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Thermodynamics of the Association Reaction of Na^+ and Br^- Ions in (70, 80, 90, and 95 Mass per Cent) 2-Butanol + Water Mixtures

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Molar conductivities of NaBr electrolyte in 2-butanol + water mixtures ($w_{\text{2-butanol}}$ = 0.7, 0.8, 0.9, 0.95) were mesaured in the temperature range from 288.15 to 308.15 K at 5 K intervals. By processing the obtained data using the conductivity equations after Fuoss-Hsia and Lee-Wheaton it was not possible to establish a reliable value for the distance of the ions in the ion-pairs formed (R). The processing was therefore repeated using the same equations with $R=q_{\text{Bjerrum}}$. The association constants (K_A) obtained by both equations at different temperatures enable calculation of the standard thermodynamic quantities (ΔH^o and ΔS^o) for the association reaction. The obtained thermodynamic quantities, together with the limiting molar conductivity (Λ_o), were compared with the analogous data from literature for HBr electrolyte in the same mixtures, and for NaBr electrolyte in *t*-butanol + water mixtures.

INTRODUCTION

Following our investigations of the association reaction of electrolytes in mixed alcohol-water solvents with a higher alcohol content, we examinated the association of $Na^+$and Br^- ions in 2-butanol + water mixtures. The investigations were based on the measurement of solution conductivity.

In our previous work,[1] we established the thermodynamics of the association reaction of Na^+ and Br^- ions in *t*-butanol + water mixtures using the equations for conductivity after Fuoss-Hsia and Lee-Wheaton. By compar-

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ing the obtained values with those obtained for HBr electrolyte in the same mixtures,[2] we found that the cation exchange (Na^+ instead of H^+) affected the thermodynamic quantities of the ion-pair formation.

In this work, our first aim is to determine whether it is possible to apply the cited equations to this system. Then, from a comparison with the analogous data for electrolyte HBr in the same mixtures,[3] we want to establish in the same way the influence of the cation exchange on the thermodynamics of the ion-pair formation. Finally, by comparing the thermodynamic quantities for NaBr electrolyte in *t*-butanol + water mixtures, we want to find out the possible influence of the organic component on these quantities with the same physical properties of mixed solvents expressed by the dielectric constant.

EXPERIMENTAL

The NaBr solutions were prepared as before.[1]

The conductivity measuring method has already been described.[2] The measured values were corrected for the conductivity of the solvent. Two parallel measurements in different cells for each molality in 70, 80, 90, and 95 mass per cent 2-butanol differed by about 0.14, 0.10, 0.07 and 0.06 S cm^2 mol^{-1} from the mean value, respectively.

The values for the density and viscosity of the solvent were taken from our previous work,[3] whereas the dielectric constants were obtained by interpolation of the literature data.[4]

RESULTS AND DISCUSSION

The measured molar conductivities for different molalities of NaBr solutions are shown in Table I. Concentrations of NaBr (c/mol dm^{-3}), relating to Table I, were obtained according to the relation $c = m \cdot d$, *i.e.* from the data for the solution molality and for solvent density.

For the investigated association reaction

$$\underset{c\alpha}{Na^+} + \underset{c\alpha}{Br^-} = \underset{c(1-\alpha)}{Na^+ \cdot Br^-} \tag{1}$$

the thermodynamic constant (K_A) is

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

where α is the degree of dissociation ($\alpha = \lambda/\lambda_{cx}$), *i.e.* the relation between the measured molar conductivity for each concentration and the molar conductivity of free ions, $y_\pm$ is the mean activity coefficient of free ions, and c^o = 1 mol dm^{-3}.

For the activity coefficient, we will use the Debye-Hückel expression

$$y_\pm^2 = \exp[-e/(1+t)] \tag{3}$$

where $e = 2\kappa q$, $t = \kappa R$; κ is the Debye parameter, q is the Bjerrum critical distance, and R is the center-to-center distance between the ions in the ion-pair formed (distance parameter).

TABLE I

Molar conductivities (Λ/S cm^2 mol^{-1}) of NaBr at various molalities in w mass per cent 2-butanol at different temperatures

$\frac{10^4 m}{\text{mol kg}^{-1}}$	T/K				
	288.15	293.15	298.15	303.15	308.15
			w = 70		
9.3940	14.71	17.53	20.81	24.35	28.20
15.804	14.23	16.93	20.05	23.42	27.12
22.206	13.80	16.42	19.42	22.67	26.31
28.599	13.47	16.06	18.94	22.10	25.53
34.991	13.25	15.76	18.57	21.64	24.96
41.394	13.02	15.46	18.25	21.27	24.57
47.797	12.80	15.21	17.93	20.91	24.10
54.200	12.62	14.97	17.63	20.53	23.66
60.603	12.44	14.77	17.40	20.23	23.34
66.993	12.27	14.59	17.19	20.00	23.03
73.394	12.16	14.43	16.99	19.77	22.76
80.089	11.95	14.18	16.68	19.42	22.33
			w = 80		
1.1959	13.75	16.56	19.81	23.41	27.30
4.1005	12.85	15.44	18.38	21.57	25.19
6.9994	12.25	14.63	17.42	20.47	23.85
9.9024	11.81	14.11	16.76	19.72	23.17
12.798	11.49	13.75	16.27	19.13	22.22
15.698	11.24	13.43	15.95	18.67	21.63
18.597	10.99	13.11	15.53	18.19	20.97
21.500	10.73	12.80	15.18	17.68	20.64
24.395	10.55	12.57	14.88	17.39	20.12
27.194	10.39	12.35	14.61	17.08	19.85
30.199	10.19	12.19	14.41	16.84	19.49
33.098	10.06	12.00	14.10	16.57	19.10
35.902	9.91	11.86	13.99	16.30	18.82
			w = 90		
1.2087	12.03	14.38	17.09	20.08	23.37

TABLE I, Continued.

$\frac{10^4 m}{\mathrm{mol\,kg^{-1}}}$	T/K				
	288.15	293.15	298.15	303.15	308.15
1.8195	11.63	13.83	16.43	19.24	22.30
2.8284	11.09	13.12	15.62	18.18	21.03
4.0805	10.51	12.43	14.68	17.10	19.74
5.5494	10.06	11.89	14.00	16.26	18.66
7.2495	9.61	11.33	13.32	15.41	17.67
9.1753	9.23	10.86	12.73	14.71	16.80
11.300	8.84	10.40	12.18	14.06	16.06
13.701	8.49	9.96	11.64	13.41	15.29
16.299	8.19	9.59	11.18	12.87	14.64
18.998	7.89	9.24	10.77	12.36	14.06
22.089	7.60	8.88	10.35	11.89	13.48
w = 95					
0.6072	10.94	13.02	15.34	17.92	20.60
1.1992	10.40	12.20	14.31	16.56	18.83
1.7982	9.86	11.55	13.41	15.36	17.47
2.7012	9.27	10.80	12.51	14.27	16.03
3.8998	8.68	10.06	11.59	13.15	14.70
5.1967	8.17	9.45	10.86	12.25	13.64
6.5996	7.75	8.93	10.22	11.49	12.77
8.2989	7.33	8.41	9.60	10.77	11.92
10.200	6.94	7.95	9.05	10.13	11.21
12.299	6.60	7.55	8.57	9.57	10.57
14.501	6.30	7.20	8.16	9.10	10.03
16.899	6.03	6.88	7.78	8.66	9.53
19.350	5.80	6.59	7.46	8.29	9.12

For $\Lambda_{c\alpha}$ we will use two theoretical equations, *i.e.* the Fuoss-Hsia[5] in the Fernández-Prini[6] (FHFP) version

$$\Lambda_{c\alpha} = \Lambda_{\mathrm{o}} - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1(c\alpha) - J_2(c\alpha)^{3/2} \tag{4}$$

and the Lee-Wheaton[7] in the Pethybridge[8] (LWP) version

$$\Lambda_{c\alpha} = \Lambda_{\mathrm{o}}(1 + C_1 e + C_2 e^2 + C_3 e^3) - \frac{B_2 (c\alpha)^{(1/2)}}{1+t}\left(1 + C_4 e + C_5 e^2 + \frac{t}{12}\right) \tag{5}$$

in wich Λ_{o} is the limiting molar conductivity, and all other symbols have their usual significance.[2]

The cited expressions were used for calculating the limiting molar conductivity, the association constant and the distance parameter by means of computer optimization after Beronius[9] (FHFPB and LWPB), where Λ_{o} and

K_A were adjusted for each chosen R. The optimization was completed after obtaining the minimal standard deviation (*sd*) between the calculated and the experimental values for conductivity.

By placing the standard deviation data in dependence on R, we obtained curves always having one minimum after LWPB, and after FHFPB having mainly one minimum, and less frequently two minima. Data for 298.15 K are given in Table II.

TABLE II

Λ_0, K_A, R and sd values obtained for NaBr in w mass per cent 2-butanol using the Fuoss-Hsia and Lee-Wheaton equations at 298.15 K

Equation	$\Lambda_0/S\ cm^2\ mol^{-1}$	K_A	R/Å	$sd/S\ cm^2\ mol^{-1}$
		w = 70		
FHFPB	23.21	75.7	8.7	0.04
LWPB	23.26	78.6	6.0	0.04
		w = 80		
FHFPB	20.82	258	9.4	0.08
LWPB	21.01	299	4.4	0.06
		w = 90		
FHFPB	19.29	1088	11.8	0.04
LWPB	19.39	1158	8.4	0.03
		w = 95		
FHFPB	17.36	2262	5.5	0.02
	(17.40)	(2531)	(22.3)	(0.02)
LWPB	17.38	2464	21.1	0.02

From these and other related data, it can be concluded that the values for Λ_0 obtained by both equations are in good agreement, the values for K_A show a slightly lesser agreement, whereas the values for R exhibit a considerable difference. It is therefore not possible with this system to obtain a reliable value for the distance parameter by using these equations with three-parameter optimization; nor is it possible to establish the character of the ion-pairs formed.

Further processing of experimental data was carried out provided the distance parameter equalled the Bjerrum critical distance ($R = q$). The values obtained for the limiting molar conductivity, the association constant and standard deviation are shown in Table III.

It is seen from the given data that the limiting molar conductivities obtained by both equations are in good agreement, and also in agreement with the values obtained by three-parameter optimization (Table II). This has also been established with HBr electrolyte in the same mixtures,[3] as well as with NaBr electrolyte in *t*-butanol + water mixtures.[1]

TABLE III

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

	$\Lambda_o/S\ cm^2\ mol^{-1}$		K_A		$sd/S\ cm^2\ mol^{-1}$		
T/K	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB	$R = q/Å$
			w=70				
288.15	16.23	16.19	69.1	63.0	0.03	0.03	10.94
293.15	19.38	19.33	72.4	66.1	0.03	0.03	11.09
298.15	23.06	23.00	78.3	71.7	0.05	0.05	11.21
303.15	27.04	26.98	82.6	75.9	0.06	0.06	11.34
308.15	31.48	31.40	89.4	82.2	0.06	0.07	11.54
			w=80				
288.15	14.39	14.37	242	229	0.05	0.05	13.68
293.15	17.33	17.29	257	243	0.08	0.09	13.83
298.15	20.77	20.72	281	265	0.09	0.10	14.01
303.15	24.55	24.50	301	284	0.11	0.13	14.20
308.15	28.79	28.72	324	306	0.11	0.13	14.42
			w=90				
288.15	13.36	13.33	896	866	0.03	0.03	16.29
293.15	16.03	15.99	996	962	0.04	0.05	16.57
298.15	19.25	19.20	1123	1085	0.04	0.05	16.88
303.15	22.80	22.73	1265	1222	0.05	0.06	17.22
308.15	26.81	26.72	1441	1390	0.05	0.06	17.60
			w=95				
288.15	12.19	12.17	1807	1773	0.03	0.03	16.95
293.15	14.62	14.59	2143	2102	0.02	0.01	17.38
298.15	17.46	17.42	2548	2499	0.03	0.02	17.85
303.15	20.70	20.65	3102	3041	0.03	0.03	18.25
308.15	24.22	24.15	3722	3648	0.02	0.02	18.70

Figure 1a) shows the depedence of the Walden product ($\Lambda_o\eta$) on the dielectric constant of the solvent for both electrolytes (NaBr and HBr) in 2-butanol + water mixtures. The increased conductivity of HBr in relation to NaBr at the same dielectric constant of the solvent results from the higher conductivity of H^+ ions in relation to Na^+ due to the contribution of the proton jump mechanism, which increases with an increase of the water content in mixture. Analogous results were obtained also in *t*-butanol + water mixtures.[1]

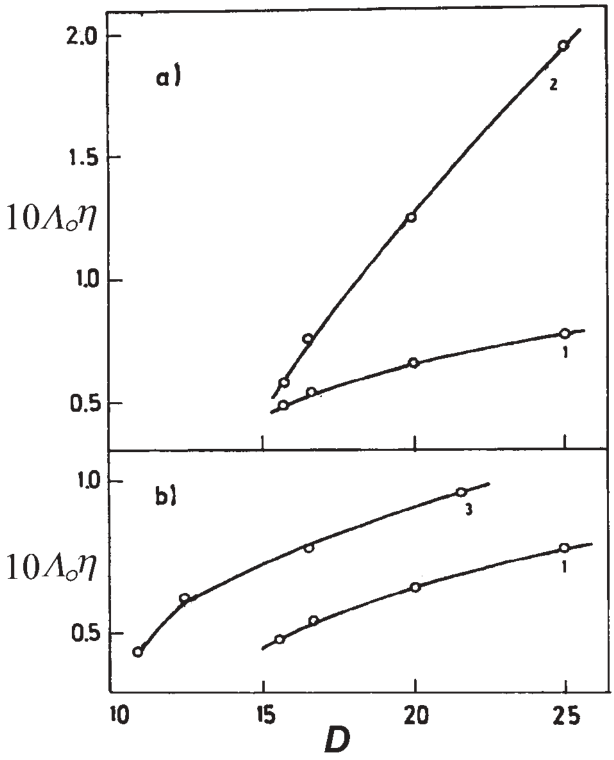

Figure 1. Variation of $\Lambda_0\eta$ with D at 298.15 K for: 1) NaBr in 2-butanol + water; 2) HBr in 2-butanol + water (Ref. 3); 3) NaBr in *t*-butanol + water mixtures (Ref. 1).

The limiting molar conductivity for NaBr in *t*-butanol + water mixtures[1] was lower at the same dielectric constant than that in 2-butanol + water mixtures, whereas the Walden product was higher (Figure 1.b). It is evident that with the same physical properties, expressed by the dielectric constant, there is an influence of the organic component in the mixed solvent.

The association constants (Table III) were slightly higher according to FHFPB than according to LWPB; the same was found in the systems already tested.[1–3] In relation to HBr electrolyte, the constants are considerably higher, which is seen in the diagram log K_A– D^{-1} (Figure 2.a). Accordingly, a cation exchange in the ion-pair will result in a higher degree of association. An analogous occurrence was found also with *t*-butanol + water mixtures.[1] However, we can see in Figure 2.b that the association constants of NaBr electrolyte at the same dielectric constants are higher in 2-butanol + water mixtures than those in *t*-butanol + water mixtures. Evidently, the degree of association at the same dielectric constant is influenced by the nature of the organic component in the mixed solvent.

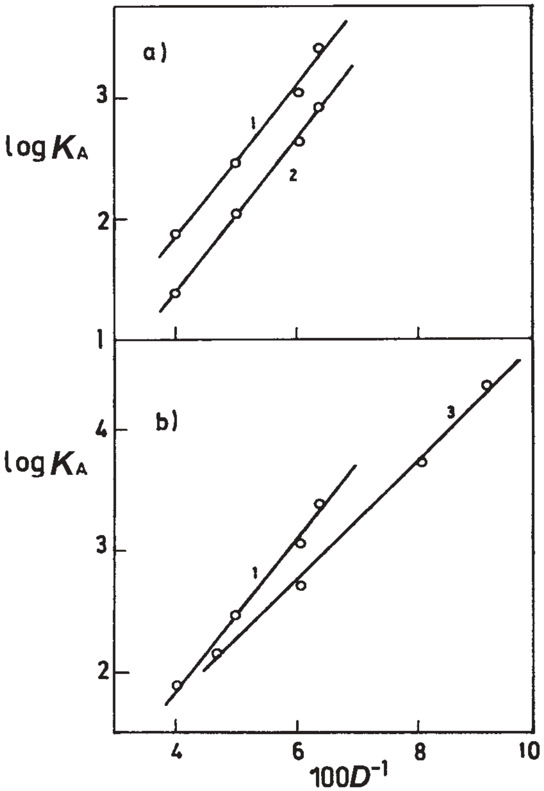

Figure 2. Variation of log K_A (obtained after FHFPB) with D^{-1} at 298.15 K for: 1) NaBr in 2-butanol + water; 2) HBr in 2-butanol + water (Ref. 3); 3) NaBr in *t*-butanol-water mixtures (Ref. 1).

Standard thermodynamic quantities for the association reaction were obtained in the usual way (ΔH^o from diagram ln K_A – $1/T$; ΔG^o and ΔS^o by using known relations). The values at 298.15 K are given in Table IV along with their standard deviations.

The association reaction is therefore endothermic and it results in increased entropy, the more so with a higher content of 2-butanol in the mixture. In comparison with HBr electrolyte in the same mixtures,[3] the endothermicity was found to be more expressed with NaBr in mixtures with a higher content of 2-butanol, and so was the increase in entropy. However, a comparison with the values for NaBr in *t*-butanol+water mixtures shows that at the same dielectric constant there was a higher endothermicity (Figure 3.a) and an increase in entropy (Figure 3.b) with the association reaction in 2-butanol+water mixtures. This again points to the influence of the organic component in the mixed solvent.

TABLE IV

Standard thermodynamic quantities for the ion-association reaction (1) calculated from association constants obtained by the Fuoss-Hsia and Lee-Wheaton equations in *w* mass per cent 2-butanol at 298.15 K

	ΔH^o/kJ mol^{-1}		ΔG^o/kJ mol^{-1}		ΔS^o/J K^{-1} mol^{-1}	
w	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB
70	9.55±0.53	9.90±0.53	–10.81±0.04	–10.59±0.05	68.3±1.8	68.7±1.8
80	10.89±0.35	10.91±0.35	–13.97±0.06	–13.84±0.06	83.4±1.2	83.0±1.2
90	17.56±0.56	17.46±0.54	–17.41±0.02	–17.33±0.03	117.3±1.9	116.7±1.8
95	26.80±0.68	26.75±0.69	–19.44±0.01	–19.39±0.01	155.1±2.3	154.8±2.3

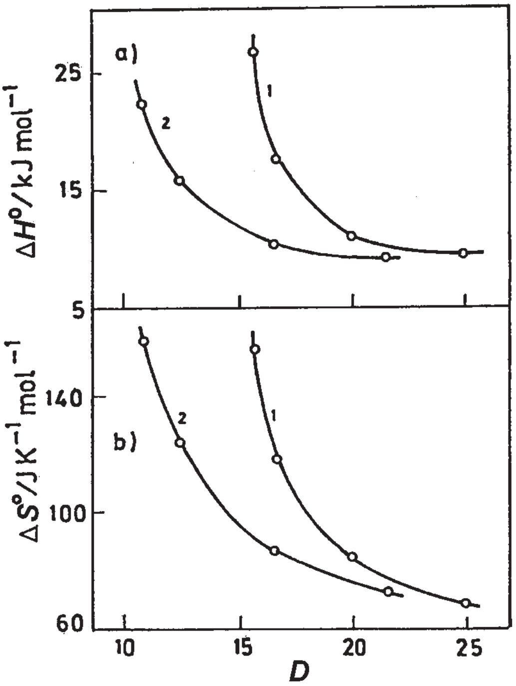

Figure 3. Variation of ΔH^o and ΔS^o with *D* at 298.15 K for NaBr in: 1) 2-butanol + water; 2) *t*-butanol + water mixtures (Ref. 1).

Thus, it can be concluded that the thermodynamics of the association reaction of Na^+ and Br^- ions in the investigated mixtures can be determined successfully by applying both (FHFPB) and (LWPB) equations, although they are based on a different model of ions in the solution, providing that

$R = q$. With a cation exchange in the ion-pair (Na^+ instead of H^+), an increased degree of association will occur also in these mixtures, and in general an increase in reaction endothermicity and increased entropy. The thermodynamic quantities of the association reaction Na^+ and Br^- ions in 2-butanol+ water and *t*-butanol+water mixtures depend on the dielectric constant of the solvent, but, at the same dielectric constants, they depend also on the nature of the organic component in a mixed solvent.

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SAŽETAK

Termodinamika asocijacijske reakcije iona Na^+ i Br^- u 70, 80, 90 i 95%-tnoj smjesi 2-butanol + voda

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Izmjerene su molarne provodnosti elektrolita NaBr u smjesama 2-butanol + voda ($w_{\text{2-butanol}}$= 0,7, 0,8, 0,9, 0,95) u temperaturnom području 288,15 do 308,15 K u intervalima od po 5 K. Obradom dobivenih podataka s pomoću jednadžbi za provodnost Fuoss-Hsia i Lee-Wheaton nije moguće dobiti pouzdanu vrijednost za polumjer nastalih ionskih parova (R). Zato je ponovljena obrada istim jednadžbama uz uvjet da je $R = q_{\text{Bjerrum}}$. Dobivene konstante asocijacije (K_A) s objema jednadžbama pri raznim temperaturama omogućuju izračunavanje standardnih termodinamičkih veličina (ΔH^o i ΔS^o) za reakciju asocijacije. Dobivene termodinamičke veličine, kao i molarna granična provodnost (Λ_o), uspoređene su s analognim literaturnim podacima za elektrolit HBr u istim smjesama, te elektrolit NaBr u smjesama *t*-butanol + voda.