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DISSOLUTION ENTHALPY OF NaI IN MIXTURES OF ETHYLENE GLYCOL + ALIPHATIC ALCOHOLS AT 313.15 K

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ABSTRACT

Measurements of the dissolution enthalpies of NaI in ethylene glycol + aliphatic alcohol (methanol, ethanol and n-propanol) mixtures have been carried out using an "isoperibol" type calorimeter at 313.15 K.

The course of the standard enthalpy of solution, $\Delta H^{\ominus}$, vs. the binary solvent composition curve is discussed and compared with corresponding curves for glycerol + n-propanol and water + n-propanol solutions of NaI.

INTRODUCTION

In our earlier works we carried out thermochemical investigations of the following systems: NaI + glycerol + water [1], NaI + glycerol + aliphatic alcohols [2] and NaI + glycerol + diols [3].

Both glycerol and ethylene glycol are exceptionally interesting solvents; they have been shown to have a significant influence on chemical compounds [4] and, moreover, as many authors suggest, they both show some common features with water.

A survey of the literature on electrolytes solutions in mixtures of glycols with aliphatic alcohols shows that such systems are rarely the subject of investigations [5,6] contrary to water + alcohol and water + glycol [7,8] solutions of electrolytes. We may suppose that the reason for this lies in the high hygroscopicity of both aliphatic alcohols and glycols and also in the high viscosity of glycols.

EXPERIMENTAL

Ethylene glycol (P.P.H. POCh Gliwice) and sodium iodide were prepared as described earlier [3]. Methanol, ethanol and n-propanol were purified and dried by the Lund–Bjerrum procedure [9].

The concentration of water in the solvents was determined by the Karl–Fischer method and did not exceed 0.02%. Solutions were prepared by weight. Measurements of the enthalpy of solution of NaI in ethylene glycol + alcohol mixtures were carried out using an "isoperibol" type calorimeter designed in our laboratory [1]. The error involved in the measurement was estimated to be ±0.5%.

RESULTS AND DISCUSSION

Values of the solution enthalpy of NaI in mixtures of ethylene glycol and aliphatic alcohols at 313.15 K are given in Tables 1–3.

The investigations were carried out over the whole region of mixed solvent composition. The salt concentration was within the range of ~ 0.002–0.01 mol kg^{-1} of solvent. Dissolution processes of NaI in all alcohol + glycol mixtures are accompanied by an exothermic effect decreasing with increasing electrolyte concentration.

On the basis of the experimental data obtained, values of the standard enthalpy of NaI, $\Delta H^{\ominus}$, have been calculated. For the NaI + ethylene glycol + methanol system, the Criss and Cobble method of calculating $\Delta H^{\ominus}$ was used [10]. Using experimental data on the electric permittivity and density of ethylene glycol + ethanol and ethylene glycol + n-propanol mixtures, we calculated $\Delta H^{\ominus}$ by means of extrapolating the graph of $\Delta H_m = \mathrm{f}(\sqrt{m})$ and from a plot of ΔH_m against $\mathrm{f}(m)$ by the least-squares method. The two procedures produce results that differ by ±20 J. The mean $\Delta H^{\ominus}$ values are collected in Table 4 which also presents the $\Delta H^{\ominus}$ values of the NaI + ethylene glycol + methanol system. Plots of $\Delta H^{\ominus} = \mathrm{f}$(mol% glycol) for all the systems investigated are shown in Fig. 1.

The observed changes have diverse characters and depend on the kind of aliphatic alcohol used. In the case of NaI + ethylene glycol + methanol, changes in $\Delta H^{\ominus}$ are slight: $\Delta H^{\ominus}_{\mathrm{NaI}}$ in pure methanol equals −32.87 kJ mol^{-1}, while in pure glycol it is −34.27 kJ mol^{-1}. The $\Delta H^{\ominus}$ curve proceeds nearly monotonically and only in the glycol-rich region can a slight extremum be observed.

A small addition of glycol (2–10%) to ethanol significantly increases the exothermicity of the process, while further additions of ethanol produce only slight changes the $\Delta H^{\ominus}$ values. We can also observe a slight maximum in solutions containing ~ 95% of glycol.

The most distinct changes of the function $\Delta H^{\ominus} = \mathrm{f}$(mol% glycol) can be seen in mixtures of ethylene glycol with n-propanol. In the alcohol-rich region (~ 20% glycol), an extreme minimum enthalpy of solution is observed which, together with the increase in glycol content, goes through a slight maximum (~ 95% glycol). Beginning with about 90 mol% glycol, the curves practically overlap in all cases.

TABLE 1

Enthalpy of solution of NaI in ethylene glycol + methanol mixtures at 313.15 K

m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})
Methanol		*60 mol% Ethylene glycol*	
0.00172	32.27	0.00151	32.82
0.00248	32.06	0.00166	32.53
0.00410	31.44	0.00323	32.19
0.00465	31.35	0.00346	32.06
0.00510	31.14	0.00618	31.31
2 mol% Ethylene glycol		*80 mol% Ethylene glycol*	
0.00204	32.40	0.00092	33.28
0.00234	32.32	0.00149	32.94
0.00544	31.14	0.00259	32.65
0.00610	31.02	0.00485	32.06
0.00843	30.60	0.00764	31.40
5 mol% Ethylene glycol		*90 mol% Ethylene glycol*	
0.00121	32.73	0.00132	33.40
0.00228	32.40	0.00245	33.15
0.00245	32.35	0.00251	33.03
0.00544	31.44	0.00371	32.65
0.00904	30.18	0.00688	32.19
10 mol% Ethylene glycol		*95 mol% Ethylene glycol*	
0.00222	32.36	0.00108	33.45
0.00289	32.11	0.00173	33.19
0.00439	31.65	0.00267	33.03
0.00533	31.44	0.00381	32.82
0.00852	30.26	0.00436	32.62
20 mol% Ethylene glycol		*Ethylene glycol*	
0.00139	32.78	0.00129	33.91
0.00186	32.69	0.00265	33.45
0.00310	32.19	0.00311	33.36
0.00395	31.90	0.00458	32.99
0.00670	31.19	0.00684	32.36

For comparison, Fig. 2 presents $\Delta H^{\ominus} = \mathrm{f}(\text{mol\% alcohol})$ curves of the previously investigated systems NaI + water + n-propanol [11] and NaI + glycerol + n-propanol [2], and also the current data.

This comparison shows the differences in behaviour of NaI solutions in water + alcohol, glycerol + alcohol and glycol + alcohol mixtures. Pair interaction coefficients, h_{xy} [3], have been calculated for NaI + ethylene glycol + n-propanol on the basis of the obtained values of $\Delta H^{\ominus}$ and compared with h_{xy} calculated earlier in NaI + glycerol + n-propanol [3] and in NaI + water + n-propanol [11]. These last data [11] were extrapolated to 313.15 K, the

TABLE 2

Enthalpy of solution of NaI in ethylene glycol + ethanol mixtures at 313.15 K

m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})
Ethanol		*40 mol% Ethylene glycol*	
0.00165	24.91	0.00126	33.86
0.00295	24.32	0.00150	33.74
0.00410	23.94	0.00330	33.28
0.00532	23.32	0.00540	32.78
0.00645	22.94	0.00718	32.16
2 mol% Ethylene glycol		*60 mol% Ethylene glycol*	
0.00220	31.14	0.00161	33.66
0.00294	30.93	0.00171	33.49
0.00430	30.43	0.00312	33.19
0.00576	29.97	0.00343	33.15
0.00765	29.22	0.00500	32.65
5 mol% Ethylene glycol		*80 mol% Ethylene glycol*	
0.00117	33.24	0.00152	33.40
0.00175	33.15	0.00236	33.19
0.00246	32.78	0.00275	33.03
0.00288	32.65	0.00442	32.61
0.00610	31.48	0.00622	31.77
10 mol% Ethylene glycol		*90 mol% Ethylene glycol*	
0.00159	33.24	0.00120	33.49
0.00245	33.03	0.00139	33.28
0.00374	32.69	0.00302	32.90
0.00612	31.98	0.00504	32.57
20 mol% Ethylene glycol		*95 mol% Ethylene glycol*	
0.00137	34.07	0.00121	33.32
0.00151	34.03	0.00218	32.94
0.00245	33.66	0.00246	32.94
0.00322	33.40	0.00397	32.40
0.00627	32.61	0.00650	31.81

temperature at which our investigations were carried out. The h_{xy} coefficients are given in Table 5.

From these values, we can see that the strongest interactions between the electrolyte and n-propanol take place in water and the weakest ones in glycerol. We may suppose that water exerts the strongest influence on electrolyte–n-propanol interactions. The high negative values of h_{xy} for NaI–glycerol and NaI–ethylene glycol in n-propanol suggest a stronger interaction between these pairs than that occurring between NaI and n-propanol. The higher solubility of the electrolyte in glycerol and glycol than in n-propanol [12] seems to support this conclusion. In the case of NaI–water

TABLE 3

Enthalpy of solution of NaI in ethylene glycol + n-propanol mixtures at 313.15 K

m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})	m (mol kg^{-1})	$-\Delta H_m$ (kJ mol^{-1})
n-Propanol		*30 mol% Ethylene glycol*	
0.00132	25.66	0.00265	35.66
0.00235	25.20	0.00385	35.46
0.00310	24.66	0.00524	34.99
0.00451	24.36	0.00867	34.12
0.00550	23.82	0.01022	33.66
2 mol% Ethylene glycol		*50 mol% Ethylene glycol*	
0.00242	31.31	0.00298	34.91
0.00501	30.22	0.00502	34.41
0.00568	29.97	0.00592	34.28
0.00785	29.05	0.00809	33.82
0.00998	28.13	0.00898	33.24
5 mol% Ethylene glycol		*80 mol% Ethylene glycol*	
0.00260	34.12	0.00235	33.57
0.00358	33.74	0.00361	33.36
0.00611	32.69	0.00501	32.94
0.00764	32.32	0.00657	32.48
0.01128	30.89	0.00880	31.90
10 mol% Ethylene glycol		*90 mol% Ethylene glycol*	
0.00290	35.08	0.00267	33.03
0.00452	34.58	0.00283	33.28
0.00593	34.07	0.00499	32.48
0.00892	33.28	0.00588	32.27
0.00944	33.15	0.01095	31.27
20 mol% Ethylene glycol		*95 mol% Ethylene glycol*	
0.00230	36.21	0.00269	32.82
0.00316	35.92	0.00487	32.36
0.00575	35.46	0.00599	32.06
0.00703	34.95	0.00822	31.48
0.01098	34.07	0.01078	30.93

in n-propanol, a significant decrease in electrolyte affinity to water can be observed in the presence of alcohol.

Since no data concerning the entropies of the previously mentioned systems are available (entropy best reflects structural changes in solutions), we will attempt to interpret the values of $\Delta H^{\ominus}$ obtained in these systems. As there are some similarities between water, glycerol and ethylene glycol, we could expect the behaviour of these solvents in mixtures with other liquids and also in their electrolyte solutions to be similar. A thermodynamic method seemed to be most suitable for such comparative investigations.

TABLE 4

Standard enthalpy of solution of NaI in ethylene glycol + alcohol mixtures at 313.15 K

Ethylene glycol + MeOH		Ethylene glycol + EtOH		Ethylene glycol + n-PrOH	
Glycol (mol%)	$-\Delta H^{\ominus}$ (kJ mol^{-1})	Glycol (mol%)	$-\Delta H^{\ominus}$ (kJ mol^{-1})	Glycol (mol%)	$-\Delta H^{\ominus}$ (kJ mol^{-1})
0	32.86	0	25.53	0	26.17
2	33.15	2	31.90	2	32.23
5	33.15	5	33.57	5	34.95
10	33.19	10	33.74	10	36.00
20	33.24	20	34.37	20	36.84
40	33.07	40	34.20	30	36.42
60	33.11	60	33.99	50	35.66
80	33.36	80	33.78	80	34.24
90	33.61	90	33.74	90	33.74
95	33.70	95	33.61	95	33.49
100	34.24	100	34.24	100	34.24

If we compare the range of water-, glycerol- and ethylene glycol-rich concentrations (Fig. 2), we see that the maxima fall in the order: water > glycerol > ethylene glycol. If we assume that the water-structure-making effect of alcohols is connected with a hydrophobic reaction, we might suppose that the height or position of the maximum $\Delta H^{\ominus}$ solution enthalpy will constitute an indirect measure of this effect. On the basis of the data

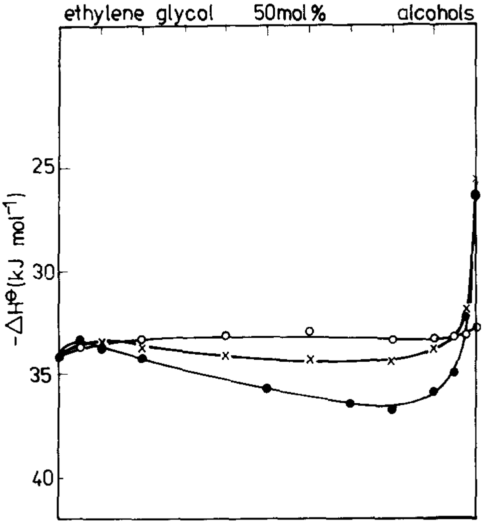

Fig. 1. Standard enthalpy of solution of NaI in ethylene glycol + alcohol mixtures as a function of mol% alcohol. (○) Methanol; (×) ethanol; (●) n-propanol; $T = 313.15$ K.

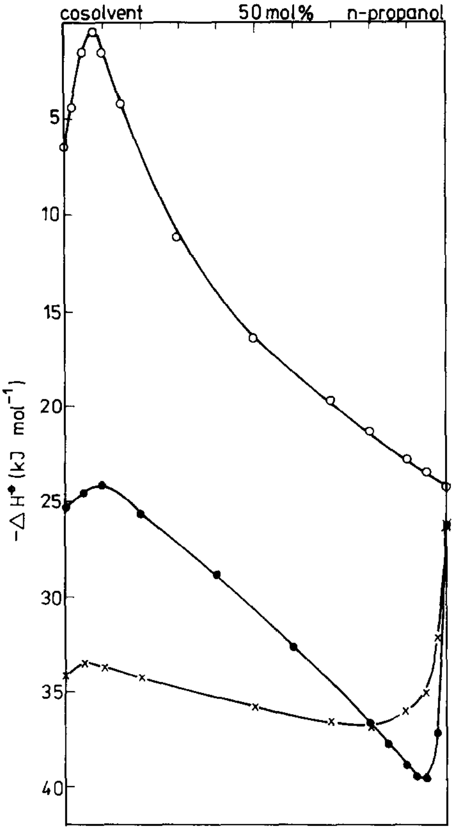

Fig. 2. Standard enthalpy of solution of NaI in n-propanol + cosolvent mixtures as a function of mol% n-propanol. (○) Water [11], $T = 298.15$ K; (●) glycerol [2], $T = 313.15$ K; (×) ethylene glycol (this work), $T = 313.15$ K.

presented we can assume that a solvophobic effect also occurs to a certain degree in glycerol, and is weakly observed in ethylene glycol.

With increasing alcohol radicals, the maximum enthalpy of NaI solution and the maxima of other solutes move towards higher water contents. The

TABLE 5

Enthalpic pair interaction coefficients, h_{xy} (J kg mol^{-2}), at 313.15 K

Pair	Solvent	h_{xy}
NaI–nPrOH	water	240
NaI–nPrOH	ethylene glycol	400
NaI–nPrOH	glycerol	550
NaI–glycerol	nPrOH	−10500
NaI–ethylene glycol	nPrOH	−5600
NaI–water	nPrOH	−135

influence of the size of the radical of the first three aliphatic alcohols on the position of a maximum cannot be observed in the NaI + glycerol + alcohol or in NaI + ethylene glycol + alcohol systems.

Another difference in the behaviours of water, glycerol and ethylene glycol is the sign of the enthalpy of solution of the substances containing hydrocarbon groups (tetrabutylammonium bromide and alcohols). The sign of the enthalpy of solution of the systems in water is negative while those of the systems in glycol and glycerol are positive [5,13–15]. So the supposed similarity of glycerol and ethylene glycol to water is, in the thermochemical sense, ambiguous.

In the case of glycol this opinion is supported by the enthalpy of solution of several aliphatic alcohols in ethylene glycol and in water, given by Nwankwo and Wadsö [5]. They considered the changes of thermal capacity, $C_{p,2}^{\infty}$, of alcohols in ethylene glycol and in water in comparison with pure alcohols. They observed a significant increase of $C_{p,2}^{\infty}$ in water solutions in contrast to that of alcohols in ethylene glycol, which shows different behaviours of these two solvents. These authors interpreted the results of their investigations from the point of view of that the hydrophobic effect plays a significant part in water–alcohol interactions. This effect was practically absent in ethylene glycol–alcohol solutions, which suggests some differences in the behaviours of glycol and water.

We may suppose that glycerol, which according to some authors [16,17] retains a hydrogen bond network in its liquid state, is a more similar solvent to water than ethylene glycol, in agreement with the results of our investigations.

Future investigations on the thermal capacity of alcohols in glycerol will provide a solid argument for the presence or absence of solvophobic interactions in glycerol.

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