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Conductometric Studies of Sodium Iodide, Sodium Tetraphenylborate, Tetrabutylammonium Iodide, and Sodium Tetrafluoroborate in 1-Propanol at Temperatures from (283.15 to 318.15) K

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The electrical conductances of dilute solutions of sodium iodide (NaI), sodium tetraphenylborate ($NaBPh_4$), tetrabutylammonium iodide (Bu_4NI), and sodium tetrafluoroborate ($NaBF_4$) in 1-propanol have been measured over the temperature range from (283.15 to 318.15). The ionic association constant, K_A, limiting molar conductances, Λ_o, and distance parameters, R, were obtained using the low concentration Chemical Model (lcCM). The smallest tendency to form ion pairs exhibits $NaBPh_4$. NaI is more associated electrolyte, Bu_4NI and particularly $NaBF_4$ are strongly associated in 1-propanol at all experimental temperatures. From the temperature dependence of the limiting molar conductivities the Eyring's activation enthalpy of charge transport was determined. The thermodynamic functions such as Gibbs energy, entropy, and enthalpy of the process of ion pair formation were calculated from the temperature dependence of the association constants. The limiting ionic conductivities and the activation enthalpy of charge transfer for these ions were estimated.

Keywords: electrolyte conductance, 1-propanol, ion association, thermodynamic functions

1. INTRODUCTION

The conductivity properties of electrolytes in various solvents are a subject of our interest for many years. In our previous paper [1], we have reported the results of the conductance measurements of sodium tetraphenylborate, tetrabutylammonium bromide, and sodium tetrafluoroborate in *N*,*N*-dimethylformamide solutions. Slight ion association was found for the examined salts in this dipolar aprotic solvent (ε_r = 36.81 at 298.15 K [2]) in the whole investigated temperature range. In this paper, we decided to study the ionic association and solvation phenomenon in protic solvent as 1-propanol (ε_r

= 20.45 at 298.15 K [3]) as a function of the temperature. This type of study allow us to understand the behavior of electrolytes in solution. A survey of the literature indicates that the electrical conductances of these electrolytes in 1-propanol as a function of the temperature have not been studied in a systematic way so far. Barthel et al. [4] have reported conductance data of tetrabutylammonium iodide and sodium iodide in 1-propanol, but in the other temperature range (-40, -30, -20, -10, 0, 10, and 25°C).

Continuing our studies on electrical conductivity, in this paper, precise conductivity measurements have been carried out for dilute solutions of NaI, $NaBPh_4$, Bu_4NI, and $NaBF_4$ in 1-propanol at T = (283.15 to 318.15) K. The choice of these electrolytes was mainly due to the fact that $NaBPh_4$, Bu_4NI and NaI can be used to split the limiting molar conductances into their ionic components. The values of limiting molar conductances of $NaBF_4$ was necessary to split the Λ_o values for the ionic liquids studied in our earlier work [5]. The obtained data were used to calculate the values of the limiting molar conductances, Λ_o, the association constants, K_A, and distance parameters, R. The Gibbs free energy, ΔG^o_A, enthalpy, ΔH^o_A, and entropy, ΔS^o_A, of ion pair formation as well as the Eyring activation enthalpy of charge transport, $\Delta H^{\ddagger}_{\lambda}$, for the electrolytes have been evaluated. A more accurate description of conductivity properties of the electrolyte and the interactions of ions with the molecules of solvent will be possible, when the analysis of the conductivity data for individual ions is made. In order to determine ionic conductivities, we used the Fuoss-Hirsch assumption about equality of ionic mobilities for Bu_4N^+ and BPh_4^- [6]. On the basis of the limiting ionic conductivities, the activation enthalpy of charge transport for ions was obtained.

2. EXPERIMENTAL

2.1. Reagents and chemicals

The specifications of used chemicals are summarized in Table 1.

Table 1. Specification of chemical samples

chemical name	source	initial mass fraction purity	purification method
1-PrOH	Aldrich	0.997	none
NaI	Aldrich	0.995	none
$NaBPh_4$	Aldrich	0.995	none
Bu_4NI	Aldrich	≥0.990	recrystallization
$NaBF_4$	Aldrich	≥0.980	recrystallization

Sodium tetraphenylborate and sodium iodide were dried in vacuo at 353.15 K, tetrabutylammonium iodide and sodium tetrafluoroborate at 333.15 and 373.15 K, respectively.

2.2. Apparatus

All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of ± $1\cdot10^{-5}$ g.

The measurement procedure was based on the method described by Bešter-Rogač *et al.* [7, 8] and used by us in our previous works [5, 9, 10]. Conductivity measurements were performed with a three-electrode cell with the use of a Precise Component Analyser type 6430B (Wayne-Kerr, UK) under argon atmosphere and at the different frequencies, ν, (0.2, 0.5, 1, 2, 3, 5, 10, 20) kHz. The temperature was kept constant within 0.003 K (Calibration Thermostat Ultra UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The details of the experimental procedure for conductometric measurements were described in our previous paper [9]. The uncertainty of the measured values of conductivity was 0.03 %.

Densities were measured with an Anton Paar DMA 5000 oscillating U-tube densimeter equipped with a thermostat with a temperature stability within ± 0.001 K. The densimeter was calibrated with extra pure water, previously degassed ultrasonically. The uncertainty of the density is ± $1\cdot10^{-5}$ g · cm^{-3}.

Viscosities were measured with a AVS 350 device (Schott Instruments, Germany). The Ubbelohde viscosimeter filled with the liquid was placed vertically in a thermostat water. An optoelectronic stopwatch with a precision of 0.01 s was used for flow time measurements. The temperature was kept constant using a precision thermostat HAAKE DC30 (Thermo Scientific). The accuracy of temperature control was 0.01 K. The uncertainty in the viscosity measurements was better than 0.1 %.

3. RESULTS AND DISCUSSION

Table 2. Densities, ρ_o, viscosities, η, and relative permittivities, ε_r, of 1-propanol at different temperatures

T/K	ρ_o/ g cm^{-3}	η/mPa s	ε_r
283.15	0.811462	2.837	22.61
288.15	0.807538	2.494	21.87
293.15	0.803546	2.202	21.15
298.15	0.799538	1.957	20.45
303.15	0.795502	1.729	19.78
308.15	0.791428	1.542	19.13
313.15	0.787314	1.381	18.50
318.15	0.783153	1.235	17.89

The densities, viscosities, and relative permittivities of 1-propanol as a function of temperature are listed in Table 2. The values of relative permittivities were obtained by interpolation from our [11-

14] and literature data [15, 16]. The values of densities and viscosities show a very good agreement with literature [3, 16, 17].

To convert molonity, $\tilde{m}$, (moles of electrolyte per kilogram of solution) into molarity, c, the values of density gradients, b, have been determined independently and used in the equation

$$c / \tilde{m} = \rho = \rho_o + b\ \tilde{m} \tag{1a}$$

where ρ_o is the density of the solvent. Molar concentrations, c, were necessary to use the conductivity equation. The density gradients and the molar conductances of the ILs in solution, Λ, as a function of IL molality, m, (moles of electrolyte per kilogram of solvent) and temperature are presented in Table 3. The relationship among m, $\tilde{m}$, and c is the following

$$\tilde{m} = c/\rho = 1 / (1 + mM) \tag{1b}$$

where M is the molar mass of electrolyte.

Table 3. Molar conductances, Λ, corresponding molar concentrations, c, and density gradients, b, for solutions of NaI, $NaBPh_4$, Bu_4NI, and $NaBF_4$ in 1-PrOH over the temperature range from (283.15 to 318.15) K

$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}
NaI, b = 0.112 kg^2 dm^{-3} mol^{-1}							
T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
0.9095	15.893	0.7860	17.955	0.8085	20.371	0.7985	23.103
2.5710	15.318	2.4065	17.271	2.4478	19.556	2.5684	22.057
4.1254	14.911	4.0523	16.786	4.1395	18.972	4.0196	21.460
5.6665	14.596	5.8064	16.423	5.7567	18.509	5.5215	20.938
8.1139	14.188	8.1810	15.951	7.9816	18.042	7.9788	20.261
11.991	13.679	12.161	15.321	12.391	17.243	11.895	19.420
16.030	13.256	16.392	14.831	16.358	16.702	16.098	18.709
24.321	12.595	23.462	14.210	23.842	15.880	24.042	17.681
40.641	11.702	39.884	13.097	39.527	14.685	39.352	16.331
		56.451	12.363			55.756	15.352
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.8989	25.625	0.9452	28.679	0.9772	31.971	0.5773	36.348
2.3872	24.587	2.4960	27.416	2.3521	30.637	2.2033	34.249
3.9000	23.854	3.9492	26.585	3.9294	29.524	3.7651	32.893
5.6071	23.198	5.5272	25.842	5.7696	28.525	5.2744	31.897
8.0774	22.405	8.1057	24.870	7.7788	27.641	7.5069	30.672

12.109	21.410	11.795	23.814	12.006	26.216	9.3262	29.880
15.888	20.721	15.865	22.903	15.866	25.216	11.534	29.041
23.733	19.577	23.149	21.652	23.548	23.716	13.143	28.491
38.839	18.050	39.436	19.756	39.677	21.595	15.434	27.811
54.983	16.906	54.901	18.538	55.701	20.191	19.405	26.821
						23.603	25.940
						38.542	23.674
						54.545	22.039
$NaBPh_4$, b = 0.097 kg^2 dm^{-3} mol^{-1}							
T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
1.1086	14.199	1.0395	16.067	1.1342	18.088	1.1028	20.387
2.5574	13.842	2.5328	15.650	2.6318	17.649	2.5377	19.915
4.1872	13.558	4.1586	15.345	4.1913	17.332	4.2484	19.525
5.7061	13.365	5.7502	15.113	5.8244	17.071	5.8849	19.232
8.0631	13.116	8.2279	14.827	8.2091	16.762	7.9634	18.925
12.255	12.775	12.618	14.441	12.463	16.333	12.260	18.422
16.361	12.529	16.335	14.186	16.335	16.024	16.183	18.058
24.067	12.184	24.991	17.730	24.511	15.514	23.786	17.498
40.985	11.683	39.192	13.203	40.256	14.817	40.685	16.622
		56.890	12.729	56.278	14.304	56.318	16.048
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.9566	23.030	1.1234	25.692	0.8604	28.875	0.9206	32.060
2.6161	22.357	2.6362	25.033	2.3552	28.045	2.4386	31.145
4.0911	21.977	4.1541	24.592	4.0103	27.477	4.3503	30.394
5.7639	21.612	5.7881	24.211	5.5146	27.038	5.8021	29.942
7.9006	21.269	8.0327	23.780	7.9531	26.495	7.8849	29.432
12.419	20.666	12.277	23.133	11.815	25.845	12.216	28.614
16.015	20.282	15.834	22.697	15.787	25.283	15.914	28.051
23.915	19.623	23.654	21.985	23.827	24.439	23.202	27.114
39.960	18.656	40.014	20.893	38.386	23.288	40.758	25.647
		55.893	20.056				

Table 3. (continued)

$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}	$10^4 c$ mol dm^{-3}	Λ S cm^2 mol^{-1}
NBu_4I, b = 0.098 kg^2 dm^{-3} mol^{-1}							
T = 283.15 K^a		T = 288.15 K		T = 293.15 K		T = 298.15 K^a	
0.5146	16.191	0.8832	17.981	0.8813	20.365	0.5070	23.483
1.7601	15.221	2.3796	16.870	2.5490	18.968	1.7342	22.023

3.1445	14.470	4.0005	15.998	4.0246	18.077	3.0982	20.899
4.7358	13.852	5.6336	15.328	5.6957	17.320	4.6660	19.983
7.1894	13.046	8.0844	14.527	8.1532	16.381	7.0834	18.793
9.2734	12.510	12.235	13.502	12.344	15.240	9.1367	18.011
11.590	12.015	16.134	12.762	16.033	14.474	11.419	17.290
		24.467	11.629	24.621	13.122		
		39.447	10.286	40.280	11.594		
		56.221	9.285				
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.8339	25.958	0.9444	28.900	0.8328	32.453	0.8779	35.990
2.4032	24.141	2.4420	26.976	2.2472	30.307	2.3704	33.465
4.0106	22.883	4.0504	25.531	3.8515	28.627	3.8370	31.736
5.5510	21.943	5.5111	24.530	5.3724	27.379	5.3954	30.313
7.9419	20.764	7.7006	23.293	7.9256	25.771	7.9057	28.544
12.468	19.149	12.079	21.484	11.931	23.936	12.026	26.415
15.727	18.290	15.892	20.327	16.138	22.520	15.717	25.016
24.687	16.515	24.033	18.511	24.371	20.495	23.402	22.857
39.007	14.698	40.271	16.247	39.273	18.181	37.166	20.395
56.860	13.229			55.596	16.550	53.487	18.500
$NaBF_4$, b = 0.050 $kg^2\ dm^{-3}\ mol^{-1}$							
T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
0.9117	14.905	0.8969	16.894	0.7973	19.164	0.8060	21.380
1.6819	13.870	1.6545	15.857	1.6179	17.948	1.6778	20.011
2.3922	13.163	2.3532	15.145	2.3746	17.137	2.4909	19.098
4.2800	11.822	4.2102	13.776	4.1253	15.771	4.0367	17.805
5.7386	11.075	5.6450	13.003	5.8372	14.799	5.6990	16.768
8.1076	10.161	7.9754	12.040	8.0820	13.826	8.0633	15.648
10.900	9.379	10.722	11.195	11.063	12.855	10.791	14.672
13.406	8.858	13.187	10.614	13.399	12.266	13.142	14.012
				15.989	11.738	15.926	13.386
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.8153	23.627	0.8214	26.060	0.7479	28.850	0.7308	31.902
1.6196	22.319	1.5866	24.698	2.4734	25.810	2.6403	27.779
2.3860	21.347	2.3550	23.656	3.9508	24.110	4.0617	25.979
3.7584	20.084	3.9660	21.998	5.4617	22.802	5.5612	24.559
5.6202	18.763	5.6012	20.747	8.0036	21.162	7.7978	22.977
7.9066	17.525	7.8898	19.388	10.565	19.887	10.579	21.564
10.689	16.431	10.725	18.129	13.080	18.900	13.034	20.653
13.072	15.705	12.996	17.347	15.746	18.056	15.538	19.955
15.997	14.890	15.913	16.481				

[a] The data from paper [4]

The conductivity data were analyzed in the framework of the low concentration Chemical Model (lcCM) [18]. This approach uses the set of equations

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

$$K_A = (1 - \alpha) / (\alpha^2 c y_\pm^2) \qquad (3)$$

and

$$\ln y_\pm = -\,(A\alpha^{1/2}c^{1/2}) / (1 + BR\alpha^{1/2}c^{1/2}) \qquad (4)$$

In these equations, Λ_o is the limiting molar conductance; α is the dissociation degree of an electrolyte; K_A is the ionic association constant; R is the distance parameter of ions; $y_\pm$ is the activity coefficient of ions on the molar scale; A and B are the Debye–Hückel equation coefficients. The analytical form of the parameters S, E, J, and $J_{3/2}$ was presented previously [18]. The values of Λ_o, K_A, and R were obtained using the well-known procedure given by Fuoss [19] and are collected in Table 4.

Table 4. Limiting molar conductances, Λ_o, association constants, K_A, distance parameters, R, and standard deviations, $\sigma(\Lambda)$, for the investigated electrolytes in 1-PrOH at different temperatures

T/K	Λ_o/S cm^2 mol^{-1}		K_A/dm^3 mol^{-1}		R/nm	$\sigma(\Lambda)$
	this work	lit.[4]	this	lit.[4]		
NaI						
283.15	16.617±0.012	16.672	143.6±0.4	150.6	12.5	0.015
288.15	18.755±0.014		154.5±0.5		12.4	0.019
293.15	21.321±0.008		172.3±0.8		12.6	0.009
298.15	24.206±0.010	24.297	196.1±1.3	205.3	12.8	0.020
303.15	27.014±0.016		216.7±3.1		12.6	0.012
308.15	30.349±0.009		246.0±4.1		12.8	0.005
313.15	33.981±0.012		280.6±3.3		12.8	0.006
318.15	38.082±0.018		321.4±4.2		13.0	0.008
$NaBPh_4$						
283.15	14.863±0.022		68.6±1.1		10.7	0.006
288.15	16.804±0.017		62.8±0.9		11.8	0.003
293.15	18.992±0.010		61.6±1.3		12.4	0.012
298.15	21.421±0.008		62.7±0.7		12.8	0.021
303.15	24.096±0.009		61.8±1.6		13.4	0.010
308.15	27.024±0.011		66.5±1.2		13.4	0.018
313.15	30.193±0.016		70.3±0.8		13.8	0.011
318.15	33.602±0.022		73.8±0.9		14.0	0.027
Bu_4NI						

283.15[a]	16.962±0.020	16.960	471.6±4.6	477.0	14.2	0.012
288.15	19.260±0.013		478.6±5.2		13.8	0.006
293.15	21.836±0.008		491.3±6.6		13.5	0.013
298.15[a]	24.659±0.021	24.660	514.4±7.1	517.0	14.2	0.018
303.15	27.823±0.009		525.8±6.2		13.9	0.012
308.15	31.243±0.015		551.4±4.6		13.8	0.008
313.15	34.949±0.012		577.3±5.4		13.6	0.011
318.15	38.946±0.014		605.2±8.2		13.6	0.010
$NaBF_4$						
283.15	17.006±0.024		1457.4±3.2		13.1	0.007
288.15	18.879±0.018		1144.9±4.1		13.2	0.013
293.15	21.009±0.016		984.0±5.6		13.5	0.029
298.15	23.348±0.010		906.5±4.2		13.7	0.041
303.15	25.848±0.012		872.0±6.1		13.9	0.023
308.15	28.579±0.026		876.1±5.3		14.1	0.008
313.15	31.539±0.027		915.4±6.0		14.4	0.009
318.15	34.689±0.014		971.7±7.1		14.6	0.017

[a] The data calculated on the basis of values given in paper [4]

As seen from Table 4, the values of association constants for examined electrolytes differ significantly. The smallest tendency to form ion pairs exhibits sodium tetraphenylborate. From a practical point of view, it can be classified as a rather strong electrolyte in 1-propanol. NaI is more associated electrolyte in 1-propanol, while Bu_4NI and $NaBF_4$ are definitely the most associated electrolytes. The data collected in Table 4 also show that the ionic association phenomenon increases with increasing temperature, with the exception of the most associated $NaBF_4$. Moreover, the values of limiting molar conductances and the association constant obtained in this paper are in very good agreement with the data determined by Barthel et al [4].

From the temperature dependence of Λ_o, the Eyring activation enthalpy of charge transport, $\Delta H_\lambda^\ddagger$, was obtained

$$\ln \Lambda_o + 2/3 \ln \rho_o = -\frac{\Delta H_\lambda^\ddagger}{RT} + D \qquad (5)$$

where D is an empirical constant. From the slope of the linear dependencies of $\ln \Lambda_o + 2/3 \ln \rho_o$ versus the inverse of the temperature ($1/T$), which are shown in Figure 1, we obtained the following $\Delta H_\lambda^\ddagger$ values: 17238, 17007, 17325 and 14800 J mol^{-1} for NaI, $NaBPh_4$, Bu_4NI, and $NaBF_4$, respectively. The values of $\Delta H_\lambda^\ddagger$ in the investigated temperature range are constant and characteristic for the studied electrolytes, because the dependences presented on the Figure 1 are highly linear. As can be seen the activation enthalpy of charge transfer for $NaBPh_4$, Bu_4NI and NaI are very similar to each other. Similar values of $\Delta H_\lambda^\ddagger$ for $NaBPh_4$ and Bu_4NI may be due to the presence of the large organic ions in these electrolytes. In the case of NaI, the comparable value of $\Delta H^{\ddagger}_{\lambda}$ may result from the large effective ionic radii. It should be noted, however, that these values refer to the electrolytes, and thus, they are the sum of the activation enthalpy of cation and anion and the more accurate analysis will be possible if the ionic limiting conductivities will be known.

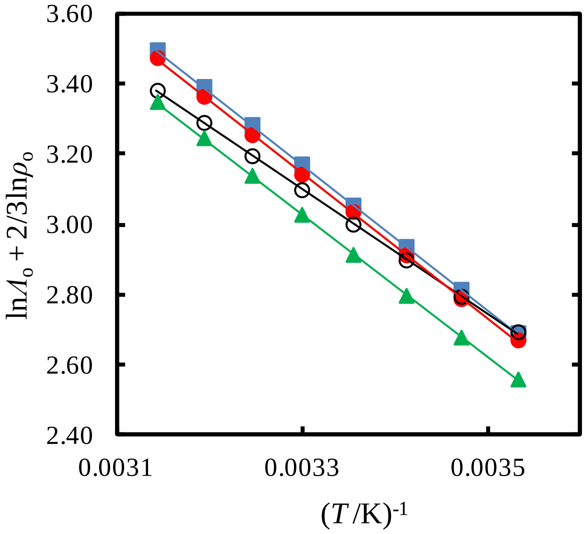

Figure 1. Plot of ln Λ_o + *2/3* ln ρ_o as a function of 1/*T* for ●, NaI; ▲, NaBPh$_4$; ■, Bu$_4$NI; and ○, NaBF$_4$in 1-PrOH.

The temperature dependence of the association constant was used to calculation of Gibbs free energy of ion formation, ΔG^o_A

$$\Delta G^o_A\ (T) = -RT\ ln\ K_A(T) \qquad (6)$$

$\Delta G^o_A(T)$ can also be expressed by the polynomial

$$\Delta G^o_A\ (T) = A_o + A_1 T + A_2 T^2 \qquad (7)$$

The values of parameters A_o, A_1, and A_2 of Eq. (7) and correlation coefficients, r^2, are summarized in Table 5.

Table 5. Coefficients of Eq. (7) and correlation coefficients, r^2, in 1-PrOH

	A_o /kJ mol^{-1}	A_1/J mol^{-1} K^{-1}	A_2/J mol^{-1} K^{-2}	r^2
NaI	-32.380	229.68	-0.5529	0.9998
NaBPh$_4$	97.848	625.06	-1.1108	0.9972
Bu$_4$NI	-20.984	105.96	-0.2931	0.9999
NaBF$_4$	-219.115	1377.2	-2.3443	0.9971

The entropy and enthalpy of ion association are defined as

$$\Delta S_{\mathrm{A}}^{\mathrm{o}} = -\left(\frac{\partial \Delta G_{\mathrm{A}}^{\mathrm{o}}}{\partial T}\right)_{\mathrm{p}} = -A_1 - 2A_2 T \qquad (8)$$

$$\Delta H_{\mathrm{A}}^{\mathrm{o}} = \Delta G_{\mathrm{A}}^{\mathrm{o}} + T\ \Delta S_{\mathrm{A}}^{\mathrm{o}} = A_{\mathrm{o}} - A_2 T^2 \qquad (9)$$

The thermodynamic functions of the ion pair formation ($\Delta G_{\mathrm{A}}^{\mathrm{o}}, \Delta S_{\mathrm{A}}^{\mathrm{o}}, \Delta H_{\mathrm{A}}^{\mathrm{o}}$) at different temperatures are presented in Figures 2, 3, and 4, respectively.

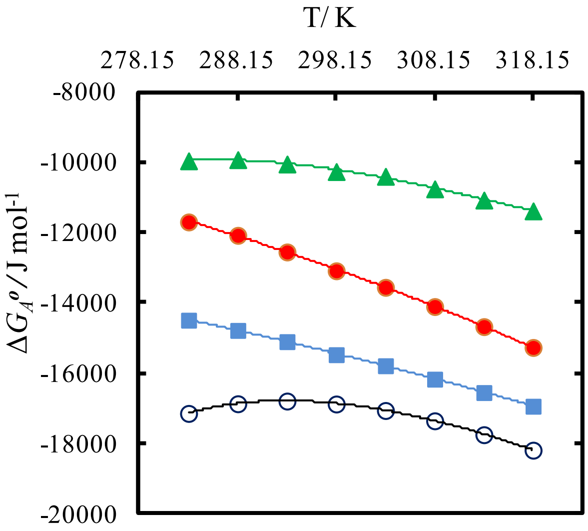

Figure 2. Variation of Gibbs free energy, $\Delta G_{\mathrm{A}}^{\mathrm{o}}$, as a function of temperature T for ●, NaI; ▲, NaBPh$_4$; ■, Bu$_4$NI; and ○, NaBF$_4$ in 1-PrOH.

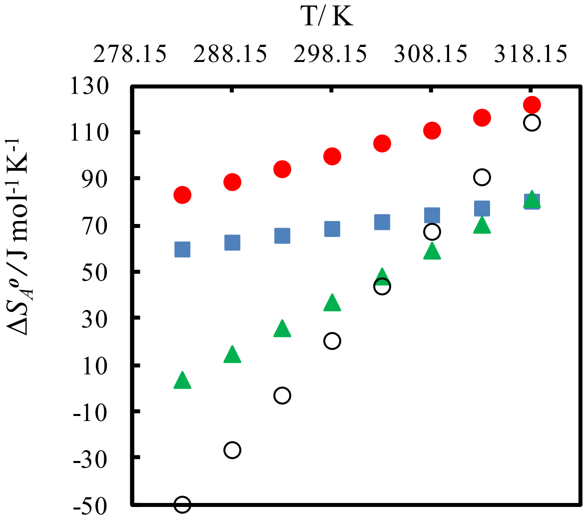

Figure 3. Variation of association entropies, $\Delta S_{\mathrm{A}}^{\mathrm{o}}$, as a function of temperature for ●, NaI; ▲, NaBPh$_4$; ■, Bu$_4$NI; and ○, NaBF$_4$ in 1-PrOH.

The values of $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ presented in Figure 2 indicate that the spontaneity of the ion pair formation increases for examined salts in the next order: NaBPh$_4$ < NaI < Bu$_4$NI < NaBF$_4$. With increasing temperature the spontaneity of the ion pair formation becomes greater. Only in the case of $NaBF_4$, the spontaneous nature of association decreases from temperature 289.15 K to 293.15 K, and then it increases with temperature. As shown in Figure 2, the dependences of ΔG_A^o = f (T) differ significantly for the individual electrolytes, therefore, to be expected also significant differences for dependences of ΔS_A^o = f (T) and ΔH_A^o = f (T).

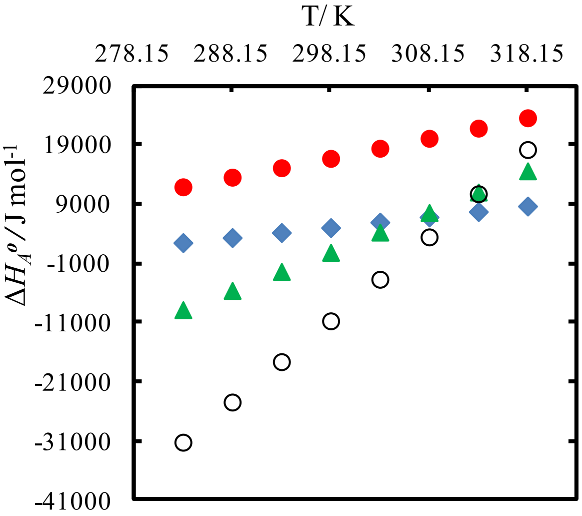

Figure 4. Variation of enthalpies, ΔH_A^o, as a function of temperature for ●, NaI; ▲, NaBPh$_4$; ■, Bu_4NI; and ○, $NaBF_4$ in 1-PrOH.

As can be seen in Figure 3, the entropies of association for Bu_4NI, NaI, and $NaBPh_4$ are positive over the range of temperatures tested. In the case of $NaBF_4$, the values of ΔS_A^o are positive above the temperature of 293.15 K. However, for each of the tested electrolytes, the values of ΔS_A^o increase with increasing temperature (the most for $NaBF_4$). A positive sign of values of ΔS_A^o mean that the desolvation of ions (at least partial) and the solvation of the ion pair formation lead, in effect, to a lower order of the solvent molecules. This effect increases with increasing temperature.

As can be seen in Figure 4, the values of enthalpy of association are positive for sodium iodide and tetrabutylammonium iodide. This endothermic effect increases with increasing temperature. Therefore, the spontaneity of the association process for these electrolytes is mainly due to the entropic effect. For other electrolytes the values of enthalpy of association change the sign and from the specified temperatures the association process becomes endothermic, which means that the association spontaneity begins to be determined by entropic effect. However, in any case, with increasing temperature the values of ΔH_A^o also increase. This effect is the strongest in the case of $NaBF_4$.

The selection of the electrolytes for this study allowed us to split the limiting molar electrolyte conductances into their ionic components on the basis of the Fuoss-Hirsch assumption [6]. The values of limiting ionic conductivities for BPh_4^-, Bu_4N^+, Na^+, I^-, BF_4^- ions and cations of the ionic liquids, i.e., 1-ethyl-3-methylimidazolium [emim]$^+$ and 1-butyl-3-methylimidazolium [bmim]$^+$ are presented in

Table 6. For the calculation we used also the values of limiting molar conductances for [emim][BF_4] and [bmim][BF_4], determined in our earlier paper [5].

Table 6. Limiting ionic conductivities, $\lambda_{\pm}^{o}$, in 1-PrOH

	$\lambda_{\pm}^{o} \cdot 10^4$/S m^2 mol^{-1}					
T/K	BPh_4^- = Bu_4N^+	Na^+	I^-	BF_4^-	$[emim]^+$	$[bmim]^+$
283.15	7.60	7.26	9.36	9.75	12.00	11.39
288.15	8.65	8.15	10.61	10.73	13.98	12.77
293.15	9.75	9.24	12.08	11.77	16.14	15.21
298.15	10.94	10.48	13.72	12.87	18.56	17.43
303.15	12.45	11.64	15.37	14.21	21.01	19.71
308.15	13.96	13.07	17.28	15.51	23.85	22.27
313.15	15.58	14.61	19.37	16.93	26.79	25.02
318.15	17.23	16.37	21.71	18.32	30.24	28.14

As seen from Table 6, the lowest values of conductivity have BPh_4^-, Bu_4N^+, and Na^+ ions. This would be expected taking into account the large size of organic ions and the effective radius of sodium ion. The same situation for these ions in DMF was described by us in paper [10] . However, in this case, the values of limiting ionic conductivities for these ions were definitely higher.

The conductivities of I^- and BF_4^- are higher, so their effective radii are smaller than the previously discussed organic ions and sodium ion. Taking into account the similar crystallographic radii of these ions (0.220 nm for I^- and 0.228 nm for BF_4^-), could be expected the similar values of ionic conductivities for these ions. A detailed analysis of the data indicates, however, some important differences between the hydrodynamic properties of these ions. Both ions undoubtedly are less solvated in 1-propanol than sodium ion (crystallographic radius equal to 0.098 nm). For temperatures higher than 288.15 K, ions I^- having a slightly smaller size than BF_4^- ions, exhibit a slightly higher conductivity, which seems quite natural. However, the ionic conductivity of I^- increases with temperature much faster than the conductivity of the BF_4^- anion. It results probably from the different properties of these ions. In contrast to ions BF_4^-, iodide ions are characterized by a high polarizability. Thus, it seems that the interaction of I^- ions with 1-propanol molecules, are strongly associated with the polarizability of these ions. These interactions are probably weakened by a temperature increase, the effective size of this ion slightly decreases, causing an additional increase in its conductivity.

In $[emim]^+$ and $[bmim]^+$ cations, the positive charge localized on the nitrogen atom is covered by a $-CH_3$ group, which hinders the cation solvation. These cations have the highest conductivity among the investigated ions, which means that they are less solvated by 1-propanol molecules, but definitely strongly than by DMF molecules [10] . The ionic conductivity of $[emim]^+$ is greater than $[bmim]^+$, due to the differences in the sizes of ethyl and butyl group occurring in these cations.

On the basis of the limiting ionic conductivities, the activation enthalpy of charge transport, $\Delta H^{\ddagger}_{\lambda}$, for these ions was obtained (Figure 5). $\Delta H^{\ddagger}_{\lambda}$ values for I^- (17498 J mol^{-1}) and BF_4^- ions (13094 J mol^{-1}) differ significantly. The value $\Delta H^{\ddagger}_{\lambda}$ for iodide ion is similar to Bu_4N^+ and BPh_4^- (17109 J mol^{-1}) and sodium ion (16897 J mol^{-1}). On the other hand, the value of $\Delta H^{\ddagger}_{\lambda}$ for BF_4^- anion is much smaller than for the other ions. This may confirm the other type of interactions with 1-propanol molecules for this ion, compared to the more polarizable iodide anion. This may confirm the other model of this ion interactions with 1-propanol molecules, compared to the more polarized iodide anion. The highest values of $\Delta H^{\ddagger}_{\lambda}$ for [emim]$^+$ (19166 J mol^{-1}) and [bmim]$^+$ (19062 J mol^{-1}) may be due to the relatively large size of these ions.

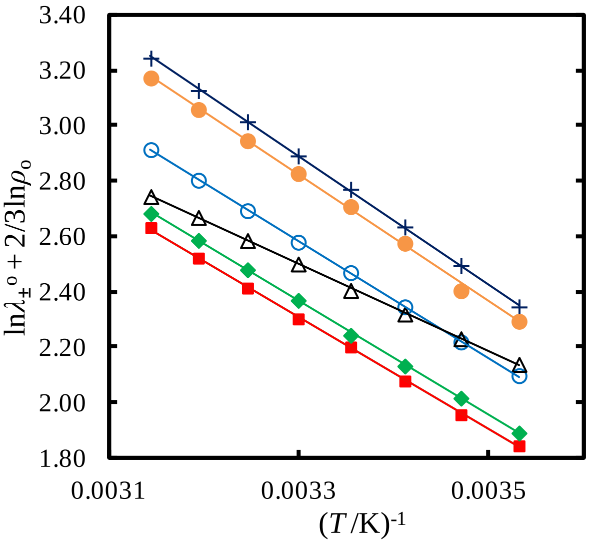

Figure 5. Plot of ln $\lambda^{o}_{\pm}$ + 2/3 ln ρ_o as a function of 1/T for ♦, BPh_4^-, Bu_4N^+; ■, Na^+; ○, I^-; Δ, BF_4^- ; +, [emim]$^+$; and ●, [bmim]$^+$ in 1-PrOH.

4. CONCLUSIONS

Molar conductances of solutions of sodium iodide, sodium tetraphenylborate, tetrabutylammonium iodide, and sodium tetrafluoroborate in protic solvent 1-propanol, have been reported at T = (283.15 to 318.15) K. Analysis of the conductivity data on the basis of Barthel's low concentration Chemical Model (lcCM) provided important information about the ion association of investigated electrolyte solutions. The electrolytes can be ordered in the following series: $NaBPh_4$ < NaI < Bu_4NI < $NaBF_4$ from the least to the most strongly associated in 1-propanol. The evaluated values of thermodynamic functions of association suggest the spontaneity of the association process, which results mainly from the entropic effects (particularly for NaI and Bu_4NI). The values of ΔS^{o}_{A} increase with increasing temperature for each electrolyte, which means that the desolvation of ions and the solvation of the ion pair formation leads to a lower order of the solvent molecules. The analysis of limiting ionic conductivities and crystallographic radii indicate that Na^+ is strongly solvated by 1-

propanol molecules, I^- and BF_4^- are less solvated, and organic ions BPh_4^- and Bu_4N^+ are poorly solvated (or unsolvated). The smallest value of activation enthalpy of charge transport for BF_4^- anion may confirm the other model of this ion interactions with 1-propanol molecules, compared to the more polarizable iodide anion, which has a similar crystallographic radius.

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