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Ion-Association Reaction of H^+ and Br^- in (70, 80, 90 and 95 Mass per cent) 2-Butanol-Water Mixtures

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Molar conductivities of HBr in 70, 80, 90 and 95 mass per cent 2-butanol-water mixtures were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The experimental values were analyzed by the conductance equations after Fuoss-Hsia and Lee-Wheaton. Values for the limiting molar conductivity (Λ_0), obtained by both equations, agree well, better than the association constants (K_A), while the distance parameters (R) differ considerably. Both equations were used to calculate the association constants at different temperatures under the condition that $R = q$ (q is the Bjerrum critical distance). These values were used to obtain standard thermodynamic quantities for the H^+ and Br^- ion association reaction. The values obtained were compared with the literature data for *tert.* butanol-water mixtures. The mechanism of H^+ ion transfer in the investigated mixtures was also discussed.

INTRODUCTION

In continuation of our studies on the ion-association reaction of H^+ and Br^- in mixed water-alcohol solvents, examinations were carried out in 2-butanol-water mixtures. Investigations were based on the HBr electrolyte conductivity measurements in these mixtures.

In our previous work[1] we studied this reaction in *tert.* butanol-water mixtures (70, 80, 90 and 95 mass per cent) by means of the Fuoss-Hsia and Lee-Wheaton equations for conductivity. These equations are based on different models of ion conductance in solution. However, neither of these equations could produce a reliable value for the ionic distance within the ion pair (distance parameter R) nor was it possible to give any preference to either equation in calculating the ion-association constant.

In this work, both equations were also used in order to determine the suitability of their application to the HBr electrolyte conductivity in 70, 80, 90 and 95 mass per

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cent 2-butanol. Further, thermodynamic quantities for the H^+ and Br^- ion-association were determined and we also tried to establish a possible change in the H^+ ion transfer mechanism in these mixtures in relation to aqueous medium.

EXPERIMENTAL

All solutions were prepared by weighing an aqueous stock-solution of HBr, redistilled water and 2-butanol (*p.a.* purity »Merck«). The stock-solution was prepared from redistilled water and 48 mass per cent HBr (*p.a.* purity »Kemika«). HBr and 2-butanol were distilled before use.

The technique and apparatus used to carry out conductance, density, and viscosity measurements were the same as previously described.[1] Two parallel conductivity measurements for each molarity differed usually by about ± 0.03 S cm^2 mol^{-1} from the mean value.

Dielectric constants of 70, 90 and 95 mass per cent 2-butanol at 288.15, 298.15 and 308.15 were determined by means of a WTW dipolmeter type DM 01; values at 293.15 and 303.15 K, as well as those of 80 mass per cent 2-butanol, were found by interpolation.

RESULTS AND DISCUSSION

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

Conductivity data processing was carried out by means of the Fuoss-Hsia[2] equation in the Fernández-Prini[3] (FHFP) version in the form

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

and by the Lee-Wheaton[4] equation in the Pethybridge[5] (LWP) version in the form

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

In equation (2), $e = 2\kappa q$, and $t = \kappa R$, where κ is the Debye parameter, q is the Bjerrum critical distance, R is the distance parameter, while the coefficients C_1–C_5 are functions of t and $\ln t$. The other symbols in equation (2), as well as those in equation (1), have their usual significance. The molar conductivity (Λ) at each HBr concentration is connected with the molar conductivity of free ions ($\Lambda_{c\alpha}$) through the degree of dissociation ($\alpha = \Lambda/\Lambda_{c\alpha}$), which is to be found in the expression for the thermodynamic equilibrium constant

$$K_A = \frac{1-\alpha}{(c/c^o)\alpha^2 y_\pm^2} \tag{3}$$

for the ion-association reaction

$$\underset{c\alpha}{H^+} + \underset{c\alpha}{Br^-} \rightleftharpoons \underset{c(1-\alpha)}{H^+ \cdot Br^-} \tag{4}$$

TABLE I

Molar conductivities (Λ/S $cm^2 mol^{-1}$) of HBr at various molalities (m/mol kg^{-1}) in x mass per cent 2-butanol at different temperatures

$10^4 m$	288.15 K	293.15 K	298.15 K	303.15 K	08.15 K
$x=70$					
3.4749	40.48	47.82	55.92	64.58	73.89
3.4760	40.30	47.64	55.71	64.32	73.51
6.9473	40.04	47.23	55.21	63.68	72.80
8.1045	39.87	47.07	54.96	63.46	72.59
9.2651	39.78	46.87	54.78	63.28	72.25
11.576	39.52	46.60	54.45	62.85	71.77
13.900	39.30	46.34	54.08	62.50	71.31
16.215	39.03	46.05	53.76	62.00	70.85
16.216	39.15	46.22	53.98	62.26	70.99
18.521	38.93	45.91	53.54	61.69	70.48
20.841	38.70	45.54	53.20	61.31	69.95
20.850	38.56	45.45	53.08	61.18	69.86
23.162	38.47	45.28	52.87	60.96	69.51
$x=80$					
2.3704	27.21	32.42	38.30	44.64	51.54
3.5605	26.68	31.75	37.54	43.66	50.52
4.7487	26.44	31.50	37.13	43.26	49.92
5.9324	26.26	31.20	36.77	42.83	49.42
7.1227	25.97	30.93	36.45	42.45	48.94
8.2939	25.79	30.61	36.07	42.02	48.41
8.3107	25.96	30.84	36.32	42.29	48.78
10.675	25.50	30.24	35.56	41.42	47.69
13.049	25.21	29.92	35.15	40.92	47.14
15.423	24.80	29.45	34.62	40.25	46.28
17.802	24.57	29.11	34.24	39.77	45.72
20.148	24.34	28.84	33.87	39.41	45.28
$x=90$					
1.8270	17.55	20.92	24.80	29.00	33.56
2.4337	17.28	20.57	24.33	28.44	32.93
3.6483	16.87	20.09	23.69	27.68	31.99
4.8681	16.44	19.53	23.02	26.84	30.95
6.0481	16.12	19.12	22.51	26.19	30.12
6.0881	16.14	19.17	22.54	26.24	30.23
7.2941	15.89	18.82	22.14	25.76	29.57
8.5196	15.58	18.46	21.70	25.20	28.95
9.7346	15.33	18.15	21.30	24.73	28.37
10.945	15.00	17.74	20.83	24.11	27.68
12.221	14.79	17.47	20.51	23.84	27.26
$x=95$					
1.2272	13.84	16.47	19.45	22.73	26.30
1.8511	13.33	15.81	18.68	21.76	25.10
2.4652	13.03	15.48	18.19	21.18	24.37
3.0814	12.77	15.14	17.78	20.61	23.65
3.6996	12.49	14.78	17.32	20.10	23.03
4.9315	12.10	14.27	16.72	19.31	22.06
6.1731	11.70	13.79	16.09	18.56	21.11
7.3906	11.46	13.47	15.71	18.07	20.52
8.6273	11.23	13.18	15.34	17.62	19.98
9.8464	10.98	12.88	14.97	17.17	19.43

TABLE II

Density (d), viscosity (η) and dielectric constant (D) of x mass per cent 2-butanol at different temperatures

T/K	288.15	293.15	298.15	303.15	308.15
			$x = 70$		
d/g cm^{-3}	0.8716	0.8675	0.8635	0.8590	0.8545
10^3 η/Pas	4.911	4.033	3.343	2.796	2.376
D	28.6	27.9	27.2	26.5	25.8
			$x = 80$		
d/g cm^{-3}	0.8512	0.8468	0.8426	0.8382	0.8337
10^3 η/Pas	4.543	3.734	3.099	2.607	2.214
D	21.8	21.2	20.6	20.0	19.6
			$x = 90$		
d/g cm^{-3}	0.8308	0.8262	0.8216	0.8174	0.8131
10^3 η/Pas	4.069	3.363	2.811	2.373	2.027
D	18.5	17.9	17.3	16.7	16.2
			$x = 95$		
d/g cm^{-3}	0.8205	0.8158	0.8113	0.8072	0.8034
10^3 η/Pas	3.927	3.270	2.731	2.316	1.966
D	17.8	17.1	16.4	15.8	15.2

The mean ion activity coefficient ($y_\pm$) in expression (3) was estimated by the Debye-Hückel equation

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

Symbols e and t were defined before.

The cited equations made it possible to calculate parameters Λ_o, K_A and R by means of an optimizing method. Optimization was carried out according to Beronius[6] where Λ_o and K_A were adjusted for each selected R. This method was applied to both equations (FHFPB and LWPB). Calculation by means of the FHFP equation was also carried out according to Justice[7] (FHFPJ), where Λ_o, K_A and the coefficient J_2 of equation (1) were adjusted simultaneously for each selected R. Values that gave a minimum of standard deviation between the calculated and experimental values for conductivity were taken to be the final values of parameters. All the calculations were carried out with a personal computer ZX Spectrum connected to the graphic printer Seikosha GP5OS.

When the obtained data for standard deviation (sd) are presented in dependence on R, curves with one or two minima are obtained. There are two well pronounced minima on the curves after FHFPB, except for 95 mass per cent 2-butanol. In all the mixtures on the curves after LWPB there is only one minimum less pronounced than those after FHFPB. Finally, the curves after FHFPJ have also only poorly pronounced minimum, except at 70 mass per cent 2-butanol which has two minima. Table III gives the values for 298.15 K. When FHFPB and FHFPJ curves have a single minimum, its values are nearer to the expected values for the second minimum and, therefore, the first one is taken as non-existing.

Table III shows that the values for Λ_o are in good mutual agreement, independently of the conductance equation (FHFPB or LWPB) and the processing method (FHFPB or FHFPJ) applied, whether there are two minima on the curve sd *versus* R or the K_A value is negative. As for the values for distance parameter R, where two mi-

TABLE III

Λ_o, K_A, R and sd values obtained for HBr in x mass per cent 2-butanol 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.
$x = 70$					
Λ_o/S cm^2 mol^{-1}	57.35	57.39	57.38	57.39	57.34
K_A	*	25.5	*	*	33.6
R/Å	0.5	21.6	11.0	68.7	60.1
sd/S cm^2 mol^{-1}	0.08	0.08	0.09	0.09	0.08
$x = 80$					
Λ_o/S cm^2 mol^{-1}	40.20	40.22	–	40.29	40.23
K_A	59.4	117.3	–	238.8	95.5
R/Å	6.3	14.4	–	37.6	9.1
sd/S cm^2 mol^{-1}	0.10	0.09	–	0.10	0.09
$x = 90$					
Λ_o/S cm^2 mol^{-1}	26.83	26.91	–	26.90	26.78
K_A	162.3	425.0	–	416.3	399.9
R/Å	2.4	25.8	–	24.7	55.4
sd/S cm^2 mol^{-1}	0.05	0.05	–	0.05	0.05
$x = 95$					
Λ_o/S cm^2 mol^{-1}	–	21.450	–	21.82	21.75
K_A	–	811.6	–	1377	897.5
R/Å	–	12.6	–	53.3	1.7
sd/S cm^2 mol^{-1}	–	0.07	–	0.05	0.04

*Negative value.

nima exist on the curves, the value of R of the first minimum is lower, sometimes even not realistic (70 and 90 mass per cent). However, even a single minimum of the curves after LWPB may be unreal, as in the case of 95 mass per cent 2-butanol. In general, even when the real values are compared, it could be concluded that it is not possible to obtain a uniform value for R by the respective conductance equations, the fact which has also been established for other solvents and electrolytes.[1,8] The data for constant K_A show that for the curves with two minima the value of the first one is lower. The values of the second minimum are comparable with that of the single minimum (curve after LWPB) and agree very well for 90 mass per cent 2-butanol, and to a somewhat lesser extent for other mixtures; the value for K_A after FHFPJ is the highest.

Further conductivity data processing was carried out with both equations after the Beronius method (FHFPB and LWPB) on the assumption that the distance parameter R is equal to the Bjerrum critical distance q.[7,9] The obtained values at different temperatures are given in Table IV.

The values from Table IV show that the limiting molar conductivities obtained by both equations, also under this condition ($R = q$), agree well, while the association constants differ slightly, and the values after LWPB are somewhat lower than those after FHFPB. This was also established in *tert.* butanol-water mixtures.[1]

TABLE IV

Λ_o, K_A and sd values obtained for HBr in x mass per cent 2- butanol using the Fuoss-Hsia and Lee-Wheaton equations for $R=q$ at different temperatures

T/K	Λ_o/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	41.81	41.78	18.8	14.5	0.11	0.10	10.14
293.15	49.43	49.40	21.5	17.1	0.12	0.12	10.21
298.15	57.83	57.79	23.0	18.5	0.13	0.12	10.30
303.15	66.87	66.81	25.0	20.3	0.16	0.16	10.40
308.15	76.54	76.48	27.4	22.5	0.18	0.17	10.51
			$x=80$				
288.15	28.49	28.44	94.8	81.9	0.07	0.07	13.30
293.15	34.00	33.94	104.4	90.8	0.09	0.09	13.44
298.15	40.24	40.16	114.9	100.5	0.09	0.09	13.60
303.15	46.95	46.85	119.8	104.7	0.12	0.12	13.78
308.15	54.35	54.24	130.1	114.7	0.13	0.13	13.83
			$x=90$				
288.15	19.09	19.05	356.8	335.8	0.05	0.05	15.67
293.15	22.84	22.80	393.4	370.5	0.07	0.06	15.92
298.15	27.17	27.11	436.6	411.2	0.07	0.06	16.20
303.15	31.94	31.86	480.5	452.5	0.09	0.08	16.50
308.15	37.21	37.12	537.9	507.3	0.10	0.09	16.73
			$x=95$				
288.15	15.01	14.99	646.3	625.7	0.05	0.06	16.29
293.15	17.99	17.96	738.3	714.5	0.06	0.06	16.67
298.15	21.43	21.40	851.0	822.9	0.07	0.07	17.09
303.15	25.28	25.23	985.8	953.4	0.07	0.08	17.44
308.15	29.60	29.53	1165	1127	0.08	0.09	17.84

The thermodynamic quantities for the H^+ and Br^- ion association reaction are calculated by means of the data for K_A at various temperatures (Table IV). Standard enthaply (ΔH^o) was determined from the linear plot ln K_A *versus* T^{-1}, while standard free energy (ΔG^o) and entropy (ΔS^o) were calculated by means of the usual equations. The values for 298.15 K are given in Table V.

From Table V it can be seen that the thermodynamic quantities for the association reaction, calculated from the data for K_A obtained by means of both equations (FHFPB and LWPB), agree well. Therefore, in order to get a better insight into the H^+ and Br^- association reaction in the investigated 2-butanol-water mixtures, no priority could be given to either equation applied, as it was also the case in *tert.* butanol-water mixtures.[1] From that table it can also be seen that quantities ΔS^o and ΔG^o change continuously with increasing the 2-butanol content in the mixture. This is the case of ΔH^o in the range of 80–95 mass per cent, while at 70 mass per cent, these values are somewhat higher. However, in this solvent, the K_A constants are relatively low (14–27), and probably their determination is less reliable.

When the data for the association constant for each temperature (Table IV) are shown in dependence on the dielectric constant (plot log K_A *versus* D^{-1}), straight lines

TABLE V

Standard thermodynamic quantities for the ion-association reaction (4) calculated from association constants obtained by the Fuoss-Hsia and Lee-Wheaton equations in x mass per cent 2-butanol at 298.15 K

x	ΔH^0/kJ mol^{-1}		ΔG^0/kJ mol^{-1}		ΔS^0/J K^{-1} mol^{-1}	
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB
70	13.03	13.78	− 7.78	− 7.23	69.8	70.5
80	11.40	12.07	−11.76	−11.43	77.7	78.8
90	15.07	15.13	−15.07	−14.92	101.1	100.8
95	21.65	21.61	−16.72	−16.64	128.7	128.3

are obtained. Figure 1 shows that the data obtained after FHFPB for 298.15 K can be expressed by the following equation:

$$\log K_A = -0.960 + 63.0/D \qquad (6)$$

This expression can be compared with the Fuoss equation:

$$K_A = \frac{4\pi NR^3}{3000}\exp(b) \qquad (7)$$

where

$$b = |z_+ z_-|\, e^2/RDkT \qquad (8)$$

(e is the electron charge, k is the Boltzmann constant while the other symbols have their usual significance), for in the plot $\log K_A$ *versus* D^{-1}, the same is represented by the straight line with the intercept. By equating the experimental values for the slope of the straight line from equation (6) with the value from the Fuoss equation: $|z_+ z_-| e^2/2.303\, RkT$, $R = 3.86$ Å is obtained, and for the intercept with the values: $3 \log R + \log(4\pi N/3000)$, $R = 3.52$ Å is obtained. By an analogous method for the *tert.* butanol-water mixtures (their straight line is also shown in Figure 1), somewhat higher values were obtained, namely, from intercept $R = 5.38$ Å and from slope $R = 5.30$ Å.[1]

From Figure 1 it can also be seen that the straight line for 2-butanol-water mixtures is above that for *tert.* butanol-water mixtures. Accordingly, the values for the association constant at the same dielectric constant in 2-butanol-water mixtures are higher than those in the corresponding *tert.* butanol-water mixtures. It is obvious that the association reaction of H^+ and Br^- ion and K_A, respectively, are influenced not only by the physical properties of the mixed solvents, expressed by the dielectric constant, but also by their chemical properties.

In order to get an insight into a possible change of the H^+ ion transfer mechanism in the investigated mixtures with respect to the water medium, the data for the product of the limiting conductivity and the viscosity coefficient ($\Lambda_0\eta$) are shown in dependence upon the dielectric constant D (Figure 2). The same figure gives the data for HBr in *tert.* butanol-water mixtures,[1] and for HCl[11] and NaCl[12], respectively, in 1-propanol-water mixtures in a wide range of alcohol content (0–100 mass per cent).

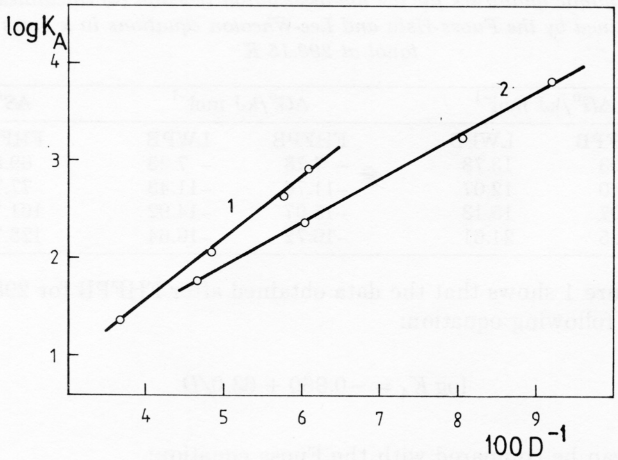

Figure 1. Variation of log K_A (obtained after FHFPB) with D at 298.15 K. Solvents: 1) 2-butanol-water (Table II and IV); 2) *tert.* butanol-water (ref. 1).

By comparison of the last two curves, increased HCl conductivity with respect to NaCl, as a result of higher conductivity of H^+ ions due to the proton jump mechanism, can be stated. This mechanism is obviously present in all the investigated mixtures, but its contribution to the overall transfer decreases with the decreasing dielectric constant. For the HBr electrolyte, the limiting conductivities at the same dielectric constants are lower in 2-butanol-water mixtures than in *tert.* butanol-water mixtures (η have similar values). Consequently, there is specific influence of the alcohol component, as stated also for the association constants. As to the mechanism of H^+ ion transfer in these mixtures, we have no data for an electrolyte with a common anion for comparison. However, a qualitative comparison can be made with the HCl electrolyte in 1-propanol-water mixtures, considering the expectation of similar conductivity values for Cl^- and Br^- ion, respectively. Namely, from the position of the lines for HBr in relation to HCl it can be concluded that the proton jump mechanism takes a certain part in the transfer of H^+ ion in 2-butanol-water and in *tert.* butanol-water mixtures, as it is the case in 1-propanol-water mixtures. However, this mechanism dominates in an aqueous medium.[13]

Finally, it has to be mentioned that still lower Λ_o can be expected in mixtures with water contents lower than those examined in this work, and that after a certain minimum an abrupt increase towards the pure alcohol takes place (this was found for HCl-electrolyte in water mixtures of 1-propanol[11] as well as 1-butanol and iso-butanol[14]). According to De Lisi and Goffredi,[14] the sharp decrease of Λ_o-values with very little amounts of water added to alcohol is a consequence of H_3O^+-formation, so that proton transitions from H_3O^+ to ROH are energetically unfavoured and those from H_3O^+ to H_2O rather improbable owing to the small number of water molecules present in the solution. As the minimum is reached, the proton-jump contribution to conductivity is gradually increased by further addition of water to the system.

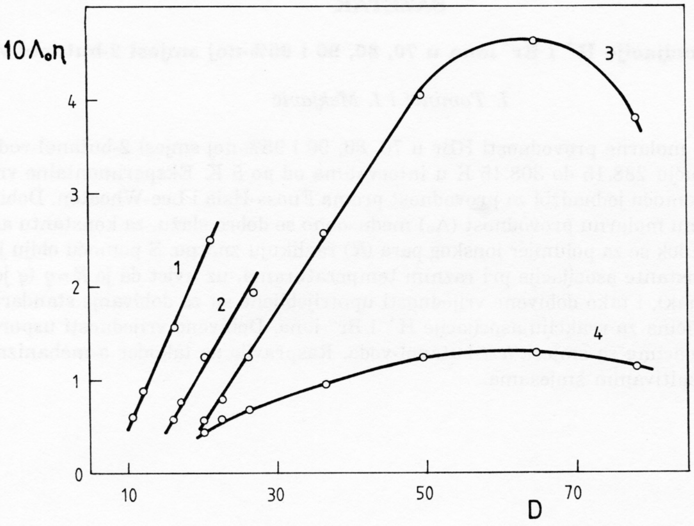

Figure 2. Variation of $\Lambda_{o}\eta$ with D at 298.15 K for: 1) HBr in *tert.* butanol-water (ref. 1); 2) HBr in 2-butanol-water (Table II and IV); 3) HCl in 1-propanol-water (ref. 11); 4) NaCl in 1-propanol-water mixtures (ref.12)

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SAŽETAK

Reakcija asocijacije H^+ i Br^- iona u 70, 80, 90 i 95%-noj smjesi 2-butanol-voda

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Izmjerene su molarne provodnosti HBr u 70, 80, 90 i 95%-noj smjesi 2-butanol-voda u temperaturnom području 288.15 do 308.15 K u intervalima od po 5 K. Eksperimentalne vrijednosti su analizirane s pomoću jednadžbi za provodnost prema Fuoss-Hsia i Lee-Wheaton. Dobivene vrijednosti za graničnu molarnu provodnost (Λ_o) međusobno se dobro slažu, za konstantu asocijacije (K_A) nešto slabije, dok se za polumjer ionskog para (R) razlikuju znatno. S pomoću obiju jednadžbi izračunane su konstante asocijacije pri raznim temperaturama, uz uvjet da je $R=q$ (q je Bjerrumov kritični razmak), i tako dobivene vrijednosti upotrijebljene su za dobivanje standardnih termodinamičkih veličina za reakciju asocijacije H^+ i Br^- iona. Dobivene vrijednosti uspoređene su s literaturnim podacime za smjese *tert*-butanol-voda. Raspravlja se također o mehanizmu prijenosa H^+ iona u ispitivanim smjesama.