Thermochimica Acta, 205 (1992) 51–63
Elsevier Science Publishers B.V., Amsterdam

Thermodynamic and conductometric studies on NaI solutions in water–*t*-butanol mixtures at 299.15 K

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(Received 22 October 1991)

Abstract

The electrical conductivity of NaI solutions and the electromotive forces of the cells: glass electrode(Na)|NaI|AgI,Ag in water–*t*-butanol systems have been measured at 299.15 K.

The values of the limiting conductivity of NaI and of the standard e.m.f. of the cells were determined. Based on the data obtained, the thermodynamic functions $\Delta G_t^{\ominus}$, $\Delta S_t^{\ominus}$ and $\Delta H_t^{\ominus}$ were calculated, taking into account the ionic association of the electrolyte.

INTRODUCTION

In order to understand and explain the nature of the interactions occurring in solutions, one has to carry out extensive investigations of the various properties of the given system using different experimental methods. The systems which have been of the greatest interest for researchers for many years include mixtures of water and *t*-butanol (TBA), and the solutions of electrolytes, as well as of non-electrolytes, in these systems. Papers on this subject are so numerous, that it is impossible to mention all of them here. Studies on the various properties of the water–*t*-butanol system have been carried out over its entire composition range. Research into electrolyte solutions in these mixtures has been restricted to water-rich systems (below 25 mol.% TBA). Measurements of the solution enthalpy of NaI were carried out, several years ago, in water–TBA mixtures in the composition range up to 98 mol.% TBA at 299.15 K [1,2]. We have recently published the results of viscosimetric measurements of NaI in the same mixtures up to about 90 mol.% TBA [3].

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In the present study, these studies were extended to include measurements of the electromotive force (e.m.f.) in the system TBA–water–NaI, in order to obtain the complete thermodynamic characteristics of the system under consideration.

The low electric permittivity of these mixtures at high alcohol content [4] suggests a considerable ionic association in the system. For this reason, we decided also to measure the conductivity of NaI solutions in water–TBA mixtures and to determine the ionic association constant of NaI. This would enable the effect of the formation of ionic pairs on the thermodynamic functions of solvation to be determined.

EXPERIMENTAL

Reagents

The *t*-butanol (Merck, Darmstadt) was heated for about 8 h under reflux over freshly calcined calcium oxide, and was then distilled and stored under an atmosphere of dry nitrogen. The specific conductivity of the freshly distilled *t*-butanol was $(1.2\text{–}2) \times 10^{-10}$ cm^{-1} Ω^{-1}.

The deionized water used was distilled three times using a Pyrex glass distillation apparatus.

The NaI, puris (Merck, Darmstadt) was dried at about 330 K in a vacuum drier for several days and then stored in a desiccator.

Conductivity measurements

The measuring apparatus, procedures of solution preparation and the measurement method are described in detail in previous papers [5,6]. Mixed solvents were prepared by weight. The mixtures, as well as the solutions, were prepared in a closed system in order to avoid incidental impurities.

E.m.f. measurements

The e.m.f. of the cells were measured with an OP-208/1 pH-meter (Radelkis, Budapest) connected to a Radelkis recorder, type OH-814/1, and a printer linked to a digital timer.

Measurement cells

A glass electrode, reversible in relation to sodium ions, type ESL-51G-05 (USSR), a silver–silver iodide electrode prepared by the thermo-electrolytic method [7] and a stirrer made of teflon, were placed in a Pyrex glass vessel.

Only those silver–silver iodide electrodes whose potentials agreed within 0.3 mV, were used.

The investigated cell was surrounded by a steel shield and placed in a thermostat filled with paraffin oil. The temperature was controlled with a thermistor in a Wheatstone bridge system; the accuracy of the temperature control was better than 0.01 K. The e.m.f. measurements were performed in the molality range 0.02–0.2 mol kg^{-1}.

More details concerning the measurement method are given in previous papers [8,9].

RESULTS AND DISCUSSION

Conductivity measurements

The molar conductivities of NaI solutions in water–*t*-butanol systems for different electrolyte concentration at 299.15 K are given in Table 1.

The conductimetric data were analysed using the equation of Fuoss and Justice [10–12] in the form

$$\Lambda = \alpha\left(\Lambda_0 - S\alpha^{1/2}c^{1/2} + Ec\,\ln(\alpha c) + J\alpha c + J_{3/2}\alpha^{3/2}c^{3/2}\right) \tag{1}$$

with

$$(1-\alpha)/\alpha^2 c y_\pm^2 = K_A \tag{2}$$

$$y_\pm = \exp - \left[\frac{A\alpha^{1/2}c^{1/2}}{1 + BR\alpha^{1/2}c^{1/2}}\right] \tag{3}$$

where Λ_0 is a limiting conductivity, α is the degree of dissociation, $(1-\alpha)$ is the molar fraction of the electrolyte occurring in the form of ionic pairs, K_A is the ionic association constant and $y_\pm$ describes the average activity coefficient of the dissociated electrolyte.

The activity coefficient of the ionic pairs were assumed to be equal to unity, as is usually the case in diluted solutions. A and B are constants from the Debye–Huckel equation

$$A = \frac{(\ln 10)\ 1.8246 \times 10^6}{(\varepsilon T)^{3/2}} \tag{4}$$

$$B = \frac{50{,}29}{(\varepsilon T)^{1/2}} \tag{5}$$

The analytical forms of the remaining parameters, i.e. S, E, J and $J_{3/2}$ are given in refs. 10–13. The value of the parameter denoting the closest distance of the approach of the ions was determined as described in ref. 14, i.e. $R = a + d$ in the case $a + d > q$ or $R = q$ in the case of $a + d < q$, where α is the sum of the crystallographic radii of the ions, d is the average distance corresponding to the size of a cell occupied by a solvent molecule, and Bjerrum's parameter is expressed in the form

$$q = e^2/2\varepsilon kT \tag{6}$$

In this case, eqn. (1) became a bi-parameter equation (Λ_0 and K_A). The determined values of Λ_0 and K_A as well as their standard deviations, and the values of R (or q) are given in Table 2. The density, ρ_0, electrical permittivity ε, and viscosity η_0, values of the TBA-water mixtures necessary for the calculation, were taken from the literature [3,4].

The limiting conductivity of NaI in the water-TBA system at 299.15 K versus the solvent composition is shown in Fig. 1, which also shows the values of Λ_0 for NaI at 298.15 K, calculated as the sum of the ionic conductivities of Na^+ and I^-, as determined by Broadwater and Kay [15] in the range of composition 0-20 mol.% TBA.

Figure 2 shows the dependence of log K_A on the reciprocal of the electrical permittivity of the mixed solvent. The present data show that the limiting conductivity of NaI decreases monotonically with the increase of the TBA content in the system. Our values of Λ_0 are similar to those calculated on the basis of Broadwater and Kay's data [15]. Small differences result from the fact that our measurements were performed at 1°C higher; moreover, Broadwater and Kay's [15] data were calculated from ionic contributions. The course of the function $\Lambda_0 = f$(composition) is, however, the same.

Figure 1 also presents the course of the changes in the Walden product versus the mixed solvent composition. The $\Lambda_0\eta$ maximum occurring for low TBA contents is, in our opinion, well explained by Broadwater and Kay [15] by the so-called "sorting effect". The values of $\Lambda_0\eta$ decrease monotonically above 20 mol.% TBA, which may be connected with a gradual exchange of water dipoles in the solvation surroundings of the ions on TBA, owing to an increase in the alcohol content. The values of the limiting conductivities of ions from ref. 3 can lead to analogous conclusions.

The relationship, log $K_A = f(1/\varepsilon)$, is a rectilinear function over almost the whole range of the mixture composition, despite the fact that R is not constant in the systems under investigation (see Table 2).

The e.m.f. measurements

The different opinions on the applicability of glass ion-selective electrodes for thermodynamic studies on electrolyte solutions in aqueous-organic systems, have led us to undertake a study of this subject [8,9,16-21]. Thus, for instance, Juillard and co-workers [22-28] have used glass ion-selective electrodes to determine the free enthalpy of transfer of electrolyte from water to various mixed solvents. However, other authors have doubted the suitability of such a procedure [29,30]. It is also believed that the applicability of a glass ion-selective electrode in a mixed solvent is restricted to systems containing less than 30 wt.% of organic cosolvent [31–33]. A detailed review of these opinions is reported in ref. 34. The results of our previous investigations concerning the application of a sodium glass electrode for thermodynamic studies in the water–methanol [8,16–18] water–*t*-butanol [9], water–isopropanol [19], water–*N*,*N*-dimethylformamide [20] and water–tetrahydrofuran [21] systems, were in very good agreement with data obtained from other methods, i.e. thermochemical, electrochemical and vapor pressure measurements. Our results have confirmed the opinion that sodium glass electrodes can be succesfully used in thermodynamic studies over wide ranges of composition and temperature.

The standard e.m.f. values of the cell: glass electrode(Na)|NaI|AgI,Ag in the water–TBA mixtures at 299.15 K versus the solution composition are given in Table 3. The standard electromotive force $E^{\ominus}$ was determined from these data by extrapolating to $m = 0$ the function

$$\begin{aligned} f(m\alpha) &= E + \frac{2R_gT}{F}\ln m\alpha - \frac{2R_gT}{F}\frac{A\sqrt{\rho_0 m\alpha}}{1 + BR\rho_0\sqrt{m\alpha}} \\ &\quad - \frac{2R_gT}{F}\ln(1 + 0.002m\alpha M_1) \\ &= E^{\ominus} - \frac{2R_gT}{F}Cm\alpha \end{aligned} \tag{7}$$

where A and B are constants from the Debye–Huckel equation (see eqns. (4) and (5)), R_g is the gas constant, T the temperature, ρ_0 the solvent density, R the ion approach parameter, M_1 the molar weight of the solvent, C the empirical constant which depends on the mixed solvent composition and temperature, and α the degree of dissociation, calculated independently from the conductivity measurements, see eqns. (1)–(3). Function (7) is obtained by substitution of the Hückel equation expressed in the molality scale

$$\ln\gamma = -\frac{A\sqrt{\rho_0 m\alpha}}{1 + BR\rho_0\sqrt{m\alpha}} + Cm - \ln(1 + 0.002m\alpha M_1) \tag{8}$$

into the equation representing the electromotive force of the cell

$$E = E^{\ominus} - \frac{2R_gT}{F}\ln\gamma_{\pm} \tag{9}$$

where $\gamma_{\pm}$ is the average activity coefficient of the dissociated part of the electrolyte (for ions), expressed in the molality scale. Parameter R, as in the case of conductivity, was chosen in accordance with the suggestion of

TABLE 1

Molar conductances Λ and corresponding concentrations c for NaI in water–t-butanol mixtures at 299.15 K

$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})	$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})	$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})
Water		*2.62 mol.% TBA*		*5.11 mol.% TBA*	
2.6605	128.19	5.9376	85.48	4.3053	63.50
5.3771	127.62	7.9342	85.21	5.8528	63.34
7.5796	127.22	9.6930	85.07	7.4152	63.20
10.594	126.78	11.109	84.88	9.3829	63.03
13.719	126.45	14.882	84.65	10.9908	62.94
16.915	126.13	17.672	84.38	14.555	62.69
20.964	125.71	21.559	84.17	18.068	62.57
25.664	125.38	24.177	84.02	21.557	62.36
30.958	124.95	37.494	83.34	24.846	62.21
35.285	124.70	43.709	83.02	37.614	61.78
44.597	124.13	49.795	82.82	45.187	61.46
54.190	123.70	59.269	82.45	51.314	61.35
63.009	123.29			60.038	61.08
71.739	122.92				
85.304	122.41				
7.57 mol.% TBA		*19.2 mol.% TBA*		*41.9 mol.% TBA*	
6.3511	50.61	1.5562	30.36	1.2142	17.62
8.5120	50.45	2.4902	30.21	2.0375	17.35
10.885	50.31	3.9926	30.05	2.9761	17.97
12.484	50.21	7.5901	29.73	3.9869	16.88
16.500	50.01	8.7205	29.66	4.8016	16.72
20.483	49.84	11.690	29.46	5.9159	16.51
24.154	49.72	14.310	29.31	7.4762	16.27
28.378	49.57	17.141	29.17	9.3926	16.01
35.883	49.32	20.011	29.07	12.965	15.60
43.732	49.12	25.726	28.82		
50.908	48.96	30.769	28.66		
58.968	48.79	36.396	28.50		
		41.528	28.35		
		48.704	28.20		
59.4 mol.% TBA		*72.2 mol.% TBA*		*78.4 mol.% TBA*	
2.8147	13.00	5.6379	11.31	5.8634	9.282
3.9453	12.48	8.6430	10.79	8.9448	8.651
5.3109	11.97	12.020	10.32	12.012	8.167
6.8411	11.51	16.695	9.81	16.301	7.633
7.9729	11.21	21.265	9.40	20.596	7.221
10.716	10.62	24.618	9.14	27.062	6.747
13.120	10.21	32.549	8.65	34.047	6.343
18.256	9.53	40.501	8.23	39.186	6.107
		49.233	7.88	45.071	5.855
		57.121	7.61	52.716	5.582
				4.639	5.240

TABLE 1 (continued)

$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})	$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})	$c \times 10^{-4}$ (mol dm^{-3})	Λ (cm^2 mol^{-1} Ω^{-1})
81.6 mol.% TBA		*90.8 mol.% TBA*			
5.7617	8.301	3.2498	5.928		
6.7541	8.069	4.1268	5.632		
7.8050	8.844	4.4624	5.540		
9.0795	7.610	4.8857	5.415		
11.013	7.305	5.3715	5.310		
13.728	6.946	6.1605	5.126		
16.054	6.681	9.3419	4.581		
19.675	6.345	12.561	4.211		
23.303	6.058	17.428	3.802		
27.002	5.815	25.624	3.338		
30.626	5.608	29.151	3.195		
38.837	5.229	33.791	3.039		
		41.727	2.818		

Fuoss [14]. When the electrolyte was almost completely dissociated, it was assumed that $\alpha = 1$. Such a procedure was justified only when the effect of the ionic association on $E^{\ominus}$ was comparable with the standard error, $\alpha E^{\ominus}$. In the remaining cases, the degree of electrolyte dissociation was calculated on the basis of the values of ionic association constants found by

TABLE 2

Limiting molar conductance Λ_0, ionic association constant K_A, their standard deviations $\sigma\Lambda_0$ and σK_A, respectively, and parameter R for NaI in water–t-butanol mixtures at 299.15 K

Mol.% TBA	Λ_0 (cm^2 mol^{-1} Ω^{-1})	$\sigma\Lambda_0$ (cm^2 mol^{-1} Ω^{-1})	K_A (dm^3 mol^{-1})	σK_A (dm^3 mol^{-1})	R (Å)
0.00	129.71	±0.02	0.4	±0.1	6.28
2.62	86.92	±0.02	1.7	±0.1	6.38
5.11	64.49	±0.01	1.3	±0.1	6.47
7.57	51.65	±0.01	1.2	±0.1	6.57
19.2	30.88	±0.01	5.8	±0.1	7.45 [a]
41.9	18.43	±0.01	127.4	±0.6	13.86 [a]
59.4	15.75	±0.01	816.7	±1.8	18.05 [a]
72.2	13.07	±0.01	2713.0	±6.0	22.21 [a]
78.4	11.80	±0.01	5704.0	±15.0	23.4 [a]
81.6	10.98	±0.01	7394.0	±13.0	23.9 [a]
90.8	8.22	±0.01	16485.0	±47.0	24.4 [a]

[a] $R = q$.

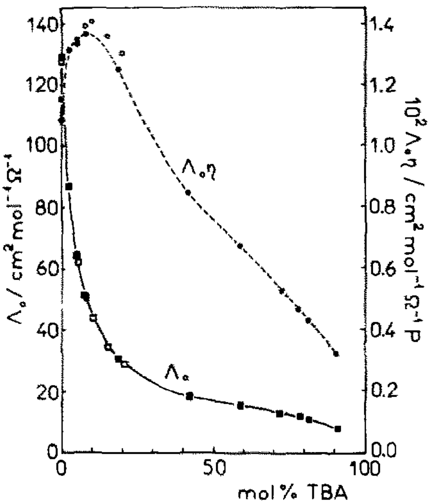

Fig. 1. Limiting molar conductivity Λ_0 and Walden product $\Lambda_0\eta_0$ for NaI in water–TBA mixtures: ●, our results at 298.15 K; ○, results obtained from ref. 5.

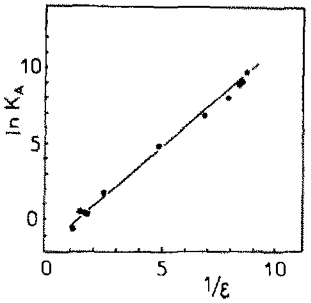

Fig. 2. Values of ln K_A as a function of $1/T$ for NaI in water–TBA mixtures at 299.15 K.

TABLE 3

Values of standard e.m.f. $E^{\ominus}$, values of the C parameter (eqn. (7)) and their standard deviation, $\sigma E^{\ominus}$ and σC

Mol.% TBA	E (V)	σE (V)	C (kg mol^{-1})	σC (kg mol^{-1})
0	−0.4969	±0.0001	0.1998	±0.0177
2.62	−0.5125	±0.0001	−0.3167	±0.0591
5.11	−0.5259	±0.0001	−0.0805	±0.0361
7.57	−0.5356	±0.0001	0.0445	±0.0610
19.20	−0.5768	±0.0001	0.9131	±0.0709
41.90	−0.6790	±0.0001	3.8994	±0.0521
59.40	−0.7764	±0.0001	6.3542	±0.0443
72.20	−0.8408	±0.0001	22.4456	±0.1176
81.60	−0.9147	±0.0001	10.2131	±0.2825

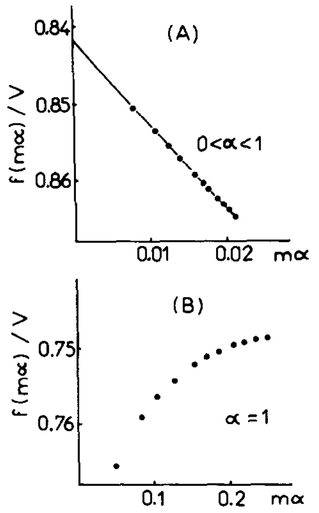

Fig. 3. The extrapolated values from eqn. (7) when the ionic association is taken (A) or not taken (B) into account in the solution containing 72.2 mol.% TBA.

conductimetry. The values of the standard electromotive force $E^{\ominus}$, of the investigated cell in the water–TBA systems, the coefficient C (eqn. (7)) and their standard errors, are listed in Table 3. It should be noted here that taking the ionic association into account affects the determination of the standard e.m.f. of the cells. Figure 3 shows the function illustrating the extrapolation equation (eqn. (7)) with and without taking into account the ionic association in the solution containing 72.2 mol.% TBA.

The same kind of linearization of function (7) was observed in all cases when the ionic association was taken into account. In our opinion, this also confirms the usefulness of glass electrodes in thermodynamic investigations of solutions in which ionic association is significant. Using the determined values of $E^{\ominus}$, we calculated the standard free enthalpy of transfer of NaI from water to water–TBA mixtures

$$\Delta G_t^{\ominus} = -F(E^{\ominus,\mathrm{mix}} - E^{\ominus,\mathrm{w}}) \qquad (10)$$

where $E^{\ominus,\mathrm{mix}}$ is the standard e.m.f. of the cell in the mixed solvent and $E^{\ominus,\mathrm{w}}$ is the standard e.m.f. of the cell in water.

The calculated enthalpies of transfer ($\Delta G_t^{\ominus}$) of NaI are given in Table 4 and are plotted in Fig. 4 versus the molar composition of the mixed solvent. Using the values of $\Delta G_t^{\ominus}$ and the values of enthalpy of transfer ($\Delta H_t^{\ominus}$) of NaI from water to the water–TBA system calculated on the basis of data

TABLE 4

Thermodynamic functions of transfer of NaI from water to water–*t*-butanol mixtures at 299.15 K

Mol. % TBA	$\Delta G_t^\ominus$ (J mol^{-1})	$\Delta H_t^\ominus$ (J mol^{-1})	$\Delta H_{t(corr)}^\ominus$ (J mol^{-1})	$\Delta S_t^\ominus$ (J mol^{-1} K^{-1})	$\Delta S_{t(corr)}^\ominus$ (J mol^{-1} K^{-1})
2.62	1485	4330		9.51	
5.11	2769	6612		12.84	
7.57	3714	6026		7.72	
19.20	7690	165		−25.15	
41.90	16200	−9885	−10256	−87.19	−88.43
59.40	22664	−17128	−21348	−133.01	−147.11
72.20	33152	−19431	−28993	−175.77	−207.33
81.60	40283	−18426	−34362	−196.25	−249.51
90.80		−17128	−36508		

from our previous papers [1,2], we determined the standard entropy of transfer ($\Delta S_t^\ominus$) of NaI in the system under investigation

$$\Delta S_t^\ominus = \frac{\Delta H_t^\ominus - \Delta G_t^\ominus}{T} \tag{11}$$

The results of the calculation are also given in Table 4. However, considering the fact that the standard enthalpies of NaI solution published in ref. 1 were determined without taking into account the ionic association, we

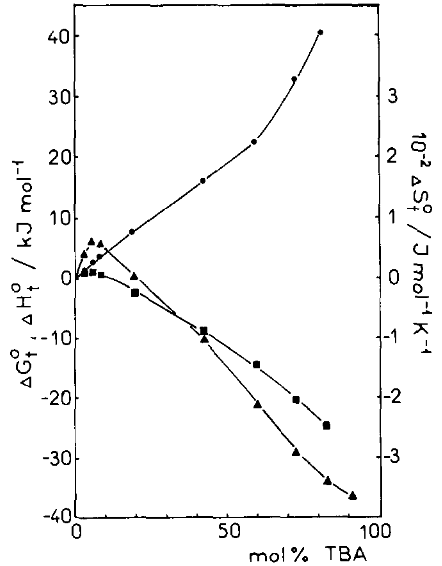

Fig. 4. Free enthalpy of transfer ($\Delta G_t^\ominus$), enthalpy ($\Delta H_t^\ominus$) and entropy ($\Delta S_t^\ominus$) of transfer of NaI from water to water–TBA mixtures at 299.15 K: ●, $\Delta G_t^\ominus$; ▲, $\Delta H_t^\ominus$; ■, $\Delta S_t^\ominus$.

decided to recalculate the $\Delta H_s^{\ominus}$ values of NaI (and $\Delta H_t^{\ominus}$) taking into consideration the process of formation of ionic pairs. For this purpose we used the method which utilizes the model given in the paper by Barthel et al. [35]. If we assume that the relative apparent enthalpy of the solution containing free ions (FI) and the ionic pairs can be expressed by the equation

$$\Phi_L = \Phi_L(\text{FI}) + (1 - \alpha)\ \Delta H_A^{\ominus} \tag{12}$$

where $\Phi_L(\text{FI})$ is the relative apparent molar enthalpy of the free ions, $\Delta H_A^{\ominus}$ is the enthalpy of ionic association and α is the degree of the electrolyte dissociation, then from

$$\Phi_L = -\Delta H_{\text{DIL}}^{\ominus} = \Delta H_s - \Delta H_s^{\ominus} \tag{13}$$

we obtain

$$\Delta H_s - \Phi_L(\text{FI}) = \Delta H_s^{\ominus} + (1 - \alpha)\ \Delta H_A^{\ominus} \tag{14}$$

In the latter equation, $\Delta H_s^{\ominus}$ is the measured solution enthalpy of the electrolyte at the given molality m.

The values of $\Phi_L(\text{FI})$ can be calculated from the formula given by Barthel et al. [35]. The dissociation degree α can be found from conductimetric data. Thus, the left side of eqn. (14) can be calculated from the experimental data

$$\Delta H_s - \Phi_L(\text{FI}) = \sigma \tag{15}$$

Giving σ as a function of $(1 - \alpha)$, we obtain the rectilinear relationship (16) which after extrapolation to $(1 - \alpha) = 0$, results in the standard solution enthalpy $\Delta H_s^{\ominus}$:

$$\sigma = \Delta H_s^{\ominus} + (1 - \alpha)\ \Delta H_A^{\ominus} \tag{16}$$

The slope of the straight line corresponds to the ionic association.

Utilizing the molal solution enthalpies of NaI in the water–TBA systems published previously [2], and the values of the ionic association constant K_A calculated in the present study, we have found, using the above-mentioned procedure, a "corrected" standard enthalpy of solution $\Delta H_s^{\ominus}$ (corr) for NaI in the system under investigation. The results are given in Fig. 5 and listed with the data omitting the ionic association reported previously [1,2]. As seen from the figure, the shapes of both curves are different within the range of high contents of *t*-butanol. Based on the corrected values of $\Delta H_s^{\ominus}$ of NaI, we have calculated the "corrected" enthalpy and entropy of transfer of NaI from water to the water–TBA mixtures. The results obtained are listed together with $\Delta G_t^{\ominus}$ in Table 4 and are shown in Fig. 5.

These data indicate that both the enthalpy and entropy of transfer of NaI from water to water–TBA systems show their maxima in the water-rich

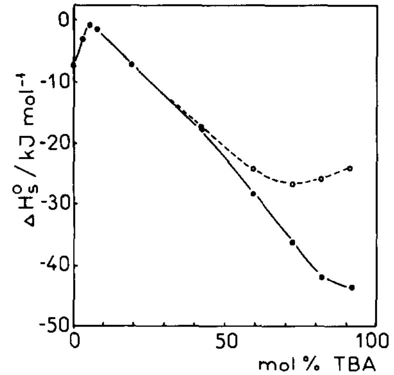

Fig. 5. Standard enthalpy of solution of NaI in water–TBA mixtures at 299.15 K: ●, "corrected values" (when ionic association is taken into account); ○, "uncorrected" values from refs. 1 and 2.

region, which is typical of water–alcohol mixtures; however, the free energy varies monotonically over the entire investigated range of the mixture composition. This results from the commonly observed compensation of the entropic and enthalpic effects in electrolyte solutions [9,16–21,36,37].

In general, it should be noted that not taking into account the ionic association during the determination of thermodynamics function values leads to significant errors in their values. These errors are usually much larger than experimental ones. Using uncorrected results may give rise to misleading conclusions.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Z. Kozłowski for discussions and for helpful suggestions. This research was sponsored by the CPBP 01.15 programme of the Polish Ministry of National Education.

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