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Standard Potentials of Silver-Silver Bromide Electrode and Thermodynamic Quantities of Hydrobromic Acid in 90 and 95 Mass per Cent 2-Methyl-1-propanol-Water Mixtures*

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The e.m.f. of the cell: Pt (or Pd), H_2 (g)/HBr (m), 90 and 95 mass per cent 2-methyl-1-propanol-water mixture/AgBr, Ag was measured at 288.15, 298,15 and 308.15 K in the HBr molality range 0.003—0.1 mol kg^{-1}. These data together with the values for the ion-pair dissociation constant of $H^+ \cdot Br^-$ were used to determine the standard e.m.f. of the cell at each temperature. The ion-pair dissociation constants of $H^+ \cdot Br^-$ were determined on the basis of conductivity measurements. The standard e.m.f. of the cell were used to calculate the standard thermodynamic quantities for the cell reaction, mean activity coefficients of HBr and standard thermodynamic quantities for HBr transfer from water to the examined mixed solvents. Standard thermodynamic quantities for the association reaction were calculated from the ion-association constants which are reciprocal values of the ion-pair dissociation constants. The standard thermodynamic quantities of transfer are compared with those of other alcohol-water mixtures while those of association reaction are compared with theoretically predicted values.

INTRODUCTION

Thermodynamic behaviour of hydrobromic acid in mixed solvents has long been a subject of interest. The aim of our investigations was to find out thermodynamic properties of hydrobromic acid in alcohol-water mixtures and, as the continuation of these studies,[1-3] this paper reports the results of investigations in 90 and 95 mass per cent 2-methyl-1-propanol-water mixtures. This alcohol has a limited solubility in water; thus from 8 to cca 83 mass per cent at 298 K there is a two-phase system.

Thermodynamic quantities are determined by measuring e.m.f. and conductivity. The e.m.f. of the cell: Pt(or Pd), H_2(g)/HBr(m), solvent/AgBr, Ag was measured in the temperature range from 288.15 to 308.15 K for different molalities (m) of HBr. From these data, as well as from values of the dissociation constant of ion-pairs $H^+ \cdot Br^-$, the standard potentials of the cell or of the Ag/AgBr electrode were determined. Namely, the studied solvents

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have a low dielectric constant (D $\leqslant$ 20), causing the association of oppositely charged ions to form ion-pairs $H^+ \cdot Br^-$, and hydrobromic acid behaves as a weak electrolyte. The ion-pair dissociation constants and their reciprocals, the ion-association constants, were determined by means of conductivity measurements in the same temperature range.

Standard potentials and their temperature dependence served to calculate the mean activity coefficients of HBr, thermodynamic quantities for the cell reaction and for the transfer of HBr, while thermodynamic quantities for the reaction of ion-association were computed from the ion-association constants and their temperature dependence.

EXPERIMENTAL

The solutions were prepared by weighing the water stock solution of HBr, 2-methyl-1-propanol (p. a. purity »Merck«) and redistilled water. The stock solution was prepared from redistilled water and HBr (p. a. purity »Kemika«), distilled before use. The preparation of the electrodes (Ag/AgBr, Pt and Pd), cell and experimental procedure were described earlier[1]. The e.m.f. was measured at temperatures 298.15, 288.15, 308.15 and again at 298.15 K by type K-4 Leeds and Northrup potentiometer with a 9828 D. C. null detector. For each molality of HBr two cells were used: one with Pt, and the other with Pd electrode.

The densities of the solvent mixtures were determined by the picnometer, the vapour pressures were estimated by Raoult's law, the dielectric constants were determined by using a WTW dipolmeter type DM 01, and coefficients of viscosity by the Ostwald viscometer.

In order to prepare the solutions intended for conductivity measurements, 2-methyl-1-propanol (p. a. purity »Merck«) had been distilled before and the mean fraction taken. Measurements were carried out by means of a Tinsley conductivity bridge type 4896 with the use of a Levell R. C. oscillator type TG200M and a Tinsley frequency selective detector amplifier type 5710. The measurements were made with 0.7, 1, 2 and 4 kHz frequencies. Plots of resistance versus reciprocal frequency were rectilinear and could easily be extrapolated to infinite frequency. This extrapolated resistance was used to calculate the conductivity of the solution. Correction was made for the conductivity of the pure mixed solvent. For each molality of HBr two cells with electrodes of bright platinum with the constants 0.1589 cm^{-1} and 0.4207 cm^{-1}, respectively, were used. The callibration of the cell was carried out by means of the potassium chloride water solution, whose conductivity was taken from literature[4].

RESULTS AND DISCUSSION

The mean values for e.m.f., corrected to 101.325 kPa hydrogen pressure, of two parallel cells are listed in Table I. The accuracy of these values for 90 and 95 mass per cent 2-methyl-1-propanol is ± 0.07 and ± 0.09 mV, respectively.

Standard Electrode Potentials

The standard e.m.f. of the cell, namely, the standard potential $E_m{}^0$ of the Ag/AgBr electrode, can be obtained using the Nernst equation:

$$E = E_m{}^{\circ} - 2k \log (m\gamma_{\pm} / m^{\circ}) = E_m{}^{\circ} - 2k \log (\alpha m\gamma'_{\pm} / m^{\circ}) \tag{1}$$

where: E is the corrected e.m.f. of the cell, $k = (RT/F)\ln 10$, $\gamma_{\mp}$ is the mean activity coefficient of HBr at molality m, $m^0 = 1$ mol kg^{-1}, α the degree of dissociation of $H^+ \cdot Br^-$, $\gamma'_{\pm}$ is the real mean activity coefficient for ionized HBr at molality αm.

TABLE I

Electromotive Force E/V *of the Cell Pt (or Pd),* H_2 *(g, 101.325 kPa)/HBr* (m) *in x Mass per Cent 2-Methyl-1-propanol/AgBr, Ag from 288.15 to 308.15 K*

m mol kg^{-1}	$x = 90$			$x = 95$		
	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K
0.003	0.23644	0.22925	0.22073	0.20523	0.19570	0.18442
0.005	0.21751	0.21008	0.20133	0.18659	0.17651	0.16534
0.007	0.20578	0.19801	0.18878	0.17442	0.16424	0.15295
0.009	0.19570	0.18786	0.17881	0.16590	0.15554	0.14428
0.012	0.18665	0.17850	0.16911	0.15604	0.14564	0.13433
0.015	0.17847	0.17034	0.16099	0.14845	0.13810	0.12650
0.025	0.16063	0.15236	0.14285	0.13129	0.12057	0.10912
0.04	0.14525	0.13689	0.12705	0.11597	0.10525	0.09375
0.06	0.13258	0.12370	0.11396	0.10271	0.09189	0.08025
0.08	0.12250	0.11364	0.10357	0.09273	0.08186	0.07030
0.1	0.11485	0.10564	0.09547	0.08466	0.07361	0.06211

By interpolating the expression for the real mean activity coefficient of ionized HBr into the equation (1), and after rearrangement the relation (2) is obtained from which E_m^o can be determined by extrapolation to $am = 0$.

$$E' = E + 2k \log (am/m^o) - \frac{2kA\,(dam)^{1/2}}{1 + aB\,(dam)^{1/2}} - 2k \log (1 + 2amM) +$$

$$\frac{2k\,(Ext)}{\ln 10} = E_m^{\,o} - 2kbam/m^o \qquad (2)$$

A and B in the above expression are Debye-Hückel constants, d is the solvent density, a is the ion-size parameter (taken as 0.5 nm), M is the mean molar mass of the solvent, (Ext) are Debye-Hückel extended terms, and b is an interaction parameter.

The data necessary to compute some terms of E' are given in Table II, the term with (Ext) was calculated by means of the data from literature,[5,6]

TABLE II

Parameters Necessary for the Evaluation of E′ *of Equation (2) in x Mass per Cent 2-Methyl-1-propanol at Different Temperatures*

T/K	288.15	298.15	308.15
	$x = 90$ ($M = 0.0564$ kg mol^{-1})		
P/kPa	1.11	2.12	3.85
d/g cm^3	0.8271	0.8185	0.8093
D_s	20.0	18.7	17.6
$10^3\,\eta$/Pas	4.421	3.119	2.272
	$x = 95$ ($M = 0.0640$ kg mol^{-1})		
P/kPa	1.00	1.89	3.49
d/g cm^3	0.8169	0.8087	0.7999
D_s	19.3	18.1	16.8
$10^3\,\eta$/Pas	4.388	3.130	2.287

while α was obtained by the method of successive approximation from the thermodynamic ion-pair dissociation constant (K_D') of $H^+ \cdot Br^-$.

The values for E_m^0 were obtained by the method of least squares and together with standard errors are presented in Table III. In the same table are the values for the standard potential E_x^0, expressed on the mol fraction scale, calculated from E_m^0 by means of the known relation.

TABLE III

Standard Potential of the Ag/AgBr *Electrode in* x *Mass per Cent 2-Methyl-1--propanol at Various Temperatures*

T/K	E_m°/V	E_x°/V	σ/V
	$x = 90$		
288.15	—0.0791	—0.2219	±0.0004
298.15	—0.0997	—0.2474	±0.0004
308.15	—0.1217	—0.2744	±0.0004
	$x = 95$		
288.15	—0.1135	—0.2500	±0.0002
298.15	—0.1371	—0.2783	±0.0003
308.15	—0.1633	—0.3093	±0.0004

The values for E_x^0 from Table III can be expressed in dependence upon temperature in the range from 288.15 to 308.15 K by the following relations:
(a) 90 mass per cent 2-methyl-1-propanol

$$E_x^\circ/V = -0.1314 + 18.47 \times 10^{-4}\ T/K - 7.5 \times 10^{-6}\ T^2/K^2 \tag{3}$$

(b) 95 mass per cent 2-methyl-1-propanol

$$E_x^\circ/V = -0.5943 + 50.85 \times 10^{-4}\ T/K - 13.5 \times 10^{-6}\ T^2/K^2 \tag{4}$$

The ion-pair dissociation constants of $H^+ \cdot Br^-$ were determined on the basis of conductivity measurements. Table IV gives the mean values for the molar conductivity of HBr from two parallel measurements. The accuracy of these values for 90 and 95 mass per cent 2-methyl-1-propanol is ± 0.04 and ± 0.02 S cm^2 mol^{-1}, respectively.

From these data the preliminary value of the molar conductivity at infinite dilution (Λ_o) was first determined from intercept at $\Lambda c = 0$ of the straight-line part of curve Λ^{-1} vs Λc. This value was used then to determine a beter value for Λ_o and for the ion-pair dissociation constant of $H^+ \cdot Br^-$ through a successive approximation procedure using the Shedlovsky equation.[7,8]

The values for Λ_o, thermodynamic ion-pair dissociation constants K_D (on the molar scale) and K_D' (on the molal scale) with their corresponding standard errors are listed in Table V. The thermodynamic constant K_D' was obtained from K_D using equation $K_D' = K_D/d$.

TABLE IV

Molar Conductivities of HBr at Various Concentrations in x Mass per Cent 2-Methyl-1-propanol at 288.15, 298.15 and 308.15 K

288.15 K		298.15 K		308.15 K	
1000 C mol l^{-1}	Λ S cm^2 mol^{-1}	1000 C mol l^{-1}	Λ S cm^2 mol^{-1}	1000 C mol l^{-1}	Λ S cm^2 mol^{-1}
		$x = 90$			
0.503	16.15	0.497	22.32	0.492	29.66
0.603	16.00	0.597	22.08	0.590	29.44
0.804	15.86	0.796	21.77	0.787	28.97
1.005	15.34	0.995	21.08	0.983	27.90
1.508	14.95	1.492	20.44	1.475	26.94
2.010	14.52	1.990	19.80	1.967	26.00
2.513	14.14	2.487	19.19	2.459	25.16
3.016	13.83	2.984	18.79	2.951	24.56
3.518	13.48	3.482	18.25	3.443	23.79
4.332	13.11	4.278	17.71	4.229	23.05
		$x = 95$			
0.503	11.92	0.497	16.35	0.492	21.70
0.603	11.69	0.597	16.05	0.590	21.20
0.804	11.53	0.796	15.73	0.787	20.75
1.005	11.26	0.995	15.32	0.984	20.17
1.508	10.75	1.492	14.56	1.476	19.02
2.010	10.38	1.990	13.96	1.968	18.15
2.513	10.04	2.487	13.48	2.460	17.45
3.015	9.75	2.985	13.07	2.952	16.85
3.518	9.51	3.482	12.72	3.444	16.35

TABLE V

Limiting Molar Conductivities Λ_0 and Ion-Pair Dissociation Constants K_D and K_D' for $H^+ \cdot Br^-$ in x Mass per Cent 2-Methyl-1-propanod at Different Temperatures

T/K	Λ_0/S cm^2mol^{-1}	1000 K_D/mol l^{-1}	1000 K_D'/mol kg^{1-}
		$x = 90$	
288.15	17.92 ± 0.10	10.45 ± 0.11	12.63 ± 0.14
298.15	25.02 ± 0.13	7.82 ± 0.08	9.55 ± 0.09
308.15	33.77 ± 0.20	5.89 ± 0.07	7.28 ± 0.09
		$x = 95$	
288.15	13.55 ± 0.06	6.71 ± 0.05	8.21 ± 0.07
298.15	18.90 ± 0.05	4.86 ± 0.03	6.01 ± 0.04
308.15	25.66 ± 0.12	3.44 ± 0.03	4.30 ± 0.04

Standard Thermodynamic Quantities for Cell Reaction

By using the standard e.m.f. of the cell (E_x^0) and its temperature coefficient (dE_x^0/dT), derived from equation (3) and (4), the standard thermodynamic quantities (ΔG^o, ΔH^o and ΔS^o) are determined by usual relations for the following reaction of the cell:

$$0.5\ H_2\,(g,\ 101.325\ kPa) + AgBr\,(s) = Ag\,(s) + (H^+ + Br^-) \qquad (5)$$

The values at 298.15 K are in table VI together with the values for 5 mass per cent 2-methyl-1-propanol[3] and water medium.[9]

TABLE VI

Standard Thermodynamic Quantities for Cell Reaction (5) in x Mass per Cent 2-Methyl-1-propanod at 298.15 K

x	ΔG^o/kJ mol^{-1}	ΔH^o/kJ mol^{-1}	ΔS^o/J K^{-1} mol^{-1}
0[9]	13.06	—21.05	—114.4
5[3]	13.16	—20.80	—113.9
90	23.87	—51.65	—253.3
95	26.85	—58.45	—286.1

The data for ΔG^o show that the reaction of the cell is nonspontaneous, the more so the higher is content of 2-methyl-1-propanol in the mixture. Thus, hydrobromic acid in the mixed solvent with increased contents of 2-methyl-1--propanol has increased free energy. This is conditioned, in the first place, by a progressive decrease of dielectric constant of the mixed solvent with the increased proportional of alcohol in it. In fact, at the same contents of alcohol in the mixture, with increasing temperature the reaction becomes more and more nonspontaneous. However, the dielectric constant of the mixed solvent decreases with increasing temperature (Table II).

On the basis of the data for ΔH^o and ΔS^o it can be seen that the reaction is exothermic and there is a decrease in entropy. In relation to water medium at 5 mass per cent 2-methyl-1-propanol exothermity is somewhat lowered and so is the decrease in entropy, while both increase considerably at higher alcohol contents in the mixture. Accordingly, both enthalpy and entropy of hydrobromic acid in 5 mass per cent 2-methyl-1-propanol are only slightly higher than in water medium, and considerably lower in 90 and 95 mass per cent alcohol. Considering that $G^o = H^o - TS^o$ and the fact that hydrobromic acid has more free energy in the mixed solvent than in water medium, it can be concluded that in 5 mass per cent 2-methyl-1-propanol the term TS^o is of lesser importance, while at 90 and 95 mass per cent mixtures it is decisive, because with the decreased enthalpy it causes a considerable increase of free energy of hydrobromic acid.

Mean Activity Coefficients of Hydrobromic Acid

The mean activity coefficient of HBr for different molalities was calculated from the equation

$$\log \gamma_{\pm} = (E_m{}^o - E)/2k - \log\,(m/m^o) \qquad (6)$$

where $E_m{}^o$ is the standard e.m.f. of the cell (Table III), and E is the e.m.f. of the cell obtained for each individual molality from the equation (2). The data for 298.15 K are in Table VII.

TABLE VII

Mean Activity Coefficients $\gamma_{\pm}$ of Hydrobromic Acid in x Mass per Cent 2-Methyl-1-propanol at 298.15 K

x	m/mol kg^{-1}						
	0.003	0.005	0.009	0.015	0.04	0.06	0.1
90	0.556	0.485	0.407	0.346	0.249	0.217	0.184
95	0.521	0.449	0.372	0.314	0.223	0.194	0.165

The values in Table VII are in accordance with the expected ones after Debye-Hückel theory. Namely, $\gamma_{\pm}$ decreases with increasing HBr molality in the given solvent, and also at a given molality with decreasing dielectric constant of the mixed solvent.

Standard Thermodynamic Quantities for Transfer of HBr from Water to Mixed Solvent

The data for standard thermodynamic quantities of the cell reaction make it possible to obtain standard thermodynamic quantities (ΔG_t^o, ΔH_t^o and ΔS_t^o) for the transfer of 1 mole of HBr from water to the mixed solvent. It was calculated according to the relation

$$\Delta X_t^o = (\Delta X^o)_s - (\Delta X^o)_w \tag{7}$$

where $X = G, H, S$, and the subscripts s and w refer to the mixed solvent and pure water, respectively.

In Table VIII are the standard thermodynamic quantities of transfer at 298.15 K together with the values for 5 mass per cent 2-methyl-1-propanol[3], as well as for isomeric butanol: 5 and 90 mass per cent 2-methyl-2-propanol,[10] for comparison.

TABLE VIII

Standard Thermodynamic Quantities for the Transfer of HBr from Water to x Mass per Cent Alcohol-Water Mixtures at 298.15 K

Alcohol	x	ΔG_t^o kJ mol^{-1}	ΔH_t^o kJ mol^{-1}	ΔS_t^o J K^{-1} mol^{-1}
2-methyl-1-propanol[3]	5	0.10	0.25	0.5
2-methyl-2-propanol[10]	5	0.10	1.02	3.1
2-methyl-1-propanol	90	10.81	—30.60	—138.9
2-methyl-2-propanol[10]	90	12.90	—27.56	—135.7
2-methyl-1-propanol	95	13.79	—37.40	—171.7

The values for ΔG_t^0 show that the transfer process gets more nonspontaneous with increased alcohol contents in the mixture. This is in accordance with the earlier established fact that hydrobromic acid has higher free energy in mixed solvent than in water. However, it should be mentioned that this is a question of the ion transfer. Therefore, if for these mixtures Feakins's interpretation is adopted, primarily given for the transfer of electrolyte to the water-methanol mixtures,[11] it can be concluded that it is in fact a non-spontaneous transfer of bromide ion, while the hydrogen ion transfer is spontaneous.

On the basis of the data for ΔH_t^0 and ΔS_t^0 it can be seen that the transfer from water to the solvent with a low alcohol content is slightly endothermic and there is an increase in entropy, while at higher contents it is considerably exothermic with the entropy decrease. This is also in accordance with the earlier established fact that hydrobromic acid has a slightly increased enthalpy and entropy in 5 mass per cent 2-methyl-1-propanol than in water medium, while in 90 and 95 mass per cent mixture they are decreased considerably. Analogous behaviour has been recorded also for isomeric butanol 2-methyl--2-propanol[10,12] and in other alcohol-water mixtures,[1,13,14] which is probably conditioned by the structure of water and mixed solvents.

Ion-Association Constants of HBr and Standard Thermodynamic Quantities for Association Reaction

The thermodynamic ion-association constants K_A for the reaction

$$H^+ + Br^- \rightleftharpoons H^+ \cdot Br^- \tag{8}$$

are reciprocal values of ion-pair dissociation constants K_D (Table V). The standard ethalpy of association ΔH^0 was determined from the linear plot of ln K_A versus T^{-1}. The standard Gibbs energy and entropy, ΔG^0 and ΔS^0, were calculated by means of the usual thermodynamic equations. The values at 298.15 K are given in Table IX.

TABLE IX

Thermodynamic Quantities for the Ion-Association Reaction (8) in x Mass per Cent 2-Methyl-1-propanol at 298.15 K

x	K_A/l mol^{-1}	ΔG^0/kJ mol^{-1}	ΔH^0/kJ mol^{-1}	ΔS^0/J K^{-1} mol^{-1}
90	127.9	—12.03	21.16	113.1
95	205.8	—13.20	24.65	126.9

Data from this table lead to the conclusion that hydrobromic acid in ionic form has higher Gibbs free energy, and lower enthalpy and entropy compared with ion-pairs $H^+ \cdot Br^-$. This fact is more pronounced for the higher alcohol content in the mixture. The same conclusion has already been reported for hydrobromic acid in 90 and 95 mass per cent 2-methyl-1-propanol with respect to water medium.

In order to compare the experimental values with those theoretically predicted from the electrostatic model of ion pairs, we calculated the ion-

-association constants according to the theories of Bjerrum,[15] Denison and Ramsey,[16] Fuoss,[17] and Yokoyama and Yamatera.[18] The values of ΔH°, ΔG° and ΔS° were determined from these data as before. The values at 298.15 K for the distance of closest approach $a = 0.5$ nm are given in Table X.

TABLE X

Theoretical Values of K_A, ΔG°, ΔH°, *and* ΔS° *for the Ion-Association Reaction (8) in x Mass per Cent 2-Methyl-1-propanol at 298.15 K*

Theory	x	K_A l mol^{-1}	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
Bjerrum[15]	90	209.1	−13.24	11.41	82.7
	95	245.5	−13.64	13.05	89.5
Denison and	90	397.1	−14.83	13.39	94.7
Ramsey[16]	95	484.5	−15.33	16.40	106.4
Fuoss[17]	90	125.2	−11.97	13.39	85.1
	95	152.7	−12.46	16.40	96.8
Yokoyama	90	162.1	−12.61	11.41	80.6
and Yamatera[18]	95	191.8	−13.03	13.72	89.7

As it can be seen from this table, the lowest values for K_A are calculated according to Fuoss, slightly higher according to Yokoyama and Yamatera, and appreciably higher according to Denison and Ramsey. The experimental value of K_A and the corresponding ΔG° for 90 mass per cent alcohol is very close to the value computed according to Fouss, while for 95 mass per cent it is close to the value according to Yokoyama and Yamatera. On the other hand, experimental values ΔH° and ΔS° are much higher than those theoretically predicted by any of the mentioned equations.

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SAŽETAK

Standardni potencijali elektrode srebro-srebro bromid i termodinamička svojstva bromovodične kiseline u 90 i 95%-tnoj smjesi 2-metil-1-propanol-voda

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Mjerena je EMS članka: Pt (ili Pd), H_2 (g)/HBr (m), smjesa 2-metil-1-propanol-voda/AgBr, Ag s 90 i 95 masenih % alkohola pri temperaturama 288,15, 298,15 i 308,15 K u području koncentracija HBr 0,003 do 0,1 mol kg^{-1} Ove vrijednosti kao i podaci za konstantu disocijacije ionskih parova $H^+ \cdot Br^-$ su omogućili dobivanje standardne EMS članka za pojedinu temperaturu. Konstante disocijacije ionskih parova $H^+ \cdot Br^-$, odnosno konstante suprotne reakcije asocijacije, su određene na osnovi mjerenja vodljivosti. Vrijednosti za standardnu EMS članka su upotrebljene za izračunavanje standardnih termodinamičkih veličina za reakciju članka, srednjih koeficijenata aktiviteta HBr kao i standardnih termodinamičkih veličina prijenosa HBr iz vode u ispitivana miješana otapala. Iz vrijednosti za konstante asocijacije iona određene su standardne termodinamičke veličine za reakciju asocijacije iona. Vrijednosti za standardne termodinamičke veličine prijenosa su uspoređene s vrijednostima dobivenim s drugim smjesama alkohol-voda, a za reakciju asocijacije s teoretski predviđenim vrijednostima.