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THERMOCHEMICAL INVESTIGATION OF NaI SOLUTIONS IN WATER-ACETAMIDE MIXTURES*

The enthalpies of solution of NaI in water-acetamide mixtures have been determined colorimetrically over the temperature range 25-85 C. The thermodynamic results obtained are correlated with results from earlier measurements on water-amide mixtures.

Amides attract considerable interest in view of their ability to dissolve various substances; for this reason they are employed in a variety of technological processes. Owing to their high dielectric constants they are also good solvents of electrolytes, the presence of H-bonds in unsubstituted and monosubstituted amides may suggest a certain similarity to water. Particularly good electrolyte-solving ability has been observed in the case of water-acetamide mixtures [1, 2].

The results obtained in [1] and [2] suggest that the thermodynamic similarities between water and acetamide solutions of electrolytes may be related to the remainders, in the liquid state, of the three-dimensional H-bond lattice which is present both in solid acetamide [3-5] and in ice [6].

In view of this we found it interesting to measure the heat of electrolyte dissolution in a mixed solvent made up of water and acetamide. The electrolyte chosen was NaI which is the most thoroughly investigated salt in organic and mixed solvents. The results obtained for water-acetamide solutions can thus be compared with those for other mixed solutions.

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Experimental

The enthalpies of solution of NaI were measured calorimetrically for a series of water-acetamide mixtures of different acetamide content in the temperature range 25-85°C. The measurements were conducted in a nonisothermal non-adiabatic calorimeter. The calorimeter proper was a 220 cm^3 Dewar vessel supplied with a stirrer, calibration heater and thermistor. Temperature changes during the measurements were determined by means of a 0-2 mV MKT recorder (GDR). The calorimeter was sensitive to $5 \cdot 10^{-4}$°C. The measurement error was estimated to be about 1%.

The water-acetamide solvents employed in the investigation were prepared by weight using twice-distilled water and dried and purified acetamide p. a. produced by Xenon-Łódź [7]. The melting point of acetamide was 81-82°C [8]. NaI was purified by a procedure described in [9].

Results and discussion

The obtained heat of solution values ΔH_m for NaI dissolved in water-acetamide mixtures at 25, 40, 60, 75 and 85°C are presented in Figs. 1-5 as functions $\Delta H_m = f(m)$.

In the case of water and mixed solutions containing less than 30 wt % of acetamide (11.5 mole %) the isoterms $\Delta H_m = f(m)$ corresponding to a temperature 25°C (for water also 40°C) may be classified as type II isoterms in the Mis'hchenko and Pronina's classification [10].

The other isotherms are of type I, i. e. the exothermicity of the heat of solution decreases as the electrolyte concentration rises. As can be seen in Figs. 1-5, changes in the shapes of isotherms $\Delta H_m = f(m)$ for the investigated systems depend on acetamide concentration in the mixed solvent and on the temperature of the solution.

In the case of water solutions of NaI, the transition from type II to type I isotherms takes place at about 45°C. This

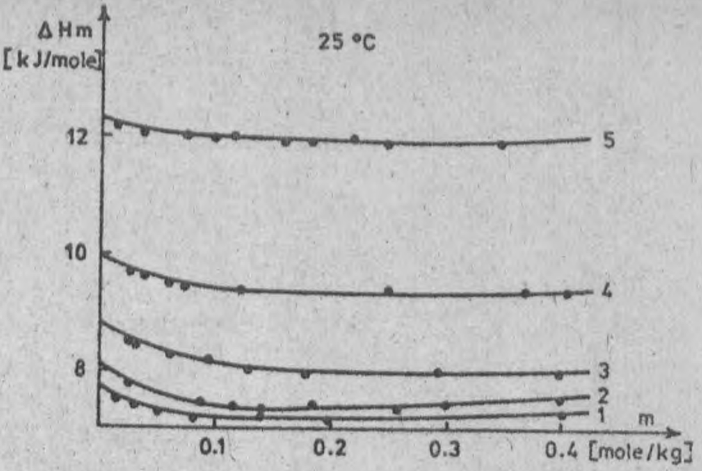

Fig. 1. Dependence of the heat of solution (ΔH_m) of NaI on concentration in water-acetamide mixtures at 25°C. 1 - water; 2 - 5 wt % (1,58 mole %) $AcNH_2$; 3 - 15 wt % (5.1 mole %) $AcNH_2$; 4 - 30 wt % (11,55 mole %) $AcNH_2$; 5 - 50 wt % (23,36 mole %) $AcNH_2$

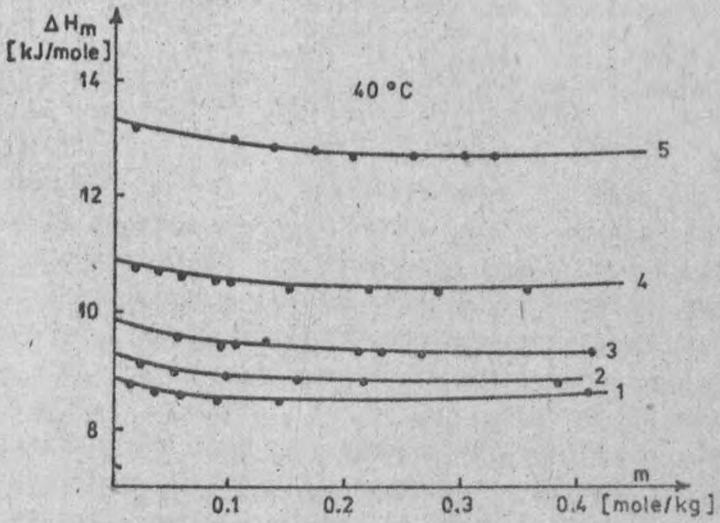

Fig. 2. Dependence of the heat of solution (ΔH_m) of NaI on concentration in water-acetamide mixtures at 40°C. 1 - water; 2 - 5 wt % (1,58 mole %) $AcNH_2$; 3 - 15 wt % (5,1 mole %) $AcNH_2$; 4 - 30 wt % (11,55 mole %) $AcNH_2$; 5 - 50 wt % (23,36 mole %) $AcNH_2$.

transition point lowers as the acetamide content in the mixed solvent increases.

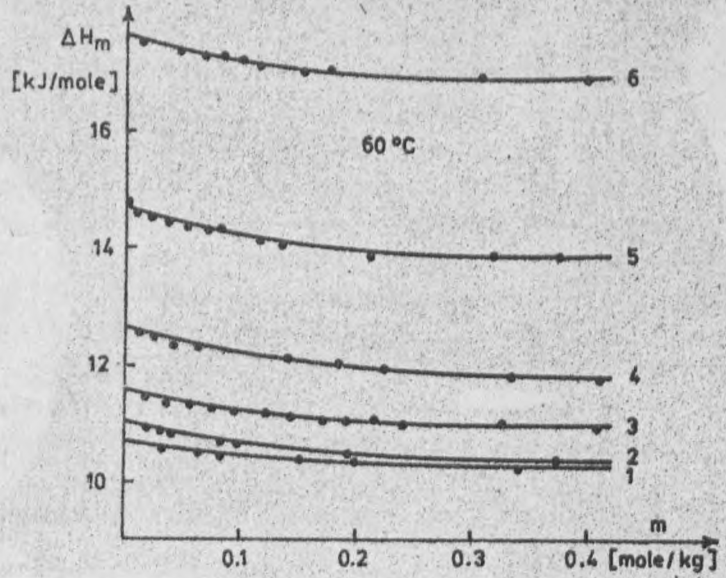

Fig. 3. Dependence of the heat of solution (ΔH_m) of NaI on concentration in water-acetamide mixtures at 60°C. 1 - water; 2 - 5 wt % (1,58 mole %) AcNH ; 3 - 15 wt % (5,1 mole %) $AcNH_2$; 4 - 30 wt % (11,55 mole %) $AcNH_2$; 5 - 50 wt % (23,36 mole %) $AcNH_2$; 6 - 70 wt % (41,55 mole %) $AcNH_2$

When the mixed solvent contained 50 wt % of acetamide, the shape of the isotherms $\Delta H_m = f(m)$ changes already at about 25°C. As is well known, type I isotherms are characteristic of strongly solvated electrolytes, for which the energetic effect related to ion desolvation grows with increasing concentration and predominates over the exothermic process of ion approaching. On the other hand, in type II isotherms $\Delta H_m = f(m)$ decisive role is played by processes of ion approaching and destruction of the solvent structure by those ions which leads to increased exothermicity of the dissolution process as the concentration of the solution increases. Addition of acetamide to water evokes a similar effect as the growth of temperature. Thus, possibly, acetamide molecules partialy disrupt the original structure of water but, as can be seen in Figs. 1-5 the effect is not very significant.

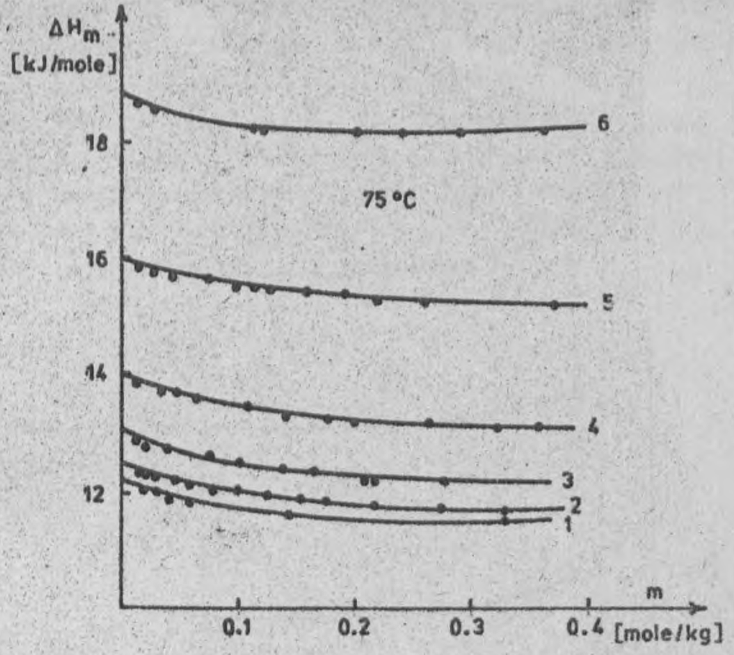

Fig. 4. Dependence of the heat of solution (ΔH_m) of NaI on concentration in water-acetamide mixtures at 75°C. 1 - water; 2 - 5 wt % (1,58 mole %) $AcNH_2$; 3 - 15 wt % (5,1 mole %) $AcNH_2$; 4 - 30 wt % (11,55 mole %) $AcNH_2$; 5 - 50 wt % (23,36 mole %) $AcNH_2$; 6 - 70 wt % (41,55 mole %) $AcNH_2$

Thermochemical investigations of NaI solutions in mixed water-formamide solvents [11] have shown that the isotherms $\Delta H_m = f(m)$ have a very small slope $\Delta(\Delta H_m)/\Delta m$ which may be related to the high dielectric constant. In the case of water-NaI-DMF system [11] the shape of the isoterm changes much faster; already in the solutions containing 20 mole % of DMF the exothermicity of the heat of solution decreases distinctly depending on the concentration (type I isotherm). This may be related to the presence of two methyl groups in a DMF molecule (lower dielectric constant, larger molecule, absence of three-dimensional H-bond lattice).

A comparison of the thermochemical properties of water mixtures with formamide, acetamide and DMF shows that the acetamide investigated in this study has intermediate properties.

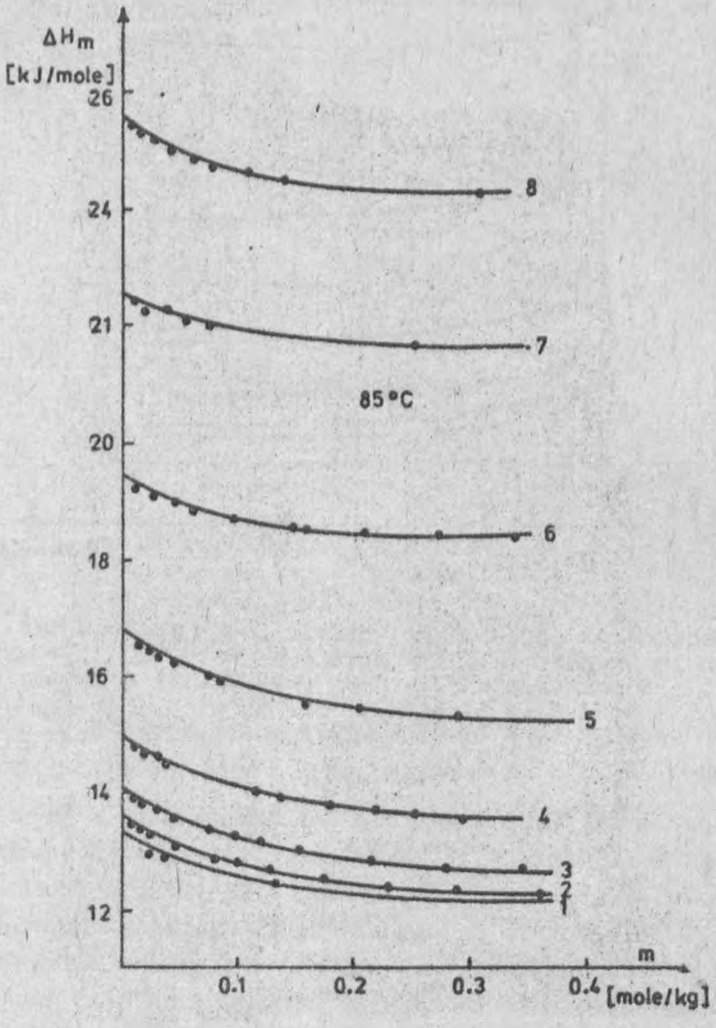

Fig. 5. Dependence of heat of solution (ΔH_m) of NaI on concentration in water-acetamide mixtures at 85° C. 1 - water; 2 - 5 wt % (1,58 mole %) $AcNH_2$; 3 - 15 wt % (5,1 mole %) $AcNH_2$; 4 - 30 wt % (11,55 mole %) $AcNH_2$; 5 - 50 wt % (23,36 mole %) $AcNH_2$; 6 - 70 wt % (41,55 mole %) $AcNH_2$; 7 - 85 wt % (63,3 mole %) $AcNH_2$; 8 - 95 wt % (85,3 mole %) $AcNH_2$

Figure 6 shows the dependence $\Delta H^{o}_{NaI} = f(x)$ for water-acetamide solutions. The heat of solution of NaI in an infinitely dilute solution were obtained by linear extrapolation of the dependence $\Delta H_{m} = f(\sqrt{m})$ because we did not have the data necessary to extrapolate the function $\varrho^{m} = f(m)$ by the method of Criss and Cobble [12, 13].

As can be seen in Fig. 6 the dependence ΔH^{o}_{NaI} in water-acetamide solutions on the mole fraction of acetamide is linear suggesting that interactions between water and acetamide molecules are very weak and that the heat of solution of NaI in an infinitely dilute solution is additive.

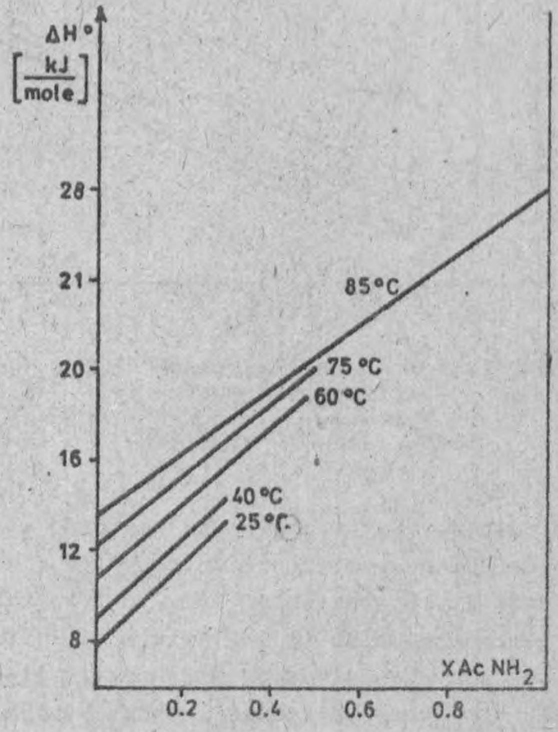

Fig. 6. Standard solution enthalpy of NaI (ΔH^{o}) in water-acetamide mixtures as a function of solvent composition

The dependence ΔH^{o}_{NaI} on the temperature in water-acetamide mixtures is presented on Fig. 7. As we can see from Fig. 7 the course of the function $\Delta H^{o}_{NaI} = f(T)$ for investigated solvents almost does not depend on the contents of acetamide in the mixed solvent.

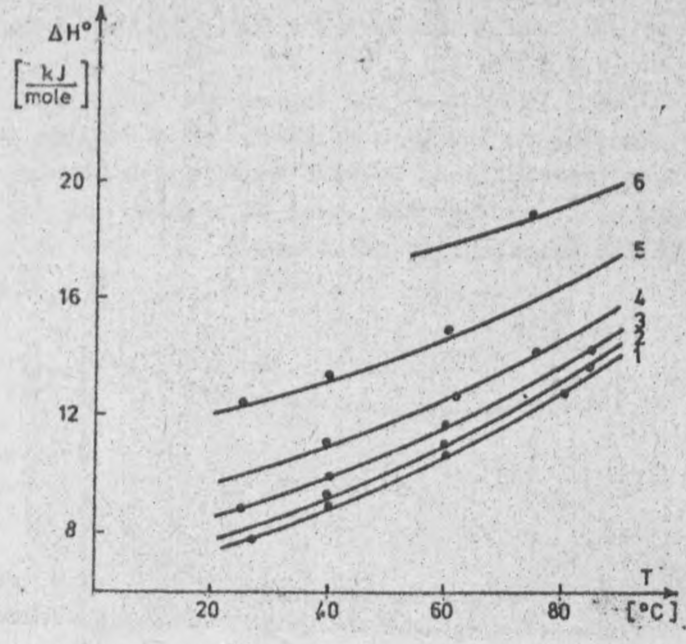

Fig. 7. Standard solution enthalpy of NaI (ΔH^{o}) in water-acetamide mixtures as a function of temperature. 1 - water; 2 - 5 wt % $AcNH_2$; 3 - 15 wt % $AcNH_2$; 4 - 30 wt % $AcNH_2$; 5 - 50 wt % $AcNH_2$; 6 - 70 wt % $AcNH_2$

In order to compare water-acetamide mixtures with other mixed solvents the dependence of function $\Delta H_m^{0.1} = f(x)$ of NaI in some mixed solvents is presented on Fig. 8 (X - the molar fraction of the organic component in the mixture). It can be seen that the function for alcohol-water mixtures is distinctly different from those for other mixtures in that there appears a minimum of heat of solution exothermicity at $x = 0.2$ for methanol and at $x = 0.09$ for isopropanol.

According to Samoilov [21, 22] the appearance of a minimum is connected with filling the gaps in water structure by alcohol molecules. This interpretation, probable as it is, is not universal and cannot be applied to other non-electrolytes even though the size of their molecules is such that they could

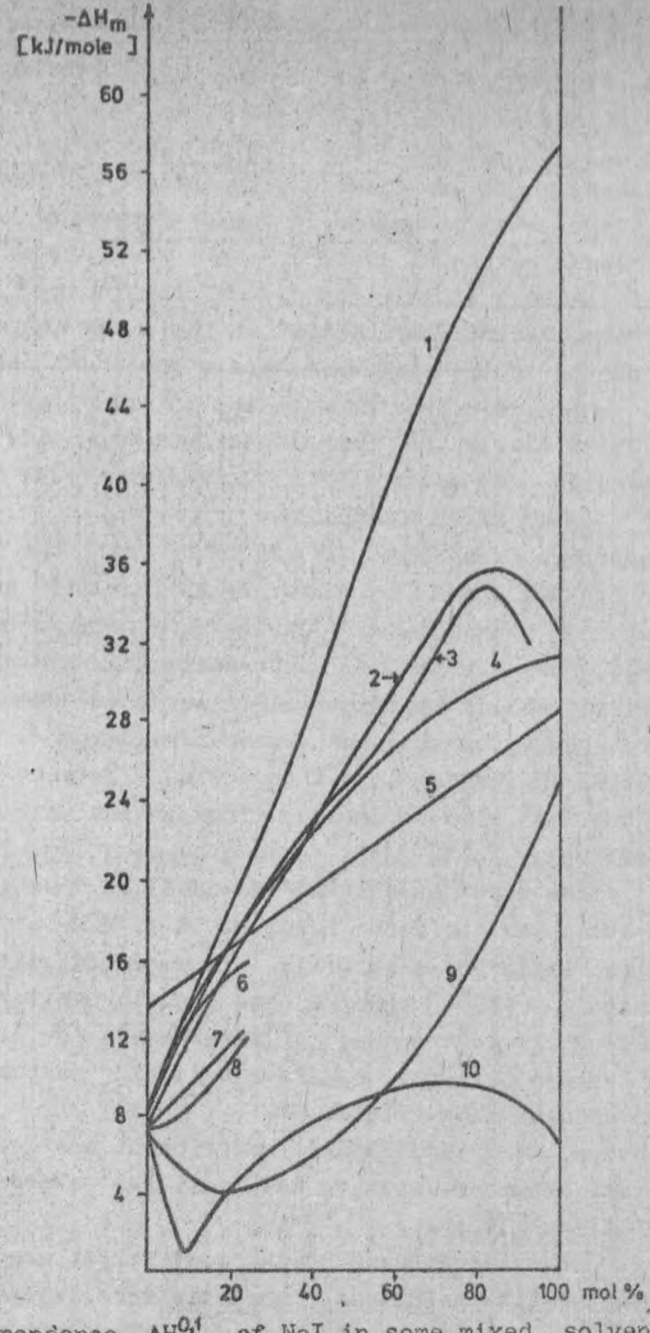

Fig. 8. Dependence $\Delta H_m^{0,1}$ of NaI in some mixed solvents as a function of mixtures composition [m_{NaI} = 0,1 mole/kg] at 25°C. 1 - water-DMF [14]; 1 - water-acetone [15]; 3 - water- acetonitrile [16]; 4 - water-formamide [14]; 5 - water-acetamide [85°C]; 6 - water-urea [17]; 7 - water-acetamide; 8 - water-propionamide [18]; 9 - water-methanol [19]; 10 - water-isopropanol [20]

fill the gaps in water structure. In the case of water-acetone and water-acetonitrile systems the functions $\Delta H_m^{0.1} = F(x)$ exhibit a distinct maximum in the range of high concentration of the organic component which explains the formation of complexes [23]. Such a maximum does not appear in water-formamide, water-acetamide (85°C) and water-DMF systems. In these systems the exothermicity of the heat of solution of NaI constantly rises with increasing non-electrolyte content in the mixed solvent.

This may be due to decreasing endothermic component of the heat of solution which is connected with the distruction of water structure. Quite likely the non-electrolyte molecules introduced to water gradually destroy the three-dimensional H-bond lattice in water forming mixed associates.

In the water-formamide system the structure of the mixed solvent changes gradually and is labile [23-25], while in case of water-DMF mixtures associates of definite composition can be discerned [26-28]. Possibly in the water-acetamide system mixed associates with H-bonds are formed. Similar phenomena may take place in water-propionamide and water-urea systems.

Some information concerning the interaction between water and non-electrolyte can also be derived from an analysis of the temperature coefficient $\Delta(\Delta H^0)/\Delta T$. As can be seen in Fig. 9 this coefficient rises most quickly in the case of water-formamide mixture attaining the zero level at 14 mole % of formamide and changes its sign to positive. In water-DMF mixtures, it attains the zero level and changes its sign to positive at 30 mole % of DMF, while in the case of water-acetamide mixtures it has negative values over the entire range of compositions investigated and changes only little.

As is well known, the temperature coefficient has negative values in the case of water solution and positive values for most organic solutions [10].

Assuming that negative values of the coefficient are characteristic of water-like solutions, then the zero value would correspond to solutions in which the original structure of water was destroyed.

Fig. 9 shows that formamide has a stronger destructive effect on the original structure of water than DMF, while in the case of acetamide this effect is very small. This may be related to the possibility of formation of a mixed three-dimensional lattice of H-bonds with both water and acetamide molecules participating.

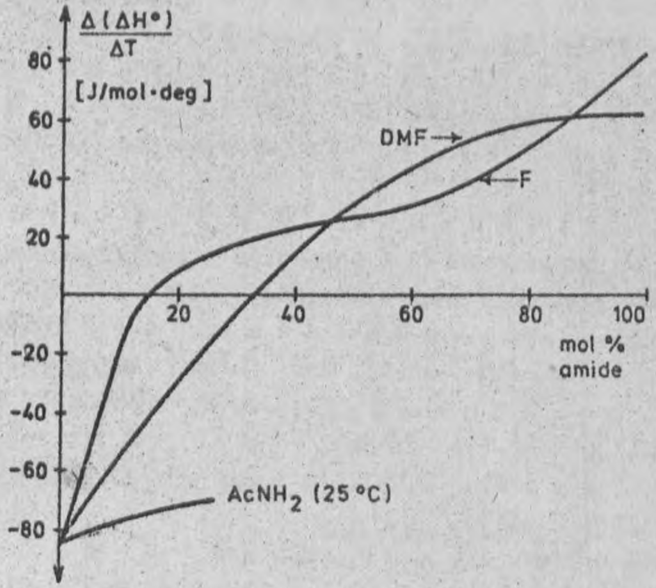

Fig. 9. The temperature coefficient of the NaI dissolution heat in water-amide mixtures at 25°C

The above conclusion is in agreement with opinion arising from densimetric [29], viscosimetric [30] and dielectric [25] studies of water-acetamide mixtures.

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TERMOCHEMICZNE BADANIA ROZTWORÓW NaI W MIESZANINIE ACETAMIDU Z WODĄ

Przeprowadzono pomiary ciepła rozpuszczania NaI w mieszaninach woda-acetamid w zakresie temperatur 25-85°C. Przedyskutowano zależność ΔH^{O}_{NaI} od składu mieszaniny i jej temperatury oraz porównano z innymi rozpuszczalnikami wodno-organicznymi.

Стефаниа Таневска-Осиньска, Марян Вольдан

ТЕРМОДИНАМИЧЕСКИЕ ИССЛЕДОВАНИЯ РАСТВОРОВ NaI В СМЕСИ ВОДА-АЦЕТАМИД

Проведено измерения теплоты растворения ΔH_m NaI в смеси вода-ацетамид в интервале температуры 25-85°C. Проведен анализ зависимости от состава смеси и температуры. Проведено сравнение смеси вода-ацетамид из другими водно-органическими растворителями.