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COMPARISON OF IONIC ENTHALPIES OF TRANSFER FROM
WATER TO MIXED SOLVENTS WITH ALCOHOL BY USE OF
TPTB AND CsI DISTRIBUTION METHODS

The enthalpy of solution of CsI in a mixed solvent consisting of n-propanol and water was measured at 298.15 K. Based on the method of Criss and Cobble, the standard enthalpy of CsI in the investigated solvent was calculated. The standard enthalpy of transfer of electrolyte was divided into ionic contributions, using the following equation $\Delta_{tr}H^{\infty}(Cs^+) = \Delta_{tr}H^{\infty}(I^-)$. The results obtained were compared with the values of ionic $\Delta_{tr}H^{\infty}$ acquired at an assumption that $\Delta_{tr}H^{\infty}(BPh_4^-) = \Delta_{tr}H^{\infty}(Ph_4P^+)$. The same analysis was carried out for aqueous mixtures containing methanol, ethanol and tert-butanol.

INTRODUCTION

Studies on standard enthalpy of solution of electrolyte in various aqueous-organic systems have been carried out for several years. Several methods for the division of standard enthalpy of transfer into ionic contributions have been proposed. One of the early methods as suggested by Lange and Mischenko [1] assumes that:

$$\Delta_{tr}H^{\infty}(Cs^+) = \Delta_{tr}H^{\infty}(I^-) \quad (1)$$

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This method has been criticized because of the difference in size of Cs^+ and I^- ions, and consequently $\Delta_{\text{tr}}H^\infty(\text{Cs}^+) \neq \Delta_{\text{tr}}H^\infty(\text{I}^-)$.

Recently the (TATB) method has been used, assuming the identity of standard enthalpies of transfer of BPh_4^- and Ph_4P^+ (or Ph_4As^+) ions from water to a bicomponent system consisting of water and organic solvent [2]. Although this method is very popular and convenient in use, its assumptions have been more frequently criticized.

In the present study, the results obtained by both methods are compared with plotted values of standard enthalpies of transfer of electrolyte from water to mixed aqueous-alcoholic solvents at a temperature of 298.15 K.

EXPERIMENTAL

Cesium iodide, analar grade (BDH Chemicals Ltd. England) was dried at a temperature of 333.15 K to constant weight. Redistilled water and n-propanol, analar grade, of Merck were used for the measurements.

The measurements of heat solution of CsI in mixtures of n-propanol and water were carried out at 298.15 K, using a non-isothermal-non-adiabatic calorimeter [3]. The estimated experimental error was 0,5%.

RESULTS AND DISCUSSION

The values of enthalpy of solution of CsI in water and aqueous n-propanol solutions are given in Tab. 1. The measurements were carried out in solutions containing from 0 to 40 mol% of n-propanol in water. When the n-propanol content in water exceeds 40 mol%, a very poor solubility of CsI is observed.

Based on the determined enthalpies of solution of CsI in water and aqueous n-propanol solutions, standard enthalpies of solution were determined by the method of Criss and Cobble [4]. The results obtained are given in Tab. 2 and illustrated in Fig. 1. The shape of curve representing $\Delta_{\text{s}}H^\infty = f(\text{mol\% of n-propanol})$ suggests that the values of standard enthalpy of

Table 1

Enthalpy of solution of CsI in water-n-propanol mixtures at 298.15 K

$\frac{m}{\text{mol kg}^{-1}}$	$\frac{\Delta_s H}{\text{kJ mol}^{-1}}$	$\frac{m}{\text{mol kg}^{-1}}$	$\frac{\Delta_s H}{\text{kJ mol}^{-1}}$
1	2	3	4
<u>0.00 mol% n-PrOH</u>		<u>5.00 mol% n-PrOH</u>	
0.0023	33.25	0.0042	36.91
0.0045	33.30	0.0045	36.89
0.0052	33.33	0.0050	36.93
0.0067	33.34	0.0059	36.99
0.0073	33.41	0.0064	37.23
0.0080	33.36	0.0079	37.18
		0.0080	37.22
		0.0097	37.17
<u>1.50 mol% n-PrOH</u>		<u>6.00 mol% n-PrOH</u>	
0.0044	34.82	0.0030	36.60
0.0052	34.81	0.0036	36.66
0.0058	34.84	0.0044	36.76
0.0062	34.84	0.0045	36.67
0.0066	35.07	0.0046	36.66
0.0071	35.05	0.0054	36.70
0.0082	34.97		
0.0084	35.09		
<u>2.50 mol% n-PrOH</u>		<u>7.50 mol% n-PrOH</u>	
0.0042	35.46	0.0025	36.12
0.0042	35.50	0.0033	36.15
0.0050	35.45	0.0036	36.31
0.0053	35.50	0.0037	36.17
0.0064	35.64	0.0037	36.22
0.0067	35.65	0.0048	36.13
0.0071	35.82	0.0053	36.31
0.0086	35.75	0.0055	36.33
		0.0056	36.36
<u>3.50 mol% n-PrOH</u>		<u>10.00 mol% n-PrOH</u>	
0.0035	36.10	0.0025	34.83
0.0042	36.07	0.0030	34.75
0.0049	36.18	0.0031	34.80
0.0057	36.19	0.0037	34.91
0.0058	36.30	0.0041	35.00
0.0059	36.21	0.0060	35.01
0.0061	36.38	0.0071	35.08
0.0066	36.37		

T a b l e 1 (cont.)

1	2	3	4
<u>15.00 mol% n-PrOH</u>		<u>40.00 mol% n-PrOH</u>	
0.0025	32.72	0.0018	20.20
0.0039	32.78	0.0022	20.28
0.0040	32.81	0.0030	20.25
0.0046	32.90	0.0046	20.22
0.0048	32.86	0.0050	20.15
0.0053	32.94	0.0053	20.32
0.0056	33.00	0.0057	20.24
<u>20.00 mol% n-PrOH</u>			
0.0032	30.37		
0.0034	30.32		
0.0041	30.43		
0.0042	30.35		
0.0044	30.37		
0.0051	30.47		

T a b l e 2

Standard enthalpies of solution of CsI in water-n-propanol mixtures and standard enthalpies of transfer of CsI from water to water-n-propanol mixtures at 298.15 K

mol% n-PrOH	$\Delta_s H^\infty$	$\Delta_{tr} H^\infty$
	kJ mol^{-1}	kJ mol^{-1}
0.0	33.13	0.00
1.5	34.40	1.27
2.5	35.02	1.89
3.5	35.62	2.49
5.0	36.54	3.41
6.0	36.40	3.27
7.5	35.88	2.75
10.0	34.52	1.39
15.0	32.31	-0.82
20.0	29.95	-3.18
40.0	20.24	-12.89

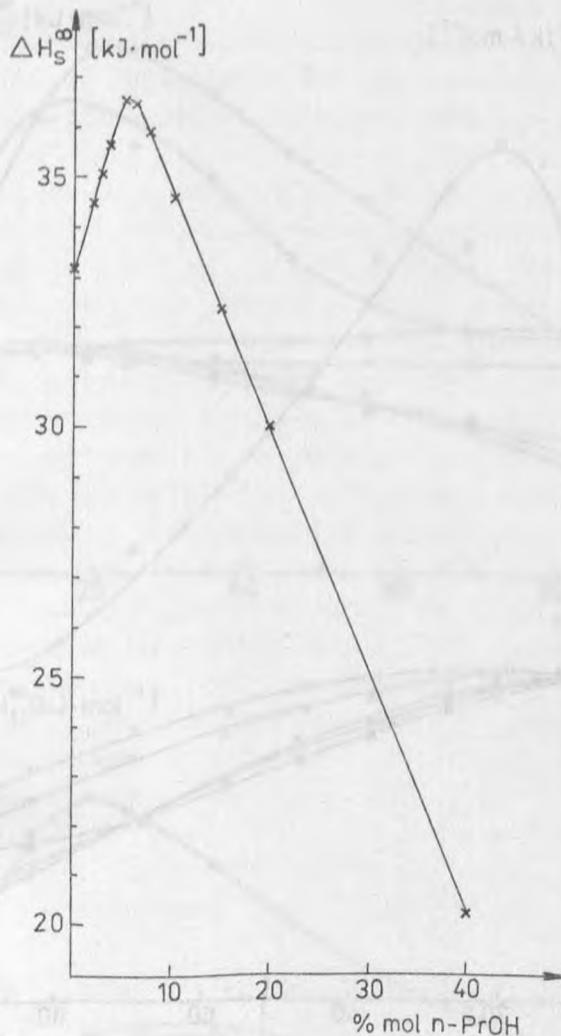


Fig. 1. Standard enthalpy of solution of CsI in *n*-PrOH-water mixtures at 298.15 K

solution of CsI increases with increasing *n*-propanol content in water and reaches maximum within the range 5-6 mol% of *n*-PrOH. The position of this maximum is similar to that of earlier curves illustrating $\Delta_S H^\infty$ for NaI [5], NaCl [6], NaBPh₄ [7] and Ph₄PCl [7] in the mixed solvent containing water and *n*-PrOH. Maxima of $\Delta_S H^\infty$ of electrolytes vs. the mixed solvent composition within

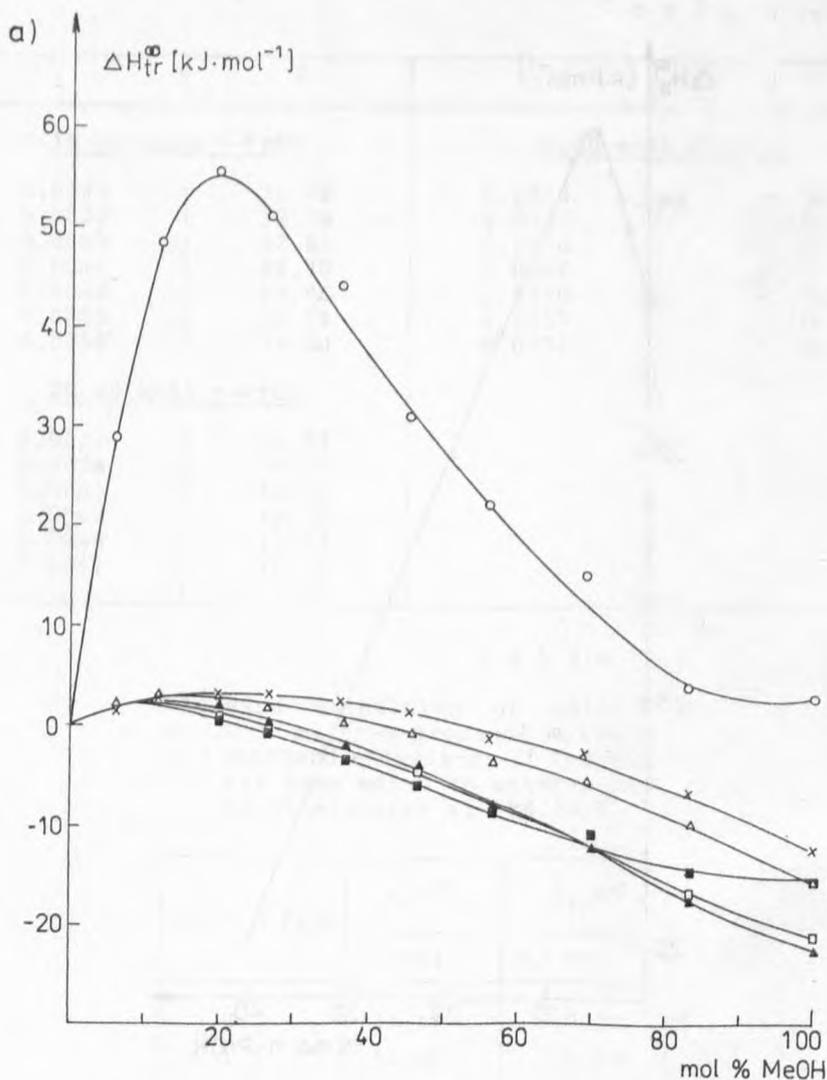
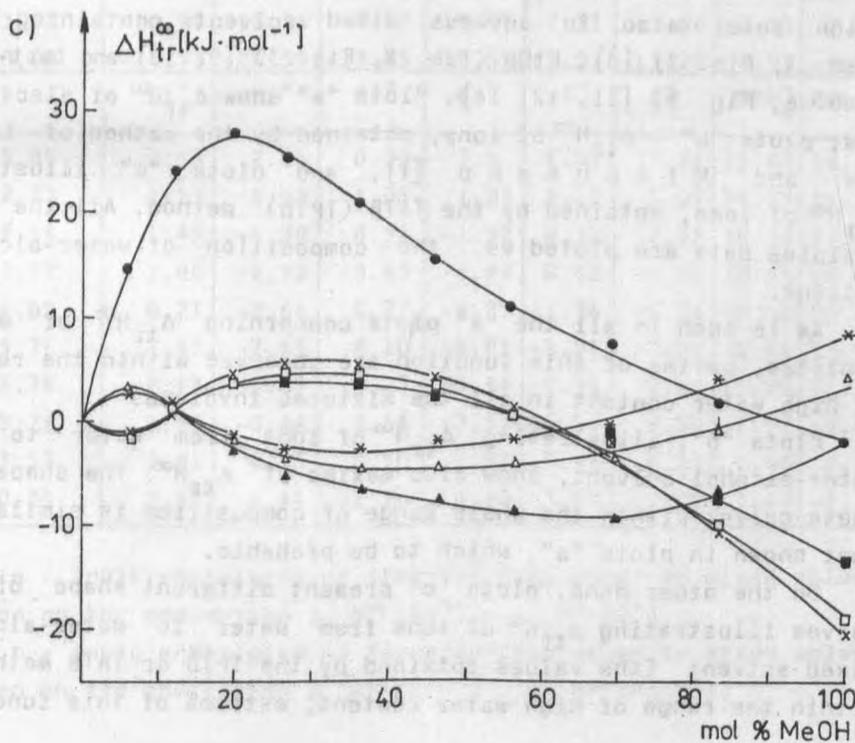
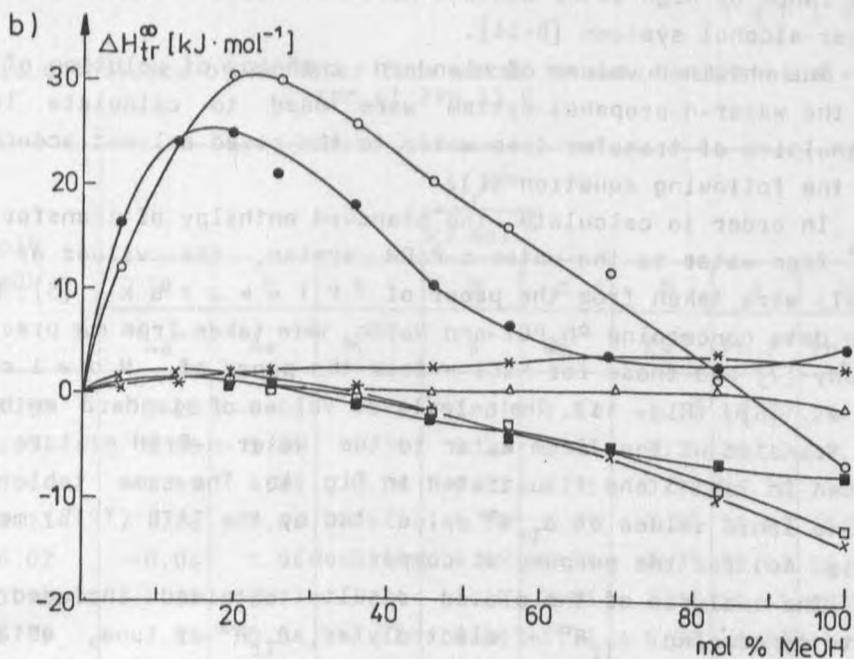


Fig. 2 a. Standard enthalpies transfer of the electrolytes from water to MeOH-water mixtures at 298.15 K: \circ - $\text{Ph}_4\text{PBPPh}_4$; \times - NaCl ; Δ - NaBr ; \blacktriangle - NaI ; \square - KI ; \blacksquare - CsI

b. Ionic enthalpies of transfer from water to MeOH-water mixtures based on the convention $\Delta_{tr}H^{\infty}(\text{Cs}^+) = \Delta_{tr}H^{\infty}(\text{I}^-)$ at 298.15 K: \blacksquare - $\text{Cs}^+ = \text{I}^-$; \times - Na^+ ; \square - K^+ ; \bullet - Ph_4P^+ ; $*$ - Cl^- ; Δ - Br^- ; \circ - BPh_4^-

c. Ionic enthalpies of transfer from water to MeOH-water mixtures based on the convention $\Delta_{tr}H^{\infty}(\text{PPh}_4^+) = \Delta_{tr}H^{\infty}(\text{BPh}_4^-)$ at 298.15 K: \bullet - $\text{Ph}_4\text{P}^+ = \text{BPh}_4^-$; \times - Na^+ ; \square - K^+ ; \blacksquare - Cs^+ ; $*$ - Cl^- ; Δ - Br^- ; \blacktriangle - I^-



the range of high water content have been also observed in other water-alcohol systems [8-14].

The obtained values of standard enthalpy of solution of CsI in the water-n-propanol system were used to calculate ionic enthalpies of transfer from water to the mixed solvent according to the following equation (1).

In order to calculate the standard enthalpy of transfer of Na^+ from water to the water-n-PrOH system, the values of $\Delta_{\text{S}}^{\text{H}^{\infty}}$ (NaI) were taken from the paper of P i e k a r s k i [5], while the data concerning Ph_4PCl and NaBPh_4 were taken from our previous study [7] and those for NaCl - from the paper of N o w i c k a et al. [6], (Fig. 4a). The calculated values of standard enthalpy of transfer of ions from water to the water-n-PrOH mixture are given in Tab. 5 and illustrated in Fig. 4b. The same table contains ionic values of $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ calculated by the TATB (TPTB) method (Fig. 4c) for the purpose of comparison.

The analysis of the plotted results obtained included also data concerning $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of electrolytes, $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions, obtained by the CsI method and $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions, obtained by the TATB method, which refer also to aqueous mixed solvents containing MeOH (Tab. 3, Fig. 2) [8], EtOH (Tab. 4, Fig. 3) [9, 10] and tert-BuOH (Tab. 6, Fig. 5) [11, 12, 14]. Plots "a" show $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of electrolytes, plots "b" - $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions, obtained by the method of L a n g e and M i s c h e n k o [1], and plots "c" illustrate $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions, obtained by the TATB (TPTB) method. All the enthalpies data are plotted vs. the composition of water-alcohol solvent.

As is seen in all the "a" plots concerning $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of electrolytes, maxima of this function are observed within the region of high water content in all the mixtures involved.

Plots "b", illustrating $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions from water to the water-alcohol solvent, show also maxima of $\Delta_{\text{tr}}^{\text{H}^{\infty}}$. The shape of these curves within the whole range of composition is similar to that shown in plots "a", which to be probable.

On the other hand, plots "c" present different shape of the curves illustrating $\Delta_{\text{tr}}^{\text{H}^{\infty}}$ of ions from water to water-alcohol mixed solvent (the values obtained by the IPTB or TATB method). Within the range of high water content, extrema of this function

Table 3

Ionic enthalpies of transfer from water to water-methanol mixtures at 298.15 K

mol% MeOH	$\Delta_{tr}H^{\infty}$ kJ mol ⁻¹							
	a	b	a	b	a	b	a	b
	Na ⁺	Na ⁺	K ⁺	K ⁺	Cs ⁺	Cs ⁺	Ph ₄ P ⁺	Ph ₄ P ⁺
5.88	1.23	-0.96	0.98	-1.21	1.07	-1.13	16.50	14.31
12.33	2.05	2.09	1.34	1.38	1.13	1.17	24.23	24.27
19.44	1.99	4.85	0.86	3.72	0.31	3.18	24.95	27.82
27.27	1.26	5.86	0.33	4.94	0.63	3.97	21.01	25.61
36.02	-0.06	5.06	-0.44	4.69	-1.74	3.39	18.03	20.88
45.76	-1.15	3.77	-1.74	3.18	-2.91	2.01	10.65	15.56
56.78	-3.85	0.84	-3.85	0.84	-4.31	0.38	6.53	11.21
69.26	-6.26	-2.30	-6.26	-2.30	-5.54	-1.59	3.62	7.61
83.52	-10.29	-10.84	-9.37	-9.92	-7.11	-7.66	2.55	2.01
100.00	-14.73	-20.59	-13.05	-18.91	-7.87	-13.72	4.23	-1.76
	Cl ⁻	Cl ⁻	Br ⁻	Br ⁻	I ⁻	I ⁻	BPh ₄ ⁻	BPh ₄ ⁻
5.88	0.65	2.85	0.90	3.1	1.07	3.26	12.08	14.31
12.33	1.13	1.09	1.09	1.05	1.13	1.09	24.35	24.27
19.44	1.49	-1.38	0.94	-1.92	0.31	-2.55	30.69	27.82
27.27	1.88	-2.72	0.63	-3.97	0.63	-5.23	30.25	25.61
36.02	0.21	-2.64	0.27	-4.85	-1.74	-6.86	26.00	20.88
45.76	2.49	-2.43	0.10	-4.81	-2.91	-7.82	20.44	15.56
56.78	2.59	-2.09	0.25	-4.44	-4.31	-9.00	15.90	11.21
69.26	3.49	-0.46	0.44	-3.51	-5.54	-9.50	11.57	7.61
83.52	3.81	4.35	0.50	1.05	-7.11	-6.57	1.46	2.01
100.00	2.55	8.41	-1.26	4.60	-7.87	-2.01	-7.07	-1.76

a - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^{\infty}(\text{Cs}^+) = \Delta_{tr}H^{\infty}(\text{I}^-)$.

b - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^{\infty}(\text{BPh}_4^-) = \Delta_{tr}H^{\infty}(\text{Ph}_4\text{P}^+)$.

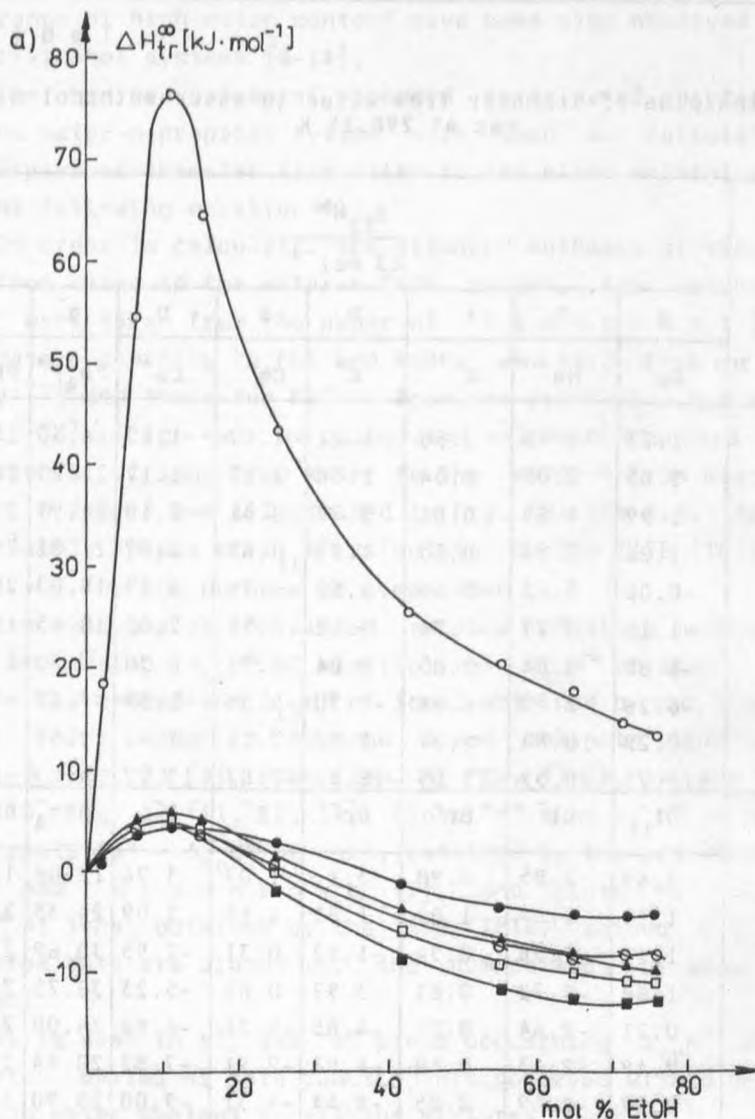
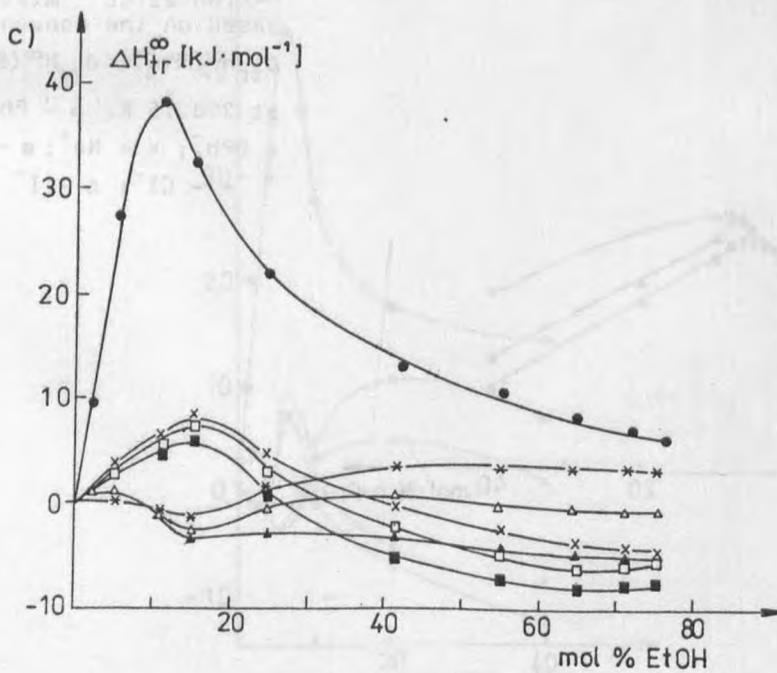
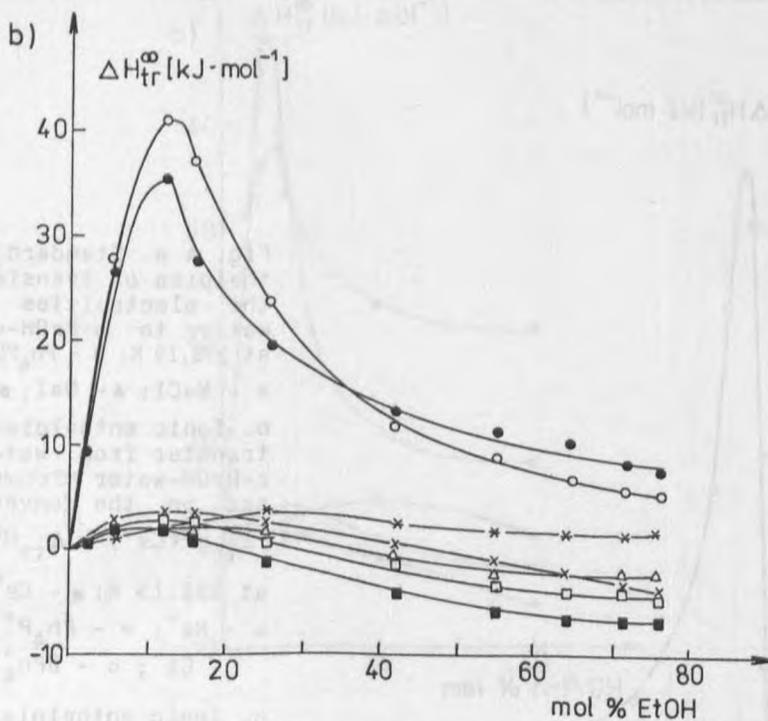


Fig. 3 a. Standard enthalpies of transfer of the electrolytes from water to EtOH-water mixtures at 298.15 K: o - Ph_4PPh_4 ; \blacktriangle - NaI; \square - KI; \bullet - CsCl; \diamond - CsBr

b. Ionic enthalpies of transfer from water to EtOH-water mixtures based on the convention $\Delta_{\text{tr}}H^\infty(\text{Cs}^+) = \Delta_{\text{tr}}H^\infty(\text{I}^-)$ at 298.15 K: \blacksquare - $\text{Cs}^+ = \text{I}^-$; \times - Na^+ ; \square - K^+ ; \bullet - Ph_4P^+ ; $*$ - Cl^- ; Δ - Br^- ; o - BPh_4^-

c. Ionic enthalpies of transfer from water to EtOH-water mixtures based on the convention $\Delta_{\text{tr}}H^\infty(\text{PPh}_4^+) = \Delta_{\text{tr}}H^\infty(\text{BPh}_4^-)$ at 298.15 K: \bullet - $\text{Ph}_4\text{P}^+ = \text{BPh}_4^-$; \times - Na^+ ; \square - K^+ ; \blacksquare - Cs^+ ; $*$ - Cl^- ; Δ - Br^-
 \blacktriangle - I^-



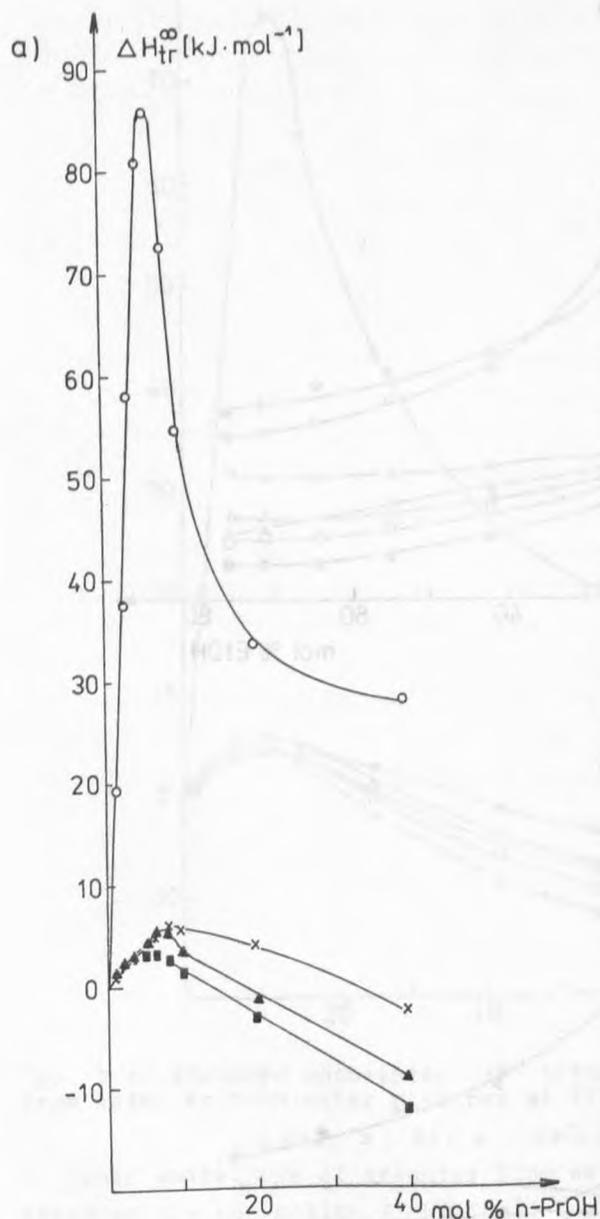


Fig. 4 a. Standard enthalpies of transfer of the electrolytes from water to n-PrOH-water at 298.15 K: o - Ph_4PPh_4 ;

x - NaCl; \blacktriangle - NaI; \blacksquare - CsI

b. Ionic enthalpies of transfer from water to n-PrOH-water mixtures based on the convention

$$\Delta_{tr} H^{\infty}(\text{Cs}^+) = \Delta_{tr} H^{\infty}(\text{I}^-)$$

at 298.15 K: \blacksquare - $\text{Cs}^+ = \text{I}^-$;

x - Na^+ ; \bullet - Ph_4P^+ ; * -

Cl^- ; o - BPh_4^-

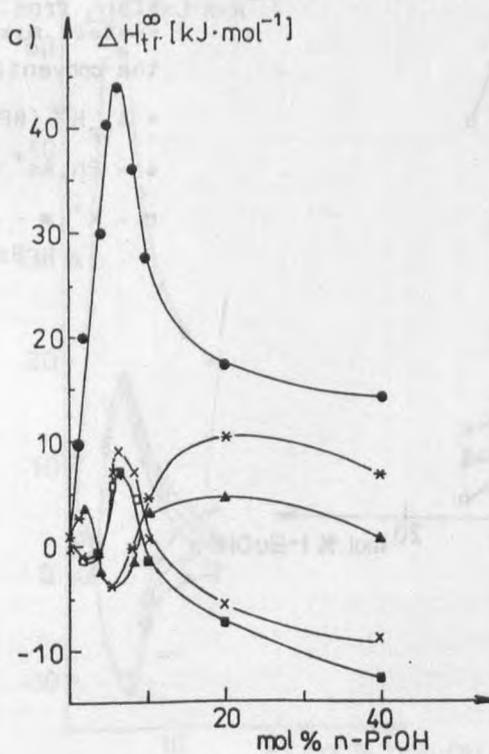
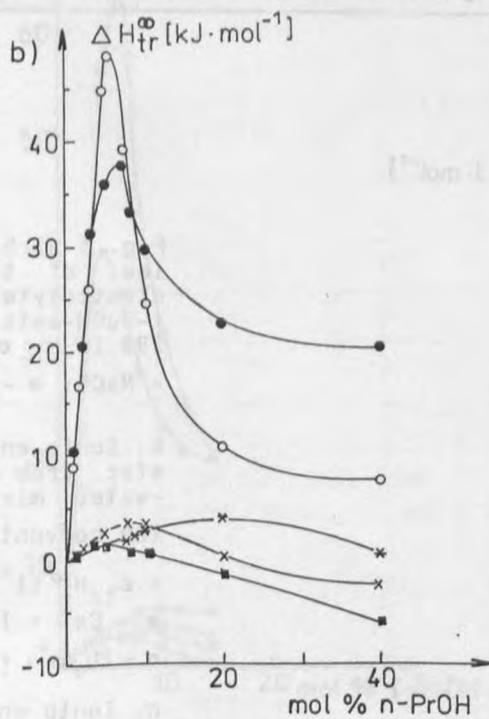
c. Ionic enthalpies of transfer from water to n-PrOH-water mixtures based on the convention

$$\Delta_{tr} H^{\infty}(\text{PPh}_4^+) = \Delta_{tr} H^{\infty}(\text{BPh}_4^-)$$

at 298.15 K: \bullet - $\text{Ph}_4\text{P}^+ =$

BPh_4^- ; x - Na^+ ; \blacksquare - Cs^+

* - Cl^- ; \blacktriangle - I^-



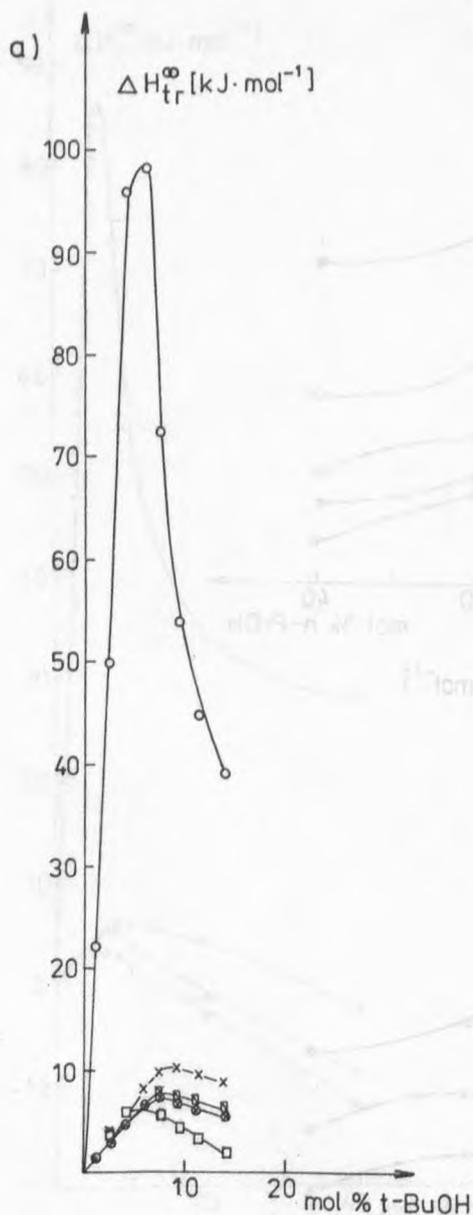


Fig. 5 a. Standard enthalpies of transfer of the electrolytes from water to t-BuOH-water mixtures at 298.15 K: o - $\text{Ph}_4\text{AsBPh}_4$; x - NaCl; ● - KBr; □ - KI; ■ - CsCl

b. Ionic enthalpies of transfer from water to t-BuOH-water mixtures based on the convention $\Delta_{tr} H^{\infty}(\text{Cs}^+) = \Delta_{tr} H^{\infty}(\text{I}^-)$ at 298.15 K: ■ - $\text{Cs}^+ = \text{I}^-$; x - Na^+ ; □ - K^+ ; ● - Ph_4As^+ ; * - Cl^- ; ○ - BPh_4^-

c. Ionic enthalpies of transfer from water to t-BuOH-water mixtures based on the convention $\Delta_{tr} H^{\infty}(\text{Ph}_4\text{As}^+) = \Delta_{tr} H^{\infty}(\text{BPh}_4^-)$ at 298.15 K: ● - $\text{Ph}_4\text{As}^+ = \text{BPh}_4^-$; x - Na^+ ; □ - K^+ ; ■ - Cs^+ ; * - Cl^- ; Δ - Br^- ; ▲ - I^-

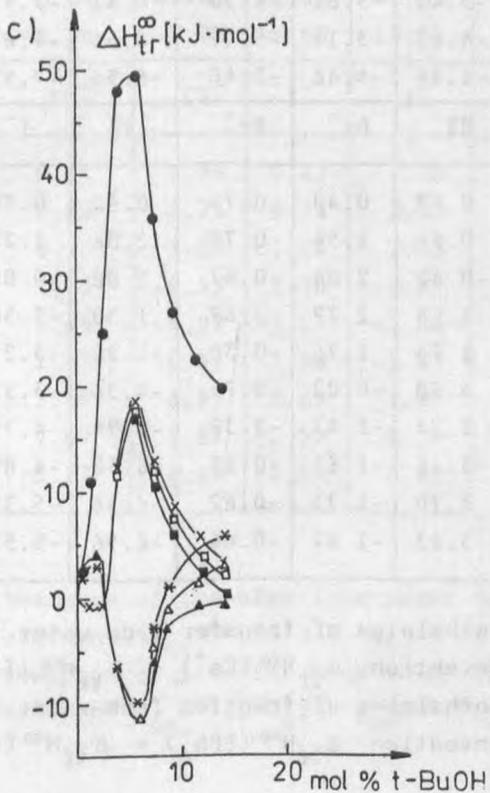
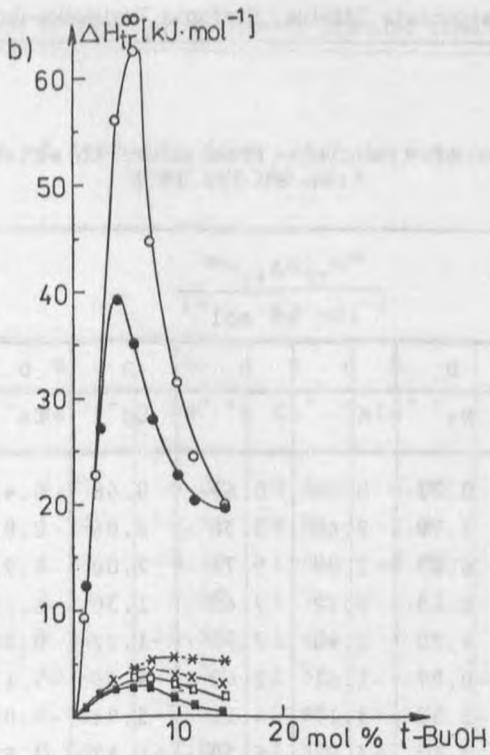


Table 4

Ionic enthalpies of transfer from water to water-ethanol mixtures at 298.15 K

mol% EtOH	$\frac{\Delta_{tr}H^\infty}{\text{kJ mol}^{-1}}$							
	a	b	a	b	a	b	a	b
	Na ⁺	Na ⁺	K ⁺	K ⁺	Cs ⁺	Cs ⁺	Ph ₄ P ⁺	Ph ₄ P ⁺
2.02	0.95	0.73	0.86	0.65	0.68	0.43	9.52	9.27
6.77	3.02	3.79	2.60	3.38	2.06	2.81	26.46	27.21
10.99	3.75	6.63	2.89	5.75	2.00	4.91	35.46	38.37
14.94	3.75	8.63	2.72	7.60	1.30	6.19	27.48	32.37
25.44	2.65	4.70	0.90	2.95	-1.22	0.84	19.74	21.80
42.07	0.57	-0.27	-1.61	-2.48	-4.36	-5.11	13.52	12.77
55.30	-1.09	-2.32	-3.19	-4.50	-5.94	-7.09	11.47	10.32
64.00	-1.90	-3.43	-3.81	-6.38	-6.42	-7.92	10.13	8.63
71.70	-2.81	-4.02	-3.14	-5.47	-6.56	-7.67	8.43	7.32
76.40	-3.45	-4.46	-4.46	-5.46	-6.56	-7.57	7.87	6.86
	Cl ⁻	Cl ⁻	Br ⁻	Br ⁻	I ⁻	I ⁻	BPh ₄ ⁻	BPh ₄ ⁻
2.02	0.24	0.49	0.48	0.73	0.68	0.90	9.05	9.27
6.77	1.40	0.64	1.54	0.79	2.06	1.29	27.98	27.21
10.99	2.48	-0.42	2.04	-0.87	2.00	-0.88	41.25	38.37
14.94	3.33	-1.56	2.22	-2.67	1.30	-3.58	37.25	32.37
25.44	3.79	1.74	1.76	-0.30	-1.22	-3.27	23.85	21.80
42.07	2.89	3.60	-0.02	0.73	-4.36	-3.52	11.93	12.77
55.30	1.95	3.23	-1.47	-0.32	-5.94	-4.71	9.09	10.32
64.00	1.89	3.46	-1.63	-0.13	-6.42	-4.89	7.10	8.63
71.70	1.88	3.70	-1.73	-0.62	-6.56	-5.35	6.11	7.32
76.40	2.22	3.23	-1.67	-0.66	-6.56	-5.55	5.85	6.86

a - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{Cs}^+) = \Delta_{tr}H^\infty(\text{I}^-)$.

b - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{BPh}_4^-) = \Delta_{tr}H^\infty(\text{Ph}_4\text{P}^+)$.

Table 5

Ionic enthalpies of transfer from water to water-n-propanol mixtures at 298.15 K

mol% n-PrOH	$\Delta_{tr}H^\infty$ kJ mol ⁻¹					
	a	b	a	b	a	b
	Na ⁺	Na ⁺	Cs ⁺	Cs ⁺	Ph ₄ P ⁺	Ph ₄ P ⁺
1.5	0.71	0.08	0.63	0.00	10.33	9.71
2.5	1.24	-0.92	0.94	-1.21	20.45	19.08
3.5	1.77	-0.42	1.24	-0.96	31.31	29.16
5.0	2.57	6.99	1.70	6.11	36.00	40.46
6.0	3.52	8.99	1.63	7.11	37.62	43.09
7.5	3.72	6.78	1.38	4.44	33.30	36.40
10.0	2.91	0.50	0.69	-1.72	29.60	27.24
20.0	0.08	-5.89	-1.59	-7.57	22.76	16.82
40.0	-2.74	-9.20	-6.05	-13.31	20.36	13.89
	Cl ⁻	Cl ⁻	I ⁻	I ⁻	BPh ₄ ⁻	BPh ₄ ⁻
1.5	0.34	0.96	0.63	1.26	9.08	9.71
2.5	0.60	2.76	0.94	3.09	16.92	19.08
3.5	0.95	3.10	1.24	3.43	26.97	29.16
5.0	1.53	-2.93	1.70	-2.72	44.88	40.46
6.0	1.46	-4.02	1.63	-3.84	48.57	43.09
7.5	2.47	-0.59	1.38	-1.67	39.46	36.40
10.0	2.49	4.89	0.69	3.09	24.83	27.24
20.0	3.89	9.87	-1.59	4.39	10.84	16.82
40.0	0.23	6.69	-6.05	0.42	7.43	13.89

a - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{Cs}^+) = \Delta_{tr}H^\infty(\text{I}^-)$.

b - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{BPh}_4^-) = \Delta_{tr}H^\infty(\text{Ph}_4\text{P}^+)$.

Table 6

Ionic enthalpies of transfer from water to water-tert-butanol mixtures at 298.15 K

mol% t-BuOH	$\frac{\Delta_{tr}H^\infty}{\text{kJ mol}^{-1}}$							
	a	b	a	b	a	b	a	b
	Na ⁺	Na ⁺	K ⁺	K ⁺	Cs ⁺	Cs ⁺	Ph ₄ As ⁺	Ph ₄ As ⁺
1.26	0.91	-0.49	0.83	-0.57	0.94	-0.46	12.38	10.98
2.63	2.07	-0.18	1.85	-0.40	1.74	-0.51	27.18	24.93
4.11	3.30	11.96	3.05	11.72	2.51	11.18	39.47	48.14
5.73	4.67	18.68	3.81	17.83	2.70	16.72	35.23	49.25
7.49	4.58	12.94	3.50	11.86	2.26	10.62	27.81	36.18
9.43	4.16	8.53	3.07	7.45	1.58	5.96	22.71	27.09
11.57	3.71	5.42	2.41	4.12	0.88	2.59	20.70	22.41
13.94	3.10	3.31	1.76	1.99	0.12	0.34	19.46	19.68
	Cl ⁻	Cl ⁻	Br ⁻	Br ⁻	I ⁻	I ⁻	BPh ₄ ⁻	BPh ₄ ⁻
1.26	0.44	1.84	0.37	1.77	0.94	2.34	9.58	10.98
2.63	0.97	3.22	0.97	3.22	1.74	3.99	22.68	24.93
4.11	2.11	-6.56	1.72	-6.95	2.51	-6.16	56.80	48.14
5.73	3.91	-10.11	2.84	-11.18	2.70	-11.32	63.26	49.25
7.49	5.19	-3.17	3.72	-4.64	2.26	-6.10	44.54	36.18
9.43	5.65	1.27	3.71	-0.67	1.58	-2.80	31.46	27.09
11.57	5.80	4.09	3.70	1.99	0.88	-0.83	24.12	22.41
13.94	5.87	5.65	3.34	3.11	0.12	-0.11	19.89	19.68

a - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{Cs}^+) = \Delta_{tr}H^\infty(\text{I}^-)$.

b - ionic enthalpies of transfer from water to mixed solvent based on the convention $\Delta_{tr}H^\infty(\text{BPh}_4^-) = \Delta_{tr}H^\infty(\text{Ph}_4\text{As}^+)$.

for cations and anions being almost like mirror reflections, are observed, which seems to be rather strange. It seems worth mentioning the assumptions of the TATB (TPTB) method:

- 1 - BPh_4^- and Ph_4P^+ or Ph_4As^+ are the same size and have the same contribution to the transfer enthalpy;
- 2 - charges of both ions are the same and fully sheathed;
- 3 - the ions react with the solvent in the same way and rather weakly.

Both ions (BPh_4^- and Ph_4P^+ or Ph_4As^+) have four phenyl groups each and hence they are likely to undergo hydrophobic hydration within the water-rich region. It has been observed in our previous studies that the maxima of $\Delta_{\text{tr}}H^\infty$ of these salts containing them are very high [15], which is associated with the hydrophobic hydration of these ions. The heights of these maxima are the higher the greater is the hydrophobicity of organic solvent [16]. If the effects of hydrophobic hydration of both ions and other interactions were the same, this would not affect the ionic $\Delta_{\text{tr}}H^\infty$ since the initial assumptions are fulfilled.

Marcus has shown in his paper [17] that the interactions of PPh_4^+ and BPh_4^- with water are not the same. Unlike the behaviour of water in the proximity of BPh_4^- , in the case of PPh_4^+ water enters between the phenyl groups of this ion. Hence the interactions between these ions and water or water-organic solvents are not the same, which probably brings about differences in the height of maximum $\Delta_{\text{tr}}H^\infty$. Probably it leads to the mirror reflexions of $\Delta_{\text{tr}}H^\infty$ (inorganic ions) mentioned earlier. Therefore the division of $\Delta_{\text{tr}}H^\infty$ (Ph_4PBPh_4 or $\text{Ph}_4\text{AsBPh}_4$) into equal contributions for BPh_4^- and Ph_4P^+ or Ph_4As^+ is not justified.

It can be seen (plots "c") that the height of extrema of $\Delta_{\text{tr}}H^\infty$ (organic ions) are the higher the greater is the hydrophobicity of solvent. In addition, in the case of an alcohol with larger molecules such as those of *n*-PrOH and *tert*-BuOH, double extrema are observed within the water-rich region, which is difficult to explain. It has been shown previously that the presence of extrema similar to mirror reflections is brought about by water present in the mixed solvent [18].

Within the region above 50 mol% of organic solvent the shapes of curves illustrating $\Delta_{\text{tr}}H^\infty$ obtained by the CsI and TATB (TPTB) methods are similar. This is the region where the behaviour of PPh_4^+ , BPh_4^- , Cs^+ and I^- is not differentiated by the hydrophobic hydration.

It is conceivable that the TATB (TPTB) method may be used for the division of $\Delta_{tr}H^\infty$ into ionic contributions in non aqueous solvents. The presence of water may lead to erroneous conclusions about interactions in solutions of because the hydrophobic hydration of organic ions used for the salts enthalpies division and of organic cosolvents.

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PORÓWNANIE JONOWYCH ENTALPII PRZENIESIENIA Z WODY DO MIESZANYCH ROZPUSZCZALNIKÓW Z ALKOHOLAMI OTRZYMANÝCH PRZEZ WYKORZYSTANIE DWÓCH METOD PODZIAŁU: TPTB (TATB) ORAZ CsI

Zmierzono entalpię rozpuszczania CsI w mieszanym rozpuszczalniku n-propanol-woda w temperaturze 298.15 K. Standardową entalpię rozpuszczania CsI w tych rozpuszczalnikach obliczono metodą Crissa i Cobble'a. Standardowa entalpia przeniesienia elektrolitów była podzielona na udziały jonowe, przy wykorzystaniu równania

$$\Delta_{tr}H^{\infty}(Cs^{+}) = \Delta_{tr}H^{\infty}(I^{-})$$

Otrzymane wartości jonowe $\Delta_{tr}H^{\infty}$ porównano z analogicznymi, uzyskanymi przy zastosowaniu metody TATB

$$\Delta_{tr}H^{\infty}(BPh_{4}^{-}) = \Delta_{tr}H^{\infty}(Ph_{4}P^{+})$$

Taką samą analizę przeprowadzono dla układów wody z metanolem, etanolem i tert-butanolem.