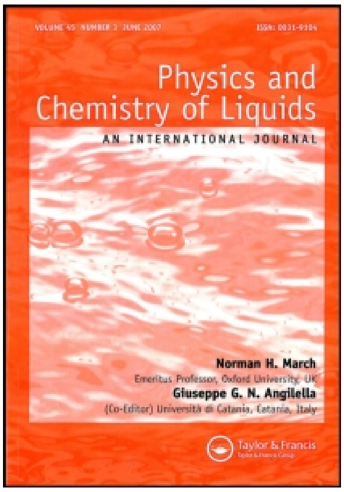

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Electrical Conductivity of NaI Solutions in Methanol—*n*-Propanol and Methanol—Isopropanol Mixtures at 298.15 K The Effect of Ion Association on the Standard Dissolution Enthalpies of NaI

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ELECTRICAL CONDUCTIVITY OF NaI SOLUTIONS IN METHANOL–*n*-PROPANOL AND METHANOL–ISOPROPANOL MIXTURES AT 298.15 K

The Effect of Ion Association on the Standard Dissolution Enthalpies of NaI

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The electrical conductivity of NaI solutions in binary methanol-*n*-propanol and methanol–isopropanol mixtures within the whole composition range has been measured and analysed using the Fuoss–Justice equation. The dependence of the equilibrium constants of ion-pair formation and the Walden products on the mixed solvents composition in studied systems has been discussed. The standard dissolution enthalpies of NaI in the same binary mixtures (published earlier) have been recalculated taking into account the ion-association process.

KEY WORDS: Equilibrium constants. Dissolution enthalpies. NaI solution enthalpy, Methanol-*n*-Propanol, Methanol-Isopropanol.

Much attention has been recently devoted to studies on electric conductance in water-organic and organic-organic mixed solvents. The results of these studies together with the results of experiments performed by means of other methods allow to observe the behaviour of ions in solutions as well as to analyse the influence of the mixed solvent properties and structure on ionic solvation process and ionic interactions.

The complex investigations of electrolyte solutions in mixed solvents have been carried out in our laboratory for many years. For this purpose we have used different experimental technics, such as calorimetry, viscosimetry and conductometry. Recently we have measured electric conductivity and determined the ion-association constant for NaI in *n*-propanol-*n*-butanol mixtures.[1] Additionally, we have performed the calorimetric measurements of dissolution enthalpy of NaI in the same mixtures.[2]

Continuing these studies we have decided to investigate the influence of alcohol molecule branching on electrolytic conductance of NaI solutions and NaI ion-association in a mixed alcoholic solvent. Methanol-*n*-propanol and methanol–isopropanol mixtures have been chosen as the mixed solvents. The systems mentioned above have already been examined calorimetrically.[3] We measured the dissolution enthalpies, ΔH_s NaI in the mixtures of methanol with *n*-propanol and with isopropanol within the whole composition range of the mixed solvent. Then the standard dissolution enthalpies, ΔH_s^0 (dissolution enthalpy in infinitely diluted solution) of NaI were determined using the extrapolation procedure as proposed by Criss and Cobble.[4]

It appeared that the standard solution enthalpy of NaI in each system exhibited distinct maximum in the range of small methanol content in contrast to other investigated systems containing two aliphatic alcohols (i.e. methanol–ethanol[3] and *n*-propanol-*n*-butanol[2]), in which the monotonous course of the dissolution enthalpy was observed. We expressed a supposition that the mentioned maxima of ΔH_s^0 appeared because in the range of high *n*-propanol or isopropanol content in the mixture with methanol there arose mixed aggregates or a lattice structure leading to the medium becoming more ordered or rigid.[3] However, since the Criss and Cobble method of ΔH_s^0 determination employed there did not encompass the ion-association process we could not exclude that the maxima of ΔH_s^0 were joined with the effect of the ion pair formation. The conductometric measurements leading to the determination of the ion pairing equilibrium constant will enable us to recalculate the NaI standard dissolution enthalpy regarding the ionic association in the system and to verify the conclusions presented above.

EXPERIMENTAL

The reagents used, NaI, Merck suprapur and methanol, *n*-propanol and isopropanol were purified and dried using the methods described in the previous papers.[2,3] The electric conductivities of the pure solvents were less than 1×10^{-7} ohm cm^{-1}. All the solutions were prepared gravimetrically.

Apparatus: The measurements of the conductivity were performed by means of E-315 A type bridge produced by "Mera-Tronic", Poland. A measuring cell similar to the Jones type vessel and connected with a 350 cm^3 Erlenmayer flask was used. The cell was made of Pyrex glass. The cell was equipped with a stirrer made of teflon and platinum, enabling the mixing of the solution components. The measuring cell was immersed into a thermostated bath keeping the temperature constant within 0.005 deg. Nujol was used as a thermostat liquid. The measuring procedure was described in detail elsewhere.[5] Taking into account the reagents purity, equipment, method of measurements and accuracy of the temperature control, the uncertainty of the measured values was less than 0.05 per cent.

The relative permittivity, ε of methanol-*n*-propanol and methanol-isopropanol mixtures was measured using the heterodyne-beat type dielectrometer with digital frequency readout constructed in the Institute of Chemistry, University of Łódź. The basic frequency was about 5 MHz. The temperature of the solution in the cell was kept constant within 0.01 deg by circulating thermostated water. The accuracy of the measurements corresponded to 0.02–0.05 units.

The densities and viscosities of some of investigated mixtures were measured—when necessary—using the methods presented earlier.[6,7]

RESULTS AND DISCUSSION

The measured molar conductivities, Λ of NaI solutions in methanol-*n*-propanol mixtures at 298.15 K are presented in Table 1 and those for NaI in methanol-isopropanol mixtures in Table 2, both as a function of the electrolyte concentration. The conductance data were analysed using the Fuoss-Justice equation[8] in the form:

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + I(\alpha c) + I_{3/2}(\alpha c)^{3/2}] \tag{1}$$

and:

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

$$\gamma_\pm = \exp\left(-\frac{A(\alpha c)^{1/2}}{1 + Bq(\alpha c)^{1/2}}\right) \tag{3}$$

$$q = e^2/B\pi\varepsilon_0\varepsilon kT \tag{4}$$

In these equations Λ_0 is the limiting conductivity, $(1-\alpha)$ is the fraction of an electrolyte acting as ion pairs, K_A is the ion association constant and $\gamma_\pm$ is mean activity coefficient of the dissociated part of an electrolyte; (the activity coefficient of the ion-pairs is assumed to be equal to unity as usual for diluted solutions). A and B are the Debye-Hückel equation coefficients. The analytical form of the remaining parameters, i.e.: S, E, I, and $I_{3/2}$ is presented elsewhere.[8-12] Following the Fuoss proposal[13] the Bjerrum's characteristic distance, q (Eq. 4) was assumed as the closest approach distance, similarly as it was done in the previous paper.[1] In this way, equation 1 became a diparametric one and it was resolved by the least squares method.[14,15] The determined Λ_0, K_A and their standard deviations as well as the Bjerrum's parameter-q values are collected in Tables 3 and 4. The solvent density (ρ_0), relative permittivity (ε) and viscosity (η_0) necessary for the calculations are given in Tables 5–9.

The limiting molar conductance, Λ_0 and the ionic association constant, K_A of NaI in methanol-*n*-propanol and methanol-isopropanol mixtures as a function of the mixed solvent composition are presented in Figures 1 and 2.

As it can be seen from these graphs, the Λ_0 decreases and K_A increases along with the growing of the propanol and isopropanol content in the mixtures.

Figure 3 shows the Walden product for NaI in methanol-*n*-propanol and methanol -isopropanol mixtures at 298.15 K. The presented function exhibits a maximum in methanol-rich region followed by a gradual decrease as the methanol content drops down in both investigated systems. The presence of these maxima means that the

Table 1 Molar conductances of NaI in methanol-*n*-propanol mixtures at 298.15 K.*

10⁴c	Λ	*10⁴c*	Λ	*10⁴c*	Λ	*10⁴c*	Λ	*10⁴c*	Λ	*10⁴c*	Λ
0 mol % *n*-Pr		5 mol % *n*-Pr		10 mol % *n*-Pr		50 mol % *n*-Pr		60 mol % *n*-Pr		70 mol % *n*-Pr	
1.1257	105.25	1.2278	97.36	3.5183	85.96	0.7635	48.31	1.4035	41.75	1.2569	35.65
2.1074	104.25	2.1678	96.49	4.7379	85.32	1.3325	47.82	1.8710	41.43	1.9348	35.21
3.0839	103.46	2.9715	95.90	5.3944	85.00	1.9369	47.40	2.5367	41.02	2.3749	34.96
4.5631	102.51	4.0888	95.22	7.0306	84.28	2.9659	46.81	3.2076	40.67	3.0897	34.59
6.0644	101.71	5.2293	94.60	9.2427	83.45	3.8150	46.39	3.7376	40.42	3.5376	34.40
7.1452	101.19	6.8657	93.83	13.461	82.14	4.5514	46.07	4.9239	39.91	4.8838	33.86
9.2307	100.31	8.6682	93.11	15.471	81.61	6.1254	45.45	5.9946	39.52	6.0087	33.46
11.710	99.39	10.410	92.47	19.781	80.59	7.5164	44.98	7.1744	39.13	7.0898	33.13
13.829	98.68	12.121	91.91	23.574	79.80	8.8711	44.59	8.2936	38.79	8.2391	32.81
16.316	97.96	15.379	90.99	27.630	79.06	10.441	44.15	10.557	38.19	10.751	32.16
20.256	96.89	18.735	90.14	31.281	78.43	13.487	43.43	12.703	37.68	12.825	31.71
		21.495	89.52	36.893	77.58	16.460	42.81	16.818	36.84		
		24.691	88.85			18.970	42.33				
		30.283	87.81			21.726	41.85				
						25.768	41.22				
20 mol % *n*-Pr		30 mol % *n*-Pr		40 mol % *n*-Pr		80 mol % *n*-Pr		90 mol % *n*-Pr		95 mol % *n*-Pr	
1.8586	75.58	2.7062	63.73	1.1300	56.79	1.2537	30.66	1.2672	26.27	1.8645	24.08
2.7426	74.96	3.4261	63.32	1.5647	56.41	1.9547	30.23	1.6970	26.00	2.5716	23.72
3.5513	74.48	4.5901	62.75	2.2311	55.96	2.7469	29.79	2.4371	25.61	3.1996	23.42
5.6133	73.43	5.5620	62.32	2.6727	55.68	3.5056	29.46	3.5988	25.10	3.6867	23.24
7.3976	72.67	6.4440	61.98	4.3088	54.81	4.1346	29.21	5.2940	24.49	4.8716	22.80
9.1868	72.04	7.3451	61.65	5.3185	54.37	5.4955	28.72	7.9671	23.72	5.8888	22.47
10.928	71.48	9.6816	60.89	6.3821	53.93	6.8307	28.31	9.1060	23.43	7.2919	22.07
12.743	70.96	11.236	60.44	7.3657	53.58	8.2088	27.91	11.534	22.91	8.3962	21.80
16.203	70.09	13.358	59.89	9.2589	52.96	9.4142	27.61	14.150	22.40	10.439	21.31
19.711	69.27	14.789	59.55	11.202	52.41	11.965	27.02	18.782	21.67	12.541	20.91
22.866	68.63	18.511	58.74	13.186	51.89	14.321	26.57				
26.043	68.06	22.103	58.05	14.938	51.47	16.862	26.13				
31.233	67.18	25.147	57.52	18.261	50.77	19.172	25.76				
		28.299	57.01			22.808	25.25				
		33.270	56.29								

* Units: c in mol · dm^{-3}, Λ in $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$.

Table 2 Molar conductances of NaI in methanol–isopropanol mixtures at 298.15 K.*

10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
10 mol % *i*-Pr		20 mol % *i*-Pr		30 mol % *i*-Pr		70 mol % *i*-Pr		80 mol % *i*-Pr		90 mol % *i*-Pr	
1.3427	84.19	2.7174	72.52	1.8737	61.86	3.1700	31.17	1.3578	27.25	2.2370	22.58
2.9745	82.92	3.9003	71.84	2.9680	61.15	5.5322	30.16	2.0987	26.76	4.3858	21.41
4.4343	82.06	5.0755	71.29	4.5008	60.36	7.9415	29.33	3.0421	26.22	6.6398	20.48
6.4286	81.10	6.6336	70.60	5.7570	59.80	9.6286	28.84	4.0931	25.71	8.7643	19.78
9.3363	79.97	8.4574	69.93	7.1011	59.28	11.957	28.25	5.3824	25.18	11.715	18.98
11.001	79.42	11.304	69.02	9.3605	58.52	14.771	27.62	6.8620	24.67	13.476	18.59
16.748	77.83	13.786	68.36	11.837	57.81	19.025	26.82	9.1149	23.95	18.805	17.57
21.146	76.80	16.124	67.79	14.198	57.24	23.533	26.12	10.638	23.54	22.452	17.00
24.634	76.10	20.628	66.80	16.716	56.67	27.751	25.54	12.751	23.07	31.143	15.94
28.600	75.38	24.989	66.01	21.190	55.80	40.567	24.08	15.845	22.40		
36.363	74.15	29.470	65.27	25.563	55.04			19.066	21.84		
43.367	73.18	33.563	64.63	29.848	54.39			22.490	21.31		
								25.641	20.88		
								31.160	20.22		
40 mol % *i*-Pr		50 mol % *i*-Pr		60 mol % *i*-Pr		93 mol % *i*-Pr		95 mol % *i*-Pr		100 mol % *i*-Pr	
3.7912	51.40	1.9199	44.24	3.1870	37.03	1.7509	21.64	1.3962	21.18	1.2708	19.37
6.5926	50.23	3.2546	43.46	5.8090	35.90	2.2950	21.25	2.1224	20.62	1.9920	18.76
8.8917	49.47	3.9499	43.14	8.6954	34.98	3.2061	20.70	4.9023	19.10	4.2056	17.38
11.982	48.57	4.8971	42.74	10.691	34.43	4.0582	20.24	7.2203	18.20	6.8161	16.26
14.086	48.07	5.4753	42.50	13.766	33.67	5.1394	19.74	9.0223	17.63	9.0336	15.53
16.863	47.42	7.5655	41.78	15.952	33.22	6.6682	19.14	11.793	16.89	11.565	14.85
21.731	46.53	9.2663	41.26	17.946	32.84	8.2778	18.60	14.811	16.24	13.956	14.31
27.229	45.65	10.890	40.84	20.343	32.42	9.9287	18.12	17.039	15.82	16.786	13.77
31.709	44.96	12.283	40.49	24.562	31.77	11.829	17.64	22.393	14.97	21.576	13.03
36.488	44.34	16.216	39.65	29.532	31.09	15.068	16.92	27.162	14.37	27.012	12.35
		19.639	39.00	34.134	30.53	18.248	16.34	32.158	13.83		
		22.693	38.46	41.677	29.70	21.077	15.89	36.591	13.41		
		25.671	38.02			23.836	15.51				
		29.054	37.52			28.509	14.93				

* Units: c in mol · dm^{-3}, Λ in cm^2 · mol^{-1} · ohm^{-1}.

Table 3 Limiting molar conductance, Λ_0 in ($\mathrm{cm^2 \cdot mol^{-1} \cdot ohm^{-1}}$), ionic association constant, K_A in ($\mathrm{dm^3 \cdot mol^{-1}}$) and Bjerrum's characteristic distance, q in (cm) for NaI in methanol-*n*-propanol mixtures at 298.15 K.

mol % Pr	Λ_0	$\delta\Lambda_0$	K_A	δK_A	$10^8 q$
0	107.95	±0.01	14.9	±0.1	8.55
5	99.95	±0.01	16.0	±0.1	8.86
10	90.09	±0.01	20.1	±0.1	9.18
20	78.32	±0.01	30.4	±0.1	9.80
30	66.79	±0.01	38.0	±0.1	10.38
40	58.63	±0.01	53.6	±0.2	10.97
50	49.69	±0.01	64.1	±0.1	11.52
60	43.58	±0.01	82.2	±0.4	12.05
70	37.28	±0.01	99.9	±0.3	12.53
80	32.21	±0.01	125.4	±0.3	12.99
90	27.76	±0.01	155.0	±0.3	13.42
95	25.91	±0.01	175.5	±0.7	13.62
100	24.29[a]	—	205.3[a]	—	—

[a] Ref. (15).

Table 4 Limiting molar conductance, Λ_0 in ($\mathrm{cm^2 \cdot mol^{-1} \cdot ohm^{-1}}$), ionic association constant, K_A in ($\mathrm{dm^3 \cdot mol^{-1}}$) and Bjerrum's characteristic distance, q in (cm) for NaI in methanol-isopropanol mixtures at 298.15 K.

mol % i-Pr	Λ_0	$\delta\Lambda_0$	K_A	δK_A	$10^8 q$
10	86.80	±0.01	20.4	±0.1	9.24
20	76.03	±0.01	25.5	±0.1	9.91
30	64.54	±0.01	35.3	±0.1	10.56
40	55.07	±0.01	51.9	±0.2	11.18
50	46.64	±0.01	68.2	±0.2	11.79
60	40.03	±0.01	96.1	±0.3	12.36
70	34.11	±0.01	137.5	±0.3	12.92
80	29.06	±0.01	195.9	±0.5	13.46
90	25.11	±0.01	313.4	±0.7	13.97
93	23.87	±0.01	364.1	±0.3	14.13
95	23.14	±0.01	393.3	±0.3	14.22
100	21.33	±0.01	527.7	±0.5	14.46

limiting conductance of the solutions decreases more slowly along with growing of each of the propanols content in the mixture than it would be expected from the increase of viscosity of the mixed solvent in methanol-rich region. The main factor of this behaviour can be in our opinion a "sorting effect".[18] Following Kay and Broadwater's explanation of the appearance of analogous $\Lambda\eta_0$ maxima in tert-butanol-water mixtures it can be supposed that in the solutions containing a large amount of methanol in the mixtures with *n*-propanol or isopropanol there is a greater percentage of methanol in ionic solvation shells than in the bulk mixture. As a result, the viscosity would be considerably smaller than the bulk viscosity, and the ion

Table 5 Density ρ_0 in ($g \cdot cm^{-3}$) of methanol-*n*-propanol mixtures at at 298.15 K.

mol % n-Pr	ρ_0	$\frac{\delta \ln \rho_0}{\delta T}$[a]
0	0.7864	−0.001174
5	0.7872	−0.001160
10	0.7879	−0.001146
20	0.7895	−0.001122
30	0.7911	−0.001102
40	0.7926	−0.001085
50	0.7939	−0.001072
60	0.7951	−0.001063
70	0.7962	−0.001057
80	0.7972	−0.001056
90	0.7982	−0.001058
93	0.7986	−0.001059
95	0.7988	−0.001061
97	0.7990	−0.001062
100	0.7993	−0.001064

[a] Interpolated data from Ref. 16.

Table 6 Density ρ_0 in ($g \cdot cm^{-3}$) of methanol–isopropanol mixtures.

mol %i-Pr	ρ_0				$\frac{\delta \ln \rho_0}{\delta T}$
	288.15 K	*298.15 K*	*308.15 K*	*318.15 K*	
0	—	0.7864	—	—	−0.001174[a]
5	0.7952	0.7859	0.7765	0.7675	−0.001183
7	0.7950	0.7857	0.7762	0.7672	−0.001189
10	0.7943	0.7854	0.7760	0.7668	−0.001177
20	0.7931	0.7846	0.7750	0.7660	−0.001166
30	0.7922	0.7838	0.7744	0.7652	−0.001161
40	0.7914	0.7831	0.7738	0.7646	−0.001153
50	0.7907	0.7826	0.7733	0.7641	−0.001146
60	0.7902	0.7821	0.7730	0.7638	−0.001136
70	0.7898	0.7817	0.7726	0.7634	−0.001137
80	0.7894	0.7814	0.7723	0.7632	−0.001130
90	0.7890	0.7811	0.7721	0.7630	−0.001121
93	0.7890	0.7810	0.7720	0.7629	−0.001125
95	0.7889	0.7810	0.7720	0.7629	−0.001121
97	0.7889	0.7810	0.7719	0.7629	−0.001122
100	0.7888	0.7810	0.7718	0.7628	−0.001124

[a] Calculated from the data in Ref. 16.

moving in a medium of lower viscosity would appear to have an excess mobility.[18] The above supposition agrees very well with the conclusions arising from our previous thermochemical studies[3] that in the case of solutions with high methanol content the salt is solvated primarily by methanol. Having at our disposal the presented above conductometric data we decided, as it was mentioned earlier, to redetermine

Table 7 Dielectric properties of methanol-*n*-propanol mixtures at different temperatures.

mol % Pr	ε					$\frac{\delta \ln \varepsilon}{\delta T}$
	288.15 K	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	
0	34.66	33.73	32.78	31.84	30.88	−0.00577
3	33.91	33.00	32.07	31.11	30.27	−0.00572
5	33.43	32.53	31.61	30.68	29.86	−0.00569
7	32.97	32.07	31.17	30.26	29.45	−0.00568
10	32.20	31.42	30.53	29.65	28.87	−0.00565
20	30.28	29.43	28.59	27.79	27.06	−0.00564
30	28.55	27.73	26.95	26.18	25.46	−0.00573
40	27.08	26.27	25.53	24.79	24.08	−0.00586
50	25.81	25.03	24.32	23.59	22.89	−0.00599
60	24.73	23.96	23.27	22.56	21.87	−0.00612
70	23.80	23.04	22.36	21.67	21.01	−0.00621
80	23.00	22.25	21.57	20.89	20.26	−0.00634
90	22.29	21.56	20.88	20.21	19.59	−0.00646
93	22.10	21.37	20.69	20.02	19.39	−0.00654
95	21.97	21.25	20.57	19.90	19.26	−0.00658
97	21.85	21.13	20.45	19.77	19.13	−0.00665
100	21.67	20.96	20.28	19.59	18.94	−0.00674

Table 8 Dielectric properties of methanol–isopropanol mixtures at different temperatures.

mol % i-Pr	ε					$\frac{\delta \ln \varepsilon}{\delta T}$
	288.15 K	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	
0	34.66	33.73	32.78	31.84	30.88	−0.00577
3	33.87	32.94	31.99	31.11	30.18	−0.00576
5	33.36	32.43	31.50	30.64	29.73	−0.00574
7	32.87	31.94	31.02	30.18	29.28	−0.00576
10	32.16	31.24	30.33	29.52	28.64	−0.00577
20	30.02	29.15	28.28	27.52	26.70	−0.00584
30	28.19	27.37	26.54	25.79	25.01	−0.00598
40	26.61	25.85	25.05	24.30	23.56	−0.00611
50	25.26	24.55	23.77	23.02	22.30	−0.00627
60	24.09	23.41	22.66	21.91	21.22	−0.00640
70	23.10	22.42	21.68	20.95	20.27	−0.00658
80	22.27	21.57	20.81	20.10	19.41	−0.00691
90	21.60	20.85	20.05	19.33	18.59	−0.00752
93	21.40	20.67	19.84	19.11	18.35	−0.00778
95	21.33	20.55	19.71	18.97	18.19	−0.00797
97	21.24	20.44	19.58	18.82	18.02	−0.00822
100	21.10	20.29	19.38	18.62	17.77	−0.00859

Table 9 Viscosity η_0 in (cP) of methanol-*n*-propanol and methanol-isopropanol mixtures at 298.15 K.

mol % Pr	η_0	
	MeOH-n-PrOH[a]	*MeOH-i-PrOH*
0	0.535	0.535
5	0.620	0.600
10	0.704	0.648
20	0.867	0.746
30	1.025	0.860
40	1.177	0.994
50	1.324	1.142
60	1.466	1.296
70	1.602	1.452
80	1.733	1.617
90	1.858	1.810
93	1.895	1.879
95	1.919	1.929
100	1.979	2.072

[a] Interpolated data from Ref. 17.

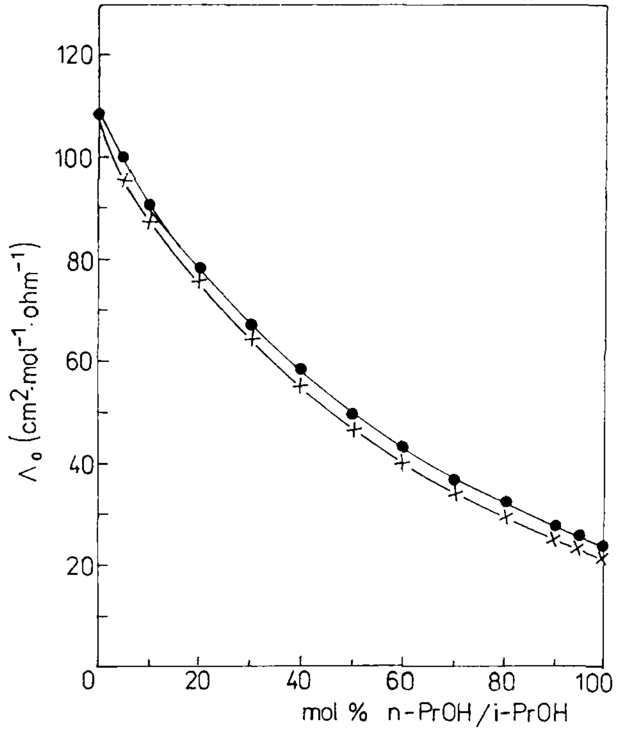

Figure 1 Limiting molar conductance, Λ_0 for NaI in methanol-*n*-propanol (●) and methanol-isopropanol (×) mixtures at 298.15 K.

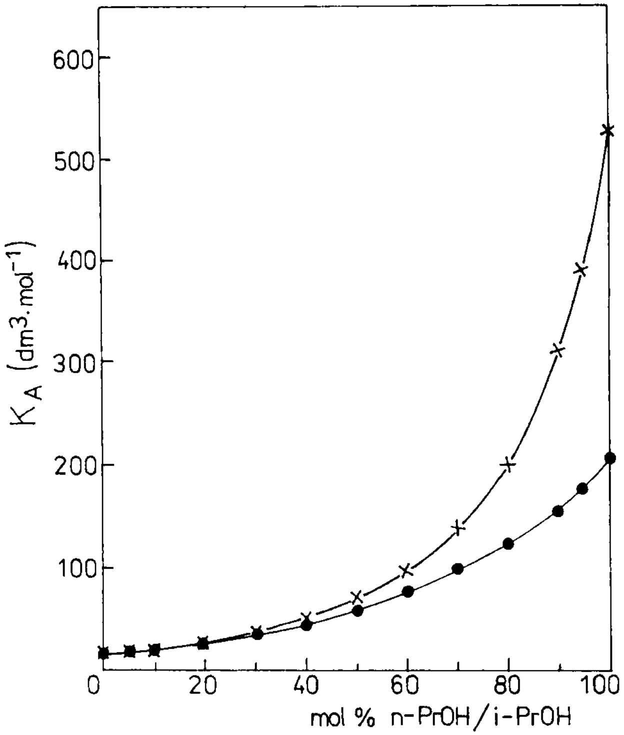

Figure 2 Ionic-association constant, K_A, for NaI in methanol-*n*-propanol (●) and methanol–isopropanol (×) mixtures at 298.15 K.

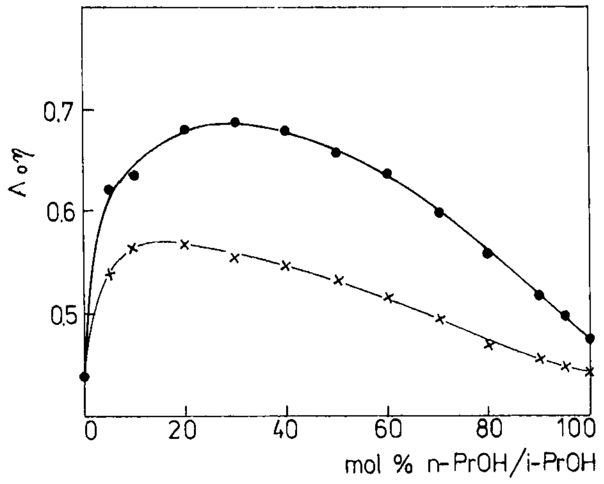

Figure 3 Limiting conductance-viscosity product, $\Lambda_0\eta$ for NaI in methanol-*n*-propanol (●) and methanol–isopropanol (×) mixtures at 298.15 K.

the standard dissolution enthalpy of NaI in methanol-*n*-propanol and methanol–isopropanol mixtures (see Ref. 2) taking into account the ionic association process. To this end the method of calculation based on the model presented in the paper of Barthel and coworkers[11] was employed. According to this method the relative apparent molal heat content of solution containing "free ions" (FI) and ion pairs is presented as a sum:

$$\Phi_L = \alpha\Phi_L(\text{FI}) + (1 - \alpha)\Delta H_A^0 \tag{5}$$

where $\Phi_L(\text{FI})$ is the relative apparent molal heat content of the solution with the "free ions", ΔH_A^0 denotes the enthalpy of ion pair formation and α is the degree of dissociation. Since:

$$\Phi_L = -\Delta H_{\text{DIL}}^0 = \Delta H_s - \Delta H_s^0 \tag{6}$$

it can be written

$$\Delta H_s - \alpha\Phi_L(\text{FI}) = \Delta H_s^0 + (1 - \alpha)\Delta H_A^0 \tag{7}$$

where ΔH_s is the experimentally determined molal enthalpy of electrolyte dissolution at given molality *m*. The $\Phi_L(\text{FI})$ values were calculated using the equation proposed by Barthel *et al.*[11] The necessary values of the electrolyte dissociation degree were obtained from conductometric measurements. Therefore, the left hand side of Eq. (7) can be calculated using the experimental data:

$$\delta = \Delta H_s - \alpha\Phi_L(\text{FI}) \tag{8}$$

Plotting the δ as a function of $(1 - \alpha)$ we obtain for each examined mixture a straight-line dependence:

$$\delta = \Delta H_s^0 + (1 - \alpha)\Delta H_A^0 \tag{9}$$

that extrapolated to $(1 - \alpha)$ equal to zero gives the standard dissolution enthalpy ΔH_s^0. The slope of the function is equal to the enthalpy of ionic association ΔH_A^0.

The redetermined standard enthalpies of NaI solution in the mixtures of methanol with *n*-propanol and with isopropanol are presented in Table 10. Moreover in Figure

Table 10 "Corrected" standard solution enthalpies, ΔH_s^0 for NaI in methanol-*n*-propanol and methanol–isopropanol mixtures at 298.15 K.

X *mol%*	$\Delta H_s^0/kJ\cdot mol^{-1}$	
	(100 − X)MeOH + X n-PrOH	*(100 − X)MeOH + X i-PrOH*
0	−31.96 ± 0.11	−31.96 ± 0.11
10	−31.62 ± 0.06	−31.56 ± 0.07
20	−31.29 ± 0.27	−30.80 ± 0.23
30	−30.54 ± 0.05	−30.14 ± 0.02
40	−29.93 ± 0.20	−29.44 ± 0.26
50	−29.27 ± 0.08	−28.49 ± 0.01
60	—	−26.73 ± 0.05
70	−27.66 ± 0.09	−24.97 ± 0.36
80	−26.54 ± 0.06	−23.86 ± 0.43
90	−25.44 ± 0.04	−23.55 ± 0.41
95	−24.58 ± 0.08	−25.80 ± 0.17
100	−26.36 ± 0.11	−28.96 ± 0.05

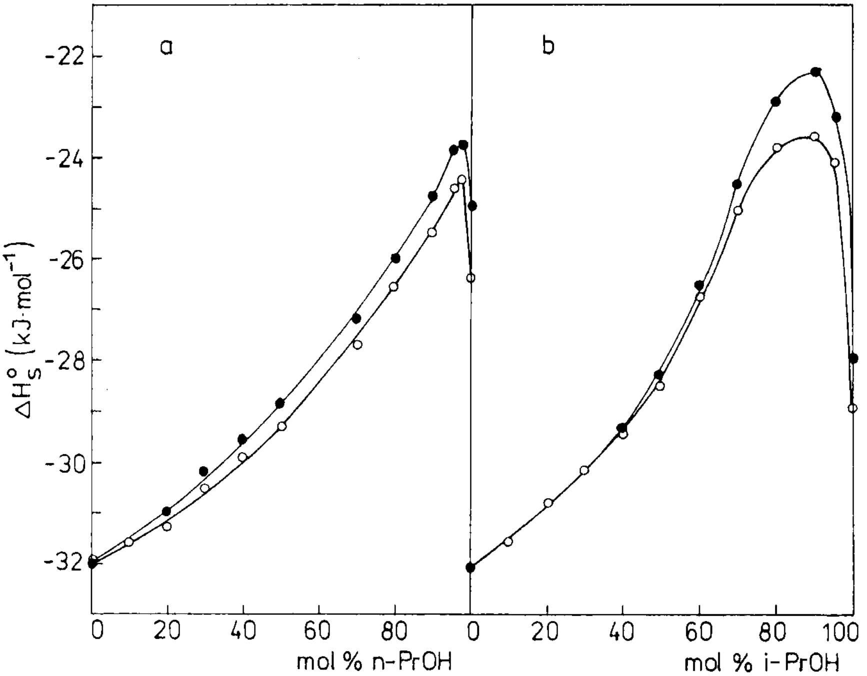

Figure 4 "Corrected" (○) and "uncorrected" (●) standard solution enthalpies, ΔH_s^0 of NaI in (a) methanol-*n*-propanol and (b) methanol–isopropanol mixtures at 298.15 K.

4 the corrected values of ΔH_s^0 are plotted as a function of the mixed solvent composition and compared with those extrapolated with the use of the already mentioned Criss and Cobble method.[4]

The unchanged shape of the $\Delta H_s^0 = f$ (solvent composition) curves and still present differences in the course of the analysed function for both mixtures in propanol-rich region suggest that the presence of the maximum of ΔH_s^0 as well as the mentioned differences are not connected, at least directly, with the ionic association of NaI in the mixtures under discussion. The different structure of both examined mixtures in the region of low methanol content seems to be the main reason of the observed phenomena.

The following observation can confirm the presented conclusion: As it is known, according to the Fuoss equation[12] the logarithm of the ion-association equilibrium constant should be a linear function of the reciprocal of solvent electric permittivity:

$$\log K_A = m + n \cdot (1/\varepsilon) \qquad (10)$$

The expected straight-line dependence is observed (Figure 5) for both investigated systems within a wide range of the mixed solvent composition. However, the separate lines characterize each of the systems. It can indicate that the growth of the ion-association constant in these, apparently so similar systems, is not only due to

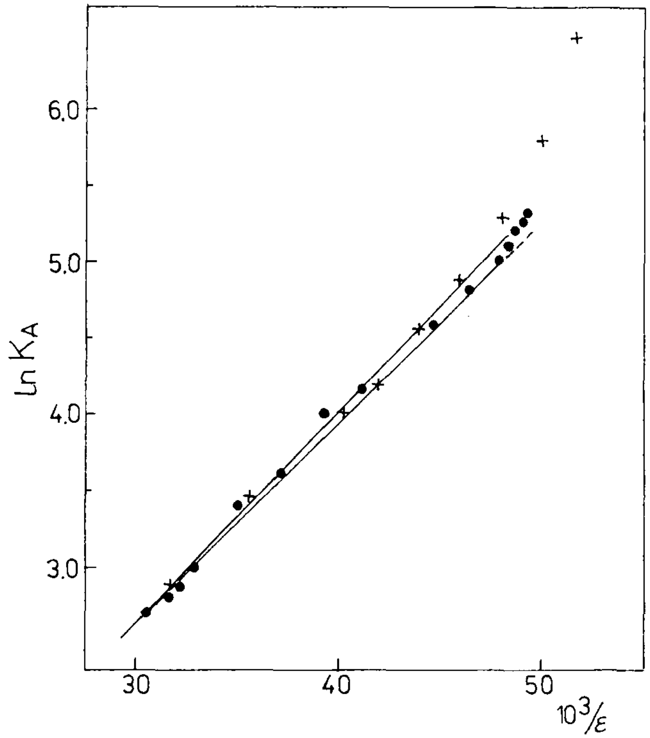

Figure 5 Logarithm of the ionic-association constant as a function of reciprocal of solvent electric permittivity for NaI solutions in methanol-*n*-propanol (●) and methanol–isopropanol (×) mixtures.

the decreasing electric permittivity but also to a change in solvent-ion or solvent-solvent interactions that are different in both mixtures.

In the range of high $1/\varepsilon$ values, that corresponds to low methanol content in the mixture, the distinct inclination of log K_A is observed. This can be due to the change in ionic solvation process caused by a drastic change in the mixed solvent structure. It should be noted that the position of the log K_A function inclination is close to the position of the maxima of NaI standard dissolution enthalpies.

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