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

I. Tominić, J. Radačić and I. Mekjavić[*]

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

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Molar conductivities of electrolyte NaBr in *tert*-butanol–water mixtures ($w_{t\text{-BuOH}}$ = 0.7, 0.8, 0.9, 0.95) were measured in a temperature range from 288.15 to 308.15 K at 5 K intervals. These data were processed by means of conductivity equations after Fuoss-Hsia and Lee-Wheaton. The obtained values for limiting molar conductivity (Λ_o), association constant (K_A) and distance parameter (R) were compared and discussed. The calculation was repeated for a two-parameter version of these equations with $R = q_{\text{Bjerrum}}$. The obtained association constants at different temperatures were used in determining the standard thermodynamic quantities of the association reaction of Na^+ and Br^- ions. These values were compared with literature data for the association of H^+ and Br^- ions.

INTRODUCTION

In our previous works[1–3] the ion-association of H^+ and Br^- in water–butanol isomer mixtures was investigated employing conductivity measurements and the Fuoss-Hsia and Lee-Wheaton equations. With these equations, however, it was not possible to determine a reliable value for the distance of ions within the formed ion-pair (distance parameter R), while comparable values were obtained for association constant (K_A) on condition that the distance parameter equals Bjerrum distance (q). The thermodynamic quantities of the investigated reaction were obtained from the temperature dependence of K_A, and for this purpose both equations, though based on different models of ions in solution, were successfully applied.

In this work, we studied the association reaction of Na^+ and Br^- ions in water-*tert*-butanol mixtures using similar methods. The aim of these investigations was to determine the suitability of, and conditions for, the application of the cited conduc-

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[*] Author to whom correspondence shoud be addressed.

tivity equations to this system, and also to establish the influence of the cation change on the thermodynamics of the association reaction.

Conductivity measurements of NaBr electrolyte were carried out in 70, 80, 90 and 95 mass per cent *tert*-butanol mixtures in a temperature range from 288.15 to 308.15 K.

EXPERIMENTAL

Solutions of definite molality were prepared by weighing the stock solution of NaBr in a particular mixed solvent and the mixed solvent itself as well. Sodium bromide used (*p.a.* purity, »Kemika«) was previously dried at 105 °C, *tert*-butanol (*p.a.* purity, »Merck«) was distilled, and the water redistilled. Maximum concentration in a particular solvent was limited by the condition that no triple ions should appear.[4]

The apparatus and technique used to carry out conductivity measurements were previously described.[1] 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 *tert*-butanol usually differed by about 0.11, 0.08, 0.06 and 0.04 S cm^2 mol^{-1} from the mean value, respectively.

The values for density, viscosity and dielectric constant of the solvents were taken from our previous work.[1]

RESULTS AND DISCUSSION

Molar conductivities for different molalities of NaBr solutions are listed in Table I. The concentration (c/mol dm^{-3}), relating to Table I, can be determined easily from the molality and density data by means of the relation $c = m \cdot d$.

Conductivity values were analyzed by using two equation, *viz.* Fuoss-Hsia[5] in the Fernández-Prini[6] (FHFP) version

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

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

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

These equations enable calculation of the limiting molar conductivity (Λ_0) for NaBr, the thermodynamic constant (K_A) for association reaction (4)

$$K_A = \frac{1-\alpha}{\frac{c}{c^0}\;\alpha^2 y_\pm^2} \tag{3}$$

$$\underset{c\alpha}{\mathrm{Na}^+} \;+\; \underset{c\alpha}{\mathrm{Br}^-} \;\rightleftharpoons\; \underset{c\,(1-\alpha)}{\mathrm{Na}^+ \cdot \mathrm{Br}^-} \tag{4}$$

and the maximal ion-distance parameter within the formed ion-pair (R).

TABLE I

Molar conductivities ($\Lambda / S\ cm^2\ mol^{-1}$) of NaBr at various molalities in w mass percent tert-*butanol at different temperatues*

$\frac{10^4\ m}{mol\ kg^{-1}}$	288.15	293.15	298.15	303.15	308.15
			w = 70%		
1.6407	12.38	15.34	18.79	22.73	26.94
3.2303	11.99	14.84	18.16	22.05	25.99
5.3537	11.65	14.45	17.60	21.24	25.22
8.0101	11.32	13.98	17.12	20.65	24.42
11.201	10.96	13.65	16.58	19.93	23.78
14.924	10.79	13.46	16.29	19.60	23.20
19.181	10.60	13.09	15.98	19.13	22.60
23.971	10.29	12.74	15.51	18.62	21.97
29.295	10.08	12.54	15.26	18.25	21.58
35.152	9.97	12.31	14.92	17.89	21.15
41.544	9.63	11.90	14.49	17.32	20.52
			w = 80%		
1.2280	9.75	12.27	14.99	18.05	21.87
3.1462	9.10	11.34	13.86	16.94	20.34
4.4375	8.86	10.94	13.47	16.38	19.43
5.9501	8.51	10.65	13.02	15.78	18.89
7.6847	8.44	10.53	12.86	15.56	18.55
9.6404	8.07	10.12	12.27	14.78	17.62
11.818	7.82	9.73	11.89	14.27	17.07
14.216	7.73	9.68	11.63	14.12	16.70
16.837	7.40	9.18	11.20	13.51	16.11
19.678	7.20	8.94	10.88	13.13	15.65
			w = 90%		
0.3500	7.88	9.87	12.07	14.58	17.24
1.0240	6.79	8.56	10.65	12.73	15.00
1.2703	6.62	8.24	10.04	11.92	14.06
1.7603	6.21	7.67	9.42	11.32	13.34
2.3297	5.98	7.39	8.97	10.70	12.66
2.9804	5.69	7.01	8.43	10.09	11.85
3.7103	5.28	6.46	7.87	9.43	11.04
4.5302	5.11	6.24	7.57	8.96	10.47
5.4197	4.85	5.90	7.13	8.49	9.85
6.3898	4.69	5.74	6.90	8.18	9.56
7.4403	4.43	5.49	6.50	7.76	8.99
8.5752	4.24	5.14	6.19	7.33	8.48
			w = 95%		
0.4994	4.82	5.76	6.86	7.73	8.68
0.5000	4.61	5.55	6.59	7.58	8.53
0.9934	3.97	4.72	5.51	6.21	6.90
2.0010	3.29	3.89	4.50	5.10	5.66
2.5981	3.05	3.59	4.13	4.66	5.16
3.1998	2.83	3.30	3.81	4.28	4.75
3.6989	2.62	3.08	3.53	3.96	4.37
4.1999	2.51	2.94	3.36	3.78	4.18
4.6986	2.46	2.87	3.29	3.68	4.07
5.2985	2.33	2.72	3.08	3.47	3.84
5.8296	2.24	2.61	2.97	3.33	3.67

In these expressions, α is the dissociation degree ($\alpha = \Lambda/\Lambda_{c\alpha}$) which represents the relation between the molar conductivity (Λ) and the molar conductivity of free ions ($\Lambda_{c\alpha}$), and $y_\pm$ is the mean activity coefficient of the free ions

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

where $e = 2\kappa q$, $t = \kappa R$; κ is the Debye parameter, and q is the previously mentioned Bjerrum critical distance. Other symbols in these equations have their usual significance.

The parameters (Λ_0, K_A and R) in both equations were calculated by computer optimization after Beronius[9] (FHFPB and LWPB), where Λ_0 and K_A were adjusted for each selected R. Optimization was terminated after obtaining the minimal standard deviation (SD) between the calculated and experimental values for conductivity.

When the standard deviation data are presented in dependence on R, we obtain curves with one or two minima, *i.e.* one or two values respectively for each parameter. According to FHFPB, the curves for 90 and 95 mass per cent *tert*-butanol have ganerally two minima, with R for the first minimum having sometimes an unrealistically low value, while the curves for 70 and 80 mass per cent generally have a single minimum. Again, according to LWPB, all curves exhibit one minimum only, with the value of R generally in agreement with that for the second minimum after FHFPB, although there are cases with unrealistically high values. For 70 mass per cent, however, the values of R after LWPB are about three times lower than those for the curves after FHFPB having only a single minimum. Accordingly, it can be concluded that with these equations, by applying this processing method (three-parameter optimization), it is not possible to obtain a reliable value for the distance parameter. As for the limiting molar conductivities obtained by means of both equations and from both minima, where they exist, their values are found to be in good mutual agreement. Finally, the association constant obtained after FHFPB, when two minima exist, has a lower value for the first minimum. The values for K_A obtained after FHFPB from the single minimum, and from the second minimum, when two of them exist, are comparable to those derived after LWPB. Thus, it can be stated that association constants determined in this way mutually differ to a lesser extent than does the distance parameter; however, these constants cannot be accepted without some uncertainty.

Further processing of the measured values was carried out using both equation (FHFPB and LWPB) on the assumption that the distance parameter is equal to the Bjerrum critical distance ($R = q$). The values obtained for Λ_0 and K_A at different temperatures are given in Table II.

From the table it is seen that the values for Λ_0 are still in very good mutual agreement, while the values for K_A after LWPB are somewhat lower in comparison to those after FHFPB; this difference decreases in percentage with an increase of the *tert*-butanol content in the mixture. Analogous results were also obtained for the HBr electrolyte.[1]

Figure 1 shows the dependence of Λ_0 on the dielectric constant of the solvent (D) at 298.15 K both NaBr and HBr electrolytes.[1]

TABLE II

Λ_0, K_A and SD values obtained for NaBr in w 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	
			w = 70%				
288.15	12.80	12.77	135	123	0.09	0.09	12.50
293.15	15.90	15.86	138	125	0.09	0.10	12.77
298.15	19.49	19.44	148	134	0.12	0.13	13.06
303.15	23.67	23.61	165	150	0.15	0.17	13.36
308.15	28.08	28.01	169	153	0.14	0.16	13.66
			w = 80%				
288.15	10.43	10.40	467	436	0.07	0.07	16.14
293.15	13.09	13.05	495	460	0.11	0.12	16.54
298.15	16.11	16.05	533	495	0.09	0.11	16.95
303.15	19.60	19.53	559	518	0.11	0.11	17.38
308.15	23.74	23.65	622	575	0.13	0.13	17.81
			w = 90%				
288.15	8.73	8.70	4025	3910	0.06	0.06	21.44
293.15	11.11	11.08	4650	4520	0.07	0.07	22.02
298.15	13.88	13.83	5250	5100	0.08	0.07	22.61
303.15	16.83	16.77	5650	5480	0.08	0.09	23.24
308.15	20.15	20.07	6185	5990	0.13	0.12	23.89
			w = 95%				
288.15	6.34	6.31	13610	13330	0.05	0.05	24.38
293.15	8.22	8.18	18130	17750	0.06	0.06	25.09
298.15	10.31	10.25	23080	22590	0.06	0.06	25.83
303.15	12.30	12.23	27110	26510	0.09	0.09	26.60
308.15	14.30	14.21	30930	30210	0.10	0.10	27.24

*Standard deviation about the fitted function.

Increased conductivity of the HBr electrolyte with respect to NaBr results from the higher conductivity of H^+ ion due to the proton jump mechanism whose contribution increases with an increase in *D*, *i.e.* the water content in the mixture.

Figure 2 shows the dependence of K_A, obtained after FHFPB at 298.15 K (Table II), on the dielectric constant of the solvent (plot log K_A versus D^{-1}), together with analogous data for the HBr electrolyte.[1]

It is seen that linear dependence was obtained for both electrolytes; but the values for NaBr are considerably higher than those for HBr, *i.e.* the extent of the association is higher for NaBr than for HBr. This can be seen from the calculated data for the fraction of ion-pair formed in the solutions of the same concentration $c = 5.10^{-4}$ mol dm^{-3} (Table III).

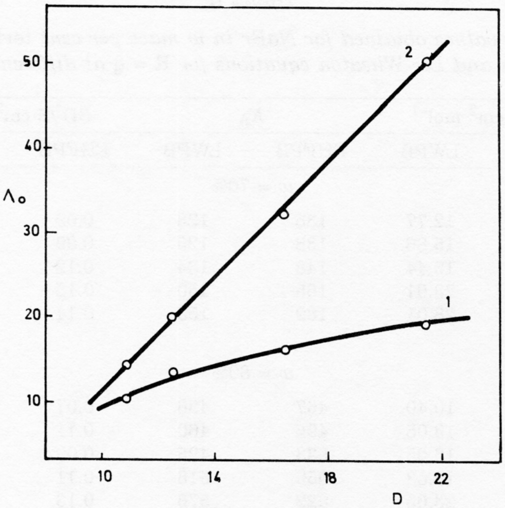

Figure 1. Variation of Λ_0 with D at 298.15 K for NaBr (1) and HBr (2).

The data for K_A at different temperatures (Table II) were used in calculating the standard thermodynamic quantities for the association reaction (4). From the slope of the straight line for ln K_A versus T^{-1}, the quantity δH^o was obtained, while δG^o

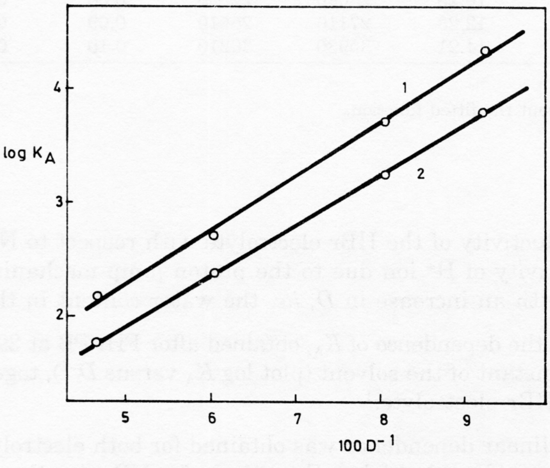

Figure 2. Variation of log K_A (obtained after FHFPB) with D^{-1} at 298.15 K for NaBr (1) and HBr (2).

TABLE III

Fraction ion-pairs formed at c = 5.10^{-4} mol dm^{-3} of different electrolytes calculated from association constants (obtained after FHFPB) in w mass per cent tert-butanol at 298.15 K

Electrolyte	*w*	70%	80%	90%	95%
NaBr		4.9%	13.4%	46.6%	69.5%
HBr[1]		2.0%	2.0%	27.5%	49.6%

and δS^o were calculated by means of the usual relations. The values at 298.15 K are given in Table IV,

The tabulated data show that the standard thermodynamic quantities obtained by means of both equations are in good agreement. The association reaction is endothermic and brings about an increase in entropy, the more so as the *tert*-butanol content in the mixture is increased. The same was also found with the HBr electrolyte,[1] but the values of δH^o and δS^o for NaBr are somewhat lower.

TABLE IV

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

w	δH^o/kJ mol^{-1}		δG^o/kJ mol^{-1}		δS^o/J K^{-1} mol^{-1}	
	FHFPB	LWPB	FHFPB	LWPB	FHFPB	LWPB
70%	9.20	8.95	–12.38	–12.14	72.4	70.7
80%	10.25	9.90	–15.56	–15.38	86.6	84.8
90%	15.61	15.47	–21.23	–21.16	123.6	122.9
95%	22.40	22.26	–24.90	–24.85	158.6	158.0

In conclusion, it can be said that in order to determine the thermodynamics for the ion-association reactions of Na$^+$ and Br$^-$, both equations (FHFPB and LWPB), assuming that $R = q$, can be used satisfactorily. Further, by changing the cation within the ion-pair (Na$^+$ instead of H$^+$), a higher degree of association results, with a slightly less pronounced reaction endothermicity and an increase in entropy. The character of the ion-pair cannot be reliably determined.

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SAŽETAK

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

I. Tominić, J. Radačić i I. Mekjavić

Izmjerene su molarne provodnosti elektrolita NaBr u smjesama *tert*-butanol–voda (ω = 0.7, 0.8, 0.9, 0.95) u temperaturnom području 288.15 do 308.15 K u intervalima od po 5 K. Iz tih podataka su s pomoću jednadžbi za provodnost prema Fuoss-Hsia i Lee-Wheaton dobivene vrijednosti za graničnu molarnu provodnost (Λ_0), konstantu asocijacije (K_A) i polumjer ionskog para (R), koje su međusobno uspoređene i raspravljene. Izračunavanje je ponovljeno za dvoparametarsku verziju tih jednadžbi uz $R = q_{\mathrm{Bjerrum}}$. Tako dobivene konstante asocijacije pri raznim temperaturama poslužile su za izračunavanje standardnih termodinamičkih veličina za reakciju asocijacije iona Na^+ i Br^-. Dobivene vrijednosti uspoređene su s literaturnim podacima za asocijaciju iona Na^+ i Br^-.