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Some remarks concerning hydrophobic effects parameters

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Abstract

The enthalpies of $NaBPh_4$ solution in binary mixtures of water with glycerol and acetonitrile were measured at 25°C. Some functions and parameters which can serve as measures of the hydrophobic effects were compared quantitatively with the semi-theoretical Kessler criterion $(\partial B_{22}/\partial P)_T$.

INTRODUCTION

Recently, considerable attention has been devoted to determining the ionic contributions in thermodynamic functions. One of the most popular methods used for dividing transfer enthalpies of salts is based on the assumption of the equality $\Delta H_{tr}^{\ominus}(BPh_4^-) = \Delta H_{tr}^{\ominus}(Ph_4P^+)$ [1]. In order to apply this method, it is necessary to know the transfer enthalpies of salts containing the above-mentioned organic ions, i.e. $NaBPh_4$ and Ph_4PCl. This study concerns solutions of this electrolyte in binary water–organic mixtures. The standard enthalpies of transfer of $NaBPh_4$ from water to mixed solvents pass through quite high maxima in the water-rich region [2–18]. Their heights tend to differ for various organic co-solvents in water–organic mixtures but this phenomenon has not been discussed so far. These maxima are probably connected with the hydrophobic hydration organic solvents and the dissolved salt containing an organic ion. To confirm this assumption, the heights of the maxima have to be correlated with the hydrophobic properties of the solvents. Thus, it would be useful to determine parameters that are measures of hydrophobic effects.

Some scientists avoid an interpretation of the phenomena occurring in solutions containing components of a definite concentration. They prefer

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solutions with a small content of substances, tending to zero, in order to make use of the pair interaction coefficients originating from the polynomials based on the McMillan–Mayer theory. In the case of the extrema considered in this paper, it would be necessary to obtain and discuss further terms of the polynomials describing triplet and higher order interactions. As is known, the magnitudes of these terms are not precise and their meaning is obscure because they also contain contributions from the lower order terms.

EXPERIMENTAL

Sodium tetraphenylborate (purum, Fluka) was purified as described by Cox et al. [1] and dried at 373 K under vacuum. Pre-evaporated glycerol (analytical grade, POCH Gliwice) was purified as described previously [19]. Acetonitrile (p.a., Aldrich) was purified and dried by means of the method described in the literature [20]. The measurements of the enthalpy of solution of $NaBPh_4$ were performed using an isoperibol calorimeter [21] at $25 \pm 0.005°C$.

Enthalpies of solution of the electrolyte were measured in the molality (m) range 0.0015–0.0126 mol kg^{-1} of mixed solvent and the content of organic solvent in the mixtures ranged from 1.0 to 50 mol.% for glycerol and from 1.0 to 8.0 mol.% for acetonitrile. The estimated experimental error was 0.5%.

RESULTS AND DISCUSSION

The enthalpies of solution $\Delta H_s(NaBPh_4)$ are presented in Tables 1 and 2. The standard enthalpies of solution $\Delta H_s^{\ominus}$ (Table 3) were calculated by the Criss and Cobble method [22]. Our value of the standard enthalpy of solution of $NaBPh_4$ in water was -20.02 kJ mol^{-1} [3]. As can be seen in Table 3 and Fig. 1, the standard enthalpy of solution of $NaBPh_4$ in the mixture of water and glycerol versus the mixed solvent compositions passes through a maximum corresponding to about 20 mol.% glycerol in water, although this solvent is considered to be hydrophilic.

The literature gives the standard enthalpy of solution values for $NaBPh_4$ in water–acetonitrile mixtures [7–9]. However, the published positions and heights of the maxima of $\Delta H_s^{\ominus}(NaBPh_4)$ are not the same. Therefore, the measurements of the enthalpies of solution in the analysed region were repeated and are presented in this paper.

As seen in Table 3 and Fig. 1, the standard enthalpies of solution of $NaBPh_4$ exhibit a maximum at approx. 6 mol.% acetonitrile.

Basing on the McMillan–Mayer theory, Kessler [23] proposed the coefficient $(\partial B_{22}/\partial P)_T$ (Table 4) (B_{22} is the second virial coefficient given by the

TABLE 1

Molar enthalpies of solution of $NaBPh_4$ in water–glycerol mixtures at 25°C

X [a]	$m \times 10^4$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	X	$m \times 10^4$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
1.0	17	17.95	10.0	21	6.55
	40	17.48		46	6.29
	65	17.15		77	6.21
	97	17.00		107	6.20
2.0	29	15.64	15.0	21	5.00
	53	15.34		45	5.22
	83	15.14		68	5.10
	111	15.19		91	5.07
3.0	18	13.74	20.0	20	4.76
	40	13.69		43	4.88
	64	13.16		69	4.82
	84	13.22		99	4.93
	106	13.21			
4.0	22	11.46	25.0	21	5.85
	46	11.45		46	5.92
	74	11.56		74	5.95
	120	11.62		105	5.93
5.0	45	10.81	30.0	17	7.66
	54	10.77		37	7.66
	66	10.62		61	7.67
	80	10.68		81	7.67
	89	10.50		104	7.66
	115	10.46			
6.0	21	9.76	40.0	20	11.31
	45	9.51		43	11.27
	77	9.44		66	11.25
	126	9.33		91	11.20
			50.0	17	15.61
				34	15.50
				59	15.28
				80	15.66

[a] Mol.% of glycerol in mixed solvent.

expression) as the most reasonable measure of hydrophobic properties.

$$2\left(\frac{\partial B_{22}}{\partial P}\right)_T = V_1^{\ominus}\frac{\partial a_{22}^*}{\partial P} + a_{22}^*\frac{\partial V_1^{\ominus}}{\partial P} + 2\frac{\partial \bar{V}_2^{\ominus}}{\partial P} - RT\frac{\partial \chi_1^{\ominus}}{\partial P}$$

$$B_{22} = -2\pi N_A \int_0^{\infty} \left[\exp \beta\omega_{22}(r) - 1\right] r^2 \, \mathrm{d}r$$

$$2B_{22} = a_{22}^* V_1^{\ominus} + 2\bar{V}_2^{\ominus} - \chi_1^{\ominus} RT$$

where $\beta = -1/kT$, $\chi_1^{\ominus}$ is the isothermic compressibility, a_{22}^* is the virial coefficient in the Lewis–Randall reference systems and $\omega_{22}(r)$ is the mean force potential.

TABLE 2

Molar enthalpies of solution of $NaBPh_4$ in water–acetonitrile mixtures at 25°C

X [a]	$m\times10^4$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	X	$m\times10^4$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
1.0	15	14.14	4.0	24	2.62
	15	14.11		26	2.56
	23	14.01		29	2.44
	24	14.01		50	2.49
	25	14.02		51	2.50
	25	14.06		55	2.50
2.0	16	9.17	7.0	24	1.49
	16	9.09		25	1.48
	26	9.10		36	1.48
	27	9.04		38	1.42
	30	8.98		54	1.40
	31	9.00		54	1.31
3.0	21	4.98	8.0	22	4.54
	24	4.96		22	4.49
	27	4.93		24	4.45
	30	4.92		33	4.47
	42	4.87		47	4.38
	49	4.80		49	4.35

[a] Mol.% of acetonitrile in mixed solvent.

TABLE 3

Standard enthalpies of solution of $NaBPh_4$ in water–glycerol and water–acetonitrile mixtures at 25°C

Water–glycerol		Water–acetonitrile	
X [a]	$-\Delta H_s^{\ominus}$ (kJ mol^{-1})	X [a]	$-\Delta H_s^{\ominus}$ (kJ mol^{-1})
1.0	17.57	1.0	14.33
2.0	15.48	2.0	9.34
3.0	13.16	3.0	5.17
4.0	11.44	4.0	2.67
5.0	10.79	7.0	1.77
6.0	9.60	8.0	4.69
10.0	6.74		
15.0	5.00		
20.0	4.69		
25.0	5.86		
30.0	7.91		
40.0	11.34		
50.0	15.48		

[a] Mol.% of organic solvent in mixtures.

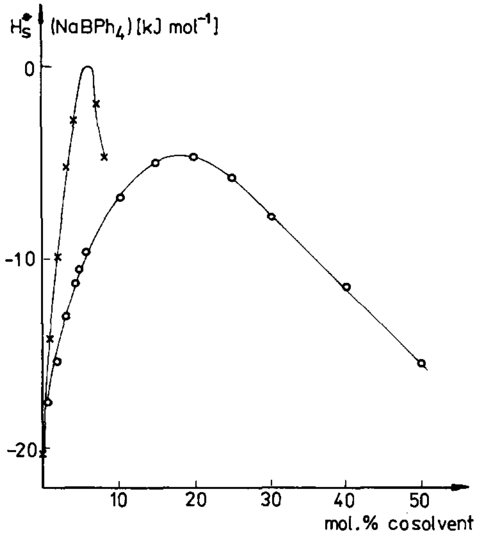

Fig. 1. Standard enthalpies of solution of $NaBPh_4$ in mixtures at 25°C: ×, $ACN-H_2O$; o, glycerol–H_2O.

TABLE 4

Parameters of hydrophobic effects

Solvent	$(\partial B_{22}/\partial P)_T \times 10^2$ [23] (cm^3 mol^{-1} bar^{-1})	$\bar{C}^{\ominus}_{p_2}$ [24] (kJ mol^{-1} K^{-1})	Depth of minimum V_ϕ [a] (cm^3 mol^{-1})	$v_{\Phi22}$ [b] (cm^3 kg mol^{-2})
MeOH	–	0.158	0.74 [26]	−0.15 [26]
EtOH	–	0.260	1.25 [26]	−0.47 [26]
n-PrOH	–	0.353	1.47 [27]	−1.10 [27]
i-PrOH	–	0.364	1.90 [28]	−1.34 [28]
t-BuOH	−9.7	0.463	2.26 [29]	−1.84 [29]
Glycerol	–	0.240	0.78 [30]	−0.38 [30]
THF	−6.6	0.294	1.20 [31]	−1.15 [31]
1,4-Dioxane	−0.8	0.222	0.61 [32]	−0.40 [32]
F	0.4	0.082	–	0.09 [33]
DMF	−1.8	0.225	1.19 [34]	−0.35 [34]
DEF	−1.4	0.400	–	–
AA (acetamide)	−0.1	0.159	–	–
DMA	−4.9	0.280	2.60 [33]	−0.80 [33]
HMPA	−31.0	0.650	3.02 [35]	−2.81 [35]
DMSO	0.3	0.180	0.91 [36]	−0.12 [36]
ACN	−1.2	0.180	0.75 [37]	−0.14 [37]

[a] The depth minima V_Φ were calculated using the density data given in the references cited.
[b] $v_{\Phi22}$ values were calculated by us on the basis of data given in the references cited.

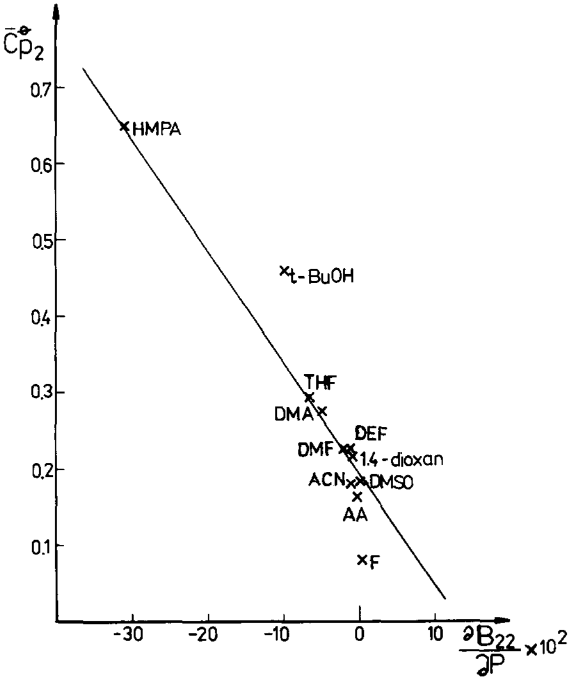

Fig. 2. The partial molar heat capacities ($\bar{C}_{p_2}^{\ominus}$) of organic solvents in water vs. the coefficients $(\partial B_{22}/\partial P)_T$ of organic solvents in water at 25°C.

The parameter $(\partial B_{22}/\partial P)_T$ is associated with the interactions of the two solute molecules, which include hydrophobic effects causing the aggregation. In this way hydrophobic molecules diminish their contact surface with water. The aggregation is connected with the reverse effects to those of the hydration and it causes a partial dehydration.

It is known that hydrophobic hydration is associated with the thermodynamic functions accompanying the dissolution process of hydrophobic substances in water. Particularly large negative enthalpies and entropies can be observed. Among the functions of hydration, only the partial molar heat capacity $\bar{C}_{p_2}^{\ominus}$ seems to be appropriate for using as a parameter of the hydrophobic hydration of solvents (Table 4). As seen in Table 4, the values of $(\partial B_{22}/\partial P)_T$ are known for a limited number of solvents. For this reason it seems to be more convenient to use $\bar{C}_{p_2}^{\ominus}$ whose values are known for many substances in water. Figure 2 shows a linear correlation of these two magnitudes. The plot indicates that points corresponding to *t*-BuOH and formamide deviate slightly from the straight line, probably owing to some errors in the values used.

According to Franks [25] the depth of the apparent molar volume minima (dep. min. V_Φ) of the solutes in water depends on the size and shape of the apolar groups. Because this characteristic of hydrocarbon

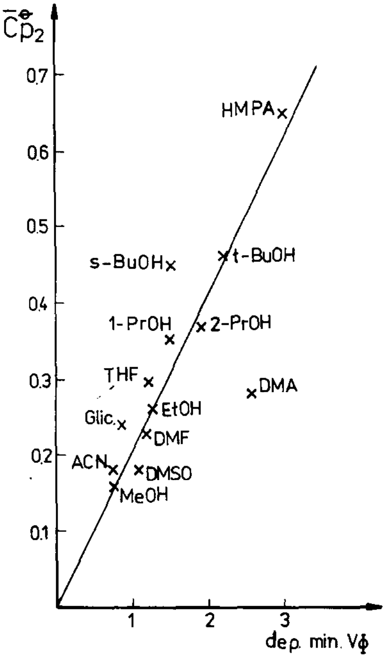

Fig. 3. The partial molar heat capacities ($\overline{C}_{p_2}^{\ominus}$) of organic solvents in water vs. the depths of minima V_Φ of organic solvents in water at 25°C.

groups is linked to the hydrophobicity, the depth of V_Φ minima can be considered as probes of hydrophobic effects. In this paper, the dep. min. V_Φ values were calculated using the literature data (Table 4).

Figure 3 shows that the function $\overline{C}_{p_2}^{\ominus} = f(\text{dep. min. } V_\Phi)$ is linear, thus indicating the possibility of assuming the depth of the V_Φ minima to be a measure of hydrophobicity.

It seemed to us that the slope of the apparent molar volume $v_{\Phi 22}$ versus the organic co-solvent content would be an even better probe. The values of $v_{\Phi 22}$ calculated from the literature data on density (Table 4) are plotted versus $\overline{C}_{p_2}^{\ominus}$ in Fig. 4, as well as versus the depth of the V_Φ minima. Again, both functions are linear, but the regression coefficients indicate that correlations for $v_{\Phi 22}$ are better than for the depth of V_Φ minima.

It is known that $\overline{C}_{p_2}^{\ominus}$ refers to the hydration in the infinite dilute solution, and it contains the temperature change of all enthalpic effects. However, both functions originating from changes of volume may instead be connected with the aggregation of pairs of molecules. The simple correlations between $\overline{C}_{p_2}^{\ominus}$, the depth of the V_Φ minima and $(\partial B_{22}/\partial P)_T$ indicate that the main contributions in these functions derive from hydrophobic effects.

In order to find out if the hydrophobic interactions in various organic cosolvents influence the heights of the enthalpy maxima of transfer of

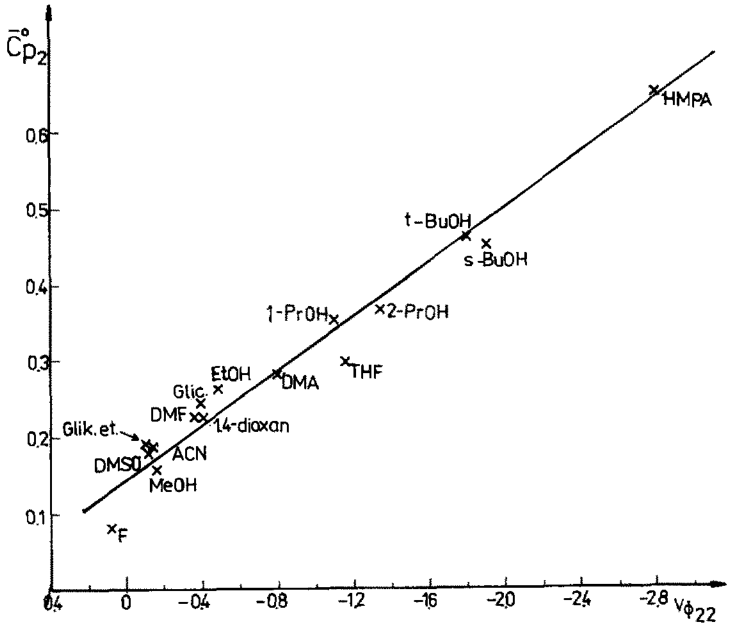

Fig. 4. The partial molar heat capacities ($C_{p_2}^{\ominus}$) of organic solvents in water vs. the coefficients $v_{\Phi 22}$ of organic solvents in water at 25°C.

NaBPh$_4$, these heights were plotted against the appropriate values of $v_{\Phi 22}$ (Fig. 5). As can be seen, two straight lines were obtained: one corresponding to solutions in alcohols and the other to solutions in aprotic solvents. Moreover, the distance between those two lines is approximately equal to the enthalpy of hydrogen bond formation. Alcohols can obviously form more hydrogen bonds with water than the aprotic solvents.

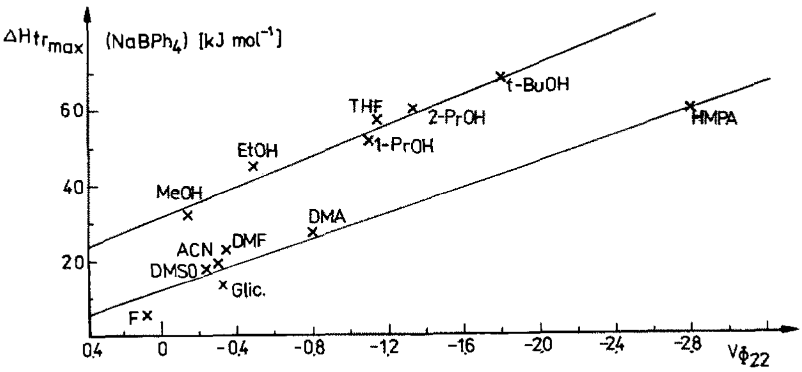

Fig. 5. The heights of the enthalpy maxima of transfer of NaBPh$_4$ in binary water–organic mixtures vs. appropriate values of $v_{\Phi 22}$ of organic solvents in water at 25°C.

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