

Scientific paper

Thermodynamics of the Association Reaction of RbBr in Binary Mixtures of 2-Butanol and Water from 288.15 to 308.15 K

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Received: 13-09-2007

Abstract

Molar conductivities of dilute solutions of rubidium 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 (Λ_0) and association constant (K_A) were determined by treating experimental data with the Lee-Wheaton conductivity equation. Thermodynamic quantities for the ion-association reaction were derived from the temperature dependence of K_A . The obtained results provide information on ion-ion and ion-solvent interactions.

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

1. Introduction

In continuation of our studies on the ion-association reactions of alkali bromides in mixtures of water and 2-butanol,^{1,2,3} we report conductance measurements of RbBr in mixtures with the alcohol mass fraction (w) 0.70, 0.80, 0.90 and 0.95 at five temperatures from 288.15 to 308.15 K. Mixed solvents are suitable for this study because even a small change in solvent composition make a significant difference in behaviour of the dissolved electrolyte. The study on conductometric properties of alkali bromides in water + N,N-dimethyl-formamide⁴ and tetrahydrofuran + water⁵ mixtures have been made at 298.15 K. Conductivity study on electrolytes over wide temperature range provide valuable information on thermodynamic behaviour of the dissolved electrolyte. The limiting molar conductivity (Λ_0), association constant (K_A) and association distance (R) were determined using the chemical model of conductivity based on the Lee-Wheaton equation. The Walden product values ($\Lambda_0\eta$), as well as the standard thermodynamic quantities for the association reaction, were derived from the temperature dependence of Λ_0 and K_A , respectively. The influence of the cation change on thermodynamic quantities was discussed from a comparison with the analogous data for LiBr,¹ NaBr² and KBr³ in the same mixtures.

2. Experimental

2-butanol (Merck, p.a.) was fractionally 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 to prepare the solutions. Water was distilled twice, and RbBr (Merck, suprapur) was dried for six hours at 393.15 K before use. The test solutions were prepared by adding a weighed amount of the mixed solvent to a weighed amount of the RbBr stock solution. The relative error on molarity and solvent composition was about 0.1%. The values for the density and viscosity of the pure solvent were taken from our previous work,³ while the relative permittivities were obtained by interpolation of literature data,⁶ and presented in Ref. (3). The molar concentration of the solution is given by the relationship

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

where m is the molality (moles of electrolyte per kilogram of solvent), d is the density of solution, and M (0.16538 kg mol⁻¹) is the molar mass of rubidium bromide. First, a small amount of the stock solution in the corresponding mixed solvent was prepared by weighing RbBr, water and 2-butanol. The solution density was determined at 293.15 K using a pycnometer. The density coefficient D was ob-

tained assuming a linear change of solution density upon its molality, $d = d_0 + Dm$, where d_0 is the density of the pure mixed solvent. The density coefficient D ($\text{kg}^2 \text{dm}^{-3} \text{mol}^{-1}$) is assumed to be independent of temperature,⁷ and its values for 0.70, 0.80, 0.90 and 0.95 alcohol mass fraction amount to 0.099, 0.044, 0.095 and 0.101, respectively.

The resistance of test solutions was measured in two parallel cells with 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 ± 0.01 K. The cell constants were determined with dilute potassium chloride solutions.⁸

3. Results and Discussion

Each molar conductivity of RbBr solutions, as presented in Table 1, is the mean value of two cells. The ave-

rage relative deviation of a single cell value from the mean amounts to $\pm 0.14\%$. All measured values were corrected for the conductivity of the solvent. Conductivity data processing was carried out by means of the Lee-Wheaton equation in Pethybridge and Taba version⁹ (LWP) and the following set of equations was used

$$A_{\text{ca}} = A_0 \left[1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3 \right] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \quad (2)$$

$$K_{\text{A,c}} = (1 - \alpha) / (c \alpha^2 y_{\pm}^2), \quad (3)$$

$$y_{\pm}^2 = \exp[-2\kappa q / (1 + \kappa R)], \quad (4)$$

$$q = \frac{e^2}{8\pi \epsilon_0 \epsilon_r \kappa T}, \quad (5)$$

Table 1. Molar conductivities (Λ) of RbBr at various molalities (m) in aqueous 2-butanol of mass fraction w at different temperatures

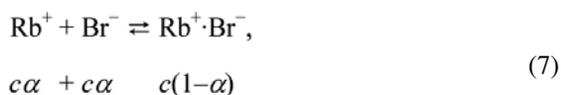
$10^4 m^a$ mol kg^{-1}	$10^4 \Lambda / \text{S m}^2 \text{mol}^{-1}$				
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$
$w = 0.70$					
2.003	16.567	19.818	23.418	27.340	31.696
6.301	16.129	19.200	22.651	26.394	30.431
10.597	15.710	18.690	22.020	25.641	29.557
14.896	15.403	18.313	21.530	25.078	28.823
19.201	15.057	17.882	21.054	24.456	28.217
23.498	14.802	17.558	20.614	23.979	27.581
27.805	14.567	17.277	20.303	23.566	27.112
32.099	14.366	17.034	20.021	23.225	26.636
36.392	14.166	16.801	19.714	22.863	26.314
40.704	13.995	16.579	19.436	22.568	25.984
45.006	13.819	16.353	19.181	22.240	25.562
49.267	13.702	16.216	18.993	22.026	25.281
53.595	13.568	16.049	18.810	21.797	25.029
57.900	13.433	15.886	18.623	21.572	24.749
61.827	13.301	15.720	18.407	21.334	24.515
$w = 0.80$					
4.099	13.368	16.012	19.025	22.376	26.035
6.433	12.824	15.329	18.167	21.326	24.781
8.644	12.430	14.838	17.569	20.572	23.898
10.862	12.116	14.456	17.097	20.003	23.221
13.083	11.803	14.081	16.632	19.450	22.515
15.286	11.559	13.777	16.281	19.010	21.982
17.509	11.353	13.526	15.960	18.620	21.528
19.727	11.152	13.274	15.646	18.261	21.095
21.941	10.979	13.069	15.397	17.957	20.775
24.159	10.795	12.830	15.124	17.644	20.431
26.386	10.654	12.657	14.918	17.399	20.118
28.597	10.518	12.504	14.711	17.145	19.754
30.800	10.374	12.325	14.500	16.894	19.455
33.018	10.237	12.155	14.303	16.663	19.172

10^4 m^a mol kg ⁻¹	$10^4 \Lambda/S \text{ m}^2 \text{ mol}^{-1}$				
	$T/K = 288.15$	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$
w = 0.90					
2.015	11.207	13.323	15.687	18.268	21.092
3.384	10.389	12.293	14.421	16.701	19.141
4.533	9.888	11.659	13.629	15.750	18.041
5.801	9.425	11.099	12.952	14.921	17.033
7.063	9.080	10.672	12.417	14.281	16.276
8.311	8.752	10.275	11.938	13.710	15.596
9.630	8.466	9.914	11.508	13.211	15.019
10.835	8.244	9.640	11.182	12.817	14.542
12.108	8.026	9.387	10.864	12.442	14.119
13.338	7.838	9.157	10.596	12.132	13.754
14.639	7.666	8.938	10.341	11.827	13.392
15.939	7.490	8.737	10.096	11.529	13.025
17.178	7.361	8.581	9.915	11.314	12.780
18.456	7.200	8.391	9.684	11.055	12.485
19.806	7.061	8.225	9.490	10.821	12.186
w = 0.95					
2.041	8.581	9.925	11.368	12.861	14.383
3.135	7.732	8.900	10.134	11.390	12.646
4.218	7.151	8.205	9.313	10.428	11.528
5.309	6.691	7.648	8.658	9.668	10.657
6.401	6.342	7.236	8.177	9.113	10.028
7.488	6.046	6.891	7.773	8.642	9.485
8.578	5.802	6.592	7.424	8.243	9.055
9.669	5.578	6.344	7.128	7.911	8.679
10.761	5.393	6.120	6.871	7.616	8.346
11.847	5.222	5.923	6.648	7.362	8.062
12.943	5.072	5.750	6.450	7.139	7.804
14.028	4.945	5.599	6.275	6.945	7.578
15.120	4.814	5.451	6.106	6.749	7.373
16.199	4.701	5.319	5.957	6.584	7.192
17.269	4.600	5.202	5.823	6.430	7.017

^a Molality can be converted to molarity using Eq. (1)

$$\kappa^2 = 16\pi N_A q \alpha c \quad (6)$$

In these expressions, Λ_{ca} is the molar conductivity of the free ions, Λ_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, κ is the Debye parameter, $\beta = 2q$, q is the Bjerrum critical distance, and ρ is defined in Ref. (9). K_{Ac} , 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. α is the degree of dissociation ($\alpha = \Lambda/\Lambda_{\text{ca}}$) and represents the ratio of the measured molar conductivity (Λ) to the molar

conductivity of free ions. y_{\pm} is the mean activity coefficient of the free ions, e is the proton charge, ϵ_r the relative permittivity of the solvent, ϵ_0 the permittivity of vacuum. The other symbols have their usual meaning. Parameters Λ_0 , K_{Ac} and R were calculated by the computer optimization according to Beronius,¹⁰ where Λ_0 and K_{Ac} were adjusted for each selected value of parameter R . The optimization is completed when the minimal standard deviation

$$\sigma^2 = \Sigma(\Lambda_{\text{exp}} - \Lambda_{\text{calc}})^2 / (n-3) \quad (8)$$

between the calculated and experimental conductivities is obtained. The initial values of Λ_0 and K_{Ac} for the iteration procedure are obtained by the Kraus-Bray method.¹¹ Each system gave a unique best set of parameters at each temperature. By plotting the standard deviation data against distance parameter (R), no significant minima were observed over the whole temperature range. Therefore, it can be concluded that it is not possible to obtain a uniform value for the distance parameter by the three-parameter fit. In

that case, the distance parameter must be fixed at some arbitrarily chosen value. There are two criteria for the choice of such a value. According to the chemical model of electrolyte solutions, oppositely charged ions of the crystallographic radii a_+ and a_- may be either in contact $R = a$, where $a = a_+ + a_-$, or separated by one or more solvent molecules $R = a + d$, the molecular diameter d is approximated by the length of an orientated solvent molecule.⁷ According to Bjerrum's physical concept of ionic association, the upper limit of integration for K_A is q (Eq. (5)). This quantity was adopted in conductometry as the distance parameter, $R = q$, by the efforts of Justice.¹² The sum of crystallographic radii of Rb^+ and Br^- (a) equals 0.343 nm.¹³ Diameter d represents the length of a water molecule, $d = 0.280$ nm,⁷ that makes $R = 0.623$ nm, a distance parameter significantly lower than Bjerrum's critical distance q in these media (see Table 2). In this case, according to Fuoss' suggestion,¹⁴ R should be equal to q . The obtained values of limiting molar conductivities, ion-association constants and standard deviations with R set at q , for all mixtures at different temperatures, are given in Table 2. To avoid thermal expansion of the solvent to the reaction enthalpy, $K_{A,c}$ was converted to the molality scale, $K_{A,m} = K_{A,c} d_o$.

The thermodynamic quantities of the ion-association reaction (Eq. (7)) were derived from the data for association constant $K_{A,m}$ at different temperatures. The stan-

dard enthalpy (ΔH°) was evaluated by the least-squares treatment of the following straight line:

$$\ln K_{A,m} = \frac{-\Delta H^\circ}{RT} + C \quad (9)$$

The standard deviation of the enthalpy was derived from the standard deviation of the corresponding slope.^(15a) The standard deviation of the reaction Gibbs energy was estimated after linearization^(15b) of the relationship

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

The standard entropy of ion-pair formation is a linear combination of two variables

$$\Delta S^\circ = \frac{1}{T} (\Delta H^\circ - \Delta G^\circ) \quad (11)$$

and its standard deviation can be obtained accordingly.^(15b)

Eyring's enthalpy of activation of the charge transport¹⁶ (ΔH^\ddagger) can be obtained from the temperature dependence of Λ_o by the equation

$$\ln \Lambda_o + 2/3 \ln d_o = -\Delta H^\ddagger/RT + C', \quad (12)$$

Table 2. Limiting molar conductivities (Λ), ion-association constants ($K_{A,c}$, $K_{A,m}$) and standard deviations (σ) of experimental Λ from the model LWP for RbBr in 2-butanol (w) + water mixtures with $R = q$

T/K	$10^4 \Lambda_o / \text{S m}^2 \text{ mol}^{-1}$	$K_{A,c}$	$K_{A,m}$	$10^4 \sigma / \text{S m}^2 \text{ mol}^{-1}$	q/nm
w = 0.70					
288.15	17.37 ± 0.03	64.6 ± 1.3	56.3 ± 1.1	0.047	1.094
293.15	20.77 ± 0.03	70.8 ± 1.1	61.4 ± 1.0	0.044	1.109
298.15	24.56 ± 0.03	76.3 ± 1.1	65.9 ± 0.9	0.049	1.121
303.15	28.70 ± 0.04	81.3 ± 1.1	69.8 ± 0.9	0.057	1.134
308.15	33.23 ± 0.03	86.9 ± 0.8	74.2 ± 0.7	0.045	1.154
w = 0.80					
288.15	14.97 ± 0.03	259.8 ± 3.1	221.1 ± 2.6	0.027	1.368
293.15	18.00 ± 0.04	278.6 ± 3.3	235.9 ± 2.8	0.034	1.383
298.15	21.48 ± 0.05	301.5 ± 3.7	254.0 ± 3.1	0.043	1.401
303.15	25.38 ± 0.07	325.6 ± 4.7	272.9 ± 3.9	0.061	1.420
308.15	29.71 ± 0.08	353.4 ± 4.9	294.6 ± 4.1	0.071	1.442
w = 0.90					
288.15	13.44 ± 0.02	1269 ± 7	1054 ± 6	0.017	1.629
293.15	16.20 ± 0.03	1436 ± 9	1186 ± 7	0.021	1.657
298.15	19.37 ± 0.04	1628 ± 9	1338 ± 7	0.025	1.688
303.15	22.92 ± 0.05	1843 ± 11	1506 ± 9	0.030	1.722
308.15	26.96 ± 0.06	2112 ± 13	1717 ± 11	0.036	1.760
w = 0.95					
288.15	12.47 ± 0.03	4055 ± 21	3327 ± 17	0.012	1.695
293.15	14.93 ± 0.04	4762 ± 24	3885 ± 20	0.014	1.738
298.15	17.78 ± 0.04	5644 ± 28	4579 ± 23	0.014	1.785
303.15	21.01 ± 0.06	6747 ± 38	5446 ± 31	0.018	1.825
308.15	24.67 ± 0.09	8146 ± 57	6544 ± 46	0.025	1.870

were d_0 is the density of solvent. The values of the standard thermodynamic quantities at 298.15 K, along with their standard deviations, are given in Table 3.

Table 3. Standard thermodynamic quantities for the ion-association reaction (Eq. (7)) calculated from $K_{A,m}$ in 2-butanol (w) + water mixtures at 298.15 K

w	$\Delta H^\circ/\text{J mol}^{-1}$	$\Delta G^\circ/\text{J mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
0.70	10059 ± 390	-10382 ± 34	68.6 ± 1.3
0.80	10620 ± 280	-13727 ± 30	81.7 ± 1.0
0.90	17920 ± 390	-17845 ± 13	120.0 ± 1.3
0.95	24940 ± 760	-20895 ± 12	153.7 ± 2.6

Figure 1 shows the concentration dependence of the experimental molar conductivity of RbBr at five temperatures in 2-butanol ($w = 0.95$) + water. Full line represents the results of the chemical model of conductivity (Eqs. (2 – 6)). The graphs for analogous data in the other three mixtures are similar.

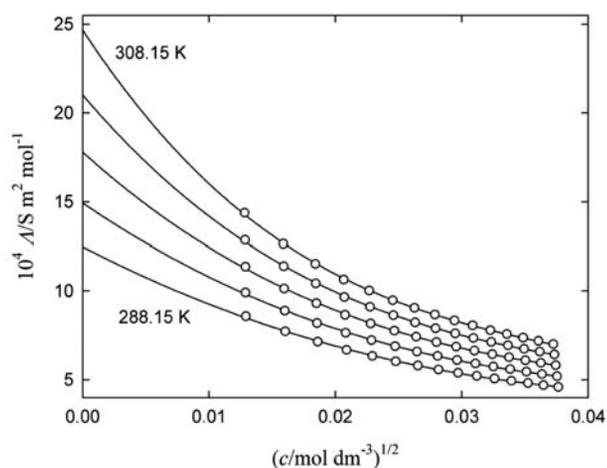


Figure 1. Molar conductivity of RbBr in aqueous 2-butanol of mass fraction 0.95 from 288.15 K to 308.15 K in steps of 5 K; \circ , experimental data; full line, calculated values.

The limiting molar conductivity increases with temperature and decreases with the alcohol addition to a mixture. Such a behaviour of Λ_0 is in agreement with the solvent viscosity.

The Walden product is almost independent of temperature, see Table 4, as found for LiBr, NaBr and KBr in the same mixtures. The variation of the Walden product $\Lambda_0\eta$ with the solvent composition gives information on ion-solvent interactions. The Walden product decreases with increasing mass fraction of alcohol, which can be explained by presolvation of ions by alcohol molecules. This presolvation of ions leads to an increase of the hydrodynamic radii of ions and decrease of their mobility.

By comparing $\Lambda_0\eta$ of RbBr with the same quantity for other alkali bromides in the same mixtures, the influence of the nature of cation can be discussed. From Figure 2 it can be observed that the dependencies of the Walden product for LiBr, NaBr, KBr and RbBr on the solvent composition at 298.15 K are similar. The values of $\Lambda_0\eta$ retain the order $\Lambda_0\eta(\text{Li}^+) < \Lambda_0\eta(\text{Na}^+) < \Lambda_0\eta(\text{K}^+) < \Lambda_0\eta(\text{Rb}^+)$ in the whole range of composition. The increase of the Walden product with increasing crystallographic radii of alkali ions indicates that the effective radius of cations follows the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$. This is the result of the stronger solvation of smaller ions which leads to their larger hydrodynamic radii. The differences in solvation of the mentioned electrolytes decrease with alcohol addition to the mixture. The similar behaviour of the Walden product was found for Li^+ , Na^+ , K^+ and Cs^+ in DMF + water mixtures.⁴

The association constant $K_{A,c}$ increases with increasing temperature. $K_{A,c}$ is low in aqueous 2-butanol of mass

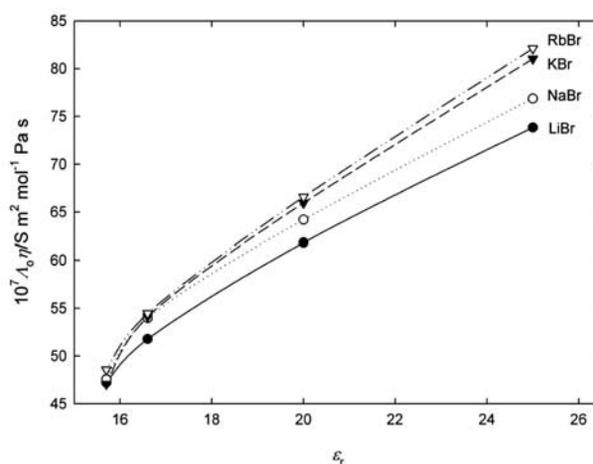


Figure 2. Variation of $\Lambda_0\eta$ with ϵ_r in 2-butanol + water mixtures at 298.15 K for: LiBr (\bullet), Ref. (1); NaBr (\circ), Ref. (2); KBr (\blacktriangledown), Ref. (3); RbBr (∇), this work.

Table 4. Walden product of RbBr in 2-butanol (w) + water mixtures at different temperatures

w	$10^7 \Lambda_0 \eta / \text{S m}^2 \text{ mol}^{-1} \text{ Pa s}$				
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$
0.70	85.30	83.77	82.10	80.25	78.95
0.80	68.01	67.21	66.57	66.17	65.78
0.90	54.69	54.48	54.45	54.39	54.65
0.95	48.97	48.82	48.56	48.66	48.50

fractions 0.70 and 0.80, while it is considerably higher for $w = 0.90$ and 0.95. This increase can be explained by the lower relative permittivity of the mixed solvent. Figure 3 shows the variation of $\ln K_{A,m}$ for alkali bromides with the inversed relative permittivity of the solvent at 298.15 K. The values of the association constant retain the order $\text{RbBr} > \text{KBr} > \text{NaBr} > \text{LiBr}$ in the whole temperature range.

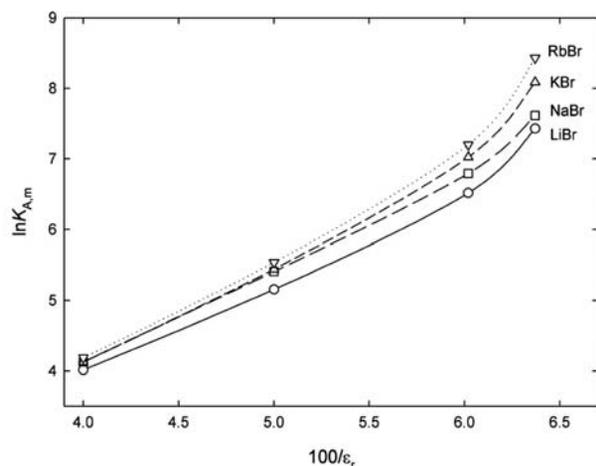


Figure 3. Variation of $\ln K_{A,m}$ with ϵ_r^{-1} in 2-butanol + water mixtures at 298.15 K for: LiBr (○), Ref. (1); NaBr (□), Ref. (2); KBr (△), Ref. (3); RbBr (▽), this work.

From Table 3 it can be concluded that the association of Rb^+ and Br^- ions is an endothermic reaction which results in an entropy increase. Both, ΔH° and ΔS° values increase with increasing 2-butanol content in the mixture. The similar behaviour show other mentioned alkali bromides, see Figure 4.

The Gibbs energy for the association reaction is negative at all temperatures and becomes more negative with

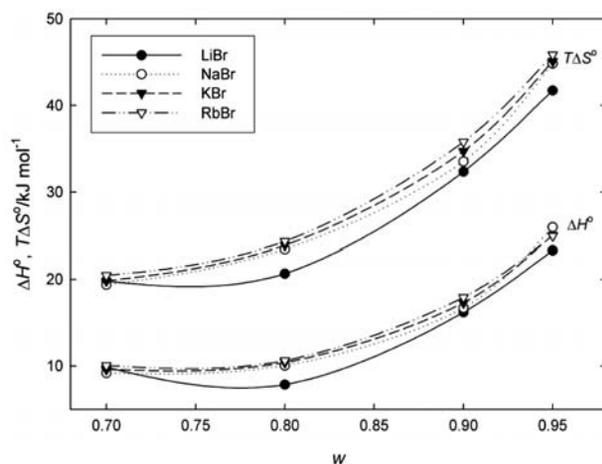


Figure 4. Thermodynamic quantities ΔH° and ΔS° for the ion-pair formation for different electrolytes in aqueous 2-butanol of mass fraction w at 298.15 K; LiBr, NaBr and KBr from Refs. (1–3), respectively.

the increasing alcohol content. That indicates a greater degree of association at lower relative permittivity. From Figure 4 it can be observed that entropy term ($T\Delta S^\circ$) dominates over association making an endothermic reaction spontaneous. This behaviour is due to considerable structural effects, probably brought by two main processes: breaking of the solvation layers and building-up of the bulk solvent. Figure 5 shows the dependence of the association Gibbs energy for alkali bromides on the alcohol content at 298.15 K. The order of the ΔG° curves, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$, suggests that ion-pair formation is weaker with more strongly solvated ions.

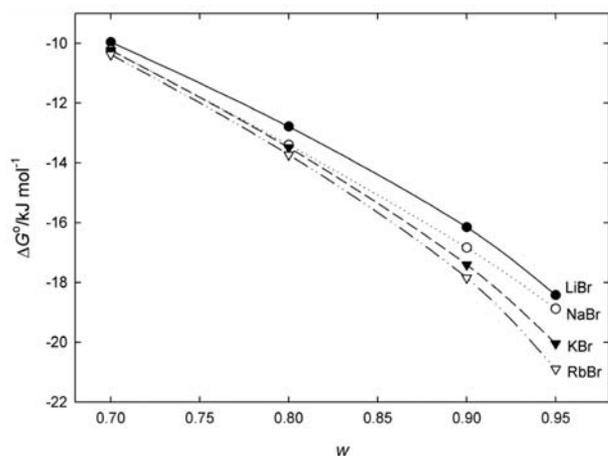


Figure 5. Values of ΔG° for the ion-pair formation as a function of the 2-butanol content (w) in 2-butanol + water mixtures at 298.15 K for: LiBr (●), Ref. (1); NaBr (○), Ref. (2); KBr (▼), Ref. (3); RbBr (▽), this work.

Eyring's enthalpy of activation of the charge transport (ΔH^\ddagger) relates to the mean of the temperature range (298.15 K). Figure 6 shows the dependence of $\ln A_0 + 2/3 \ln d_0$

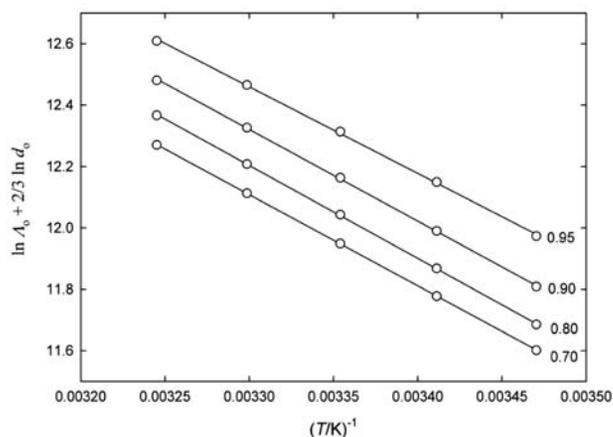


Figure 6. Dependences of $(\ln A_0 + 2/3 \ln d_0)$ on $1/T$ for RbBr in aqueous 2-butanol of mass fractions 0.70, 0.80, 0.90 and 0.95. The activation energy of the transport process ΔH^\ddagger was determined according to Eq. (12).

In d_0 upon $1/T$ for RbBr in all investigated mixtures. The activation energy of the ionic movement is obtained from the slope of the straight lines. Thus, $\Delta H^\ddagger/\text{kJ mol}^{-1}$ for RbBr in aqueous 2-butanol of the mass fraction 0.70, 0.80, 0.90 and 0.95 amounted to 23.45, 24.81, 25.15 and 24.69, respectively. Corresponding values in Ref. (3) for LiBr, NaBr and KBr are very close: for example in the mixture with $w = 0.95$ they are 24.59, 24.85, 24.30, respectively.

4. Acknowledgment

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

5. References

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Povzetek

Izmerili smo molske prevodnosti razredčenih raztopin rubidijevega bromida v binarnih mešanicah 2-butanola in vode v temperaturnem območju med 288.15 in 308.15 K v intervalih po 5 K. Dobljene podatke smo analizirali z Lee-Wheatonovo enačbo za prevodnost elektrolitov ter določili molske prevodnosti pri neskončnem razredčenju (Λ_0) ter konstante asociacije ionov (K_A). Iz temperaturne odvisnosti K_A smo izpeljali termodinamske količine za opis asociacije ionov, ki nam dajejo informacije o ion-ion ter ion-topilo interakcijah v raztopinah.