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Stefania Taniowska-Ostńska, Henryk Piekarski

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IN NONAQUEOUS AND MIXED SOLVENTS

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This paper constitutes a review of the results of investigations on electrolyte solutions in some organic solvents that behaves similarly to water from thermochemical point of view as well as in some water - organic mixed solvents. The investigations have been carried out in Physical Chemistry Department of University of Łódź in recent years.

Electrolyte solutions have been receiving considerable attention in recent years as evidenced by the large number of publications devoted to them. There is no doubt that knowledge of their properties has a lot to contribute to the progress in various fields of science, technology and industry and appropriate studies can thus be regarded as a promising area of research.

In the early investigations most attention was devoted to aqueous solutions of electrolytes, while in recent years solutions in nonaqueous solvents have been attracting increasingly more interest. This change of focus seems to be fully justified in view of the increasing range of industrial applications of such solutions.

From the point of view of applications considerable attention is now being paid to three-component systems involving the dissolved electrolyte and mixed solvent. Observed by several methods properties of these solutions don't allow to elucidate clearly their intermolecular interactions and structure. The maxima, minima, or inflections frequently observed in the various functions studied are interpreted as resulting from structural changes in the mixed solvent, complex formation, change in solvation or selective solvation.

In this paper we intend to focus our attention on the results of thermochemical investigation on electrolytic solutions in pure and mixed solvents.

In 1931 E. Lange published his experimental data concerning integral enthalpy of dilution of aqueous electrolyte solutions with an aim of testing their agreement with the predictions of the limiting law of Debye and Hückel [1]. It turned out that in the range of concentrations exceeding the region of applicability of the limiting law, various electrolytes behave differently, i.e. in some cases ΔH_m^O changes its sign (Fig. 1). It remains unclear why ions whose structure is similar to that of noble gases interact differently enough to change the sign of ΔH_m^O .

According to some authors and ourselves among them the reason lies in differences in the effect of ions on water which, in turn, effect interactions among ions.

Following Lange's research M i s h c h e n k o [2] in a long series of thermochemical experiments involving both aqueous and nonaqueous solutions of electrolyte was able to demonstrate that the above-mentioned different plot of ΔH_m^O takes place only in the case of aqueous solutions. In addition to that he established a number of characteristics which differentiate aqueous and nonaqueous solutions (Fig. 2). These include the plot of $\Delta H_m^O = f(c)$, changes in the plot of $\Delta H_m = f(m)$ with changing temperature, the sign of the temperature derivative of ΔH_m or ΔH^O , and others.

Finally, he also proposed a classification of aqueous solutions of electrolytes on the basis of the plots of isotherms $\Delta H_m = f(m)$.

Studies conducted thus far of the entropy of aqueous electrolyte solutions have shown that in solution of type I (Fig. 2) the excess of partial molal entropy of the solvent ΔS_1^{-E} has the negative sign while the positive sign of ΔS_1^{-E} is related to the solutions of the II type electrolyte. As is known negative values of entropy constitute evidence of the structure making effect of solute on solvent, while positive values are evidence of the structure breaking effect [3, 4]. Thus electrolyte of the

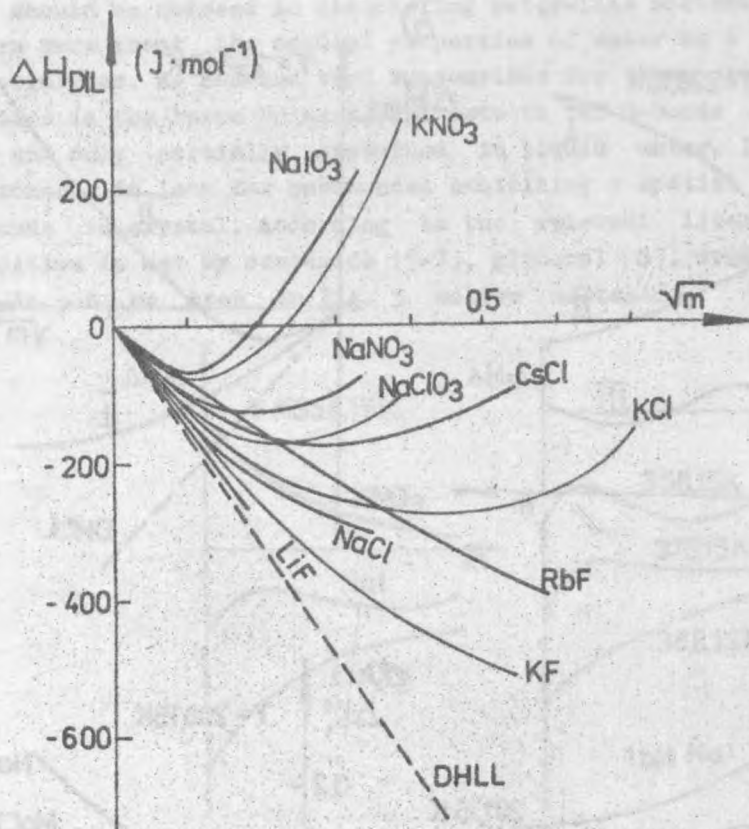


Fig. 1. Dilution enthalpy ΔH_{DIL} in aqueous electrolyte solutions at 298.15 K, according to Lange [1].

I-st type order the water structure and those of the II-nd type destroy it*.

Taking into account differences in the behaviour of aqueous and nonaqueous electrolyte solutions we set in our laboratory about looking for other solvents of electrolytes which share water's special properties.

* Authors of this paper use the notions "structure breaking" and "structure making" as has been proposed by Frank and Evans basing on entropy and viscosity data [3].

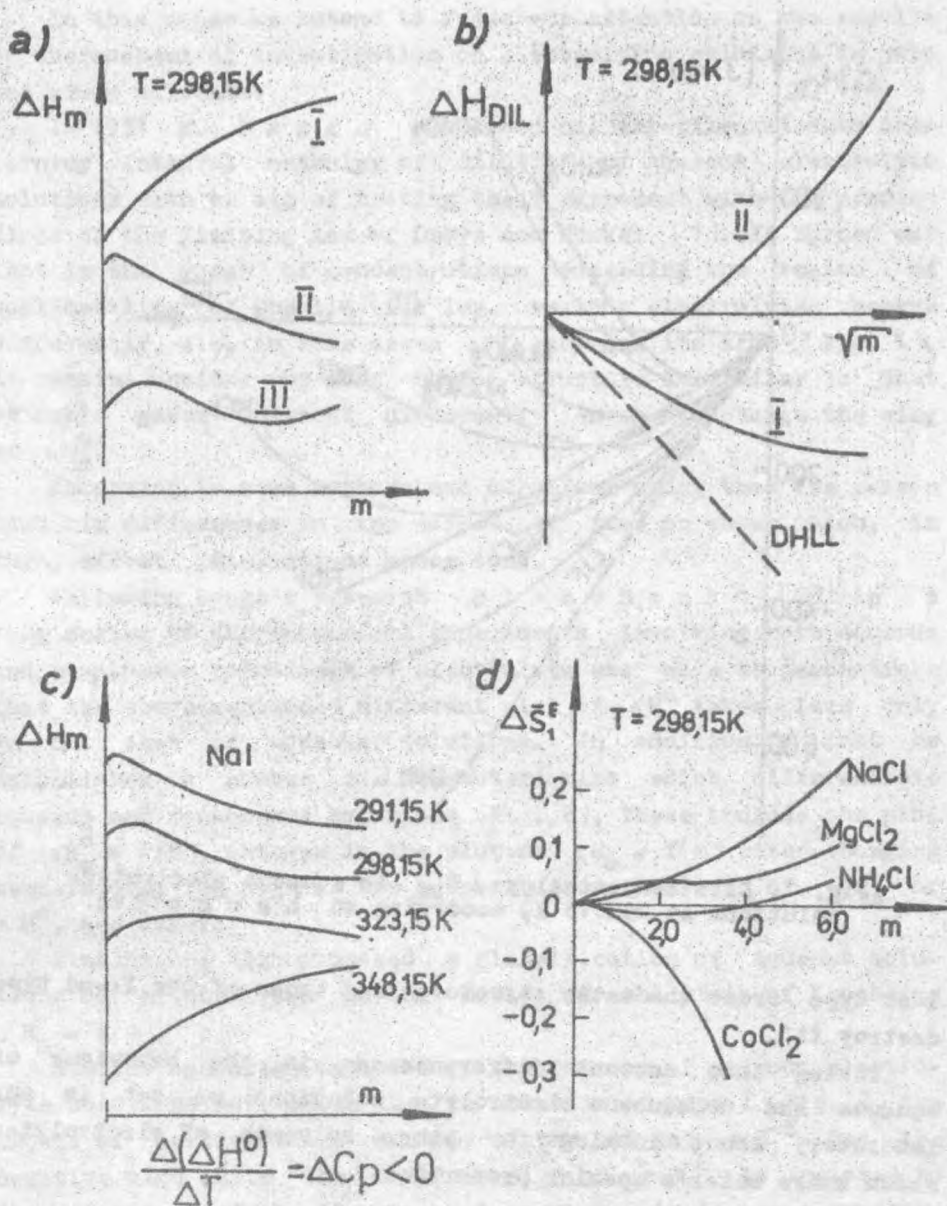


Fig. 2. Thermochemical characteristics of aqueous solutions of electrolyte: a) types of the heat of solution isotherms, b) heat of dilution isotherms (DHLL - Debye-Hückel limiting law), c) effect of temperature on $\Delta H_m = f(m)$ isotherms for NH_4Cl in water, d) excess of relative partial molal entropy of water \bar{S}_1^E in aqueous solutions of electrolyte at 298.15 K.

Should we succeed in discovering water-like solvents we might learn more about the special properties of water as a solvent of electrolytes. We assumed that responsible for those peculiar properties is the three dimensional network of H-bonds present in ice and only partially disturbed in liquid water. It was thus reasonable to look for substances exhibiting a spatial system of H-bonds in crystal. According to the relevant literature, this condition is met by acetamide [5-7], glycerol [8], urea [9].

As can be seen in Fig. 3 molten acetamide, distinctly

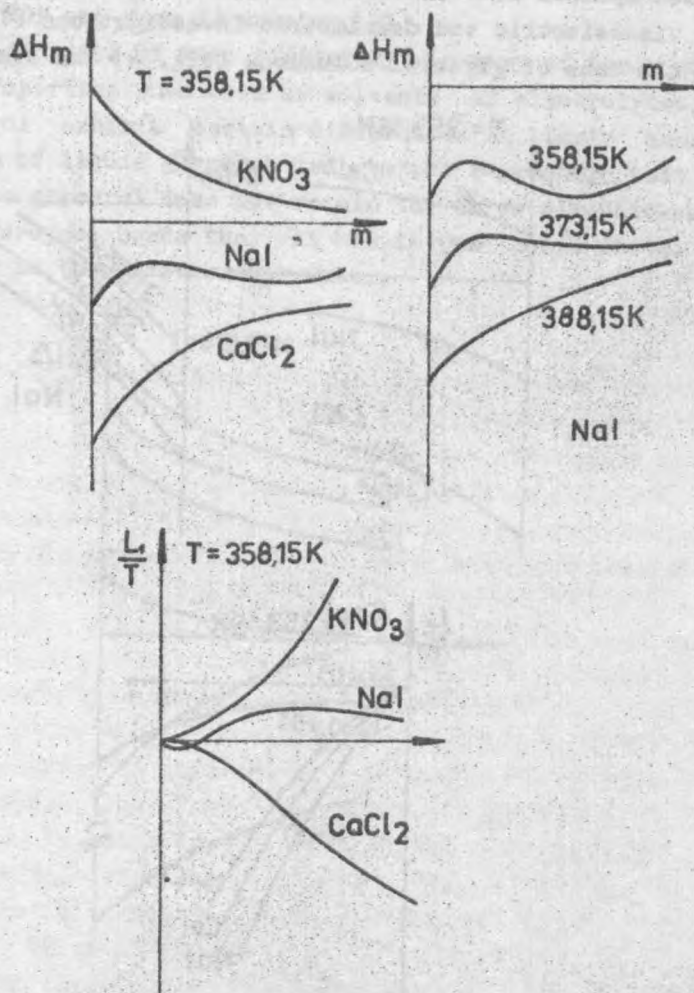


Fig. 3. Thermochemical properties of electrolyte solutions in molten acetamide.

different from water in chemical terms, behaves similarly to water from thermochemical point of view when it is used as a solvent of electrolytes. Isotherms of ΔH_m for dissolved salts: NaI, KNO_3 , $CaCl_2$ belong to 3 types of heat of solution curves distinguished by Mishchenko, in keeping with Lange's findings in relation to aqueous solutions. Similarly as in the case of aqueous solutions ΔC_p has a negative sign [10-12]. It thus seems likely that in the molten state the solvent retains partially disturbed spatial network of H-bonds. This view is also supported by our viscosimetric and densimetric investigations [13-14].

In the case of glycerol solutions (Fig. 4) the similarity to

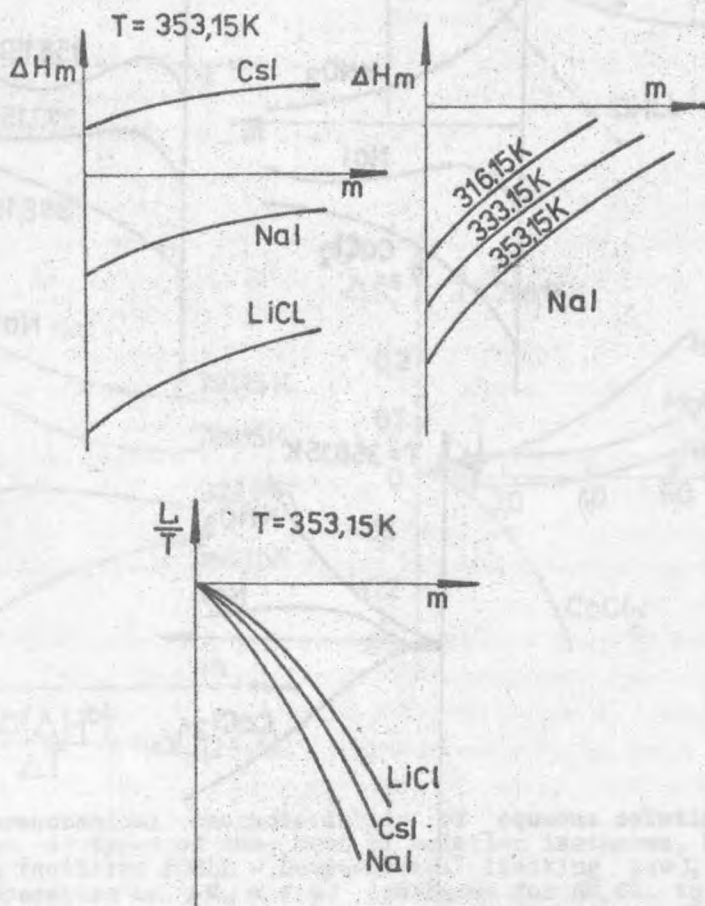


Fig. 4. Thermochemical properties of electrolyte solutions in glycerol.

water is, contrary to expectations, smaller and all enthalpic isotherms studied: LiCl, NaI, CsI are of one, i.e. I-st type, in terms of Mishchenko's classification, which makes glycerol solutions similar to non-aqueous solutions, while ΔC_p had a negative sign, similarly as in water [15, 16].

Supplementary viscosimetric and spectroscopic investigations [17-19] lead to the conclusion - consistent with thermochemical data, that the salts studied indeed have a structure making effect on glycerol. The same view can be reached from volume functions [20] and near IR spectra [21].

Thus, in spite of the similarity in many of their physico-chemical properties when used as solvents of electrolytes, water and glycerol exhibit certain differences in their behaviour. Examination of liquid glycerol led to the suggestion that in the liquid state glycerol does not retain the three dimensional lattice of hydrogen bonds that it has in the solid state. This is opposite to the behaviour of water.

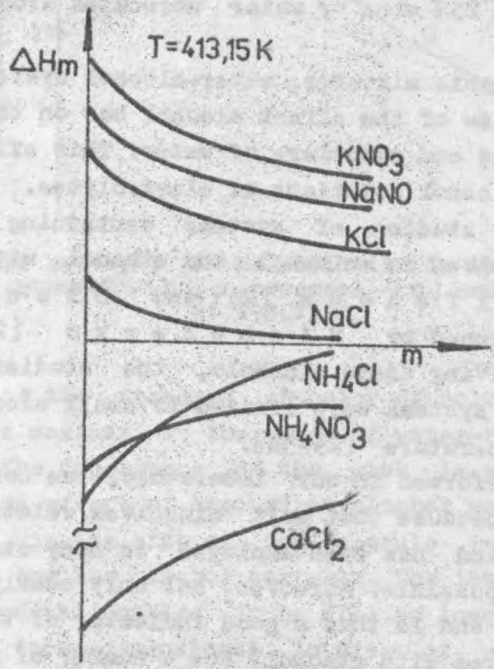


Fig. 5. Enthalpy of solution of some electrolytes in molten urea.

Solutions in molten urea (Fig. 5) behave similarly as in water, i.e. they exhibit two types of curve, but ammonium salts, which belong to the 2nd type when dissolved in water, are of the 1-st type in urea because of their chemical interactions with the solvent.

Summarizing the above discussion we conclude that it is not only in water that plots of isotherms ΔH_{DIL} or ΔH^0 for various electrolytes are different, that it is not only the structure of water that can be disturbed by electrolyte and that not only in aqueous solutions the sign of ΔC_p is negative.

The specific properties of water manifest themselves also in the features distinguishing water-organic mixtures from among other liquid systems. According to N a b i e r u k h i n and R o g o v [22] the unusual behaviour of the above-mentioned systems is due to fact that the non-electrolyte fills the gaps in the structure of water. Other authors attribute the anomalous behaviour to the formation of clathrate-like structures [23] of "ice-bergs" [4, 24, 25] etc. by water molecules around the dissolved molecules.

Among water-organic mixtures, water-alcohol systems occupy a special place in view of the effect alcohol has on the distinctly different properties and structure of water. This effect is also present in water-alcohol solutions of electrolytes.

Thermochemical studies of systems containing a number of electrolytes dissolved in methanol and ethanol with water were pioneered by W o l f e n d e n [26] and S l a n s k y [27] and were then continued by M i s h c h e n k o [28]. Apart from the work involving these alcohols, the studies on electrolyte-alcohol-water systems were limited to small alcohol contents and mostly one temperature [29-38].

In research performed in our laboratory, we concentrated on solutions of NaI because that salt dissolves relatively well in organic solvents and has been employed in many studies, which makes comparisons possible. Moreover, NaI only weakly affects the structure of water and is thus a good indicator of the behaviour of water in mixtures with alcohol. For a number of years now we have conducted systematic studies of NaI solutions in the first seven aliphatic alcohols with water [39-44]. (Fig. 6 and 7).

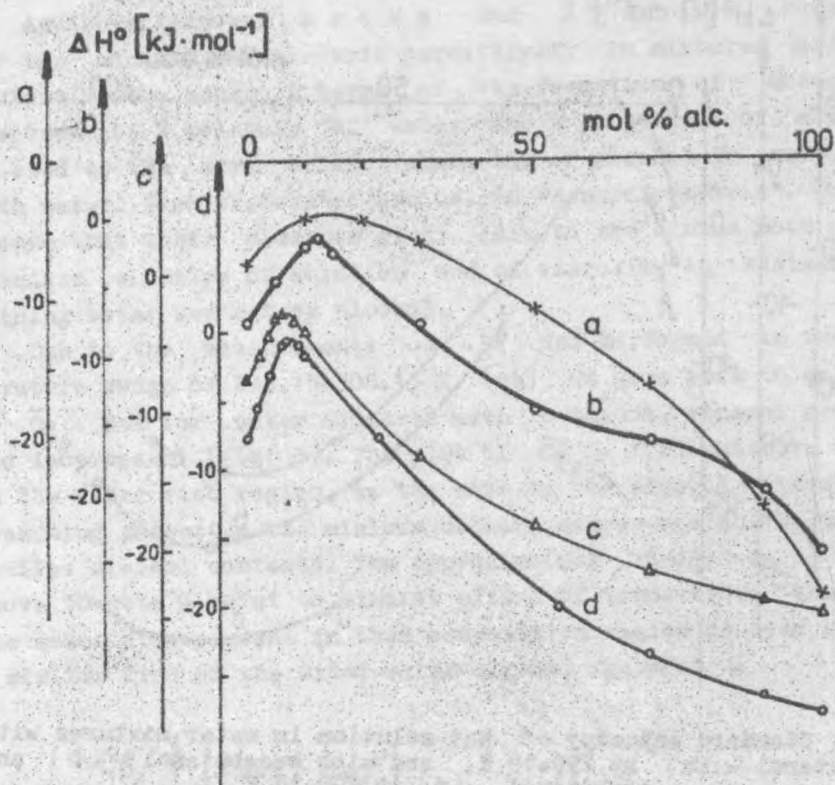


Fig. 6. Standard enthalpy of NaI solution in water mixtures with methanol-(a), ethanol-(b), n-propanol-(c) and isopropanol-(d) at 298.15 K.

The plot of the standard enthalpy of solution vs. alcohol content shows a maximum in the range of water-rich compositions (Fig. 6, 7). The appearance of the peak is attributed to the structure making effect of monohydroxyalcohol molecules on water [2, 32, 45-49]. As the size of the molecule increases the peak shifts towards smaller alcohol contents. The increasing size of the alcohol radical enables it to fill an increasing number of gaps in the three-dimensional lattice of water or to form clusters, depending on how one wishes to view the structure of water. The same kind of conclusion about the stabilizing or structure making effect of alcohol on water follows from studies

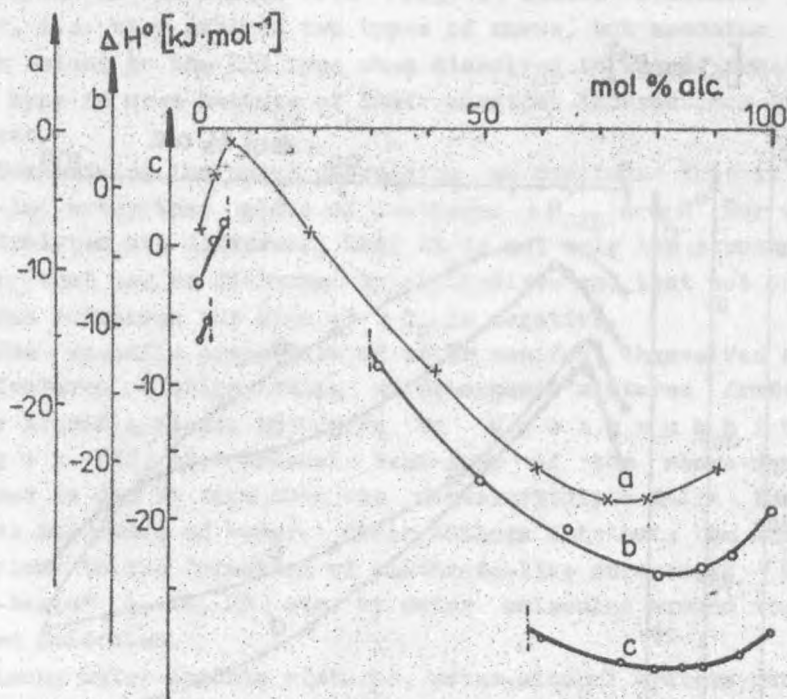


Fig. 7. Standard enthalpy of NaI solution in water mixtures with tert-butanol - (a) at 299.15 K, and with sec-butanol - (b) and isobutanol - (c) at 298.15 K.

of all known electrolyte solutions in water-alcohol mixtures carried out by all experimental procedures available [21, 50-55]. One example are our studies of viscosity carried out simultaneously [53-55]. The results obtained indicate maximum stabilizing effect of alcohols on water; this conclusion is suggested by the appearance of relative viscosity minima which correspond to the same compositions as maxima of ΔH° .

In water-butanol mixtures we observed, for the first time, the appearance of a minimum of standard enthalpy of solution of salts in the range of high alcohol content [40] (Fig. 7). An analysis of IR spectra [51], of electric permittivity [56] and viscosity [54] for butanol-water mixtures containing no electrolyte suggests that the observed plot of $\Delta H^\circ = f(x)$ for

those mixtures, is related to the properties or structure of the mixture and not to ion solvation.

As is well-known, Brown and Ives [56] accounted for the minimum of electric permittivity in mixtures of tert-butanol with water in terms of the formation of associates composed of 1 molecule of water and 4 molecules of alcohol, related to the more acidic character of alcohol in comparison with water. Such associates are called "centrosymmetric". One may assume that their presence gives rise to the minima both of the standard enthalpy of solution and of viscosity in systems containing water and excess alcohol.

Due to the measurements of ΔH° NaI performed in the temperature range of 298.15-308.15 K [44] we were able to calculate \bar{C}_{p2}° NaI for water mixtures with methanol, ethanol propanol and isopropanol (Fig. 8). The plot of $\bar{C}_{p2}^{\circ} = f(x)$ exhibits minima in the water rich region. As the size of the alcohol molecule and branching increases the minimum becomes deeper and shifts towards smaller alcohol contents. The approximately similar \bar{C}_{p2}° values above 50 mole % point to similar effect of temperature change on the associates present in this composition region or even suggest a similar kind of the mixed water-alcohol aggregates.

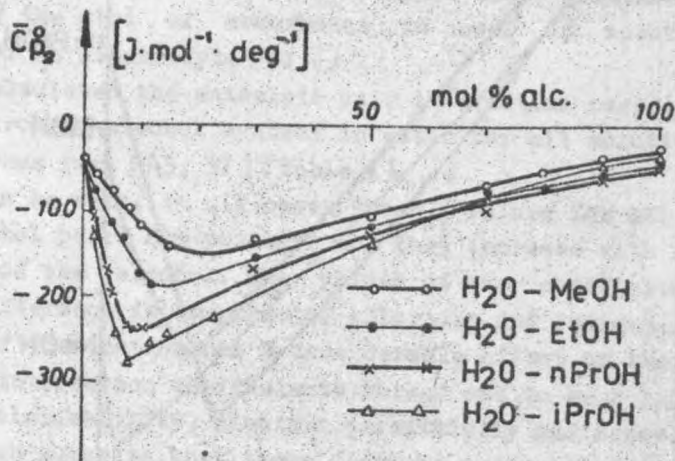


Fig. 8. Partial molal heat capacity (\bar{C}_{p2}°) for NaI in water-alcohol mixtures at 298.15 K

From above presented results concerning ΔH° NaI and its temperature derivative one can draw conclusion about the decisive effect of the mixed solvent structure on the behaviour of ionic solution.

The consistency of the presented characteristics of NaI solutions became disturbed when we turned to 1:2 electrolytes, especially CaCl_2 [57].

As can be seen in Fig. 9, similarly as in the case of NaI, maxima of enthalpy of solution appears in the range of small alcohol contents with the exception of methanol. The plateau extending from 0 to 17% suggests the presence of two mutually compensating effects: a stabilizing effect of alcohol on water

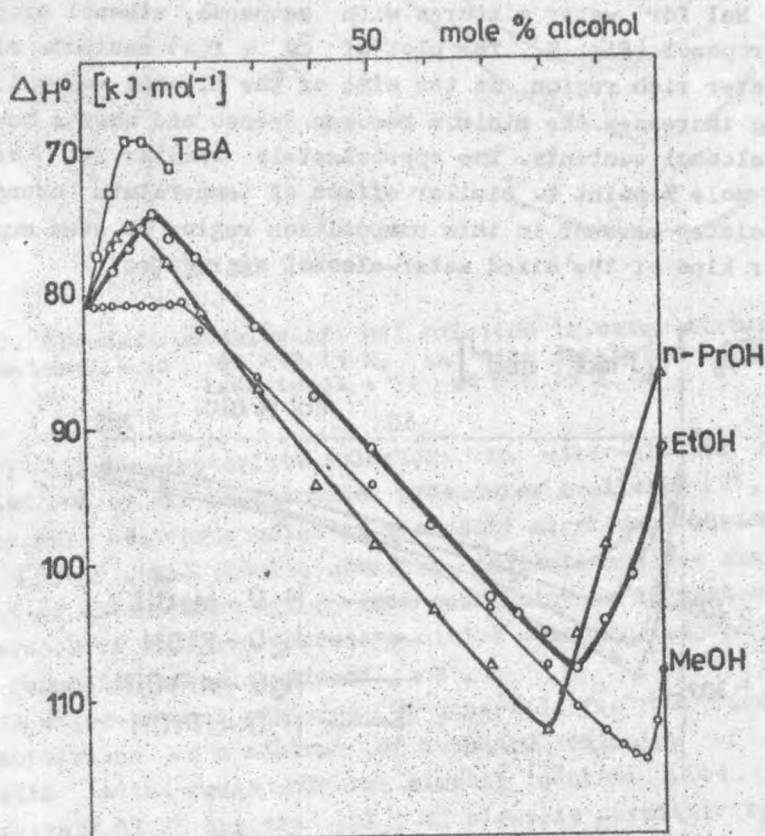


Fig. 9. Standard solution enthalpy ΔH° for CaCl_2 in water-alcohol mixtures at 298.15 K.

which produces an increase of the enthalpy of NaI solution, and the opposite effect due to which methanol molecules become built into ion hydration shells. This is a tentative explanation and we can only repeat after Covington and Newman that "methanol-water is one of the hardest solvent systems to understand". In the range of alcohol-rich solutions we observed, for the first time, minima in mixtures of water with the first three alcohols. The presence of these minima, not observed in NaI solutions, is not easy to explain. Possibly, the effect of NaI on the structure of the mixtures is too weak for all properties of the mixtures to become evident. Addition of CaCl_2 , which contains 3 ions including a divalent cation, distinctly reveals the structure of the system thanks to stronger solvation. One may also assume that in mixtures of methanol, ethanol and propanol with water there arise associates similar to those suggested by Brown and Ives, but that their number is smaller than in butanol solutions with water, possibly because of the stronger tendency of the former to form chain associates.

This suggestion is supported by the similar positions of the minima of ΔH_o HCl in methanol and ethanol with water [58], the extremum of excess volumes in methanol-water mixtures [59] the change of the plot of absorbance in near IR spectra in the absence of an electrolyte [51].

We calculated the enthalpic pair interaction coefficients h_{xy} for electrolyte-alcohol systems in water for all solutions investigated thus far [43, 57] (Table 1).

As can be seen, in all cases the h_{xy} values for all electrolyte-alcohol pairs are positive and they increase with increasing radical of the alcohol. The values of the coefficients show little difference in the case of chlorides and iodides, but the change of the cation has a considerable effect on their values. The pair interaction coefficients turned out to be a linear function of polarizability, electric permittivity and Kosover's constant, which suggests that those features are related to the energy of interactions.

In the Table 1 are also collected the calculated values of pair interaction coefficients h_{xy} (electrolyte-water) in alcohols. By contrast with the positive values of h_{xy} (NaI-water)

the negative values of h_{xy} (CaCl_2 -water) seem to point to a stronger affinity of CaCl_2 to water than is the case with NaI . As the alcohols radical increases, the interaction of ions with water increases too.

Table 1

Electrolyte-alcohol pair interaction enthalpies h_{xy} ($\text{J} \cdot \text{kg} \cdot \text{mol}^{-2}$)
at 298.15 K in water solution

Alcohol	Electrolyte		
	NaI	NaCl	CaCl_2
Methanol	+157	+150	+49
Ethanol	+298	+290	+162
Propanol	+395	+370	+340
Isopropanol	+509		
Isobutanol	+600		
s-Butanol	+643		
t-Butanol	+720	+483	+599
	+711*		

* literature data

Electrolyte-water pair interaction enthalpies h_{xy} ($\text{J} \cdot \text{kg} \cdot \text{mol}^{-2}$)
at 298.15 K in alcohol solution

Solvent	Electrolyte	
	NaI	CaCl_2
Methanol	+583	-1083
Ethanol	+551	-1167
Propanol	+177	-1225
Isopropanol	+173	
Isobutanol	-1370	
s-Butanol	-1420	

On the basis of these investigations, the compositions of the mixtures may be divided into the following five ranges

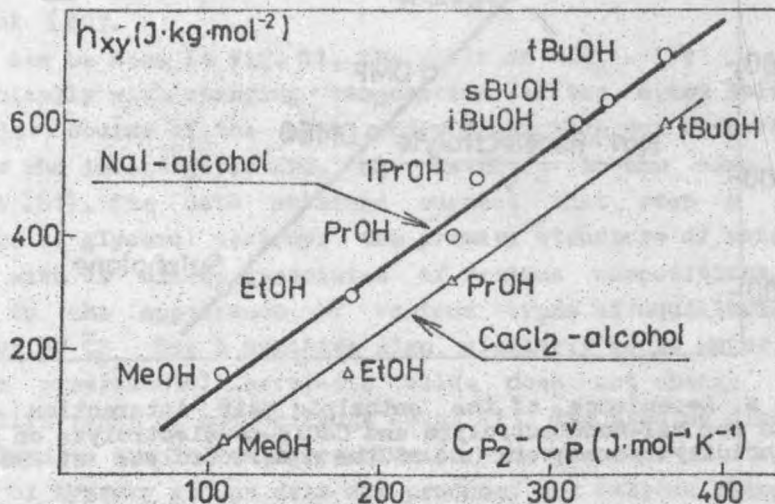
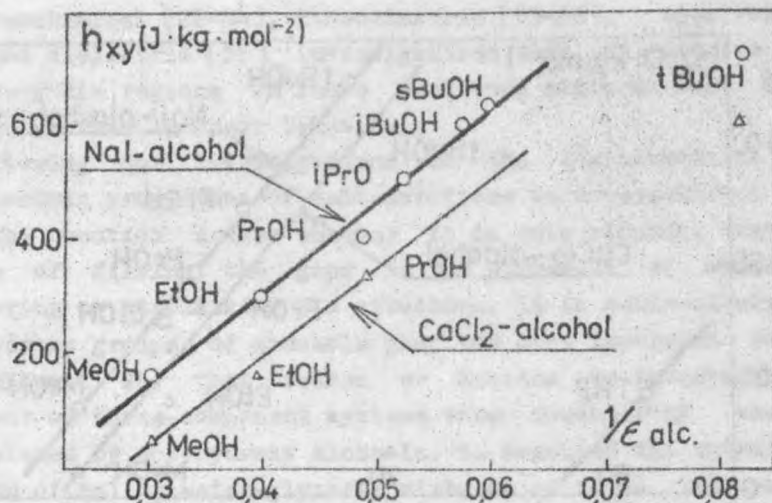


Fig. 10. Dependence of the enthalpic pair interaction coefficients for NaI-alcohol and CaCl₂-alcohol pairs on reciprocal of the alcohol electric permittivity $1/\epsilon$ and heat capacity of transfer of alcohol molecule from vapour phase to high dilution in water ($C_{P_2}^o - C_P^v$) at 298.15 K.

1. 0-5 or 9 mol %- stabilizing effect of alcohol on the structure of water
2. 5/9-15 mol % - addition of alcohol begins to disturb the ordered structure of water

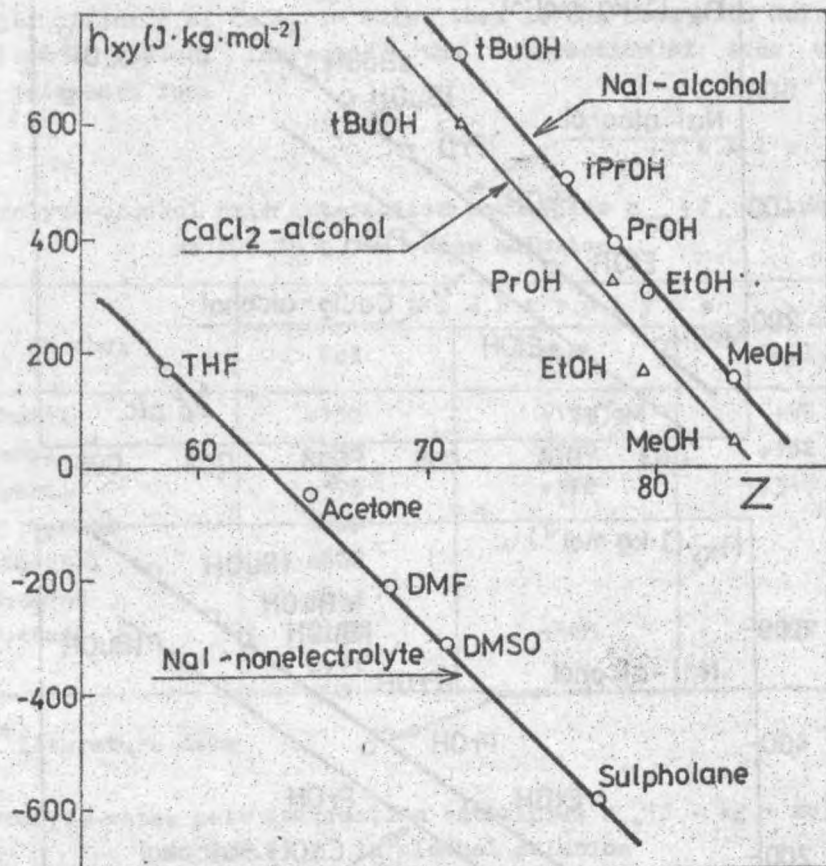


Fig. 10 a. Dependence of the enthalpic pair interaction coefficients for NaI-nonelectrolyte and CaCl_2 -nonelectrolyte on Kosower's acidity parameter (z) of the nonelectrolyte at 298.15 K.

3. 15-80 mol % - the three-dimensional lattice of hydrogen bonds is destroyed and associates of various compositions, shapes and size arise
4. 80-90 mol % - a composition corresponding to the highest possible number of "centrosymmetric" associates
5. 90-100 mol % - structure characteristic of alcohols arises.

Ending this discussion on electrolyte solutions in water-alcohol mixtures, it seems interesting to state that the results

of thermochemical [26-44], viscosimetric [53-55], spectroscopic [31] and dielectric [56] investigations let us observe some characteristic regions in above mentioned mixtures that differ from one another in their behavior.

Following our investigations of the thermochemical and viscosimetric properties of salt solutions in water-alcohol mixtures the question arises whether it is only alcohols that are capable of filling the gaps in the structure of water or of ordering or stabilizing its structure. It is quite likely that the hydroxy groups of alcohols play the most important role in that effect. For that reason we decided to investigate the behaviour of three-component systems when monohydroxy alcohols are replaced by polyhydroxy alcohols. We measured the enthalpy of solution of NaI in water-glycerol mixtures at three temperatures higher than 25°C because of the considerable viscosity of glycerol [60].

As can be seen in Fig. 11, the plots of $\Delta H_0 = f(x)$ change monotonically with changing composition of the mixed solvents. A similar course of the plot under discussion was observed by Krestov who investigated KNO_3 and $\text{Ca}(\text{NO}_3)_2$ in the same mixed solvent [61]. The data obtained suggest that even a small addition of glycerol destroys the primary structure of water and forms with it mixed associates of various compositions, which leads to the appearance of various types of equilibria. The function of $\bar{C}_{P_2}^0$ has a negative sign similarly as in water, and -within experimental error-its value does not change over the entire range of compositions (Fig. 11). The studies discussed above lead to the following conclusion: the presence of a sizable number of hydroxy groups does not produce any extrema changes of the properties.

Our subsequent studies concerned the effect of other hydrophilic substances on the structure of water. The next solvent which, in contradistinction to alcohols, does not contain the OH group, i.e. formamide, was investigated in the same way in the temperature range of 5-35°C [62-65].

Formamide, being capable of forming hydrogen bonds, combines with water molecules thus disturbing its primary structure. The thermal effect of NaI solution changes monotonically with changing formamide content in the system (Fig. 12).

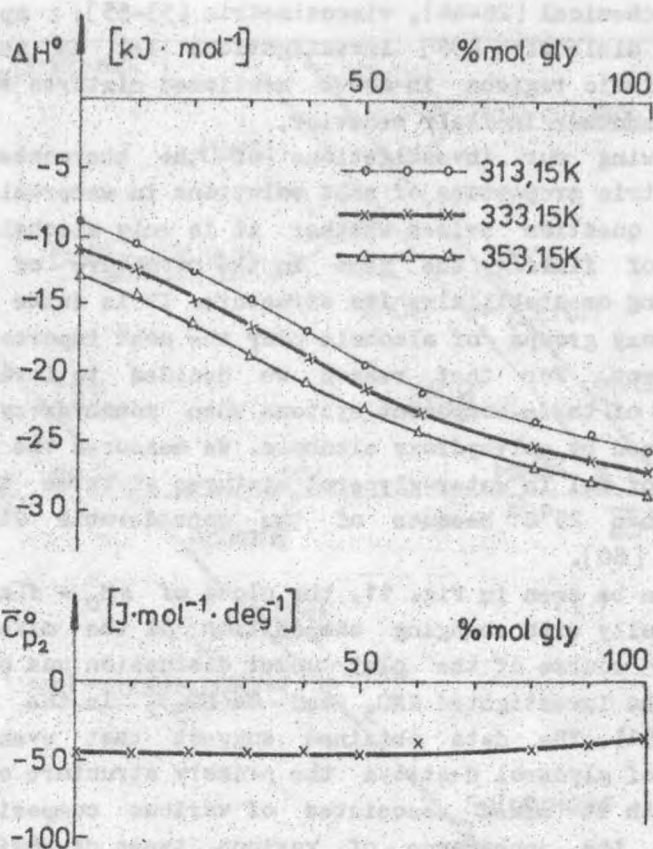


Fig. 11. Standard solution enthalpy (ΔH°) and partial molal heat capacity ($\bar{C}_{p_2}^\circ$) for NaI in water-glycerol mixtures.

The viscosity plotted in the function of solvent composition changes in a similar way [66]. Our results show that this solvent too does not have a stabilizing effect on the structure of water.

We are thus left with the possibility that ordering of the structure of water is related to the presence of CH_3 groups in the molecule of the organic solvent and their absence gives rise to hydrophilic character of the given solvent. For that reason we selected for our investigations DMF, whose molecule contains two CH_3 groups. In the opinion of several authors e.g. Shakhparonov [67], DMF has an ordering effect on the

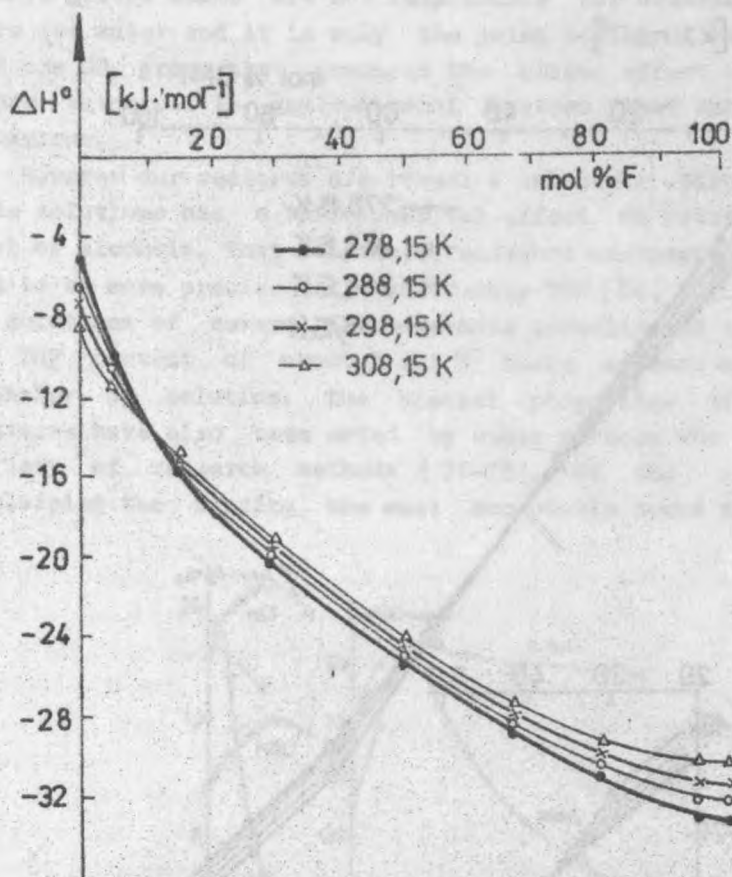


Fig. 12. Standard solution enthalpy (ΔH°) for NaI in water-formamide solutions.

structure of water. It follows from our results that the shape of ΔH° NaI in DMF solutions (Fig. 13) is similar to the shape of that function in systems, containing formamide [63].

The maximum of enthalpy which would testify to the structure ordering effect does not appear, so addition of DMF disturbs the structure of water although it does so in a less violent way than was the case with solutions containing formamide. The inflection point at ~ 60 mol %, seems to testify to the change of hydration shells of ions into solvation shells DMF. Our view is confirmed by the study of H o l t z carried out by nuclear resonance

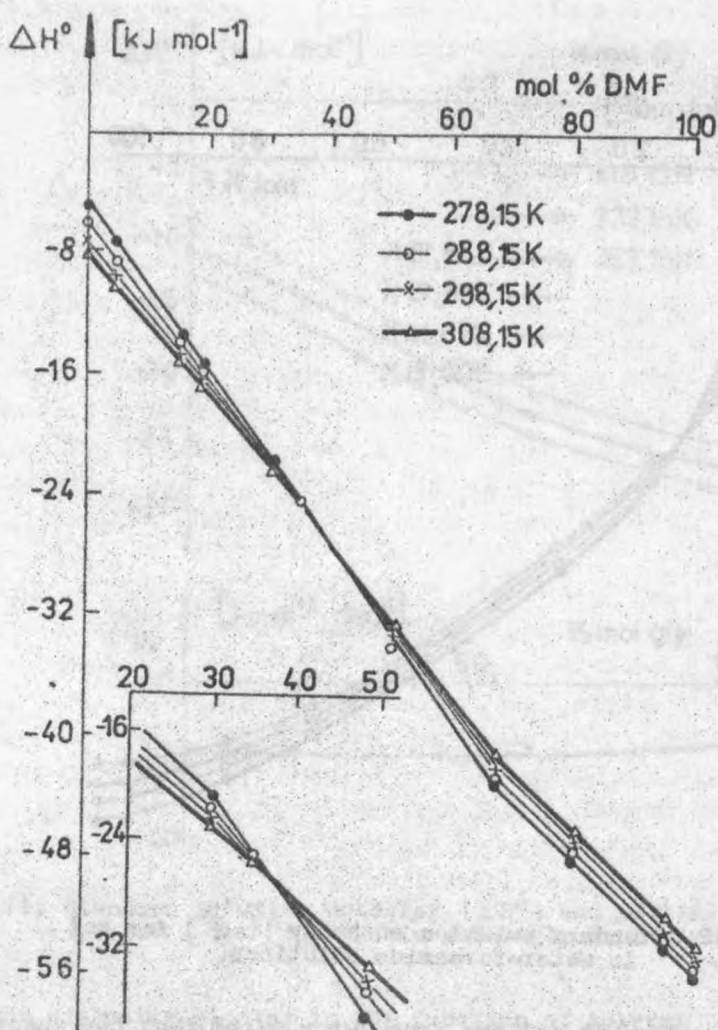


Fig. 13. Standard solution enthalpy (ΔH°) for NaI in water-N,N-dimethylformamide solutions.

[68]. The dependence of the relative viscosity of NaI solutions is very similar in systems containing F and DMF [66] which supports the conclusion of thermochemical investigations about the disordering effect of DMF on the structure of water, contrary to the opinions of other authors. Having investigated the last of the systems discussed above we came to the conclusion that

methyl groups alone are not responsible for ordering the structure of water and it is only the joint action of methyl groups and one OH group that produces the unique effect on water. In other words, it is water-alcohol systems that exhibit unusual behaviour.

However our research did reveal a substance which in electrolyte solutions has a thermochemical effect on water similar to that of alcohols. That substance, somewhat unexpectedly, is ether and to be more precise tetrahydrofuran THF [69, 70]. In the case of solutions of several salts we have investigated in the range of THF content of about 5 mol % there appears a maximum of enthalpy of solution. The special properties of water-THF mixtures have also been noted by other authors who employed a variety of research methods [71-73]. Of the attempts at explaining the finding the most acceptable seems to be the one

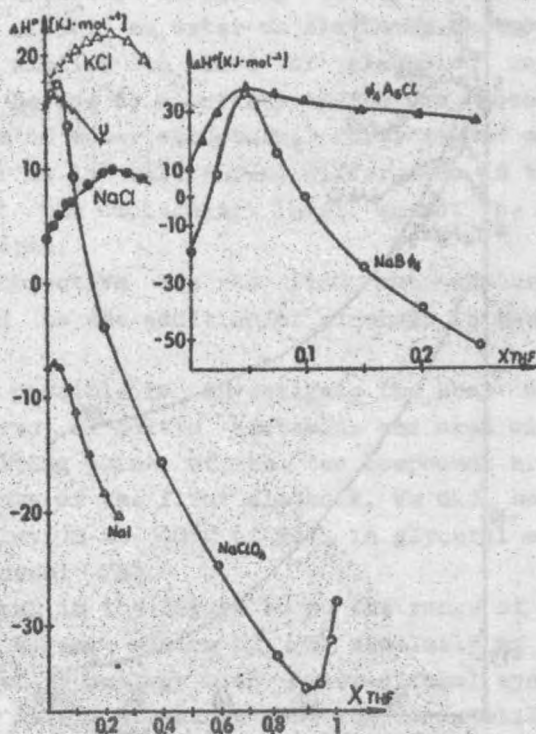


Fig. 14. Standard solution enthalpy of some electrolytes and urea in water-tetrahydrofuran (THF) mixtures at 298.15 K.

according to which there arise quasi-clathrates of type II with a ratio of 1 to 17 [72, 73]. A similar view regard to solutions containing tert-butanol is gaining increasingly more support in the literature [74]. The only electrolyte of those studied thus far which dissolves in solutions with high THF content is NaClO_4 . Its heat of solution curve resembles those for tert-butanol-water solutions of NaI. In the vicinity of 60 mol % THF there appears a minimum of ΔH° . In view of the low electric permittivity of THF ($\epsilon \approx 7$) it seems necessary to take into account ion association. The study under discussion has yet to be completed.

Another solvent whose solutions exhibit a similarity to water-alcohol solutions in terms of the plot of $\Delta H^\circ = f(x)$ is hexamethylphosphortriamide HMPT, which is a strongly basic amide of medium electrical permittivity equal to 29.6 [75, 76].

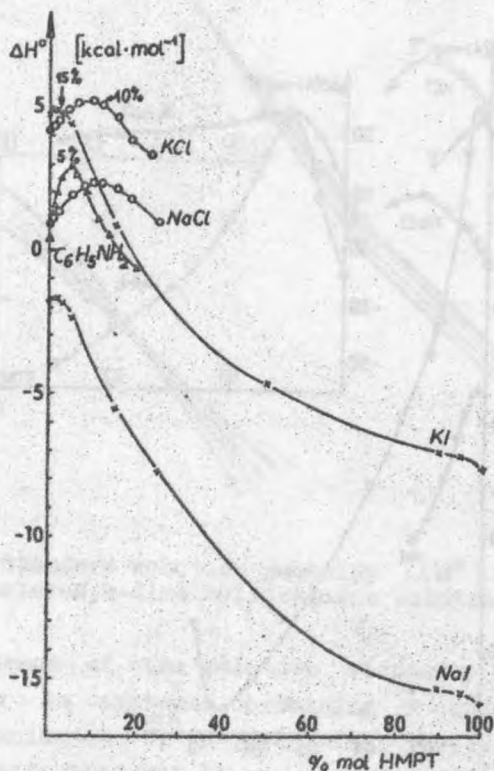


Fig. 15. Standard solution enthalpy of some electrolytes and aniline in water-hexamethylphosphortriamide (HMPT) at 298.15 K.

The maxima of solution enthalpies for salts in water-rich solutions are probably not connected with the possibility of large HMPT molecules filling the gaps in the structure of water.

Investigations of the solutions of tetraalkylammonia salts [77] also confirm their similarity to alcohol solutions.

A special property of the isotherms of solution enthalpies for salts in water-HMPT and water-THF mixtures is the dependence of their shapes on the anion of the dissolved salt. In contrast to water-alcohol systems, in which the position of the maximum of ΔH° for salt did not depend on the kind of dissolved substance, in systems with HMPT chlorides exhibit a maximum at 10% mol HMPT, iodides at 1.5% mol HMPT. In the case of solutions with THF chlorides exhibit a maximum at 25% mol THF and iodides and other anions at 5% mol of THF.

It follows from the foregoing discussion that there are solvents whose effect on water—as shown by thermochemical investigations—is similar to that of alcohols. However, the similarity may be due to a variety of factors, such as ordering or stabilization of water structure, formation of clathrate-like aggregates, etc. As is well known, differences in the behaviour of solutions at the molecular level cannot be explained in thermodynamic terms.

Our next objective was to find out whether water-like solvents respond to the addition of alcohols in the same way as water.

It was not possible to investigate the heat of solution of salts in mixtures of molten acetamide and urea with alcohols because the melting points of the two compounds are higher than the boiling points of the first alcohols. We did, however, study the heat of solution at 40°C of NaI in glycerol with methanol, ethanol and propanol [78].

As can be seen in the figure 16 in the range of glycerol-rich solutions there appear maxima of ΔH° similarly as in alcohol-water solutions. By analogy with water-alcohol systems they can be presumed to have a structure ordering or stabilizing effect. The minima of enthalpy in solutions containing small amounts of glycerol may also indicate the existence of spatial associates just as was the case with alcohol-water systems. The calculated

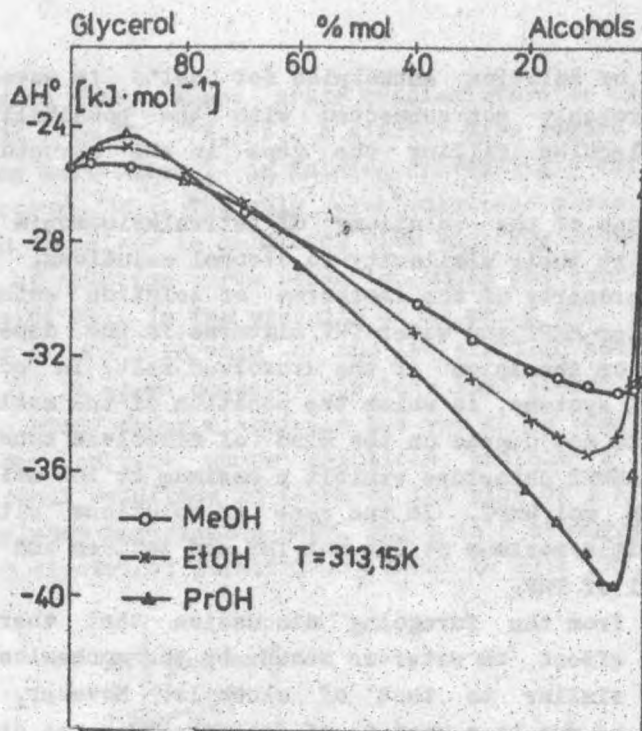


Fig. 16. Standard solution enthalpy ΔH° for NaI in the mixtures of glycerol with aliphatic alcohols at 313.15 K.

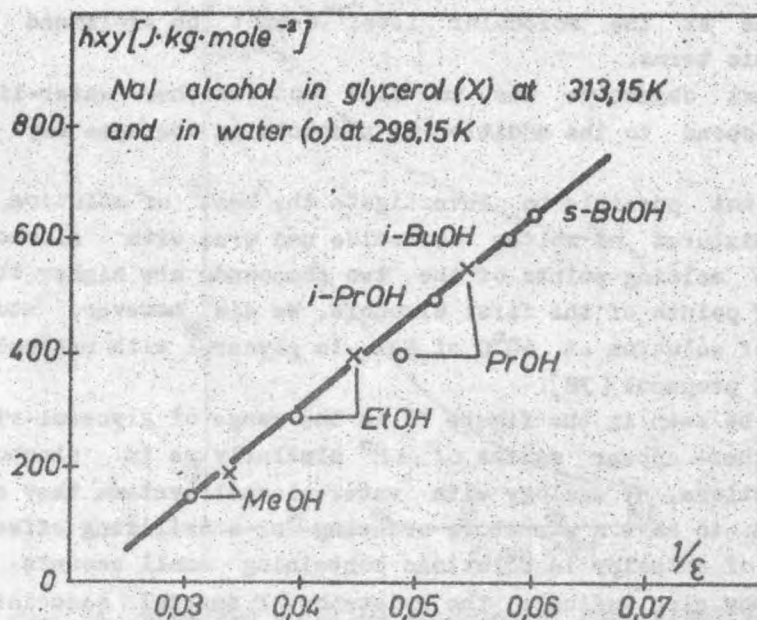


Fig. 17. Enthalpic pair interaction coefficients h_{xy} of NaI-alcohol in glycerol and in water solutions.

pair interaction coefficients h_{xy} in glycerol are compared with the values for aqueous solutions in the Fig. 17.

At the sizes of the alcohol radicals increase so do the positive values of h_{xy} thus indicating the growing affinity of NaI to glycerol and water and decreasing interactions with alcohols.

In alcohol-rich solutions, interactions between NaI and glycerol increase with increasing size of the alcohol molecules more distinctly than in water. This finding confirms the better solubility of NaI in glycerol than in alcohols.

The observed similarity of glycerol to water in solutions containing salts and alcohols made us try and find out whether

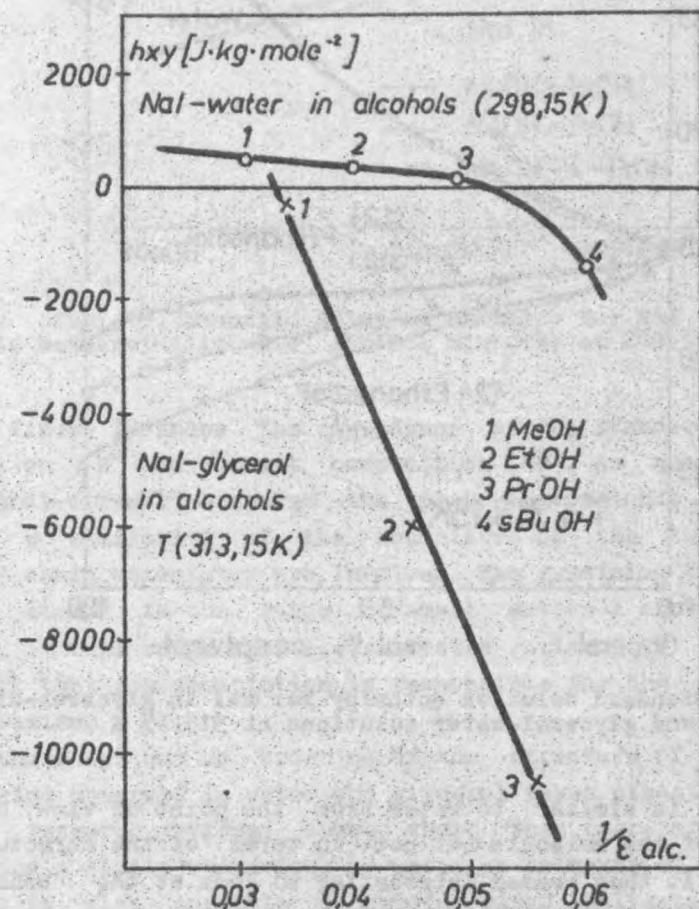


Fig. 17 a. Enthalpic pair interaction coefficients h_{xy} of NaI-water and NaI-glycerol in alcohol solutions.

similarly as in water polyhydroxy alcohols behave differently in that they do not produce any extrema points in the plots. To that aim we conducted a calorimetric investigation of NaI solutions in glycerol mixtures with glycols [79]. The absence of extremes confirms the similarity of glycerol to water (Fig. 18).

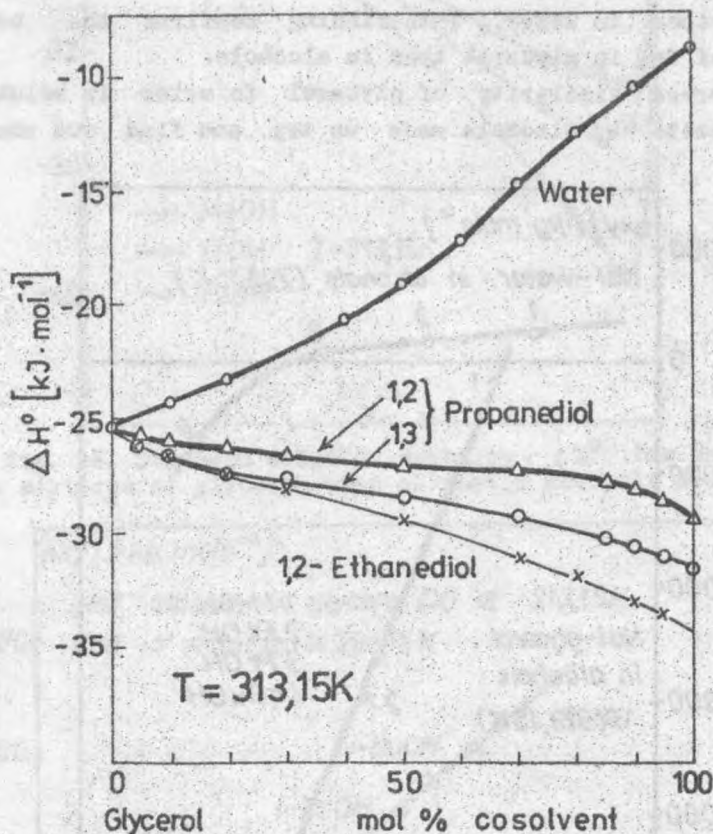


Fig. 18. Standard solution enthalpy for NaI in glycerol-diols and glycerol-water solutions at 313.15 K.

Methanol is similar to water from the point of view of the structure of the molecule but not in terms of the structure of the liquid. It thus seemed interesting to look at the behaviour of the electrolyte in mixed solvents composed of methanol and the next three alcohols.

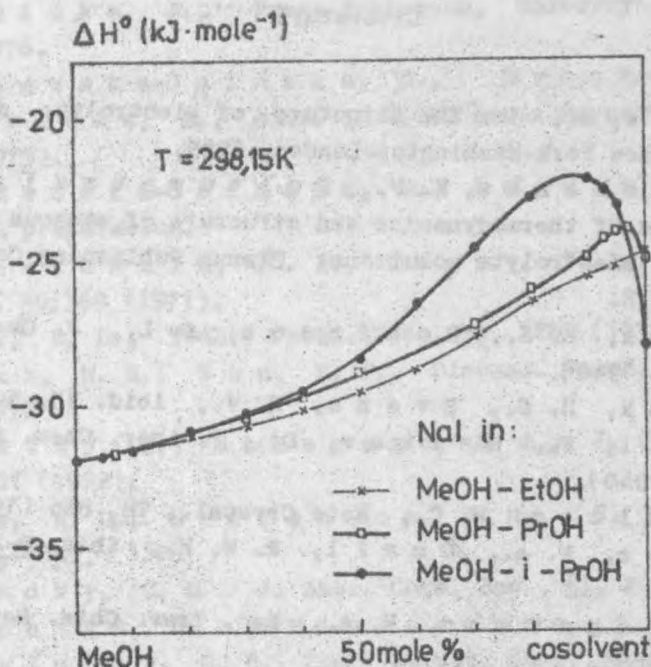


Fig. 19. Standard solution enthalpy for NaI in methanol-aliphatic alcohol mixtures at 298.15 K.

The figure 19 shows the dependence of the standard enthalpy of solution ΔH° on solvent composition [80]. As can be seen, in methanol-ethanol mixtures the plot is monotonic which may suggest a similarity of the associates of the two alcohols. Probably chain associates are involved. The remaining two systems exhibit maxima in the range of small methanol contents. Presumably, in this range spatial associates arise. It cannot be ruled out that ion association is responsible for the appearance of the maximum.

In those systems no ordering of the structure of methanol of the kind observed in water and glycerol takes place.

The research reviewed above shows that there are solvents exhibiting a similar behaviour to water as solvents of electrolytes. It is also possible to obtain mixed solvents which in thermochemical terms behave similarly to water-alcohol mixtures. Consequently, the division of solvents into aqueous and non-aqueous solvents is not so obvious.

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Stefania Taniewska-Osińska, Henryk Piekarski

WŁASNOŚCI ROZTWORÓW ELEKTROLITÓW
W ROZPUSZCZALNIKACH NIEWODNYCH I MIESZANYCH

Niniejsza praca stanowi przegląd badań nad roztworami elektrolitów w niewodnych i wodno-organicznych mieszanych rozpuszczalnikach prowadzonych w ostatnich latach w Zakładzie Chemii Fizycznej Uniwersytetu Łódzkiego.

Department of Physical Chemistry,
Institute of Chemistry,
University of Łódź,
ul. Nowotki 18
91-416 Łódź, Poland

