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Enthalpies of transfer of $MgCl_2$ from water to water–methanol mixtures at 298.15 K

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Abstract

Enthalpies of transfer of magnesium chloride from water to water–methanol mixtures were determined over the entire range of mixed solvent compositions. The $\Delta H_t^{\ominus}$ values of the electrolyte were estimated from the heat of dilution of the concentrated solutions. The results are compared with the values of $\Delta H_t^{\ominus}$ for other alkaline earth metal chlorides in water–methanol mixtures.

INTRODUCTION

For some time, research in our laboratory has concentrated on the calorimetric investigation of water–alcohol solutions of alkaline earth metal chlorides. So far, we have determined the enthalpy of solution $\Delta H_s^{\ominus}$ of calcium chloride in mixtures of the first three alcohols of the homologous series with water over the entire range of mixed solvent compositions [1] and in mixtures of water with *t*-butyl alcohol up to 40 wt.% alcohol [2]. Measurements of $\Delta H_s^{\ominus}$ for $SrCl_2$ and $BaCl_2$ in water–methanol, water–ethanol [3] and water–*t*-butyl alcohol [2] mixtures were carried out in water-rich mixtures because of the limited solubilities of these salts. Changes in the enthalpy of electrolytes containing a common anion examined with changes in solvent composition make it possible to compare the properties of alkaline earth metal cations. In order to systematize the results obtained, it seemed interesting to examine how the course of this function changes in the presence of $MgCl_2$. As is known, direct measurements of the heat of solution of such a hygroscopic salt involve considerable error. Thus, in the present study, we present the values of enthalpy of transfer for $MgCl_2$ from water to mixtures of water–methanol, as determined by the method we used previously for the system magnesium chloride–water–*t*-butyl alcohol [2].

EXPERIMENTAL

Methanol (puriss, POCh, Poland) was purified by the standard method [4]. The water–alcohol mixtures were prepared by weight. All the calorimetric measurements were performed using an isoperibol calorimeter as described previously [1]. The temperature inside the calorimeter was determined using three thermistors working in a Wheatstone bridge system. The voltage of the unbalanced bridge was measured by means of a Keithley K-148 nanovoltmeter. The temperature in the thermostat was stable to $\pm 1 \times 10^{-5}$ K. The experimental precision was ±0.5%. Enthalpies of transfer of magnesium chloride were estimated from the heat of dilution by the method proposed previously [5] and then modified as described in ref. 2.

The molality ($m = 1.53$ mol kg^{-1}) of the basic concentrated aqueous solution of $MgCl_2$ was estimated by potentiometric titration using a silver nitrate solution.

RESULTS AND DISCUSSION

The values of the transfer enthalpy for magnesium chloride with varying compositions of water–methanol mixtures as determined by the above method are given in Table 1 and illustrated in Fig. 1. As can be seen, the transfer enthalpy curve of $MgCl_2$ is characterized by a maximum in the water-rich region and a minimum in methanol-rich mixtures. For the purpose of comparison, Fig. 1 shows changes in $\Delta H_t^{\ominus}$ for all the alkaline earth metal chlorides studied earlier [1–3]. Transfer enthalpies of Ca, Sr and Ba chlorides were estimated from measurements of the heat of solution $\Delta H_s^{\ominus}$, of these salts in water and in the mixtures. This comparison shows that within the range of water-rich mixtures, $\Delta H_t^{\ominus}$ maxima are characteristic for $MgCl_2$ as well as for $SrCl_2$ and $BaCl_2$ and occur at

TABLE 1

Enthalpies of transfer of $MgCl_2$ from water to water–methanol mixtures at 298.15 K

x_2 [a]	$\Delta H_t^{\ominus}$ (kJ mol^{-1})	x_2 [a]	$\Delta H_t^{\ominus}$ (kJ mol^{-1})
5	1.72	60	−3.26
10	3.56	70	−4.36
15	4.25	80	−6.39
20	4.11	90	−8.14
30	0.71	95	−7.56
40	−3.15	100	−7.17
50	−5.31		

[a] Mol.% of methanol.

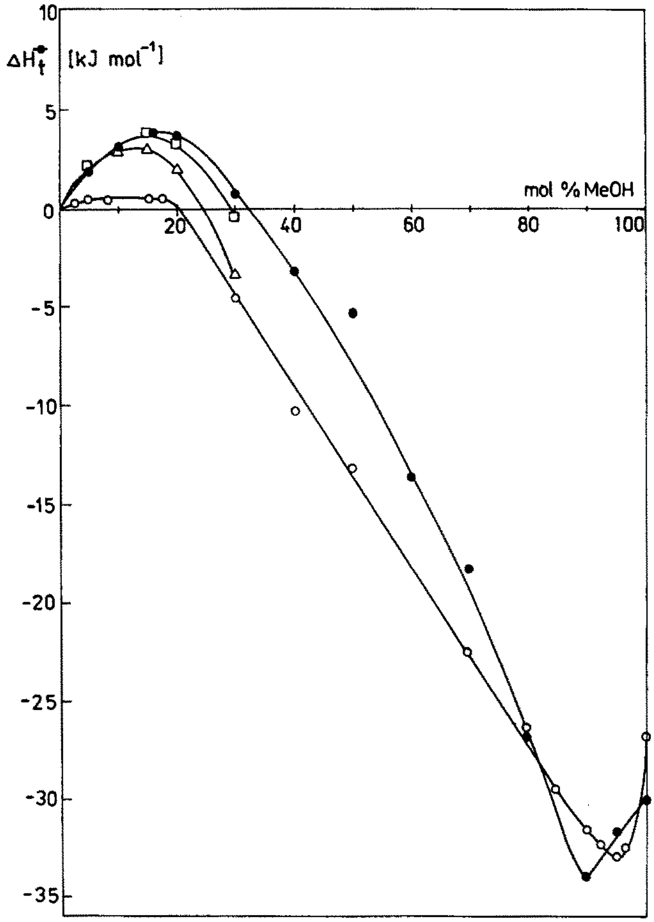

Fig. 1. Variations of the enthalpies of transfer (kJ mol^{-1}) of alkaline earth metal chlorides with the methanol content of the mixture: ●, $MgCl_2$; ○, $CaCl_2$; □, $SrCl_2$; △, $BaCl_2$.

approx. 15 mol.% methanol in water. Previously, maxima were also observed in water–methanol mixtures of alkaline metal chlorides [6–8]. In these systems the enthalpy of transfer passes through a maximum which is also in the region of 15–20 mol.% of methanol. In the water-rich region, $\Delta H_t^{\ominus}$ values are positive for both the alkaline earth metal chlorides (Fig. 1) and the alkaline metal chlorides. Many authors believe that the maximum is associated with the effect of reinforcement of the water structure by added methanol [9,10]. Probably, within this range of solvent composition, the structural ordering of the system is greater than in pure water. Of the presented electrolytes, only in the case of $CaCl_2$ does the transfer enthalpy not show considerable changes with an increase in methanol content in water, up to about 17 mol.% of alcohol.

It is also seen from the function $\Delta H_t^{\ominus} = f(\text{mol.\% methanol})$, shown in Fig. 1, that there is a growing similarity in the shape of the curves in the systems $MgCl_2$–water–methanol and $CaCl_2$–water–methanol with increasing methanol content in water. In alcohol-rich mixtures a minimum is observed in the curve $\Delta H_t^{\ominus} = f$(mol.% methanol) at about 95 mol.% in the case $CaCl_2$ and at approx. 90 mol.% in the case of $MgCl_2$. Such a minimum is not observed in the water–methanol solutions of alkaline metal chlorides [7,8]. It can be deduced that the above differences in the nature of the changes in $\Delta H_t^{\ominus} = f$(mol.% methanol) for the 1:1 and 1:2 electrolytes are connected with the different abilities of mono- and bivalent cations to form ionic associations. A considerable decrease in the dielectric constant of the mixed solvent within the range of high-methanol contents is favourable to the association process. Attempts to account for the presence of all the chemical species in solution (according to the single- or multi-stage mechanism of association) have been made in the case of symmetric electrolytes [11,12]. In asymmetric electrolytes, such attempts have just begun.

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