HEATS OF SOLUTION OF SOME SODIUM AND POTASSIUM SALTS IN WATER AND IN WATER–METHANOL MIXTURES

Ján BENKO and Oľga VOLLÁROVÁ

Department of Physical Chemistry, Comenius University, 842 15 Bratislava

The enthalpies of solution ΔH_s^0 were determined for NaSCN, KSCN, NaBrO$_3$, KBrO$_3$, NaClO$_3$, KClO$_3$, NaIO$_4$, KMnO$_4$, KNO$_2$ and NaNO$_2$ in water–methanol mixtures. The transfer functions ΔH_t^0 of the salts and anions were calculated based on the extrathermodynamic TPTB assumption. The ΔH_t^0 values of the anion obtained from the sodium and potassium salts were compared. The differences observed, particularly at higher concentrations of the cosolvent, are discussed with respect to the interactions between the solvent molecules and the solute–solvent interactions.

The problem of the role of solvent in chemical processes has been attracting interest for a long time and continues to be topical. The assessment of interactions in mixed aqueous solvents is based on the thermodynamic transfer functions ΔH_t^0, ΔG_t^0, ΔS_t^0 whose changes are related with the differences in the solvation of the solute in water and in aqueous–nonaqueous media. Feakins and Waghorne[1] demonstrated that while ΔG_t^0 changes monotonically with the solvent composition up to rather high cosolvent concentrations, ΔH_t^0 passes through significant extremes which better mirror the solute–solvent interactions as well as the changes in the interactions between the solvent molecules. The ΔH_t^0 value can be calculated from the temperature dependence of solubility of the solute but the $\ln K_S = f(1/T)$ dependence is nonlinear even over a narrow temperature region[2] (ΔT about 10 °C). Calorimetric measurements of enthalpies of solution and dilution are more convenient and more precise[3]. The ΔH_t^0 value does not include the crystal lattice energy of the solute, it only includes the energy changes associated with the solvation effects. The solute–solvent interaction is of a complex nature because the three-dimensional "water structure" is affected both by the addition of cosolvent, as expressed by the excess mixing functions G^E, H^E and S^E, and the solute which either can contribute to the arrangement of the solvent molecules owing to its hydrophobic nature, or on the contrary, can disturb the arrangement by solvation effects. Information on the solvation of substances in a solvent is used when examining the solvent effect on the kinetics of ionic reactions, where the transfer enthalpy of the ion must be taken into account and this value cannot be determined directly by an experiment. Its calculation relies on the generally adopted extrathermodynamic principle which is based on the

assumption that the contributions of tetraphenylphosphonium tetraphenylborate (TPTB) cations and anions are the same over the entire cosolvent concentration region[4].

The present work was aimed at obtaining the enthalpies of solution of some salts in water and in water–methanol mixtures; the salts were chosen to enable us to assess the additivity of the ion transfer functions calculated based on the extrathermodynamic assumptions. Information on the electrolyte–solvent interactions was also derived from the ΔH_t^0 vs ΔH^E correlation dependences[5] as well as from the pair interaction parameters h_{ne} (ref.[6]).

EXPERIMENTAL

All chemicals used were of reagent grade purity and were dried prior to use. The enthalpies of solution and dilution were measured on an Entalpiograf isoperibolic calorimeter manufactured by the Technical University in Brno. The voltage change between a pair of thermistors in a differential bridge setup indicates the temperature difference between the vessel in which the process under study takes place (dissolution, dilution) and a vessel containing the same volume of solvent (100 ml). (R is about 15 kΩ at 23 °C, and temperature changes of $2 . 10^{-4}$ to $2 . 10^{-1}$ °C are associated with voltage changes at the bridge of 0 to 1 000 mV.) The time for which the process measured proceeded (40 – 60 s) was sufficiently short for the isoperibolic conditions to be obeyed. The instrument was calibrated by using known values of enthalpies of solution of some salts in water and in water–methanol mixtures[7 – 10]; alternatively, the instrument was calibrated electrically, and a very good agreement between the two ways of calibration was obtained. The enthalpies of solution were measured over the concentration region of 20 to 2 mmol dm^{-3}. Over this region the changes in the experimental values of enthalpies of solution with changes in the salt concentrations were not higher than the experimental errors involved in the measurement; therefore, the values measured were taken as the standard enthalpies of solution. The enthalpies of dilution were measured for a roughly 200-fold dilution of solutions of NaSCN, KSCN, NaNO$_2$ (4.0 mol dm^{-3}) and KNO$_2$ (2.86 mol dm^{-3}) in water and in water–methanol mixtures (x_2 = 0.100 and 0.228). Owing to the good solubility of these salts in water and in the mixed solvent, no correction of the enthalpy of dilution for the dilution of water in the mixed system was necessary.

RESULTS AND DISCUSSION

The experimental values of the enthalpies of solution and enthalpies of dilution in water and in water–methanol mixtures are given in Tables I and II as averages of 3 to 6 independent measurements, along with the standard deviations. The higher ΔH_t^0 values for the potassium salts in comparison with the sodium salts (with the exception of nitrites) is due to a higher lattice energy of the former. The difference tends to decrease with increasing concentration of the cosolvent, as is the case with other sodium and potassium salts[7 – 10]. The endothermic effect observed was appreciable at x_2 (MeOH) = 0.100 – 0.160, at which the changes in the arrangement of molecules in the solvation shell of the ions are most energy-demanding due to the high share of structurally bonded solvent molecules[11].

The difference between the enthalpies of solution or dilution in water and in the mixed solvent was used to calculate the transfer function of the substance studied:

$\Delta H_t^0 = \Delta H_s^0(x_2) - \Delta H_s^0(H_2O)$. It is an unfavourable fact that the error of the transfer function of the salt $\partial\Delta H_t^0$ is given by the sum of errors of the enthalpies of solution in water and in the mixed medium. An additional uncertainty in the transfer function is associated with the choice of the transfer function of the "co-ion", which involves an error as well. Table III gives the ΔH_t^0 values for some univalent anions, calculated from those of the sodium or potassium salts. The transfer functions of the sodium and potassium ions were obtained by using the extrathermodynamic TPTB assumption[4]. The transfer function $\Delta H_t^0(Na^+)$ was calculated from the enthalpies of solution of the salts according to the equations[12]

$$\Delta H_t^0(Ph_4P^+Ph_4B^-) = \Delta H_t^0(Ph_4P^+Cl^-) + \Delta H_t^0(Na^+Ph_4B^-) - \Delta H_t^0(Na^+Cl^-) \qquad (1)$$

$$\Delta H_t^0(Ph_4P^+Ph_4B^-) = 2\,\Delta H_t^0(Ph_4P^+) = 2\,\Delta H_t^0(Ph_4B^-) \qquad (2)$$

$$\Delta H_t^0(Na^+) = \Delta H_t^0(Na^+Ph_4B^-) - \Delta H_t^0(Ph_4B^-)\,. \qquad (3)$$

The transfer functions ΔH_t^0 for potassium and the other alkali metal cations have been calculated by Abraham and coworkers[12] from the enthalpies of dilution of the chlorides[3].

With regard to the above facts as well as to the precision of determination of the enthalpy of solution ΔH_s^0 and dilution ΔH_d^0 (Tables I and II, respectively), the error of the transfer function is estimated to $\partial\Delta H_t^0 \approx \pm 1$ kJ mol^{-1}. Within this error, the ΔH_t^0(anion) values obtained from the enthalpies of solution and dilution on the one hand and from the sodium and potassium salts on the other hand appear to be in a good

TABLE I
Enthalpies of solution of some salts in water and in water (1)–methanol (2) mixtures at various mole fractions x_2, $T = 298.2$ K

Salt	H_2O	$x_2 = 0.047$	$x_2 = 0.100$	$x_2 = 0.160$	$x_2 = 0.228$
NaSCN	6.7 ± 0.2	8.9 ± 0.1	9.9 ± 0.2	10.4 ± 0.1	8.7 ± 0.3
KSCN	24.2 ± 0.1	26.5 ± 0.1	27.3 ± 0.5	27.6 ± 0.2	24.5 ± 0.2
NaBrO$_3$	26.8 ± 0.2	30.5 ± 0.2	31.8 ± 0.1	31.0 ± 0.2	30.7 ± 0.5
KBrO$_3$	41.5 ± 0.2	45.3 ± 0.2	46.3 ± 0.5	44.6 ± 0.5	44.1 ± 0.4
NaClO$_3$	21.8 ± 0.1	24.3 ± 0.2	26.5 ± 0.3	25.4 ± 0.4	24.6 ± 0.4
KClO$_3$	41.5 ± 0.2	44.5 ± 0.3	46.5 ± 0.4	44.7 ± 0.3	43.9 ± 0.3
NaNO$_2$	13.8 ± 0.1	15.8 ± 0.3	16.2 ± 0.2	16.7 ± 0.2	15.8 ± 0.3
KNO$_2$	13.1 ± 0.2	14.6 ± 0.2	15.0 ± 0.3	16.2 ± 0.2	15.3 ± 0.3
NaIO$_4$	32.9 ± 0.2	36.5 ± 0.2	40.7 ± 0.4	41.9 ± 0.7	40.4 ± 0.3

agreement. Within this cosolvent concentration region (up to $x_2 = 0.228$), the TPTB assumption on the additivity of the transfer functions of ions is satisfied with a precision given by the experimental error. For cosolvent concentrations in excess of $x_2 = 0.228$, we performed a similar analysis based on published ΔH_t^0 data of sodium and potassium halides[8,10] and nitrates[9] (Fig. 1). While a good agreement was observed at low cosolvent concentrations, as shown in Table III, differences were found at higher cosolvent concentrations; the ΔH_t^0(anion) values derived from the potassium salt data were lower than those derived from the sodium salt data. In discussing this difference one must allow for the facts that the precision of determination of ΔH_s^0 decreases with increasing cosolvent concentration and that the transfer functions for sodium and potassium ions have not been determined in the same way. The fact that all ΔH_t^0(anion) values calculated from potassium salt data are lower (Fig. 1) indicates that the ion pairs, whose concentration increases with relative permittivity of medium, may exert an effect. It is known from literature[13 − 15] that potassium ions form better ion pairs than

TABLE II
Enthalpies of dilution of some salts in water and in water (1)–methanol (2) mixtures at various mole fractions x_2, $T = 298.2$ K

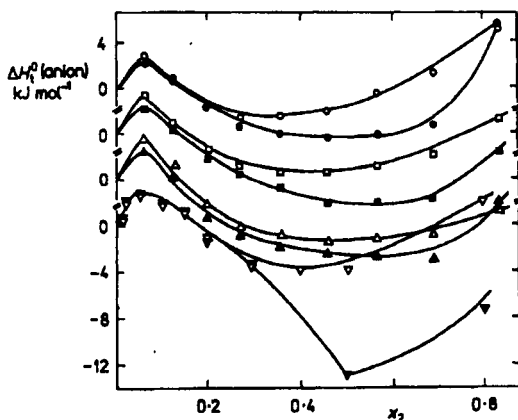| Salt	H_2O	$x_2 = 0.100$	$x_2 = 0.228$
NaSCN	6.8 ± 0.4	9.8 ± 0.4	6.8 ± 0.5
KSCN	9.6 ± 0.4	12.6 ± 0.3	9.8 ± 0.2
NaNO₂	4.9 ± 0.5	6.9 ± 0.4	5.6 ± 0.4
KNO₂	3.1 ± 0.2	4.9 ± 0.3	3.7 ± 0.3

FIG. 1
Transfer enthalpies ΔH_t^0(anion) calculated from enthalpies of solution of the sodium and potassium salts, in dependence on the MeOH mole fraction x_2: ○ Cl⁻(Na⁺), ● Cl⁻(K⁺), □ Br⁻(Na⁺), ■ Br⁻(K⁺), △ I⁻(Na⁺), ▲ I⁻(K⁺), ▽ NO₃⁻(Na⁺), ▼ NO₃⁻(K⁺); $T = 298.2$ K

sodium ions and that their association constants increase with relative permittivity of the solvent. Including the ion pair formation in the expression for $\Delta H_t^0(anion)$, we obtain the equation

$$\Delta H_t^0(anion) = \Delta H_t^0(salt) - \Delta H_t^0(cation) - \Delta H^0(associate). \qquad (4)$$

The last right-hand term in Eq. (4) is the enthalpy associated with the formation of ion pairs; it can be different for the sodium and potassium salts. This is consistent with the fact that increase in the cosolvent concentration is accompanied by a decrease in the difference between the experimental ΔH_s^0 values of sodium and potassium salts. Other factors affecting the ion pair formation include the effect of cosolvent and solute on the solvent structure. At methanol mole fractions x_2 about 0.15 the structure of water is arranged to the highest extent; additional increase in the cosolvent concentration brings about decomposition of the structure, which can, due to the assumed ion solvation, affect unfavourably the formation of contact ion pairs. A similar effect of disturbance of the solvent structure arises from an addition of electrolyte over the entire cosolvent concentration region[5]. The interaction of electrolyte (e) with cosolvent (n) can be expressed via the enthalpy pair interaction coefficient h_{ne} (refs[6,16]), which is calculated from the equations

$$\Delta H_t^0(e) / x_n = b + cx_n \qquad (5)$$

TABLE III
Transfer functions of some anions, calculated from their sodium and potassium salt data, for various MeOH mole fractions x_2; $T = 298.2$ K. Transfer functions calculated from enthalpies of dilution are given in parentheses

Anion	$x_2 = 0.047$	$x_2 = 0.100$	$x_2 = 0.160$	$x_2 = 0.228$
$SCN^-[Na^+]$	3.0	2.1 (1.9)	-0.1	-3.3 (-5.3)
$SCN^-[K^+]$	3.5	1.8 (1.7)	0.2	-5.1 (-5.2)
$BrO_3^-[Na^+]$	4.5	3.9	0.4	-1.4
$BrO_3^-[K^+]$	5.0	3.5	-0.1	-2.8
$ClO_3^-[Na^+]$	3.8	3.6	-0.2	-2.5
$ClO_3^-[K^+]$	4.2	3.7	0.0	-3.0
$NO_2^-[Na^+]$	2.8	1.3 (0.9)	-0.9	-3.3 (-4.6)
$NO_2^-[K^+]$	2.7	0.6 (0.5)	-0.1	-3.2 (-4.8)
$NO_3^-[Na^+]^a$	2.9	2.1	0.9	-1.4
$NO_3^-[K^+]^a$	3.1	2.3	1.0	-1.5
$ClO_4^-[Na^+]^b$	4.3	5.2	3.4	1.6
$IO_4^-[Na^+]$	4.4	6.7	5.2	2.2

[a] Ref.[9]; [b] ref.[12].

and

$$h_{ne} = b\, M_w\, /\, 2\, v\, ,\qquad\qquad(6)$$

where parameter b is related with the McMillan–Mayer pair interaction coefficient[17], M_W is molar mass of water and v is the number of ions in electrolyte. The pair interaction coefficients between methanol and electrolyte in water were calculated using data from Table I; their values were $h_{ne} = 200$ to 430 J kg mol^{-2}, which is consistent with the published data of $h_{ne} = 200$ and 157 J kg mol^{-2} for potassium nitrate[9] and sodium iodide[16], respectively. The fact that the values are invariably positive indicates that the electrolyte–methanol interactions are weak in the water-rich region where preferential solvation by water can be assumed. A similar analysis has been carried out for the methanol-rich region[18]. The positive h_{ne} values for electrolyte and water in methanol point to weak electrolyte–water interactions.

The above facts can account for the good agreement between the transfer functions of electrolytes obtained from the enthalpies of solution and dilution in the water-rich region. The difference in the transfer function values at higher cosolvent concentrations[3] can be contributed to, in addition to the associates, also by changes in the electrolyte solvation. De Valera and coworkers[3] measured the enthalpies of dilution by diluting small volumes of aqueous solutions of electrolytes (about 4 mol kg^{-1}) in water–methanol mixture and subtracting the enthalpy associated with the enthalpy of mixing of water in methanol. While solvation of electrolyte by methanol probably does not take place in water-rich mixtures, as borne out by the positive h_{ne} values, at higher methanol concentrations, resolvation can occur, water molecules can be replaced by methanol[19,20], which can be mirrored by the transfer function value so obtained.

Furthermore, we analyzed the solute–solvent interaction using Eq. (7) describing the relation between the ion or molecule transfer enthalpy[5] and the excess mixing enthalpy H^E, derived assuming that preferential solvation of solute does not occur:

$$\Delta H_t^0 / x_B = [(\Delta H_{12}^0)_B - (\Delta H_{12}^0)_A] - (\alpha n + \beta N)\Delta H^E / x_B + (\alpha n + \beta N)(\Delta H_A^{0}{}^* - \Delta H_B^{0}{}^*). \qquad(7)$$

Here $(\Delta H_{12}^0)_A$ and $(\Delta H_{12}^0)_B$ are enthalpies involving the solute–solvent interactions in solvents A and B, respectively; n is the number of solvent molecules in the close environment of solute; α is the fraction of bonds between the solvent molecules disturbed by solute; N and βN have a meaning similar to that of n and αn, respectively, but include the number of bonds altered due to the effect of solute in the whole solute environment; $\Delta H_A^{0}{}^*$ and $\Delta H_B^{0}{}^*$ are enthalpies of evaporation[5] of the pure solvents extrapolated to zero pressure. In the case of nonpreferential solvation the $\Delta H_t^0 / x_B$ vs $\Delta H^E / x_B$ dependence will be linear (the H^E values for the water–methanol system are taken from ref.[21]). Application of this equation to the electrolytes examined showed a behaviour similar to that found in the case of halides[5], for bulkier molecules such as $NaClO_4$ or

$NaIO_4$, however, deviations were observed (Fig. 2). The data for NaI (ref.[16]) and $NaNO_3$ (ref.[9]) were also evaluated in this manner and departures from linearity were also observed in the water-rich region. These deviations, along with the positive h_{ne} values, point to a preferential solvation by water in the region up to $x_2 \approx 0.1$. Because of the narrow cosolvent concentration region, the dependence of ΔH_t^0 on the partial enthalpy of mixing of water $L(H_2O)$, which is linear in the case preferential solvation by water[5], could not be evaluated. The results obtained give evidence that at low concentrations of cosolvent the extrathermodynamic assumption of the additivity of the transfer functions is satisfied, whereas at higher concentration, a higher number of factors play a role, so that no unambiguous conclusion can be drawn.
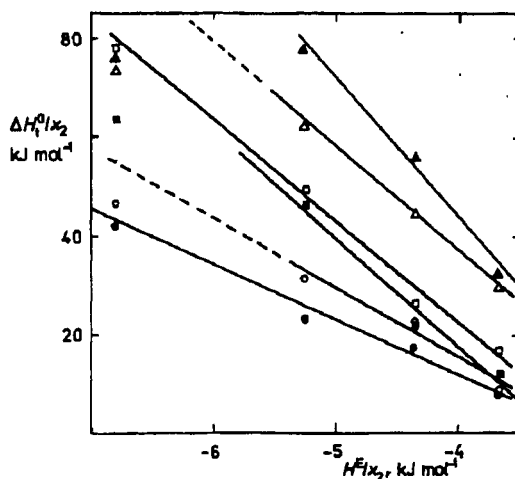

FIG. 2
Interrelation between $\Delta H_t^0 / x_2$ and H^E / x_2 in water–methanol mixture for O NaSCN, ● $NaNO_2$, ☐ $NaBrO_3$, ■ $NaClO_3$, △ $NaClO_4$, ▲ $NaIO_4$; $T = 298.2$ K

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Translated by P. Adámek.