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Ion-Association Reaction of H^+ and Br^- in (70, 80, 90 and 95 Mass per Cent) *tert*-Butanol-Water Mixture*

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The molar conductivity of the solutions of HBr in 70, 80, 90, and 95 mass per cent *tert*-butanol was measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The measured values were processed by the conductance equations after Fuoss-Hsia and Lee-Wheaton using different calculating methods. The obtained values for limiting molar conductivity (Λ_0), distance parameter (R) and association constant (K_A) were compared and discussed. The association constants obtained at different temperatures under the condition $R = q$ (q is Bjerrum critical distance) were used to calculate the standard thermodynamic quantities for the association reaction of H^+ and Br^- ions. The obtained values for K_A were also compared with the theoretically predicted values.

INTRODUCTION

In our previous work[1] we determined the constants and other thermodynamic quantities for the association reaction of H^+ and Br^- ions in 90 and 95 mass per cent 2-methyl-1-propanol (*iso*-butanol). Association constants were obtained by the Shedlovsky[2] conductance equation and used in determination of standard potentials of silver-silver bromide electrode in these solvents.

In this work we studied the association of the electrolyte HBr in *tert*-butanol-water mixtures with 70, 80, 90, and 95 mass per cent alcohol and used other theoretical conductance equations for data processing. Namely, there are a number of different equations in the literature and the purpose of our work was to test the possibility of their application to this electrolyte. In this sense two equations were chosen: the Fuoss-Hsia[3] equation, which is based on the model of ions as the hard spheres, and the Lee-Wheaton[4] equation which is derived from the »new model« of ions in a solution, using the concept of Gurney cosphere round every single ion.

As HBr conductivity measurements in these solvents were carried out in the temperature range from 288.15 to 308.15 K, it was possible, using

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the equations mentioned above, to determine association constants at different temperatures, *i. e.* their temperature dependence. These data served to calculate thermodynamic quantities for the association reaction of H^+ and Br^- ions.

EXPERIMENTAL

Solutions of the desired molality were prepared by weighing the water stock solution of HBr, 98.5 mass per cent tert. butanol and redistilled water. The stock solution was prepared from redistilled water and 48 mass per cent HBr (p. a. purity »Kemika«) distilled before use. The stock solution molality was determined gravimetrically by precipitation with the $AgNO_3$ solution. Tert. butanol (p. a. purity »Merck«) had also been distilled before use. As it is solid at room temperature, its mixture with 1.5 mass per cent of redistilled water was prepared by weighing.

Resistance measurements were carried out by means of the equipment described before[1] at 0.7, 1, 2, and 4 kHz frequencies at 5 temperatures series, 298.15—293.15—288.15—303.15—308.15 K. At the end of most series the temperature was reinstated to 298.15 K and excellent reproducibility of the measured resistance was established. Each concentration was measured simultaneously in two cells with electrodes of bright platinum. The cell constants (0.1590 and 0.4212 cm^{-1}, respectively) were determined by calibration by means of the KCl water solutions[5].

The resistance dependence on the reciprocal value of frequency could be well presented with a straight line. The resistance at infinite frequency, obtained by the method of least squares, was used to calculate the molar conductivity of the solution. No correction for solvent conductivity was made for it was assumed that in the acid medium it was suppressed[6].

Densities of the solvent mixtures, needed to transfer the molality into molarity, were determined by a pycnometer at 288.15, 298.15 and 308.15 K temperatures, and the values at 293.15 and 303.15 K were obtained by graphic interpolation. Viscosity coefficients were determined by an Ostwald viscometer at 5 working temperatures. Dielectric constants were derived from Åkerlöf's relations[7], while those for 95 mass per cent *tert*-butanol were obtained by graphic interpolation.

RESULTS AND DISCUSSION

The mean values for the molar conductivity of HBr from two parallel cells are listed in Table I. The accuracy of these values for 70, 80, 90 and 95 mass per cent *tert*-butanol is 0.14, 0.06, 0.03 and 0.06 S cm^2 mol^{-1}, respectively. The values for the density, viscosity coefficient and dielectric constant of the solvents are given in Table II.

Conductivity data processing was carried out by means of the Fuoss-Hsia equation in Fernández-Prini version[8] (FHFP) in the form

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

where $\Lambda_{c\alpha}$ is the molar conductivity of free ions, while the other symbols have their usual significance. The molar conductivity (Λ) obtained for each concentration (c) is connected with $\Lambda_{c\alpha}$ according to the equation

$$\alpha = \frac{\Lambda}{\Lambda_{c\alpha}} \qquad (2)$$

The thermodynamic constant for the association reaction

$$H^+ + Br^- \rightleftharpoons H^+ \cdot Br^- \qquad (3)$$

is given by the expression

$$K_A = \frac{1 - \alpha}{(c/c^0)\, \alpha^2\, y^2 \pm} \qquad (4)$$

TABLE I

Molar conductivities (Λ/S cm^2 mol^{-1}) of HBr at various concentrations (c/mol dm^{-3}) in x mass per cent tert-*butanol at different temperatures*

288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ	10^4 c	Λ
				$x = 70$					
4.0323	32.83	4.0140	39.72	3.9952	47.74	3.9755	55.96	3.9558	65.07
5.0379	32.74	5.0150	39.59	4.9916	47.44	4.9670	55.71	4.9424	64.77
8.0626	32.35	8.0260	39.13	7.9885	46.71	7.9491	55.00	7.9097	63.87
12.094	32.00	12.039	38.69	11.983	46.18	11.924	54.27	11.865	63.02
14.111	31.76	14.047	38.36	13.981	45.82	13.912	53.83	13.843	62.46
16.114	31.63	16.041	38.27	15.966	45.69	15.887	53.49	15.808	62.09
18.137	31.51	18.054	38.06	17.970	45.29	17.881	53.33	17.793	61.85
20.155	31.30	20.064	37.78	19.970	45.11	19.871	52.93	19.773	61.33
24.187	30.84	24.078	37.26	23.965	44.36	23.847	52.14	23.729	60.47
28.210	30.45	28.082	36.77	27.951	43.84	27.813	51.48	27.675	59.59
32.214	29.96	32.068	36.16	31.918	43.10	31.761	50.51	31.603	58.53
				$x = 80$					
1.0092	20.90	1.0041	25.61	0.9990	31.05	0.9939	37.03	0.9885	43.64
1.5125	20.57	1.5049	25.20	1.4973	30.56	1.4895	36.43	1.4816	42.86
3.0272	20.04	3.0120	24.55	2.9968	29.69	2.9812	35.34	2.9653	41.56
4.0356	19.75	4.0154	24.18	3.9951	29.17	3.9743	34.72	3.9531	40.80
5.0427	19.52	5.0173	23.83	4.9920	28.78	4.9661	34.22	4.9395	40.22
6.0517	19.27	6.0213	23.51	5.9909	28.38	5.9598	33.75	5.9279	39.60
7.0553	19.10	7.0198	23.32	6.9844	28.12	6.9481	33.45	6.9110	39.20
8.0628	18.83	8.0223	22.97	7.9818	27.72	7.9403	32.89	7.8979	38.58
9.0682	18.72	9.0227	22.85	8.9771	27.50	8.9305	32.65	8.8827	38.29
10.080	18.60	10.030	22.68	9.9790	27.23	9.9272	32.36	9.8741	37.91
12.097	18.26	12.036	22.26	11.975	26.80	11.913	31.77	11.849	37.25
14.110	17.96	14.039	21.91	13.968	26.32	13.895	31.19	13.821	35.51
				$x = 90$					
1.5118	11.00	1.5041	13.54	1.4963	16.53	1.4879	19.63	1.4794	23.11
2.0168	10.55	2.0066	12.95	1.9962	15.68	1.9850	18.68	1.9736	21.91
2.5222	10.37	2.5094	12.71	2.4964	15.39	2.4824	18.31	2.4681	21.43
3.0234	10.06	3.0081	12.32	2.9925	14.86	2.9757	17.65	2.9586	20.63
3.5265	9.89	3.5087	12.09	3.4905	14.57	3.4710	17.27	3.4510	10.11
4.0311	9.72	4.0108	11.86	3.9899	14.28	3.9676	16.89	3.9447	19.70
5.0410	9.42	5.0156	11.46	4.9895	13.76	4.9616	16.29	4.9330	18.94
7.0581	8.72	7.0225	10.58	6.9860	12.67	6.9469	14.89	6.9069	17.28
9.0779	8.29	9.0321	10.06	8.9851	11.98	8.9348	14.06	8.8834	16.27
				$x = 95$					
0.5058	7.65	0.5032	9.35	0.5005	11.33	0.4976	13.10	0.4946	14.96
0.7574	7.37	0.7534	8.94	0.7495	10.80	0.7451	12.53	0.7406	14.34
1.0090	6.98	1.0037	8.46	0.9984	10.10	0.9926	11.72	0.9867	13.34
1.2610	6.76	1.2544	8.18	1.2478	9.72	1.2405	11.25	1.2311	12.75
1.6357	6.43	1.6271	7.76	1.6185	9.16	1.6091	10.55	1.5995	11.91
2.0198	6.16	2.0092	7.39	1.9986	8.70	1.9870	9.99	1.9751	11.27
2.5188	5.87	2.5056	7.00	2.4924	8.22	2.4779	9.40	2.4631	10.58
3.0309	5.59	3.0150	6.65	2.9991	7.77	2.9817	8.89	2.9639	9.96
4.0281	5.20	4.0069	6.17	3.9858	7.16	3.9626	8.16	3.9390	9.10
5.0411	4.90	5.0147	5.78	4.9882	6.71	4.9592	7.60	4.9296	8.46

TABLE II

Density (d), *viscosity* (η) *and dielectric constant* (D) *of* x *mass per cent* tert-*butanol at different temperatures*

T/K	288.15	293.15	298.15	303.15	308.15
$x = 70$					
$d/g\ cm^{-3}$	0.8594	0.8555	0.8515	0.8473	0.8431
D	23.20	22.31	21.45	20.63	19.84
$10^3\ \eta/Pas$	8.050	6.266	4.931	3.939	3.214
$x = 80$					
$d/g\ cm^{-3}$	0.8361	0.8319	0.8277	0.8234	0.8190
D	17.96	17.23	16.53	15.86	15.22
$10^3\ \eta/Pas$	7.884	6.117	4.807	3.839	3.116
$x = 90$					
$d/g\ cm^{-3}$	0.8120	0.8079	0.8037	0.7992	0.7946
D	13.52	12.94	12.39	11.86	11.35
$10^3\ \eta/Pas$	7.374	5.671	4.416	3.518	2.835
$x = 95$					
$d/g\ cm^{-3}$	0.8000	0.7958	0.7916	0.7870	0.7823
D	11.89	11.36	10.85	10.36	9.89
$10^3\ \eta/Pas$	7.146	5.472	4.220	3.331	2.681

where c° is 1 mol dm^{-3}, and $y_{\pm}$ denotes the mean activity coefficient, which can be estimated by the Debye-Hückel equation

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

In this equation $e = 2\varkappa q$, and $t = \varkappa R$, where $\varkappa$ is the Debye parameter, q is the Bjerrum critical distance, and R is the maximum center-to-center distance between the ions in the ion-pair (distance parameter).

Conductivity data processing was also carried out by the Lee-Wheaton equation in Pethybridge version[9] (LWP) in the form

$$\Lambda_{c\alpha} = \Lambda_0 (1 + C_1 e + C_2 e^2 + C_3 e^3) - \frac{B_2 (c\alpha)^{1/2}}{1 + t} (1 + C_4 e + C_5 e^2 + t/12) \tag{6}$$

In this equation the $C_1 - C_5$ coefficients are expressed as the power series of t and ln t, B_2 is the coefficient which, for this type of electrolyte, corresponds numerically to the relaxation term of the limiting slope S, while the other symbols were mentioned above.

The cited equations contain parameters Λ_o, K_A and R, and the calculation consists of their adjustment (optimizing), by using a computer, in order to determine the values that give minimum deviations between the calculated and experimental values for conductivity. In this work, all the calculations were carried out with a personal computer ZX Spectrum connected to the graphic printer Seikosha GP50S.

Optimization was carried out according to Beronius[10], namely, after this method Λ_o and K_A were adjusted for each selected R. The initial Λ_o was evaluated by extending the curve $\Lambda - c$ to $c = 0$, K_A was chosen arbitrarily, for the initial R the value of 1 Å was taken, and increased by steps of changeable size. In contrast to Beronius, who calculated α from equations (1) and (2), in this work it was calculated by (4) and (5) while the initial α was roughly estimated by the Λ/Λ_0 ratio. This method was applied to both equations (FHFPB and LWPB).

Calculation by means of the FHFP equation was also carried out by the Kay method[11] (FHFPK), according to which all the three parameters were adjusted simultaneously, and according to Justice[12] (FHFPJ), where Λ_0, K_A and coefficient J_2 of equation (1) for each selected R were optimized at the same time.

Out of the values obtained by these calculating methods, we present only those referring to 80 mass per cent tert. butanol at 298.15 K. Figure 1 gives the graphic presentation of the standard deviation (sd) dependence on R; Table III gives the values for Λ_0, K_A and R corresponding to the minimal sd.

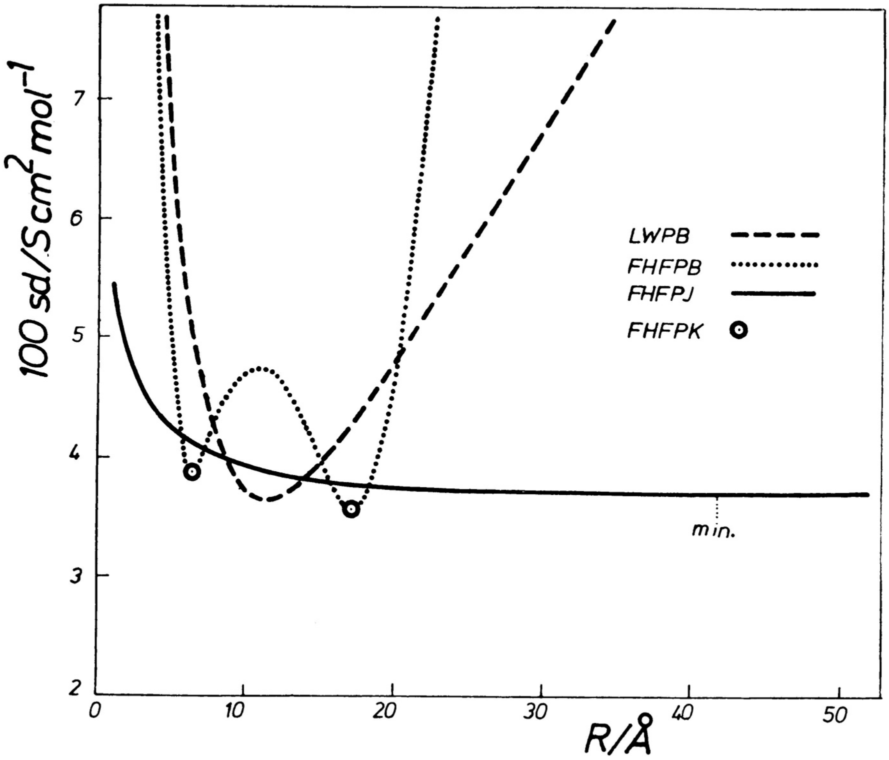

Figure 1. Dependence of standard deviation (*sd*) on distance parameter (*R*) for different calculating methods for 80 mass per cent tert. butanol at 298.15 K.

Figure 1 shows that by processing according to FHFPB two minima were obtained, the LWPB curve exibits one between them, while at FHFPJ a poorly pronounced minimum was obtained at a higher value of R. The values after FHFPK correspond to the minima according to FHFPB, for the Beronius

TABLE III

Λ_o, K_A, R *and sd values obtained for HBr using the Fuoss-Hsia and Lee-Wheaton equations in 80 mass per cent* tert-butanol *at 298.15 K*

Method	FHFPB		FHFPK		FHFPJ	LWPB
	I min.	II min.	I min.	II min.	min.	min.
$\Lambda_o/S\ cm^2\ mol^{-1}$	32.50	32.57	32.50	32.57	32.62	32.56
K_A	100.5	236.8	99.7	236.8	444.2	194.0
$R/Å$	6.6	17.4	6.6	17.4	42.0	11.5
$sd/S\ cm^2\ mol^{-1}$	0.04	0.04	0.04	0.04	0.04	0.04

method is, in fact, a modified Kay method. For other mixtures the form of the curves is similar, but in some the value of parameter R at the first minimum is low having no physical significance, while the curves after LWPB have a poorly pronounced minimum behind the second minimum of FHFPB.

Table III shows that the limiting molar conductivities obtained by different methods agree well, the K_A values differ; however, if the values of the first minimum are neglected, the value of the second minimum is slightly higher than the one after LWPB, while the value after FHFPJ is the highest. The values for R, even if those for the first minimum are neglected, differ considerably. This is similar in other investigated mixtures.

For the sake of comparison with other electrolytes, the data by Goffredi and Shedlovsky[6] for HCl in 90 mass per cent 1-propanol at 298.15 K ($D = 22.86$), and by Beronius and Lindbäck[13] for LiBr in 1-octanol at 298.15 K ($D = 9.85$), were processed in the same way. With Beronius and Lindbäck only the concentration region from $0.42394 \cdot 10^{-4}$ to $3.0533 \cdot 10^{-4}$ mol dm^{-3} was taken, i. e. to $c_{max} = 3.2 \cdot 10^{-7}\ D^3$, where triple ions did not occur[14]. The results of processing are shown in Table IV; those after FHFPK are left out for they are the same as after FHFPB.

TABLE IV

Λ_o, K_A, R and *sd values obtained for HCl in 90 mass per cent 1-propanol (Ref. 6) and LiBr in 1-octanol (Ref. 13) using the Fuoss-Hsia and Lee-Wheaton equations at 298.15 K*

Method	FHFPB		FHFPJ		LWPB
	I min.	II min.	I min.	II min.	min.
	HCl				
$\Lambda_o/S\ cm^2\ mol^{-1}$	36.814	36.940	36.839	36.833	36.950
K_A	33.7	78.0	42.1	68.8	74.6
$R/Å$	4.9	10.1	5.7	73.3	7.2
$sd/S\ cm^2\ mol^{-1}$	0.005	0.012	0.004	0.003	0.011
	LiBr				
$\Lambda_o/S\ cm^2\ mol^{-1}$	3.923	3.936	3.903	3.878	3.933
K_A	55410	56740	53950	53980	56380
$R/Å$	12.9	34.9	4.2	135.6	28.3
$sd/S\ cm^2\ mol^{-1}$	0.001	0.001	0.001	0.001	0.001

Table IV shows that two minima were obtained for both electrolytes processed after FHFPB and FHFPJ, while LWPB gave only one between them. The limiting molar conductivities agree well. The values for K_A in HCl referring to the second minima are comparable with those after LWPB, while for LiBr the values do not differe significantly. However, the values for R, even if those of the first minimum are neglected, differ considerably.

Therefore, it can be concluded that for the electrolyte HBr in the investigated mixtures of tert. butanol, as well as for HCl in 90 mass per cent 1-propanol and LiBr in 1-octanol, the applied equations for conductance do not make it possible to obtain a uniform value for the distance parameter R, as found for other electrolytes[15]. Further, the limiting molar conductivities Λ_0 obtained by both equations and for both minima agree satisfactorily. However, the association constant K_A depends on R, but if the values for the first minimum (lower R) are exempted, those for the second minima do not differ considerably from the values obtained after LWPB.

Further processing by both equations was carried out after the Beronius method (FHFPB and LWPB) supposing that the distance parameter R is equal to Bjerrum critical distance q[12,13,16,17]. The obtained values for all the mixtures at different temperatures are given in Table V.

TABLE V

Λ_0, K_A *and* sd *values obtained for HBr in* x *mass per cent* tert-*butanol 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}		$R=q$/Å
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB	
			$x=70$				
288.15	34.76	34.66	47.1	33.5	0.20	0.19	12.50
293.15	42.13	42.00	50.0	35.3	0.25	0.23	12.77
298.15	50.65	50.48	57.8	41.7	0.25	0.23	13.06
303.15	59.59	59.38	59.7	42.4	0.33	0.30	13.36
308.15	69.46	69.20	65.2	46.4	0.38	0.34	13.66
			$x=80$				
288.15	21.81	21.75	193.1	163.9	0.04	0.04	16.14
293.15	26.79	26.72	210.1	177.8	0.04	0.04	16.54
298.15	32.58	32.48	235.4	199.6	0.03	0.04	16.95
303.15	38.95	38.83	254.9	215.6	0.05	0.05	17.38
308.15	45.99	45.84	275.9	232.6	0.06	0.07	17.81
			$x=90$				
288.15	12.99	12.89	1309	1188	0.06	0.06	21.44
293.15	16.20	16.07	1493	1354	0.07	0.07	22.02
298.15	20.10	19.92	1766	1603	0.10	0.10	22.61
303.15	24.30	24.06	1983	1797	0.13	0.12	23.24
308.15	29.09	28.79	2276	2060	0.14	0.14	23.89
			$x=95$				
288.15	9.22	9.18	4317	4131	0.04	0.03	24.38
293.15	11.52	11.46	5189	4965	0.05	0.04	25.09
298.15	14.48	14.39	6729	6445	0.06	0.06	25.82
303.15	17.16	17.05	7644	7312	0.10	0.10	26.60
308.15	20.21	20.07	9010	8611	0.15	0.14	27.41

It can be seen from Table V that the values for the association constant obtained after LWPB for all the mixtures are somewhat lower than those after FHFPB.

The data for the association constant at different temperatures made it possible to calculate the thermodynamic quantities for the association reaction (3). Namely, the standard enthalpy ΔH° was determined from the linear plot ln K_A versus T^{-1}, while the standard Gibbs energy and entropy, ΔG° and ΔS°, were calculated by means of the usual thermodynamic equations. The values at 298.15 K are in Table VI.

TABLE VI

Standard thermodynamic quantities for the ion-association reaction (3) calculated from association constants obtained by the Fuoss-Hsia and Lee-Wheaton equations in x mass per cent tert-butanol *at 298.15 K*

x	ΔH°/kJ mol^{-1}		ΔG°/kJ mol^{-1}		ΔS°/J K^{-1} mol^{-1}	
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB
70	12.26	12.36	—10.06	—9.25	74.9	72.5
80	13.44	13.22	—13.54	—13.13	90.5	88.4
90	20.58	20.49	—18.53	—18.29	131.2	130.1
95	27.64	27.55	—21.85	—21.74	166.0	165.3

From this table it can be concluded that the thermodynamic quantities, calculated from the data for K_A obtained by means of Fuoss-Hsia (FHFPB) and Lee-Wheaton (LWPB) equations, mutually agree. Therefore, no priority could be given to either equation applied. The values themselves prove that the association of H^+ and Br^- ions is an endothermic reaction, which brings about an increase of entropy. Both, ΔH° and ΔS° values increase with a higher content of *tert.* butanol in the solvent.

Finally, the data obtained for the association constant were compared with those predicted theoretically according to the theories by Bjerrum[18], Denison and Ramsey[19], Fuoss[20], and Yokoyama and Yamatera[21]. Namely, according to the theory by Denison and Ramsey in the diagram log K_A versus D^{-1} a straight line is expected passing through the origin; The Fuoss theory predicts a straight line with a finite intercept, whereas Bjerrum and Yokoyama and Yamatera predict curves which are concave downwards[17]. Our data for the 298.15 K temperature are shown in Figure 2.

As seen from Figure 2, by applying the data calculated according to both equations, straight lines are obtained, which can be presented by expressions

$$\text{for FHFPB: } \log K_A = -0.406 + 45.8/D \tag{7}$$

$$\text{and for LWPB: } \log K_A = -0.652 + 48.4/D \tag{8}$$

Therefore, the Fuoss equation was applied, which is as follows:

$$K_A = \frac{4\pi N R^3}{3000} \exp(b) \tag{9}$$

where

$$b = |z_+ z_-| e^2/RDkT \tag{10}$$

In these expressions e is the electron charge, k is the Boltzmann constant while the other symbols have their usual significance.

From equation (9) it follows that in the plot log K_A versus D^{-1} the slope of the straight line is: $|z_+ z_-| e^2/2.303\ RkT$, and the intercept is 3 log$R$ + log

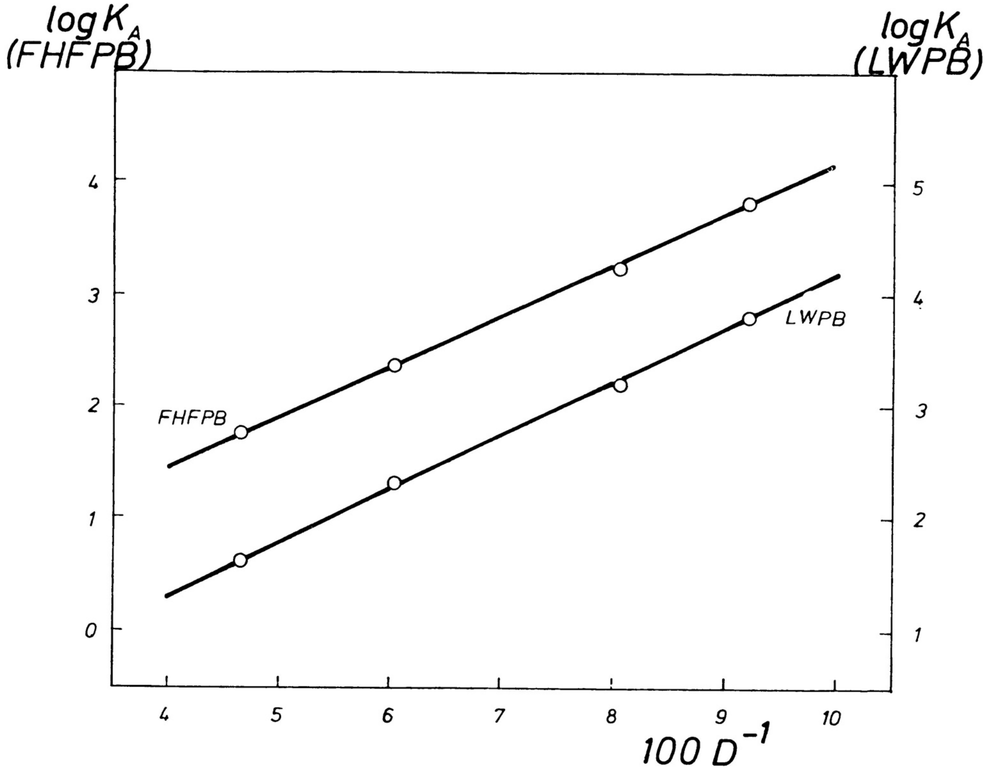

Figure 2. Variation of log K_A from Table V with D at 298.15 K.

($4\pi N/3000$). By equating these expressions with the experimental values for the slope and intercept, for equation (7) it follows from the slope $R = 5.30$ Å, and from the intercept $R = 5.38$ Å, while for equation (8) from the slope $R = 5.02$ Å, and from the intercept $R = 4.45$ Å.

The values for the distance parameter R, obtained by both equations agree fairly well, gathering around the value of 5 Å, which is fairly near the value otained by summing up the effective ion radius for H_3O^+ of 2.8 Å[22] and Br^- of 1.95 Å[23]. A good agreement of the values for R from the straight line slope and intercept, also gathering around the quantity of 5 Å, was found for other temperatures, too.

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SAŽETAK

Reakcija asocijacije iona H^+ i Br^- u 70, 80 90 i 95%-noj smjesi *tert*-butanol-voda

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Mjerena je molarna provodnost HBr u smjesama *tert*-butanol-voda koje sadrže 70, 80, 90 i 95% (masenih) alkohola u temperaturnom području od 288,15 do 308,15 K, u intervalima od po 5 K. Mjerene vrijednosti obrađene su s pomoću jednadžbi za provodnost prema Fuoss-Hsia i Lee-Wheatonu, primjenjujući razne metode računanja. Dobivene vrijednosti za graničnu molarnu provodnost (Λ_0) radius ionskog para (R) i konstantu asocijacije (K_A) su međusobno uspoređene i raspravljene. Konstante asocijacije dobivene pri različitim temperaturama uz uvjet $R = q$ (q je Bjerrumov kritični razmak) poslužile su za izračunavanje standardnih termodinamičkih veličina za reakciju asocijacije iona H^+ i Br^-. Dobivene vrijednosti za K_A također su uspoređene s teorijski predviđenim vrijednostima.