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INTERACTIONS IN ELECTROLYTE SOLUTIONS IN GLYCEROL–WATER AND GLYCEROL–METHANOL MIXTURES FROM THE HEAT OF SOLUTION ENTHALPY

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ABSTRACT

The enthalpy of solution of *n*-Bu_4NBr in glycerol–water and glycerol–methanol mixtures was measured throughout the entire range of composition at 313.15 K. The dependence of the standard enthalpy of solution $\Delta H^{\ominus}$ on the concentration of glycerol in the solvent is discussed.

INTRODUCTION

The ability of glycerol to stabilize highly organized biological macromolecules is a well-known phenomenon [1–3]. The mechanism of this process is not easy to define. However, it seems that an explanation for the stabilizing abilities of glycerol may be determined from other effects rather than from its modification of the structure of water.

It is known that the peculiar characteristics of water as a solvent are clearly seen in water containing hydrocarbons or chemical compounds with apolar groups with one or two functional groups. Interactions which occur in these types of solutions are called hydrophobic interactions. We believe that investigations of water–glycerol mixtures and their electrolyte solutions (both the simple NaI type and the tetraalkylammonium salts (R_4NBr)) are of extra significance due to some similarity in the physical properties of glycerol and water [4].

Therefore, we have conducted calorimetric measurements of the solution enthalpy of tetrabutylammonium bromide (*n*-Bu_4NBr) in glycerol–water and glycerol–methanol mixtures. The glycerol–methanol mixture was chosen for our investigations since we expected the behaviour of this solution to be different from that of the water–glycerol solution.

We believe that the calorimetric data (ΔH_m) obtained and the behaviour of the standard enthalpy of solution in relation to the composition of the mixed solvent may provide information about the interactions in glycerol–water solutions.

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EXPERIMENTAL

Tetrabutylammonium bromide (puriss, Fluka A.G. Fuchs) was dried in vacuum at 50 °C. Glycerol (P.P.H. Polish Chemicals, Gliwice) was prepared as described previously [4]. Methanol was purified and dried by the Lundt–Bjerrum procedure [5]. The concentration of water in the solvents was determined by the Karl–Fischer method and did not exceed 0.02%. Double-distilled deionized water was used. The solutions were prepared by weight.

Measurements of the enthalpy of solution of n-Bu_4NBr were carried out using an isoperibol-type calorimeter designed in our laboratory [4]. The error involved in the measurement was estimated to be $\pm 0.5\%$.

RESULTS AND DISCUSSION

Measurements of the enthalpy of solution of n-Bu_4NBr in glycerol–water and glycerol–methanol solutions were carried out over the entire range of mixed solvent composition at 313.15 K. This temperature was selected as the viscosity of glycerol is much reduced at this temperature compared with that at 298.15 K. The high viscosity of glycerol at 298.15 K would make it virtually impossible to conduct the calorimetric measurements. The salt (n-Bu_4NBr) concentration was varied within the range ≈ 0.002–0.008 mol (kg solvent)$^{-1}$. The results of the measurements are shown in Tables 1 and 2.

Glycerol–water solutions

Dissolution of n-Bu_4NBr in glycerol–water mixtures is accompanied by an endothermic effect. On the basis of the ΔH_m values and using the method of Criss and Cobble [6] values of the standard enthalpies of solution $\Delta H^{\ominus}$ were calculated and are shown in Table 3. The $\Delta H^{\ominus}$ value obtained by us in water at 313.15 K can be compared with the value of Mastroianni and Criss [7] who determined this function within the temperature range 278.15–368.15 K. From the data of Mastroianni and Criss the heat effect which accompanies the dissolution of n-Bu_4NBr in water below the temperature of ≈ 309 K is exothermic, whereas above this temperature n-Bu_4NBr dissolves in water with a positive effect. Our $\Delta H^{\ominus}$ data obtained at a temperature of 313.15 K are in good agreement with those of Mastroianni and Criss [7].

In Fig. 1(a) the standard enthalpy of solution $\Delta H^{\ominus}$ is presented as a function of the composition of the glycerol–water mixture. The dependence of $\Delta H^{\ominus}$ on the concentration of glycerol shows a maximum corresponding to a value of about 30 mol% glycerol. A similar dependence is shown by the same function in the n-Bu_4NBr–H_2O–t-BuOH system at 298.15 K [8], although the maximum occurs at a lower concentration of alcohol ($\approx 8\%$). The existence of a maximum is attributed to the stabilization of the water

TABLE 1

Enthalpy of solution of n-Bu_4NBr in glycerol–water mixtures at 313.15 K

m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
Water		40 mol% glycerol	
0.00532	2.60	0.00197	30.96
0.00667	2.50	0.00240	31.05
0.00764	2.60	0.00294	30.96
0.01327	2.51	0.00526	31.22
0.01776	2.59	0.00532	31.00
0.02814	2.51	0.00811	31.34
2 mol% glycerol		60 mol% glycerol	
0.00421	5.49	0.00230	29.79
0.00688	5.53	0.00364	29.87
0.00766	5.49	0.00469	29.96
0.01090	5.87	0.00650	30.04
0.01134	5.87	0.00818	30.00
0.01425	5.91	0.01063	30.17
5 mol% glycerol		80 mol% glycerol	
0.00311	8.97	0.00112	28.95
0.00637	8.72	0.00198	28.91
0.00772	8.97	0.00200	28.95
0.00955	8.76	0.00488	29.12
0.00984	8.88	0.00646	29.25
0.01258	8.80	0.00767	29.25
10 mol% glycerol		90 mol% glycerol	
0.00285	17.14	0.00216	28.66
0.00432	17.22	0.00276	28.74
0.00622	17.26	0.00375	28.82
0.00949	17.30	0.00435	28.78
0.01259	17.18	0.00606	28.95
0.01458	17.30	0.00767	28.99
20 mol% glycerol		100 mol% glycerol	
0.00348	24.59	0.00245	28.37
0.00394	24.59	0.00292	28.32
0.00454	24.68	0.00412	28.53
0.00705	24.72	0.00490	28.58
0.00718	24.72	0.00602	28.70
0.00953	24.76	0.00858	28.87

structure due to the filling up of cavities in the water by t-BuOH. The maximum observed in the water–glycerol mixture is much lower and only a slight stabilizing effect may occur in such solutions. Our opinion is confirmed by the data of Paola and Belleau [9] on the heat capacity and apparent molal volume of the tetraalkylammonium salts in glycerol–water

TABLE 2

Enthalpy of solution of n-Bu_4NBr in glycerol–methanol mixtures at 313.15 K

m (mol kg^{-1})	ΔH_m (kJ mol^{-1})	m (mol kg^{-1})	ΔH_m (kJ mol^{-1})
Methanol		60 mol% glycerol	
0.00102	16.34	0.00101	30.45
0.00112	16.32	0.00189	30.59
0.00194	16.32	0.00307	31.88
0.00222	16.34	0.00430	31.02
0.00387	16.32	0.00485	31.10
0.00635	16.31	0.00582	31.18
2 mol% glycerol		80 mol% glycerol	
0.00100	18.98	0.00141	30.45
0.00175	19.06	0.00265	30.88
0.00196	18.98	0.00367	31.00
0.00313	19.00	0.00432	31.88
0.00467	19.02	0.00525	32.05
0.00602	18.99	0.00610	32.47
5 mol% glycerol		90 mol% glycerol	
0.00151	21.41	0.00110	29.46
0.00174	21.48	0.00129	29.49
0.00271	21.38	0.00236	30.10
0.00350	21.50	0.00350	30.92
0.00462	21.41	0.00413	31.38
0.00615	21.39	0.00515	31.42
10 mol% glycerol		95 mol% glycerol	
0.00104	22.83	0.00144	29.32
0.00110	22.85	0.00231	29.45
0.00178	22.89	0.00355	29.34
0.00242	22.93	0.00449	30.88
0.00292	22.89	0.00541	31.08
0.00390	23.04	0.00610	31.25
20 mol% glycerol		100 mol% glycerol	
0.00100	26.82	0.00245	28.37
0.00124	26.80	0.00292	28.32
0.00168	26.88	0.00412	28.53
0.00243	26.94	0.00490	28.58
0.00362	26.96	0.00602	28.70
0.00486	27.05	0.00858	28.87

mixtures. Structural hydration or solvation effects are lower in glycerol–water than in water.

In an earlier paper [10] we presented data on the enthalpy of solution of NaI in glycerol–water mixtures (Fig. 1(b)). The dependence of the function

TABLE 3

Standard enthalpy of solution (kJ mol^{-1}) of n-Bu_4NBr in glycerol–water and glycerol–methanol mixtures at 313.15 K

Glycerol–water		Glycerol–methanol	
Glycerol (mol%)	$\Delta H^{\ominus}$	Glycerol (mol%)	$\Delta H^{\ominus}$
0	2.60	0	16.32
2	5.69	2	19.02
5	8.88	5	21.29
10	17.09	10	22.84
20	24.34	20	26.73
30	31.34	40	29.75
40	31.00	60	30.37
60	29.75	80	30.17
80	28.91	90	29.67
90	28.58	95	29.41
100	28.28	100	28.28

$\Delta H^{\ominus}$ = f(mol% glycerol) is monotonic. We believe that in the presence of NaI glycerol and water form mixed associated molecules through hydrogen bonds.

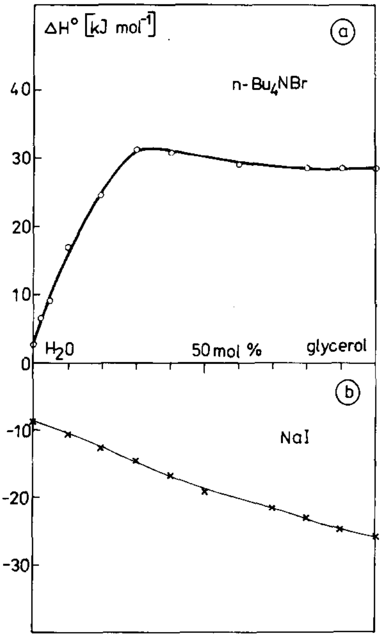

Fig. 1. Standard enthalpy of solution of (a) n-Bu_4NBr and (b) NaI in glycerol–water mixtures at 313.15 K.

Glycerol–methanol solutions

Dissolution of n-Bu_4NBr in methanol, glycerol and glycerol–methanol mixtures is accompanied by an endothermic effect. Data on the dependence of the enthalpy of solution ΔH_m on the concentration of salt in the solution are shown in Table 2 and were used to calculate the standard enthalpy of solution $\Delta H^{\ominus}$. The $\Delta H^{\ominus}$ value obtained by us for the n-Bu_4NBr–methanol system at 313.15 K is in good agreement with the data obtained by Shin and Criss [11].

In Fig. 2(a) the dependence of $\Delta H^{\ominus}$ on the concentration of glycerol in the n-Bu_4NBr–glycerol–methanol system is presented. This dependence is different from that observed in the glycerol–water solution. However, the results are not surprising. According to many workers [11–13] interactions between methanol and n-Bu_4NBr do not lead to solvophobic effects. From the point of view of investigations of heat capacity [11], methanol solutions of tetraalkylammonium salts show a totally different behaviour compared with water solutions of these salts.

We believe that glycerol–methanol solutions of n-Bu_4NBr contain systems which are different from those in glycerol–water. A very slight maximum on the curve $\Delta H^{\ominus}$ = f(mol% glycerol) seems to indicate a lack of any peculiar effects in this mixture.

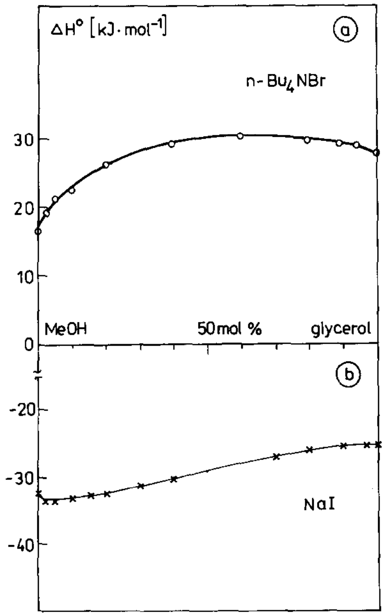

Fig. 2. Standard enthalpy of solution of (a) n-Bu_4NBr and (b) NaI in glycerol–methanol mixtures at 313.15 K.

If we compare the plot $\Delta H^{\ominus} = f(\text{mol\% glycerol})$ for the n-Bu_4NBr–glycerol–methanol system with an analogous plot for the NaI–glycerol–methanol system [14] (Fig. 2(b)) we can see that there are some very small changes in $\Delta H^{\ominus}$ in the NaI–glycerol–methanol system as the composition of the solution changes; this is similar to the observations in the n-Bu_4NBr–glycerol–methanol system investigated in this work.

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