

Scientific paper

Ion-Association Reaction of Rb^+ and Br^- in 2-Methylpropan-2-ol + Water Mixtures

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Abstract

The molar conductivity of RbBr solutions in 2-methylpropan-2-ol (*tert*-butanol) + water mixtures at alcohol mass fractions of 0.70, 0.80 and 0.90 was measured at temperatures from 288.15 to 308.15 K at 5 K intervals. The limiting molar conductivity (Λ_0) and the ion-pair formation constant (K_A^0) were determined by the Lee-Wheaton conductivity equation. Thermodynamic quantities, Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0), for the ion-association reaction were derived from the temperature dependence of K_A^0 ; the activation energy of the ionic movement (ΔH^*) was derived from the temperature dependence of Λ_0 . These values were compared with those obtained earlier for HBr and NaBr in the same mixtures.

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

1. Introduction

Our previous thermodynamic studies of the association of $\text{HBr}^{1,2}$ and alkali metal bromides^{3–8} in binary mixtures of water with two isomeric butanols were carried out using conductivity measurements. In this work we report conductometric data for low-concentration rubidium bromide solutions in 2-methylpropan-2-ol + water mixtures with alcohol mass fraction $w = 0.70, 0.80$ and 0.90 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 Bjerrum's critical distance q . The limiting molar conductivity (Λ_0), the association constant (K_A^0) and Walden product ($\Lambda_0 \eta_0$) were derived. Standard Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) changes for the association reaction of Rb^+ and Br^- were calculated from the temperature dependence of K_A^0 ; the association constant. Eyring's enthalpy of activation for charge transport (ΔH^*) was derived from the temperature dependence of the limiting conductivity. The obtained quantities were compared with those for HBr^1 and NaBr^3 in the same mixtures. The influence of the organic solvent on the behaviour of rubidium, sodium and hydrogen ions was discussed by comparison of the Walden product and K_A^0 in 2-methylpropan-2-ol + water mixtures with those in butanol-2-ol + water mixtures.^{7,4,2}

2. Experimental

The organic solvent 2-methylpropan-2-ol (Merck, p.a.) was fractionally distilled in a Vigreux column immediately before use and the middle fraction of distillate, collected at a head temperature of 355 K, was used to prepare mixtures. Water was distilled twice (specific conductivity $\approx 10^{-6} \text{ S cm}^{-1}$), and RbBr (Merck, suprapur) was dried for six hours at 398.15 K before use. Solvent mixtures and the concentrated stock solution were prepared by weight without buoyancy correction; 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.⁹

Measurements were performed at five temperatures in the range from 288.15 to 303.15 K using a dipping type conductivity cell Orion (model 018001) with two electrodes of bright platinum. The cell constant ($0.10402 \pm 0.00002 \text{ cm}^{-1}$) was determined by calibration with aqueous potassium chloride solutions¹⁰ in the concentration range from 0.001 to 0.05 mol dm^{-3} . The conductivity cell was connected to a precision component analyser Wayne-Kerr (model 6430A). The resistance (R) of the test solutions was measured at four frequencies $f = 500, 800, 1000$ and 2000 Hz . Its dependence on reciprocal frequency was well presented by a straight line and

the intercept (R_0) obtained by the method of least squares.¹¹

The experimental procedure begins by weighing the pure solvent into a glass reaction cell. Traces of dissolved CO_2 were removed from the liquid by a short bubbling of high-purity nitrogen. The reaction cell was then hermetically closed with a teflon lid and placed into a Thermo-Haake Circulator DC10-V15/B which maintained the temperature ± 0.01 K. After achievement of thermal equilibrium, the resistance at four frequencies was determined. Then the known weight of stock solution was added into the cell using a syringe and the resistance readings repeated. Between these two operations the test solution was homogenized through a short-run spin of a teflon magnetic stirrer bar activated by an immersible stirrer Cyclone (model 1 – 100 HMC).

Molarity ($c/\text{mol dm}^{-3}$) was determined as

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

where m is molality (moles of electrolyte per kilogram of solvent), $d / \text{kg dm}^{-3}$ is the solution density, and M ($0.16538 \text{ kg mol}^{-1}$) is the molar mass of rubidium bromide. The stock solution density at 293.15 K, as well as the densities of 2-methylpropan-2-ol + water mixtures (d_0) at all working temperatures, were determined by a digital density meter Anton Paar (model DMA 4500 M). Knowing d and m of the stock and d_0 , the density coefficient $D / \text{kg}^2 \text{ dm}^{-3} \text{ mol}^{-1}$ was obtained assuming a linear change of the solution density upon its molality:

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

Its values at 293.15 K for 0.70, 0.80, and 0.90 alcohol mass fraction (w) amount to 0.108, 0.104 and 0.083, respectively, and were assumed to be independent on temperature.¹² The relative error in molarity and solvent composition was about ± 0.1 %.

3. Results and Discussion

The properties of 2-methylpropan-2-ol + water mixtures are given in Table 1. The viscosity and permittivity values of the pure solvent were taken from Ref. 1. Molar conductivity for the RbBr solutions of different concentrations is given in Table 2.

The limiting molar conductivity, Λ_0 , and association constant, K_{Λ} , were determined using a chemical model of conductivity based on the Lee-Wheaton equation¹³ in the Pethybridge and Taba version¹⁴ (LWPT)

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

$$\rho = \frac{Fe}{3\pi\eta_0}, \quad q = \frac{e^2}{8\pi\epsilon_0\epsilon_r kT} \quad (4)$$

$$\kappa^2 = 16\pi N_{\Lambda} q \alpha c \quad (5)$$

$\Lambda_{c\alpha}$ is the molar conductivity of the free ions and Λ_0 the same quantity 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 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 is the relative permittivity of the solvent; other symbols have their usual meanings. Standard equilibrium constant $K_{\Lambda,c}^{\circ}$, subscript c indicating the molarity scale, for the association reaction (7) is given by the expression:

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



where $c^{\circ} \equiv 1 \text{ mol dm}^{-3}$, $c\alpha$ and $c(1-\alpha)$ are the equilibrium

Table 1. Density, viscosity¹ and relative permittivity¹ of 2-methylpropan-2-ol + water mixtures.^a

| | 288.15 K | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
|-----------------------------|----------|----------|----------|----------|----------|
| $w = 0.70$ | | | | | |
| $d_0 / \text{kg dm}^{-3}$ | 0.86018 | 0.85594 | 0.85163 | 0.84726 | 0.84283 |
| $10^3 \eta_0 / \text{Pa s}$ | 8.050 | 6.266 | 4.931 | 3.939 | 3.214 |
| ϵ_r | 23.20 | 22.31 | 21.45 | 20.63 | 19.84 |
| $w = 0.80$ | | | | | |
| $d_0 / \text{kg dm}^{-3}$ | 0.83681 | 0.83247 | 0.82802 | 0.82349 | 0.81889 |
| $10^3 \eta_0 / \text{Pa s}$ | 7.884 | 6.117 | 4.807 | 3.839 | 3.116 |
| ϵ_r | 17.96 | 17.23 | 16.53 | 15.86 | 15.22 |
| $w = 0.90$ | | | | | |
| $d_0 / \text{kg dm}^{-3}$ | 0.81332 | 0.80876 | 0.80413 | 0.79943 | 0.79465 |
| $10^3 \eta_0 / \text{Pa s}$ | 7.374 | 5.671 | 4.416 | 3.518 | 2.835 |
| ϵ_r | 13.52 | 12.94 | 12.39 | 11.86 | 11.35 |

^a w is the mass fraction of 2-methylpropan-2-ol in the mixture.

Table 2. Molar conductivity ($\Lambda / \text{S cm}^2 \text{mol}^{-1}$) of RbBr at various concentrations ($c / \text{mol dm}^{-3}$) in aqueous 2-methylpropan-2-ol mixtures of alcohol mass fraction w at different temperatures.

| 288.15 K | | 293.15 K | | 298.15 K | | 303.15 K | | 308.15 K | |
|----------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|
| $10^4 \cdot c$ | Λ |
| $w = 0.70$ | | | | | | | | | |
| 2.5260 | 11.156 | 2.4503 | 14.097 | 2.3620 | 17.360 | 2.4415 | 20.820 | 2.5262 | 24.491 |
| 4.9375 | 10.979 | 4.8553 | 13.827 | 4.8120 | 17.013 | 4.9253 | 20.281 | 4.8965 | 23.861 |
| 7.4502 | 10.766 | 7.2916 | 13.538 | 7.3125 | 16.645 | 7.2317 | 19.841 | 7.2051 | 23.284 |
| 9.8462 | 10.566 | 9.5485 | 13.291 | 9.5931 | 16.327 | 9.5009 | 19.457 | 9.5548 | 22.783 |
| 12.111 | 10.397 | 11.760 | 13.080 | 11.845 | 16.048 | 11.815 | 19.105 | 11.806 | 22.356 |
| 14.409 | 10.245 | 14.000 | 12.882 | 14.048 | 15.804 | 14.251 | 18.787 | 14.156 | 21.967 |
| 16.651 | 10.108 | 16.152 | 12.725 | 16.254 | 15.589 | 16.534 | 18.517 | 16.332 | 21.664 |
| 18.799 | 9.987 | 18.369 | 12.567 | 18.454 | 15.392 | 18.747 | 18.275 | 18.460 | 21.388 |
| 21.030 | 9.882 | 20.545 | 12.421 | 20.650 | 15.209 | 20.924 | 18.057 | 20.596 | 21.131 |
| 23.189 | 9.781 | 22.632 | 12.292 | 22.874 | 15.043 | 23.057 | 17.861 | 22.675 | 20.897 |
| 25.300 | 9.691 | 24.710 | 12.176 | 24.980 | 14.892 | 25.200 | 17.676 | 24.801 | 20.675 |
| 27.389 | 9.601 | 26.652 | 12.074 | 27.169 | 14.740 | 27.382 | 17.503 | 26.785 | 20.486 |
| 29.454 | 9.523 | 28.649 | 11.977 | 29.119 | 14.618 | 29.489 | 17.346 | 28.846 | 20.302 |
| 31.480 | 9.447 | 30.577 | 11.877 | 31.189 | 14.498 | 31.535 | 17.205 | 30.791 | 20.137 |
| 33.243 | 9.376 | 32.497 | 11.794 | 33.079 | 14.393 | 33.309 | 17.088 | 32.714 | 19.987 |
| $w = 0.80$ | | | | | | | | | |
| 3.3494 | 8.109 | 3.4083 | 10.025 | 3.3818 | 12.086 | 3.2404 | 14.803 | 3.1940 | 17.668 |
| 4.4182 | 7.910 | 4.4927 | 9.751 | 4.4523 | 11.738 | 4.2713 | 14.375 | 4.2308 | 17.479 |
| 5.4711 | 7.728 | 5.5815 | 9.510 | 5.5325 | 11.432 | 5.3195 | 13.979 | 5.2723 | 16.993 |
| 6.5238 | 7.566 | 6.6081 | 9.288 | 6.5552 | 11.164 | 6.3074 | 13.639 | 6.2771 | 16.572 |
| 7.5477 | 7.422 | 7.6808 | 9.092 | 7.5735 | 10.928 | 7.3178 | 13.349 | 7.3629 | 16.157 |
| 8.5391 | 7.286 | 8.7028 | 8.917 | 8.5860 | 10.719 | 8.2821 | 13.085 | 8.3382 | 15.824 |
| 9.5200 | 7.167 | 9.7119 | 8.765 | 9.5889 | 10.527 | 9.2508 | 12.846 | 9.2840 | 15.536 |
| 10.541 | 7.053 | 10.688 | 8.629 | 10.582 | 10.351 | 10.195 | 12.632 | 10.237 | 15.267 |
| 11.493 | 6.952 | 11.652 | 8.501 | 11.541 | 10.196 | 11.151 | 12.430 | 11.201 | 15.017 |
| 12.437 | 6.862 | 12.602 | 8.386 | 12.484 | 10.053 | 12.062 | 12.252 | 12.110 | 14.803 |
| 13.357 | 6.768 | 13.540 | 8.277 | 13.401 | 9.923 | 12.964 | 12.090 | 13.014 | 14.599 |
| 14.288 | 6.692 | 14.479 | 8.176 | 14.381 | 9.791 | 13.842 | 11.936 | 13.899 | 14.419 |
| 15.161 | 6.623 | 15.377 | 8.082 | 15.217 | 9.686 | 14.784 | 11.784 | 14.745 | 14.254 |
| $w = 0.90$ | | | | | | | | | |
| 1.3247 | 4.671 | 1.3186 | 5.751 | 1.2630 | 7.140 | 1.2611 | 8.572 | 1.2295 | 9.894 |
| 1.7369 | 4.455 | 1.7243 | 5.476 | 1.6818 | 6.748 | 1.6587 | 8.092 | 1.6362 | 9.285 |
| 2.1616 | 4.266 | 2.1312 | 5.239 | 2.0899 | 6.425 | 2.0563 | 7.686 | 2.0371 | 8.790 |
| 2.5721 | 4.102 | 2.5343 | 5.032 | 2.5019 | 6.148 | 2.4463 | 7.349 | 2.4218 | 8.387 |
| 2.9835 | 3.964 | 2.9209 | 4.863 | 2.8784 | 5.926 | 2.8240 | 7.065 | 2.8136 | 8.041 |
| 3.3832 | 3.846 | 3.3131 | 4.704 | 3.2518 | 5.731 | 3.1984 | 6.819 | 3.1872 | 7.752 |
| 3.7709 | 3.741 | 3.6927 | 4.569 | 3.6235 | 5.559 | 3.5618 | 6.605 | 3.5629 | 7.494 |
| 4.1484 | 3.650 | 4.0740 | 4.447 | 3.9855 | 5.406 | 3.9290 | 6.411 | 3.9232 | 7.276 |
| 4.5221 | 3.563 | 4.4448 | 4.338 | 4.3414 | 5.270 | 4.2955 | 6.238 | 4.2815 | 7.075 |
| 4.9015 | 3.487 | 4.8032 | 4.240 | 4.7026 | 5.143 | 4.6476 | 6.086 | 4.6308 | 6.896 |
| 5.2914 | 3.414 | 5.1600 | 4.151 | 5.0566 | 5.030 | 4.9768 | 5.954 | 4.9703 | 6.745 |
| 5.6616 | 3.348 | 5.5046 | 4.072 | 5.4062 | 4.924 | 5.3180 | 5.829 | 5.3048 | 6.598 |
| 6.0141 | 3.287 | 5.8501 | 3.996 | 5.7504 | 4.829 | 5.6671 | 5.709 | 5.6340 | 6.470 |

concentrations of the fraction of free ions and ion pairs, respectively; α is the degree of dissociation and represents the ratio ($\alpha = \Lambda / \Lambda_{ca}$) of the stoichiometric molar conductivity (Λ) to that of free ions. The mean activity coefficient of the free ions is given by the relationship:

$$y_{\pm}^2 = \exp[-2\kappa q / (1 + \kappa R)] \quad (8)$$

The chemical model is obtained by combining ex-

pressions for $K_{A,c}^{\circ}$ and α ,

$$\Lambda = \frac{\Lambda_{ca}}{1 + K_{A,c}^{\circ} (c/c^{\circ}) \alpha y_{\pm}^2} \quad (9)$$

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

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

The model was resolved by an iterative procedure, the computer optimization according to Beronius:¹⁵ Λ_0 and $K_{A,c}^o$ were adjusted for each selected value of R until the minimal value of the variance

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

was achieved (n is the number of solutions tested in one run). The derived values of the parameters Λ_0 and $K_{A,c}^o$ change uniformly with temperature, while the distance parameter R covers a wide range of values, showing an irregular trend with temperature (no significant minima in the plot $\sigma(R)$ was obtained for any solvent composition). Therefore, the experimental data were processed by a two-parameter fit, $\Lambda = f(c; \Lambda_0, K_{A,c}^o)$, i.e. with the value of R fixed at the Bjerrum critical distance ($R = q$, as recommended by Justice¹⁶) for the reasons explained earlier.^{7,8} The values obtained for Λ_0 and $K_{A,c}^o$ by this condition are listed in Table 3. Standard deviations of Λ_0 and $K_{A,c}^o$ were estimated as suggested in the literature,¹⁷ and the numeral 3 in Eq. (11) was switched to 2. To avoid the influence of the solvent thermal expansion to the reaction enthalpy, $K_{A,c}^o$ was converted to the molality scale, $K_{A,m}^o = K_{A,c}^o d_o / \text{kg dm}^{-3}$.

Fig. 1 shows the concentration dependence of the experimental molar conductivity of RbBr at five temperatures in 2-methylpropan-2-ol ($w = 0.90$) + water; full line represents the results of the LWPT conductivity model. Analogous plots for the other two mixtures are similar.

Viscosity and permittivity should have the opposite effects on the limiting molar conductivity. Since η_0 decreases with increasing temperature much faster than ϵ_r (Table 1), Λ_0 increases (Table 3). With increasing alcohol mass

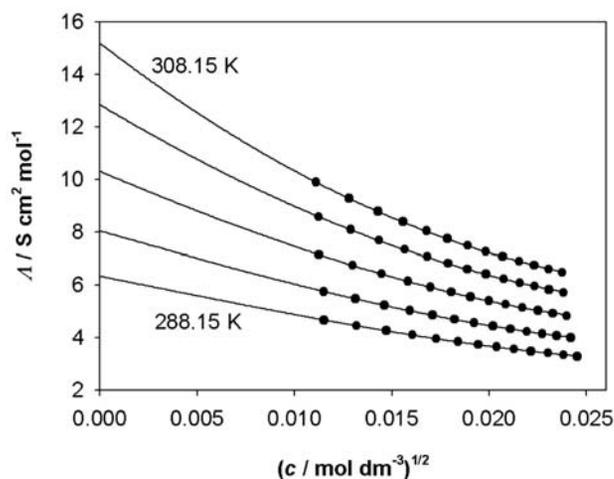


Figure 1. Molar conductivity of RbBr in aqueous 2-methylpropan-2-ol mixture with $w = 0.90$ from 288.15 K to 308.15 K; ●, experimental data; full line, calculated values.

fraction, on the other hand, the decrease of permittivity prevails over that of η_0 and Λ_0 of RbBr diminishes – molecules bound as dipoles to the ions are slowing them by their inertia. Similar behaviour was found earlier for HBr and NaBr in the same mixtures,^{1,3} as well as for all three electrolytes in the mixtures of butanol-2-ol with water.^{7,24}

Walden product $\Lambda_0 \eta_0$ of an electrolyte, as derived from the Stokes model, is proportional to the sum of reciprocal hydrodynamic radii of cation and anion, $\Lambda_0 \eta_0 \propto (1/r_+ + 1/r_-)$, and sensitive to changes in the ion-solvent interactions. Fig. 2 shows its dependence on solvent permittivity for the same three electrolytes in aqueous 2-methylpropan-2-ol and butan-2-ol at 298.15 K.

Table 3. Limiting molar conductivities (Λ_0), ion-association constants ($K_{A,c}^o$, $K_{A,m}^o$) and standard deviations (σ) of experimental Λ from the model LWPT for RbBr in 2-methylpropan-2-ol (w) + water mixtures with $R = q$.

| T/K | $\Lambda_0 / \text{S cm}^2 \text{ mol}^{-1}$ | $K_{A,c}^o$ | $K_{A,m}^o$ | $100\sigma / \text{S cm}^2 \text{ mol}^{-1}$ | q/nm |
|------------|----------------------------------------------|------------------|------------------|----------------------------------------------|---------------|
| $w = 0.70$ | | | | | |
| 288.15 | 12.01 ± 0.01 | 98.65 ± 0.44 | 84.85 ± 0.38 | 0.44 | 1.250 |
| 293.15 | 15.13 ± 0.01 | 102.4 ± 0.4 | 87.61 ± 0.32 | 0.45 | 1.277 |
| 298.15 | 18.69 ± 0.01 | 111.0 ± 0.4 | 94.51 ± 0.38 | 0.65 | 1.306 |
| 303.15 | 22.35 ± 0.01 | 115.6 ± 0.6 | 97.91 ± 0.46 | 0.94 | 1.336 |
| 308.15 | 26.34 ± 0.02 | 124.0 ± 1.0 | 104.5 ± 0.9 | 1.9 | 1.367 |
| $w = 0.80$ | | | | | |
| 288.15 | 9.47 ± 0.02 | 442.9 ± 4.2 | 370.6 ± 3.5 | 1.1 | 1.614 |
| 293.15 | 11.84 ± 0.01 | 497.6 ± 2.5 | 414.2 ± 2.1 | 0.73 | 1.654 |
| 298.15 | 14.37 ± 0.01 | 535.9 ± 1.9 | 443.7 ± 1.6 | 0.63 | 1.695 |
| 303.15 | 17.68 ± 0.01 | 584.3 ± 2.3 | 481.1 ± 1.9 | 0.89 | 1.738 |
| 308.15 | 21.72 ± 0.02 | 637.9 ± 2.3 | 522.4 ± 1.9 | 0.85 | 1.781 |
| $w = 0.90$ | | | | | |
| 288.15 | 6.33 ± 0.02 | 3572 ± 29 | 2905 ± 23 | 0.79 | 2.145 |
| 293.15 | 8.05 ± 0.03 | 4232 ± 51 | 3423 ± 42 | 1.4 | 2.203 |
| 298.15 | 10.31 ± 0.04 | 5181 ± 61 | 4166 ± 49 | 1.7 | 2.262 |
| 303.15 | 12.85 ± 0.06 | 6182 ± 68 | 4942 ± 55 | 1.9 | 2.324 |
| 308.15 | 15.19 ± 0.06 | 7060 ± 68 | 5610 ± 54 | 1.9 | 2.389 |

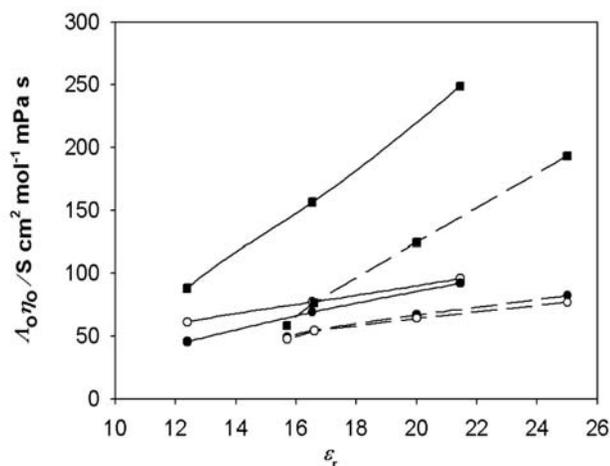


Figure 2. Variation of $\Lambda_0 \eta_0$ with ϵ_r at 298.15 K for HBr (■), NaBr (○) and RbBr (●) in mixtures of water with 2-methylpropan-2-ol (full lines) and butanol-2-ol (dashed lines).

By adding alcohol to water the network pattern of water molecules is gradually decomposing and ϵ_r decreasing. Both effects favour the formation of a region of half-oriented loosely held molecules between the ionic primary shell of strongly bound molecules and the bulk solution. Such a secondary shell is more sensitive, in terms of its width and content, to changes in w , and so is mainly responsible for the positive slope of the Walden curves for NaBr and RbBr (Fig. 2). They suggest the relation of hydrodynamic radii $r(\text{Rb}^+) > r(\text{Na}^+)$ in the mixtures with 2-methylpropan-2-ol and the reversed one in those with butanol-2-ol; divergences are generally small, except in the former mixtures at w approaching 0.90. Difference in the Walden products for a salt in two isodielectric solvent mixtures (vertical cut in Fig. 2) most likely reflects the structural difference of the two isomers – the stretched hydrocarbon tail of the latter is longer than the spherical diameter of the former, so ensuring a greater r to ions.

The product $\Lambda_0 \eta_0$ for hydrobromic acid is high when the proton (H^+) conductivity is governed by the hydrogen bond transfer among neighbouring water molecules („proton jumps“). With the amount of water decreasing in respect to butanol (their mole ratio is lowered four times within the investigated composition range) the migration of entities H_3O^+ is replacing the jumps and Walden product for HBr is approaching the salt values (Fig. 2).

The magnitude of the Walden product decrease with increasing temperature is suitably expressed by a relative quantity, $\Delta_{\text{rel}} W = (W_{15} - W_{35}) / W_{25}$. Its values for NaBr³ and RbBr (Table 4) in aqueous 2-methylpropan-2-ol are similar and falling with the alcohol enrichment, barring the deviating NaBr values near $w = 0.90$. The solvent influence is obvious: the input heat breaks the solvent structure, ion attracts liberated molecules into secondary shell, so increasing its hydrodynamic radius. $\Delta_{\text{rel}} W$ is most pro-

minent in systems with the best organized bulk-structure and consequently the thinnest secondary shell ($w = 0.70$), because the degree of disorder produced by heating, as well as the consequent relative enlargement of the shell, are then the greatest. Since $\Delta_{\text{rel}} W$ for the same salts in aqueous butanol-2-ol^{4,7} is 2 to 3 times lower (at $w = 0.90$ there is no temperature dependence at all), that mixtures must have a less developed structure in relation to those with 2-methylpropan-2-ol.

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

| w | $10^3 \Lambda_0 \eta_0 / S \text{ cm}^2 \text{ mol}^{-1} \text{ Pa s}$ | | | | |
|------|------------------------------------------------------------------------|----------|----------|----------|----------|
| | 288.15 K | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| 0.70 | 96.68 | 94.80 | 92.16 | 88.04 | 84.66 |
| 0.80 | 74.66 | 72.43 | 69.08 | 67.87 | 67.68 |
| 0.90 | 46.68 | 45.65 | 45.53 | 45.21 | 43.06 |

The association constant increases with increasing temperature and alcohol content (Table 3 for RbBr) as a consequence of the permittivity decrease. The dependence of $\log K_{A,m}^0$ on ϵ_r^{-1} for HBr, NaBr and RbBr in aqueous media with 2-methylpropan-2-ol^{1,3} and butanol-2-ol^{2,4,7} at 298.15 K is linear (Fig. 3). The lines for the salts almost overlap, while that for HBr is translated considerably downward: H^+ is less inclined to association than alkali metal cations because it is by far more strongly solvated (the Gibbs energy of formation of the cluster H_3O^+ in the gas phase is about ten times more negative than that of $\text{K}(\text{H}_2\text{O})^+$).¹⁸

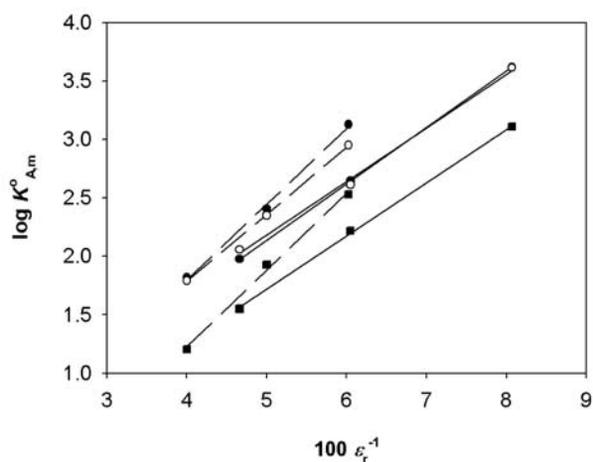


Figure 3. Variation of $\log K_{A,m}^0$ with ϵ_r^{-1} at 298.15 K for HBr (■), NaBr (○) and RbBr (●) in mixtures of water with 2-methylpropan-2-ol (full lines) and butanol-2-ol (dashed lines).

The difference between two types of butanolic mixtures at the same ϵ_r (Fig. 3) stems from differences in the chemical nature of two isomers.

Using data for $K_{A,m}^{\circ}$ and Λ_0 at different temperatures (Table 3) the standard enthalpy of the association reaction (ΔH°) and the activation enthalpy of the charge transport (ΔH^*) were evaluated by a least-squares treatment assuming

$$\ln K_{A,m}^{\circ} = -\Delta H^{\circ} / RT + C \quad (12)$$

$$\ln \Lambda_0 + 2/3 \ln d_0 = -\Delta H^* / RT + C' \quad (13)$$

The standard deviation of each enthalpy was derived from the corresponding slope.¹¹

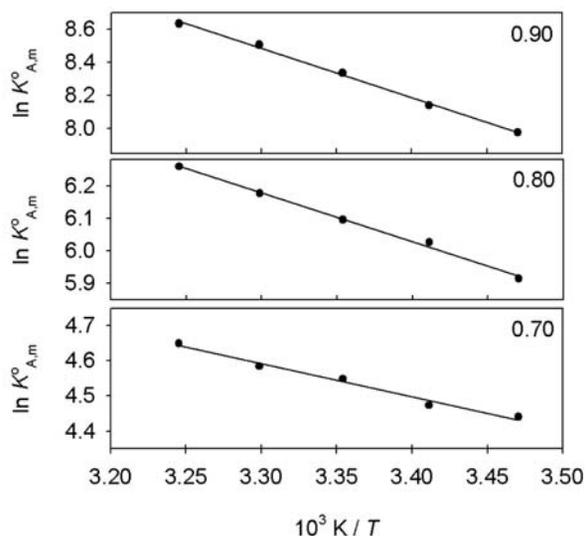


Figure 4. Dependence of $\ln K_{A,m}^{\circ}$ on T^{-1} for RbBr in 2-methylpropan-2-ol + water mixtures of different alcohol mass fraction w .

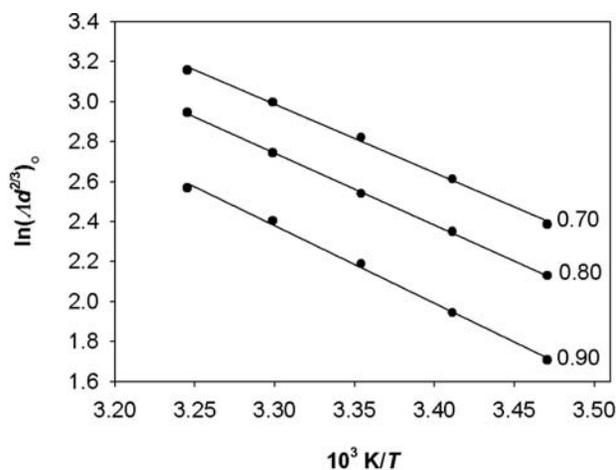


Figure 5. Dependence of $\ln(\Lambda d^{2/3})_0$ on T^{-1} for RbBr in 2-methylpropan-2-ol + water mixtures of different alcohol mass fraction w .

Fig. 4 shows that good straight lines can be drawn through experimental points. The points in Fig. 5, on the other hand, exhibit a noticeable curvature and accordingly an increased standard deviation (s_p); similar features, but of lesser intensity, were found for NaBr and HBr in the same mixtures.^{3,1} They result from the ΔH^* decrease with increasing temperature which manifests in solvents of stronger structure.^{19a}

The Gibbs energy and entropy changes (ΔG° and ΔS°), as well as their standard deviations, were calculated as described before.^{7,8}

Results are gathered in Table 5 for RbBr and presented in Fig. 6 for all three electrolytes for the sake of comparison.

The complex quantity ΔH^* encompasses the energy needed for the ion jump into a prepared „hole“, as well as the work in building up the hole itself. As the solvent molar volume or the ionic size is increased, the first contribution decreases, while the second increases.^{19b} The curves describing the ΔH^* dependence on w for two alkali metal bromides are therefore very close and have a small slope (Fig. 6.); corresponding values in 2-butanolic mixtures are lower for about 4 kJ mol⁻¹ (HBr²) to 5 kJ mol⁻¹ (NaBr,⁴ RbBr⁷).

The standard Gibbs energy change for the association of ions Rb⁺ and Br⁻ points out the spontaneity of the process; its values are becoming more negative with the increasing 2-methylpropan-2-ol content (Table 5). The sa-

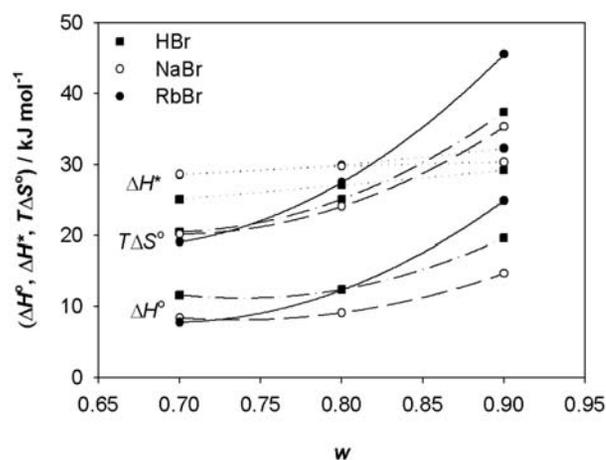


Figure 6. Variation of thermodynamic quantities of the ionic movement activation (ΔH^*) and the ion-pair formation (ΔH° , ΔS°) with 2-methylpropan-2-ol mass fraction for HBr,¹ NaBr³ and RbBr (Table 5) at $T = 298.15$ K.

Table 5. Activation enthalpy of ionic movement and thermodynamic quantities of the ion-association reaction for RbBr in 2-methylpropan-2-ol + water mixtures at 298.15 K.

| w | $\Delta H^*/\text{kJ mol}^{-1}$ | $\Delta H^{\circ}/\text{kJ mol}^{-1}$ | $\Delta G^{\circ}/\text{kJ mol}^{-1}$ | $\Delta S^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$ |
|------|---------------------------------|---------------------------------------|---------------------------------------|----------------------------------------------------|
| 0.70 | 28.5 ± 0.9 | 7.8 ± 0.6 | -11.28 ± 0.01 | 63.9 ± 1.9 |
| 0.80 | 29.9 ± 0.4 | 12.4 ± 0.5 | -15.11 ± 0.01 | 92.1 ± 1.6 |
| 0.90 | 32.2 ± 1.0 | 24.9 ± 0.8 | -20.66 ± 0.03 | 152.7 ± 2.7 |

me general form of the ΔG° dependence on w could be derived for the other two electrolytes using data from Fig. 3; curves for RbBr and NaBr would be almost overlapping, while that for HBr shifted fairly upwards.

Since the ion association is also endothermic (Table 5), the term $T\Delta S^\circ$ must exceed ΔH° (Fig. 6) in order to make the process spontaneous. That indicates considerable structural changes in the system, among which the crumbling of solvation shells around pairing ions is the most emphasized. The ascending entropy curves (Fig. 6) reflect therefore an enhanced solvation of the free ions. However, it is quite peculiar that huge Rb^+ ion (2.4 times greater than Na^+ by surface) would be better solvated with discrete molecules, as suggested by its steeper curve. There must be some special kind of the Rb^+ – 2-methylpropan-2-ol interactions, possibly a size-selective cation attachment to bends of the alcohol winding chains. That could also explain a deflection of rubidium curve from the sodium one for the Walden product (Fig. 2), as well as for ΔH^* and ΔH° (Fig. 6), when w is approaching its upper limit. There needs to say that no such deflection exists in butanol-2-ol + water mixtures.⁸

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Povzetek

Izmerili smo molske prevodnosti razredčenih raztopin RbBr v mešanica h t-butanola in vode z molskimi deleži alkohola 0.70, 0.80 in 0.90 v temperaturnem območju med 288.15 in 308.15 K. Z uporabo Lee-Wheatonove enačbe smo iz eksperimentalnih podatkov določili limitne vrednosti molskih prevodnosti (Λ_0) ter konstante asociacije ionov (K_A) RbBr v proučevanih topilih. Iz vrednosti K_A ter njene temperaturne odvisnosti smo dobili vse termodinamske parametre procesa ionske asociacije: Gibbsovo energijo (ΔG°), entalpijo (ΔH°) in entropijo (ΔS°). Iz temperaturne odvisnosti Λ_0 pa smo določili aktivacijsko energijo za gibanje ionov (ΔH^\ddagger). Vse tako dobljene parametre smo primerjali z literaturnimi vrednostmi za HBr in NaBr v istih topilih.