [$BaCl_2$] (kJ mol^{-1})
0	51.13	13.50		
	50.74 [b]	12.61 [b]		
	51.12 [c]	13.51 [d]		
5	48.88	11.35	47.06	9.55
10	47.97	10.70	43.92	7.55
15	47.36	10.40	44.19	8.34
20	47.94	11.55	46.04	9.92
30	51.41	16.88	51.97	13.70
40			55.82	
50			61.85	
60			67.03	

[a] Mol% alcohol.
[b] From ref. 6.
[c] From ref. 14.
[d] From ref. 15.

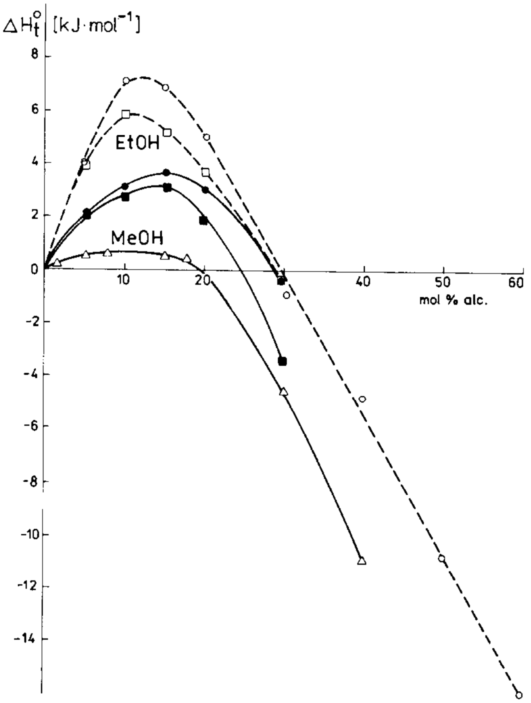

Fig. 1. Variation in the standard enthalpies of transfer (kJ mol^{-1}) of $CaCl_2$, $SrCl_2$ and $BaCl_2$ with the alcohol content of the mixture: △, $CaCl_2$ + water + methanol; ●, $SrCl_2$ + water + methanol; ■, $BaCl_2$ + water + methanol; ○, $SrCl_2$ + water + ethanol; □, $BaCl_2$ + water + ethanol.

gated, which indicates a similarity in the behaviour of these salts and 1 : 1 type electrolytes. On comparing the present results with those obtained earlier for $CaCl_2$ in the same solvents [7], it became clear that only with the water–ethanol mixtures were the shapes of the solution enthalpy curves for the three alkaline earth metal chlorides similar. In the water–methanol mixtures, the behaviour of $CaCl_2$ was different from that of the Sr^{2+} and Ba^{2+} chlorides investigated in the present work.

Some indication as to the solvation change which occurs when salts of 1 : 1 or 1 : 2 valency type are added to a mixed solvent is given by the variation in the enthalpy of transfer of solutes $\Delta H_t^{\ominus}$ with solvent composition (Fig. 1). In the water-rich region, $\Delta H_t^{\ominus}$ values are positive for both the alkaline earth metal chlorides $SrCl_2$ and $BaCl_2$ and the alkali metal chlorides, i.e. NaCl and KCl [5,18]. Probably, within this range of solvent composition, the structural ordering of the system is greater than in pure water.

To sum up, the maxima are observed at a methanol mole fraction of ca. 0.15 and an ethanol mole fraction of ca. 0.10 for all the salts investigated so far. The amplitudes of the maxima are not distinctly different for 1 : 1 and 1 : 2 electrolytes, in contrast to the case of corresponding systems containing a water–*t*-butyl mixed solvent [8]. However, what is clearly seen is a dependence between the cation valency and the solvent composition at which the enthalpies of transfer change their sign (from positive to negative). Negative values of $\Delta H_t^{\ominus}$ for bivalent cation salts appear at lower content of alcohol than for 1 : 1 salts.

Further work on 1 : 2 electrolytes in alcohol–water solutions is in progress.

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