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Water-diol mixtures as solvents of electrolytes. Part 1. Enthalpies of solution of $NaBPh_4$ and Ph_4PCl in water with ethanediol-1,2, propanediol-1,2 and butanediol-1,2

Anetta Pietrzak, Bożenna Nowicka, Stefania Taniewska-Osińska *

Department of Physical Chemistry, University of Łódź Pomorska 18, 91–416 Łódź, Poland

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Abstract

Heats of solution of $NaBPh_4$ and Ph_4PCl in the mixtures of ethanediol-1,2, propanediol-1,2 and butanediol-1,2 with water in almost the whole composition range were measured at 25°C. Plots of the determined standard enthalpies of solution, $\Delta_{sol}H^\circ$, vs. diols content in mixed solvents were examined. Close positions of $\Delta_{sol}H^\circ$ maxima to the apparent molar volume minima, V_ϕ, are discussed for solutions of the salts in water with diols as well as in water with alcohols. The linear correlation of $\Delta_{tr}H^\circ$ maxima positions vs. the number of equivalent CH_2 groups included in diol and alcohol molecules was found.

Keywords: Enthalpy of solution; Enthalpy of transfer; Isoperibol calorimetry; $NaBPh_4$; Ph_4PCl; Water-diol mixtures

1. Introduction

As is well known the maxima of standard enthalpy of solution of electrolytes and nonelectrolytes appear in the water-rich region in aqueous solutions of alcohols [1–9]. Similar maxima of $\Delta_{sol}H^\circ$ are not observed for solutions of inorganic salts in most water-aprotic solvent mixtures [10–14] as well as in systems containing formamide [10] and ethanediol-1,2 [15].

The situation is quite different for $NaBPh_4$ and Ph_4PCl, which dissolve with a heat effect, exhibiting maxima in all binary solvents, composed of water and organic

* Corresponding author.

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cosolvents (e.g. alcohols [1,4–6, 9], aprotic solvents [12–14, 16–20], urea [21] and formamide [22]).

It seemed worthwhile to determine the unknown solution enthalpy for salts containing organic ions in mixtures of water with diols and to observe the character of $\Delta_{sol}H^{\circ} = f$(composition) curves. We have measured enthalpies of solution of $NaBPh_4$ and Ph_4PCl in mixtures of water with ethanediol-1,2, propanediol-1,2 and butanediol-1,2.

2. Experimental

Sodium tetraphenylborate, tetraphenylphosphonium chloride (Fluka, pro analysis) and solvents: ethanediol-1,2, propanediol-1,2, butanediol,-1,2 (Aldrich, pro analysis) were purified for experiments in the way described earlier [19, 23, 24]. The diol with water mixtures were prepared by weight. The measurements of heat of the salt solution in the mixed solvents were performed in an "isoperibol" calorimeter [25]. The salt concentrations in solutions did not exceed $5 \cdot 10^{-3}$ mol kg^{-1} of solvent over the whole range of mixed solvent compositions. The enthalpies of solution of Ph_4PCl in butanediol-1,2 - water mixtures were measured only up to 90 mol% diol content because of the extremly low solubility. The total uncertainty in the enthalpy of solution was about $\pm$ 0.5%.

3. Results and discussion

Standard enthalpies of solution, $\Delta_{sol}H^{\circ}$, of $NaBPh_4$ and Ph_4PCl in the investigated mixtures were determined using the Debye–Hückel limiting law [26]. The $\Delta_{sol}H^{\circ}$ values are included in Table 1. The enthalpies of transfer of electrolytes from water to water-diol mixtures, $\Delta_{tr}H^{\circ}$, defined as:

$$\Delta_{tr}H^{\circ} = \Delta_{sol}H^{\circ}(\text{mixture}) - \Delta_{sol}H^{\circ}(\text{water})$$

are presented in Fig. 1 as a function of the mixed solvent composition.

As it can be seen in the figure, $\Delta_{tr}H^{\circ}$ for both salts containing tetraphenyl ions exhibit maxima in the water-rich range, corresponding to 15 mol% of ethanediol-1,2, to 12.5 mol% of propanediol-1,2 and to 7.5 mol% of butanediol-1,2. The positions of these $\Delta_{tr}H^{\circ}$ maxima do not depend on the kind of dissolved salts but they depend on the size of apolar groups in the diol molecules, similarly to the solutions in water-alcohol binary solvents. These observations suggest that $\Delta_{sol}H^{\circ}$ maxima positions illustrate only properties of cosolvents, that is probably their hydrophobic character. To verify the last supposition, it would be necessary to know the solvent ability to hydrophobic interactions.

According to Franks' supposition [27], the size and shape of apolar groups in cosolvent molecules influence the position of the minima of apparent molar volume V_{ϕ}. curves vs. organic solvent content.

Table 1
Standard enthalpies of solution of $NaBPh_4$ and Ph_4PCl in water–diol mixtures at 25°C, $\Delta_{sol}H^{\circ}$/kJ mol^{-1}.

Mol% diol	Ethanediol-1,2		Propanediol-1,2		Butanediol-1,2	
	$NaBPh_4$	Ph_4PCl	$NaBPh_4$	Ph_4PCl	$NaBPh_4$	Ph_4PCl
0.0	−19.91[a]	−8.79[a]	−19.91	−8.79	−19.91	−8.79
2.5	−13.64		−9.93	2.45	−3.45	9.26
5.0	−9.44	3.66		10.73	10.94	20.90
7.5	−4.90	6.21	6.13	16.11	17.32	21.24
10.0	−2.94	8.97	10.54	17.95	13.24	18.79
12.5			14.49	19.90		
15.0	−0.50	10.03	13.24	18.08	2.63	13.21
20.0	−2.26	9.49	9.45	15.38	−3.46	11.58
30.0	−7.20	8.11	−1.24	11.48	−11.61	9.04
40.0	−14.89	6.55	−8.38	8.48	−17.33	7.14
50.0	−20.87	5.52	−13.95	5.94	−20.17	6.88
60.0	−27.53	4.89	−19.68	5.74	−23.82	6.44
70.0	−32.05					
80.0	−37.51	4.53	−29.49	5.38	−29.04	5.72
90.0	−42.02	3.34			−33.01	5.02
100.0	−47.58	2.88	−36.98	4.89	−36.50	–

[a] Values agree with the data published earlier [19].

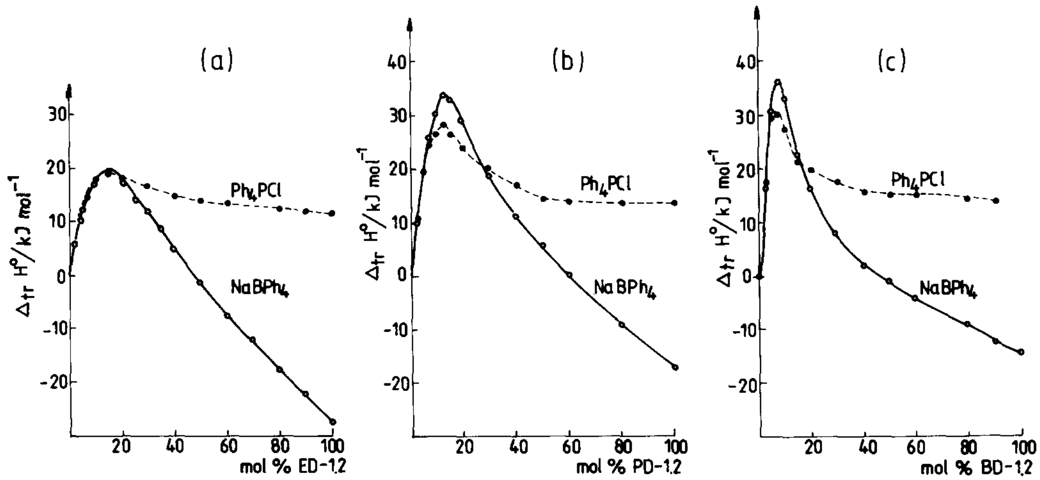

Fig. 1. Enthalpies of transfer of $NaBPh_4$ and Ph_4PCl from water to water-ethanediol-1,2 (a), water-propanediol-1,2 (b) and water-butanediol-1,2 (c) mixtures at 25°C as a function of mol% diol-1,2.

In Table 2, the positions of V_{ϕ} minima and $\Delta_{sol}H^{\circ}$ maxima of $NaBPh_4$ (Ph_4PCl) in water-diol and water-alcohol mixtures are juxtaposed. The positions of these extrema appear to be the same within the limits of error. The above comparison shows that also the positions of the solution enthalpy maxima characterize the hydrophobicity of alcohols and investigated diols.

Table 2
Minima positions of the apparent molar volume, V_ϕ, for the water–organic mixtures and the maxima positions of the standard enthalpies of $NaBPh_4$ in these mixtures, $\Delta_{sol}H^\circ$ (in mol% cosolvent)

Organic solvent	V_ϕ [a] (min)	$\Delta_{sol}H^\circ(NaBPh_4)$ (max)
Methanol	17	17
Ethanol	11	12
Propanol-1	5	6
Propanol-2	7	7.5
tert-Butanol	5	5
Ethanediol-1,2	15	15
Propanediol-1,2	10	12.5
Butanediol-1,2	5	7.5

[a] Data from Refs. [28 and 29].

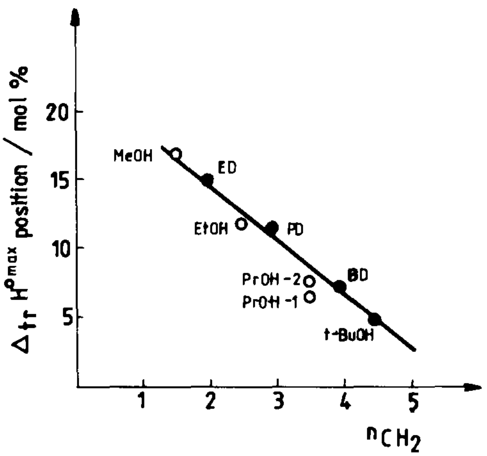

Fig. 2. Maxima positions of the enthalpies of transfer of $NaBPh_4$ from water to water-alcohol and water-diol mixtures vs. number of CH_2 equivalent groups.

Correlation between the maxima of $\Delta_{sol}H^\circ(NaBPh_4)$ positions discussed here and the number of hydrophobic CH_2 groups included in alcohol and diol molecules (Fig. 2) was found. Savage and Wood suggestion [30], that CH_3 group is equivalent to 1.5 CH_2 group and CH group corresponds to 0.5 CH_2 group was assumed by us. The calculation of CH_2 groups number is only approximative, because it includes the suppositions of the lack of interactions among the hydrophobic groups, as well as the lack of effects of hydrophilic groups inlcuded in the molecules of organic solvents. Common straight line for diols and alcohols points to the similar behaviour of both the solvent groups in the mixtures with water used as electrolytes solvents.

It can be supposed that the appearance of $\Delta_{sol}H^\circ$ maxima for the diol-water mixtures results, similarly to the mixtures of alcohols with water, from the competitive hydrophobic hydration of $NaBPh_4$ and cosolvent molecules. The linear correlation found here proves that the positions of $\Delta_{sol}H^o(NaBPh_4)$ maxima depend on the hydrophobicity of hydrocarbon groups included in solvent molecules. Probably, the number of OH^- groups does not influence the correlation presented.

The hydrophobic properties of the investigated cosolvents determined in this way increase as follows:

methanol < ethanediol-1,2 < ethanol < propanediol-1,2 < propanol-1

= propanol-2 < butanediol-1,2 < tert-butanol.

It is worth to mention that the correlation of c^o_{p2} and $\Delta_{hyd}H$ [31], describing hydrophobic effects, with number of $-CH_2-$ groups is presented by two straight lines, one for solutions containing alcohols, the second one for solutions with diols.

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