

Scientific paper

# Conductometric Study of Ammonium Bromide in 2-Butanol + Water Mixtures

Vesna Sokol,\* Renato Tomaš and Ivo Tominić

Faculty of Chemistry and Technology, University of Split, N. Tesle 10, 21000 Split, Croatia

\* Corresponding author: E-mail: vsokol@ktf-split.hr

Received: 10-12-2008

## Abstract

Molar conductivities of dilute solutions of ammonium bromide in binary mixtures of 2-butanol and water were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The limiting molar conductivity ( $\Lambda_0$ ) and the ion-pair formation constant ( $K_A$ ) were determined by the Lee-Wheaton conductivity equation. Thermodynamic quantities, Gibbs energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ), for the ion-association reaction were derived from the temperature dependence of  $K_A$ . The activation energy of the ionic movement ( $\Delta H^\ddagger$ ) was derived from the temperature dependence of  $\Lambda_0$ . The obtained thermodynamic quantities, together with Walden product, were compared to those for alkali metal bromides and interpreted in terms of the ionic size, as well as solvent basicity, structure and permittivity.

**Keywords:** Ammonium bromide, 2-butanol + water mixtures, association to ion-pairs, thermodynamic quantities

## 1. Introduction

It is well known that precise conductivity measurements provide important information on ion-ion and ion-solvent interactions. Recently, the conductometric studies of ion association in dilute aqueous lithium, sodium, potassium and ammonium cyclohexylsulfamate solutions,<sup>1</sup> as well as KCNS,  $\text{NH}_4\text{CNS}$ ,  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$  in 2-ethoxyethanol,<sup>2</sup> have been reported.

In our previous studies<sup>3–7</sup> the influence of the alkali metal ions (so called  $d^0$  – cations<sup>8a</sup>) on the transport and equilibrium properties of the corresponding bromides, as well as its change with solvent composition, were examined in 2-butanol + water mixtures of the alcohol mass fraction ( $w_B$ ) 0.70, 0.80, 0.90, and 0.95 – there is a two-phase system between  $w_B$  0.175 and 0.648 at 298.15 K.<sup>9</sup>

As the protic cation  $\text{NH}_4^+$  exhibits a different kind of interaction, comparison with alkali cations could be interesting. This paper presents a conductometric study of ammonium bromide in the same mixtures at temperature ranging from 288.15 K to 308.15 K.

## 2. Experimental

Physical properties of the mixed solvents (density, viscosity and relative permittivity) were reported earlier;<sup>5</sup> permittivities were obtained by the interpolation of litera-

ture data.<sup>10</sup> 2-Butanol (Merck, p.a.) was fractionally distilled in a Vigreux column immediately before use, and the middle fraction of the distillate, collected at a head temperature of 372.0 – 372.6 K, was used for solution preparations. Water was distilled twice (specific conductivity  $\sim 10^{-6}$  S  $\text{cm}^{-1}$ ), and  $\text{NH}_4\text{Br}$  (Merck, extra pure) was dried for six hours at 393 K before use. Solutions of definite molality were prepared by weighing the pure mixed solvent and the concentrated stock solution of  $\text{NH}_4\text{Br}$  in that solvent. The molarity ( $c/\text{mol dm}^{-3}$ ) can be determined from the molality and density data by means of the relation:

$$c = md/(1 + Mm), \quad (1)$$

where  $m$  is the molality (moles of electrolyte per kilogram of solvent),  $d$  is the density of solution, and  $M$  (0.09881  $\text{kg mol}^{-1}$ ) is the molar mass of ammonium bromide. The solution density was determined at 293.15 K by a pycnometer. The density coefficient  $D$  ( $\text{kg}^2 \text{dm}^{-3} \text{mol}^{-1}$ ) was obtained assuming a linear change of solution density upon its molality:

$$d = d_0 + Dm, \quad (2)$$

where  $d_0$  is the density of the pure mixed solvent. The density coefficient is assumed to be independent of temperature,<sup>11</sup> and its values for 0.70, 0.80, 0.90 and 0.95

alcohol mass fraction ( $w_B$ ) amount to 0.128, 0.058, 0.139, and 0.216, respectively. The relative error in molarity and solvent composition was about 0.1%. Two parallel measurements in different cells were carried out for each molarity by a precision component analyser Wayne-Kerr (model 6430A) at four frequencies ( $f = 500, 800, 1000$  and  $2000$  Hz) and extrapolated against  $f^{-1}$  to infinite frequency. Cells were immersed in a Thermo-Haake Circulator DC10-V15/B maintaining the temperature within  $\pm 0.01$  K. The cell constants were determined with dilute potassium chloride solutions.<sup>12</sup> The measured values of conductivity were corrected for the conductivity of the solvent. The average relative deviation of a single cell value from the mean amounts to  $\pm 0.15\%$  in 0.95 mass fraction of 2-butanol and  $\pm 0.14\%$  in other mixtures.

### 3. Results and Discussion

Molar conductivities for different molalities of  $\text{NH}_4\text{Br}$  solutions are given in Table 1.

Conductivity data were analyzed by the Lee-Wheaton equation in Pethybridge and Taba version<sup>13</sup> (LWPT), and the following set of equations was used:

$$A_{\text{ca}} = A_o \left[ 1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3 \right] - \frac{\rho \kappa}{1 + \kappa R} \left[ 1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \quad (3)$$

$$K_{A,c} = (1 - \alpha) / (c \alpha^2 y_{\pm}^2), \quad (4)$$

$$y_{\pm}^2 = \exp[-2\kappa q / (1 + \kappa R)], \quad (5)$$

$$\rho = \frac{Fe}{3\pi\eta}, \quad q = \frac{e^2}{8\pi\epsilon_0\epsilon_r kT}, \quad (6)$$

$$\kappa^2 = 16\pi N_A q \alpha c. \quad (7)$$

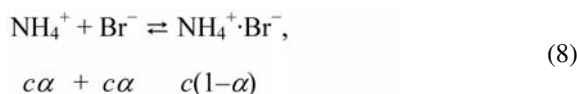
**Table 1.** Molar conductivities ( $\Lambda$ ) of  $\text{NH}_4\text{Br}$  at various molalities ( $m$ ) in aqueous 2-butanol mixtures with alcohol mass fraction  $w_B$  at different temperatures

$10^4 m^a$ mol kg <sup>-1</sup>	$\Lambda/S$ cm <sup>2</sup> mol <sup>-1</sup>				
	$T/K = 288.15$	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$
$w_B = 0.70$					
6.3011	17.059	20.420	24.125	28.185	32.600
10.595	16.539	19.785	23.340	27.237	31.486
14.903	16.161	19.312	22.780	26.561	30.680
19.184	15.869	18.956	22.349	26.042	30.063
23.502	15.620	18.641	21.963	25.578	29.496
27.793	15.432	18.403	21.668	25.228	29.092
32.100	15.252	18.180	21.394	24.891	28.693
36.340	14.984	17.865	21.006	24.445	28.165
40.693	14.818	17.653	20.743	24.128	27.785
44.989	14.649	17.448	20.517	23.852	27.466
49.289	14.525	17.297	20.324	23.619	27.185
53.637	14.377	17.120	20.116	23.374	26.889
57.888	14.275	16.986	19.948	23.165	26.651
62.307	14.104	16.783	19.701	22.880	26.319
$w_B = 0.80$					
2.0042	14.750	17.744	21.129	24.881	29.016
6.5754	13.776	16.527	19.597	22.980	26.690
8.8973	13.355	16.000	18.957	22.208	25.772
11.200	13.016	15.571	18.425	21.561	24.994
13.502	12.770	15.270	18.051	21.107	24.443
15.798	12.514	14.956	17.666	20.643	23.889
18.098	12.241	14.620	17.263	20.156	23.315
20.387	12.086	14.437	17.027	19.872	22.970
22.697	11.908	14.213	16.769	19.570	22.614
24.962	11.751	14.021	16.526	19.265	22.255
27.290	11.592	13.821	16.290	18.986	21.916
29.561	11.451	13.649	16.075	18.735	21.626
31.898	11.312	13.478	15.877	18.495	21.340
34.456	11.153	13.286	15.638	18.207	21.000

$10^4 m^a$ mol kg <sup>-1</sup>	$\Lambda/S$ cm <sup>2</sup> mol <sup>-1</sup>				
	$T/K = 288.15$	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$
	$w_B = 0.90$				
2.0200	11.925	14.195	16.715	19.468	22.464
3.2692	11.327	13.440	15.773	18.290	21.001
4.5128	10.884	12.888	15.083	17.445	19.970
5.7602	10.480	12.372	14.446	16.663	19.027
7.1511	10.051	11.878	13.878	16.025	18.323
8.3751	9.831	11.569	13.457	15.460	17.604
9.5466	9.549	11.221	13.045	14.976	17.018
10.839	9.343	10.974	12.737	14.608	16.578
12.107	9.097	10.672	12.376	14.179	16.077
13.389	8.912	10.447	12.100	13.855	15.698
14.661	8.770	10.270	11.886	13.598	15.395
15.759	8.562	10.022	11.596	13.253	14.991
17.225	8.499	9.941	11.496	13.128	14.839
18.158	8.353	9.765	11.283	12.880	14.557
19.703	8.154	9.527	10.998	12.547	14.163
	$w_B = 0.95$				
2.3581	9.556	11.147	12.845	14.603	16.390
3.4954	8.825	10.245	11.742	13.274	14.814
4.6544	8.287	9.585	10.945	12.328	13.698
5.7963	7.864	9.077	10.329	11.595	12.849
6.8981	7.540	8.677	9.858	11.043	12.208
8.0760	7.237	8.318	9.424	10.535	11.621
9.1958	6.992	8.018	9.073	10.125	11.155
10.397	6.758	7.738	8.738	9.740	10.716
11.495	6.581	7.530	8.531	9.457	10.392
12.591	6.417	7.332	8.269	9.194	10.094
13.779	6.250	7.134	8.033	8.925	9.788
14.874	6.114	6.973	7.847	8.712	9.547
16.076	5.980	6.811	7.658	8.495	9.301
17.133	5.868	6.680	7.504	8.319	9.102

<sup>a</sup> Molality can be converted to molarity using Eqs. (1, 2).

In these expressions,  $\Lambda_{ca}$  is the molar conductivity of the free ions,  $\Lambda_0$  is the molar conductivity at infinite dilution, coefficients  $C_1$ – $C_5$  are the functions of  $t$  and  $\ln t$  ( $t = \kappa R$ ),  $R$  is the greatest centre-to-centre distance between the ions in the ion-pair formed,  $\kappa$  is the Debye parameter,  $\beta = 2q$ ,  $q$  is the Bjerrum critical distance.  $K_{A,c}$ , subscript  $c$  indicating the molarity scale, is the thermodynamic equilibrium constant for the association reaction



where  $c\alpha$  and  $c(1-\alpha)$  are the equilibrium concentrations of the fraction of free ions and ion pairs, respectively,  $\alpha$  is the degree of dissociation ( $\alpha = \Lambda/\Lambda_{ca}$ ) and represents the ratio of the measured molar conductivity ( $\Lambda$ ) to the molar conductivity of free ions, while  $y_{\pm}$  is the mean activity coefficient of the free ions. The other symbols have their usual meaning. Parameters  $\Lambda_0$ ,  $K_{A,c}$  and  $R$  were calculated by the computer optimization according to Beronius,<sup>14</sup>

where  $\Lambda_0$  and  $K_{A,c}$  were adjusted for each selected value of parameter  $R$ . The optimization is completed when the minimal standard deviation

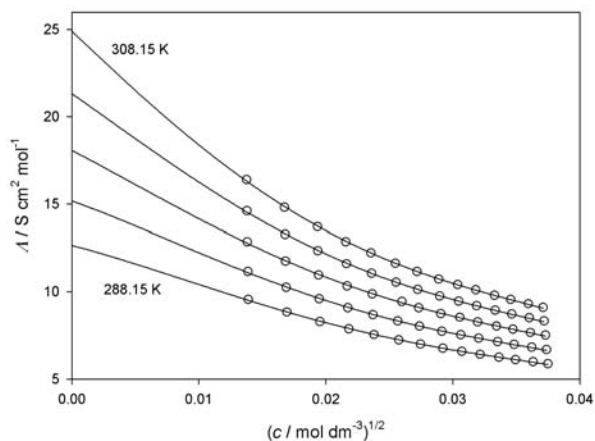
$$\sigma^2 = \sum (\Lambda_{\text{exp}} - \Lambda_{\text{calc}})^2 / (n-3) \quad (9)$$

between the calculated and experimental conductivities is obtained. The obtained values of parameters  $\Lambda_0$  and  $K_{A,c}$  were changing uniformly over the whole temperature range, while the distance parameter  $R$  covered a wide range of values, showing irregular trend with temperature. Further processing of the measured values is carried out using a two-parameter fit, which means that  $R$  must be fixed in accord with some of the existing criteria. The distance parameter can be fixed at the Bjerrum's critical distance,  $R = q$ , as recommended by Justice,<sup>15</sup> or at  $R = a + d$  where  $d$  is the length of an orientated solvent molecule.<sup>16</sup> The sum  $a$  of Pauling's radii of  $\text{NH}_4^+$  and  $\text{Br}^-$  equals 0.343 nm,<sup>8b</sup> for a water molecule  $d = 0.280$  nm,<sup>16</sup> which makes  $R = a + d = 0.623$  nm. From Table 2 it can be observed that this value is significantly lower than Bjerrum's critical distance  $q$  in

**Table 2.** Limiting molar conductivities ( $\Lambda_0$ ), ion-association constants ( $K_{A,c}$ ,  $K_{A,m}$ ) and standard deviations ( $\sigma$ ) of experimental  $\Lambda$  from the model LWPT for  $\text{NH}_4\text{Br}$  in 2-butanol ( $w_B$ ) + water mixtures with  $R = q$

$T/\text{K}$	$\Lambda_0/\text{S cm}^2 \text{mol}^{-1}$	$K_{A,c}$	$K_{A,m}$	$\sigma/\text{S cm}^2 \text{mol}^{-1}$	$q/\text{nm}$
$w_B = 0.70$					
288.15	$18.32 \pm 0.03$	$63.2 \pm 1.1$	$55.1 \pm 1.0$	0.036	1.094
293.15	$21.98 \pm 0.03$	$67.8 \pm 1.1$	$58.8 \pm 1.0$	0.042	1.109
298.15	$26.03 \pm 0.04$	$72.5 \pm 1.2$	$62.6 \pm 1.0$	0.050	1.121
303.15	$30.47 \pm 0.05$	$77.2 \pm 1.2$	$66.3 \pm 1.0$	0.059	1.134
308.15	$35.35 \pm 0.06$	$82.4 \pm 1.3$	$70.4 \pm 1.1$	0.067	1.154
$w_B = 0.80$					
288.15	$15.79 \pm 0.02$	$210.4 \pm 2.3$	$179.1 \pm 2.0$	0.027	1.368
293.15	$19.04 \pm 0.03$	$226.6 \pm 2.5$	$191.9 \pm 2.1$	0.034	1.383
298.15	$22.72 \pm 0.04$	$246.1 \pm 2.7$	$207.4 \pm 2.3$	0.042	1.401
303.15	$26.81 \pm 0.05$	$266.5 \pm 2.9$	$223.4 \pm 2.4$	0.051	1.420
308.15	$31.35 \pm 0.06$	$288.2 \pm 3.2$	$240.3 \pm 2.7$	0.061	1.442
$w_B = 0.90$					
288.15	$13.78 \pm 0.03$	$828.0 \pm 8.8$	$687.9 \pm 7.3$	0.031	1.629
293.15	$16.58 \pm 0.04$	$934.7 \pm 9.1$	$772.2 \pm 7.5$	0.034	1.657
298.15	$19.75 \pm 0.05$	$1059 \pm 10$	$870.4 \pm 8.1$	0.040	1.688
303.15	$23.30 \pm 0.06$	$1204 \pm 11$	$984.1 \pm 9.0$	0.048	1.722
308.15	$27.27 \pm 0.08$	$1376 \pm 14$	$1119 \pm 11$	0.061	1.760
$w_B = 0.95$					
288.15	$12.64 \pm 0.04$	$2184 \pm 19$	$1792 \pm 16$	0.021	1.695
293.15	$15.18 \pm 0.04$	$2584 \pm 20$	$2108 \pm 16$	0.022	1.738
298.15	$18.07 \pm 0.06$	$3079 \pm 25$	$2498 \pm 20$	0.026	1.785
303.15	$21.32 \pm 0.07$	$3697 \pm 27$	$2984 \pm 22$	0.026	1.825
308.15	$24.92 \pm 0.08$	$4450 \pm 32$	$3575 \pm 26$	0.029	1.870

these media. In that case, Fuoss<sup>17</sup> suggests that  $R$  should be fixed to  $q$ . The values so obtained for the limiting molar conductivity ( $\Lambda_0$ ), and the association constant ( $K_{A,c}$ ), along with the standard deviation of experimental  $\Lambda$  from the model ( $\sigma$ ), are listed in Table 2. Standard deviations of  $\Lambda_0$  and  $K_{A,c}$  were estimated as suggested in the literature.<sup>18</sup> To avoid the influence of the solvent thermal expansion on the reaction enthalpy,  $K_{A,c}$  was converted to the molality scale,  $K_{A,m} = K_{A,c} d_o$ .



**Figure 1.** Molar conductivity of  $\text{NH}_4\text{Br}$  in aqueous 2-butanol mixtures with  $w_B = 0.95$  from 288.15 K to 308.15 K; o, experimental data; full line, calculated values.

Fig. 1 shows the concentration dependence of the experimental molar conductivity of  $\text{NH}_4\text{Br}$  at five temperatures in 2-butanol ( $w = 0.95$ ) + water. Full line represents the results of the LWPT conductivity model. The graphs for analogous data in the other three mixtures are similar.

The limiting molar conductivity  $\Lambda_0$  increases with temperature in all 2-butanol + water mixtures as the result of the solvent viscosity decrease. The decrease of  $\Lambda_0$  values with increasing mass fraction of alcohol indicates the greater solvation of  $\text{NH}_4\text{Br}$  ions. The similar dependences of  $\Lambda_0$  on the temperature and the solvent composition were found earlier for alkali bromides in the same mixtures.<sup>3–7</sup> The values of limiting molar conductivity for alkali bromides are very close to that of  $\text{NH}_4\text{Br}$ , keeping mainly the same relation at all temperatures and solvent compositions. Thus for  $\text{LiBr}$ ,  $\text{NaBr}$ ,  $\text{KBr}$ ,  $\text{RbBr}$ ,  $\text{CsBr}$  and  $\text{NH}_4\text{Br}$  they amount to 18.42, 19.20, 19.25, 19.37, 19.49 and 19.75, respectively, at  $T = 298.15$  K and  $w_B = 0.90$ .

The values of  $K_{A,c}$  for these electrolytes mainly retain the relation  $\text{LiBr} < \text{NH}_4\text{Br} < \text{NaBr} < \text{KBr} < \text{RbBr} < \text{CsBr}$  regardless of the solvent composition and temperature. Only,  $\text{NH}_4\text{Br}$  exchanges places with  $\text{KBr}$  in  $w_B = 0.70$ , and with  $\text{NaBr}$  in  $w_B = 0.95$ . With increasing alcohol content the association equilibrium is shifting to the right as a consequence of the mixture permittivity decrease.

The Walden product  $\Lambda_0 \eta$  of the same electrolytes in pure water and its mixtures with 2-butanol is presented in Figures 2a and 2b. 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. The differences in cation solvation and mobility gradually diminish as the fraction of 2-butanol increases.

Alkali metal cations exhibit an electrostatic ion-dipole interaction depending exclusively on their size.<sup>8a</sup> Pauling's radii (in nanometers) follow the order:  $\text{Li}^+$  (0.060) <  $\text{Na}^+$  (0.095) <  $\text{K}^+$  (0.133) <  $\text{Rb}^+$  (0.148) <  $\text{Cs}^+$  (0.169).<sup>8b</sup> The same order is generally followed by the Walden product (Figure 2) emphasizing small  $\text{Li}^+$  as the most solvated cation of the group. Though being of rubidium size, the  $\text{NH}_4^+$  departs from the group of greater cations. Its smaller hydrodynamic radius is due to localized interactions with solvent through H-bonding.<sup>8a</sup>

The standard thermodynamic quantities for the association reaction of  $\text{NH}_4^+$  and  $\text{Br}^-$  ions were obtained from the  $K_{A,m}$  values listed in Table 2. The reaction enthalpy ( $\Delta H^\circ$ ) was determined from the slope of the straight line

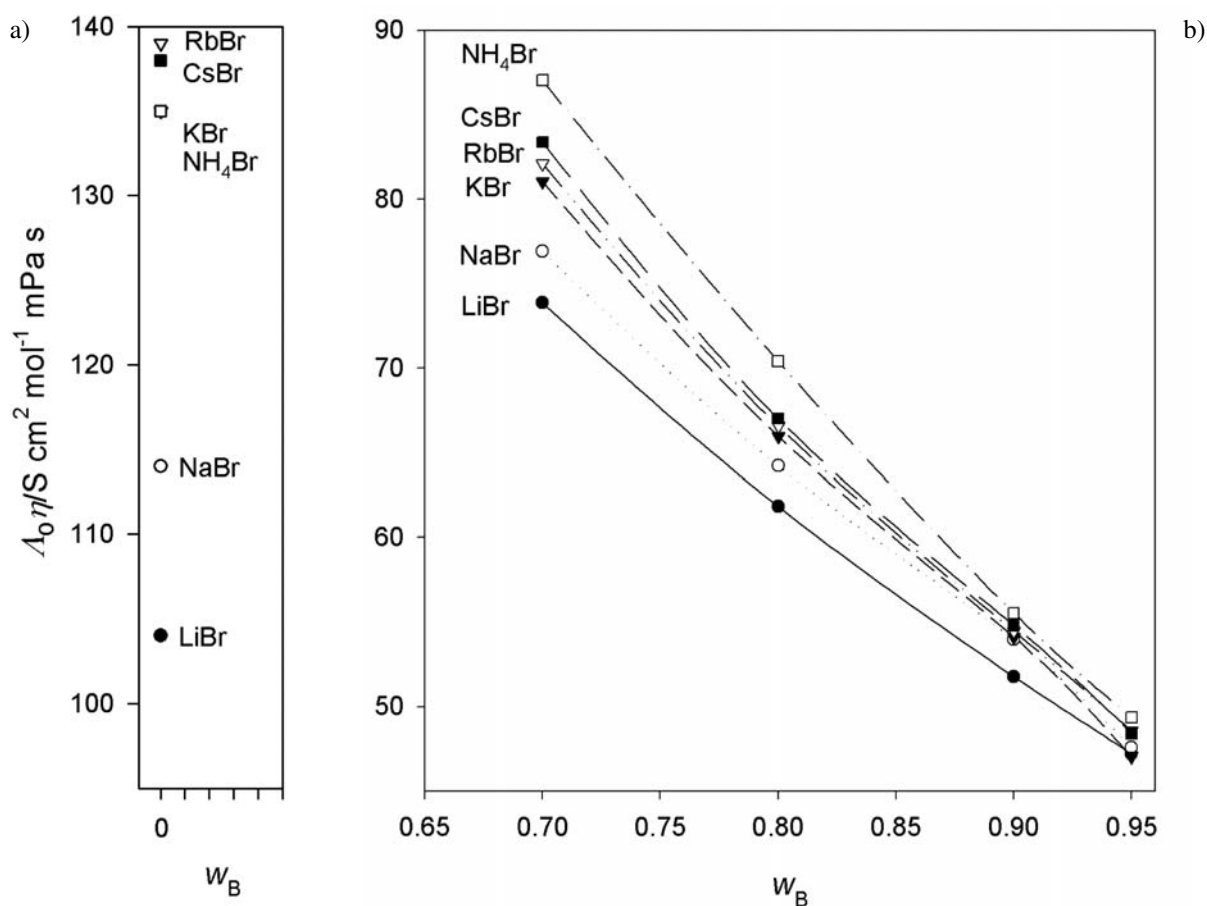
$\ln K_{A,m}$  versus  $1/T$ , Gibbs energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated by the usual equations:

$$\Delta G^\circ = -RT \ln K_{A,m}, \quad (10)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T. \quad (11)$$

The values of thermodynamic quantities and their standard deviations at 298.15 K for  $R = q$  are shown in Table 3.

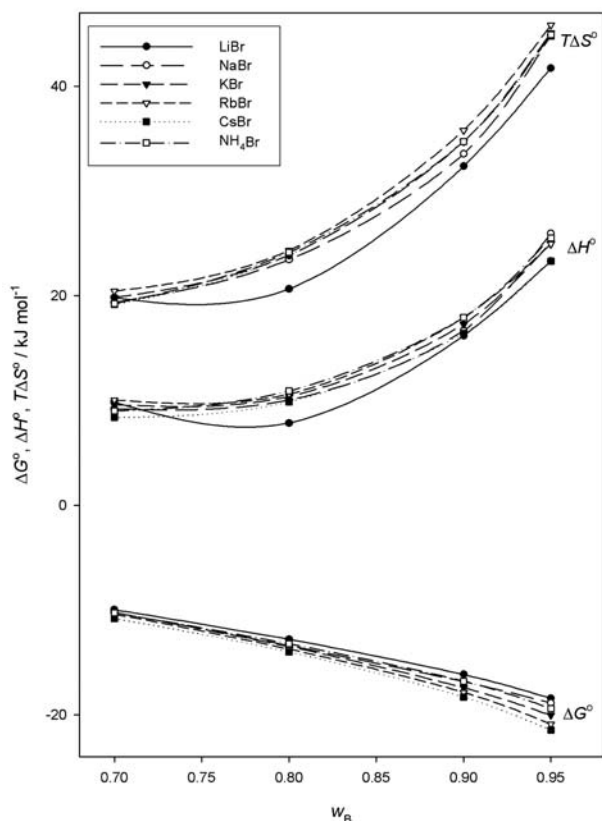
The ion-association reaction is endothermic and has a positive entropy change. The  $\text{NH}_4\text{Br}$  curve is blended with those of previously investigated alkali bromides, see Figure 3. The entropy term ( $T\Delta S$ ) dominates over enthalpy ( $\Delta H$ ) indicating a considerable structural break-down at association: the disorder caused by degradation of the ionic solvation shells is by far greater than the order produced by building up the bulk-solvent structure with liberated molecules. As that structure is becoming stronger, the curves are falling less steeply until are levelled in the  $w_B$  region between 0.70 and 0.75 (Figure 3). The azeotropic mixture composition of  $w_B = 0.68$  at 361.65 K<sup>20</sup> is probably shifted to that region at the room temperature.



**Figure 2.** Walden product for different electrolytes at 298.15 K in: **a)** water—calculated from data in Ref. (19); **b)** 2-butanol + water mixtures; LiBr,<sup>3</sup> NaBr,<sup>4</sup> KBr,<sup>5</sup> RbBr,<sup>6</sup> CsBr<sup>7</sup> and NH<sub>4</sub>Br (this work).

**Table 3.** Activation enthalpy of ionic movement and thermodynamic quantities of the ion-association reaction for  $\text{NH}_4\text{Br}$  in 2-butanol + water mixtures at 298.15 K

$w_B$	$\Delta H^\ddagger/\text{J mol}^{-1}$	$\Delta H^\circ/\text{J mol}^{-1}$	$\Delta G^\circ/\text{J mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
0.70	$23750 \pm 310$	$9009 \pm 53$	$-10255 \pm 40$	$64.6 \pm 0.2$
0.80	$24810 \pm 240$	$10920 \pm 190$	$-13224 \pm 27$	$81.0 \pm 0.6$
0.90	$24650 \pm 180$	$17940 \pm 410$	$-16780 \pm 23$	$116.4 \pm 1.4$
0.95	$24540 \pm 160$	$25510 \pm 620$	$-19393 \pm 20$	$150.6 \pm 2.1$

**Figure 3.** Values of  $\Delta H^\circ$ ,  $T\Delta S^\circ$  and  $\Delta G^\circ$  for the ion-pair formation as a function of the 2-butanol mass fraction ( $w_B$ ) in 2-butanol + water mixtures at 298.15 K for: LiBr,<sup>3</sup> NaBr,<sup>4</sup> KBr,<sup>5</sup> RbBr,<sup>6</sup> CsBr,<sup>7</sup>  $\text{NH}_4\text{Br}$ , (this work).

It is expected that the ion association of the stronger solvated ions is less favourable. This is confirmed by the order of the  $\Delta G^\circ$  curves in Figure 3,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ . Again,  $\text{NH}_4^+$  is following a different pattern: instead of being found under  $\text{Cs}^+$ , its curve is overlapping that of  $\text{Na}^+$ .

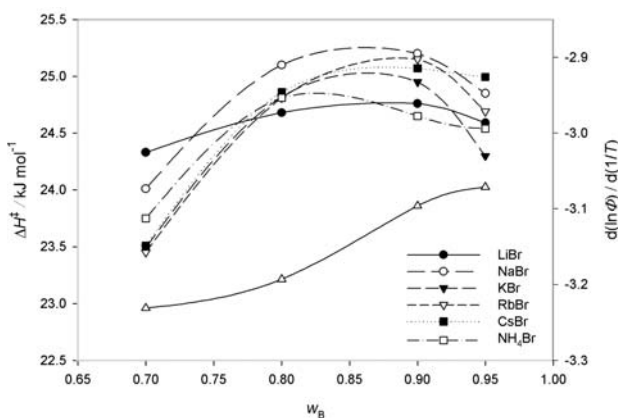
The activation enthalpy of the charge transport ( $\Delta H^\ddagger$ ) presented in Table 3 refers to the mean of the tem-

perature range (298.15 K).  $\Delta H^\ddagger$  was evaluated by the least-squares treatment of the straight line:

$$\ln \Lambda_0 + 2/3 \ln d_0 = -\Delta H^\ddagger/RT + C'. \quad (12)$$

Table 4 shows the standard deviation ( $s_r$ ) of experimental points from the regression straight line ( $\ln \Lambda_0 + 2/3 \ln d_0$ ) versus  $1/T$ . The line through points exhibits a slight curvature with its slope falling as the temperature is raising. This phenomenon is more pronounced in structured solvents, as reflected by the higher standard deviation from the regression straight line ( $s_r$ ). Considerable decrease of  $s_r$  with increasing 2-butanol content in the mixture (Table 4) indirectly points to a “weaker” structure of the mixed solvent. According to Brummer and Hills<sup>21</sup> the heat of activation at constant pressure is a complex quantity which depends on the temperature:

$$\Delta H^\ddagger = \Delta U^\ddagger + (\pi + P)\Delta V^\ddagger, \quad (13)$$

**Figure 4.** Activation enthalpy of the charge transport,  $\Delta H^\ddagger$ , and the temperature gradient of fluidity  $\Phi$  ( $-\Delta-$ ) in aqueous 2-butanol with mass fraction  $w_B$  at 298.15 K; LiBr, NaBr, KBr, RbBr and CsBr from Refs. [3] to [7], respectively.**Table 4.** The standard deviation ( $s_r$ ) of experimental points from the regression straight line ( $\ln \Lambda_0 + 2/3 \ln d_0$ ) versus  $1/T$  for different electrolytes in 2-butanol + water mixtures

$w_B$	LiBr	NaBr	KBr	RbBr	CsBr	$\text{NH}_4\text{Br}$
0.70	0.0058	0.0046	0.0060	0.0062	0.0069	0.0066
0.80	0.0034	0.0043	0.0044	0.0038	0.0050	0.0052
0.90	0.0055	0.0031	0.0037	0.0029	0.0038	0.0039
0.95	0.0028	0.0030	0.0038	0.0011	0.0018	0.0034

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,  $\pi$  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.<sup>21</sup> This can explain the closeness and similar shape of all curves in Figure 4. The shape of the curve, representing the dependence of the solvent fluidity (reciprocal viscosity) temperature gradient upon the mixed solvent composition, is similar.

## 4. Acknowledgment

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

## 5. References

1. D. Rudan Tasic, T. Župec, C. Klofutar, M. Bešter-Rogač, *J. Solution Chem.* **2005**, *34*, 631–644.
2. R. De, C. Guha, B. Das, *J. Solution Chem.* **2006**, *35*, 1505–1514.
3. V. Sokol, I. Tominić, R. Tomaš, M. Višić, *Croat. Chem. Acta* **2005**, *78*, 43–47.
4. I. Tominić, V. Sokol, I. Mekjavić, *Croat. Chem. Acta* **1998**, *71*, 705–714.
5. V. Sokol, R. Tomaš, M. Višić, I. Tominić, *J. Solution Chem.* **2006**, *35*, 1687–1698.
6. V. Sokol, R. Tomaš, I. Tominić, *Acta Chim. Slov.* **2008**, *55*, 308–314.
7. V. Sokol, R. Tomaš, I. Tominić, *Polish J. Chem.* **2008**, *82*, 1585–1596.
8. J. M. G. Barthel, H. Krienke, W. Kunz, *Physical Chemistry of Electrolyte Solutions-Modern Aspects*, Steinkopff/Darmstadt, Springer/New York, **1998**. a) p. 4;b) p. 37.
9. K. Ochi, T. Saito, K. Kojima, *J. Chem. Eng. Data* **1996**, *41*, 361–364.
10. A. Bald, J. Gregorowicz, A. Szejgis, *J. Electroanal. Chem.* **1992**, *340*, 153–167.
11. M. Bešter-Rogač, R. Neueder, J. Barthel, *J. Solution Chem.* **1999**, *28*, 1071–1086.
12. J. Barthel, F. Feuerlein, R. Neueder, R. Wachter, *J. Solution Chem.* **1980**, *9*, 209–219.
13. A. D. Pethybridge, S. S. Taba, *J. Chem. Soc. Faraday Trans. I* **1980**, *76*, 368–376.
14. P. Beronius, *Acta. Chem. Scand. A* **1974**, *28*, 77–82.
15. J. C. Justice, *Electrochim. Acta* **1971**, *16*, 701–712.
16. M. Bešter-Rogač, R. Neueder, J. Barthel, *J. Solution Chem.* **1999**, *28*, 1071–1086.
17. R. M. Fuoss, *J. Phys. Chem.* **1978**, *82*, 2427–2440.
18. D. M. Himmelblau, *Process Analysis by Statistical Methods*, John Wiley and Sons/ New York, **1970**, p. 197.
19. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Second Revised Edition, Dover Publications Inc., Mineola, New York, **2002**, p. 463.
20. Handbook of Chemistry and Physics, Edited by Weast R. C., CRC Press, Cleveland, Ohio, 56<sup>th</sup> edn, **1975–1976**, p. D-9.
21. S. B. Brummer, G. J. Hills, *J. Chem. Soc. Faraday Trans.* **1961**, *57*, 1816–1837.

## Povzetek

V temperaturnem območju med 288.15 in 308.15 K smo izmerili smo molske prevodnosti razredčenih raztopin amonijskega bromida v mešanici 2-butanol in vode. Z uporabo Lee-Wheatonovih enačb za prevodnost elektrolitov smo določili molsko prevodnost pri neskončnem razredčenju,  $\Lambda_0$ , ter konstanto asociacije ionov,  $K_A$ . S pomočjo znane temperaturne odvisnosti  $K_A$  smo izračunali termodinamske parametre procesa asociacije ionov, Gibbsovo prosto energijo,  $\Delta G^\circ$ , entalpijo,  $\Delta H^\circ$ , in entropijo,  $\Delta S^\circ$ . Iz temperaturne odvisnosti  $\Lambda_0$  smo ocenili aktivacijsko energijo gibanja ionov v raztopinah,  $\Delta H^\ddagger$ . Dobljene vrednosti smo primerjali z vrednostmi za bromide alkalijskih kovin ter jih interpretirali glede na vpliv velikosti ionov ter lastnosti topil.