Conductometric Study of Cesium Bromide in Aqueous Butan-2-ol of Lower Mass Fraction

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Molar conductivities of dilute solutions of cesium bromide in binary mixtures of butan-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_o) and the ion-pair formation constant (K_A) were determined by the Lee-Wheaton conductivity equation. Thermodynamic quantities, Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$), for the ion-association reaction were derived from the temperature dependence of K_A. The activation enthalpy of the charge transport ($\Delta H^{\ddagger}$) was derived from the temperature dependence of Λ_o. The obtained thermodynamic quantities, together with Walden product, were discussed in terms of solvent basicity, structure permittivity and viscosity.

Keywords: cesium bromide, butan-2-ol + water mixtures, association to ion-pairs, thermodynamic quantities

1. INTRODUCTION

Precise conductivity measurements provide important informations on ion-ion and ion- solvent interactions. Recently, the conductometric studies of ion association in dilute aqueous lithium, sodium, potassium and ammonium cyclohexylsulfamate solutions [1], as well as in 2-ethoxyethanol solutions of KCNS, NH$_4$CNS, NaNO$_3$ and NH$_4$NO$_3$ have been reported [2].

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.).

In previous studies [3-6] the influence of the alkali metal ions (so called d^0 – cations [7]) on

the transport and equilibrium properties of the corresponding bromides, as well as their change with solvent composition, were examined in butan-2-ol + water mixtures of the alcohol mass fraction (w_B) 0.70, 0.80, 0.90 and 0.95. There is a two-phase system in the w_B range from 0.175 to 0.648 at 298.15 K [8]. This paper presents a conductometric study of cesium bromide in mixtures of lower w_B (0.05, 0.08, 0.10, 0.12 and 0.15) at temperatures ranging from 288.15 K to 308.15 K.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Butan-2-ol, p.a., and cesium bromide, suprapure, were purchased from Merck (Germany). CsBr was dried for 5 hours prior use at 383.15 K to constant mass. Butan-2-ol was distilled in a Vigreux column, the first fraction was thrown away, and the middle fraction of the distillate, collected at a head temperature of 372.0–372.6 K, was used in preparation of mixed solvents and stock-solutions.

Preparation of tested solutions of increasing molality was described earlier [9] in detail. The maximum tested concentration was limited by the condition that no triple ions should appear [10].

2.2. Apparatus

The viscosity (η) and density (ρ_o of the pure mixed solvent were determined by an Ostwald viscometer and Anton Paar Density Meter DMA 4500, respectively, and are listed in Table 1. The uncertainty in measurements of time and density were $\pm$ 0.1 s and $\pm$ 0.00005 g cm^{-3}, respectively.

Measurement of resistance of the tested solutions was described earlier [9] in detail. The cell constant (0.10402 cm^{-1}) was determined with dilute potassium chloride solutions [11].

The solution molarity (c/mol dm^{-3}) can be calculated from its molality (m/mol kg^{-1}) and density (ρ/kg dm^{-3}) using:

$$c = \frac{\rho m}{1 + mM} \qquad (1)$$

where M is the solute molar mass (M_{CsBr} = 0.21281 kg mol^{-1}). The stock-solution density was determined at all working temperatures by the Anton Paar DMA 4500. The density coefficient (D) was obtained at 298.15 K assuming a linear change of solution density upon its molality:

$$\rho = \rho_o + mD \qquad (2)$$

In mixtures of the alcohol fraction 0.05, 0.08, 0.10, 0.12 and 0.15 the values of D (kg^2 dm^{-3} mol^{-1}) amount to 0.164, 0.165, 0.167, 0.162 and 0.165, respectively, and are assumed to be independent on temperature [12].

The relative error in molarity and solvent composition was about $\pm$ 0.1%.

3. RESULTS AND DISCUSSION

The density, viscosity and relative permittivity of the tested mixed solvents are given in Table 1; permittivity values were interpolated from literature [13]. Conductivities of the CsBr solutions in those solvents are given in Table 2.

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

w_B		T/K				
		288.15	293.15	298.15	303.15	308.15
0.05	ρ_o / g cm^{-3}	0.9919	0.9909	0.9896	0.9880	0.9862
	η / 10^3 Pa s	1.4123	1.2233	1.0624	0.9311	0.8417
	ε_r	78.4	76.7	75.0	73.3	71.5
0.08	ρ_o / g cm^{-3}	0.9883	0.9871	0.9856	0.9839	0.9819
	η / 10^3 Pa s	1.7978	1.5452	1.3359	1.1801	1.0253
	ε_r	76.2	74.5	72.8	71.0	69.2
0.10	ρ_o / g cm^{-3}	0.9861	0.9847	0.9830	0.9811	0.9790
	η / 10^3 Pa s	2.1124	1.8002	1.5341	1.3404	1.1637
	ε_r	74.7	73.0	71.3	69.5	67.7
0.12	ρ_o / g cm^{-3}	0.9839	0.9822	0.9803	0.9782	0.9758
	η / 10^3 Pa s	2.4677	2.0866	1.7584	1.5150	1.3352
	ε_r	73.2	71.6	69.8	68.0	66.2
0.15	ρ_o / g cm^{-3}	0.9800	0.9779	0.9755	0.9729	0.9703
	η / 10^3 Pa s	2.8884	2.4129	2.0219	1.7307	1.5054
	ε_r	71.0	69.3	67.6	65.7	63.9

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

288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
				$w_B = 0.05$					
10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ
114.21	135.58	116.76	99.192	117.58	109.95	116.73	121.30	114.22	135.58
106.56	136.04	109.30	99.457	110.04	110.35	109.33	121.75	106.56	136.04
98.769	136.20	101.73	99.821	102.40	110.49	101.87	122.24	98.769	136.20
90.849	136.71	94.435	100.04	94.525	110.98	94.158	122.72	90.849	136.71
82.803	137.35	86.576	100.45	86.808	111.49	86.340	123.16	82.803	137.35
74.599	137.85	78.532	100.90	78.766	112.01	78.461	123.77	74.599	137.85
66.151	138.44	70.440	101.32	70.355	112.61	70.390	124.46	66.151	138.44
57.584	139.13	62.169	101.82	62.010	111.87	62.094	124.42	57.584	139.13
48.804	139.92	53.734	102.38	53.552	112.71	53.669	125.19	48.804	139.92
39.988	140.56	45.119	102.95	44.890	113.48	45.072	125.98	39.988	140.56
30.783	139.44	36.349	103.56	36.500	114.37	36.245	127.12	30.783	139.44
21.903	140.33	27.502	104.20	27.615	115.36	27.273	128.37	21.903	140.33
12.772	141.26	18.465	105.08	18.367	116.69	18.411	129.71	12.772	141.26
6.7889	143.89	9.0815	106.16	9.0919	118.15	9.1984	131.29	6.7889	143.89
				$w_B = 0.10$					
10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ
116.80	71.793	116.57	82.486	119.77	93.693	117.12	105.69	116.70	118.60
109.33	71.984	109.19	82.722	112.05	93.976	109.76	105.99	109.37	118.95
101.82	72.177	101.73	82.969	104.21	94.270	102.15	106.33	101.88	119.32
94.301	72.403	93.999	83.254	96.372	94.568	94.485	106.66	94.271	119.84
86.427	72.637	86.248	83.528	88.183	94.891	86.620	107.02	86.448	120.22

78.498	72.875	78.237	83.782	80.033	95.231	78.585	107.40	78.481	120.63
70.422	73.158	70.133	83.890	71.703	95.577	70.423	107.81	70.346	121.11
62.100	73.156	61.827	84.195	63.160	95.964	62.084	108.27	62.052	121.60
53.656	73.419	53.356	84.614	54.552	96.363	53.597	108.76	53.587	122.16
44.984	73.502	44.766	85.048	45.740	96.799	45.099	109.25	44.941	122.73
36.159	73.895	36.086	85.248	36.694	97.269	36.246	109.81	36.255	123.33
27.186	74.230	27.207	85.829	27.502	97.824	27.223	110.45	27.321	124.08
18.022	74.481	18.377	86.302	18.016	98.471	17.991	111.19	18.299	124.88
8.5838	74.951	9.0258	86.632	9.1011	99.367	8.6419	112.28	8.8006	125.99

| $w_B = 0.15$ | | | | | | | | | |
10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ
160.51	60.085	124.71	70.622	120.07	81.764	118.93	92.799	117.08	105.02
150.76	60.231	116.84	70.825	112.72	81.969	111.47	93.034	109.77	105.27
140.81	60.409	108.80	71.027	105.18	82.202	103.91	93.294	102.23	105.59
131.27	60.584	100.70	71.267	97.537	82.436	96.145	93.561	94.642	105.90
121.13	60.775	92.222	71.487	89.631	82.706	88.279	93.854	86.843	106.23
110.71	60.970	83.647	71.734	81.449	82.958	79.977	94.187	78.816	106.61
99.769	61.183	74.818	71.994	72.951	83.245	71.549	94.553	70.567	107.01
88.891	61.411	65.866	72.296	64.549	83.536	63.221	94.905	62.278	107.41
77.072	61.690	56.550	72.579	55.854	83.869	54.707	95.303	53.922	107.87
65.413	61.982	47.374	72.895	46.847	84.234	45.906	95.720	45.294	108.35
53.301	62.306	38.283	73.230	37.935	84.630	36.757	96.227	36.561	108.93
40.955	62.693	29.188	73.622	28.738	85.080	27.562	96.770	27.612	109.58
28.001	63.137	19.957	74.028	19.105	85.637	18.203	97.433	18.436	110.34
14.483	63.731	10.157	74.655	9.1836	86.431	8.7763	98.296	8.8124	111.38

| $w_B = 0.08$ | | $w_B = 0.12$ | |
| 298.15 K | | 298.15 K | |
10^4 c	Λ	10^4 c	Λ
117.02	100.98	117.17	89.112
109.63	101.25	109.86	89.350
102.06	101.56	102.36	89.589
94.419	101.92	94.597	89.850
86.592	102.25	86.801	90.126
78.613	102.60	78.828	90.420
70.453	102.98	70.607	90.737
62.254	103.39	62.213	91.069
53.754	103.79	53.798	91.432
45.115	104.24	45.174	91.852
36.297	104.75	36.413	92.271
27.270	105.31	27.496	92.746
17.971	106.05	18.218	93.339
8.7629	106.93	9.0085	94.075

Conductivity data were analyzed by the Lee-Wheaton equation in Pethybridge and Taba version (LWPT) [14], and the following set of equations were used:

$$q = \frac{e^2}{8\pi\varepsilon_0\varepsilon_r kT} \tag{3}$$

$$\beta = 2q \tag{4}$$

$$\rho = \frac{Fe}{3\pi\eta} \tag{5}$$

$$\kappa^2 = 16\pi N_A q c \alpha \tag{6}$$

$$y_\pm^2 = e^{\frac{-2\kappa q}{1+\kappa R}} \tag{7}$$

$$K_{A,c} = \frac{c°(1-\alpha)}{c\alpha^2 y_\pm^2} \tag{8}$$

$$\Lambda_{c\alpha} = \Lambda_o\left[1 + C_1\beta\kappa + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3\right] - \frac{\rho\kappa}{1+\kappa R}\left[1 + C_4\beta\kappa + C_5(\beta\kappa)^2 + \frac{\kappa R}{12}\right] \tag{9}$$

$$\Lambda = \alpha\Lambda_{c\alpha} \tag{10}$$

The quantities Λ and $\Lambda_{c\alpha}$ are the molar conductivities of the electrolyte at c (stoichiometric), and of its ionized part at the equilibrium concentration $c\alpha$, respectively, Λ_o is the same quantity at infinite dilution; α is the degree of dissociation, coefficients C_1–C_5 are the functions of κR [14], R is the greatest centre-to-centre distance between the ions in the formed ion-pair, κ is the Debye parameter and q is the Bjerrum critical distance. $K_{A,c}$ is the thermodynamic equilibrium constant in the molarity scale, Eq. (8), for the association reaction,

$$Cs^+ + Br^- \ \square \ \ Cs^+ \cdot Br^- \tag{11}$$

$$c\alpha \quad c\alpha \qquad c(1\text{-}\alpha)$$

where $c(1-\alpha)$ is the equilibrium concentration of ion pairs, $y_\pm$ is the mean activity coefficient of the free ions and $c° = 1$ mol dm^{-3}. Symbols F, N_A and k represent in turn constants of Faraday, Avogadro and Boltzmann; e is the elementary charge and ε_0 the vacuum permittivity.

Parameters Λ_o and $K_{A,c}$ were calculated by the computer optimization according to Beronius [15]. The distance parameter was fixed at the Bjerrum's critical distance, R = q, as recommended by Justice [16] and at R = a + s, where are a represents the sum of crystallographic radii of Cs^+ and Br^- (0.364 nm) and s is the diameter of a water molecule (0.280 nm) [17], respectively, to investigate for possible difference in these two criteria. The optimization was completed when the difference in Λ_o of the last two iterative steps would drop below 1.0×10^{-7}.

The determined limiting molar conductivity (Λ_o), association constant (K_A) and standard deviation (σ^2) of experimental conductivities (Λ_{exp}) from the LWPT model (Λ_{calc})

$$\sigma^2 = \frac{\sum(\Lambda_{exp} - \Lambda_{calc})^2}{n-2} \tag{12}$$

are listed in Table 3 and Table 4.

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

$$K_{A, m} = K_{A, c} \cdot \rho_o \qquad (13)$$

The standard deviation of Λ_o and both constants were estimated according to literature suggestions [18].

Table 3. Limiting molar conductivities (Λ_o), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviations (σ) of experimental Λ from the model LWPT for CsBr in butan-2-ol (w_B) + water mixtures with R = q.

T / K	Λ_o/S cm^2 mol^{-1}	$K_{A, c}$	$K_{A, m}$	σ /S cm^2 mol^{-1}	R = q/nm
		$w_B = 0.05$			
288.15	96.17±0.06	1.61±0.10	1.60±0.10	0.09	0.370
293.15	108.50±0.03	3.17±0.05	3.14±0.05	0.05	0.371
298.15	120.41±0.19	3.18±0.28	3.15±0.28	0.27	0.374
303.15	134.20±0.13	4.26±0.17	4.21±0.17	0.18	0.376
308.15	147.57±0.13	2.47±0.13	2.44±0.13	0.10	0.379
		$w_B = 0.10$			
288.15	76.74±0.11	0.49±0.24	0.48±0.24	0.12	0.388
293.15	88.85±0.06	1.41±0.11	1.39±0.11	0.08	0.390
298.15	101.49±0.04	1.83±0.06	1.80±0.06	0.06	0.393
303.15	114.67±0.03	2.08±0.06	2.04±0.06	0.06	0.397
308.15	128.88±0.07	2.06±0.10	2.02±0.10	0.11	0.400
		$w_B = 0.15$			
288.15	65.35±0.01	1.52±0.03	1.49±0.03	0.02	0.409
293.15	76.31±0.03	1.71±0.08	1.68±0.08	0.05	0.411
298.15	88.23±0.02	1.62±0.05	1.58±0.05	0.04	0.415
303.15	100.39±0.03	1.85±0.05	1.80±0.05	0.05	0.419
308.15	113.77±0.02	2.01±0.03	1.95±0.03	0.03	0.424
		$w_B = 0.08$			
298.15	109.26±0.05	1.65±0.08	1.63±0.08	0.08	0.385
		$w_B = 0.12$			
298.15	96.07±0.03	1.60±0.05	1.57±0.06	0.05	0.401

The distance in contact ion pair in tested butan-2-ol + water mixtures (a =0.364 nm) is very close to value of q (0.370 – 0.424 nm). Fuoss [10] suggests increasing 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 Λ_o while for K_A the differences were expressed, see Table 3 and Table 4. Standard deviations (σ) in about 40 % cases are lower for R = a + s and model showed better adjustment.

The concentration dependence of the CsBr molar conductivity at five temperatures in butan-2-ol ($w_B = 0.05$, 0.10, 0.15) + water mixtures are shown in the Figures 1-6; theoretical lines are drawn in accord with both criteria, R = q and R = a + s.

Table 4. Limiting molar conductivities (Λ_o), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviations (σ) of experimental Λ from the model LWPT for CsBr in butan-2-ol (w_B) + water mixtures with R = a + s

T / K	Λ_o/S cm^2 mol^{-1}	$K_{A,c}$	$K_{A,m}$	σ /S cm^2 mol^{-1}
		$w_B = 0.05$		
288.15	96.15±0.05	2.14±0.09	2.12±0.09	0.08
293.15	108.48±0.03	3.69±0.05	3.66±0.05	0.05
298.15	120.39±0.19	3.70±0.28	3.66±0.28	0.28
303.15	134.16±0.13	4.78±0.18	4.72±0.18	0.19
308.15	147.50±0.13	2.98±0.14	2.94±0.14	0.10
		$w_B = 0.10$		
288.15	76.72±0.11	0.99±0.23	0.98±0.23	0.12
293.15	88.82±0.06	1.92±0.11	1.89±0.11	0.08
298.15	101.46±0.03	2.35±0.06	2.31±0.06	0.05
303.15	114.64±0.03	2.60±0.05	2.55±0.05	0.05
308.15	128.85±0.06	2.58±0.09	2.53±0.09	0.10
		$w_B = 0.15$		
288.15	65.32±0.01	1.98±0.02	1.94±0.02	0.01
293.15	76.29±0.03	2.20±0.07	2.15±0.07	0.05
298.15	88.20±0.02	2.11±0.04	2.06±0.04	0.03
303.15	100.36±0.02	2.35±0.04	2.29±0.04	0.03
308.15	113.74±0.01	2.51±0.02	2.44±0.02	0.02
		$w_B = 0.08$		
298.15	109.23±0.04	2.18±0.07	2.15±0.07	0.07
		$w_B = 0.12$		
298.15	96.05±0.03	2.1±0.05	2.06±0.05	0.05
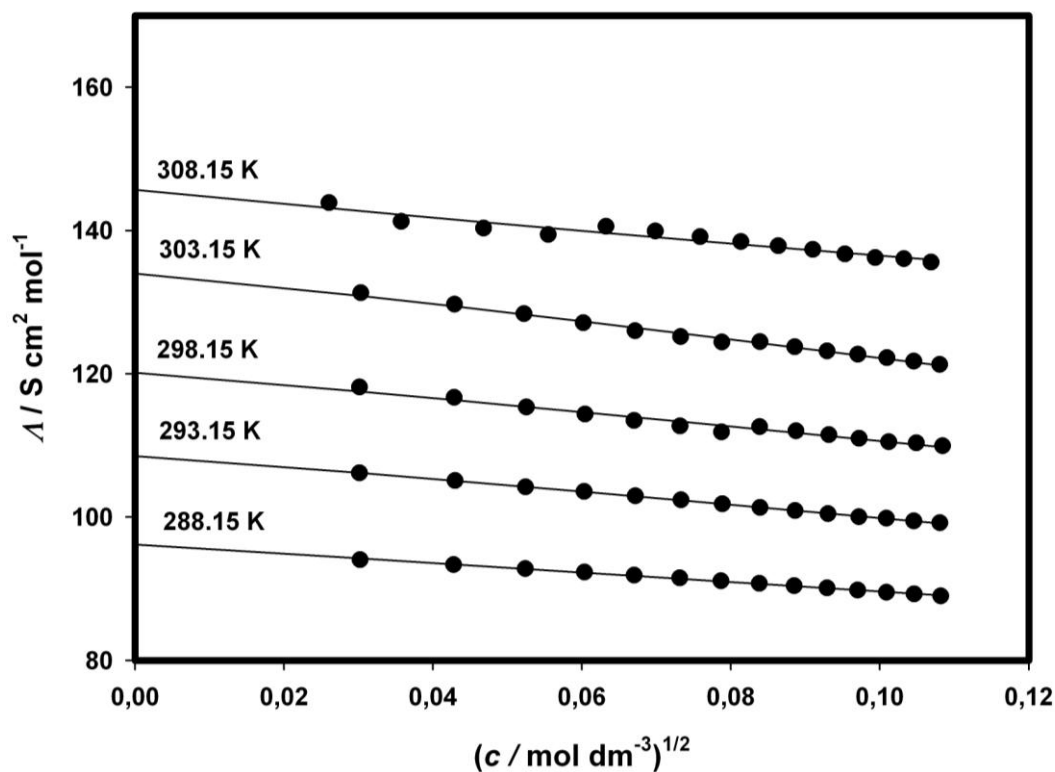
Figure 1. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B = 0.05 from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, (R = q).
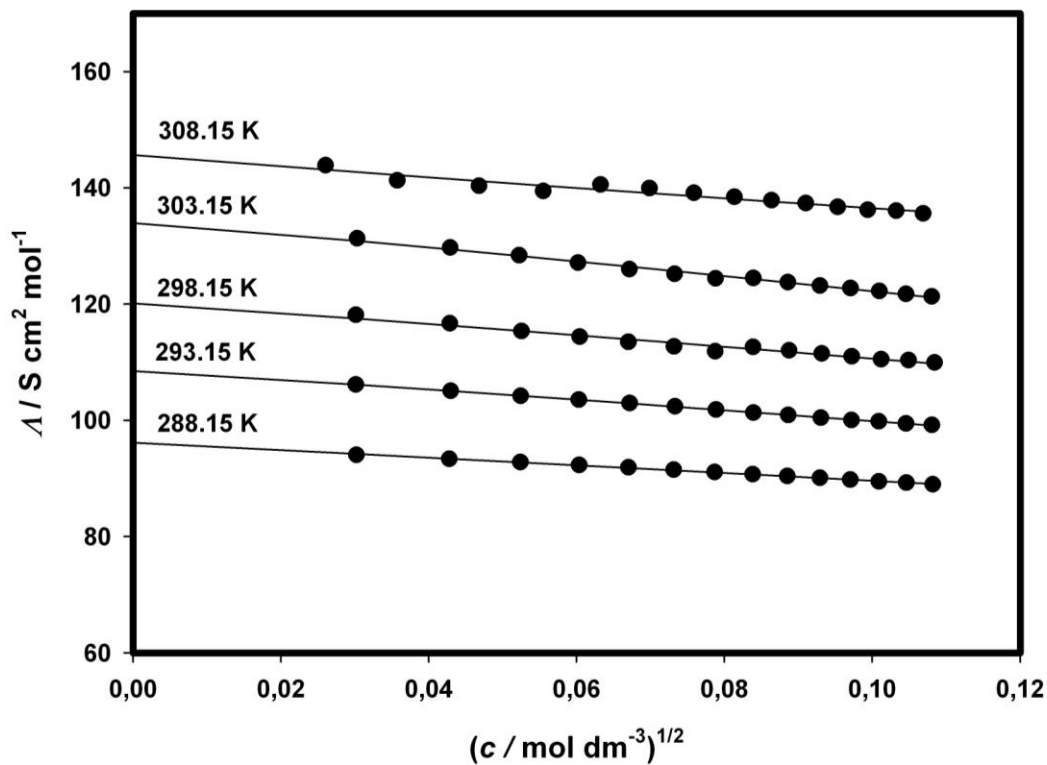
Figure 2. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B = 0.05 from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, (R = a + s).
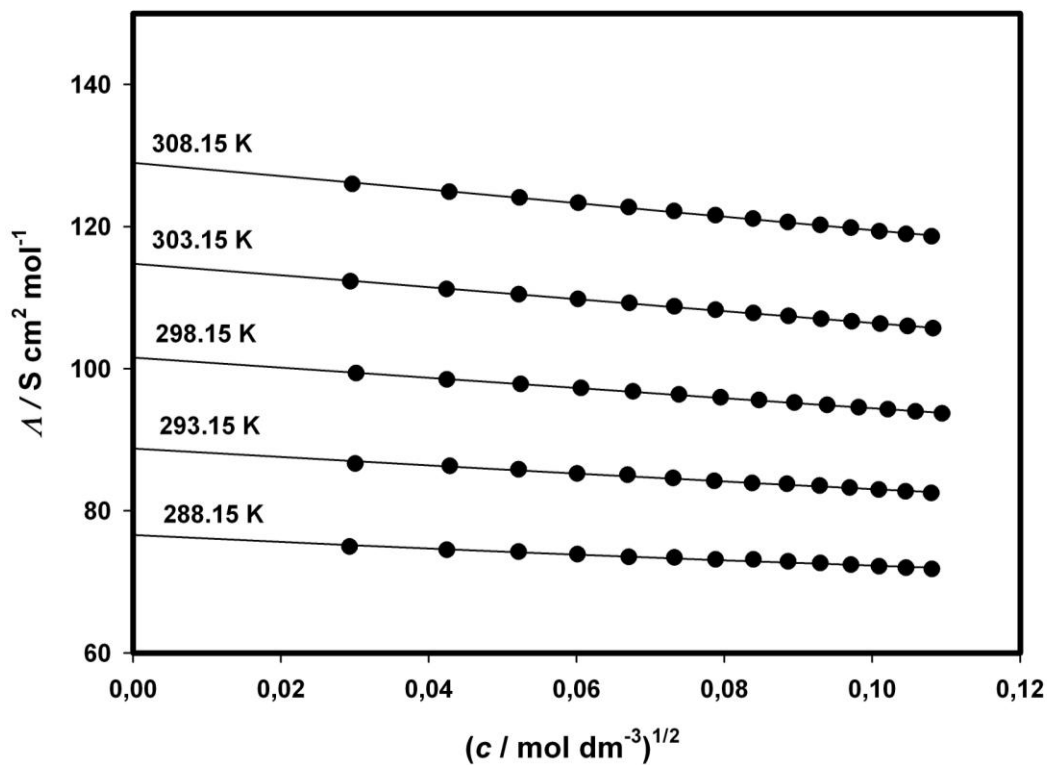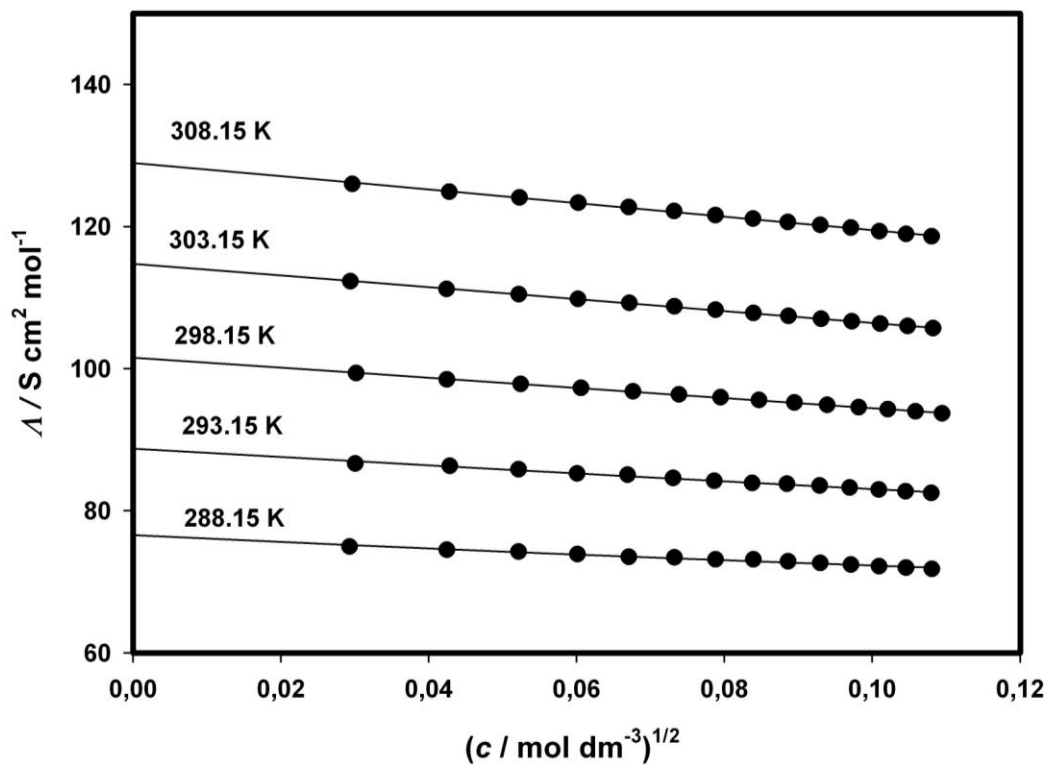

Figure 3. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B = 0.10 from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values,(R = q).

Figure 4. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B = 0.10 from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, (R = a + s).
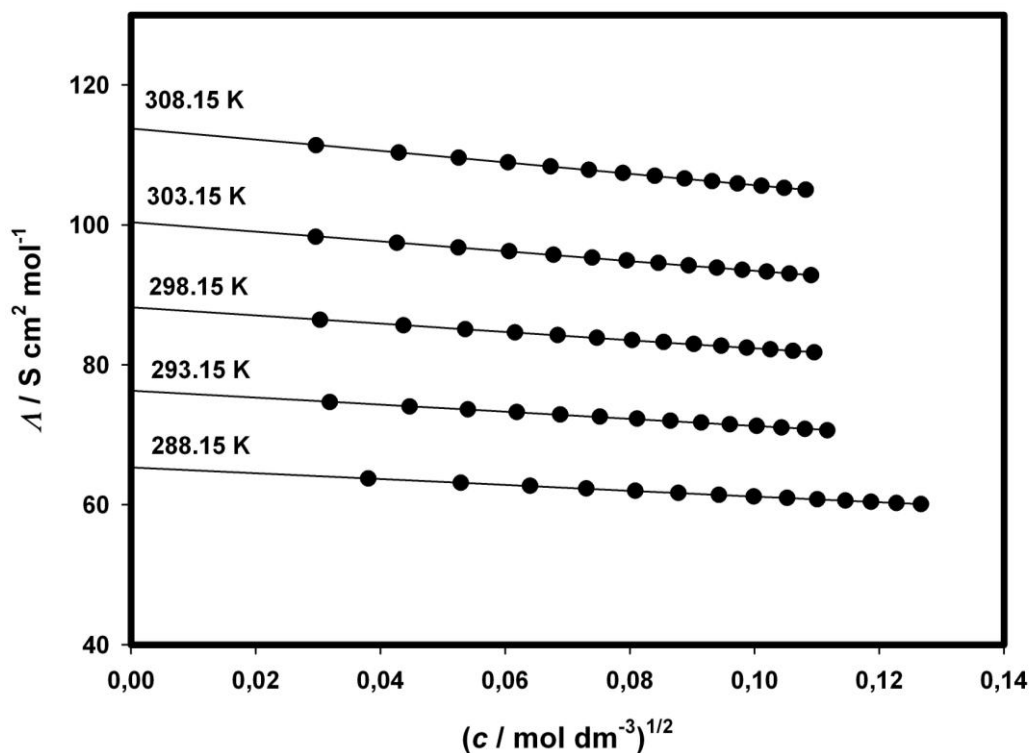

Figure 5. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B = 0.15 from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, (R = q).
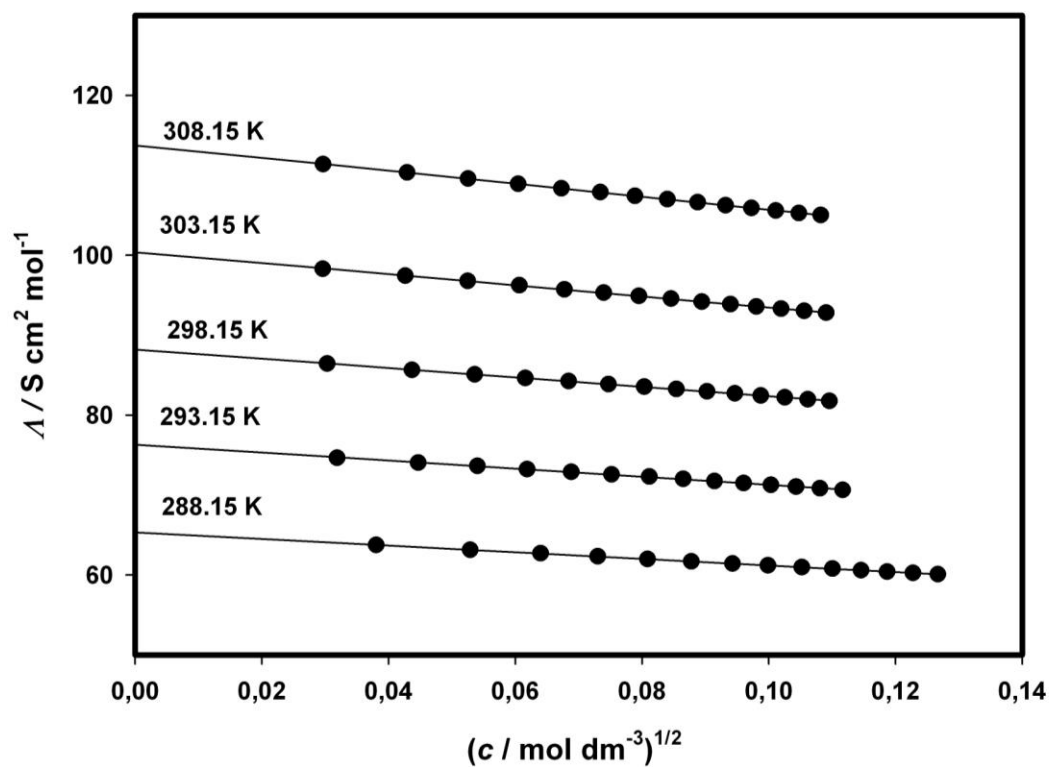
Figure 6. Molar conductivity of CsBr in aqueous butan-2-ol mixture with $w_B = 0.15$ from 288.15 K to 308.15 K; dots, experimental data; full line, calculated values, (R = a + s).
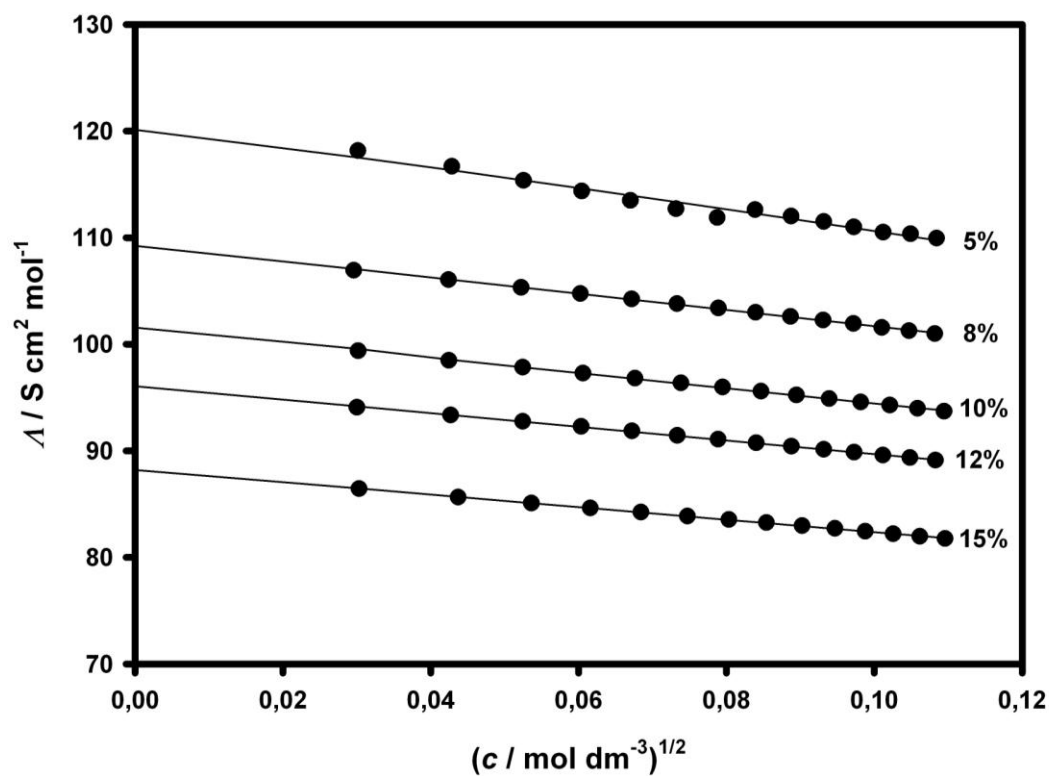

Figure 7. Molar conductivity of CsBr in aqueous butan-2-ol mixture with $w_B = 0.05$, 0.08, 0.10, 0.12 and 0.15 at 298.15 K; dots, experimental data; full line, calculated values, (R = q).
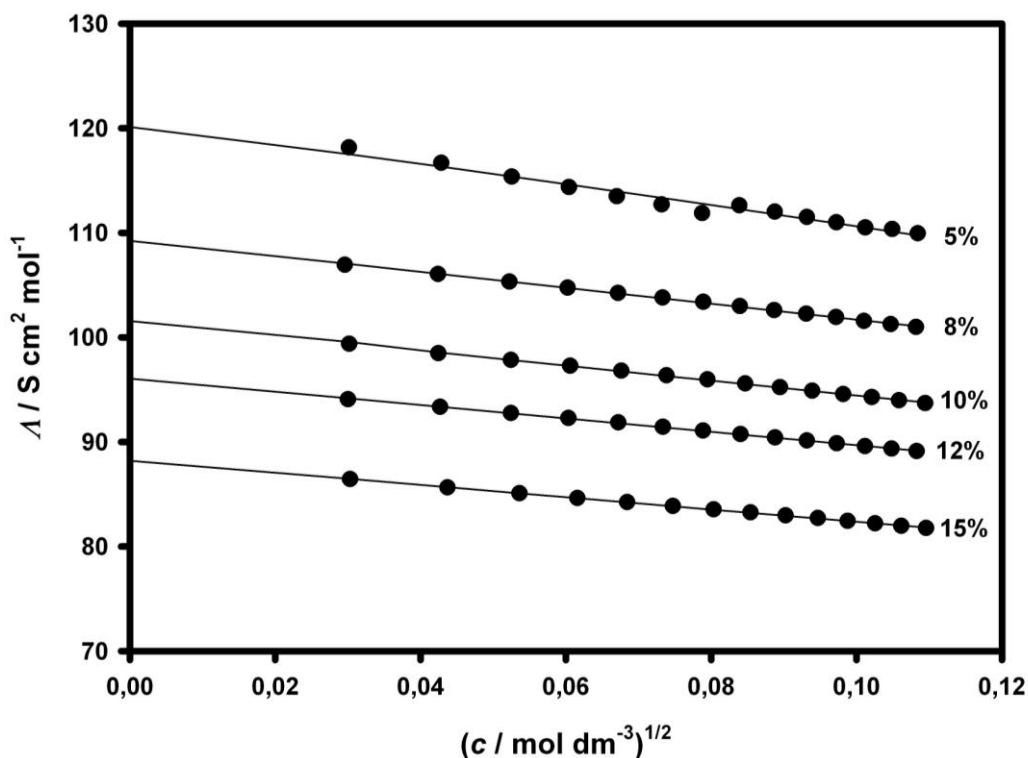
Figure 8. Molar conductivity of CsBr in aqueous butan-2-ol mixture with w_B =0.05, 0.08, 0.10, 0.12 and 0.15 at 298.15 K; dots, experimental data; full line, calculated values, (R = a + s).

Generally, it can be said that conductivity increases for all solvent mixtures by temperature increase due the viscosity decrease. Viscosity increases by increasing alcohol content (w_B) what results in conductivity decrease. The relative permittivity decreases with w_B increase, what results in conductivity increase. The increase of viscosity has higher rate than decrease of permittivity and it predominates what results in conductivity decrease, see Table 1 and Figures 7-8.

The second part of comparison is thermodynamic quantities. First were calculated K_A for all solvent mixtures and data are given in Table 3 and Table 4. It can be seen that values of K_A are small and positive. Generally, K_A increases with temperature. Similar cases were shown in earlier investigations [1, 12, 19]. Due the low K_A, it is reasonably to conclude there is no much ion pairs. The standard thermodynamic quantities ($\Delta H°$, $\Delta S°$, $\Delta G°$) as well as the activation enthalpy of the charge transport ($\Delta H^{\ddagger}$) were calculated using equations (14)-(17) and given in Table 5 and Table 6:

$$\ln K_A = -\frac{\Delta H°}{RT} + C \tag{14}$$

$$\Delta G° = -RT \ln K_A \tag{15}$$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{16}$$

$$\ln \Lambda_o + \frac{2}{3} \ln \rho_o = -\frac{\Delta H^{\ddagger}}{RT} + C' \tag{17}$$

$\Delta H°$ and $\Delta H^{\ddagger}$ were evaluated by the least-squares treatment of the straight lines represented by Eq. (14) and Eq. (17).

Table 5. Thermodynamic quantities ($\Delta H^{\ddagger}$, $\Delta H°$, $\Delta S°$, $\Delta G°$) for CsBr in mixed solvents butan-2-ol + water at 298.15 K. Results for 0.70, 0.80, 0.90 and 0.95 are taken from Ref. [6], R = q.

w_B	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta G°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
0.05	15.6 ± 0.2	47.1 ± 1.1[*a]	−2.8 ± 0.2	167.5 ± 3.9
0.10	18.9 ± 0.3	28.4 ± 5.4[*b]	−1.5 ± 0.08	100 ± 18
0.15	20.2 ± 0.3	10.0 ± 2.3[*c]	−1.1 ± 0.08	37.4 ± 7.8
0.70	23.8 ± 0.3	9.0 ± 0.1	−10.3 ± 0.04	64.6 ± 0.2
0.80	24.8 ± 0.2	10.9 ± 0.2	−13.2 ± 0.02	81.0 ± 0.6
0.90	24.7 ± 0.20	17.9 ± 0.4	−16.8 ± 0.02	116.4 ± 1.4
0.95	24.5 ± 0.2	25.5 ± 0.6	−19.4 ± 0.02	150.6 ± 2.1

*Evaluated by the least-squares treatment that did not involve $K_{A,m}$: a) at 293.15 K, 308.15 K, b) 288.15 K, 308.15 K, c) 293.15 K

Table 6. Thermodynamic quantities ($\Delta H^{\ddagger}$, $\Delta H°$, $\Delta S°$, $\Delta G°$) for CsBr in mixed solvents butan-2-ol + water at 298.15 K, R = a + s.

w_B	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta G°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
0.05	15.6 ± 0.2	38.8 ± 0.2[*a]	−3.2 ± 0.2	140.9 ± 0.9
0.10	18.9 ± 0.3	22.2 ± 4.1[*b]	−2.1 ± 0.06	81 ± 14
0.15	20.2 ± 0.3	8.6 ± 1.7[*c]	−1.8 ± 0.05	34.7 ± 5.7

*Evaluated by the least-squares treatment that did not involve $K_{A,m}$: a) at 293.15 K, 308.15 K, b) 288.15 K, 308.15 K, c) 293.15 K

$\Delta H°$ and $\Delta S°$ 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 (mainly for cation). $\Delta G°$ has negative value in all cases what indicates the reaction spontaneity. The addition of butan-2-ol in the mixture results in the entropy and enthalpy decrease.

Conductometric methods are not suitable for accurate determination of small K_A, and especially their temperature dependence (Eq. 14). The proof of mentioned above can be seen in value of standard deviations of $\Delta H°$ and $\Delta S°$, Table 5 and Table 6.

Increase of☐☐ $\Delta G°$ in function of w_B increase, Table 5 and Table 6, is related with K_A decrease, Table 3 and Table 4, because ☐$\Delta G°$ and K_A are connected with Eq. 13 while in mixtures with higher w_B the situation is different (Table 5).

The activation enthalpy of the charge transport increases as the mass fraction of alcohol increases. According to Brummer and Hills [20a] the heat of activation at constant pressure is a complex quantity which depends on the temperature:

$$\Delta H^{\ddagger} = \Delta U^{\ddagger} + (\pi + P)\Delta V^{\ddagger} \tag{16}$$

where $\Delta V^{\ddagger}$ is the volume of activation, i.e. the partial molar volume change required for the unit displacement (one jump) of a mole of ions, $\Delta U^{\ddagger}$ is the internal energy change referring to the same displacement at constant volume, π is the internal pressure of the solvent $(\partial U/\partial V)_T$. $\Delta V^{\ddagger}$ increases and the corresponding internal energy $\Delta U^{\ddagger}$ decreases with increasing ionic size, and increasing solvent molar volume, as well [20b].
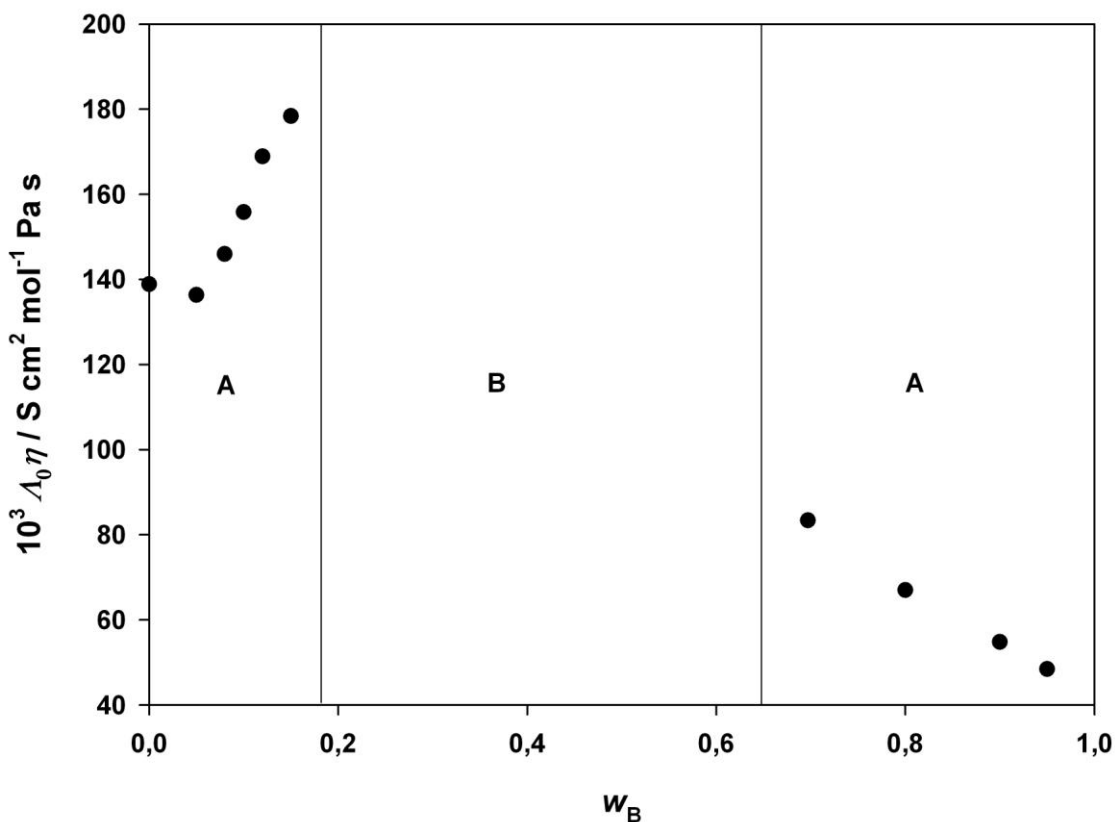

Figure 9. Walden product for CsBr at 298.15 K in water (Ref. [23]) and butan-2-ol + water mixtures; w_B =0.05, 0.08, 0.10, 0.12, 0.15 (this work), 0.70, 0.80, 0.90 and 0.95 (Ref. [6]). A − mono-phase system; B − two-phase system.

The Walden product, $\Lambda_o\eta$, of the same electrolyte in pure water and in the mixtures of water + butan-2-ol is presented in Figure 9. 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. Higher Walden product in the mixtures with low organic solvent content was observed earlier [21] 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. In described case, microscopic viscosity (around the ion) has slower growth than the macroscopic viscosity (space around cation is richer with water molecules) what leads to the ion mobility increase as the result of Stokes Law. 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. Increase of solvent "basicity" leads to a bigger size of solvation shells surrounding cations and, in the matter of speaking, cation mass growths and reduces its mobility as well as Walden product. In the literature was reported case of Walden product fluctuation as a function of the organic component fraction in mixed solvent [22] and for small fraction change, Walden product showed both maximum and minimum.

4. CONCLUSIONS

Precise conductivity measurements provide important information on ion-ion and ion- solvent interactions. According the shown results, reaction of association can not be ignored in mixed solvents with low fraction of organic component. For tested $w_B = 0.05 - 0.15$, K_A has very same value, in same order of magnitude. Generally, it can be stated that by increase butan-2-ol content in mixed solvent, conductivity reduces in tested temperature range. For all tested mixed solvents, $\Delta G°$ has negative value what indicates reaction spontaneity. $\Delta H°$ and $\Delta S°$ have positive values what indicates endothermic reaction and increasing system disorder. Increasing system disorder can be explained by dissolution of solvation shells surrounding the free ions during the association process. The activation enthalpy of the charge transport increases as the mass fraction of alcohol increases. Walden product growths by w_B in tested mixed solvents what is different acting than in mixed solvents with $w_B \geq 0.70$ what was explained by "sorting effect".

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