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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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Adam Bald^a; Jerzy Gregorowicz^a; Adam Szejgis^a

^a Department of Chemical Didactics, University of Łódź, Lindleya 3, Łódź, Poland

To cite this Article Bald, Adam , Gregorowicz, Jerzy and Szejgis, Adam(1993) 'Thermodynamic and Conductometric Studies on NaI Solutions in Water-Isobutanol Mixtures at 298.15 K', *Physics and Chemistry of Liquids*, 26: 2, 121 – 133

To link to this Article: DOI: 10.1080/00319109308030826

URL: <http://dx.doi.org/10.1080/00319109308030826>

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THERMODYNAMIC AND CONDUCTOMETRIC STUDIES ON NaI SOLUTIONS IN WATER-ISOBUTANOL MIXTURES AT 298.15 K.

ADAM BALD,* JERZY GREGOROWICZ and ADAM SZEJGIS

*Department of Chemical Didactics, University of Łódź, Lindleya 3,
90-131 Łódź, Poland.*

(Received 30 October 1992)

The electric conductivity of NaI solutions in water-isobutanol mixtures in the complete miscibility range of the alcohol has been measured and analysed using the Fuoss-Justice equation. The electromotive force of the cell: glass electrode (Na)|NaI|AgI, Ag in the same binary mixtures has been determined. The standard enthalpies of solution of NaI have been recalculated and the thermodynamic functions ΔG° and ΔS° have also been calculated taking into account ion association.

KEY WORDS: Ion association, EMF, Electrical conductivity.

INTRODUCTION

Solutions of electrolytes in water-organic solvents mixtures have been the object of numerous investigations by many authors. Thermodynamic studies of electrolyte solutions in mixed solvents have been carried out in our laboratory for many years. For this purpose we have used different experimental techniques such as conductivity, relative permittivity and density measurements over a wide range of the temperatures and also the measurements the electromotive forces (e.m.f.) of the cells containing glass sodium electrode.

Glass ion-selective electrodes have been used mainly to determine the Gibbs energy of transfer and the activity coefficients of electrolytes.^{1–8} In the previously published papers^{9–16} we have calculated the values of the free enthalpies, enthalpies and entropies of transfer of electrolytes from the e.m.f. data of the cells containing the ion-selective electrodes. They were compared with the results obtained from e.m.f. measurements of the cell with amalgam electrode^{9–12,14–16}, vapour pressure measurements¹⁹ and calorimetric measurements.^{10,12–14,16} In our opinion such a procedure is the best way to verify the results. These investigations lead us to the conclusion that the glass ion-selective electrodes are characterized by excellent accuracy, reproducibility and the simplicity of the methods of taking measurements. The authors' opinions in this subject are in agreement with suggestions included in Refs. 1–6. A

* To whom correspondence should be addressed.

review of the opinions of other authors has been given in Ref. 17. The review of the above-mentioned opinions, including also the analytical aspect of the applicability of the glass electrodes in mixed solvents was made by Pungor *et al.*¹⁸ Recently our studies have been devoted to electrolyte solutions 1:1 in the mixtures at low electric permittivities. In these studies the influence of ion association on thermodynamic function of transfer was analysed and discussed.²⁴⁻²⁶ We have also measured electric conductivity and determined the ion-association constant for NaI in the mixtures of tert-butanol and sec-butanol with water.^{28,29} In addition we have redetermined the standard enthalpies of solution of NaI (ΔH_s°) taking into account the ion-pair formation.^{28,29}

Continuing our studies we have decided to investigate NaI solutions in water-isobutanol mixtures.

The system mentioned above has already been examined calorimetrically.^{19,20} Owing to a relatively low electric permittivity of these mixtures at high alcohol contents²¹ [for isobutanol 17.53 (Ref. 22)] it seemed advisable to redetermine the ΔH_s° of NaI in the system taking into account the ion-pairs formation.

For this the electric conductance was measured for NaI solutions in the mixed solvent under investigation. We have also extended these studies, including measurements of the electromotive force (e.m.f.) in the system water-isobutanol-NaI, which would permit one to obtain full thermodynamic characteristics of the system under consideration.

EXPERIMENTAL

Reagents: isobutanol, (i-BuOH) produced by Koch and Light Laboratories Ltd. (England) was purified according to the procedure given in Ref. 19 and stored under the atmosphere of dry nitrogen. The specific conductivity of the freshly distilled isobutanol was $1.2-2 \cdot 10^{-10} \text{ cm}^{-1} \text{ ohm}^{-1}$. Deionized water was distilled three times using a Pyrex-Glass distillation apparatus. NaI-puris, of Merck-Darmstadt, was dried at a temperature of about 330 K in a vacuum drier for several days and then stored in a desiccator. All the solutions were prepared by weight. The mixtures as well as the solutions were prepared in a closed system to avoid incidental impurities.

Apparatus and procedure

The method and apparatus for measuring conductivity and procedures of the solution preparation were described in our previous paper.²³ Taking into account the purity of reagents, equipment, method of taking measurements and accuracy of the temperature control, the error of the measured values was less than 0.05%. E.m.f. of the cells was measured by means of a precise pH-meter type OP-208/1 (made by Radelkis-Budapest), connected with a recorder, a printer and a digital timer.

The input impedance of pH-meter was greater than 10^{12} ohm . A glass electrode, reversible to sodium ions, type ESL-51G-05 (made in the USSR) and a silver-silver iodide electrode prepared by the thermal-electrolytic method²⁷ were used. Only those silver-silver iodide electrodes were used whose potentials agreed within 0.01 mV. A glass electrode ESL-51G-05 (resistance ca. 50 Mohm) was applied in all our previous

investigations.⁹⁻¹⁶ The e.m.f. measurements were performed in the molality range 0.02–0.3 mol kg⁻¹. The reproducibility of the e.m.f. values was better than 0.3 mV. Temperature was controlled with a thermistor in a Wheatstone bridge system; the error of the temperature control was less than 0.01 K. All the solutions were prepared by weighing.

The details of measuring procedure, cell design as well as the response time and equilibrium potential of glass electrode was described in detail elsewhere.⁹⁻¹⁶ The density, ρ_0 , of water-isobutanol mixtures was measured using the methods presented earlier.²⁴ The temperature was kept constant within 0.01 K. The accuracy of the density measurements corresponded to 1×10^{-4} kg/dm⁻³. The density values of the water-isobutanol system are collected in Table 1. The viscosity and relative permittivity values of the water-isobutanol mixtures was taken from data given in the literature^{22,28} (Table 2).

RESULTS AND DISCUSSION

(i) Analysis of the results of the conductivity measurements. The molar conductances of NaI solutions in water-isobutanol systems for different electrolyte concentration at 298.15 K are given in Table 3. The conductometric data were analysed by means of Fuoss-Justice³¹⁻³³ equation:

$$\Lambda = \alpha[\Lambda_0 - S\alpha^{1/2}c^{1/2} + E(\alpha c) \ln(\alpha c) + J(\alpha c) + J_{3/2}\alpha^{3/2}c^{3/2}] \quad (1)$$

Table 1 Density, ρ_0 , of water-isobutanol mixtures at different temperatures.

mol % <i>i</i> -BuOH	$\rho_0/\text{kg dm}^{-3}$					
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.00	0.9991	0.9982	0.9970	0.9956	0.9940	0.9922
0.15	0.9981	0.9972	0.9960	0.9946	0.9930	0.9910
0.31	0.9970	0.9961	0.9949	0.9934	0.9918	0.9900
0.50	0.9958	0.9949	0.9937	0.9922	0.9905	0.9887
0.79	0.9942	0.9931	0.9920	0.9904	0.9887	0.9869
1.31	0.9914	0.9903	0.9890	0.9873	0.9856	0.9836
1.84	0.9889	0.9876	0.9862	0.9844	0.9826	0.9804
57.88	0.8362	0.8323	0.8292	0.8241	0.8202	0.8157
64.07	0.8300	0.8262	0.8226	0.8180	0.8140	0.8096
71.78	0.8235	0.8197	0.8258	0.8116	0.8075	0.8031
72.06	0.8232	0.8194	0.8155	0.8114	0.8072	0.8028
75.77	0.8205	0.8167	0.8127	0.8086	0.8044	0.8000
77.35	0.8193	0.8155	0.8116	0.8073	0.8033	0.7989
84.93	0.8144	0.8104	0.8065	0.8022	0.7983	0.7939
88.46	0.8121	0.8083	0.8043	0.8001	0.7961	0.7919
91.12	0.8105	0.8066	0.8027	0.7985	0.7946	0.7903
91.77	0.8102	0.8063	0.8024	0.7983	0.7942	0.7900
92.94	0.8095	0.8056	0.8017	0.7975	0.7935	0.7891
96.63	0.8073	0.8033	0.7997	0.7955	0.7915	0.7874
100.00	0.8051	0.8015	0.7977	0.7937	0.7897	0.7856

Table 2 The values of the electric permittivity, ϵ , and $\delta \ln \epsilon / \delta T$, viscosities, η , densities, ρ_0 , and $\delta \ln \rho_0 / \delta T$ at 298.15 K taken to the calculations.

mol % <i>i</i> -BuOH	$\epsilon^{(a)}$	$\left(\frac{\partial \ln \epsilon}{\partial T}\right)^{(a)}$	$\eta^{(b)}$ (P)	$\rho_0^{(c)}$ (kg dm ⁻³)	$\left(\frac{\partial \ln \rho_0}{\partial T}\right)^{(c)}$
1.38	73.45	-0.00550	0.01135	0.9889	-0.000297
59.30	18.19	-0.00842	0.03121	0.8276	-0.000969
74.20	17.29	-0.00715	0.03037	0.8139	-0.000989
79.60	17.05	-0.00720	0.03035	0.8100	-0.000997
84.60	16.92	-0.00743	0.03058	0.8067	-0.001007
87.80	16.96	-0.00768	0.03090	0.8047	-0.001005
96.80	17.21	-0.00874	0.03263	0.7995	-0.000983
100.00	17.53	-0.00921	0.03356	0.7977	-0.000966

^(a) Interpolated values from data in Ref. (22).^(b) Interpolated values from data in Ref. (30).^(c) Interpolated values from the data obtained in this work (Table 1).

The analytical form of the parameters S , E , J and $J_{3/2}$ has been presented elsewhere.³¹⁻³⁴

The degree of dissociation, α , and the association constant, K_A , were calculated from the relationship:

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

where y_{\pm} is the activity coefficient and

$$\ln y_{\pm} = - \frac{A \alpha^{1/2} c^{1/2}}{1 + B R \alpha^{1/2} c^{1/2}} \quad (3)$$

A and B are coefficients of the Debye-Hückel equation. We adopted the ion distance parameter, R , according to Fuoss'³⁵ suggestions. In this way Eq. (1) becomes diparametric equation (Λ_0 and K_A) and was resolved by a least-squares method.^{28,29,32,36}

The values of Λ_0 and K_A thus determined as well as their standard errors ($\sigma \Lambda_0$ and σK_A) and the values of R are given in Table 4. The molar conductance, Λ_0 , of NaI in water-isobutanol systems at 298.15 K as a function of mixed solvent composition is shown in Figure 1. As follows from the presented data the limiting conductance of NaI is decreasing monotonically with the increase of isobutanol content in the system. Figure 2 shows the dependence of K_A versus mixed solvent composition. As can be seen from these data, in the system with higher isobutanol content, ionic association becomes significant. The relationship $K_A = f(\text{composition})$ is a nonlinear function in the complete miscibility range of the alcohol. The K_A values increase rapidly with the increasing of alcohol content in the system (see Figure 2).

Having the above conductometric data we were able to recalculate standard dissolution enthalpy of NaI in water-isobutanol mixtures (previously published [Ref. 19]) taking into account the ionic association process. For this purpose, the method presented by Barthel *et al.*²¹ was employed. In this method the relative apparent molal heat content of solutions containing "free ions" (FI) and ion pairs is expressed by the equation:

$$\Phi_L = \alpha\Phi_L(FI) + (1 - \alpha)\Delta H_A^\circ \quad (4)$$

where $\Phi_L(FI)$ is the relative apparent molal heat content of a solution with a "free ions", ΔH_A° is the enthalpy of association and α is the degree of dissociation.

Taking into account

$$\Phi_L = -\Delta H_{DIL}^\circ = \Delta H_s - \Delta H_s^\circ \quad (5)$$

one can write an expression determining the enthalpy of solution at infinite dilution:

$$\Delta H_s - \alpha\Phi_L(FI) = \Delta H_s^\circ + (1 - \alpha)\Delta H_A^\circ \quad (6)$$

where ΔH_s is the enthalpy of solution at a molality m and ΔH_s° is the standard enthalpy of solution. The $\Phi_L(FI)$ values were calculated using the formula given in the above mentioned paper of Barthel *et al.*²¹ Having the molal dissolution enthalpies NaI in the water-i-butanol systems²⁰, and the values of the ionic association constant, K_A , calculated in the present study, we have found, by the above mentioned procedure, a "corrected" ($\Delta H_{s(\text{corr.})}^\circ$) standard enthalpies of NaI solution in the system under investigation. The plot of ΔH_s° vs. mol% isobutanol both taking into account ionic association and neglecting it (Figure 3), have the same character but in the alcohol rich region ionic association diminishes the standard enthalpy of solution (ΔH_s°) as well as enthalpy of transfer, ΔH_t° , (see also Figure 5).

(ii) Analysis of the results of e.m.f. measurements. The standard electromotive force, E° , of the cell: glass electrode (Na)|NaI|AgI,Ag was determined from the experimental data by extrapolation to $m = 0$ the function:

$$f(m\alpha) = E + \frac{2R_g T}{F} \ln m\alpha - \frac{2R_g T}{F} \frac{A\sqrt{\rho_0 m\alpha}}{1 + BR\sqrt{\rho_0 m\alpha}} - \frac{2R_g T}{F} \ln(1 + 0.002m\alpha M_1) = E^\circ - \frac{2R_g T}{F} C m\alpha \quad (7)$$

where R_g —gas constant, T —temperature, ρ_0 —solvent density, R —ion approach parameter, M_1 —molar weight of the solvent, C —empirical constant which depended on the mixed solvent composition and temperature, α —degree of dissociation (calculated independently from conductivity measurements, Eqs. 1, 2, 3).

Table 3 Molar conductances, Λ , and corresponding concentrations, c , for NaI in water-isobutanol mixtures at 298.15 K.

$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)
1.38 mol % <i>i</i> -BuOH		59.30 mol % <i>i</i> -BuOH		74.20 mol % <i>i</i> -BuOH		79.60 mol % <i>i</i> -BuOH	
5.7352	106.50	1.4277	18.96	1.4030	16.66	2.8215	15.27
7.8971	106.23	2.0027	18.66	1.9423	16.31	3.3877	14.99
9.7576	106.04	2.5954	18.41	3.1218	15.68	4.2112	14.65
11.153	105.91	2.9959	18.24	4.0634	15.28	4.6731	14.47
14.887	105.56	3.3730	18.11	5.2621	14.85	5.5136	14.16
19.188	105.23	3.8678	17.93	6.2753	14.54	6.8021	13.77
21.731	105.03	4.9381	17.61	8.2782	13.99	7.8797	13.47
26.144	104.75	5.9550	17.33	9.3133	13.76	9.1587	13.16
34.073	104.30	6.7173	17.14	11.285	13.36	10.540	12.86
40.255	103.97	7.7611	16.90	14.201	12.84	11.568	12.66
47.087	103.67	8.5722	16.73			12.996	12.40
53.429	103.40	9.5554	16.53			13.922	12.24
62.509	102.99	10.361	16.38				
		11.285	16.22				
		13.002	15.96				

$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)		$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)		$c \cdot 10^4$ (mol dm^{-3})	Λ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	
	87.80 mol % <i>i</i> -BuOH			96.90 mol % <i>i</i> -BuOH			100 mol % <i>i</i> -BuOH	
1.6857	14.07		2.1016	11.72		1.0715	11.06	
2.1412	13.80		2.5522	11.47		1.2328	10.93	
2.5751	13.55		3.0644	11.20		1.5117	10.71	
3.3621	13.18		3.3927	11.06		1.7720	10.52	
4.3390	12.77		4.0759	10.77		2.1446	10.28	
5.0677	12.51		5.0603	10.40		2.652	10.00	
6.0174	12.22		6.0729	10.07		3.0514	9.78	
6.7365	12.01		7.049	9.80		3.5327	9.57	
7.6425	11.76		7.9537	9.58		4.0782	9.35	
8.4535	11.57		8.8317	9.38		5.1308	8.96	
9.4012	11.36		9.8566	9.18		6.176	8.66	
10.116	11.22		10.792	9.00		7.0942	8.41	
11.553	10.94		11.701	8.84		8.0398	8.19	
13.151	10.68		13.524	8.56		8.9625	8.00	
14.764	10.44		15.250	8.32		9.9719	7.80	

Table 4 Limiting molar conductance, Λ_0 , ionic association constant, K_A , standard errors, σD_0 , and σK_A , and parameter R for NaI in water-isobutanol mixtures at 298.15 K.

<i>mol %</i> <i>i-BuOH</i>	Λ_0 ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	$\sigma \Lambda_0$ ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)	K_A ($\text{dm}^3 \text{mol}^{-1}$)	σK_A ($\text{dm}^3 \text{mol}^{-1}$)	R (\AA)
1.38	108.31	± 0.02	0.6	± 0.1	6.33
59.30	20.32	± 0.01	249.4	± 0.6	15.40*
74.20	18.29	± 0.01	461.7	± 1.5	16.21*
79.60	17.83	± 0.01	523.7	± 1.5	16.43*
87.80	15.94	± 0.01	613.0	± 2.0	16.66*
96.80	13.95	± 0.01	856.5	± 2.0	16.28*
100.00	12.56	± 0.01	1058.0	± 3.0	15.98*

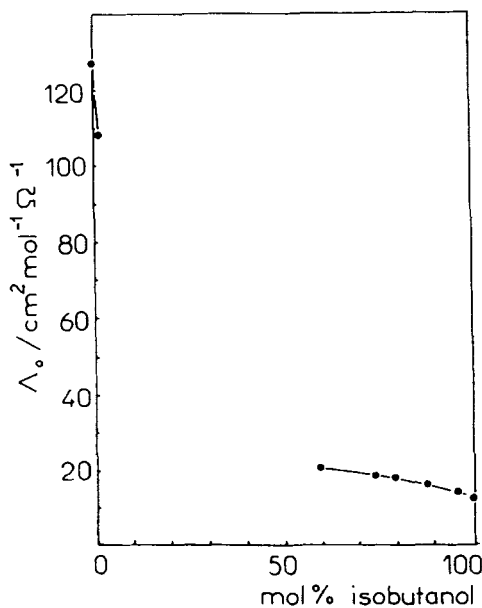
* $R = q$.

Function (7) is obtained by substitution of the Hückel equation expressed in the molality scale:

$$\ln \gamma_{\pm} = - \frac{A \sqrt{\rho_0 m \alpha}}{1 + BR \sqrt{\rho_0 m \alpha}} + Cm - \ln(1 + 0.002 m \alpha M_i) \quad (8)$$

into the equation representing the electromotive force of the cell:

$$E = E^\circ - \frac{2R_g T}{F} \ln m \gamma_{\pm} \quad (9)$$

**Figure 1** Limiting molar conductivity Λ_0 for NaI in water-isobutanol mixtures at 298.15 K.

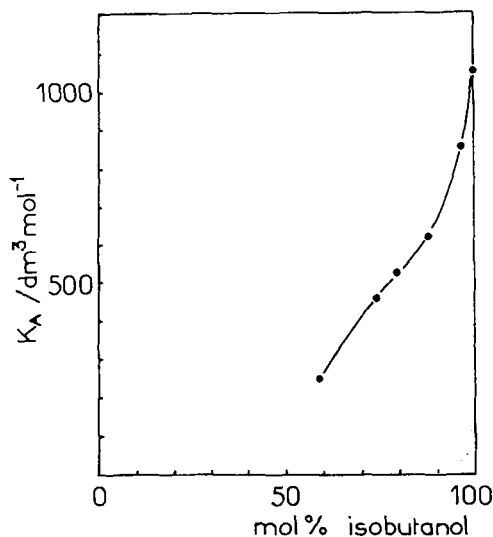


Figure 2 Values of K_A as a function of content for NaI in water-isobutanol mixtures at 298.15 K.

where γ_{\pm} —average activity coefficient of the dissociated part of the electrolyte (for ions).

The parameter R , as in the case of conductivity, was chosen in accordance with the suggestion of Fuoss.³⁵ When the electrolyte was practically completely dissociated it was assumed that $\alpha = 1$. Such a procedure was only justified when the effect of the ionic association on E° was comparable with standard error σE° . In the remaining

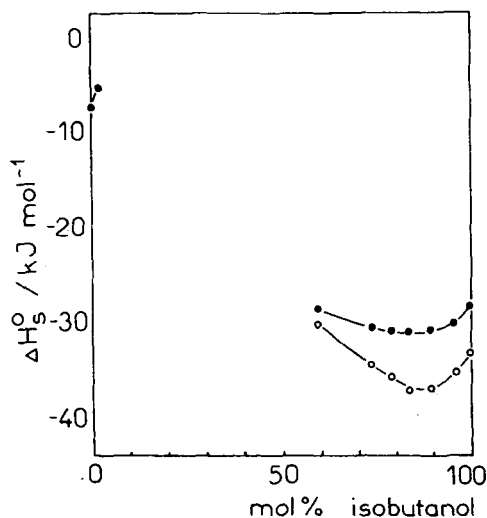


Figure 3 Standard enthalpy of solution of NaI in water-isobutanol mixtures at 298.15 K. \circ —“corrected values” (when ionic association is taken into account, \bullet —“uncorrected values” from paper [20].

Table 5 Values of standard e.m.f., E° , values of the C parameter (Eqn. 7) and standard errors σE° and σC .

<i>mol %</i> <i>i-BuOH</i>	E° (V)	σE° (V)	C (kg mol^{-1})	σC (kg mol^{-1})
0	-0.4960	± 0.0001	0.1998	± 0.0177
1.38	-0.5037	± 0.0001	0.3474	± 0.0116
74.20	-0.7801	± 0.0001	11.7793	± 0.0974
79.60	-0.8031	± 0.0001	12.4865	± 0.0808
87.80	-0.8445	± 0.0002	10.2434	± 0.1084
96.80	-0.9023	± 0.0002	4.6097	± 0.0519
100.00	-0.9311	± 0.0002	-2.3152	± 0.1530

cases, the degree of the electrolyte dissociation was calculated on the basis of the values of ionic association constants determined conductometrically. The values of standard electromotive force E° of the investigated cell in the water-*i*-butanol systems, coefficient C (equation 7) and their standard errors (σE° and σC) are listed in Table 5.

It should be noticed here that there is an effect of taking into account the ionic association on the determination of the standard e.m.f. of the cells. Figure 4 shows the function illustrating the extrapolation equation (equation 7) with and without taking into account the ionic association in the solution containing 87.80% mol of isobutanol. The same kind of linearisation of the function (7) was observed in all

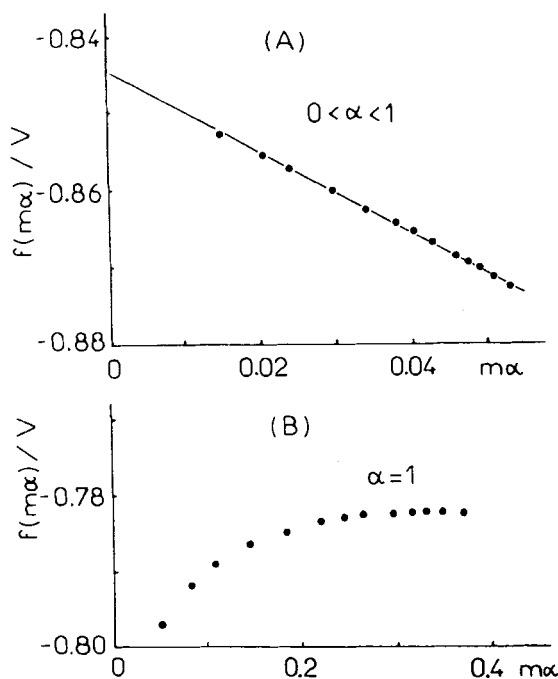


Figure 4 The extrapolated values from equation (7) when the ionic association is taken (A) or not taken into account in the solution containing 87.80 mol% *i*-butanol.

cases, when the ionic association was taken into account.^{28,29} Using the determined values of E° we calculated the free enthalpy of transfer of the NaI from water to the water-isobutanol mixtures

$$\Delta G_i^\circ = -F(E^{\circ,\text{mix}} - E^{\circ,\text{w}}) \quad (10)$$

where $E^{\circ,\text{mix}}$ —standard e.m.f. of the cell in the mixed solvent, $E^{\circ,\text{w}}$ —standard e.m.f. of the cell in water.

The calculated free enthalpies of transfer (ΔG_i°) of NaI are given in Table 6 and in Figure 5 versus the composition of the mixed solvent. Using the values of ΔG_i° and the values of enthalpy of transfer (ΔH_i°) of NaI from water to the water-isobutanol system calculated on the basis of data from papers^{19,20}, we determined the standard entropy of transfer (ΔS_i°) of NaI in the system under investigation:

$$\Delta S_i^\circ = \frac{\Delta H_i^\circ - \Delta G_i^\circ}{T} \quad (11)$$

The results of the calculation are also recorded in Table 6.

Based on the corrected values of ΔH_i° of NaI, we have calculated "corrected" enthalpy and entropy of transfer of NaI from water to the water-isobutanol mixtures. The obtained results are listed together with ΔG_i° in Table 6 and in Figure 5.

It follows from these data, that both the enthalpy and entropy of transfer of NaI from water to the water-isobutanol systems show the increasing tendency due to adding a small amount of alcohol that is typical for other water-alcohol mixtures.

In the immiscibility gap of the investigated system the maxima of enthalpy and entropy are observed in the other water-alcohol mixtures. In the isobutanol rich region (in the miscibility range), ΔS_i° and ΔH_i° are gradually decreasing. However, ΔH_i° show minima at ca. 85 mol % of isobutanol. The free enthalpy of transfer varies monotonically over the investigated range of the mixture composition. This results from the commonly observed compensation of the entropic and enthalpic effects in electrolyte solutions.^{9-16,37,38} As seen from the above mentioned results, for electrolyte solutions in which ion association processes can occur, their presence must be taken into consideration, in order to determine corrected values of thermodynamic

Table 6 Thermodynamic function of transfer of NaI from water to water-isobutanol mixtures at 298.15 K.

<i>mol %</i> <i>i-BuOH</i>	ΔG_i° ($J \text{ mol}^{-1}$)	ΔH_i° ($J \text{ mol}^{-1}$)	$\Delta H_{i(\text{corr.})}^\circ$ ($J \text{ mol}^{-1}$)	ΔS_i° ($J \text{ mol}^{-1} \text{ K}^{-1}$)	$\Delta S_{i(\text{corr.})}^\circ$ ($J \text{ mol}^{-1} \text{ K}^{-1}$)
1.38	740	1950		4.1	
74.20	27410	-22790	-26830	-168.4	-181.9
79.60	29630	-23070	-27860	-176.8	-192.8
87.80	33630	-23090	-29300	-190.2	-211.1
96.80	39200	-22460	-27640	-206.8	-224.2
100.00	41980	-20530	-25570	-209.6	-226.6

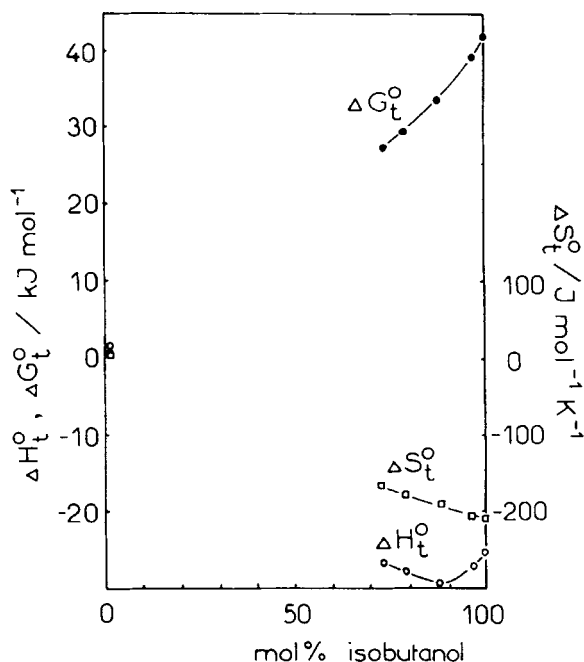


Figure 5 Free enthalpy of transfer (ΔG_t^0), enthalpy (ΔH_t^0) and entropy of transfer (ΔS_t^0) of NaI from water to water-isobutanol mixtures at 298.15 K. ●— ΔG_t^0 , ○— ΔH_t^0 , and □— ΔS_t^0 .

function of solvation. The omission of the ionic association process during determination of thermodynamic functions leads to very important errors. Moreover, the use of uncorrected results may lead to misleading conclusions, because these errors are usually much larger than the experimental ones.

The above mentioned considerations lead us to the further studies on the influence of ionic association on the value of thermodynamic function of transfer. Appropriate studies are already under way and results will be reported in a subsequent paper.

Acknowledgement

This work is dedicated to Professor Zygmunt Kozłowski on the occasion of his 70th birthday. This research was sponsored by Polish Ministry of National Education.

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