CROATICA CHEMICA ACTA
CCACAA **78** (1) 43–47 (2005)

ISSN-0011-1643
CCA-2976
Original Scientific Paper

Thermodynamics of the Association Reaction of Li^+ and Br^- Ions in 2-Butanol + Water Mixtures from Conductivity Measurements

Vesna Sokol,[a,*] Ivo Tominić,[a] Renato Tomaš,[a] and Marija Višić[b]

[a] *Department of Physical Chemistry, Faculty of Chemical Technology, University of Split, Teslina 10, 21000 Split, Croatia*

[b] *Department of Chemistry, Faculty of Natural Sciences, Mathematics and Education, University of Split, Teslina 12, 21000 Split, Croatia*

RECEIVED SEPTEMBER 16, 2003; REVISED APRIL 22, 2004; ACCEPTED JUNE 17, 2004

Keywords
association distance
2-butanol + water mixtures
conductivity
lithium bromide
thermodynamic quantities
Walden product

Molar conductivity of LiBr solutions in 2-butanol + water mixtures ($w_{2\text{-BuOH}}$ = 0.7, 0.8, 0.9, 0.95) was measured at five temperatures in the temperature range from 288.15 to 308.15 K. The limiting molar conductivity (Λ_0), association constant (K_a) and association distance (R) were calculated using the Lee-Wheaton equation. Three-parameter adjustment did not produce uniform values of R. Consequently, the treatment was repeated by the two-parameter version of this equation with R fixed at q (q is Bjerrum's critical distance). The Walden product values, as well as the standard thermodynamic quantities for the association reaction at 298.15 K, were derived from the temperature dependent Λ_0 and K_a, respectively. All quantities obtained are reported and discussed.

INTRODUCTION

Following our investigations of association reactions of electrolytes in mixtures of water and 2-butanol,[1,2] we investigated LiBr in 2-butanol (70, 80, 90 and 95 % (mass fractions, w)) + water mixtures conductometrically in the temperature range from 288.15 to 308.15 K. Information on ion-ion and ion-solvent interactions can be obtained from conductivity measurements. The limiting molar conductivity (Λ_0), association constant (K_a) and association distance (R) were determined using the chemical model of conductivity based on the Lee-Wheaton equation. As the thus obtained R was randomly scattered within a broad range of values, the new sets of Λ_0 and K_a were derived by setting R at q (Bjerrum's critical distance). From the temperature dependence of the association constant, thermodynamic quantities of the association reaction of Li^+ and Br^- ions were calculated. Values of the Walden product ($\Lambda_0\,\eta$) and the limiting molar conductivity (Λ_0) of LiBr solutions were compared with the same quantities for HBr[1] and NaBr[2] in the same mixtures. Also, the influence of the cation change on thermodynamic quantities was discussed.

EXPERIMENTAL

LiBr-hydrate (Merck, *suprapur*) is a mixture of mono- and dihydrate of unknown ratio. Before preparing the LiBr stock solution, the water content in the lithium bromide sample was accurately determined gravimetrically by precipitation with $AgNO_3$ (Merck, *p.a.*) solution (0.1 mol dm^{-3}). 2-butanol

* Author to whom correspondence should be addressed. (E-mail: vsokol@ktf-split.hr)

TABLE I. Relative permittivities (ε_r) of 2-butanol (w/%) + water mixtures at different temperatures [a]

w [b]	ε_r				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
70	26.5	25.7	25.0	24.3	23.5
80	21.2	20.6	20.0	19.4	18.8
90	17.8	17.2	16.6	16.0	15.4
95	17.1	16.4	15.7	15.1	14.5

[a] Values are obtained by interpolation of the literature data.[4]
[b] Mass fractions, $w \times 100$.

(Merck, *p.a.*) was distilled, the first fraction was thrown away, and the middle fraction of the distillate was used to prepare the solutions. Water was redistilled. The solutions at the reported molalities were prepared by adding a weighed amount of the mixed solvent to a weighed amount of the LiBr stock solution. Molality of the stock solution of LiBr did not exceed the maximum concentration permitted,[3] given by the relation $c_{max} = 3.2 \times 10^{-7}\ \varepsilon_r^3$, where ε_r is the relative permittivity. All the measured values were corrected for the conductivity of the solvent. Conductometric values are the result of extrapolation to infinite frequency. To measure the resistance of solutions, two different conductometric cells were used. Solvent density and viscosity were taken from our previous work,[1] while relative permittivities were obtained by interpolation of literature data[4] (Table I). Equipment and the performing technique for conductometric measurements were previously described.[5]

RESULTS AND DISCUSSION

Each molar conductivity given in Table II is the mean value of two cells. The average relative deviation of a single cell value from the mean for 70, 80, 90 and 95 % (w) 2-butanol amounts to 0.7 %, 0.5 %, 0.4 % and 0.3 %, respectively. Concentration of the solutions in Table II can be easily calculated from the molality and density values by means of the expression $c = m\rho$.

The Lee-Wheaton equation,[6] as given by Pethybridge[7] (LWP),

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

was used to analyze the conductometric data. In equation (1) $e = 2\kappa q$, $t = \kappa R$, where κ is Debye's parameter, q is Bjerrum's critical distance, R is the centre-to-centre distance between the ions in the ion-pair formed (distance parameter), while coefficients $C_1 - C_5$ are the functions of t and ln t. The remaining symbols in Eq. (1) have their usual meaning.[5]

Equation LWP was used to calculate the limiting molar conductivity (Λ_0), association constant (K_a) for the association reaction (2) and the association distance (R).

Table II. Molar conductivities (Λ/S cm^2 mol^{-1}) of LiBr at various molalities (m_{LiBr}/mol kg^{-1}) in (w/%) 2-butanol at different temperatures

$10^4 m$	Λ				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			w = 70		
2.9619	14.733	17.640	20.965	24.673	28.684
7.9028	14.182	17.025	20.226	23.719	27.547
12.085	13.763	16.508	19.556	22.904	26.571
17.694	13.512	16.132	19.128	22.381	25.916
22.597	13.305	15.866	18.779	21.996	25.423
27.496	13.015	15.538	18.400	21.494	24.897
32.404	12.827	15.279	18.102	21.123	24.460
37.294	12.675	15.093	17.882	20.868	24.139
42.193	12.541	14.902	17.654	20.614	23.801
47.101	12.371	14.716	17.432	20.332	23.484
52.102	12.222	14.539	17.203	20.100	23.220
56.903	12.140	14.429	17.075	19.949	23.052
62.616	12.005	14.258	16.844	19.656	22.715
			w = 80		
7.9245	11.968	14.359	17.047	20.004	23.315
12.928	11.409	13.669	16.117	19.011	22.070
15.397	11.191	13.386	15.883	18.621	21.583
17.922	10.992	13.134	15.564	18.097	20.997
20.446	10.793	12.887	15.235	17.850	20.744
22.926	10.631	12.727	15.049	17.636	20.449
25.427	10.413	12.430	14.677	17.326	20.031
27.931	10.354	12.329	14.594	17.076	19.784
30.431	10.155	12.179	14.421	16.798	19.544
32.930	10.070	12.046	14.179	16.636	19.140
			w = 90		
3.1523	10.798	12.905	15.173	17.767	20.435
4.6515	10.353	12.232	14.450	16.816	19.357
6.1543	9.957	11.817	13.875	16.092	18.439
7.6499	9.650	11.381	13.376	15.486	17.751
9.1551	9.363	11.021	12.933	14.929	17.084
10.654	9.101	10.743	12.547	14.501	16.503
12.154	8.887	10.448	12.206	14.125	16.056
13.654	8.671	10.236	11.891	13.768	15.724
15.153	8.502	9.999	11.595	13.437	15.315
16.656	8.349	9.815	11.445	13.160	14.992
18.158	8.182	9.585	11.199	12.888	14.674
19.654	8.039	9.459	10.958	12.652	14.350
			w = 95		
2.9685	9.283	10.902	12.606	14.452	16.378
4.0758	8.833	10.286	11.851	13.550	15.246
5.1627	8.384	9.768	11.239	12.780	14.337
6.2710	8.071	9.380	10.772	12.221	13.650
7.3696	7.786	9.013	10.347	11.714	13.077
8.4708	7.539	8.738	9.981	11.306	12.602
9.5702	7.327	8.444	9.655	10.919	12.180
10.696	7.133	8.205	9.389	10.590	11.773
11.783	6.956	8.014	9.137	10.290	11.436
12.870	6.787	7.825	8.894	10.024	11.122
15.070	6.506	7.479	8.516	9.557	10.573
16.171	6.381	7.330	8.331	9.327	10.345
17.271	6.263	7.189	8.159	9.159	10.143

$$\mathrm{Li^+ + Br^- \rightleftharpoons Li^+ \cdot Br^-} \quad (2)$$

$$c\alpha + c\alpha \qquad c(1\text{-}\alpha)$$

$$K_a = \frac{1-\alpha}{(c/c^\circ)\alpha^2 y_\pm^2} \quad (3)$$

In these expressions, α is the degree of dissociation ($\alpha = \Lambda/\Lambda_{c\alpha}$) and represents the ratio of the measured molar conductivity (Λ) to the molar conductivity of free ions ($\Lambda_{c\alpha}$). The mean activity coefficient of free ions, $y_\pm^2$, is given by:

$$y_\pm^2 = \exp(-e/(1+t)) \quad (4)$$

Symbols e and t were previously defined. Parameters Λ_0, K_a and R were calculated by computer optimization according to Beronius,[8] where Λ_0 and K_a were adjusted for each selected value of parameter R. Optimization is finished when the minimal standard deviation ($\sigma^2 = \Sigma(\Lambda_{exp} - \Lambda_{calc})^2/(n-3)$) between the calculated and experimental conductivity values is obtained. Thus, each system gave a unique best set of parameters at each temperature. While the best Λ_0 and K_a showed an expected trend with temperature, this trend for R was quite irregular and covered a broader range of values. In such a situation, the calculation must be repeated by fixing R according to some preselected criterion. Literature offers R set at q or $a + d$. The sum of crystallographic radii of Li^+ and Br^- (a) equals 2.55 Å[9] and the diameter of a water molecule d = 2.80 Å,[5] which makes $a + d$ = 5.35 Å, a value significantly lower than Bjerrum's critical distance q in these media (see Table III). When this is the case, Fuoss[10] suggests that R should be identified with q, the quantity adopted in conductometry as a distance parameter by the efforts of Justice.[11] The values of Λ_0, K_a and σ_Λ (standard deviation of the experimental Λ from the model LWP), obtained by the treatment of our data with R set at q, are given in Table III.

Table III. Λ_0, K_a and σ_Λ values obtained for LiBr in (*w*/%) 2-butanol using the Lee-Wheaton equation with $R = q$ at different temperatures[(a)]

T/K	Λ_o/S cm^2 mol^{-1}	K_a	σ_Λ/S cm^2 mol^{-1}	$R = q$/Å
		w = 70		
288.15	15.45(±0.02)	55.1(±1.0)	0.030	10.94
293.15	18.57(±0.02)	61.4(±0.9)	0.031	11.09
298.15	22.09(±0.03)	64.3(±1.0)	0.039	11.21
303.15	25.99(±0.05)	69.3(±1.4)	0.064	11.34
308.15	30.25(±0.06)	74.2(±1.5)	0.077	11.54
		w = 80		
288.15	13.93(±0.04)	185(±4)	0.026	13.68
293.15	16.75(±0.06)	194(±5)	0.033	13.83
298.15	19.95(±0.09)	206(±6)	0.054	14.01
303.15	23.52(±0.09)	216(±6)	0.053	14.20
308.15	27.58(±0.12)	235(±6)	0.068	14.42
		w = 90		
288.15	12.81(±0.02)	646(±4)	0.013	16.29
293.15	15.41(±0.03)	726(±7)	0.024	16.57
298.15	18.42(±0.04)	822(±8)	0.030	16.88
303.15	21.76(±0.02)	917(±4)	0.015	17.22
308.15	25.37(±0.06)	1022(±9)	0.035	17.60
		w = 95		
288.15	12.12(±0.02)	1522(±9)	0.013	16.95
293.15	14.58(±0.02)	1797(±8)	0.011	17.38
298.15	17.29(±0.02)	2079(±8)	0.011	17.85
303.15	20.44(±0.04)	2461(±11)	0.015	18.25
308.15	23.95(±0.06)	2941(±17)	0.021	18.70

(a) Standard deviation is given in parentheses.

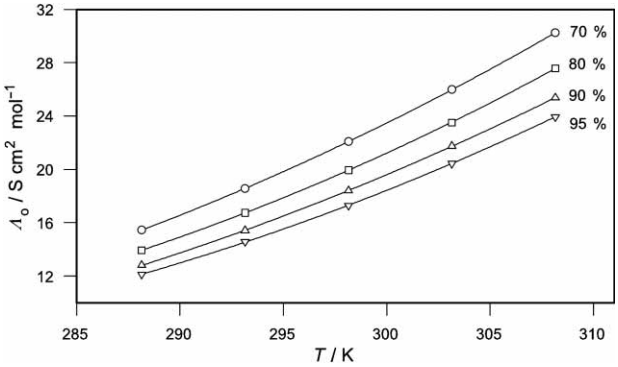

Figure 1. Temperature dependence of Λ_0(LiBr) in 70, 80, 90 and 95 % (*w*) 2-butanol (LWP for $R = q$).

Table IV. Walden product ($10^3\ \Lambda_0\ \eta$ / S cm^2 mol^{-1} Pa s) for LiBr in (*w*/%) 2-butanol at different temperatures

w	$10^3\ \Lambda_0\ \eta$				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
70	75.87	74.89	73.85	72.67	71.87
80	63.28	62.54	61.83	61.32	61.06
90	52.12	51.82	51.78	51.64	51.42
95	47.60	47.68	47.22	47.34	47.09

Figure 1 shows the temperature dependence of the limiting molar conductivity Λ_0 of particular systems. The limiting molar conductivity decreases as the mass fraction of alcohol increases at all temperatures. The increase of Λ_0 with an increase of temperature is due to the decrease of solvent viscosity.

From the dependence of the Walden product $\Lambda_0\eta$ on the solvent composition information can be obtained on ion-solvent interactions. Data from Table IV show that the Walden product dependence on the temperature of lithium bromide is very small (70 and 80 % (*w*) 2-butanol) or almost nonexistent (90 and 95 % (*w*) 2-butanol). Barthel *et al.*[12] measured the conductivity of lithium bro-

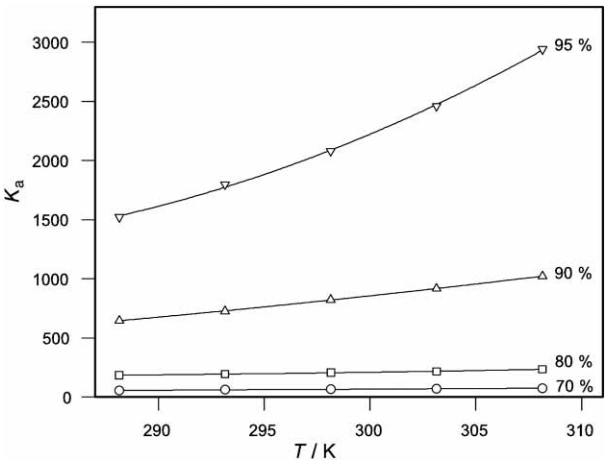

Figure 2. Temperature dependence of the association constant of Li^+ and Br^- ions in different mixtures of 2-butanol (w/%) + water (LWP for $R = q$).

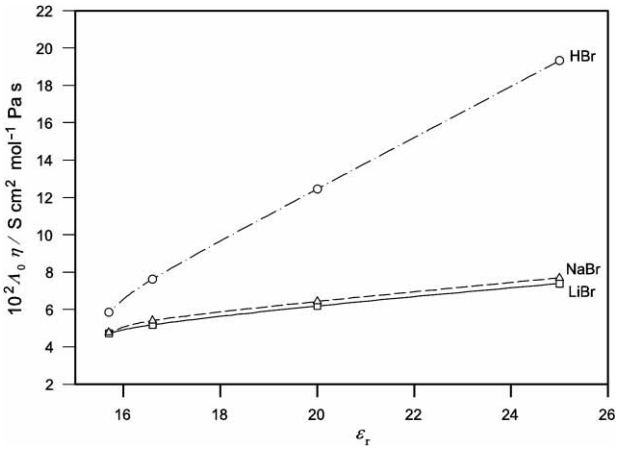

Figure 3. Dependence of the Walden product ($\Lambda_0\eta$) for HBr, NaBr and LiBr on the relative electric permittivity (ε_r) of 2-butanol + water mixtures at 298.15 K.

mide in mixtures of propylene carbonate and acetonitrile ($0 \le w_{PC} \le 1$) in the temperature range from –35 to 75 °C. The results of their investigations also show that Λ_0 increases with an increase in temperature, which is the result of the decrease of solvent viscosity, leading to a Walden product almost independent of temperature.

At constant temperature, the Walden product decreases with increasing alcohol content, which is possibly the consequence of presolvation of ions by alcohol molecules, causing an increase of the hydrodynamic radii of ions and a decrease of their mobility. The same behaviour is shown by HBr[1] and NaBr[2] in the same solvent mixtures.

Figure 2 shows the change of K_a with the increase of temperature. Association constants in 70 and 80 % (w) 2-butanol have similar values, while in 90 and particularly in 95 % (w) 2-butanol, the association constant is considerably higher. Increase of ion association with the increase of alcohol content can be explained in terms of the mixture permittivity decrease. The same behaviour is exhibited by electrolytes HBr[1] and NaBr[2] in the same mixtures. The values of K_a for these three electrolytes retain the relation NaBr > LiBr > HBr at all temperatures.

Standard thermodynamic quantities for the association reaction of Li^+ and Br^- ions are obtained from the temperature dependence of K_a as given in Table III. The standard enthalpy change ($\Delta H°$) was determined from the slope of line ln K_a *versus* 1/T, and the standard Gibbs energy ($\Delta G°$) and entropy ($\Delta S°$) changes were calculated using the known relations $-RT \ln K_a$ and $(\Delta H° - \Delta G°)/T$, respectively. The values of thermodynamic quantities and their standard deviation at 298.15 K are shown in Table V. The association reaction is endothermic. The change in entropy is positive and it increases with the increase of alcohol content in the mixed solvent. The same behaviour was found for HBr[1] and NaBr[2] electrolytes. As the alcohol content increases, quantities $\Delta H°$ and $\Delta S°$ for the three mentioned electrolytes are in the order NaBr > LiBr > HBr, while in 70 % 2-butanol the order is HBr > LiBr > NaBr.

Table V. Standard thermodynamic quantities for the ion-association reaction (2) calculated from association constants obtained by the Lee-Wheaton equation for $R = q$ in (w/%) 2-butanol at 298.15 K[(a)]

w	$\Delta H°$ / J mol^{-1}	$\Delta G°$ / J mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
70	10600(±700)	–10324(±38)	70.2(±2.3)
80	8610(±680)	–13207(±78)	73.2(±2.3)
90	16970(±150)	–16640(±25)	112.7(±0.5)
95	24070(±690)	–18939(±9)	144.3(±2.3)

[(a)] Standard deviation is in parentheses.

From the $\Delta G°$ dependence for the association reactions of LiBr, NaBr and HBr on electric permittivity of 2-butanol + water mixed solvent, one can conclude that the yield of ion pairs increases as alcohol content increases.

Comparing the Walden product and thermodynamic quantities of the association reaction of LiBr with the same quantities for HBr and NaBr in the same mixtures of 2-butanol and water, the influence of the nature of cations on these quantities can be discussed. The values at 298.15 K obtained by the LWP equation for $R = q$ were compared. The values of the Walden product in dependence on the solvent permittivity are shown in Figure 3.

The curve for HBr stands out considerably among the other curves. This is due to the »proton jump« mechanism. The differences of the Walden product between electrolytes diminish with the increase of alcohol content. Although the crystallographic radius of lithium ion is smaller than that of sodium, NaBr shows a larger Walden product than LiBr. The same relation of the Walden product was found for NaBr and LiBr in the mixtures *N*,*N*-di-

methylformamide + water.[13] This indicates the larger hydrodynamic radius of solvated lithium ions.

This work is part of an extensive research program in which, along with the previously investigated HBr[1] and NaBr[2], the behaviour of other alkali bromides in 2-butanol + water mixtures at different temperatures will be investigated. The research will be extended to other mixed solvents in order to get more information about the influence of the organic solvent on the behaviour of the mentioned electrolytes. For this purpose, conductivity measurements of HBr[5,14] and NaBr[15] have already been carried out.

Acknowledgement. – This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia (Project No. 0011008).

REFERENCES

1. I. Tominić and I. Mekjavić, *Croat. Chem. Acta* **64** (1991) 9–18.
2. I. Tominić, V. Sokol, and I. Mekjavić, *Croat. Chem. Acta* **71** (1998) 705–714.
3. R. M. Fuoss and F. Accascina, *Electrolytic Conductance*, Interscience, New York, 1959, p. 253.
4. A. Bald, J. Gregorowicz, and A. Szejgis, *J. Electroanal. Chem*. **340** (1992) 153–167.
5. I. Tominić and I. Mekjavić, *Croat. Chem. Acta* **63** (1990) 27–36.
6. W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. 2* (a) **74** (1978) 743–766, 1456–1482; (b) **75** (1979) 1128– 1145.
7. A. D. Pethybridge and S. S. Taba, *J. Chem. Soc., Faraday Trans. 1* **76** (1980) 368–376.
8. P. Beronius, *Acta. Chem. Scand*., *Ser. A* **28** (1974) 77–82.
9. J. O′M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Vol 1, Mac Donald, London, 1970, p. 64.
10. R. M. Fuoss, *J. Phys. Chem*. **82** (1978) 2427–2440.
11. J. C. Justice, *Electrochim. Acta* **16** (1971) 701–712.
12. J. Barthel, R. Neueder, P. Rawytsch, and H. Roch, *J. Electroanal. Chem*. **471** (1999) 78–87.
13. A. Szejgis, A. Bald, J. Gregorowicz, and C. M. Kinart, *Phys. Chem. Liq*. **34** (1997) 189–199.
14. I. Tominić and I. Mekjavić, *Croat. Chem. Acta* **64** (1991) 189–197.
15. I. Tominić, J. Radačić, and I. Mekjavić, *Croat. Chem. Acta* **67** (1994) 307–314.

SAŽETAK

Termodinamika asocijacijske reakcije iona Li^+ i Br^- u smjesama 2-butanol + voda iz mjerenja provodnosti

Vesna Sokol, Ivo Tominić, Renato Tomaš i Marija Višić

Mjerena je molarna provodnost otopina LiBr u smjesama 2-butanol + voda ($w_{2\text{-BuOH}}$ = 0,7, 0,8, 0,9, 0,95) pri pet temperatura u temperaturnome području od 288,15 do 308,15 K. Granična molarna provodnost (Λ_0), asocijacijska konstanta (K_a) i asocijacijski razmak (R) izračunani su Lee-Wheatonovom jednadžbom. Podešavanje triju parametara nije dalo ujednačene vrijednosti parametra R. Stoga je obrada ponovljena dvoparametarskom verzijom jednadžbe uz $R = q$ (q je Bjerrumov kritični razmak). Vrijednosti Waldenova produkta, kao i standardne termodinamičke veličine za reakciju asocijacije pri 298,15 K, izvedene su iz temperaturne ovisnosti Λ_0, odnosno K_a. Sve su dobivene veličine prikazane i raspravljene.