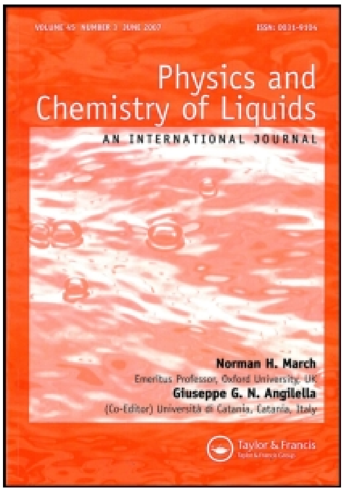

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VISCOSITY OF NaI SOLUTIONS IN WATER-tert-BUTANOL MIXTURES AT 35 AND 40°C.

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Viscosity of water-tert-butanol mixtures and of NaI solutions in those mixtures at 35 and 40°C have been measured. Results are discussed in terms of the effect of alcohol on the water structure and of NaI on the structure of water-alcohol mixtures. Temperature coefficients of viscosity have been calculated for several water-alcohol and water-amide mixtures. We conclude that it is precarious to describe structures basing on $\Delta\eta/\Delta t$ values. It can be only presumed that whatever structure of solution arises, it is unstable when its temperature coefficient of viscosity is large. Plots of relative viscosities of NaI solutions (at various concentration of NaI) in water-tert-butanol mixtures have minima at about 6 mol% alcohol i.e. the composition range in which water structure exhibits the maximum ordering effect by tert-butanol molecules. A comparison of viscosities and standard solutions enthalpies for NaI solutions in water-alcohol and water-amide systems is made.

KEY WORDS: Temperature coefficient of viscosity, water-tert-butanol mixtures, NaI solution viscosity.

INTRODUCTION

We have investigated earlier the physicochemical properties of electrolyte solutions in water-alcohol mixtures. Results of viscosity studies involving NaI solutions in water-monohydric alcohols i.e. methanol (MA), ethanol (EA), *n*-propanol (NPA), isopropanol (IPA), isobutanol (IBA), sec-butanol (SBA) at 25°C and tert-butanol (TBA) at 26°C and IPA at 15 and 40°C, have already been published[1–5]. The present work reports the results of viscosity studies of NaI solutions (0.5, 1.0 and 2.0 mol NaI/100 moles of mixed solvent) in water-TBA mixtures over the whole range of mixed solvent compositions at 35 and 40°C. We have also compared the viscosities of NaI solutions in water-alcohol and water-amide mixtures.

EXPERIMENTAL

The viscosity measurements were made by means of Ubbelohde-type viscometers with flow times of 200–500 s for various solutions. The liquids used as standards were water[6] and *n*-butanol[7]. The viscosity was calculated from Eqn. (1):

$$\eta/\rho = Kt - L/t \tag{1}$$

where η is the viscosity, ρ is the density, t—the efflux time and K and L are characteristic constants of the viscometer. The applied viscometer equipment was similar to that described by Out *et al.*[8] The Ubbelohde-type viscometer was connected by optical fibres to an electronic clock working with a precision of 2×10^{-3} s. The temperature stability was *ca* ± 0.001°C. The accuracy of viscosity data was better than $\pm 3 \times 10^{-3}$ cP.

Following its freezing out, TBA (produced by BDH Chemicals Ltd) was dried with freshly calcinated CaO and distilled. The water content, determined by gas chromatography (Perkin-Elmer F-11) did not exceed 0.05%. The specific conductivities of TBA and double destilled water were better than 0.1 and 1 μS/cm, respectively. Sodium iodide (Merck, analytical grade) was dried under vacuum at 70°C.

All solutions were prepared by weight.

RESULTS AND DISCUSSION

The viscosities of water-TBA mixtures at 35 and 40°C are collected in Table 1 and shown in Figure 1. We were unable to find in the literature any data for water-TBA viscosity at 35°C, and only found some indirect data of Westmeier[9] for 40°C, obtained by interpolation of unpublished results of other investigators. A comparison of our data with those by Westmeier shows a good agreement in the range of 0–10 mol% TBA and in pure TBA. They diverge quite considerably in the 20–90 mol% TBA, with the largest difference—of about 8%—in the middle range of the mixture compositions.

The curves of viscosity of water-TBA mixtures *vs.* alcohol content at 35, 40 and

Table 1 Viscosities of water-TBA mixtures at 35 and 40°C.

mol% TBA	*35°C* η*	*40°C* η*
0	0.7194	0.6531
5	1.541	1.311
7	—	1.540
10	2.188	1.840
20	2.951	2.453
30	3.186	2.615
40	3.219	2.618
50	3.116	2.534
60	2.973	2.409
70	2.837	2.290
80	2.707	2.188
90	2.635	2.120
95	2.606	2.087
100	2.646	2.066

* Units of η: cP

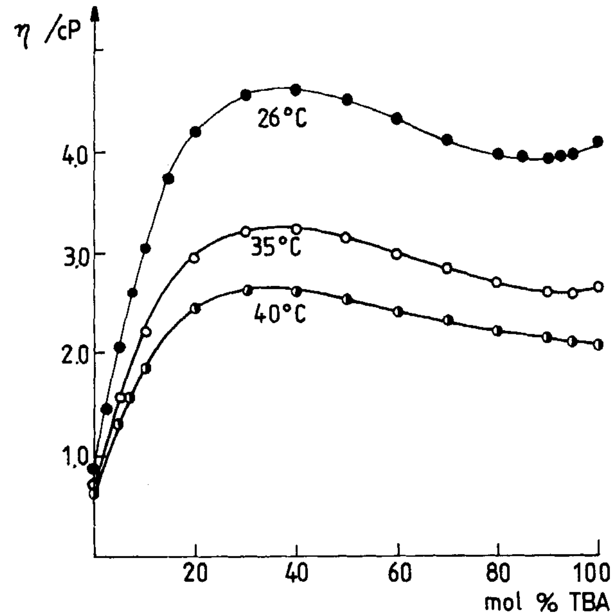

Figure 1 Viscosity for water-tert-butanol systems at various temperatures.

26°C[2,3] (Figure 1) exhibit maxima at about 35–38 mol% TBA and minima at about 90 mol% TBA. Viscosity maxima are not unique for water-alcohol systems, being observed also for mixtures of water with other organic solvents[10–18] including, among others, mono- and disubstituted amides e.g. N-methylformamide (NMF) and N,N-dimethylformamide (DMF)[10–12] (Figure 2). The appearance of viscosity maxima for NMF and DMF may well be due to the presence of hydrophobic groups in their molecules. On the other hand, the absence of the viscosity maximum for water-formamide mixtures (the viscosity plot is monotonic) is probably due to the strong hydrophilicity of formamide (F). When mixed with water, tetrahydrofuran (THF) and hexamethylphosphotriamide (HMPA) probably form clathrates[13–15,19,20] whose composition doesn't correspond with viscosity maximum positions.

According to some authors[20,21] TBA has a structure making effect or hydrophobic hydration effect on water due to the presence of $—CH_3$ groups, and it is quite likely that clathrate-like structures arise in water-rich region[23–25] but not corresponding with the viscosity maximum.

The viscosity minimum observed for the water-TBA system (Figure 1) in the range of alcohol-rich compositions occurs also for other systems involving higher alcohols, both normal and branched[2,7] beginning with IPA. We suggested in our previous paper[2] that the appearance of minima of viscosity and of electric permittivity is due to the formation of "centrosymmetric" associates made up of one water molecule and four alcohol molecules (the Brown and Ives model[25]). The same kind of opinion was put forward by D'Aprano *et al.*[7] concerning water-*n*-pentanol (NPeA) and water-*n*-hexanol (NHeA) systems. Electric permittivity and viscosity minima are

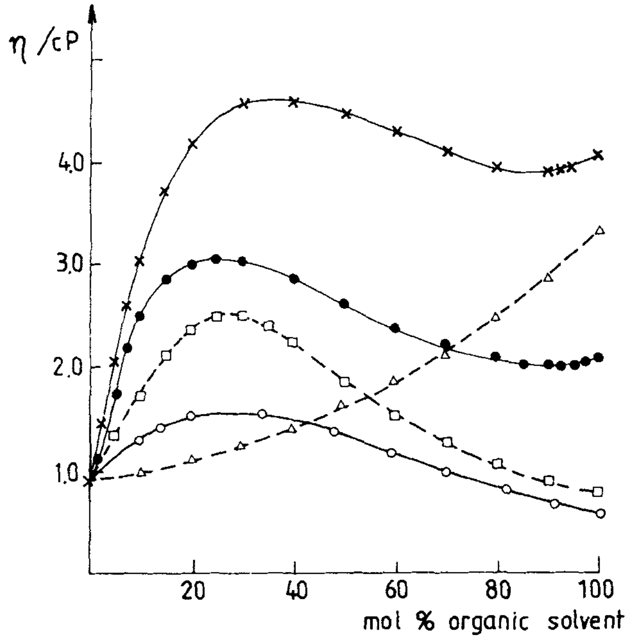

Figure 2 Viscosity of water mixtures with chosen alcohols and amides at 25°C; ○—methanol[1], ●—isopropanol[2,3], ×—tert-butanol[2,3] at 26°C, △—formamide,[10] □—N,N-dimethylformamide.[10]

observed at almost the same composition range for a given alcohol in all water-alcohol mixtures containing four or more carbon atoms in the molecule[2,7,27,28] but for water-IPA and water-NBA systems the viscosity minima are observed only.

As the temperature increases, the viscosity minima become smoother (Figure 1) which is probably due to a decreased number or absence of centrosymmetric water-alcohol associates (viscosity minimum for water-TBA disappears at 40°C).

Analysing the results of viscosity studies in water-TBA system (Figure 1, Table 2) it can be noticed that the temperature coefficient of viscosity (its absolute value) increases with increasing of alcohol content in the mixture, up to the composition corresponding to maximum viscosity, following which it falls slightly down to *ca.* 90 mol% i.e. viscosity minimum. It then rises again attaining, in pure TBA, somewhat higher values than those corresponding to maximum viscosity. The values of the temperature coefficients in pure TBA being so close to those in the range of maximum viscosity may suggest that in both cases associates arise whose structure may be similar to those in pure alcohol i.e. chain multimers stabilised by hydrogen bonds[25–29]

For a comparison the temperature coefficients of viscosity for other water-alcohol systems as well as those for water-amide systems investigated in an earlier study[10] are collected in Table 2. The coefficients for pure alcohols increase as the carbon chain length and branching of the molecule increase (higher value of the coefficient for isopropanol than for *n*-butanol and, likewise, higher values for tert-butanol than for *n*-pentanol and *n*-hexanol). This is the opposite of the ability of alcohol molecules to form long chain self-associates[25–28]. Such behaviour of the temperature coefficient

Table 2 Temperature coefficients of viscosity for 25–35°C, *-for 25–40°C, **-for 26–35°C; x_2-molar fraction of organic solvent.

Pure solvents		*Mixtures with water*			
		Maximum viscosity range		*Minimum viscosity range*	
Solvent	$\Delta\eta/\Delta t$	x_2	$\Delta\eta/\Delta t$	x_2	$\Delta\eta/\Delta t$.
Methanol	0.007^{30}	0.026	0.038^{31}	—	—
		0.273	0.035^{30}	—	—
Ethanol	0.019^{30}	0.243	0.055^{30}	—	—
Isopropanol*	0.073^{3}	0.250	0.123^{3}	0.925	0.070^{3}
n-Butanol	0.058^{7}	—	—	0.922	0.060^{5}
tert-Butanol**	0.143^{3}	0.300	0.138	0.900	0.128
		0.400	0.138		
n-Pentanol	0.085^{7}	—	—	0.831	0.085^{7}
n-Hexanol	0.119^{7}	—	—	0.807	0.112^{7}
Water	0.017^{6}	—	—	—	—
Formamide	0.076^{10}	—	—	—	—
N,N-Dimethylformamide	0.007^{10}	0.300	0.063^{10}	—	—

of viscosity indicates that the larger the molecule and the more it is branched, the more susceptible do the associates become to temperature changes.

The markedly higher temperature coefficients of viscosity for pure formamide than for water and DMF was previously attributed to the ability of formamide to form long chains via hydrogen bonds[10]. However, the $\Delta\eta/\Delta t$ values for TBA are about twice as high as those for formamide, which can hardly have anything to do with the presumed formation of longer chain associates of TBA as compared with formamide. In the case of TBA the ability to form hydrogen bonds is limited by the structure of the molecule and it should not be expected associates involving a large number of molecules[28–29].

In water-alcohol systems, in the range of viscosity maxima, the temperature coefficients of viscosity are usually much larger than those for the corresponding pure alcohols (with the exception of TBA) i.e. the structure of solutions whose composition corresponds to viscosity maxima is less stable than of pure alcohol. The different behaviour of mixtures with TBA may be related to the fact that, of all the alcohols under consideration, it is the only tertiary one. Molar heat, which is taken to be a good indicator of the structures of the solutions, does not exhibit extreme points in the range of compositions corresponding to viscosity maxima. Consequently, it does not point to the existence of any particular type of associates.

However, the values of the temperature coefficients of viscosity for pure alcohols and water-alcohol systems in the composition range of viscosity minima (Table 2) are very close, the structures of pure alcohols and that of solutions are different i.e. centrosymmetric water-alcohol associates are probably formed in the composition range of viscosity minima (the minima of the electric permittivity data[25–28] supports this view[24–27]).

It is thus impossible to draw definite conclusions about structure from the $\Delta\eta/\Delta t$

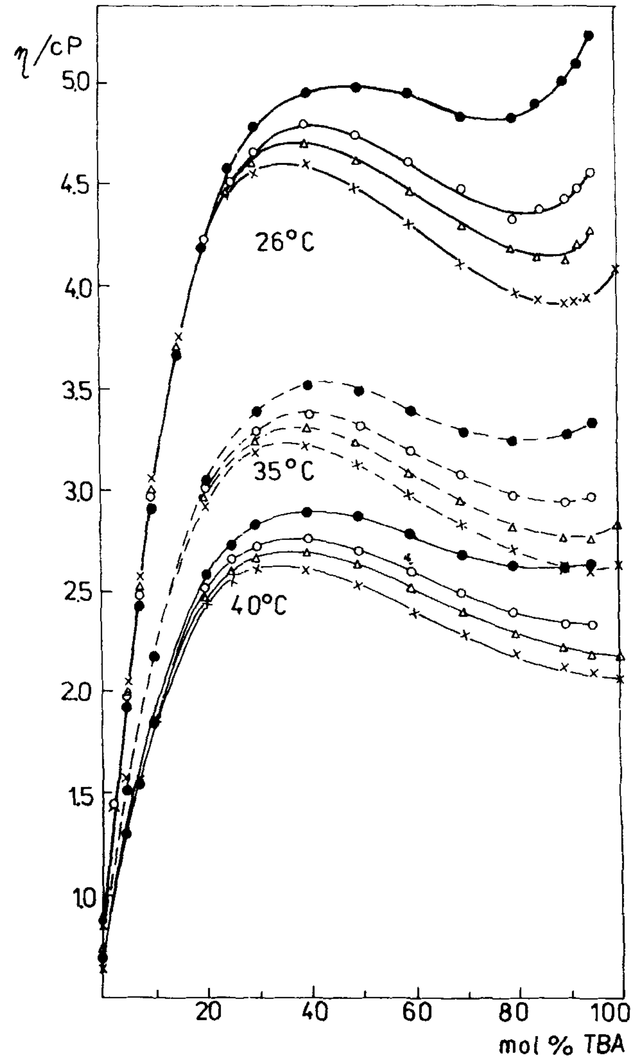

Figure 3 Viscosity of NaI solutions in water-tert butanol mixtures at various temperatures; *x*—solvent, △—0.5, ○—1.0, ●—2.0 mol NaI/100 mol mixed solvent.

values. All what is allowed to presume is that whatever solution structure arises, it is less stable when its temperature coefficients of viscosity are larger.

The viscosity curves for NaI solutions in water-TBA mixtures *vs.* mixed solvent composition (Figure 3, Table 3) have shapes analogous to those for pure solvent. The only exception is the plot for the system with concentration of 2 mol NaI/100 mol solvent at 40°C, where a viscosity minimum is observed: at that temperature the curve for the mixed solvent exhibit no minimum. We made a suggestion in previous work[2] that the increased depth of the viscosity minimum accompanying increased salt concentration could be due, among other factors, to the presence in the solution of spherical aggregates made up of ions and solvation shells. Their effect on the

Table 3 Viscosities of NaI solutions in water-TBA systems at 35 and 40°C (in cP).

mol% TBA	*35°C*			*40°C*		
	*0.5**	*1.0**	*2.0**	*0.5**	*1.0**	*2.0**
0	0.7284	0.7413	0.7534	0.6621	0.6703	0.6902
5	1.531	1.520	1.515	1.306	1.304	1.308
7	—	—	—	1.541	1.543	—
10	2.184	2.178	2.176	1.849	1.852	1.869
20	2.973	3.007	3.041	2.497	2.525	2.581
30	3.261	3.394	3.388	2.675	2.735	2.826
40	3.315	3.379	3.512	2.706	2.759	2.876
50	3.231	3.316	3.493	2.637	2.699	2.879
60	—	3.200	3.406	2.524	2.598	2.780
70	2.961	3.088	3.305	2.395	2.502	2.687
80	2.838	2.975	3.257	2.306	2.406	2.622
90	2.784	2.946	3.274	2.231	2.350	2.628
95	2.769	2.947	3.347	2.204	2.340	2.644
100	2.848	—	—	2.181	—	—

* mol NaI/100 mol solvent.

viscosity could be like that of centrosymmetric water-alcohol associates. This suggestion is strengthened by the appearance of a viscosity minimum in the plot for 2 moles NaI/100 moles of solvent at 40°C and its absence in the plots for pure solvent or low concentrations.

As the salt concentration increases, the maximum shifts toward higher TBA contents in the mixture, and the minimum shifts in the opposite direction. The shift of the minimum viscosity towards lower TBA contents may be due to higher affinity of ions to water molecules as compared with alcohol, even under conditions of a large excess of alcohol.

If electric permittivity and viscosity minima are to appear, the water molecules captured by ions have to be replaced by others so that water-centric mixed water-alcohol associates—responsible for them—may arise. For this reason an increase of ion content should lead to shift of the viscosity minimum towards higher water contents. Obviously, this does not rule out other interpretations of the above finding.

Plots of the relative viscosities of NaI solutions with various concentrations in water-TBA mixtures in the entire range of mixture compositions and at several temperatures are shown in Figure 4. Each curve corresponds to a definite salt concentration expressed in mol/100 mol solvent. The minima in the water-rich region i.e. at about 6 mol% TBA are observed in each case. As it is known[2,22–25,32–37] these minima are attributed to the compositions in which the water structure is the most ordered. The fact that the position of the relative viscosity minimum is independent of the salt concentration[1,2] indicates that it is related to the structure of the mixed solvent, with the salt concentration affecting the depth of the minimum only. Thus, the higher the salt concentration and the lower the temperature, the deeper the minimum. As temperature increases, the minimum shifts towards lower alcohol contents in the system. Desnoyers *et al.*[35] have observed similar shifts of apparent

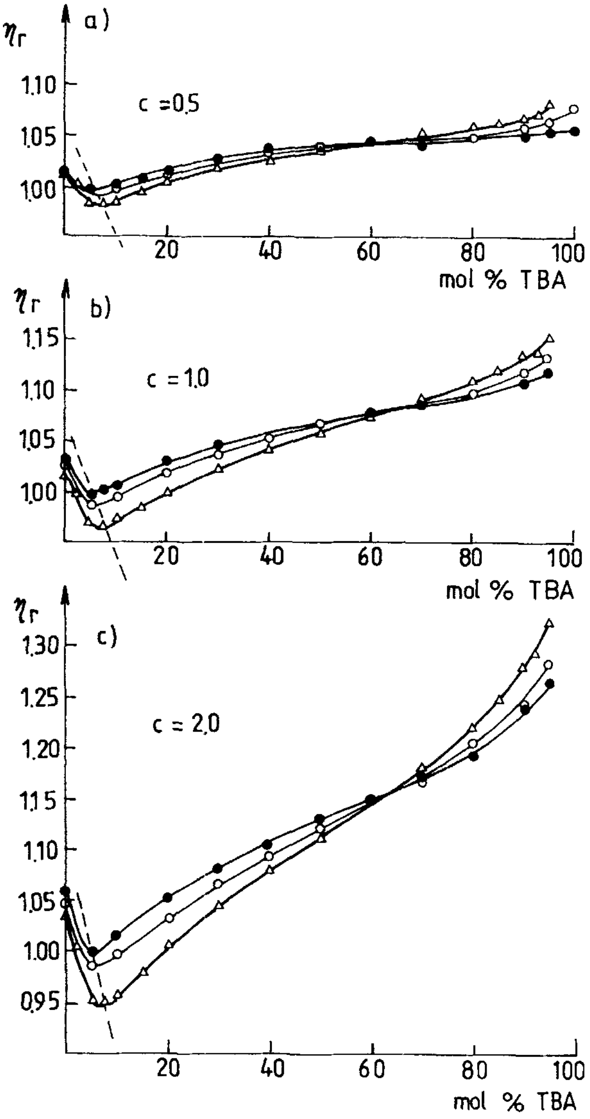

Figure 4 Relative viscosity of NaI solutions in water-tert-butanol mixtures at various temperatures; c—salt concentration in mol/100 mol solvent, △—26°C, ○—35°C, ●—40°C.

molal volumes minima and apparent molal heat capacities maxima of TBA in water with increasing temperature.

Relative viscosity isotherms for NaI solutions in the same concentration intersect at about 65 mol% TBA, which means that at that point the temperature coefficients of the relative viscosity of such solutions change their sign from positive to negative. Positive values of the coefficients probably point to a structure breaking effect of

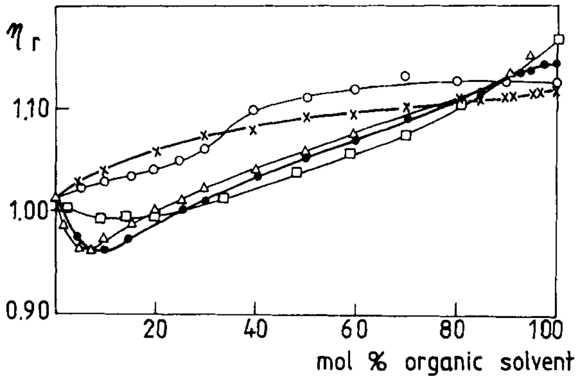

Figure 5 Relative viscosity of NaI solutions with concentration 1 mol salt/100 mol mixed solvent at 25°C in water-organic solvent mixtures: □—methanol[1], ●— isopropanol,[2,3] △—tert-butanol,[2,3] ×—formamide,[10] ○—N,N-dimethylformamide.[10]

electrolyte on the mixed solvent and their negative values above 65 mol% TBA suggest a structure making effect.

A comparison of the relative viscosities of NaI solutions in water-alcohol (MA, IPA, TBA) systems with those in water-amide (F, DMF) indicates that the effects of

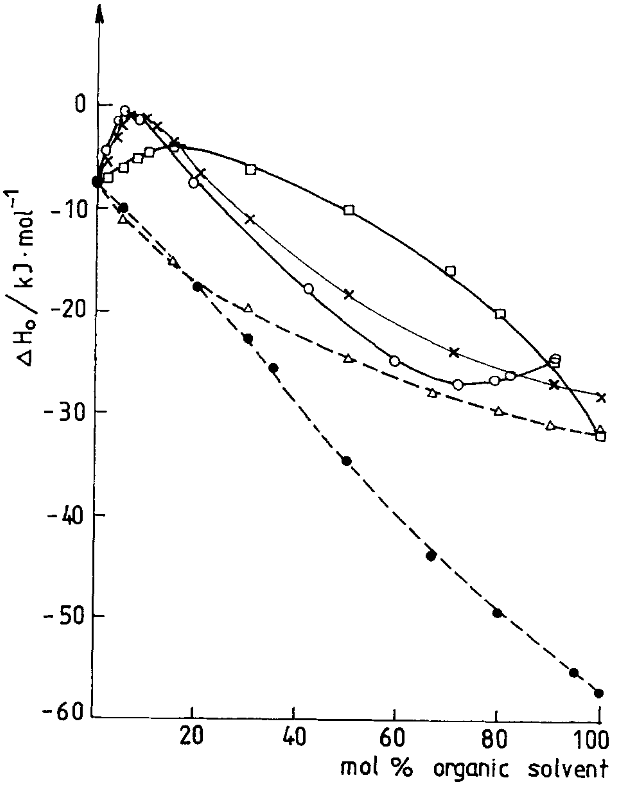

Figure 6 Standard enthalpies of NaI solution in water-organic solvent mixtures at 25°C; □—methanol,[35] ×—isopropanol,[35] ○—tert-butanol,[37] △—formamide,[38] ●—N,N-dimethylformamide.[38]

alcohols and amides on water structure are different. This is evident from the differences in two sets of curves in Figure 5.

An analysis of the curves of standard solution enthalpies for NaI in water-alcohol[35,37] and water-amide[38] systems also points to differences in the behaviour of two types of solvent (Figure 6). The plots of $\Delta H^{\circ}(\mathrm{NaI}) = f(x_2)$ for water-alcohol systems exhibit maxima in the range of water structure stabilisation being brought by small amounts of alcohols. In water-amide systems, on the other hand, the standard solution enthalpy values decrease monotonically as the amide content in the mixtures increases. Such shapes of the isotherms may be attributed to a structure breaking effect of both amides on water, the opposite of the effect of alcohols.

The sign of the relative viscosity temperature coefficients for NaI solutions in water-alcohol and water-amide systems suggests that in the case of alcohols the structure making effect of NaI occurs in the range of high alcohol content (above 80 mol% IPA[2] and 65 mol% TBA) while in the case of amides it takes place in water-rich mixtures i.e. above *ca.* 30 mol% F and DMF[10].

These results and discussion point to differences in behaviour of two- and three- component solutions involving alcohols, especially TBA and systems containing amides.

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