Thermochimica Acta, 169 (1990) 347–352
Elsevier Science Publishers B.V., Amsterdam

Note

ANALYSIS OF THE THERMODYNAMIC CHARACTERISTICS OF THE SOLVATION OF IONS IN PROTIC SOLVENTS AT VARIOUS TEMPERATURES USING MODEL CONCEPTS *

A.M. KOLKER, A.N. KINCHIN and L.P. SAFONOVA

Institute of Non-aqueous Solution Chemistry of the U.S.S.R. Academy of Sciences,
1 Akademicheskaya Str., Ivanovo 153045 (U.S.S.R.)

(Received 3 December 1989)

Our laboratory of the Institute of Non-aqueous Solution Chemistry of the U.S.S.R. Academy of Sciences performs systematic investigations on the influence of low temperatures on the thermodynamic properties of non-aqueous solutions of electrolytes. The majority of non-aqueous solvents are known to have low melting points. However, for various reasons investigators do not pay much attention to this very important region of low temperatures though it is of great practical and scientific interest.

The present paper will deal with the influence of low temperatures on the thermodynamic characteristics of the solvation of ions in protic solvents, particularly in monoatomic alcohols.

EXPERIMENTAL

We have measured the enthalpies of solution of a number of 1-1 electrolytes, viz. halides of the alkali metals, of tetraalkylammonium, of tetraphenylphosphonium, and sodium tetraphenylborate in ethanol and *n*-propanol over the temperature range −50° to +55°C.

The measurements were conducted on the specially constructed hermetic microcalorimeter (Fig. 1). A massive copper block inside a Dewar vessel was used as a thermostatic shell and was cooled by liquid or gaseous nitrogen. A resistance thermometer and a heater were situated inside the block walls to control the temperature. The errors of the measurements of the thermal

---

* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.

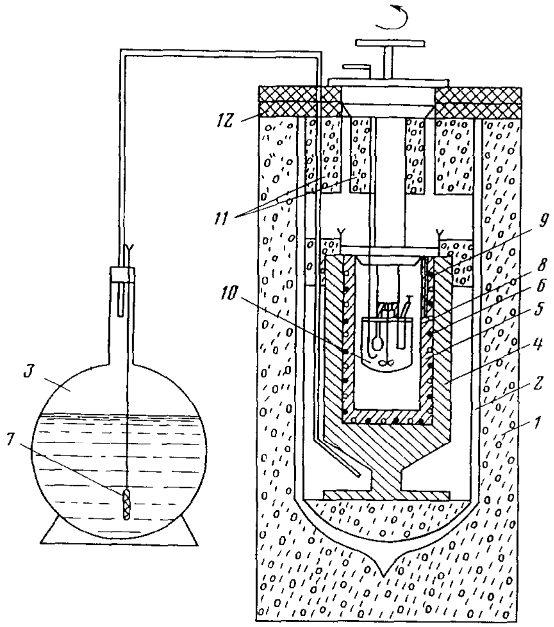

Fig. 1. The low-temperature calorimeter. 1, 11, 12, thermal isolator; 2, Dewar vessel; 3, liquid nitrogen; 4, massive copper block of the thermostat; 5, thermostatic shell; 6, heater for the thermostatic shell; 7, heater; 8, copper resistance thermometer; 9, precision platinum resistance thermometer; 10, hermetic cell of the microcalorimeter.

effects of the solution of salts in this calorimeter did not exceed 0.5%. Experimental data on $\Delta H^{\mathrm{m}}_{\mathrm{soln}}$ have been given elsewhere [1–3].

RESULTS

To obtain the standard thermodynamic characteristics of a solution we used the extrapolation equation which takes the process of ionic association into account

$$\Delta_{\mathrm{soln}}H^{\mathrm{m}} = \Delta_{\mathrm{soln}}H^{0} + \frac{\nu}{2}\,\Delta_{\mathrm{dil}}H_{\mathrm{DH}} + (1-\alpha)\,\Delta_{\mathrm{ass}}H^{0}$$

where $\Delta_{\mathrm{dil}}H_{\mathrm{DH}}$ is the contribution from the dilution of the completely dissociated part of the electrolyte which was calculated on the basis of the second approximation of the Debye–Hückel theory, α is the degree of dissociation, $\Delta_{\mathrm{ass}}H^{0}$ is the enthalpy change on the association of ions. $\Delta_{\mathrm{ass}}H^{0}$ was found from association constant data or, if the latter were not available, from the minimization conditions.

The values obtained for the standard enthalpies of solution of electrolytes at different temperatures are shown in Fig. 2.

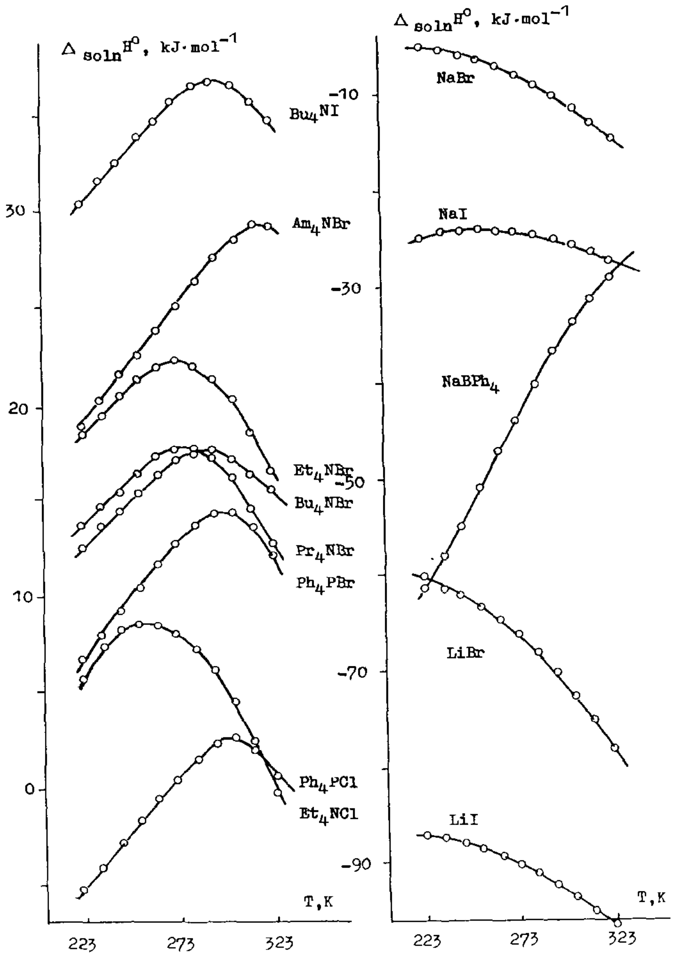

Fig. 2. Temperature dependence of $\Delta_{soln}H^0$ of 1-1 electrolytes in ethanol.

All the temperature dependences of the enthalpies of solution of all the tetraalkylammonium and tetraphenylphosphonium salts are characterized by a maximum. The position of the maximum is displaced toward higher temperatures with increasing radius of the tetraalkylammonium ion and a common anion. NaI also yields a small maximum.

A similar picture can be observed for the solutions of electrolytes in propanol (Fig. 3).

Using the values of the heat capacities of crystalline salts, the thermodynamic characteristics of the solvation of electrolytes are obtained from the temperature dependences of the enthalpies of solution of electrolytes.

Division of the total characteristics into ionic constituents is made on the basis of the assumption of the equality between their change with temperature for a pair of ions: tetraphenylphosphonium and tetraphenylborate.

$$\Delta_{solv}C_p^0(BPh_4^-) = \Delta_{solv}C_p^0(Ph_4P^+)$$

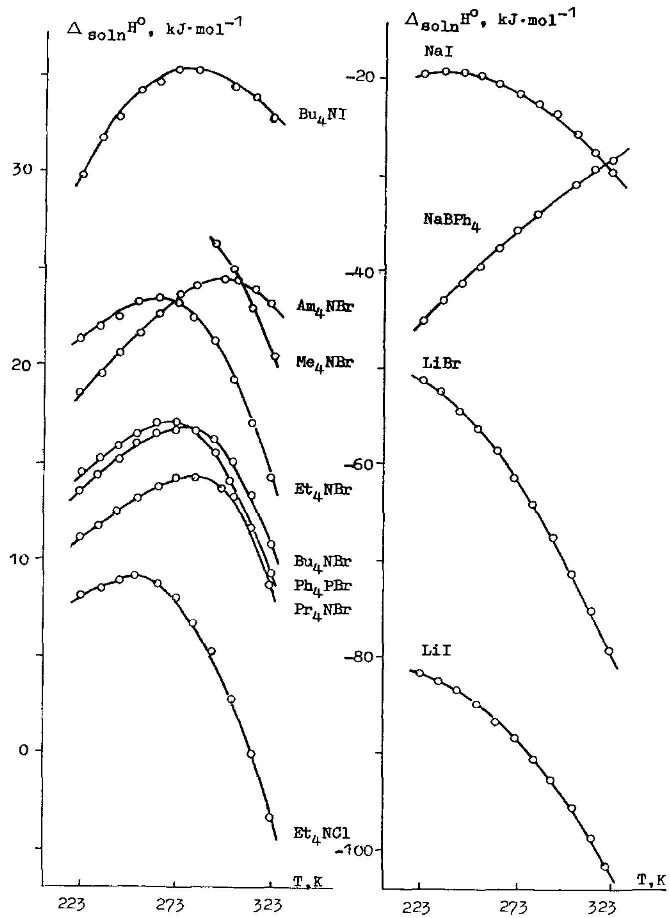

Fig. 3. Temperature dependence of $\Delta_{\text{soln}}H^0$ of 1-1 electrolytes in *n*-propanol.

or

$$\Delta_{\text{tr}}H^0_{\text{solv}}(T \to 298)\text{Ph}_4\text{P}^+ = \Delta_{\text{tr}}H^0_{\text{solv}}(T \to 298)\text{BPh}_4^-$$

The temperature dependence of the differences in the changes of enthalpies of solvation of individual ions at the given temperature and at 298 K is shown in Fig. 4. In the solvents studied, one can observe a transition from negative to positive temperature coefficients of the enthalpies of solvation of ions in the dependence on their nature and size. For halide ions, the temperature coefficients are always negative. For cations, it is positive except for the lithium ion in propanol.

So, the extremes in the temperature dependences of the enthalpies of solution of electrolytes (Figs. 2 and 3) are determined by the counter-influence of temperature on the enthalpies of solvation of the cation and anion which form the given salt.

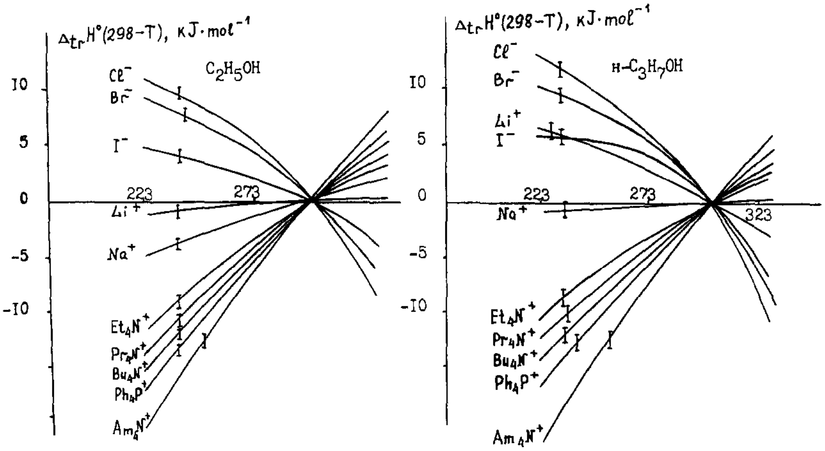

Fig. 4. Temperature dependence of $\Delta_{tr}H^0_{solv}(T \rightarrow 298\ K)$ in ethanol and propanol.

Analysis of the influence of temperature on the state of ions in solution can be performed using various models. We used the approach based on the representation of the total solvation characteristic in the form of contributions from the electrostatic interaction of the ion with solvent ($\Delta_{el}Y_i^0$), formation of the cavity of appropriate size within the solvent ($\Delta_{cav}Y_i^0$) and contributions from other interactions of the ion with the solvent ($\Delta_{int}Y_i^0$) and from its structural changes ($\Delta_{str}Y_i^0$).

$$\Delta_{solv}Y_i^0 = \Delta_{el}Y_i^0 + \Delta_{cav}Y_i^0 + \Delta_{str}Y_i^0 + \Delta_{int}Y_i^0$$

The electrostatic contribution was calculated from various continuum models: the Abraham equation for a two-layer model [4], modified the Born equation by accounting for the change in dielectric permeability of solvent vs. its distance to the ionic centre [5], an equation based on Debye's theory for the dielectric permeability of the medium [6]. The contribution from cavity formation was calculated from the equations of the scaled particle theory, taking account of the temperature changes in the diameter of the solvent solid sphere.

The calculations show that the electrostatic interaction yields a negative temperature coefficient in the enthalpic and entropic characteristics of solvation of ions.

The contribution from cavity formation yields a positive temperature coefficient in the thermodynamic characteristics of solvation of ions. The greater the ionic size, the greater is the magnitude of the contribution.

So, the positive temperature coefficients of the enthalpies of solvation of tetraalkylammonium, tetraphenylborate and tetraphenylphosphonium cations are conditioned by the determining influence of the contribution from the cavity formation on the changes of $\Delta_{solv}H_i^0$. The effects of cavity formation will not be determining for the ions of the alkali metals. The structural contribution evidently comes to the fore here; a concrete interpretation of this contribution is difficult at the moment.

As shown above, the halide ions have negative temperature coefficient of the enthalpies of solvation which is not in agreement with the scheme given.

This peculiarity of anions is connected first of all with their ability to form hydrogen bonds with the molecules of protic solvents. Increase in temperature leads to a substantial displacement of the equilibrium from the formation of hydrogen bonds between the solvent molecules to the solvent–anion bonds. Here the total energy of the hydrogen bonds between the alcohol molecules decreases with increasing temperature more than that between the proton of the hydroxyl group and anion. This results in the negative temperature coefficient of the enthalpies and entropies of solvation of anions.

If the present model is correct, then this should not be observed in the aprotic solvents. This will be shown by future investigations which we have already undertaken, e.g. in acetonitrile.

REFERENCES

1 S.L. Solovyov, A.N. Kinchin, A.M. Kolker and L.P. Safonova, Dep. VINITI, Moscow, 29.12.86, N° 8944-B-86.
2 S.L. Solovyov, L.P. Safonova, A.N. Kinchin and A.M. Kolker, Dep. VINITI, Moscow, 27.07.86, N° 5351-B-86.
3 S.L. Solovyov, A.N. Kinchin, L.P. Safonova and A.M. Kolker, Dep. VINITI, Moscow, 05.05.88, N° 3489-B-88.
4 M.H. Abraham, J. Liszi and L. Meszaros, J. Chem. Phys., 70 (1979) 2491.
5 T. Abe, J. Am. Chem. Soc., 90 (1986) 713.
6 M. Burher and T.L. Porter, J. Phys. Chem., 90 (1986) 3406.