

Conductometric Study of Sodium Chloride in Aqueous 2-methylpropan-2-ol of Mass Fraction 0.10, 0.30, 0.50, 0.70, 0.80 and 0.90

Perica Bošković^{1,*}, Vesna Sokol¹, Ante Prkić², Josipa Giljanović²

¹Department of Physical Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia

²Department of Analytical Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia.

*E-mail: perica@ktf-split.hr

Received: 14 February 2014 / Accepted: 17 March 2014 / Published: 14 April 2014

Molar conductivities of dilute solutions of sodium chloride in binary mixtures of 2-methylpropan-2-ol and water were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The limiting molar conductivity (Λ_0) and the ion-pair formation constant (K_A) were determined by the Lee-Wheaton conductivity equation. Thermodynamic quantities, Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), for the ion-association reaction were derived from the temperature dependence of K_A . The activation enthalpy of the charge transport (ΔH^*) was derived from the temperature dependence of Λ_0 . The obtained thermodynamic quantities, together with Walden product, were discussed in terms of solvent basicity, structure permittivity and viscosity.

Keywords: sodium chloride, 2-methylpropan-2-ol + water mixtures, association to ion-pairs, thermodynamic quantities

1. INTRODUCTION

A review of old and recent literature shows an increasing interest in transport properties of electrolytes in pure solvents or solvent mixtures [1-5]. The mixed solvents are suitable for investigation of ion-pair formation because addition of even small amounts of water to organic component changes significantly physical properties of the mixture (see Table 1.).

The conductometric method is well-suited to investigate interactions in electrolyte solutions. Conductivity measurements should cover a wider temperature range to make thermodynamics of these processes better understood.

Numerous systematic investigations on mixed solvent electrolyte systems were carried out in

our laboratory over the last two decades and were subject of a series of publications concerning the proper evaluation of ion-ion, ion-solvent and solvent-solvent interactions in solutions[6-13]. Searching the older and newer literature we were not able to find a conductivity investigation made for the low concentration sodium chloride solutions in 2-methylpropan-2-ol - water mixtures.

In our previous work [11] the ion-pair association of alkali halides in binary mixtures of water with 2-methylpropan-2-ol was studied at five temperatures from 288.15 K to 308.15 K. The systems water - 2-methylpropan-2-ol and alkali chlorides were investigated conductometrically [14] at 298.15 K.

The present work reports conductometric data for the low concentration sodium chloride solutions in 2-methylpropan-2-ol - water mixtures with alcohol mass fraction $w_B = 0.10, 0.30, 0.50, 0.70, 0.80$ and 0.90 at 288.15, 293.15, 298.15, 303.15 and 308.15 K.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Water was distilled twice (specific conductivity $\approx 10^{-6} \text{ S cm}^{-1}$) and NaCl (Merck, suprapur) was dried for six hours at 393.15 K before use. 2-methylpropan-2-ol (Merck, absolute, 99.8 %) was used without further purification. Solvent mixtures and the concentrated stock solutions were prepared by weight. The test solution concentration range was covered by adding stock to solvent. The maximum tested concentration was limited by the condition that no triple ions should appear [15]. Molarity ($c / \text{mol dm}^{-3}$) was determined as

$$c = \frac{dm}{1 + mM} \quad (1)$$

where m is molality (moles of electrolyte per kilogram of solvent), $d / \text{kg dm}^{-3}$ is the solution density and M the molar mass of electrolyte. By assuming a linear dependence of the solution density upon its molality,

$$d = d_o + Dm \quad (2)$$

(d_o is the solvent density), the density gradient $D / \text{kg}^2 \text{ dm}^{-3} \text{ mol}^{-1}$ was obtained. Its values at 293.15 K for the alcohol mole fraction (w_B) of 0.10, 0.30, 0.50, 0.70, 0.80 and 0.90 amount to 0.0412, 0.0373, 0.0328, 0.0261, 0.0224 and 0.0829, respectively, and are assumed to be independent on temperature [16]. The relative error in molarity and solvent composition was about $\pm 0.1 \%$.

2.2. Apparatus

The stock solution density at 293.15 K, as well as the densities of 2-methylpropan-2-ol - water mixtures at all working temperatures, were determined by a digital density meter Anton Paar (model DMA 4500 M) with the uncertainty of $\pm 0.00005 \text{ kg dm}^{-3}$.

The viscosity of 2-methylpropan-2-ol - water mixtures was measured at each temperature using an Ostwald viscometer. The uncertainty in measurements of time was about $\pm 0.1 \%$.

Measurement of resistance by a component analyser Wayne - Kerr (model 6430 A) was described earlier in detail [11].

3. RESULTS AND DISCUSSION

3.1. Solvent properties and solution conductivity

The density, viscosity and relative permittivity of the tested mixed solvents are given in Table 1; permittivity values were interpolated from literature [17]. Conductivities of the NaCl solutions in those solvents are given in Table 2.

Table 1. Density (d_o), viscosity (η) and relative permittivity (ϵ_r) of the 2-methylpropan-2-ol (w_B) + water mixtures at different temperatures

		T/K				
w_B		288.15	293.15	298.15	303.15	308.15
0.10	$d_o / \text{g cm}^{-3}$	0.98474	0.98344	0.98186	0.98004	0.97801
	$\eta / 10^3 \text{ Pa s}$	2.019	1.681	1.423	1.228	1.067
	ϵ_r	73.55	71.75	69.98	68.27	66.59
0.30	$d_o / \text{g cm}^{-3}$	0.95233	0.94864	0.94495	0.94126	0.93751
	$\eta / 10^3 \text{ Pa s}$	4.906	3.774	2.989	2.519	2.077
	ϵ_r	55.76	54.18	52.64	51.14	49.69
0.50	$d_o / \text{g cm}^{-3}$	0.90647	0.90245	0.89840	0.89428	0.89014
	$\eta / 10^3 \text{ Pa s}$	7.105	5.523	4.433	3.614	2.981
	ϵ_r	37.87	36.59	35.36	34.17	33.01
0.70	$d_o / \text{g cm}^{-3}$	0.86067	0.85643	0.85212	0.84774	0.84331
	$\eta / 10^3 \text{ Pa s}$	8.050	6.266	4.931	3.939	3.214
	ϵ_r	23.20	22.31	21.45	20.63	19.84
0.80	$d_o / \text{g cm}^{-3}$	0.83713	0.83277	0.82832	0.82380	0.81919
	$\eta / 10^3 \text{ Pa s}$	7.884	6.117	4.807	3.839	3.116
	ϵ_r	17.96	17.23	16.53	15.86	15.22
0.90	$d_o / \text{g cm}^{-3}$	0.81378	0.80923	0.80460	0.79991	0.79514
	$\eta / 10^3 \text{ Pa s}$	7.374	5.671	4.416	3.518	2.835
	ϵ_r	13.52	12.94	12.39	11.86	11.35

Table 2. Molar conductivities ($\Lambda / \text{S cm}^2 \text{ mol}^{-1}$) of NaCl in aqueous 2-methylpropan-2-ol mixtures with alcohol mass fraction w_B at various concentrations ($c / \text{mol dm}^{-3}$) and temperatures (T / K)

288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
$w_B = 0.10$									
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
8.9013	55.207	7.9530	64.709	8.5984	74.316	8.2602	85.329	8.5837	96.554
18.091	54.521	17.098	63.737	17.879	73.939	17.096	83.325	17.246	95.767
27.082	54.702	26.230	63.019	26.787	74.102	26.104	83.047	26.031	94.635
35.926	54.535	34.887	62.646	34.826	74.044	34.835	81.863	34.613	94.921
44.534	54.197	43.356	62.194	43.249	73.625	43.481	81.756	43.146	94.448
53.107	54.119	51.640	61.838	51.547	73.064	51.859	81.063	51.629	93.912
61.183	53.884	59.686	62.372	59.794	72.742	60.088	80.923	59.864	93.592
69.371	53.910	67.873	62.051	68.009	72.375	67.894	81.051	67.949	93.065
77.308	53.789	75.873	61.745	76.186	72.192	75.874	81.036	75.864	92.956

85.151	53.608	83.545	61.586	83.728	71.873	83.676	80.762	83.568	92.671
93.013	53.447	91.184	61.831	91.365	71.570	91.331	80.855	91.151	92.311
100.61	53.294	98.655	61.585	98.862	71.383	98.857	80.496	98.573	91.937
108.01	53.148	106.13	61.418	106.34	71.112	106.26	80.373	105.74	91.636
115.42	53.017	113.18	61.217	113.74	70.869	113.47	80.075	112.88	91.354
$w_B = 0.30$									
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A
7.3811	28.414	7.5744	35.545	7.6523	43.123	7.4424	51.179	7.7399	59.437
15.963	28.072	16.179	35.047	16.152	42.561	15.908	50.645	16.377	58.658
24.531	27.813	25.036	34.700	25.137	42.168	24.324	50.191	24.844	58.409
33.486	27.605	33.761	34.415	33.448	41.852	32.993	49.803	33.148	57.915
42.056	27.453	42.305	34.179	41.987	41.587	41.495	49.489	41.294	57.833
50.545	27.309	50.814	33.980	50.409	41.353	49.680	49.217	49.273	57.503
58.868	27.196	59.067	34.227	58.688	41.144	57.644	48.974	57.114	57.134
66.893	27.097	67.057	34.075	66.727	40.975	65.601	48.749	64.961	56.870
74.826	26.995	74.759	33.982	74.514	40.793	73.229	48.552	72.999	56.582
82.601	26.906	82.527	33.829	82.171	40.639	80.968	48.354	80.733	56.328
90.202	26.831	90.063	33.716	89.588	40.497	88.621	48.181	88.256	56.166
97.700	26.742	97.610	33.614	97.139	40.355	96.015	48.018	95.602	56.072
105.21	26.671	104.96	33.515	104.39	40.234	103.22	47.869	102.45	55.345
112.54	26.606	112.34	33.422	111.41	40.311	110.34	47.812	109.58	55.486
$w_B = 0.50$									
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A
7.1389	16.931	6.8399	21.066	7.7030	25.095	7.2115	30.395	6.9775	36.361
15.011	16.585	15.217	20.547	16.436	25.387	15.312	29.434	14.804	35.387
22.910	16.272	23.329	20.101	25.014	24.993	23.279	28.841	22.541	34.738
30.545	16.040	31.661	20.229	33.709	24.647	31.242	28.414	30.382	34.315
38.174	15.863	39.619	20.055	42.555	24.362	39.455	28.054	38.196	33.883
46.145	16.207	47.285	19.886	51.321	24.111	47.188	27.750	46.079	33.524
53.837	16.076	54.951	19.740	59.738	23.892	54.826	27.486	53.649	33.207
61.357	15.961	62.365	19.598	68.166	23.657	62.397	27.259	61.083	32.955
68.706	15.779	69.593	19.472	68.429	26.261	69.686	27.048	68.556	32.662
76.156	15.688	76.898	19.350	84.405	23.344	76.919	26.865	75.675	32.426
83.377	15.778	84.041	19.248	92.498	23.194	83.801	26.689	82.764	32.213
90.026	15.536	90.999	19.144	100.22	23.068	90.759	26.539	89.821	32.016
97.062	15.467	97.869	19.051	107.77	22.955	97.461	26.391	96.522	31.829
103.75	15.392	104.78	18.963	115.35	22.845	104.10	26.261	103.33	31.667
$w_B = 0.70$									
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A
6.5488	9.1348	5.6746	11.506	6.4763	14.611	6.9381	17.529	6.0522	20.931
13.651	8.8187	12.573	11.157	13.680	13.787	14.429	16.527	13.087	19.626
21.084	8.5469	19.526	10.751	21.128	13.175	21.768	15.834	19.846	19.037
28.432	8.3541	26.426	10.442	28.746	12.805	29.053	15.265	26.627	18.348
35.787	8.0819	33.350	10.141	36.074	12.434	36.126	14.819	33.278	17.795
43.148	7.8870	40.134	9.9066	43.839	12.097	43.117	14.447	39.803	17.351
50.505	7.7269	47.179	9.6926	51.008	11.834	50.016	14.130	46.499	16.961
57.904	7.5762	54.261	9.4973	58.479	11.591	56.977	13.847	53.253	16.603
65.127	7.4448	61.645	9.3212	65.656	11.381	64.259	13.582	59.864	16.291
72.347	7.3329	68.952	9.1635	72.784	11.191	71.293	13.355	66.442	16.022
79.463	7.2275	76.107	9.0177	79.687	11.029	78.102	13.149	72.683	15.778
86.212	7.1072	83.023	8.8921	86.027	10.887	84.999	12.967	78.936	15.554
92.979	7.0238	88.999	8.7880	92.827	10.744	91.672	12.807	85.133	15.355
99.749	6.9426	95.705	8.6844	99.423	10.618	98.182	12.646	91.240	15.156
$w_B = 0.80$									
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A

3.4222	6.9207	2.2554	8.9891	2.2158	11.161	2.1891	13.956	2.1224	16.655
4.5737	6.7893	3.4239	8.8431	3.3616	10.939	3.3393	13.539	3.2792	16.033
5.7299	6.6470	4.5844	8.6346	4.4978	10.669	4.4713	13.129	4.3821	15.512
6.9089	6.5129	5.7232	8.4344	5.6121	10.415	5.5822	12.769	5.4792	15.070
8.0933	6.3794	6.8326	8.2504	6.7274	10.178	6.6758	12.451	6.5527	14.679
9.2771	6.2622	7.9433	8.0812	7.8259	9.9639	7.7426	12.177	7.6208	14.366
10.428	6.1564	9.0627	7.9274	8.9104	9.7691	8.7915	11.930	8.6930	14.042
11.607	6.0516	10.181	7.7842	9.9669	9.5955	9.8302	11.708	9.7209	13.773
12.713	5.9604	11.256	7.6583	11.026	9.4376	11.959	11.290	10.748	13.531
13.806	5.8754	12.349	7.5385	12.111	9.2857	12.970	11.139	11.739	13.314
14.862	5.8036	13.407	7.4309	13.199	9.1441	13.976	10.982	12.723	13.118
15.907	5.7326	14.537	7.3233	14.251	9.0178	14.986	10.833	13.714	12.917
		15.571	7.2307	15.287	8.8998			14.677	12.758
$w_B = 0.90$									
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A	$10^4 c$	A
0.4209	2.9712	0.4197	5.3729	0.4488	6.8548	0.4206	7.1243	0.4164	9.4990
0.9196	3.7706	0.9205	5.4461	0.9172	6.7804	0.9118	7.6739	0.8748	9.5716
1.4041	3.8154	1.3989	5.2564	1.3790	6.4833	1.3999	7.4514	1.3391	9.1182
1.8815	3.7558	1.8870	5.0355	1.8311	6.1955	1.8759	7.1537	1.8055	8.6629
2.3662	3.6684	2.3736	4.8843	2.2883	5.9361	2.3443	6.8689	2.2745	8.2527
2.8286	3.5787	2.8643	4.7033	2.7404	5.7087	2.8097	6.6127	2.7142	7.9113
3.2901	3.4907	3.3607	4.5394	3.1956	5.5050	3.2665	6.3858	3.1632	7.5474
3.7455	3.4082	3.8458	4.3958	3.6255	5.3420	3.7243	6.1836	3.6191	7.3379
4.2008	3.3331	4.3172	4.2704	4.0647	5.1797	4.1662	6.0070	4.0778	7.0986
4.5959	3.2676	4.7824	4.1565	4.4702	5.0489	4.5920	5.8505	4.5069	6.8899
5.0528	3.2018	5.2389	4.0568	4.8920	4.9240	5.0489	5.6966	4.9542	6.6979
5.5234	3.1352	5.6749	3.9679	5.2941	4.8139	5.4804	5.5650	5.3938	6.5101
5.9790	3.0753	6.1217	3.8845	5.7079	4.7559	5.9196	5.4421	5.8044	6.3799
6.4272	3.0210	6.5631	3.8077	6.1079	4.6638	6.3321	5.3335	6.2071	6.2555

3.2. Model and data processing

The limiting molar conductivity Λ_0 and association constant K_A were determined using a chemical model of conductivity based on the Lee-Wheaton equation [18] in the Pethybridge and Taba version [19], LWPT,

$$\Lambda_{c\alpha} = \Lambda_0 \left[1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3 \right] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \quad (3)$$

$$\rho = \frac{Fe}{3\pi\eta}, \quad q = \frac{e^2}{8\pi\epsilon_0\epsilon_r kT}, \quad \kappa^2 = 16\pi N_A q c \alpha, \quad (4a,b,c)$$

$\Lambda_{c\alpha}$ is the molar conductivity of free ions and Λ_0 the same quantity at infinite dilution, coefficients $C_1 - C_5$ are the functions of κR [19], R is the greatest centre-to-centre distance between ions in the ion-pair formed, κ is the Debye parameter, $\beta = 2q$ (q is the Bjerrum critical distance), e is the proton charge, ϵ_r relates the solvent permittivity to that of vacuum (ϵ_0); other symbols have their usual meaning.

Thermodynamic equilibrium constant $K_{A,c}$ (subscript c indicating the molarity scale) for the association reaction



is given by the expression

$$K_{A,c} = \frac{c^0(1-\alpha)}{c\alpha^2 y_{\pm}^2} \quad (6)$$

where $c^0 = 1 \text{ mol dm}^{-3}$, $c\alpha$ and $c(1-\alpha)$ are the equilibrium concentrations of the fraction of free ions and ion pairs, respectively; α is the degree of dissociation represented by the ratio of the stoichiometric molar conductivity to that of free ions,

$$\alpha = \frac{\Lambda}{\Lambda_{c\alpha}} \quad (7)$$

The mean activity coefficient of the free ions is given by the relationship:

$$y_{\pm} = e^{\frac{-\kappa q}{1+\kappa R}} \quad (8)$$

The chemical model is obtained by combining equations (6) and (7),

$$\Lambda = \frac{c^0 \Lambda_{c\alpha}}{c^0 + K_{A,c} c \alpha y_{\pm}^2} \quad (9)$$

With the numerator described by some theoretical equation, in this case (3), the chemical model becomes a function of concentration and three adjustable parameters:

$$\Lambda = f(c; \Lambda_0, K_{A,c}, R) \quad (10)$$

The model was resolved by an iterative procedure: parameters Λ_0 and $K_{A,c}$ were adjusted according to Beronius [20] for each selected value of R until the standard deviation (σ) of experimental conductivities from the calculated ones,

$$\sigma^2 = \frac{\sum (A_{\text{calc}} - A_{\text{exp}})^2}{n-3} \quad (11)$$

would have achieved its minimal value (n is the number of solutions tested in one run). The values of parameters Λ_0 and $K_{A,c}$ so derived change uniformly with temperature, while the distance parameter R covers a wide range of values, showing irregular trend with temperature (no significant minima in the plot $\sigma - R$ was obtained for any solvent composition). The experimental data were therefore processed by a two-parameter fit, $\Lambda = f(c; \Lambda_0, K_{A,c})$, *i.e.* R had to be chosen in accord with some of the existing criteria. The distance parameter was fixed at the Bjerrum's critical distance, $R = q$, as recommended by Justice [21] and at $R = a + s$, where a represents the sum of crystallographic radii of Na^+ and Cl^- (0.276 nm) and s is the diameter of a water molecule (0.280 nm) [22], respectively, to investigate for possible difference in these two criteria. The optimization was completed when the difference in Λ_0 of the last two iterative steps would drop below 1.0×10^{-7} .

In order to avoid the influence of the solvent thermal expansion on the reaction enthalpy, $K_{A,c}$ was converted to the molality scale:

$$K_{A,m} = K_{A,c} d_0 / \text{kg dm}^{-3} \quad (12)$$

The standard deviation of Λ_0 and both constants were estimated according to literature suggestions [23].

Table 3. Limiting molar conductivities (Λ_0), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviations (σ) of experimental Λ from the model LWPT for NaCl in aqueous 2-methylpropan-2-ol mixtures with alcohol mass fraction w_B with $R = q$

T / K	$\Lambda_0 / S \text{ cm}^2 \text{ mol}^{-1}$	$K_{A,c}$	$K_{A,m}$	$\sigma / S \text{ cm}^2 \text{ mol}^{-1}$	$R = q/nm$
$w_B = 0.10$					
288.15	56.73±0.07	-	-	0.07	0.394
293.15	65.67±0.25	-	-	0.15	0.397
298.15	77.69±0.08	-	-	0.04	0.400
303.15	86.14±0.11	-	-	0.08	0.404
308.15	99.07±0.13	-	-	0.18	0.407
$w_B = 0.30$					
288.15	29.07±0.01	1.39±0.07	1.32±0.07	0.02	0.520
293.15	36.32±0.05	0.07±0.03	0.07±0.03	0.08	0.526
298.15	44.23±0.03	1.91±0.16	1.80±0.15	0.05	0.532
303.15	52.61±0.02	1.92±0.16	1.81±0.15	0.02	0.539
308.15	61.37±0.04	1.83±0.32	1.71±0.30	0.08	0.546
$w_B = 0.50$					
288.15	17.46±0.09	2.91±1.27	2.63±1.15	0.09	0.766
293.15	21.93±0.04	6.61±0.52	5.97±0.50	0.05	0.779
298.15	27.14±0.02	10.96±0.16	9.85±0.14	0.02	0.793
303.15	31.46±0.04	13.92±0.33	12.45±0.29	0.04	0.807
308.15	37.88±0.02	13.30±0.13	11.84±0.11	0.02	0.821
$w_B = 0.70$					
288.15	10.27±0.03	81.5±1.6	70.1±1.4	0.03	1.250
293.15	12.93±0.01	89.1±0.5	76.3±0.4	0.01	1.277
298.15	16.21±0.02	99.1±0.9	84.4±0.8	0.02	1.306
303.15	19.68±0.03	111.3±1.2	94.37±1.0	0.03	1.336
308.15	23.37±0.04	112.5±1.27	94.9±1.1	0.05	1.367
$w_B = 0.80$					
288.15	7.92±0.07	325±21	272±18	0.05	1.614
293.15	10.23±0.06	384±15	320±12	0.05	1.654
298.15	12.91±0.03	460.8±7.1	381.7±5.9	0.02	1.695
303.15	16.06±0.04	528.5±9.5	435.4±7.8	0.04	1.738
308.15	19.19±0.03	582.7±6.2	477.4±5.1	0.02	1.781
$w_B = 0.90$					
288.15	4.67±0.05	1322±77	1076±63	0.03	2.145
293.15	6.69±0.07	2259±95	1828±76	0.05	2.203
298.15	8.54±0.06	2944±79	2368.4±63	0.04	2.262
303.15	10.12±0.09	3156±89	2525±71	0.04	2.324
308.15	13.00±0.09	4437±96	3528±76	0.04	2.389

Table 4. Limiting molar conductivities (Λ_0), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviations (σ) of experimental Λ from the model LWPT for NaCl in aqueous 2-methylpropan-2-ol mixtures with alcohol mass fraction w_B with $R = a + s$

T / K	$\Lambda_0 / S \text{ cm}^2 \text{ mol}^{-1}$	$K_{A,c}$	$K_{A,m}$	$\sigma / S \text{ cm}^2 \text{ mol}^{-1}$
$w_B = 0.10$				
288.15	56.81±0.08	-	-	0.08
293.15	65.32±0.14	-	-	0.14
298.15	77.47±0.09	-	-	0.08

303.15	85.85±0.14	-	-	0.13
308.15	99.29±0.17	-	-	0.16
$w_B = 0.30$				
288.15	29.07±0.01	1.51±0.08	1.44±0.08	0.02
293.15	36.21±0.08	1.31±0.09	1.24±0.08	0.09
298.15	44.23±0.03	2.00±0.16	1.89±0.16	0.05
303.15	52.61±0.02	1.98±0.08	1.86±0.08	0.03
308.15	61.39±0.09	1.76±0.36	1.65±0.36	0.08
$w_B = 0.50$				
288.15	17.53±0.07	2.47±1.06	2.24±10.96	0.09
293.15	21.96±0.05	5.54±0.59	4.99±0.53	0.06
298.15	27.21±0.01	10.28±0.13	9.23±0.11	0.01
303.15	31.55±0.03	13.25±0.26	11.85±0.23	0.03
308.15	37.99±0.02	12.55±0.15	11.17±0.13	0.02
$w_B = 0.70$				
288.15	10.65±0.07	114.6±4.6	98.7±3.9	0.05
293.15	13.44±0.06	127.7±3.4	109.3±3.4	0.05
298.15	16.76±0.08	139.0±3.6	118.4±2.9	0.07
303.15	20.46±0.09	162.2±3.9	137.5±3.3	0.08
308.15	25.17±0.09	199.1±3.1	167.9±2.6	0.04
$w_B = 0.80$				
288.15	8.07±0.09	370±29	309±24	0.06
293.15	10.39±0.08	433±24	360±20	0.07
298.15	13.23±0.07	547±16	452±13	0.04
303.15	16.41±0.09	617±21	508±17	0.07
308.15	19.59±0.09	674±18	552±14	0.06
$w_B = 0.90$				
288.15	4.81±0.07	1610±120	1310±96	0.04
293.15	6.88±0.10	2660±150	2160±120	0.07
298.15	8.82±0.09	3490±130	2810±110	0.06
303.15	10.63±0.15	4040±170	3230±140	0.06
308.15	13.76±0.18	5700±190	4530±150	0.06

The distance in contact ion pair in tested 2-methylpropan-2-ol + water mixtures ($a = 0.276$ nm) is very different to very wide range of values of q (0.394 – 2.389 nm). Fuoss [15] suggests to increase the upper limit of association to involve the influence of long distance forces ($\propto r^{-2}$). The criteria $R = a + s$ was chosen because of mentioned reasons. Solving LWPT model in both cases gave very similar results for A_0 while for K_A the differences were expressed, see Table 3 and Table 4. Standard deviations (σ) in about 30 % cases are lower for $R = a + s$ for lower mass fraction and model showed better adjustment.

Figures 1 and 2 show the concentration dependence of the experimental molar conductivity (Λ_{exp}) for NaCl at five temperatures in the 2-methylpropan-2-ol ($w_B = 0.80$) - water mixture; full lines are drawn through points computed by the LWPT conductivity model (Λ_{calc}); theoretical lines are drawn in accord with both criteria, $R = q$ and $R = a + s$. Analogous plots for the other five mixtures are similar.

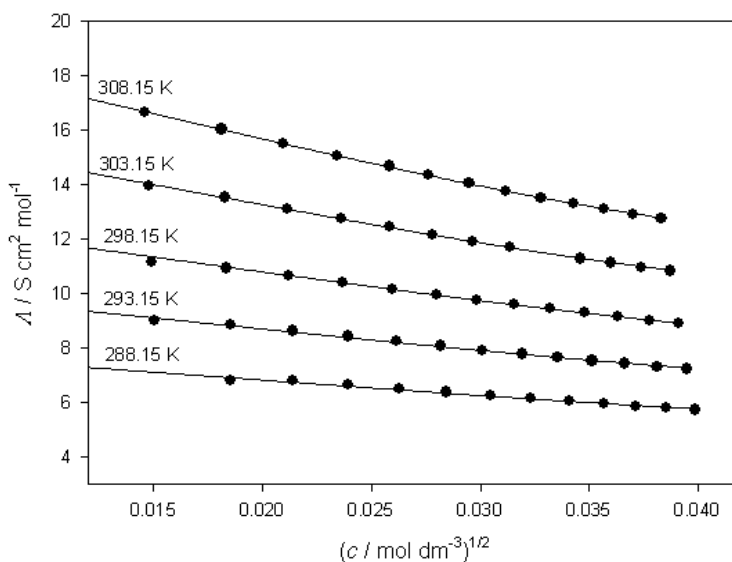


Figure 1. Molar conductivity of NaCl in aqueous 2-methylpropan-2-ol mixtures with $w_B = 0.80$ from 288.15 K to 308.15 K, $R = q$; dots, experimental data; full line, calculated values.

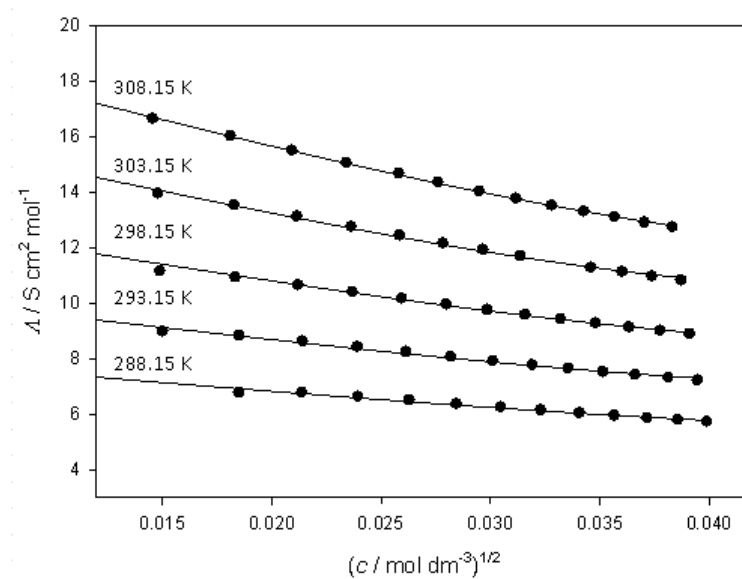


Figure 2. Molar conductivity of NaCl in aqueous 2-methylpropan-2-ol mixtures with $w_B = 0.80$ from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, $R = a + s$.

In media of lower permittivity (ϵ_r) the interactions ion - dipole (shell 1) - dipoles (shell 2) are stronger and the hydrodynamic radii r of ions accordingly greater. Limiting molar conductivity is inversely proportional to the medium viscosity and moving-sphere radius, $\lambda_o \propto 1 / \eta r$, as derived from the Stokes model, meaning that opposite changes in η and ϵ_r should have the same influence on λ_o . Up to the 2-methylpropan-2-ol mass fraction of 0.3 the increasing η and decreasing ϵ_r (Table 1) both contribute to the λ_o descend which is therefore very steep (Table 3 and 4). Constants of the ionic equilibria, K_A are increasing with the 2-methylpropan-2-ol content (Table 3 and 4) as expected – lower ϵ_r enhances the attraction of oppositely charged ions.

3.3. Limiting molar conductivities and Walden product

Tables 3 and 4 show the limiting electrolyte conductances obtained from the data in Table 2 with the help of two parameter fits. The values of λ_o increase monotonically with increase in temperature due to the increase of the mobility of the free ions as can be seen in Table 3 and 4. The results indicate that the mobility of the free ions is completely controlled by the bulk viscosity.

The limiting conductivity can be interpreted as a quantity free of ion-ion interaction, which describes the mechanism of ionic migration in the solvent. The temperature dependence of λ_o can be approximated in the framework of the kinetic theory of conductance [24] by the equation

$$\ln \lambda_o + \frac{2}{3} \ln d = -\frac{\Delta H^*}{RT} + B \tag{13}$$

which connects the enthalpy of activation of the charge transport ΔH^* to the limiting conductance λ_o and the solvent density d . B is the integration constant. The experimental points of Eq. (13) and "best" straight lines are shown in Fig. 3 for sodium chloride.

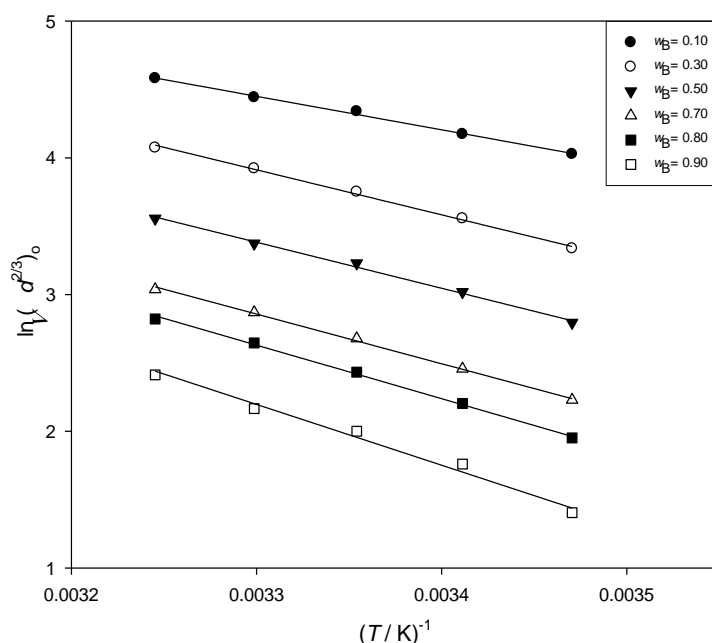


Figure 3. Plot of $\ln (\lambda_o d^{2/3})_o$ against T^{-1} for NaCl in 2-methylpropan-2-ol (w_B) - water mixtures.

Values for ΔH^* from the slope of the function at the left-hand side of Eq. (13) versus the inverse temperature are given in Table 5.

Table 5. Enthalpy of activation of the charge transport ΔH^* in 2-methylpropan-2-ol (w_B) - water mixtures in the temperature range from 288 K to 308 K

w_B	$\Delta H^* / \text{kJ mol}^{-1}$
0.10	20.32 ± 0.70
0.30	27.18 ± 0.85
0.50	27.78 ± 1.01
0.70	30.00 ± 0.76
0.80	32.29 ± 0.87
0.90	35.82 ± 2.41

The activation enthalpy of the charge transport, within a reasonable limit of error, increases as the mass fraction of alcohol increases (Table 5). This contribution is intended as a first basic study of conductivity phenomena and further investigations will be necessary to make the split into individual ion contribution.

The Walden product, $\Lambda_0 \eta$, of the electrolyte in pure water and in the mixtures of water + 2-methylpropan-2-ol is presented in Figure 4. The descent of this quantity with increasing alcohol content can be explained by presolvation of ions by alcohol molecules leading to an increase of hydrodynamic radius and consequent decrease of ion mobility.

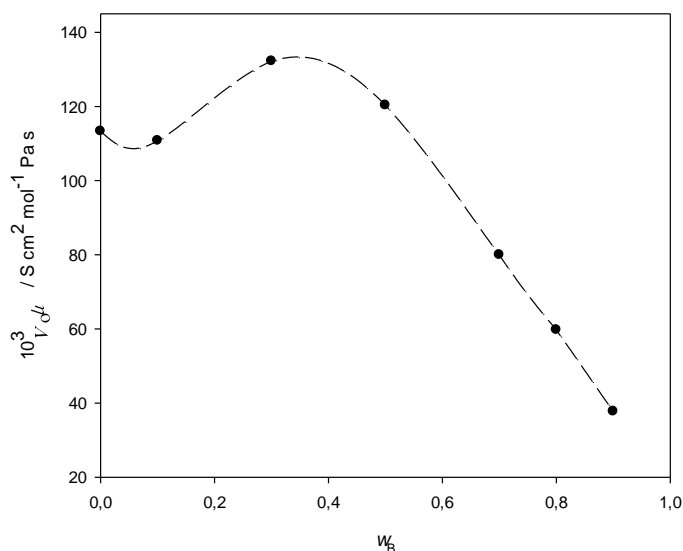


Figure 4. Walden product for NaCl at 298.15 K in: a) water-calculated from data in Ref. [25]; b) 2-methylpropan-2-ol + water mixtures; $w_B = 0.10, 0.30, 0.50, 0.70, 0.8$ and 0.90 , at 298.15 K.

Higher Walden product in the mixtures with low organic solvent content was observed earlier [26] and it can be explained by “sorting effect”. According the “sorting effect”, cation mobility increases by adding organic solvent to water due the difference between composition of solvation shell around cation and the remain of mixed solvent. On the other hand, possible cause of Walden product decrease in solvent mixtures with higher organic component content can be explained by “basicity” of solvent. In the literature was reported case of Walden product fluctuation as a function of the organic component fraction in mixed solvent [12, 27] and for small fraction change, Walden product showed both maximum and minimum.

3.4. Thermodynamic quantities

The temperature-dependent equilibrium constants K_A for the ion association reaction allows the investigation of the thermodynamics of this process. First were calculated K_A for all solvent mixtures and data are given in Table 3 and Table 4. Generally, K_A increases with temperature. Small constants of the equilibria, obtained conductometrically in lower alcohol mass fraction w_B (0.10, 0.30, 0.50), are not quite reliable and were excluded for calculating the standard thermodynamic quantities. The standard thermodynamic quantities (ΔH° , ΔS° , ΔG°) in higher alcohol mass fraction w_B (0.70, 0.80, 0.90) were calculated using equations (14)-(16) and given in Table 6 and Table 7:

$$\ln K_A = -\frac{\Delta H^\circ}{RT} + C \quad (14)$$

$$\Delta G^\circ = -RT \ln K_A \quad (15)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (16)$$

ΔH° was evaluated by the least-squares treatment of the straight lines represented by Eq. (14).

Table 6. Thermodynamic quantities (ΔH° , ΔS° , ΔG°) of the ion-association reaction for NaCl in mixed solvents 2-methylpropan-2-ol + water at 298.15 K, $R = q$

w_B	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
0.70	12.8 ± 1.4	-11.39 ± 0.02	81.3 ± 4.8
0.80	22.0 ± 1.2	-15.20 ± 0.04	125 ± 4.0
0.90	40.8 ± 6.1	-19.80 ± 0.06	203 ± 20

Table 7. Thermodynamic quantities (ΔH° , ΔS° , ΔG°) of the ion-association reaction for NaCl in mixed solvents 2-methylpropan-2-ol + water at 298.15 K, $R = a + s$

w_B	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
0.70	19.8 ± 2.2	-12.23 ± 0.06	107 ± 7.6

0.80	23.0 ± 2.0	-15.63 ± 0.07	130 ± 6.7
0.90	43.6 ± 4.6	-20.22 ± 0.09	214 ± 15

ΔH° and ΔS° have positive values what suggests that association reaction is endothermic and results with system disorder increase (Tables 6 and 7). The system disorder increase is related to destruction of solvation shell structure during the association process. ΔG° have negative value in all cases what indicates the reaction spontaneity. Decrease of ΔG° in function of w_B increase, Table 6 and Table 7, is related with K_A increase, Table 3 and Table 4, because ΔG° and K_A are connected with Eq. 15.

4. CONCLUSIONS

Precise conductivity measurements provide important information on ion-ion and ion - solvent interactions. The present work reports conductometric data for the low concentration sodium chloride solutions in 2-methylpropan-2-ol - water mixtures with alcohol mass fraction $w_B = 0.10, 0.30, 0.50, 0.70, 0.80$ and 0.90 in temperature range from 288.15 to 308.15 K.

The values of Λ_0 increase monotonically with increase in temperature due to the increase of the mobility of the free ions. The results indicate that the mobility of the free ions is completely controlled by the bulk viscosity.

The activation enthalpy of the charge transport, within a reasonable limit of error, increases as the mass fraction of alcohol increases. Higher Walden product in the mixtures with low organic solvent content was observed earlier [26] and it can be explained by "sorting effect". In the literature was also reported case of Walden product fluctuation as a function of the organic component fraction in mixed solvent [12, 27] and for small fraction change, Walden product showed both maximum and minimum.

ΔH° and ΔS° have positive values what suggests that association reaction is endothermic and results with system disorder increase. The system disorder increase is related to destruction of solvation shell structure during the association process. ΔG° have negative value in all cases what indicates the reaction spontaneity. The thermodynamic quantities of the association reaction Na^+ and Cl^- depend on the dielectric constant of the solvent but they also depend on the nature of the organic component in a mixed solvent.

ACKNOWLEDGMENT

This work is supported by a grant from the Ministry of Science, Education and Sports of the Republic of Croatia.

References

1. H. J. Gores, J. Barthel, *Naturwissenschaften*, 70 (1983) 495-503.
2. M. Bešter-Rogač, R. Neueder, J. Barthel, *J. Solution Chem.*, 29 (2000) 5161.

3. J. I. Bhat, H. R. Shivakumar, *J. Mol. Liq.*, 111 (2004) 101.
4. B. Ramsauer, M. M. Meier, R. Neueder, W. Kunz, *Acta Chim. Slov.*, 56 (2009) 30-39.
5. J. I. Bhat, M. N. Manjunatha, *Indian J. Chem. Tech.*, 17 (2010) 462.
6. I. Tominić, V. Sokol, I. Mekjavić, *Croat. Chem. Acta*, 71 (1998) 705.
7. V. Sokol, I. Tominić, R. Tomaš, M. Višić, *Croat. Chem. Acta*, 78 (2005) 43.
8. V. Sokol, R. Tomaš, M. Višić, I. Tominić, *J. Solution Chem.*, 35 (2006) 1687.
9. V. Sokol, R. Tomaš, I. Tominić, *Acta Chim. Slov.*, 55 (2008) 308.
10. V. Sokol, R. Tomaš, I. Tominić, *Polish J. Chem.*, 82 (2008) 1585.
11. V. Sokol, R. Tomaš, P. Bošković, *Acta Chim. Slov.*, 59 (2012) 920.
12. A. Prkić, V. Sokol, P. Bošković, *Int. J. Electrochem. Sci.*, 8 (2013) 4886.
13. P. Bošković, V. Sokol, R. Tomaš, A. Prkić, *Int. J. Electrochem. Sci.*, 8 (2013) 10961-10975.
14. T. L. Broadwater, R. L. Kay, *The Journal of Physical Chemistry*, 74(1970) 21
15. R. M. Fuoss, F. Accascina, *Electrolyte Conductance*, Interscience/New York, 1959, p. 253.
16. M. Bešter-Rogač, R. Neueder, J. Barthel, *J. Solution Chem.*, 28 (1999) 1071.
17. A. Bald, J. Gregorowicz, A. Szejgis, *J. Electroanal. Chem.* 340 (1992) 153.
18. W. H. Lee, R. J. Wheaton, *J. Chem. Soc. Faraday Trans. II*, 74 (1978) 743, 1456; 75 (1979) 1128.
19. A. D. Pethybridge, S. S. Taba, *J. Chem. Soc. Faraday Trans. I*, 76 (1980) 368.
20. P. Beronius, *Acta. Chem. Scand. A.*, 28 (1974) 77.
21. J. C. Justice, *Electrochim. Acta* 16 (1971) 701.
22. J. G. Speight, Editor-in-Chief, *Lange's Handbook of Chemistry*, 16th Edition, McGraw-Hill Inc., New York, 2005, p 5.152.
23. D. M. Himmelblau, *Process Analysis by Statistical Methods*, John Wiley and Sons, New York, 1970, p 197.
24. S. B. Brummer, G. J. Hills, *J. Chem. Soc. Faraday Trans.* 57 (1961) a) 1816, b) 1823.
25. W. M. Haynes, Editor-in-Chief, *Handbook of Chemistry and Physics*, 93rd Edition, CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2012, p 5.77
26. A. Szejgis, A. Bald, J. Gregorowicz, C. M. Kinartm, *Phys. Chem. Liq.*, 34 (1997) 189.
27. J. I. Bath, M. K. Shetty, *J. Mol. Liq.*, 160 (2011) 140.