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Conductometric Study of Potassium Chloride in Ethanol - Water Mixtures

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The molar conductivities of dilute solutions of potassium chloride in binary mixtures of ethanol and water were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The experimental data were treated by the Lee-Wheaton conductivity equation and parameters Λ_o and K_A derived. The ionic limiting molar conductivities (λ_o) were obtained using the literature values of the cation limiting transference number $t_o(K^+)$ from the same temperature range. The ionic Walden product $\lambda_o\eta$, thermodynamic quantities for the ion-association reaction (ΔG^o, ΔH^o and ΔS^o) and the activation enthalpy of the ionic movement ΔH_i^* were calculated and discussed in terms of the ionic size, as well as solvent viscosity, permittivity, structure and basicity.

Keywords: ethanol - water mixtures, potassium chloride, limiting ionic conductivity, association to ion-pairs, thermodynamic quantities

1. INTRODUCTION

Studies of electrolytic conductance provide very important information concerning ions in solution. Mixed solvents are suitable for such studies because even a small change in solvent composition may lead to a significant difference in behaviour of the dissolved electrolyte. The formation of pairs and higher aggregates of oppositely charged ions occurs in a medium of low relative electrical permittivity. Conductivity measurements should cover a wider temperature range to make thermodynamics of these processes better understood.

In our previous works [1-7] the ion-pair association of alkali bromides in binary mixtures of water with two isomeric butanols was studied at five temperatures from 288.15 K to 308.15 K. The systems water - ethanol - KCl were investigated conductometrically [8] at 283.15 K (only three water-rich systems) and 298.15 K (the whole composition range).

The present work reports conductometric data for the low concentration potassium chloride solutions in ethanol - water mixtures with alcohol mole fraction x_E = 0.05, 0.10, 0.20, 0.40 and 0.60 at 288.15, 293.15, 298.15, 303.15 and 308.15 K. Data were processed by the Lee-Wheaton conductivity model with the distance parameter R fixed at $R = a + s$ (where a represents the sum of ionic radii and s is the length of a water molecule) and two parameters, the limiting molar conductivity (Λ_o) and the association constant (K_A), were derived. Limiting transference numbers of KCl (t_o at 298.15 K [9]) and their change with temperature [10] enabled the splitting of Λ_o into ionic contributions (λ_o). The ionic conductivity λ_o and its temperature dependence served to calculate the ionic Walden product $\lambda_o\eta$ and Eyring's enthalpy of activation of ionic movement (ΔH_i^*).

An insight into the ion-association thermodynamics can still be get from the equilibrium constant K_A, though they are slight and wobbling with temperature.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Water was distilled twice (specific conductivity ≈ 10^{-6} S cm^{-1}) and KCl (Merck, suprapur) was dried for six hours at 393.15 K before use. Ethanol (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 [11]. Molarity (c / mol dm^{-3}) was determined as

$$c = \frac{dm}{1 + mM} \tag{1}$$

where m is molality (moles of electrolyte per kilogram of solvent), d / kg dm^{-3} is the solution density and M the molar mass of electrolyte (0.07455 kg mol^{-1} for KCl). By assuming a linear dependence of the solution density upon its molality,

$$d = d_o + Dm \tag{2}$$

(d_o is the solvent density), the density gradient D / kg^2 dm^{-3} mol^{-1} was obtained. Its values at 293.15 K for the alcohol mole fraction (x_E) of 0.05, 0.10, 0.20, 0.40 and 0.60 amount to 0.0463, 0.0492, 0.0437, 0.0415 and 0.0511, respectively, and are assumed to be independent on temperature [12]. The relative error in molarity and solvent composition was about ± 0.1 %.

2.2. Apparatus

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

The viscosity of ethanol - water mixtures was measured at each temperature using an Ostwald viscometer. The uncertainty in measurements of time was about ± 0.1 %.

Measurement of resistance by a component analyser Wayne - Kerr (model 6430 A) was described earlier in detail [6].

3. RESULTS AND DISCUSSION

3.1. Solvent properties and solution conductivity

The density and viscosity of ethanol - water mixtures were already reported at 293.15, 298.15 and 303.15 K [13]. Still, Table 1 contains only our new values.

The relative permittivity of the pure solvent was obtained by interpolation from literature data [14].

Molar conductivity of potassium chloride is given in Table 2.

Table 1. Density , viscosity and relative permittivity of ethanol - water mixtures[a]

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
x_E = 0.05					
d_o / kg dm^{-3}	0.98059	0.97931	0.97776	0.97597	0.97392
η / mPa s	1.907	1.597	1.373	1.194	1.054
ε_r	75.25	73.50	71.72	70.03	68.32
x_E = 0.10					
d_o / kg dm^{-3}	0.96764	0.96535	0.96299	0.96048	0.95791
η / mPa s	2.728	2.239	1.866	1.596	1.375
ε_r	68.60	67.40	65.74	64.11	62.60
x_E = 0.20					
d_o / kg dm^{-3}	0.94076	0.93715	0.93352	0.92979	0.92597
η / mPa s	3.515	2.866	2.373	2.007	1.706
ε_r	58.62	57.11	55.61	54.20	52.81
x_E = 0.40					
d_o / kg dm^{-3}	0.88851	0.88438	0.88020	0.87595	0.87165
η / mPa s	3.070	2.569	2.179	1.882	1.634
ε_r	44.25	42.85	41.80	40.55	39.40
x_E = 0.60					
d_o / kg dm^{-3}	0.84936	0.84508	0.84075	0.83636	0.83197
η / mPa s	2.372	2.057	1.786	1.574	1.392
ε_r	35.33	34.25	33.20	32.20	31.18

[a] x_E is the mole fraction of ethanol in the mixture.

Table 2. Molar conductivity (Λ / S cm^2 mol^{-1}) of KCl in aqueous ethanol (x_E) at different concentrations (c / mol dm^{-3}) and temperatures

288.15 K		**293.15 K**		**298.15 K**		**303.15 K**		**308.15 K**	
10^4 *c*	Λ	10^4 *c*	Λ	10^4 *c*	Λ	10^4 *c*	Λ	10^4 *c*	Λ
x_E = 0.05									
27.204	76.162	28.198	86.342	9.5743	101.881	36.091	111.122	27.848	**123.848**
35.093	75.804	36.777	85.966	18.295	101.068	44.629	110.610	35.998	**123.085**
43.188	75.582	44.955	85.640	27.560	100.419	52.611	110.159	52.439	**121.987**
51.548	75.300	53.513	85.316	36.826	99.772	60.736	109.733	60.579	**121.490**
60.358	75.037	61.442	85.003	44.269	99.413	68.646	109.283	68.274	**121.245**
68.583	74.798	69.248	84.794	59.624	98.763	76.364	109.004	75.760	**120.880**
76.989	74.610	77.246	84.536	67.285	98.457	84.047	108.599	83.635	**120.407**
85.277	74.398	85.176	84.364	74.628	98.161	91.666	108.332	91.182	**120.017**
93.770	74.176	92.687	84.132	82.134	97.874	98.677	108.031	98.552	**119.709**
101.84	73.815	100.32	83.945	88.987	97.666	105.80	107.716	105.74	**119.385**
109.39	73.831	108.08	83.751	96.128	97.381				
x_E = 0.10									
8.8470	56.064	43.083	63.965	10.283	75.847	51.098	84.792	27.214	**97.839**
17.687	55.425	51.172	63.701	19.089	75.188	59.002	84.396	35.702	**97.235**
26.362	55.114	59.138	63.464	27.879	74.706	67.746	84.093	44.201	**96.786**
34.823	54.767	66.924	63.263	36.902	74.286	75.431	83.842	52.340	**96.345**
43.432	54.390	74.503	63.064	45.273	73.932	83.813	83.570	60.337	**95.918**
51.320	54.150	81.809	62.899	53.588	73.622	91.206	83.325	68.265	**95.545**
59.456	53.921	89.394	62.744	61.541	73.365	99.512	83.087	75.823	**95.237**
67.699	53.693	96.557	62.574	69.626	73.100	106.76	83.852	83.432	**94.917**
75.264	53.468	103.826	62.469	77.375	72.832			90.961	**94.566**
82.841	53.296			85.983	72.586			98.274	**94.287**
90.275	53.237			93.589	72.390			105.52	**94.003**
97.598	53.079			101.18	72.180				
104.86	52.938			108.51	71.982				
x_E = 0.20									
8.0247	39.746	7.4406	47.268	7.5826	55.512	16.919	64.433	8.2714	**74.525**
16.436	39.250	15.113	46.676	23.072	54.315	25.392	63.814	17.091	**73.568**
24.797	38.914	22.809	46.254	30.744	53.897	33.722	63.387	25.745	**72.889**
32.984	38.580	30.327	45.895	38.141	53.551	42.127	62.912	33.908	**72.353**
41.033	38.376	37.641	45.607	52.199	53.024	50.179	62.639	41.639	**71.944**
48.970	38.168	44.947	45.354	59.487	52.787	57.782	62.343	49.518	**71.571**
56.633	37.968	52.083	45.112	66.265	52.590	65.461	62.059	57.243	**71.259**
64.315	37.810	59.303	44.907	72.888	52.413	72.689	61.799	64.883	**70.897**
71.955	37.651	66.148	44.727	79.524	52.241	79.988	61.562	72.360	**70.517**
79.977	37.515	72.621	44.569	86.125	52.073	87.252	61.360	79.621	**70.242**
87.246	37.359	79.258	44.509	92.504	51.920	94.572	61.319	86.901	**70.011**
94.377	37.239	86.020	44.283			101.30	61.135	93.908	**69.899**
101.37	37.150	92.181	44.161					100.71	**69.708**
x_E = 0.40									
15.339	31.617	7.6959	38.113	7.3843	43.792	15.887	49.779	7.5573	**58.066**
23.588	31.136	15.840	37.304	15.415	42.880	23.749	48.998	15.509	**56.883**

39.109	30.752	23.954	36.710	23.423	42.212	31.493	48.420	23.336	**55.984**
46.580	30.479	31.694	36.263	31.227	41.678	39.057	47.893	31.111	**55.262**
53.829	30.238	39.213	36.247	38.811	41.264	46.465	47.447	38.641	**54.650**
68.134	30.0920	46.852	35.905	46.253	40.868	53.850	47.033	46.115	**54.146**
74.903	29.914	54.150	35.619	53.558	40.520	60.909	46.668	53.431	**53.667**
81.843	29.743	61.450	35.351	60.939	40.201	68.129	46.329	60.545	**53.171**
88.531	29.588	68.578	35.105	68.125	39.917	75.060	46.020	67.606	**52.833**
95.188	29.445	75.275	34.896	74.978	39.663	81.897	45.745	74.459	**52.409**
		82.012	34.705	81.819	39.424	88.533	45.475	81.162	**52.119**
		88.775	34.507	88.536	39.204	95.170	45.248	87.781	**51.843**
		94.815	34.321	95.405	39.006			94.201	**51.589**
x_E =0.60									
6.8141	31.571	7.1942	36.252	7.2441	40.655	7.1279	46.021	6.4895	**52.477**
13.966	30.648	14.464	35.119	15.368	39.311	15.101	44.441	13.988	**50.604**
20.963	29.966	21.433	34.309	22.729	38.383	22.895	43.318	21.064	**49.312**
27.899	29.418	28.068	33.649	29.945	37.653	30.189	42.478	27.588	**48.426**
34.736	28.947	34.441	33.119	37.217	36.999	37.612	41.705	34.311	**47.530**
41.345	28.545	41.147	32.631	44.187	36.457	44.778	41.085	40.700	**46.893**
47.790	28.196	47.728	32.203	50.906	35.989	51.497	40.527	46.974	**46.235**
54.180	27.882	54.005	31.828	57.597	35.563	58.250	40.036	52.974	**45.683**
60.325	27.593	60.298	31.486	64.202	35.183	65.046	39.577	58.943	**45.184**
66.457	27.336	66.488	31.172	70.643	34.843	71.617	39.168	64.807	**44.726**
72.534	27.092	72.598	30.883	76.929	34.522	77.993	38.802	70.826	**44.266**
78.383	26.875	78.412	30.626	83.100	34.237			76.465	**43.895**
84.227	**26.671**	**84.291**	**30.392**					**81.949**	**43.536**

3.2. Model and data processing

The limiting molar conductivity Λ_o and association constant K_A were determined using a chemical model of conductivity based on the Lee-Wheaton equation [15] in the Pethybridge and Taba version [16], LWPT,

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

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

$\Lambda_{c\alpha}$ is the molar conductivity of free ions and Λ_o the same quantity at infinite dilution, coefficients $C_1 - C_5$ are the functions of κR [16], 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_o); other symbols have their usual meaning.

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

$$\mathrm{K^+ + Cl^- \rightleftarrows K^+{\cdot}Cl^-} \qquad (5)$$
$$c\alpha \quad c\alpha \qquad c(1-\alpha)$$

is given by the expression

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

where $c^{\mathrm{o}} = 1$ 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,

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

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

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

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

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

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

$$\Lambda = f\,(c;\ \Lambda_{\mathrm{o}},\ K_{\mathrm{A},c},\ R) \qquad (10)$$

The model was resolved by an iterative procedure: parameters Λ_{o} and $K_{\mathrm{A},c}$ were adjusted according to Beronius [17] for each selected value of R until the standard deviation (σ) of experimental conductivities from the calculated ones,

$$\sigma^2 = \frac{\sum(\Lambda_{\mathrm{calc}} - \Lambda_{\mathrm{exp}})^2}{n-3} \qquad (11)$$

would have achieved its minimal value (n is the number of solutions tested in one run). The values of parameters Λ_{o} and $K_{\mathrm{A},c}$ 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, $\Lambda = f(c;\ \Lambda_{\mathrm{o}},\ K_{\mathrm{A},c})$, *i.e.* R had to be chosen in accord with some of the existing criteria. A solvent separated ion-pair was used as a model with $R = a + s$; a represents the sum of radii of $\mathrm{K^+}$ and $\mathrm{Cl^-}$ (314 pm, according to Pauling [18]) and s for aqueous mixtures is the length of a water molecule, (280 pm [12]), which makes $R = 594$ pm. The values of Λ_{o} and $K_{\mathrm{A},c}$ obtained by this condition, along with standard deviation σ of experimental Λ from the model (9), are listed in Table 3; numeral 3 in Eq. (11) was switched to 2. Standard deviations of Λ_{o} and $K_{\mathrm{A},c}$ were estimated as suggested in the literature [19]. To avoid the influence of the solvent thermal expansion to the reaction enthalpy, $K_{\mathrm{A,c}}$ was converted to the molality scale, $K_{\mathrm{A},m} = K_{\mathrm{A},c}\, d_{\mathrm{o}}$ / kg dm^{-3}.

Fig. 1 shows the concentration dependence of the experimental molar conductivity (Λ_{exp}) for KCl at five temperatures in the ethanol ($x_{\mathrm{E}} = 0.60$) - water mixture; full lines are drawn through points computed by the LWPT conductivity model (Λ_{calc}). Analogous plots for the other four mixtures are similar.

Table 3. Limiting molar conductivity (Λ_o), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviation (σ) of experimental Λ from the model LWPT (with R fixed at 594 pm) for KCl in ethanol (x_E) - water mixtures

T/K	Λ_o/S cm^2 mol^{-1}	$K_{A,c}$	$K_{A,m}$	σ/S cm^2 mol^{-1}
		$x_E = 0.05$		
288.15	78.78 ± 0.06	0.99 ± 0.13	0.97 ± 0.13	0.06
293.15	89.40 ± 0.02	0.80 ± 0.04	0.79 ± 0.04	0.02
298.15	104.03 ± 0.02	1.31 ± 0.04	1.28 ± 0.04	0.03
303.15	116.03 ± 0.03	1.80 ± 0.05	1.75 ± 0.05	0.03
308.15	128.59 ± 0.07	1.64 ± 0.10	1.60 ± 0.10	0.07
		$x_E = 0.10$		
288.15	57.22 ± 0.04	2.56 ± 0.13	2.48 ± 0.13	0.05
293.15	66.95 ± 0.02	1.20 ± 0.05	1.16 ± 0.05	0.01
298.15	77.67 ± 0.01	1.58 ± 0.03	1.52 ± 0.03	0.02
303.15	89.36 ± 0.04	1.52 ± 0.08	1.46 ± 0.08	0.02
308.15	101.93 ± 0.03	2.12 ± 0.06	2.03 ± 0.06	0.03
		$x_E = 0.20$		
288.15	40.70 ± 0.02	3.15 ± 0.10	2.96 ± 0.09	0.03
293.15	48.38 ± 0.03	3.57 ± 0.17	3.34 ± 0.16	0.05
298.15	56.84 ± 0.04	3.21 ± 0.16	3.00 ± 0.15	0.05
303.15	66.83 ± 0.05	2.36 ± 0.17	2.19 ± 0.16	0.06
308.15	76.52 ± 0.04	2.74 ± 0.12	2.54 ± 0.11	0.06
		$x_E = 0.40$		
288.15	33.28 ± 0.06	3.11 ± 0.46	2.76 ± 0.41	0.06
293.15	39.58 ± 0.07	6.71 ± 0.49	5.94 ± 0.43	0.10
298.15	45.60 ± 0.02	9.55 ± 0.10	8.41 ± 0.09	0.02
303.15	53.02 ± 0.01	9.86 ±0.06	8.64 ± 0.05	0.01
308.15	60.65 ± 0.02	10.62 ± 0.11	9.26 ± 0.10	0.03
		$x_E = 0.60$		
288.15	33.53 ±0.01	25.19 ± 0.04	21.40 ± 0.04	0.01
293.15	38.65 ± 0.02	28.65 ± 0.18	24.21 ± 0.15	0.02
298.15	43.42 ± 0.01	27.68 ± 0.08	23.27 ± 0.07	0.01
303.15	49.21 ± 0.01	29.69 ± 0.07	24.83 ± 0.06	0.01
308.15	55.98 ± 0.02	32.38 ± 0.18	26.94 ± 0.15	0.02

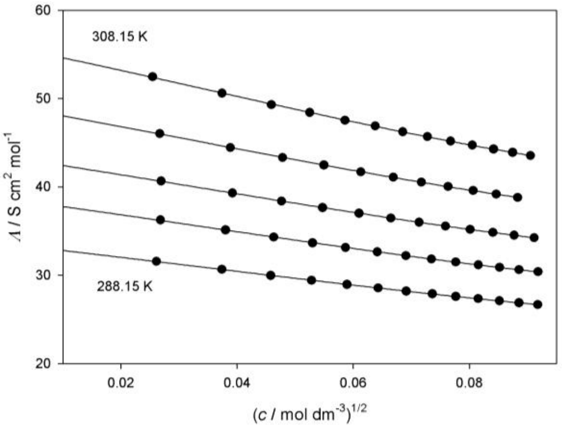

Figure 1. Molar conductivity of KCl in ethanol - water mixture with x_E = 0.60 from 288.15 K to 308.15 K: experimental data (●); values calculated by LWPT using Λ_o and $K_{A,c}$ from Table 3 (lines).

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 ethanol mole fraction of 0.2 the increasing η and decreasing ε_r (Table 1) both contribute to the Λ_o descend which is therefore very steep (Table 3 and Fig. 2). From $x_E = 0.2$ on the relative decrease in permittivity is about twofold greater than that in viscosity, the effect of η is more than compensated by that of ε_r and Λ_o is slightly descending. With increasing temperature, on the other hand, the latter decrease is four to eight times greater than the former (Table 1) and Λ_o is ascending (Table 3).

Small constants of the ionic equilibria obtained conductometrically are not quite reliable. Still, barring two values, K_A is increasing with the ethanol content (Table 3) as expected – lower ε_r enhances the attraction of oppositely charged ions. Despite somewhat higher scatter with temperature a positive general trend in K_A is recognized, except for the structurally critical water-rich region (as indicated by the viscosity curve in Fig. 2) where it is undoubtedly negative.

3.3. Ionic limiting conductivity and Walden product

The cation limiting transference numbers for KCl in aqueous ethanol at 298.15 K [9] were chosen as points of reference. The temperature effect on those numbers in the ethanol (x_E = 0.05, 0.10, 0.15, 0.20 and 0.30) - water mixtures (expressed by slope of the straight line $\frac{\ln(1-t_+)}{t_+}$ against $\frac{1}{T}$ [10]) served to derive the $t_o(K^+)$ values at the remaining four temperatures (Table 4); those for $x_E = 0.4$ were obtained by extrapolation and probably are less accurate.

The limiting conductivities of K^+ and Cl^- (Table 5) were determined by the relations $\lambda_o(K^+) = t_o(K^+)\Lambda_o(KCl)$ and $\lambda_o(Cl^-) = \Lambda_o(KCl) - \lambda_o(K^+)$, using data from Tables 3 and 4; corresponding water values were calculated through the parameters [20] of assumedly linear function $\lambda_o(T)$. Curves of their change with composition at 298.15 K and the curve for Λ_o already discussed have the same shape (Fig. 2), since the transference numbers are always near 0.5.

Table 4. The cation limiting transference number for KCl in ethanol (x_E) - water mixtures from its temperature dependence [10] with respect to the value at 298.15 K [9]

	x_E						
***T* / K**	0.05	0.10	0.15	0.20	0.30	0.40	**0.60**
288.15	0.5084	0.5168	0.5134	0.5085	0.4938	0.4862^{b}	
293.15	0.5057	0.5125	0.5113	0.5063	0.4930	0.4861^{b}	
298.15^{a}	0.5031	0.5091	0.5087	0.5036	0.4915	0.4856	**0.4883**
303.15	0.5006	0.5063	0.5056	0.5003	0.4895	0.4846^{b}	
308.15	**0.4982**	**0.5045**	**0.5021**	**0.4965**	**0.4868**	**0.4832^{b}**	

^{a}Literature data [9]; ^{b}extrapolated values

Table 5. The ionic limiting molar conductivity λ_o / S cm^2 mol^{-1} in ethanol (x_E) - water mixtures at different temperatures

	x_E											
	0.00[a]		0.05		0.10		0.20		0.40		**0.60**	
***T* / K**	K^+	Cl^-	K^+	Cl^-	K^+	Cl^-	K^+	Cl^-	K^+	Cl^-	K^+	$\mathbf{Cl^-}$
288.15	60.4	61.3	40.05	38.73	29.57	27.65	20.70	20.00	16.18	17.10	-	-
293.15	67.4	68.3	45.21	44.19	34.31	32.64	24.49	23.88	19.24	20.34	-	-
298.15	74.4	75.4	52.33	51.69	39.54	38.13	28.63	28.22	22.15	23.46	21.20	**22.22**
303.15	81.4	82.5	58.09	57.95	45.24	44.12	33.44	33.40	25.69	27.33	-	-
308.15	**88.4**	**89.6**	**64.06**	**64.52**	**51.43**	**50.51**	**37.99**	**38.53**	**29.31**	**31.34**	**-**	**-**

[a] From empirical straight lines $\lambda_o(T)$ [20]

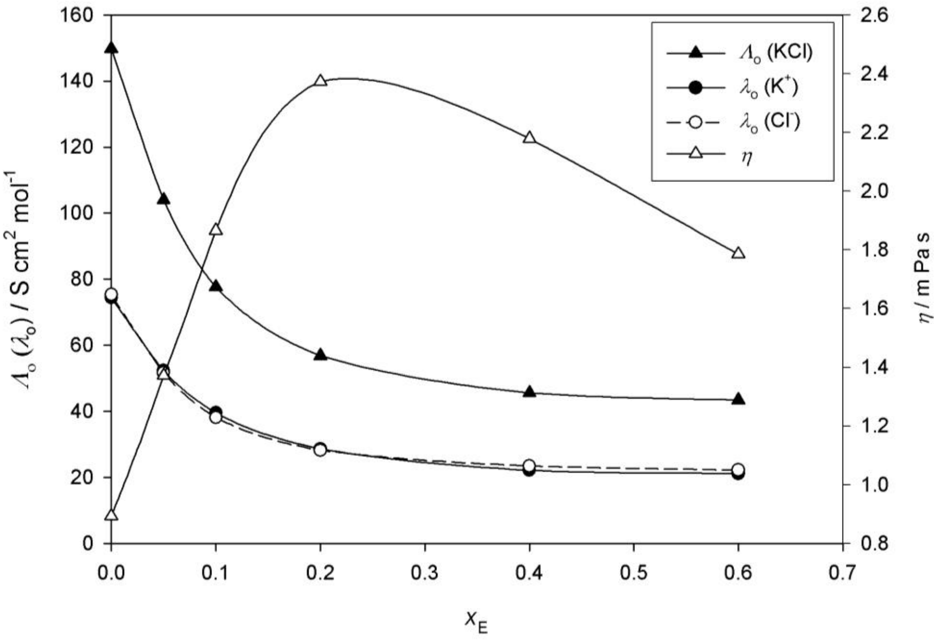

Figure 2. The dependence of the limiting molar conductivities (Λ_o(KCl), λ_o(K$^+$), λ_o(Cl$^-$) and viscosity on the ethanol mole fraction (x_E) in mixtures with water at 298.15 K.

The ionic Walden products ($\lambda_o \eta$) were obtained by multiplying each datum from Table 5 by the appropriate viscosity; values of η for mixtures were taken from Table 1, those for water in the temperature range 283.15 - 313.15 K [21a] were shown graphically and interpolated at 298.15 K and 308.15 K.

All results are listed in Table 6, but only those at 288.15, 298.15 and 308.15 K are presented against x_E in Fig. 3 in order to keep it transparent; barring few overlaps, the curves for 293.15 K and 303.15 K would lie between the previous ones and basically have their shape.

Table 6. Walden product ($W = \lambda_o\eta$ / S cm^2 mol^{-1} mPa s) of the ions K$^+$ and Cl$^-$ in ethanol (x_E) - water mixtures at different temperatures and ΔW as a measure of its dependence on temperature

	x_E											
	0.00[a]		0.05		0.10		0.20		0.40		**0.60**	
***T* / K**	K$^+$	Cl$^-$	K$^+$	Cl$^-$	K$^+$	Cl$^-$	K$^+$	Cl$^-$	K$^+$	Cl$^-$	K$^+$	**Cl$^-$**
288.15	68.8	69.8	76.38	73.85	80.67	75.43	72.74	70.31	49.68	52.50	-	-
293.15	67.5	68.4	72.20	70.57	76.82	73.07	70.20	68.45	49.43	52.26	-	-
298.15	66.2	67.1	71.86	70.97	73.78	71.14	67.93	66.96	48.25	51.12	37.87	**39.68**
303.15	64.9	65.8	69.36	69.19	72.21	70.41	67.11	67.03	48.36	51.43	-	-
308.15	63.7	64.5	67.52	68.01	70.71	69.45	64.81	65.73	47.89	51.22	-	-
ΔW[b]	**7.7**	**7.9**	**12.3**	**8.2**	**13.5**	**8.4**	**11.7**	**6.8**	**3.7**	**2.5**	**-**	**-**

[a] η from [21a]; [b] $\Delta W = \dfrac{100(W_{298} - W_{308})}{W_{298}}$

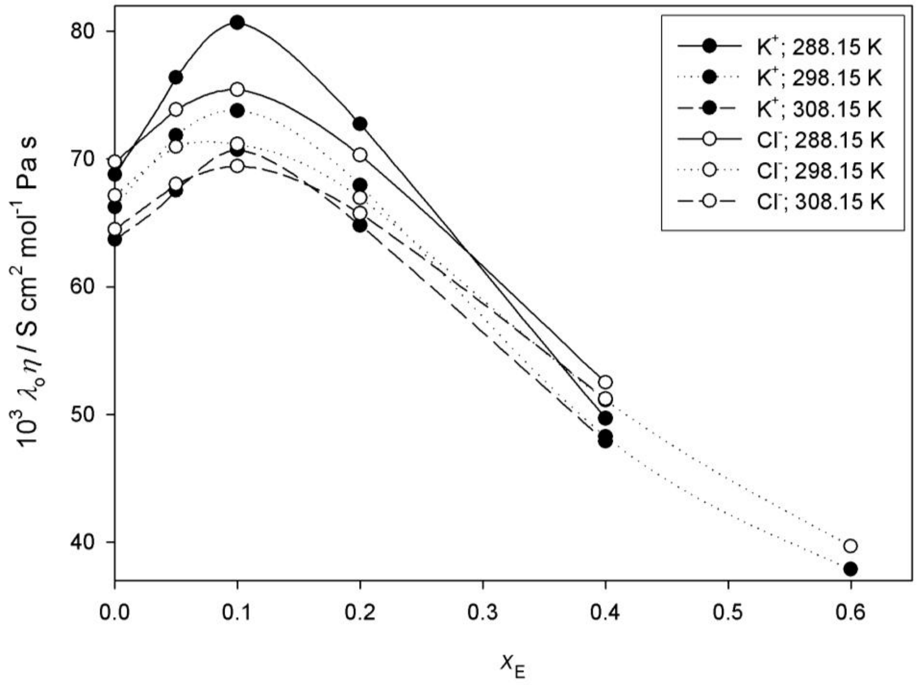

Figure 3. The ionic Walden products for KCl in dependence on the mole fraction of ethanol in aqueous mixture (x_E) at three temperatures.

An ion and the bulk-solvent are competing for molecules in the secondary shell (shell 2). In principle larger ion and the more developed bulk-structure make that shell thiner, and vice versa. In the region of the enhanced water structure the secondary shell contribution to the hydrodynamic radius r is the least and Walden product W exhibits a maximum (Fig. 3 observed earlier [7, 22, 23] as well); the temperature dependence of that contribution "modulates" the sum of the bare-ion radius and the primary shell width (shell 1, a monolayer of oriented molecules) but never making $r(\text{K}^+) > r\ (\text{Cl}^-)$, for the $W(\text{K}^+)$ maximum is always exceeding that of Cl$^-$. By further addition of ethanol the steadily decreasing ε_r and crumbling water structure both favour the broadening of shell 2, r is growing up and W is falling down, accordingly; the $W(\text{Cl}^-)$ decrease is less steep (Fig. 3) owing most likely to the inductive effect of numerous ethyl-groups which is weakening H-bonds with anion by making the mixtures more basic [24].

The relative ε_r decrease with increasing temperature ($\Delta\varepsilon_r$) is about 10 % in all systems (Table 1), still the relative Walden product decrease (ΔW) is far away from constancy showing maximum at x_E = 0.1 (Table 6). Uniformed influence of $\Delta\varepsilon_r$ on ΔW is most likely modulated by the structural contribution [6]: a given quantity of heat will produce a greater disorder in a better organized bulk-structure, more molecules will be liberated and an ion will elongate its r to a greater extent by attracting them into its initially thiner shell 2.

The chloride ion is less sensitive to the effect described (Table 6) out of its lower surface charge density.

3.4. Thermodynamic quantities

The standard enthalpy of the association reaction (ΔH^o) and the activation enthalpy of the charge transport (ΔH_i^*), both assumed as independent on temperature, were calculated by a least-squares treatment of the expressions,

$$\ln K_{A,m}^{o} = -\frac{\Delta H^{o}}{RT} + C \qquad (12)$$

$$\ln(\lambda d^{2/3})_{o} = -\frac{\Delta H_{i}^{*}}{RT} + C' \qquad (13)$$

using data for $K_{A,m}^{o}$ (Table 3) and λ_o (Table 5) at different T; density data for water and mixtures were taken from literature [21b] and Table 1, respectively. The standard deviation of each enthalpy was derived from the corresponding slope [25]. Four specially discrepant points, omitted in Fig.4, were excluded from data processing: at 288.15 K for x_E of 0.10 and 0.40, at 293.15 K for x_E = 0.05, at 303.15 K for x_E = 0.20. For the mixture with x_E = 0.100 the rejected $K_{A,m}$ value was replaced by one recalculated by the LWPT model from the pairs (c, Λ) reported at 283.15 K [8]. The experimental points of Eq. (13) and "best" straight lines are shown in Fig. 5 for potassium ion.

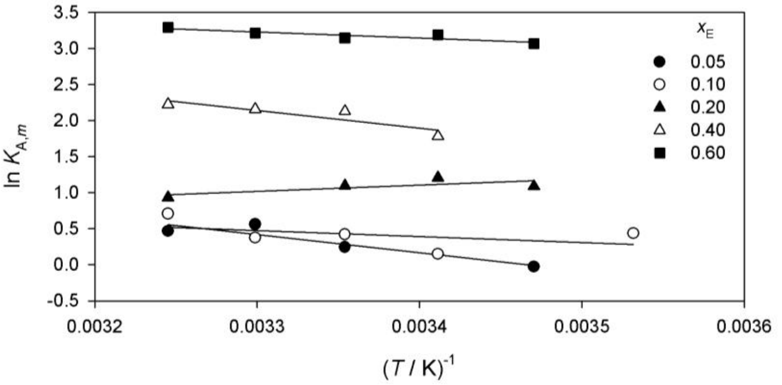

Figure 4. Plot of ln $K_{A,m}$ against T^{-1} for KCl in ethanol (x_E) - water mixtures.

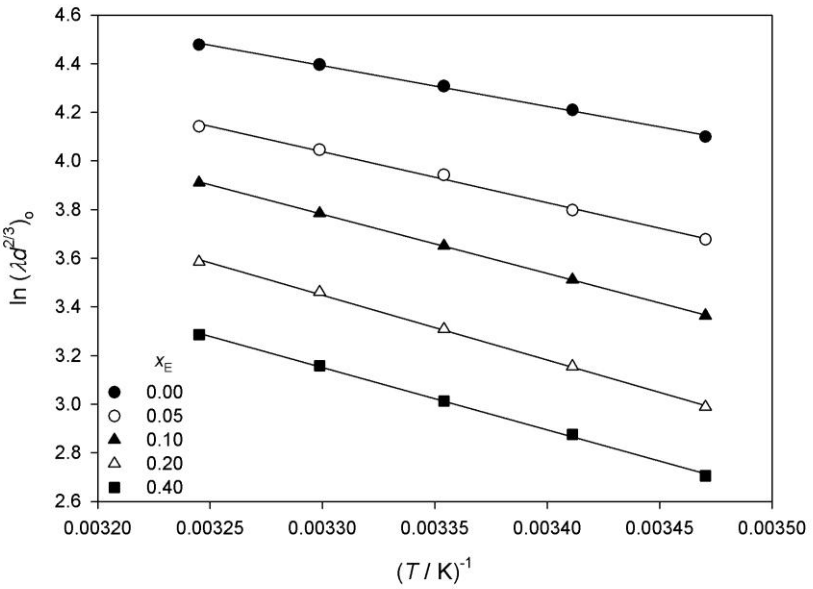

Figure 5. Plot of ln $(\lambda d^{2/3})_o$ against T^{-1} for K^+ in ethanol (x_E) - water mixtures.

The Gibbs energy and entropy changes ($\Delta G°$ and $\Delta S°$), as well as their standard deviations, were computed as described before [4, 5]. All thermodynamic data for association are listed in Table 7 and presented graphically in Fig. 6 against x_E.

Table 7. Thermodynamic quantities for the association of ions K^+ and Cl^- in ethanol (x_E) - water mixtures at 298.15 K

x_E	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
0.05	- 0.6 ± 0.09	20.9 ± 6.0	**72 ± 20**
0.10	- 1.0 ± 0.05	7.0 ± 7.6	**27 ± 26**
0.20	- 2.7 ± 0.1	-7.2 ± 4.7	**-15 ± 16**
0.40	- 5.3 ± 0.03	20.6 ± 7.5	**87 ± 25**
0.60	**- 7.8 ± 0.01**	**7.2 ± 1.9**	**50 ± 6**

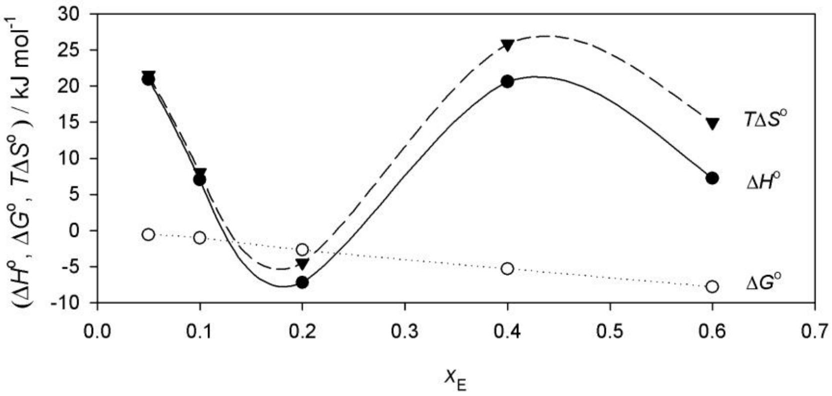

Figure 6. Thermodynamic quantities of the ion-association reaction for KCl in aqueous ethanol of mole fraction x_E at 298.15 K.

Unlike Gibbs energy, the enthalpy and entropy change reflects the structural changes accompanying the pairing of ions. In spite of an aggravating uncertainty in ΔH^{o} and ΔS^{o} the minimum in the structurally critical water-rich region is not a random occurence: the heat and order changes resulting from the break of shells around approaching ions compensate for those consorting the creation of solvent-separated pair and the building up of bulk-solvent.

The activation enthalpy of ionic movement is listed in Table 8 and its dependence on x_E presented in Fig.7.

Table 8. Activation enthalpy of ionic movement for K^+, Cl^- and composite in ethanol (x_E) - water mixtures in the temperature range from 288 K to 308 K

x_E	$\Delta H^*_{K^+}$ / kJ mol^{-1}	$\Delta H^*_{Cl^-}$ / kJ mol^{-1}	ΔH^* / kJ mol^{-1}
0.00	13.9 ± 0.3	13.9 ± 0.3	**13.9 ± 0.3**
0.05	17.4 ± 0.6	18.9 ± 0.6	**18.2 ± 0.6**
0.10	20.2 ± 0.1	22.0 ± 0.3	**21.1 ± 0.2**
0.20	22.2 ± 0.4	23.9 ± 0.3	**23.0 ± 0.3**
0.40	21.3 ± 0.4	21.8 ± 0.3	**21.6 ± 0.4**
0.60	-	-	**18.2 ± 0.3**

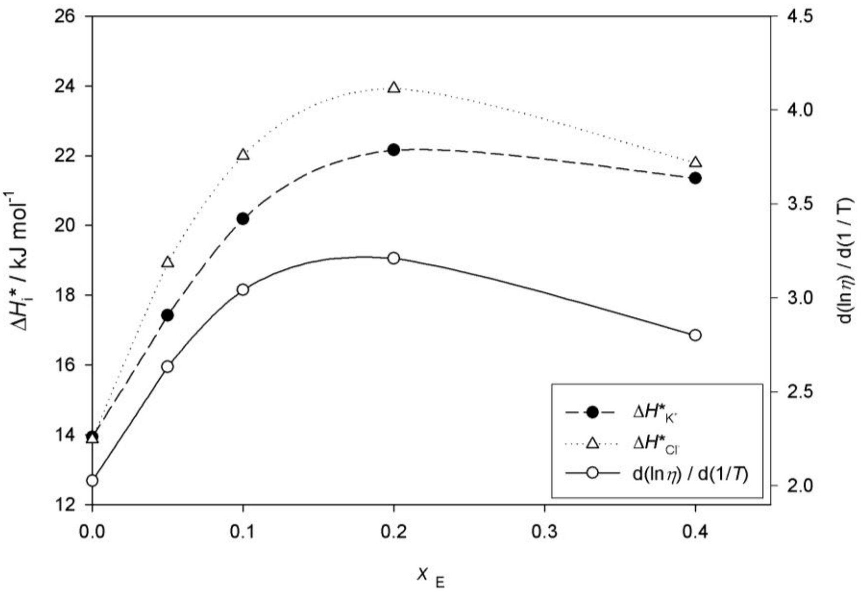

Figure 7. Activation enthalpy of the charge transport for K^+ and Cl^- and the temperature gradient of viscosity in aqueous ethanol of mole fraction x_E.

The ions K^+ and Cl^- differ very slightly in that quantity, so the composite enthalpy (obtained through Λ_o instead of λ_o) should have practically the same standard deviation [26]. The solvent flow and the ion migration are governed by similar transport mechanisms [12] as indicated by the shape of curves in Fig.7.

4. CONCLUSIONS

The present work reports conductometric data for the low concentration potassium chloride solutions in ethanol - water mixtures with alcohol mole fraction x_E = 0.05, 0.10, 0.20, 0.40 and 0.60 in temperature range from 288.15 to 308.15 K. Molar conductivity decreases by increasing the proportion of ethanol in the mixture and increases with increasing temperature. In the region of the enhanced water structure the secondary shell contribution to the hydrodynamic radius of ions is the least and Walden product exhibits a maximum. ΔH^o and ΔS^o exhibit the minimum in the structurally critical water-rich region because the heat and order changes resulting from the break of shells around approaching ions compensate for those consorting the creation of solvent-separated pair and the building up of bulk-solvent. The solvent flow and the ion migration are governed by similar transport mechanisms as indicated by the values of the activation enthalpy of the charge transport for K^+ and Cl^- and the temperature gradient of viscosity in aqueous ethanol mixtures.

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