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Ion solvation in methanol–organic cosolvent mixtures¹ Part 5. Enthalpies of transfer of inorganic ions in mixtures of methanol and propylene carbonate at 298.15 K

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Abstract

The enthalpies of solution of NaBr, NaI and NaClO₄ in methanol + propylene carbonate mixtures were measured at 298.15 K. From these data, together with literature data that refer to (n-Bu)₄NBr, (n-Bu)₄NB(n-Bu)₄ and (n-Bu)₄NClO₄, the enthalpies of transfer of the individual ions Na⁺, Br⁻, I⁻, ClO₄⁻ and (n-Bu)₄N⁺, from methanol to methanol + propylene carbonate mixtures were calculated employing the assumption $\Delta_{tr}H^\infty(n\text{-Bu})_4\text{N}^+ = \Delta_{tr}H^\infty\text{B}(n\text{-Bu})_4^-$. The dependences of the single-ion transfer enthalpies on the mixed solvent composition are discussed.

Keywords: Cosolvent; Electrolyte; Heat of transfer; Methanol; Propylene carbonate; Solvation

1. Introduction

According to the opinion of many authors, water is not the best reference solvent when the thermodynamic properties of electrolyte solutions are analysed. The less “structured” solvents, like *N,N*-dimethylformamide, acetonitrile or even methanol are a better choice [5]. In order to verify this, systematic investigations of the thermochemical properties of electrolyte solutions in binary organic mixtures containing the solvents mentioned above have been carried out at our laboratory

¹ The previous papers in this series are refs. 1–4.

over many years. Among others, we have measured the dissolution enthalpies of NaI in mixtures of methanol (MeOH) with aliphatic alcohols [1], nitromethane (NM) [2], acetonitrile (AN) [2], *N,N*-dimethylformamide (DMF) [2], ethylene glycol (EG) [6] and glycerol (Gly) [7]. In addition, the single-ion transfer enthalpies from methanol to its mixtures with DMF [3] and AN [4] have been determined. This paper is devoted to the results of the thermochemical investigations of ion solvation in methanol + propylene carbonate (PC) mixtures. Electrolyte solutions in mixtures of methanol with propylene carbonate have already been examined in many laboratories using different experimental methods, including calorimetry. Kondo et al. [8] measured the dissolution enthalpies of several organic salts in this mixed solvent and determined the enthalpies of transfer of several ions from PC to mixtures of PC with MeOH. The thermochemical properties of inorganic salts in these mixtures have not been examined so far. Therefore, we decided to measure the enthalpies of solution of NaBr, NaI and NaClO₄ in mixtures of methanol with propylene carbonate over the whole range of the binary solvent composition at 298.15 K. By studying these salts, it was possible to analyse the influence of the nature of the anion on the thermochemical behaviour of the system, which seemed to be interesting in the light of the results of Kondo et al. [8] that the anions are very sensitive to the properties of the mixed solvent. In addition, data from ref. 8 could be used to calculate the transfer enthalpies of Na⁺ and I⁻ ions in the MeOH + PC mixtures.

2. Experimental

Propylene carbonate (Fluka AG) was stirred over molecular sieves (J.T. Baker Type 5A) for 48 h and then distilled under reduced pressure ($T = 353$ K at $p = 1.33$ mbar). Methanol (POCH-Gliwice) was dried as described earlier [1,2].

The salts NaBr, NaI and NaClO₄ (all p.a. Merck) were used without purification. They were dried under reduced pressure at 333 K for several days and were kept in a desiccator over P₂O₅.

The methanol + propylene carbonate mixtures were prepared by weight in a dry box.

The dissolution enthalpies were measured with a non-isothermal–non-adiabatic-type calorimeter. The glass calorimeter vessel of capacity approx. 100 cm³, equipped with a calibration heater, thermistor and stirrer–ampoule holder, was tightly closed with a “Teflon” lock. A thin-walled glass ampoule containing the sample of salt to be dissolved was attached to the ampoule holder and crushed against the bottom of the calorimetric vessel during the experiment. The thermistor (10 kΩ) was connected to a Wheatstone bridge. The voltage of the unbalanced bridge was measured using a Keithley K-148 nanovoltmeter connected to a digital voltmeter and a recorder. The overall temperature sensitivity of the calorimeter was found to be approx. 3×10^{-5} K. The ampoule-breaking heat effect in the reaction vessel was negligible. The calorimeter was in a hermetically closed brass jacket with a capacity

of about 1 dm³, within a water thermostat. The temperature stability of the thermostat was better than 1×10^{-3} K. The range of electrolyte concentrations in the mixed solvent was 0.002–0.02 mol kg⁻¹. The uncertainties in the measured enthalpies did not exceed $\pm 0.5\%$ of the obtained value.

3. Results

The standard solution enthalpies $\Delta_{\text{sol}}H^\infty$ for NaBr, NaI and NaClO₄ in the mixtures of methanol with propylene carbonate at 298.15 K were obtained by graphical extrapolation of the measured dissolution enthalpies in each investigated mixture as a function of the square root of the salt concentration to $m = 0$.

The standard solution enthalpies of the salts in pure methanol and pure propylene carbonate determined as described above agree reasonably well with the literature data: for NaBr in methanol $\Delta_{\text{sol}}H^\infty = -18.95$ kJ mol⁻¹ (-18.0 kJ mol⁻¹ [9], -16.95 kJ mol⁻¹ [10]); for NaI in methanol $\Delta_{\text{sol}}H^\infty = -31.73$ kJ mol⁻¹ (-29.87 kJ mol⁻¹ [10], -31.88 kJ mol⁻¹ [1], -32.05 kJ mol⁻¹ [11]); for NaI in propylene carbonate $\Delta_{\text{sol}}H^\infty = -21.05$ kJ mol⁻¹ (-21.09 kJ mol⁻¹ [12], -21.51 kJ mol⁻¹ [13]); for NaClO₄ in methanol $\Delta_{\text{sol}}H^\infty = -11.13$ kJ mol⁻¹ (-10.9 kJ mol⁻¹ [14]); and for NaClO₄ in propylene carbonate $\Delta_{\text{sol}}H^\infty = -12.85$ kJ mol⁻¹ (-12.76 kJ mol⁻¹ [12]). Because NaBr dissolves slowly in pure PC, its dissolution enthalpy in this solvent could not be determined directly. The $\Delta_{\text{sol}}H^\infty$ value in this case was calculated from the standard dissolution enthalpy of NaBr in pure DMF (-29.83 kJ mol⁻¹ [10]) and from the enthalpy of transfer of NaBr from DMF to PC ($\Delta_{\text{tr}}H^\infty = 32.61$ kJ mol⁻¹ [10])

$$\Delta_{\text{sol}}H^\infty(\text{NaBr in PC}) = \Delta_{\text{sol}}H^\infty(\text{NaBr in DMF}) + \Delta_{\text{tr}}H^\infty(\text{DMF} \rightarrow \text{PC}) \quad (1)$$

Using the data above in Eq. (1), we obtained; $\Delta_{\text{sol}}H^\infty(\text{NaBr in PC}) = -29.83$ kJ mol⁻¹ + 32.61 kJ mol⁻¹ = 2.78 kJ mol⁻¹.

4. Discussion

The molar enthalpies of transfer $\Delta_{\text{tr}}H^\infty$ of NaBr, NaI and NaClO₄ from methanol to the mixtures of methanol with propylene carbonate as a function of the molar composition of the mixed solvent are shown in Table 1 and in Fig. 1. The $\Delta_{\text{tr}}H^\infty$ values were calculated according to the formula

$$\Delta_{\text{tr}}H^\infty = \Delta_{\text{sol}}H^\infty(\text{M}) - \Delta_{\text{sol}}H^\infty(\text{MeOH}) \quad (2)$$

where $\Delta_{\text{sol}}H^\infty(\text{M})$ and $\Delta_{\text{sol}}H^\infty(\text{MeOH})$ denote the standard solution enthalpies of the given salt in MeOH + PC mixtures and in pure methanol, respectively.

As can be seen from Fig. 1, the shape of the $\Delta_{\text{tr}}H^\infty = f(x)$ function depends on the investigated salt. The dissolution enthalpies of NaBr and NaI change only insignificantly in the methanol-rich range, while that for NaClO₄ decreases rapidly when a small amount of PC is added to MeOH. However, in the range of high-PC

Table 1

Molar enthalpy of transfer of electrolytes $\Delta_t H^\infty$ in kJ mol^{-1} from methanol to methanol + propylene carbonate mixtures at 298.15 K

mol% PC	NaBr	NaI	NaClO ₄
10	-0.29	-0.17	-4.98
25	-0.50	-1.05	-7.53
50	+0.75	-0.84	-6.86
75	+2.22	-0.29	-5.43
90	+5.31	+2.01	-3.93
100	+(21.71) ^a	+9.41	-1.67

^a Value calculated as explained in the text.

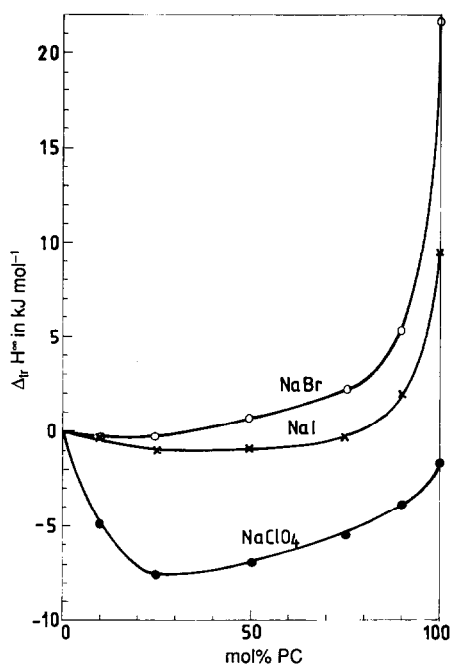


Fig. 1. Enthalpy of transfer of electrolytes from methanol to methanol + propylene carbonate mixtures at 298 K.

content, the transfer enthalpies of salts with a halide anion change drastically. It can be supposed that ion–solvent interactions are responsible for the observed course of the analysed function, the more so as the functions illustrating different physico-chemical properties, e.g. electric permittivity ϵ , density ρ , viscosity η , of the PC + MeOH mixture run monotonically over the whole range of the mixed solvent composition [15]. The curves illustrating the transfer enthalpies of the investigated sodium salts as a function of the mixed solvent composition exhibit a slight minimum corresponding to approx. 25 mol% of PC content. This fact can only be

fortuitous, but it also indicates the particular behaviour of the mixture, whose composition corresponds to the molar ratio MeOH:PC = 3:1. It is noteworthy that a semi-empirical molecular orbital calculation showed considerable electron density on the ring oxygens as well as on the carbonyl oxygen in the propylene carbonate molecule [16]. Therefore, at least theoretically, mixed H-bonded associates of (MeOH)₃·(PC) type can be formed in the investigated mixed solvent.

In order to gain some insight into the ionic solvation phenomena, it seemed advisable to determine the single-ion transfer (or solvation) enthalpies in the investigated systems. In their earlier work Kondo et al. [8] calculated the single-ion quantities in MeOH + PC mixtures for B(*n*-Bu)₄⁺, Br⁻ and ClO₄⁻ ions. To this aim the authors applied a method that assumed equality of the $\Delta_{tr}H^\infty$ values for tetra-*n*-butyl-ammonium and tetra-*n*-butylborate ions (the TBATBB method), instead of the generally accepted TATB method [17]. As stated in one of our recent papers, although the values of the ionic contributions obtained by means of these methods are different, the shapes of the curves illustrating the single-ion transfer enthalpies as a function of the mixed solvent composition are essentially the same. Consequently, an analysis of the $\Delta_{tr}H^\infty = f(x)$ function for the individual ions leads to conclusions that are qualitatively identical, independent of which of the two presented calculation methods is employed [4]. Therefore, the $\Delta_{tr}H^\infty$ values obtained in our laboratory were combined with the appropriate data from ref. 8 and the molar transfer enthalpies for individual ions from methanol to methanol + propylene carbonate mixtures were calculated. The calculations were performed by means of the multiple linear regression method.

The determined ionic transfer enthalpies are shown in Table 2 and plotted in Fig. 2 as a function of the mixed solvent composition. The $\Delta_{tr}H^\infty$ values for Br⁻ and ClO₄⁻ ions are very close to the analogous values in ref. 8.

The monotonic course of the $\Delta_{tr}H^\infty = f(x)$ function for both inorganic (Na⁺) and organic (Bu₄N⁺ [8]) cation suggests that the solvation shells of these ions change gradually from those typical for methanolic solution to those typical for solution in pure PC. The decrease in the exothermic solvation effect of the cations probably results from the lower solvation ability of PC in comparison with MeOH (the donor number, DN, is equal to 15.1 for PC and 19.1 for MeOH [18]). A more complex shape of the $\Delta_{tr}H^\infty = f(x)$ function is observed for halide anions. The

Table 2

Single-ion transfer enthalpies $\Delta_{tr}H^\infty$ in kJ mol⁻¹ from methanol to methanol + propylene carbonate mixtures at 298.15 K

mol% PC	Na ⁺	Br ⁻	I ⁻	ClO ₄ ⁻	(<i>n</i> -Bu) ₄ N ⁺
10	3.08	-3.45	-3.25	-7.97	-0.40
25	4.58	-5.40	-5.63	-11.80	0.71
50	8.82	-8.32	-9.66	-15.45	2.58
75	12.58	-10.54	-12.87	-17.83	3.62
90	15.07	-9.74	-13.06	-19.00	4.08
100	17.74	3.66	-8.32	-19.09	3.98

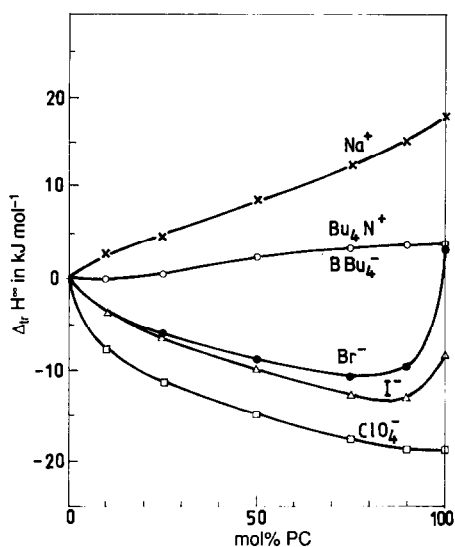


Fig. 2. Single-ion transfer enthalpies in methanol + propylene carbonate mixtures.

curves for Br^- and I^- ions show a decrease within the methanol-rich region, then they exhibit a minimum and a sharp increase in the PC-rich region. It is known that the propylene carbonate molecule does not have a well developed centre of positive charge and so it will interact relatively weakly with anions [16,19–21], while methanol molecules can interact strongly with the halide ions [22,23]. Methanol and propylene carbonate mix endothermically, which suggests that the self-association of methanol would be partially broken in these mixtures [8]. The free methanol molecules released can solvate the considered anions more easily, so that an exothermic effect of transfer of Br^- and I^- ions from pure methanol to the MeOH + PC mixtures is observed. When the amount of methanol is not sufficient to form ionic solvation structures, the process of anionic desolvation occurs. This gives a sharp increase in the $\Delta_{\text{tr}}H^\circ$ values for Br^- and I^- anions in the high-PC range. This endothermic shift is smaller in the case of the iodide anion. It is possible that the “soft”, more polarisable I^- ion interacts more strongly with the PC molecule than Br^- ion, and the desolvation of the iodide anion occurs to a smaller extent than that of the bromide ion.

The transfer enthalpy for the ClO_4^- anion decreases monotonically with increasing PC content in the mixture. According to the opinion of many authors, the ClO_4^- ion is only weakly solvated [16,23,24] or non-solvated [15] by PC molecules. However, the perchlorate anion, in which the electron delocalisation is greater than in Br^- and I^- ions, exhibits strong ion–dipole interaction with the solvent molecule. This effect is probably stronger for PC than for MeOH molecules, due to the higher dipole moment of the PC molecule. As a result $\Delta_{\text{tr}}H^\circ$ decreases significantly upon addition of a small amount of PC to methanol.

Finally, it is noteworthy that from the thermochemical point of view, the electrolyte solutions in MeOH + PC mixtures behave like solutions in MeOH + AN mixtures investigated earlier [2]. The shapes of the $\Delta_{tr}H^\infty = f(x)$ curves are similar in both systems. However, in the case of individual ionic transfer enthalpies, some differences can be observed. The $\Delta_{tr}H^\infty$ for single ions in MeOH + AN mixtures exhibit a sharp increase both for inorganic cations and halide anions [4]. It is possible that the rapid desolvation of ions within the range of small methanol content refers to both cations and anions in the MeOH + AN mixtures, while for the MeOH + PC mixtures it refers only to halide anions. In order to elucidate this matter, thermochemical investigations of some salt solutions in PC + AN mixtures have recently been undertaken.

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