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Conductometric Study of Hydrobromic Acid in 2-Propanol + Water Mixtures

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Molar conductivity of HBr in 2-propanol + water mixtures, with alcohol mass fractions of 70, 80, 90 and 95 %, was determined at five temperatures in the region from 288.15 to 308.15 K. Data were processed by the Lee-Wheaton conductivity equation, with parameter R set at q (Bjerrum's pairing distance) and the following quantities were obtained: limiting molar conductivity (Λ_0) and activation energy of the ionic movement ($\Delta H^{\ddagger}$), as well as the equilibrium constant (K) and the thermodynamic quantities for the ion-association reaction. Some of these quantities were compared with those obtained earlier for NaBr in the same mixed solvent. Differences in the behaviour of hydrogen and sodium ions were interpreted in terms of their size, as well as solvent basicity, structure, and permittivity.

INTRODUCTION

Thermodynamics of the electrochemical cell, which included silver-silver bromide and hydrogen electrodes, was examined in 70 % (w) 2-propanol[1] assuming complete dissociation of hydrobromic acid. Later literature data in similar systems laid some doubt upon that assumption. Following the report on molar conductivities of NaBr in 2-propanol + water mixtures,[2] we decided to scatter any doubt and, at the same time, to compare qualitatively the behaviour of Na^+ and H_3O^+. For that purpose, conductivities of low-concentration HBr solutions were determined in 2-propanol + water mixtures with alcohol mass fractions, w = 70, 80, 90 and 95 % at five temperatures. Data were processed by the Lee-Wheaton conductivity model with parameter R fixed at Bjerrum's pairing distance q. The obtained equilibrium constant K for the ion-association reaction served to investigate the thermodynamics of this reaction, as well as to re-analyze the potentiometric data in 70 % 2-propanol. The obtained limiting molar conductivity (Λ_0) values were used to evaluate the Walden product and the activation energy $\Delta H^{\ddagger}$ of the ionic movement.

EXPERIMENTAL

Density of 2-propanol + water mixtures was determined at 288.15, 298.15 and 308.15 K using a pycnometer, while the values at 293.15 and 303.15 K were obtained by graphic interpolation. Viscosity was measured at each temperature using an Ostwald viscometer. The relative permittivity of 70,

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TABLE I. Density (ρ_0), viscosity (η) and relative permittivity (ε_r) of 2-propanol + water mixtures at different temperatures[(a)]

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			w = 70 %		
ρ_0 / g cm^{-3}	0.8645	0.8604	0.8563	0.8521	0.8478
$10^3\eta$ / Pa s	4.217	3.471	2.890	2.418	2.054
ε_r	30.48	29.57	28.70	27.84	27.02
			w = 80 %		
ρ_0 / g cm^{-3}	0.8408	0.8368	0.8327	0.8283	0.8238
$10^3\eta$ / Pa s	3.699	3.074	2.580	2.189	1.874
ε_r	25.31	24.51	23.74	23.00	22.28
			w = 90 %		
ρ_0 / g cm^{-3}	0.8169	0.8128	0.8086	0.8043	0.8000
$10^3\eta$ / Pa s	3.116	2.635	2.235	1.922	1.656
ε_r	21.74	21.01	20.31	19.64	18.99
			w = 95 %		
ρ_0 / g cm^{-3}	0.8046	0.8004	0.7962	0.7920	0.7877
$10^3\eta$ / Pa s	2.868	2.441	2.085	1.796	1.563
ε_r	20.34	19.65	18.97	18.30	17.69

[(a)] w is the mass fraction of 2-propanol.

80, 90 and 100 % 2-propanol was evaluated from Åkerlöf's relations,[3] and interpolated graphically for 95 % alcohol. All data are collected in Table I. Standard deviation in the density and viscosity measurements was estimated at 0.01 % and 0.3 % of the reported values, respectively.

Analytical reagent grade 2-propanol (Kemika, Zagreb) was fractionally distilled before use. Preparation and standardization of the water stock solution of HBr has already been described.[4] In order to avoid trace losses while mixing separately the weighed liquid components, each working solution was prepared by weighing, in turn, the stock solution, redistilled water and 2-propanol, all in the same flask. Solution molalities were recalculated according to the real weights, and are given in Table II. The thus introduced solvent composition error was practically negligible: the mean relative deviation of the 2-propanol mass fraction from its declared value was only ±0.01 %.

The resistance of solutions was measured using a Tinsley 4896 conductivity bridge connected with a Levell TG200M RC oscillator and a Tinsley 5710 frequency selective detector amplifier. The cells, calibration, temperature program, frequency range, and extrapolation to infinite frequency were the same as before.[4] Each temperature was maintained within ±0.02 K. Since the solutions were acidic, no correction for solvent conductivity was made.[5]

Molality was converted to molarity through the simple formula $c = m\rho_0$. The error, thus introduced into the highest concentration, was estimated to be about +0.01 %. Care was taken for the highest molarity not to exceed the value given by the expression $c_{\max} = 3.2 \times 10^{-7}\ \varepsilon_r^{\,3}$, at 298.15 K.[6]

Each molar conductivity, as presented in Table II, is the mean value of two cells. The average relative deviation of a single cell value from the mean amounts to ±0.5 % for 70 % 2-propanol, and to ±0.3 % for the other mixtures.

CALCULATIONS

Oppositely charged ions tend to form ion pairs in a medium of low relative permittivity. At constant temperature, free ions and ion pairs are at their equilibrium concentrations $c\alpha$ and $c(1–\alpha)$, respectively. This state is described by the thermodynamic equilibrium constant for the ion-association reaction (K). Since ion pair is a non-conducting entity, the degree of dissociation (α) can be given by the ratio of the molar conductivity of electrolyte (Λ) to that of free ions ($\Lambda_{c\alpha}$). By combining the expressions for K and α, one obtains:

$$\Lambda = \frac{\Lambda_{c\alpha}}{1 + K(c/c^\circ)\alpha y_\pm^2} \tag{1}$$

where c° = 1 mol dm^{-3}. The mean activity coefficient ($y_\pm$)

$$y_\pm = \exp\left(-\frac{\kappa q}{1+\kappa R}\right) \tag{2}$$

refers to the dissociated part of the electrolyte; hence the distance parameter R must be the least distance that two free ions can approach before they merge into an ion pair. Or, in other words, R is the furthest distance of separation of two paired ions. The parameters κ and q are related by:

TABLE II. Molar conductivities (Λ / S cm^2 mol^{-1}) of HBr in 2-propanol + water mixtures at various molalities (m) (a)

$10^4\ m$ / mol kg^{-1}	Λ / S cm^2 mol^{-1}				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
w = 70 %					
4.6515	45.04	53.24	62.28	72.31	82.95
5.8099	44.93	53.13	62.04	72.14	82.67
6.9775	44.52	52.57	61.52	71.42	81.89
8.1285	44.50	52.50	61.53	71.36	81.75
10.4592	44.38	52.43	61.34	71.19	81.55
12.7875	44.09	51.98	60.83	70.59	80.77
15.1078	43.89	51.77	60.60	70.19	80.51
17.4321	43.66	51.51	60.23	69.99	80.08
19.7571	43.72	51.65	60.32	70.04	80.18
22.0821	43.68	51.58	60.29	69.78	79.95
24.4117	43.55	51.38	60.03	69.55	79.64
w = 80 %					
4.7775	32.97	38.82	45.42	52.63	60.54
5.9681	32.69	38.51	45.07	52.27	60.06
5.9703	32.78	38.59	45.09	52.33	60.04
7.1654	32.58	38.31	44.87	52.00	59.75
8.3694	32.32	38.03	44.38	51.53	59.19
10.7537	32.20	37.89	44.14	51.32	58.87
13.1478	31.75	37.34	43.53	50.56	58.08
20.3231	31.15	36.65	42.75	49.59	56.79
22.0883	31.03	36.51	42.50	49.29	56.49
23.8834	30.86	36.26	42.28	48.96	56.12
w = 90 %					
4.9264	23.25	27.19	31.66	36.58	41.93
6.1508	23.00	26.91	31.38	36.18	41.44
7.3747	22.77	26.63	30.97	35.78	40.94
8.6130	22.62	26.45	30.79	35.52	40.66
10.4557	22.36	26.15	30.38	35.05	40.12
11.8292	22.21	25.93	30.16	34.74	39.73
14.7784	21.80	25.45	29.57	34.05	38.89
17.2200	21.60	25.20	29.20	33.69	38.46
19.6867	21.45	24.97	29.00	33.38	38.08
22.1361	21.19	24.70	28.62	32.90	37.55
24.6226	21.04	24.50	28.37	32.66	37.19
w = 95 %					
3.7453	19.51	22.76	26.41	30.48	34.97
3.7487	19.47	22.70	26.39	30.42	34.88
4.9970	19.03	22.17	25.72	29.62	33.91
6.2386	18.82	21.91	25.45	29.16	33.47
7.5695	18.62	21.69	25.12	28.92	33.07
7.5711	18.56	21.65	25.08	28.87	32.99
10.0014	18.19	21.18	24.49	28.13	32.09
12.4846	17.85	20.74	23.98	27.50	31.33
14.9831	17.57	20.40	23.57	27.00	30.72
17.5068	17.36	20.13	23.22	26.61	30.26
20.0088	17.06	19.80	22.84	26.12	29.66
22.5095	16.86	19.56	22.55	25.78	29.25
24.9881	16.69	19.33	22.27	25.43	28.84

(a) w is the mass fraction of 2-propanol; at each temperature, molarity is related to the reported molality by the expression: $c = m\,\rho_0$.

$$\kappa^2 = 16000\ \pi N_A\, qc\alpha \qquad (3)$$

$$q = \frac{e^2}{8\pi\varepsilon_0\varepsilon_r kT} \qquad (4)$$

If it is assumed that the dissociated part of a weak electrolyte acts like a hypothetic completely dissociated strong electrolyte of the same type, $\Lambda_{c\alpha}$ in Eq. (1) can be replaced by any theoretical equation for conductivity in order to make Eq. (1) a conductivity model. The model founded on the Lee-Wheaton equation,

$$\Lambda_{c\alpha} = \Lambda_0\,[1 + C_1\beta\kappa + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\rho\kappa}{1+\kappa R}\left[1 + C_4\beta\kappa + C_5(\beta\kappa)^2 + \frac{\kappa R}{12}\right] \qquad (5)$$

with coefficients C_1–C_5, as given by Pethybridge and Taba[7] (model LWP), was used in this work. Λ_0 is the molar conductivity at infinite dilution and $\beta = 2\,q$. Other symbols in Eqs. (3) – (5) are either defined in the cited literature or have their usual significance.

The model was considered as a non-linear function of three parameters, $\Lambda = \Lambda(\Lambda_0, K, R)$, and was resolved by an iterative procedure. A broader range of R was scanned by a series of successive steps of definite size (usually 100 pm). For each step, the parameters Λ_0 and K are obtained at the end of a sequence of alternating linearizations and least-square optimizations of the model (the Gauss-Seidel method[8a]), when Λ_0 satisfies the criterion for convergence. In a row of three-parameter sets, the »best« is the one by which the model is best fitted to experimental data, *i.e.*, the minimal standard deviation ($\sigma(\Lambda)$) is attained. The step size is then lowered by an order of magnitude, and the search is continued in the region around the »best« R. This procedure is repeated until the final »best triplet« of parameters (Λ_0, K, R) is established when the step size equals 0.1 pm.

All »best triplets« mainly comprised an acceptable Λ_0 and a K, but R exhibited its well-known scatter. Uniform values of parameter R over the whole temperature range were obtained for HBr only in the mixture with w (2-propanol) = 95 % (450–590 pm). In 70 % 2-propanol, the LWP model yielded an extremely low R (about 10 pm) and a negative K, both without physical meaning. In other systems, the »best« distance parameter R covered a wide range of values. Thus, in 80 % 2-propanol, they ranged from 250 to 1780 pm, showing quite an irregular trend with the temperature – an abrupt rise followed by a sudden fall.

When the three-parameter fit fails, the distance parameter R must be fixed at some arbitrarily chosen value. There are two criteria for the choice of such a value. According to the chemical model of electrolyte solutions, two paired ions of the crystallographic radii a_+ and a_- may be either in contact ($R = a$, where $a = a_+ + a_-$) or separated by one or more solvent molecules – the molecular diameter d is approximated by the length of an orientated molecule.[9] According to Bjerrum's physical concept of ionic association, the upper limit of integration for K is q (Eq. 4). This quantity was adopted in conductometry as the distance parameter, $R = q$, by the efforts of Justice.[10]

Sum of the radii of H_3O^+ and Br^- ions can be fixed at 475 pm,[4] and $d(H_2O)$ can be taken to be 280 pm, which makes $a + d = 755$ pm, a value lower than q in these media (see Table III). In such a case, Fuoss[11] recommends that R should be identified with q »to allow for the longer range of Coulomb forces in solvents of lower dielectric constant«. Values of the limiting molar conductivity (Λ_0), ion-association constant (K), and standard deviation of experimental Λ from the model (σ_Λ), obtained by data treatment with R set at q, are shown in Table III. Standard deviations of Λ_0 and K were estimated as suggested in the literature.[8b]

The standard enthalpy of the ion-association reaction (ΔH°) and Eyring's enthalpy of activation of the charge transport[9] ($\Delta H^\ddagger$) were evaluated by the least-squares treatment of the following straight lines:

$$\ln K = -\Delta H^\circ/RT + C \qquad (6)$$

$$\ln \Lambda_0 + 2/3\ \ln \rho_0 = -\Delta H^\ddagger/RT + C \qquad (7)$$

The standard deviation of each enthalpy was derived from the standard deviation of the corresponding slope.[12a] The standard entropy of ion-pair formation is a linear combination of two variables:

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \qquad (8)$$

and its standard deviation can be obtained accordingly.[12b] The standard deviation of the reaction Gibbs' energy had to be estimated previously by linearization[12b] of the relationship:

$$\Delta G^\circ = -RT \ln K \qquad (9)$$

Results of the calculation with Eqs. (6) – (9) at 298.15 K are gathered in Table IV.

RESULTS AND DISCUSSION

Standard potentials (E°_m) of the electrode Ag|AgBr in 70 % 2-propanol have been determined assuming complete dissociation of HBr.[1] Repeated mathematical treatment of the potentiometric data at 298.15 K, using $K = 4.4$ from Table III, has shown that the ion-pair mole fraction in end solutions of the set (0.003 and 0.1 mol kg^{-1}) is 0.7 % and 6.1 %, respectively. The resulting new value for E°_m was by five tenths of a millivolt lower than the old one. The differences found at the other two temperatures were also too small to influence the discussion.[1]

TABLE III. Λ_0, K, and σ_Λ for HBr in 2-propanol + water mixtures obtained at different temperatures with $R = q$[(a)]

T / K	Λ_0 / S cm^2 mol^{-1}	K	σ_Λ / S cm^2 mol^{-1}	$R = q$ / pm
		w = 70 %		
288.15	46.33 (±0.09)	2.7 (±2.1)	0.11	951
293.15	54.77 (±0.13)	3.4 (±2.7)	0.17	964
298.15	64.16 (±0.13)	4.4 (±2.2)	0.16	976
303.15	74.61 (±0.14)	6.2 (±2.2)	0.18	990
308.15	85.61 (±0.17)	7.2 (±2.3)	0.21	1003
		w = 80 %		
288.15	34.67 (±0.05)	33.1 (±2.0)	0.06	1145
293.15	40.86 (±0.06)	34.9 (±2.1)	0.07	1163
298.15	47.90 (±0.07)	40.3 (±2.1)	0.09	1180
303.15	55.63 (±0.08)	41.0 (±2.2)	0.10	1198
308.15	64.05 (±0.07)	45.3 (±1.7)	0.09	1217
		w = 90 %		
288.15	25.07 (±0.03)	74.4 (±2.0)	0.03	1334
293.15	29.43 (±0.03)	83.4 (±1.6)	0.03	1356
298.15	34.43 (±0.05)	94.4 (±2.3)	0.05	1380
303.15	39.86 (±0.05)	102.0 (±2.0)	0.05	1403
308.15	45.85 (±0.06)	113.3 (±2.2)	0.06	1428
		w = 95 %		
288.15	21.16 (±0.04)	136.2 (±4.0)	0.06	1425
293.15	24.77 (±0.05)	150.6 (±4.0)	0.06	1450
298.15	28.88 (±0.06)	168.3 (±4.0)	0.07	1477
303.15	33.44 (±0.08)	189.1 (±5.2)	0.10	1506
308.15	38.59 (±0.09)	218.1 (±5.4)	0.11	1533

[(a)] Standard deviation is in the parentheses; w is the mass fraction of 2-propanol.

It is seen from Figure 1 that the Walden product $\Lambda_0\eta$ for HBr is slightly temperature dependent (in 95 % 2-propanol there is no dependence at all) and steeply descends with increasing 2-propanol concentration in the mixture. Decrease of the Walden product for NaBr can be ascribed to the steadily elongating hydrodynamic radius of the cation. Namely, it is known that the mixed-solvent basicity increases with gradual addition of alcohol to water, and the solvation of the cation (Na^+) becomes more intensive accordingly. At the same time, the solvent structure weakens and the molecules are more easily attracted to secondary solvation shells. Solvation of the anion (Br^-) would have an opposite trend, but, as the anion is usually larger ($a(Br^-) / a(Na^+) = 2.0$), it is too feeble to compensate for the cationic effects. For HBr, one would expect these effects to be more pronounced and its isotherm to be positioned beneath that of NaBr. The real position of the curves is quite opposite (Figure 1) be-

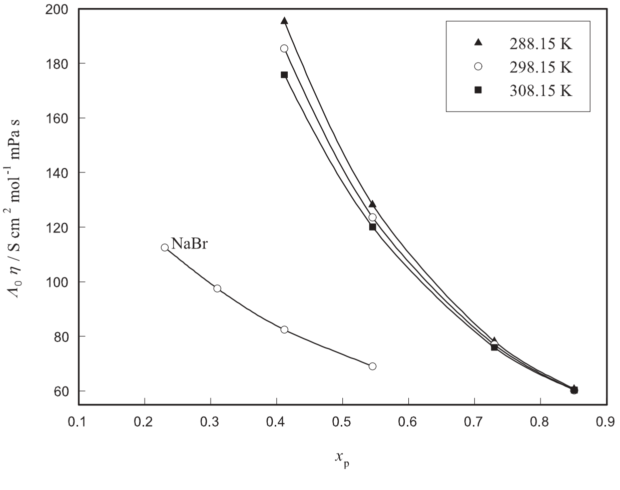

Figure 1. Dependence of the Walden product for HBr on the mole fraction of 2-propanol in the mixture (x_p). The curve for NaBr[2] is shown for comparison.

TABLE IV. Standard thermodynamic quantities of the ion-association reaction (ΔG°, ΔH° and ΔS°) and activation energy of the ionic movement ($\Delta H^\ddagger$) for HBr in 2-propanol + water mixtures at 298.15 K [(a)]

w / %	ΔG° / J mol^{-1}	ΔH° / kJ mol^{-1}	ΔS° / J K^{-1} mol^{-1}	$\Delta H^\ddagger$ / J mol^{-1}
70	–3680 (±1300)	37.4 (±2.2)	137.7 (±8.6)	22230 (±240)
80	–9160 (±130)	11.6 (±1.4)	69.6 (±4.6)	22190 (±160)
90	–11270 (±60)	15.4 (±0.5)	89.5 (±1.8)	21790 (±130)
95	–12710 (±60)	17.2 (±0.9)	100.4 (±2.9)	21660 (±30)

[(a)] Standard deviation is in parentheses; w is the mass fraction of 2-propanol.

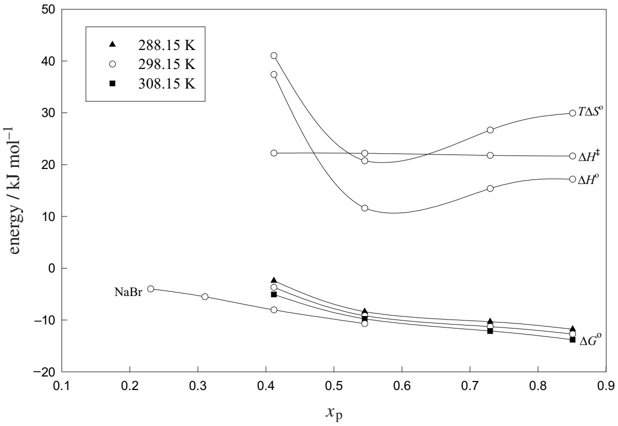

Figure 2. Dependence of the thermodynamic quantities of the ion-association reaction and the activation energy of the ionic movement for HBr on the mole fraction of 2-propanol in the mixture (x_p). The ΔG°(NaBr)[2] is shown for comparison.

cause besides its migratory capability, the conductance of H_3O^+ is significantly affected by the so-called »proton-jumping«.

If hydrogen ion is really solvated more strongly than Na^+, hydrobromic acid would be less inclined to associate than sodium bromide. This is confirmed by the order of the reaction Gibbs' energies (ΔG°) in Figure 2. With alcohol enrichment, the association equilibrium is shifted toward ion pairs owing to the decrease of medium permittivity. With increasing temperature the reaction becomes more exergonic, in accordance with its endothermity ($\Delta H^\circ > 0$). The entropy term ($T\Delta S^\circ$) dominates over association and its change with solvent composition is far from the monotony of the ΔG° curve. This points to considerable structural effects, which most probably result from the competition of two processes: breaking of the solvation layer and building-up of the bulk solvent. Since ΔS° is positive throughout, the former prevails and hydrobromic acid may be recognized as a structure-maker in these media.

The activation energy $\Delta H^\ddagger$ of the ionic movement shows a hardly noticeable decrease with increasing 2-propanol mole fraction. If the temperature-dependent conductances of NaBr were reported, it could be interesting to check the $\Delta H^\ddagger$ independence of solute properties.[9]

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SAŽETAK

Konduktometrijski studij bromidne kiseline u smjesama 2-propanol + voda

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Molarna provodnost HBr u smjesama 2-propanol + voda, sa 70, 80, 90 i 95 % masenih udjela alkohola, određena je pri pet temperatura u području od 288,15 K do 308,15 K. Podaci su obrađeni jednadžbom Lee-Wheaton (uz parametar R izjednačen s Bjerrumovim razmakom q) i dobivene su sljedeće veličine: granična molarna provodnost (Λ_0) i aktivacijska energija ionskog gibanja ($\Delta H^{\ddagger}$), te ravnotežna konstanta (K) i termodinamičke veličine za reakciju ionske asocijacije. Neke od tih veličina uspoređene su s onima za NaBr u istom miješanom otapalu. Razlike u ponašanju vodikovoga i natrijevoga iona protumačene su kako njihovom veličinom, tako i bazičnošću, strukturom i permitivnošću otapala.