Ion-Association Reaction of H$^+$ and Br$^-$ in (90 and 95 Mass per Cent) 1-Butanol-Water, and (90 and 95 Mass per Cent) 2-Methyl-2-Propanol-Water Mixtures*

*I. Tominić and I. Mekjavić***

Laboratory of Physical Chemistry, Faculty of Technology, University of Split,
58000 Split, Teslina 10, Croatia, Yugoslavia

The molar conductivities of HBr in the 90 and 95 mass per cent 2-methyl-2-propanol-water and 1-butanol-water mixtures, respectively, were measured in the temperature range from 288.15 to 308. 15 K at 5 K intervals. By means of the conductance equations after Fuoss-Hsia and Lee-Wheaton the limiting molar conductivity (Λ_0), association constant (K_A) and the radius of the ion pair (R) were obtained from these data. The data for R differ considerably, so that K_A and Λ_0 were also calculated with the same equations under the condition that $R = q$ (q is the Bjerrum critical distance). The influence of the dielectric constant on K_A and Λ_0 was established and discussed and comparison was made with analogous literature data for 2-butanol-water and tert. butanol-water mixtures. From the data for K_A at different temperatures (under the condition $R = q$) the standard thermodynamic quantities for association reaction of H$^+$ and Br$^-$ were determined.

INTRODUCTION

This work is a final report of our studies on the ion-association reaction of H$^+$ and Br$^-$ in the butanol isomer-water mixtures with a higher content of alcohol. The mixtures containing 70, 80, 90 and 95 mass per cent of alcohol were tested with tert. butanol[1] and 2-butanol.[2] However, the tests with 1-butanol and 2-methyl-1-propanol were possible only in 90 and 95 mass per cent mixtures because they are one-phase systems.

The association reaction was studied by means of the conductivity measurements of the HBr solutions using the Fuoss-Hsia and the Lee-Wheaton equations for data

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** To whom correspondence should be addressed.

processing. The association constants obtained at different temperatures made it possible to determine the thermodynamic quantities for the association reaction.

In our previous work[3] on standard potentials of Ag/AgBr electrode in the 90 and 95 mass per cent 2-methyl-1-propanol mixtures, in the 288.15 – 298.15 – 308.15 K temperature range, the HBr conductivity data were given and the association constants were determined by the Shedlovsky equation. In this work, however, the conductivity measurements were carried out again in the same temperature range, but at 5 K intervals.

EXPERIMENTAL

The solutions of HBr were prepared as before.[2]

The measuring methods of conductivity, density and viscosity[1], as well as the dielectric constant[2], had already been described.

Two parallel conductivity measurements for each molarity differed mainly by about ±0.04 S cm^2 mol^{-1} from the mean value.

RESULTS AND DISCUSSION

The molar conductivities of different molalities of HBr solutions are listed in Table I, and the data for density, viscosity and dielectric constant of the solvents are given in Table II. The concentrations of HBr (c/mol dm^{-3}), which go along with Table I, can be easily obtained from molality and solvent density according to the $c = m.d$ relation.

The tabled values make it possible to calculate the thermodynamic constant of the equilibrium (K_A) for the H$^+$ and Br$^-$ ion-association reaction, the maximal distance between the ions in the ion pair (distance parameter R) and the limiting molar conductivity of HBr (Λ_o).

The thermodynamic constant for the association reaction

$$\begin{array}{ccc} \text{H}^+ + \text{Br}^- & \rightleftharpoons & \text{H}^+\cdot\text{Br}^- \\ c\alpha \quad\quad c\alpha & & c(1-\alpha) \end{array} \tag{1}$$

was given by the expression

$$K_A = \frac{1-\alpha}{(c/c^0)\alpha^2 y_\pm^2} \tag{2}$$

In this expression α is the dissociation degree ($\alpha = \Lambda/\Lambda_{c\alpha}$) relating the measured molar conductivity (Λ)) and the molar conductivity of the free ions ($\Lambda_{c\alpha}$). For $\Lambda_{c\alpha}$, two theoretical equations were used: the Fuoss-Hsia[4] in the Fernández-Prini[5] (FHFP) version

$$\Lambda_{c\alpha} = \Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \, ln(c\alpha) + J_1 c\alpha - J_2(c\alpha)^{3/2} \tag{3}$$

and the Lee-Wheaton[6] in the Pethybridge[7] (LWP) version

$$\Lambda_{c\alpha} = \Lambda_0(1 + C_1 e + C_2 e^2 + C_3 e^3) - \frac{B_2(c\alpha)^{1/2}}{1+t}(1 + C_4 e + C_5 e^2 + t/12) \tag{4}$$

TABLE I

Molar conductivity (Λ)/S cm² mol⁻¹) of HBr at various molalities (m/mol kg⁻¹) in x mass per cent alcohol at different temperatures

10⁴m	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
		x = 90% 2-methyl-1-propanol			
6.0756	16.36	19.26	22.60	26.15	29.99
7.2909	16.18	19.11	22.31	25.84	29.73
9.7229	16.00	18.81	21.95	25.44	29.21
12.154	15.46	18.22	21.23	24.51	28.09
18.231	15.05	17.65	20.57	23.70	27.09
24.307	14.60	17.12	19.91	22.90	26.12
30.384	14.20	16.62	19.28	22.17	25.27
		x = 95% 2-methyl-1-propanol			
6.1431	12.02	14.15	16.49	19.05	21.88
7.3717	11.77	13.85	16.16	18.63	21.35
9.8290	11.58	13.61	15.80	18.24	20.86
12.286	11.30	13.25	15.38	17.73	20.25
18.428	10.78	12.60	14.60	16.76	19.07
24.572	10.40	12.11	13.98	16.03	18.18
30.716	10.05	11.73	13.49	15.44	17.47
		x = 90% 1-butanol			
6.0299	19.79	22.99	26.52	30.34	34.49
7.2359	19.56	22.71	26.19	29.94	34.09
9.6478	19.35	22.44	25.84	29.53	33.55
12.060	19.02	22.07	25.37	28.94	32.86
18.089	18.25	21.14	24.29	27.66	31.34
24.119	17.70	20.48	23.53	26.76	30.29
30.149	17.27	19.93	22.87	25.98	29.36
		x = 95% 1-butanol			
6.0991	14.84	17.15	19.67	22.37	25.31
7.3189	14.66	16.87	19.38	22.04	24.88
9.7585	14.41	16.63	19.01	21.59	24.39
12.198	14.13	16.28	18.60	21.09	23.80
18.297	13.50	15.51	17.70	20.04	22.56
24.396	13.04	14.95	17.00	19.23	21.61
30.495	12.64	14.48	16.48	18.60	20.83

Again, $y_{\pm}$ is the mean activity coefficient which can be estimated by means of the Debye-Hückel equation

$$y_{\pm}^2 = \exp[-e/(1 + t)] \qquad (5)$$

where $e = 2\kappa q$, $t = \kappa R$, κ is the Debye parameter, and q is the Bjerrum critical distance. The other symbols in the cited equations have their usual significance.

The calculation of the mentioned parameters (Λ_o, K_A, R) by means of the above expressions was carried out by computer optimization according to Beronius[8] using both equations for conductivity (FHFPB and LWPB) and after Justice[9] using the

TABLE II

Density (d), viscosity (η)) and dielectric constant (D) of x mass per cent alcohol at different temperatures

T/K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			x = 90% 2-methyl-1-propanol		
$d/\mathrm{g\ cm^{-3}}$	0.8271	0.8228	0.8185	0.8139	0.8093
$10^3\eta/\mathrm{Pas}$	4.421	3.698	3.119	2.650	2.272
D	20.0	19.3	18.7	18.1	17.6
			x = 95% 2-methyl-1-propanol		
$d/\mathrm{g\ cm^{-3}}$	0.8169	0.8128	0.8087	0.8043	0.7999
$10^3\eta/\mathrm{Pas}$	4.388	3.697	3.130	2.674	2.287
D	19.3	18.7	18.1	17.5	16.8
			x = 90% 1-butanol		
$d/\mathrm{g\ cm^{-3}}$	0.8334	0.8292	0.8249	0.8207	0.8165
$10^3\eta/\mathrm{Pas}$	3.553	3.052	2.635	2.291	2.002
D	20.4	19.8	19.2	18.6	18.1
			x = 95% 1-butanol		
$d/\mathrm{g\ cm^{-3}}$	0.8239	0.8198	0.8157	0.8115	0.8072
$10^3\eta/\mathrm{Pas}$	3.403	2.941	2.550	2.234	1.959
D	19.6	19.0	18.4	17.8	17.2

FHFP equation (FHFPJ). Optimization terminates when the minimum of the standard deviation (sd) between the calculated and experimental values for conductivity is obtained.

The survey of the obtained values could be suitably carried out on the basis of the graphic representation of the standard deviation (sd) depending on R. These dependencies are the curves: at FHFPB with two well pronounced minima, at LWPB with one not so well pronounced minimum, while at FHFPJ there are also two but very poorly pronounced minima (except for the 90 mass per cent 2-methyl-1-propanol, which has only one). Accordingly, the values of R at the minimal sd are different: for the first minimum (FHFPB and FHFPJ) they are generally low and mainly not realistic, for the second minimum at FHFPB and the single minimum at LWPB they are different but with comparable values, while those of the second minimum at FHFPJ are high and not comparable with the former values. For all the minima of different curves the values for Λ_o agree well mutually. Finally, the values for K_A of the FHFPB second minimum and of the LWPB single minimum are of different, though comparable, extents; the K_A values of the first FHFPB minimum are low (for 1-butanol mixtures even negative) while those at the FHFPJ are mainly negative for both minima.

As with the present processing of experimental data no reliable value was obtained for the distance parameter R, and the values for K_A were mutually different, further processing was carried out under the condition that the distance parameter was equal to the Bjerrum critical distance ($R = q$), a procedure very often applied.[10-12] The so obtained data for K_A and Λ_o at different temperatures by means of both equations after Beronius (FHFPB and LWPB) are given in Table III.

TABLE III

Λ_0 K_A and sd values obtained for HBr in x mass per cent alcohol using the Fuoss-Hsia and Lee-Wheaton equations for $R = q$ at different temperatures

T/K	Λ_0/S cm^2 mol^{-1}		K_A		sd/S cm^2 mol^{-1}		$R = q/\text{Å}$
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB	
			x = 90% 2-methyl-1-propanol				
288.15	18.26	18.20	146.8	127.6	0.08	0.08	14.50
293.15	21.67	21.58	164.4	143.4	0.08	0.08	14.77
298.15	25.50	25.39	183.4	160.8	0.10	0.10	14.98
303.15	29.71	29.58	203.3	178.7	0.13	0.13	15.23
308.15	34.35	34.20	224.9	198.7	0.17	0.16	15.40
			x = 95% 2-methyl-1-propanol				
288.15	13.74	13.69	203.9	185.8	0.04	0.03	15.02
293.15	16.30	16.24	231.9	211.9	0.04	0.04	15.24
298.15	19.18	19.11	265.4	243.2	0.03	0.03	15.48
303.15	22.33	22.25	295.4	271.1	0.06	0.06	15.75
308.15	25.94	25.83	342.5	314.6	0.07	0.07	16.14
			x = 90% 1-butanol				
288.15	22.08	22.00	136.5	119.4	0.08	0.07	14.21
293.15	25.75	25.66	149.4	131.1	0.09	0.09	14.39
298.15	29.80	29.70	161.6	142.0	0.09	0.09	14.59
303.15	34.26	34.13	178.1	156.8	0.11	0.10	14.82
308.15	39.16	39.00	194.2	171.5	0.12	0.12	14.98
			x = 95% 1-butanol				
288.15	16.88	16.84	168.2	153.3	0.04	0.04	14.79
293.15	19.60	19.55	187.4	171.1	0.06	0.06	15.00
298.15	22.62	22.55	209.7	191.8	0.05	0.05	15.23
303.15	25.88	25.80	231.5	211.7	0.06	0.06	15.48
308.15	29.48	29.38	257.0	235.2	0.08	0.08	15.76

The Table shows that the values obtained for Λ_0 agree mutually well, while the K_A constants differ insignificantly (those after LWPB are slightly lower). This was also stated in the tert. butanol-water[1] and 2-butanol-water[2] mixtures.

Considering these data and those for mixtures of tert. butanol and 2-butanol, it can be generally concluded:

– The limiting molar conductivity Λ_0 can be reliably determined in all the tested mixtures with both equations (FHFPB and LWPB) applied, regardless of the processing method (FHFPB or FHFPJ) and under both calculation conditions (minimal sd and $R = q$). At 90 and 95 mass per cent 2-methyl-1-propanol, the Λ_0 agrees well also with the values obtained by the equation after Shedlovsky.[3]

– The association constants K_A can be reliably determined by both equations (FHFPB and LWPB) under the condition $R = q$. It should be mentioned, however, that the values can be very often compared also with the values of the second minimum at FHFPB as well as of the single minimum at the LWPB obtained under the condition of the minimal sd.

– No reliable value can be obtained for the distance parameter R by the applied equations.

In order to get an insight into the influence of the dielectric constant on the limiting molar conductivity, Figure 1 shows the data at 298.15 K (plot Λ_o versus D) of all the tested mixtures for comparison.

As seen from the figure, Λ_o increases in all the tested mixtures by increasing the dielectric constant. This increase is linear for the tert. butanol, slightly curved for the 2-butanol, while for the 2-methyl-1-propanol and 1-butanol there is a common straight line. Accordingly, in these latter mixtures, although for only a narrow area of dielectric constants, the specific character of each individual alcohol is not expressed. In other mixtures, however, this influence does exist, so that in relation to the latter mixtures at the same dielectric constant Λ_o increases in the direction to 2-butanol and tert. butanol, respectively.

It should be mentioned that De Lisi and Goffredi[13] found from the dependence of $\Lambda_o\eta$ for hydrogen chloride upon dielectric constant of some alcohols that this Walden product decreases from methanol to ethanol, and then increases progressively from ethanol to 1-butanol through 1-propanol, while the values for 2-methyl-1-propanol and 2-propanol show some differences. Our data, when shown graphically in the same way, give plots which resemble those in Figure 1. The straight line for tert. butanol-water
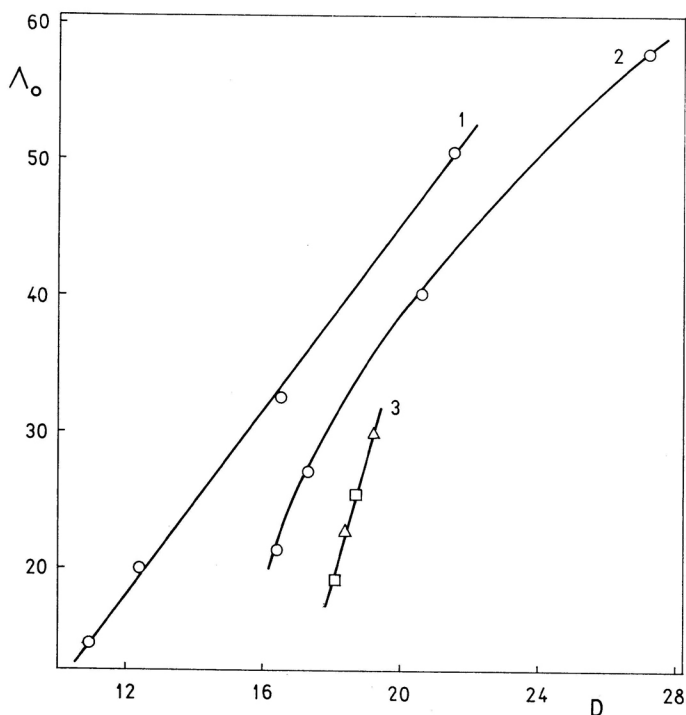

Figure 1. Variation of Λ_o with D at 298.15 K. Solvents: 1) tert. butanol-water (ref. 1); 2) 2-butanol- water (ref. 2); 3) 2-methyl-1-propanol (□) and 1-butanol- water (Δ) mixtures (Tables II and III).

mixtures and a slightly curved line for 2-butanol mixtures still remain while the common straight line for 2-methyl-1-propanol and 1-butanol mixtures is now separated into two very close and almost parallel straight lines (different η – Table II). In this last case, a straight line through two points must be a good approximation because the area of dielectric constant is very narrow (18.1 – 18.7 for 2-methyl-1-propanol and 18.4 – – 19.2 for 1-butanol) and water mass percentage is of such extent that ion-transfer mechanism remains unchanged (beyond ca 2 mass % of water in the mixture all the protons exist as hydronium ions[13]). Accordingly, it can be asserted that the product $\Lambda_o\eta$ is slightly influenced by these last two alcohols.

In order to get an insight into the influence of the dielectric constant of the solvent on the association constant, Figure 2 shows the data obtained after the FHFPB at 298.15 K (plot log K_A versus D^{-1}) of all tested mixtures for comparison.

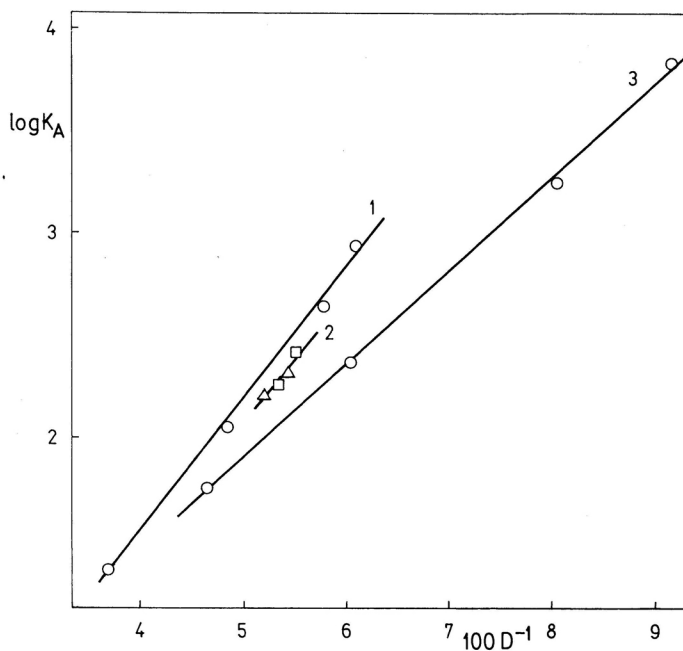Figure 2. Variation of log K_A (obtained after FHFPB) with D^{-1} at 298.15 K. Solvents: 1) 2-butanol-water (ref. 2); 2) 2-methyl-1-propanol ($\square$) and 1-butanol-water ($\triangle$) (Tables II and III); 3) tert. butanol-water mixtures (ref. 1).

As seen from the Figure, the data for the mixtures of 2-methyl-1-propanol and 1-butanol can be approximated by the common straight line, while the other mixtures have individual straight lines. The position of the straight lines in the figure shows that, at the same dielectric constant, the constants K_A in the 2-butanol mixtures are

the highest, while in the tert. butanol they are the lowest. So, for instance, it follows from the plot that in the mixture with $D = 18.5$ $K_A = 260$ when alcohol is 2-butanol (ca 86 mass per cent), $K_A = 210$ for 2-methyl-1-propanol (ca 92 mass per cent) or 1-butanol (ca 95 mass per cent) and $K_A = 130$ when alcohol is tert. butanol (ca 76 mass per cent).

From Figure 2 the common straight line for 2-methyl-1-propanol and 1-butanol mixtures can be represented by the relation

$$\log K_A = -1.349 + 67.9/D \tag{6}$$

It is possible to compare this expression with the theoretical equation after Fuoss[14]

$$K_A = (4\pi N R^3/3000) \, exp(e^2/RDkT) \tag{7}$$

where e is the electron charge, k is the Boltzmann constant, and the other symbols have their usual significance. Namely, this equation in the plot $\log K_A$ versus D^{-1} represents also the straight line with the intercept. By comparison, the slope of the straight line from equation (6) and the slope of the straight line from the Fuoss equation $(e^2/2.303 \, RkT)$ one obtains $R = 3.6$ Å, while R-values obtained in the same way for the mixtures of 2-butanol and tert. butanol were 3.9 Å and 5.3 Å, respectively. It is obvious that the values 3.6 and 3.9 Å are too low and unrealistic, because the minimal value should be $R = 4.75$ Å; for the effective radius for H_3O^+ and Br^- they are 2.8 Å[15] and 1.95 Å[16], respectively. Therefore, it could certainly be asserted that there are no ideal systems here (ions as rigid charged spheres in a continuum) for which, by applying the Fuoss equation, a reliable datum for R can be obtained from the slope.[17] Otherwise, in case of such behaviour, and with $R = 4.75$ Å in the above mentioned example ($D = 18.5$), $K_A = 157$ results from Fuoss equation (7) for all the tested mixtures.

Finally, from the values obtained for K_A at various temperatures (Table III), the thermodynamic quantities for the ion association reaction (1) can be calculated. Namely, ΔH° is obtained from the slope of the straight line $\ln K_A$ versus T^{-1}, and ΔG° and ΔS° by means of the usual relations. The data at 298.15 K are in Table IV.

By comparing the obtained values, it can be concluded that the standard thermodynamic quantities obtained by both equations, which are otherwise based on a dif-

TABLE IV

Standard thermodynamic quantities for the ion-association reactions (1) calculated from association constants obtained by the Fuoss-Hsia and Lee-Wheaton equations for $R = q$ in x mass per cent alcohol at 298.15 K

Alcohol	ΔH°/kJ mol^{-1}		ΔG°/kJ mol^{-1}		ΔS°/J K^{-1}mol^{-1}	
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB
90% 2-methyl-1-propanol	15.74	16.33	−12.92	−12.59	96.1	97.0
95% 2-methyl-1-propanol	18.88	19.18	−13.84	−13.62	109.7	110.0
90% 1-butanol	13.00	13.33	−12.61	−12.29	85.9	85.9
95% 1-butanol	15.64	15.79	−13.25	−13.03	96.9	96.7

ferent model of ions in the solution, agree mutually well, the fact which was also established in the mixtures with tert. butanol[1] and 2-butanol.[2] Therefore, in order to get an insight into the thermodynamics of the association reaction, both equations (under the condition $R = q$) can serve equally well. The data show that the association reaction is endothermic and results in increased entropy the higher is the alcohol content in the mixture. The trend of the increase, however, is better pronounced for $\Delta H°$.

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SAŽETAK

Reakcija asocijacije iona H$^+$ i Br$^-$ u 90- i 95%-noj smjesi 1-butanol-voda i 2-metil-1-propanol-voda

I. Tominić i I. Mekjavić

Izmjerene su molarne provodnosti HBr u 90- i 95%-noj smjesi 1-butanol-voda odnosno 2-metil-1-propanol-voda u temperaturnom području 288.15 do 308.15 K u intervalu po 5 K. Upotrebom jednadžbi za provodnost prema Fuoss-Hsia i Lee-Wheaton dobiveni su iz tih podataka granična molarna provodnost (Λ_0), konstanta asocijacije (K_A) i radius ionskog para (R). Podaci za R znatno se međusobno razlikuju, pa su K_A i Λ_0 također izračunani istim jednadžbama, ali uz uvjet $R = q$ (q je Bjerrumov kritični razmak). Ustanovljen je i raspravljen utjecaj dielektričke konstante otapala na K_A i Λ_0 i izvršena usporedba s analognim literaturnim podacima za smjese 2-butanol-voda i *tert*-butanol-voda. Iz podataka za K_A pri raznim temperaturama (uz uvjet $R = q$) određene su standardne termodinamičke veličine za reakciju asocijacije iona H$^+$ i Br$^-$.