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ENTHALPY OF SOLUTION OF NaI IN GLYCEROL—WATER MIXTURES AT VARIOUS TEMPERATURES

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ABSTRACT

The enthalpy of solution of NaI in glycerol—water mixtures has been measured throughout the whole mixed solvent composition range at 313.15, 333.15 and 353.15 K. The course of the standard enthalpy of solution, ΔH^0, in relation to the content of glycerol in the solvent has been discussed.

INTRODUCTION

In an earlier paper [1] we reported the results of the thermochemical study of glycerol solutions of several electrolytes. In view of the considerable interest in glycerol, we decided to extend our calorimetric study to water—glycerol mixtures of sodium iodide, which is a convenient compound to study because of its relatively good solubility in glycerol. Furthermore, its solutions in organic solvents as well as in mixed solvents have been studied by many investigators, which makes for easy comparison of various systems.

Unlike solutions in pure glycerol, water—glycerol solutions of electrolytes have attracted a lot of attention. The work devoted to them includes studies of their viscosity [2,3], conductivity [4], EMF [5—7], volume [11], NMR spectra [12] and thermodynamic [9,10] and acoustic properties [8], and others. Investigations on water—glycerol mixtures are easier to conduct in view of their considerably lower viscosity and better solubility of electrolytes in mixed solvents. The results obtained are usually discussed in terms of the interactions between the two solvents or of the effect of glycerol on the structure of water.

Other studies described in the literature concern the stabilizing effect of glycerol on natural proteins in water. Based on their work on the apparent molar volume and thermal capacity, Di Paola and Belleau [11] found that in water solutions of glycerol specific interactions contribute to the abovementioned stabilizing effect observed in biological systems rather than provoke structural changes. It is hoped that the results reported here will shed some more light on the nature of such interactions.

EXPERIMENTAL

Glycerol and sodium iodide were prepared as described previously [1], and the water used was twice distilled. The water—glycerol mixtures were prepared by weight and contained 0—100 mole % glycerol. The measurements were performed at 313.15, 333,15 and 353.15 K, using an "isoperibol" calorimeter, in the concentration range 0.008—0.05 mole NaI/kg solvent. In view of the higher glycerol viscosity at 313.15 K, the measurement error was 2%; at higher temperatures it did not exceed 1.5%.

RESULTS AND DISCUSSION

Dissolution enthalpies of NaI in water—glycerol systems throughout the entire glycerol concentration range are collected in Table 1. In each case, the exothermic effect accompanying the process of NaI dissolution can be observed; the effect becomes greater as glycerol concentration increases.

The standard dissolution enthalpy, ΔH^0 (Table 2), was calculated using the procedure of Guggenheim and Prue [13]. The electric permitivities of the solvent were adopted from Åkerlöf [14], and the density data from Timmermans [15]. It follows from Fig. 1 that the $\Delta H^0 = f(x\%)$ plots do not exhibit any extrema, and change monotonically with changes in solvent concentration. Krestov and Egorova [16] who studied KNO_3—water—glycerol and $Ca(NO_3)_2$—water—glycerol systems obtained similar $\Delta H^0 = f(x)$ plots. Such plots change monotonically also in the case of NaI—water—DMSO [17] and NaI—formamide—water systems [18], while those for NaI—water—alcohols [19,20], NaI—water—acetonitrile [21] and NaI—water—acetone [22] do exhibit maxima.

The absence of maxima in the $\Delta H^0 = f(x\%)$ plots for water—glycerol solutions of NaI can be related to the absence of any marked ordering effect of glycerol on the structure of water. Basumullick and Kundu [23] place glycerol between monoalcohols which are thought to have an ordering effect on the structure of water [24], and polyalcohols, which are said to destroy it [25]. The special properties of glycerol as a solvent are due first of all to its ability to form intra- and intermolecular hydrogen bonds [26], and to the existence in glycerol of various conformations regardless of its density.

Recent studies on acoustic spectra indicate that among the various possible structures of associates, of particular importance are glycerol dimers with two hydrogen bonds. Rabichev et al. [26] suggest that the decomposition of such dimers in the process of mixing with water and formation of water—glycerol bonds is the main factor responsible for the marked change of the physico-chemical properties of glycerol, such as viscosity or boiling point (1% of water by weight causes the viscosity and boiling point to decrease by 25% and 60—65° C, respectively).

It seems justified to say that in water—glycerol solutions there arise extensive hydrogen bonds between the two components which lead to various types of equilibria. The collective hydrogen bonds theory successfully accounts for the experimental data on the viscosity [2,3], dielectric con-

TABLE 1

Enthalpy of solution of NaI in glycerol—water mixtures at various temperatures

313.15 K		333.15 K		363.15 K	
m (mole kg^{-1})	$-\Delta H_m$ (kcal mole^{-1})	m (mole kg^{-1})	$-\Delta H_m$ (kcal mole^{-1})	m (mole kg^{-1})	$-\Delta H_m$ (kcal mole^{-1})
Water					
0.01114	2.09	0.01170	2.60	0.01123	2.91
0.02351	2.05	0.02532	2.59	0.01976	2.90
0.03644	2.01	0.03809	2.56	0.03156	2.86
0.05588	2.00	0.05341	2.53	0.04229	2.82
10 mole % glycerol					
0.00970	2.40	0.00691	2.91	0.01444	3.32
0.01973	2.35	0.01672	2.91	0.02843	3.32
0.02917	2.29	0.02520	2.90	0.04509	3.28
0.03881	2.26	0.04172	2.88	0.06434	3.27
20 mole % glycerol					
0.00932	2.84	0.00871	3.51	0.01046	3.72
0.01979	2.80	0.01734	3.44	0.02202	3.69
0.03093	2.69	0.02503	3.43	0.03525	3.63
0.04229	2.62	0.03652	3.42	0.05683	3.60
30 mole % glycerol					
0.01060	3.32	0.01041	3.87	0.00870	4.28
0.02081	3.26	0.01720	3.84	0.01905	4.23
0.03479	3.18	0.02403	3.83	0.03619	4.17
0.04859	3.08	0.03582	3.77	0.05270	4.13
40 mole % glycerol					
0.00721	3.85	0.00717	4.39	0.00952	4.68
0.01730	3.76	0.01385	4.36	0.01933	4.69
0.03212	3.65	0.02267	4.30	0.03093	4.60
0.04401	3.57	0.03235	4.26	0.04487	4.52
50 mole % glycerol					
0.01129	4.41	0.00944	4.88	0.00871	5.14
0.02290	4.30	0.01647	4.83	0.01683	5.09
0.03224	4.27	0.02313	4.79	0.03114	5.02
0.04518	4.15	0.03487	4.70	0.04486	4.97
60 mole % glycerol					
0.00423	4.95	0.01365	5.22	0.00843	5.53
0.01404	4.80	0.03082	5.17	0.01685	5.44
0.03072	4.68	0.04278	5.11	0.02821	5.34
0.04269	4.57	0.05418	5.04	0.03917	5.25
80 mole % glycerol					
0.00876	5.25	0.00637	5.80	0.00652	6.18
0.01762	5.16	0.01488	5.71	0.01566	6.10
0.02888	4.96	0.02174	5.65	0.02251	5.95
0.03967	4.76	0.02995	5.60	0.03139	5.92
90 mole % glycerol					
0.00944	5.50	0.00972	5.95	0.00335	6.40
0.01996	5.42	0.01843	5.81	0.01114	6.35
0.03066	5.25	0.02603	5.73	0.01942	6.21
0.04101	4.91	0.03415	5.63	0.03133	6.12
100 mole % glycerol					
0.00762	5.76	0.00867	6.24	0.01312	6.52
0.01668	5.55	0.01772	6.15	0.02341	6.42
0.02729	5.32	0.02811	5.95	0.03388	6.36
0.09752	5.12	0.04184	5.82	0.04709	6.24

TABLE 2

Standard enthalpy of solution (kcal mole^{-1}) of NaI in water—glycerol mixtures at various temperatures

Glycerol (mole %)	—ΔH^0 (kcal mole^{-1})		
	313.15 K	333.15 K	353.15 K
0	2.15	2.65	3.03
10	2.52	2.97	3.42
20	3.00	3.55	3.90
30	3.50	4.00	4.45
40	4.00	4.50	4.90
50	4.60	5.02	5.35
60	5.08	5.45	5.80
80	5.55	6.02	6.43
90	5.80	6.22	6.64
100	6.05	6.45	6.84

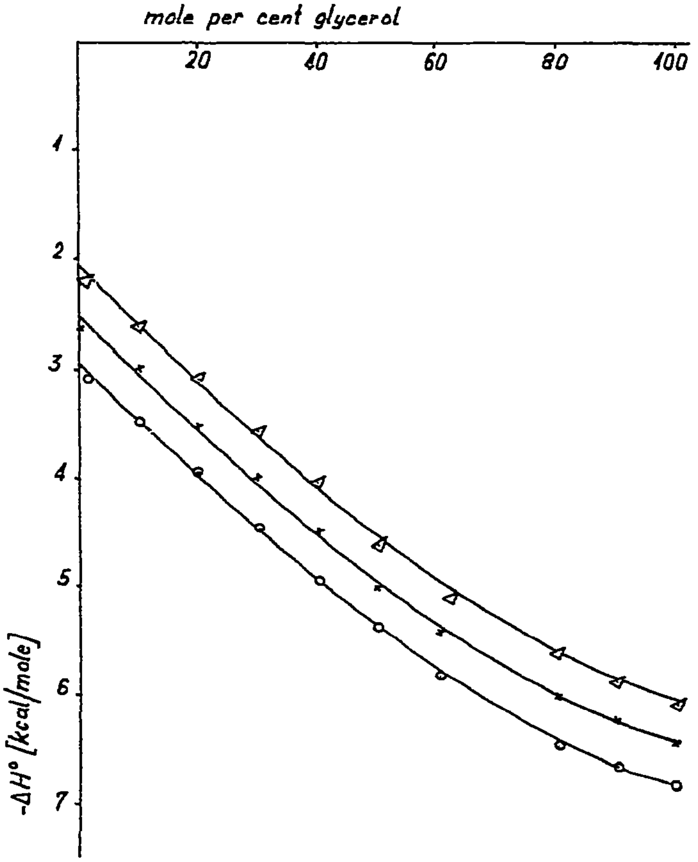

Fig. 1. Standard enthalpy of solution of NaI in glycerol—water mixtures. △, 313.15 K; ×, 333.15 K; ○, 353. 15 K.

stants [14], and the Walden product [4] of water—glycerol mixtures; the plots illustrating the dependence of these quantities on glycerol concentration do not exhibit any extrema. Ageno and Frontall [27] suggest that the monotonic character of the changes in these plots is related to the ability of glycerol to form more than one independent hydrogen bond (similar to glycol). The experimental data on the volume properties and some thermodynamic properties, as well as NMR spectra and dielectric relaxation data, all indicate that hydrophilic substance + water systems, i.e. also glycerol + water, can be described most adequately in terms of a model which assumes the existence of an extensive glycerol—water complex (through H-bonds). The size and member of the labile complexes change permanently along mixed solvent composition which leads to the monotonic character of the curves $\Delta H^0 = f(x\%)$.

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