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Standard Potentials of Silver-Silver Bromide Electrode and Related Thermodynamic Quantities in 2-Propanol-Water Mixtures

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The standard potentials (E°_{m}) of silver—silver bromide electrode in 2-propanol—water mixtures (containing 30, 50, 70 and 90 wt-% 2-propanol) have been determined at 15, 25 and 35 °C using a cell of the type

Pt (Pd), H_2 (g) | HBr (m), x wt-% 2-propanol—water mixture | AgBr, Ag with m in the range from 0.003 to 0.1 mol kg^{-1}.

Values of E°_{m} varied with temperature in each solvent according to equations

a) 30 wt-% 2-propanol

$$E^{\circ}_{m} / \mathrm{V} = 0.05720 - 5.50 \times 10^{-4} (t/^{\circ}\mathrm{C} - 25) - 6.15 \times 10^{-6} (t/^{\circ}\mathrm{C} - 25)^2$$

b) 50 wt-% 2-propanol

$$E^{\circ}_{m} / \mathrm{V} = 0.04023 - 8.49 \times 10^{-4} (t/^{\circ}\mathrm{C} - 25) - 4.50 \times 10^{-6} (t/^{\circ}\mathrm{C} - 25)^2$$

c) 70 wt-%-2-propanol

$$E^{\circ}_{m} / \mathrm{V} = 0.00575 - 12.37 \times 10^{-4} (t/^{\circ}\mathrm{C} - 25) - 5.95 \times 10^{-6} (t/^{\circ}\mathrm{C} - 25)^2$$

d) 90 wt-% 2-propanol

$$E^{\circ}_{m} / \mathrm{V} = -0.0764 - 20.55 \times 10^{-4} (t/^{\circ}\mathrm{C} - 25) - 13.5 \times 10^{-6} (t/^{\circ}\mathrm{C} - 25)^2$$

These values have been used to calculate 1) standard thermodynamic quantities for cell reaction and the reaction involving HBr formation, 2) mean activity coefficients of HBr, 3) the primary medium effect, and 4) standard quantities for transfer of HBr from water to each mixed solvent. Results for 4) are discussed in terms of acid-base properties and structure of solvent.

INTRODUCTION

In a previous paper[1], the authors have studied thermodynamic properties of hydrobromic acid in 10 wt-% 2-propanol-water mixture. It was found that this mixed solvent is a stronger base than water and has also a more developed structure than water.

In present paper our further investigations with some other 2-propanol-water mixtures are reported. Study was done using the cell

$$\text{Pt (Pd)}, H_2 \text{ (g)} \mid \text{HBr } (m),\ x \text{ wt-\% 2-propanol-water mixture} \mid \text{AgBr, Ag} \qquad (1)$$

with $x = 30$; 50; 70 and 90. Measurements of emf. of cell (1) were made in temperature range from 15 to 35 °C and for molalities of hydrobromic acid from 0.003 to 0.1 mol kg^{-1}.

EXPERIMENTAL

Preparation of solutions and electrodes (AgBr and Pt), purification of gas and all experimental procedure are described earlier[1].

This time in addition to Pt electrodes Pd electrodes were used as well. Each Pd electrode was prepared by paladizing a Pt foil of 0.8 × 1 cm in 1 M HCl solution containing 2% of $PdCl_2$ over a period of 20 minutes at current density of 10 mA/cm^2. For each molality of hydrobromic acid, two parallel measurements were made: one in cell with Pt electrode and the other in the cell with Pd electrode. For both electrodes by changing hydrogen flow we reached the potential of satisfactory stability. However, potential of Pd electrode was more stable.

Solutions of HBr in 90 wt-% 2-propanol had a great resistance and measurements of emf. by Feussner compensator in conjuction with a galvanometer (sensitivity 4×10^{-9} A/mm scale) were not reliable. Therefore, when we used 90 wt-% 2-propanol and 70 wt-% 2-propanol only at lower concentrations of HBr, emf. was measured by Type K-4 Leeds & Northrup potentiometer with 9828 D.C. null detector which had satisfactory sensitivity.

Conductance measurements of hydrobromic acid in 90 wt-% 2-propanol were performed by using a Type MA 5691 Iskra conductometer. The purpose of these measurements was to determine the ionization constant of HBr.

RESULTS

Values of the emf. of cell (1) were corrected to 1 atm pressure of hydrogen and are given in Table I. Required data for vapour pressure of 2-propanol-water mixtures were obtained by interpolation of values from literature[2,3]. The accuracy for two parallel measurements for 30; 50 and 70 wt-% were approximately ± 0.06 mV, and for 90 wt-% 2-propanol about ± 0.09 mV.

TABLE I

Electromotive force E/V of the cell Pt (Pd), H (g, 1 atm) | HBr (m) in x wt-% 2-propanol | AgBr, Ag from 15 to 25 °C

m	$x = 30$			$x = 50$		
mol kg^{-1}	t = 15 °C	t = 25 °C	t = 35 °C	t = 15 °C	t = 25 °C	t = 35 °C
0.003	0.35515	0.36053	0.36464	0.34342	0.34592	0.34723
0.005	0.33077	0.33534	0.33876	0.31942	0.32116	0.32194
0.009	0.30322	0.30688	0.30936	0.29297	0.29354	0.29338
0.015	0.27892	0.28193	0.28368	0.26948	0.26949	0.26868
0.025	0.25542	0.25753	0.25854	0.24704	0.24638	0.24488
0.04	0.23415	0.23556	0.23571	0.22648	0.22523	0.22315
0.06	0.21538	0.21624	0.21598	0.20860	0.20686	0.20431
0.08	0.20256	0.20316	0.20246	0.19635	0.19416	0.19121
0.1	0.19204	0.19231	0.19140	0.18627	0.18404	0.18074

m	$x = 70$			$x = 90$		
mol kg^{-1}	t = 15 °C	t = 25 °C	t = 35 °C	t = 15 °C	t = 25 °C	t = 35 °C
0.003	0.31730	0.31622	0.31260	0.25692	0.24946	0.23899
0.005	0.29436	0.29265	0.28828	0.23690	0.22870	0.21822
0.009	0.26925	0.26672	0.26198	0.21434	0.20580	0.19488
0.015	0.24800	0.24484	0.23950	0.19590	0.18690	0.17551
0.025	0.22693	0.22303	0.21730	0.17720	0.16842	0.15707
0.04	0.20752	0.20345	0.19714	0.16074	0.15170	0.13998
0.06	0.19162	0.18710	0.18052	0.14626	0.13698	0.12535
0.08	0.17984	0.17485	0.16799	0.13636	0.12672	0.11486
0.1	0.17082	0.16577	0.15851	0.12741	0.11802	0.10588

Standard Electrode Potentials

The expression for emf. of cell (1) is

$$E = E^{\circ}_{m} - 2\,\mathrm{k} \log (m \gamma_{\pm}) \tag{2}$$

where E°_{m} is standard molal potential of the cell or of the Ag/AgBr electrode, k is 2.3026 RT/F, and $\gamma_{\pm}$ is the mean activity coefficient for HBr at molality m.

The standard electrode potential E°_{m} was determined by extrapolation to $m = 0$ of equation (3)

$$E' = E + 2\,k \log m - \frac{2\,k\,A\,(d\,m)^{1/2}}{1 + \mathring{a}\,B\,(d\,m)^{1/2}} - 2\,k \log (1 + 0.002\ M_{xy}\,m) = E^{\circ}_{m} - 2\,k\,b\,m \tag{3}$$

Above relation is obtained by inserting the expression for activity coefficient (4) in equation (2)

$$\log \gamma_{\pm} = -\frac{A\,(d\,m)^{1/2}}{1 + \mathring{a}\,B\,(d\,m)^{1/2}} + b\,m - \log (1 + 0.002\ M_{xy}\,m) \tag{4}$$

A and B in equations (3) and (4) are Debye-Hückel constants (for their calculation dielectric constants are required and were taken from Åkerlöf[4]), d is the solvent density (obtained by interpolation of data from literature[2,3]), $\mathring{a}$ is the ion-size parameter (5 Å), b is the parameter of interaction, and M_{xy} is mean molecular weight of solvent.

In solvent mixture with 90 wt-% 2-propanol, where the dielectric constant is smaller than 25, ion-pair formation occurs and hydrobromic acid behaves as a weak electrolyte. In this case for the determination of E°_{m}, the ionization constant of HBr[5,6] must be known. According to this method, the following equation could be given, for emf. of the cell

$$E = E^{\circ}_{m} - 2\,k \log (\alpha\,m\,g_{\pm}) \tag{6}$$

where α is degree of ionization and $g_{\pm}$ activity coefficient of HBr as a strong electrolyte at ionic concentration $\alpha\,m$.

The standard electrode potential E°_{m} was determined by extrapolation to $\alpha\,m = 0$ of equation (7)

$$E' = E + 2\,k \log (\alpha\,m) - \frac{2\,k\,A\,(d\,\alpha\,m)^{1/2}}{1 + \mathring{a}\,B\,(d\,\alpha\,m)^{1/2}} = E^{\circ}_{m} - 2\,k\,b\,\alpha\,m \tag{7}$$

which is obtained by inserting the relation for activity coefficient (8), (where the term with M_{xy} is neglected), in equation (6)

$$\log g_{\pm} = -\frac{A\,(d\,\alpha\,m)^{1/2}}{1 + \mathring{a}\,B\,(d\,\alpha\,m)^{1/2}} + b\,\alpha\,m \tag{8}$$

The ionization degree α has been calculated by means of thermodynamic ionization constant (expressed on the molal scale) from relation

$$K_{m} = \alpha^{2}\,m\,g^{2}_{\pm} / (1 - \alpha) \tag{9}$$

where the activity coefficient of undissociated molecules (or of ion pairs) was taken as unity. The calculation procedure was as follows: first a preliminary α-value was determined by solving eqn. (9) where $g_{\pm} = 1$. This value was then used for calculating the first value of $g_{\pm}$ according to expression $\log g_{\pm} = -A\,(d\,\alpha\,m)^{1/2} / [1 + \mathring{a}\,B\,(d\,\alpha\,m)^{1/2}]$. The obtained value for $g_{\pm}$ was then inserted in eqn. (9). After solving the eqn. (9) a better value for α was determined. The procedure was repeated until a constant value for α was obtained.

Values for E°_{m}, obtained by least squares method, with corresponding standard errors, are given in Table II. The standard potentials on concentration scale, E°_{c}, and on the mole fraction scale, E°_{N}, were calculated from equations

$$E^{\circ}_{c} = E^{\circ}_{m} + 2\,k \log d \tag{10}$$

$$E^{\circ}_{N} = E^{\circ}_{m} - 2\,k \log (1000/M_{xy}) \tag{11}$$

and are also given in Table II.

TABLE II

Standard potential of the Ag/AgBr electrode in x wt-% 2-propanol-water mixture from 15 to 35 °C

x	t/°C	E°_{m}/V	E°_{c}/V	E°_{N}/V
30	15	0.06208	0.05970 ± 0.00022	—0.12566
	25	0.05720	0.05443 ± 0.00021	—0.13706
	35	0.05109	0.04777 ± 0.00018	—0.14969
50	15	0.04827	0.04364 ± 0.00017	—0.12981
	25	0.04023	0.03503 ± 0.00014	—0.14403
	35	0.03129	0.02533 ± 0.00013	—0.15915
70	15	0.01753	0.01020 ± 0.00020	—0.14849
	25	0.00575	—0.00231 ± 0.00024	—0.16603
	35	—0.00722	—0.01610 ± 0.00016	—0.18476
90	15	—0.0572	—0.0675 ± 0.0009	—0.2073
	25	—0.0764	—0.0875 ± 0.0008	—0.2317
	35	—0.0983	—0.1103 ± 0.0008	—0.2588

The values for E°_{m} in Table II can be represented as a function of temperature in the range from 15 to 35 °C, according to the following equations:

a) 30 wt-% 2-propanol

$$E^{\circ}_{m}/\mathrm{V} = 0.05720 - 5.50 \times 10^{-4}\,(t/^{\circ}\mathrm{C} - 25) - 6.15 \times 10^{-6}\,(t/^{\circ}\mathrm{C} - 25)^{2} \tag{12}$$

$$E^{\circ}_{m}/\mathrm{V} = -0.32563 + 31.177 \times 10^{-4}\,T/\mathrm{K} - 6.15 \times 10^{-6}\,T^{2}/\mathrm{K}^{2} \tag{12.a}$$

b) 50 wt-% 2-propanol

$$E^{\circ}_{m}/\mathrm{V} = 0.04023 - 8.49 \times 10^{-4}\,(t/^{\circ}\mathrm{C} - 25) - 4.50 \times 10^{-6}\,(t/^{\circ}\mathrm{C} - 25)^2 \qquad (13)$$

$$E^{\circ}_{m}/\mathrm{V} = -0.10668 + 18.344 \times 10^{-4}\,T/\mathrm{K} - 4.50 \times 10^{-6}\,T^2/\mathrm{K}^2 \qquad (13.a)$$

c) 70 wt-% 2-propanol

$$E^{\circ}_{m}/\mathrm{V} = 0.00575 - 12.37 \times 10^{-4}\,(t/^{\circ}\mathrm{C} - 25) - 5.95 \times 10^{-6}\,(t/^{\circ}\mathrm{C} - 25)^2 \qquad (14)$$

$$E^{\circ}_{m}/\mathrm{V} = -0.15418 + 23.104 \times 10^{-4}\,T/\mathrm{K} - 5.95 \times 10^{-6}\,T^2/K^2 \qquad (14.a)$$

d) 90 wt-% 2-propanol

$$E^{\circ}_{m}/\mathrm{V} = -0.0764 - 20.55 \times 10^{-4}\,(t/^{\circ}\mathrm{C} - 25) - 13.5 \times 10^{-6}\,(t/^{\circ}\mathrm{C} - 25)^2 \qquad (15)$$

$$E^{\circ}_{m}/\mathrm{V} = -0.6638 + 59.95 \times 10^{-4}\,T/\mathrm{K} - 13.5 \times 10^{-6}\,T^2/\mathrm{K}^2 \qquad (15.a)$$

Ionization constant for HBr in 90 wt-% 2-propanol at different temperatures was determined by conductivity measurements[7]. Data for molar conductivities of HBr are listed in Table III.

TABLE III

Molar conductivities of HBr at various concentrations in 90 wt-% 2-propanol at 15, 25 and 35 °C

$t = 15\ ^{\circ}\mathrm{C}$		$t = 25\ ^{\circ}\mathrm{C}$		$t = 35\ ^{\circ}\mathrm{C}$	
$\frac{1000\ c}{\mathrm{mol\ l^{-1}}}$	$\frac{\Lambda}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{1000\ c}{\mathrm{mol\ l^{-1}}}$	$\frac{\Lambda}{\mathrm{S\ cm^2\ mol^{-1}}}$	$\frac{1000\ c}{\mathrm{mol\ l^{-1}}}$	$\frac{\Lambda}{\mathrm{S\ cm^2\ mol^{-1}}}$
1.008	21.70	1.000	29.58	0.989	38.75
0.907	21.20	0.900	29.29	0.890	38.15
0.806	22.00	0.800	29.86	0.791	39.44
0.706	22.05	0.700	30.01	0.692	39.34
0.605	22.25	0.600	30.54	0.593	40.40
0.504	22.80	0.500	30.48	0.495	39.70
0.403	23.48	0.400	32.04	0.396	41.59
0.302	23.37	0.300	31.37	0.297	42.29
0.202	23.98	0.200	32.95	0.198	43.35
0.101	24.60	0.100	34.33	0.099	45.10
0.091	25.10	0.090	33.87	0.089	45.95
0.081	25.02	0.080	34.35	0.079	45.23
0.071	25.24	0.070	34.60	0.069	45.74

From these data, the preliminary value for Λ_o, was first obtained from intercept[8] at $\Lambda c = 0$ of a least-squares line of Λ^{-1} vs. Λc. This value was used for calculating the Z variable acording to equation[9]

$$Z = (B_1 \Lambda_o + B_2)\,(\Lambda_o)^{-3/2}\,(\Lambda\, c)^{1/2} \qquad (16)$$

where c is concentration (mol/1), and B_1 and B_2 are Onsager coefficients. The ionization degree α was determined from relation

$$\alpha = \Lambda/\Lambda_o\, F\,(Z) \qquad (17)$$

where $F(Z)$ functions for different Z values were obtained from Fuoss's table[9]. Calculated values for α were used for determination of the mean molar activity coefficient from equation

$$\log f_{\pm} = - A\,(\alpha\, c)^{1/2}/[1 + å\, B\,(\alpha\, c)^{1/2}] \qquad (18)$$

Finally, better value for Λ_o was obtained by using expression

$$F(Z)/\Lambda = \frac{1}{\Lambda_o} + \frac{c\,\Lambda\, f_{\pm}^{2}/F(Z)}{K_c\,\Lambda_o^{2}} \qquad (19)$$

In other words, a plot of $F(Z)/\Lambda$ *vs.* $c\,\Lambda\, f_2^{\pm}/F(Z)$ will determine $(1/\Lambda_o)$ and $(1/K_c\,\Lambda_2^{\mathrm{o}})$ as the intercept and slope, respectively, and consequently Λ_o and the ionization constant K_c can be calculated. The value of Λ_o so obtained can be reiterated to obtain a second approximation for Λ_o and K_c. This procedure was repeated until the reciprocal of intercept gave the same value of Λ_o as that used in calculating Z and α.

From these values for constant K_c (on the molar scale) thermodynamic ionization constants were calculated from equation $K_m = K_c/d$. Values for Λ_o, K_c and K_m with their corresponding standard errors are listed in Table IV.

TABLE IV

Limitimg molar conductivities Λ_o *and ionization constants* K_c *and* K_m *for HBr in 90 wt-%* *2-propanol-water mixture at 15, 25 and 35* °C

t/°C	Λ_o/S cm^2 mol^{-1}	1000 K_c/mol l^{-1}	1000 K_m/mol kg^{-1}
15	26.0 ± 0.3	5.84 ± 0.14	7.18 ± 0.18
25	35.6 ± 0.5	5.59 ± 0.15	6.93 ± 0.18
35	47.4 ± 0.7	4.50 ± 0.14	5.65 ± 0.18

Standard Thermodynamic Quantities for Cell Reaction and for Reaction Involving Formation of Hydrobromic Acid

Standard thermodynamic quantities ΔG°, ΔH° and ΔS° for reaction (20) were obtained from E°_{m} and from temperature coefficinet dE°_{m}/dT [derived from eqns. (12.a)—(15.a)], by means of Gibbs-Helmholtz equation.

$$0.5\,H_2\,(g,\ 1\ atm) + AgBr\,(s) = Ag\,(s) + (H^+ + Br^-)\ (std.\ state,\ m = 1\ in\ x\ wt\text{-}\%\ 2\text{-}propanol) \qquad (20)$$

From these data and from literature[10] values for $\Delta_f G^{\circ}$ and $\Delta_f H^{\circ}$ of AgBr formation from its elements, and S° for AgBr, H_2 and Ag, $\Delta_f G^{\circ}$ and $\Delta_f H^{\circ}$ for HBr formation reaction (21) and S° for hydrobromic acid were calculated.

$$0.5\,H_2\,(g,\ 1\ atm) + 0.5\,Br_2\,(l) = (H^+ + Br^-)\ (std.\ state,\ m = 1\ in\ x\ wt\text{-}\%\ 2\text{-}propanol) \qquad (21)$$

Values are given in Table V.

TABLE V

Standard thermodynamic quantities at 25 °C: ΔG°, ΔH° *and* ΔS° *for reaction (20);* $\Delta_f G^\circ$, $\Delta_f H^\circ$ *for reaction (21), and standard entropy* S^o_{HBr}

x	$(\Delta G^\circ)_{20}$ J mol^{-1}	$(\Delta H^\circ)_{20}$ J mol^{-1}	$(\Delta S^\circ)_{20}$ J K^{-1} mol^{-1}	$(\Delta_f G^\circ)_{21}$ J mol^{-1}	$(\Delta_f H^\circ)_{21}$ J mol^{-1}	S^o_{HBr} J K^{-1} mol^{-1}
30	—5519	—21327	— 53.02	—102420	—121701	76.70
50	—3882	—28303	— 81.91	—100783	—128677	47.81
70	— 555	—36157	—119.41	— 97456	—136531	10.31
90	7372	—51748	—198.29	— 89529	—152122	—68.57

Mean Activity Coefficients of HBr

The mean activity coefficients for HBr in mixtures 2-propanol-water were calculated from equation

$$\log \gamma_{\pm} = (E^o_m - E)/2\,k - \log m \tag{22}$$

where E^o_m values are taken from Table II. E values for different molalities were obtained from eqns. (3) and (7). Activity coefficient refers to a value of unity for infinitely dilute solutions in respective solvents. Values at 25 °C are given in Table VI.

TABLE VI

Mean activity coefficients ($\gamma_{\pm}$) *of hydrobromic acid in* x *wt-%* *2-propanol at 25 °C*

x	m/mol kg^{-1} 0.003	0.005	0.009	0.015	0.04	0.06	0.1
30	0.914	0.893	0.865	0.836	0.777	0.751	0.721
50	0.873	0.843	0.804	0.766	0.684	0.650	0.608
70	0.791	0.747	0.698	0.637	0.532	0.491	0.444
90	0.603	0.533	0.455	0.391	0.291	0.260	0.230

Primary Medium Effect

Primary medium effect ($\log {}^{s}_{w}\gamma^{o}_{\pm}$) was calculated from relation

$$\log {}^{s}_{w}\gamma^{o}_{\pm} = ({}^{w}E^o_m - {}^{s}E^o_m)/2\,k \tag{23}$$

in which ${}^{s}E^o_m$ is the determined value for E^o_m in each mixed solvent, and ${}^{w}E^o_m$ value for the corresponding water solution[11]. Term, ${}^{s}_{w}\gamma^{o}_{\pm}$, represents the mean activity coefficient of hydrobromic acid at infinite dilution in the respective solvent mixture referred to unity at infinite dilution in aqueous state.

Data for temperature of 25 °C are given in Table VII.

TABLE VII

Primary medium effect ($\log^{s}_{w} \gamma^{o}_{\pm}$) *of* x *wt-$^{0}/_{0}$ 2-propanol on hydrobromic acid at 25 ^{0}C*

	$x = 30$	$x = 50$	$x = 70$	$x = 90$
$\log {}^{s}_{w}\gamma^{o}_{\pm}$	0.1171	0.2605	0.5519	1.2463
${}^{s}_{w}\gamma^{o}_{\pm}$	1.309	1.822	3.564	17.630

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

Standard Gibbs free energy for transfer process

$$\mathrm{HBr\ (in\ H_2O) = HBr\ (in\ x\ wt\text{-}^{0}/_{0}\ 2\text{-}propanol)}$$

was calculated from equation

$$\Delta_t G^{\circ} = F\,({}^{w}E^{o}_{N} - {}^{s}E^{o}_{N}) = \Delta\, E^{o}_{N} \tag{24}$$

where ${}^{w}E^{o}_{N}$ is standard emf. of the cell on mole fraction scale in water, and ${}^{s}E^{o}_{N}$ the corresponding value in a particular mixed solvent. From results listed in Table II for 2-propanol-water mixtures and for water solution[11] respectively at different temperatures the following temperature dependance was obtained:

a) 30 wt-$^{0}/_{0}$ 2-propanol

$$\Delta_t G^{\circ}/J = 22008 - 148.05\ T/\mathrm{K} + 25.09 \times 10^{-2}\ T^2/\mathrm{K}^2 \tag{25}$$

b) 50 wt-$^{0}/_{0}$ 2-propanol

$$\Delta_t G^{\circ}/J = 890 - 27.50\ T/\mathrm{K} + 91.66 \times 10^{-3}\ T^2/\mathrm{K}^2 \tag{26}$$

c) 70 wt-$^{0}/_{0}$ 2-propanol

$$\Delta_t G^{\circ}/J = 5480 - 77.49\ T/\mathrm{K} + 23.16 \times 10^{-2}\ T^2/\mathrm{K}^2 \tag{27}$$

d) 90 wt-$^{0}/_{0}$ --propanol

$$\Delta_t G^{\circ}/J = 55079 - 441.24\ T/\mathrm{K} + 96.49 \times 10^{-2}\ T^2/\mathrm{K}^2 \tag{28}$$

Other thermodynamic functions can be obtained from the standard relations, namely

$$\Delta_t S^{\circ} = -\,d\,(\Delta_t G^{\circ})/\mathrm{d}T \tag{29}$$

$$\Delta_t H^{\circ} = \Delta_t G^{\circ} + T\,\Delta_t S^{\circ} \tag{30}$$

Transfer Gibbs energy can be expressed as the sum of an electrostatic and a chemical part

$$\Delta_t G^{\circ} = \Delta_t G^{\circ}\,(\mathrm{el}) + \Delta_t G^{\circ}\,(\mathrm{chem}) \tag{31}$$

The electrostatic part in transfer energy was obtained from Born equation

$$\Delta_t G^{\circ}\,(\mathrm{el}) = 1/2\, N_A\, e^2\, (D_s^{-1} - D_w^{-1})\,(r_+^{-1} + r_-^{-1}) \tag{32}$$

where N_A is Avogadro's constant, e the unit charge, D_s and D_w dielectric constant for the mixed solvent and water, r_+ and r_- are the effective radii of the cation and anion, taken as 2.8 Å[12] and 1.95 Å[13] respectively.

Table VIII summarizes the values of these thermodynamic quantities together with values for 10 wt-% 2-propanol[1].

TABLE VIII

Standard thermodynamic quantities for the transfer of HBr from water to x wt-% 2-propanol at different temperatures

x	t/°C	$\Delta_t G^\circ$ J mol^{-1}	$\Delta_t G^\circ$ (el) J mol^{-1}	$\Delta_t G^\circ$ (chem) J mol^{-1}	$\Delta_t H^\circ$ J mol^{-1}	$\Delta_t S^\circ$ J K^{-1} mol^{-1}
10[1]	15	275	723	—448	3516	11.24
	25	180	776	—596	2582	8.06
	35	115	827	—712	1617	4.88
30	15	179	2736	—2557	1176	3.46
	25	170	2915	—2745	—295	—1.56
	35	211	3103	—2892	—1817	—6.58
50	15	577	6102	—5525	—6721	—25.32
	25	839	6517	—5678	—7528	—27.15
	35	1120	6956	—5836	—7814	—28.98
70	15	2381	12470	—10089	—13750	—55.98
	25	2964	13353	—10389	—15108	—60.61
	35	3593	14299	—10706	—16512	—65.25
90	15	8052	20423	—12371	—25037	—114.83
	25	9296	22034	—12738	—30694	—134.13
	35	10734	23754	—13020	—36544	—153.43

DISCUSSION

From data in Table V the continuous change of standard thermodynamic quantities with increasing amount of 2-propanol in mixed solvent can be seen. This change is more explicit starting from 70 wt-% to 90 wt-% 2-propanol.

Values for mean activity coefficients (Table VI), are decreased with increasing HBr concentration. The same effect occurs when (at a given molality) the dielectric constant of solvent is decreasing. This all is in accordance with Debye-Hückel theory. However, in 90 wt-% 2-propanol, the decrease of $\gamma_\pm$ values is more pronounced with increasing HBr values.

It is evident that in the solvent range from 70 to 90 wt-% 2-propanol, ion association phenomenon occurs and the HBr is behaving like a weak electrolyte. In 90 wt-% 2-propanol (dielectric constant is 20.3 at 25 °C), a remarkable ion association occurs evidenced by ionization constant values (Table IV). Similar behaviour has been reported for hydrobromic acid in dioxane-water mixtures with more than 65 wt-% dioxane.[6].

From values of Gibbs free energy change computed for transfer of HBr from water to mixed solvent, it is evident that this is not a spontaneous process. This is more explicit in solvents with a higher 2-propanol contents (Table VIII). Considering values for electrostatic part [$\Delta_t G^0$ (el)], (although the calculation of these involves some uncertainties, especially due to dielectric saturation and the choice of effective ionic radii [eqn. (32)]), negative values for the chemical part of free energy [$\Delta_t G^0$ (chem)] are obtained. Consequently, the chemical reaction in transfer process is spontaneous and increases with increasing amount of 2-propanol in the mixture.

In previous work[1], it was already mentioned that this spontaneous reaction couldn't be expected for the transfer process of both ions. Here we can consider Feakins's interpretation[14], given for water-methanol mixture. For 2-propanol, it was supposed to be more »basic« than water and water molecules in 2-propanol-water mixture are more »basic« from those in pure water. Thus it can be deduced, that for hydrogen ion transfer the change in free energy is a negative value, and for bromide ion transfer a positive value. Summary values for $\Delta_t G^0$ (chem) being negative, it can be conclude that $\Delta_t G^0$ (chem) for the hydrogen ion transfer is more negative than the positive value for bromide ion transfer. Therefore, all tested mixtures of 2-propanol--water are more basic than water, even more so with higher amount of 2-propanol in the mixture.

The changes in enthalpy and entropy in the transfer process give us an insight into the solvent structure. From data in Table VIII, we can see that values for $\Delta_t H^0$ and $\Delta_t S^0$ in 10 wt-% 2-propanol are positive and decrease as the temperature increases. In 30 wt-% 2-propanol these values are only positive at 15 °C, and at 25 °C are becoming negative. With an increase in amount of 2-propanol in solvent, values are getting more negative, as well as with a temperature increase.

We can assume that structure-forming processes are exothermic and accompanied with an entropy decrease. Structure-breaking processes are endothermic and leading to an entropy increase. Transfer process of ions from water to another solvent involves a number of changes connected with structure building up and breaking down[15]. We can conclude that with lower amounts of 2-propanol, where the total sum for $\Delta_t H^0$ and $\Delta_t S^0$ are positive, ions break down more structure in mixed solvent than in water. With higher amounts of 2-propanol the reverse case takes place. Consequently, mixed solvent with less than 30 wt-% 2-propanol is a more structured solvent than water. Above this amount, water is the more structured solvent. Therefore, we can assume that smaller additions of 2-propanol to water (up to mole fraction *cca* 0.1), enhance the three-dimensional structure of water. Higher amounts of 2-propanol are breaking down this structure. This was indeed found for some other lower alcohols.[14,16,17] Finally we would like to mention that Roy and Bothwell[18,19] were testing thermodynamic properties of hydrochloric acid in the 2-propanol-water mixtures in range from 8.03 to 87.81 wt-% 2-propanol. Comparison of data for standard thermodynamic quantities for transfer process of HCl with corresponding values for HBr in Table VIII suggest similar behaviour of both acids in these mixed solvents.

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SAŽETAK

Standardni potencijali elektrode srebro-srebro bromid i odgovarajuće termodinamičke veličine u smjesama 2-propanol-voda

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Određeni su standardni potencijali Ag/AgBr elektrode u smjesama 2-propanol-voda, koje sadržavaju 30, 50, 70 i 90 tež. % 2-propanola, pri temperaturi 15, 25 i 35 ^{0}C na osnovi mjerenja EMS članka:

$$\mathrm{Pt\,(Pd),\ H_2\,(g)\ |\ HBr\,(m),\ smjesa\ 2\text{-}propanol\text{-}voda\ |\ AgBr,\ Ag}$$

u području koncentracija HBr od 0,003 do 0,1 mol kg^{-1}.

Vrijednosti E°_{m} ovise o temperaturi u pojedinom otapalu prema jednadžbi:

a) 30 tež.% 2-propanol

$$E^{\circ}_{m}\ /\mathrm{V} = 0{,}05720 - 5{,}50 \times 10^{-4}\,(t/^{0}\mathrm{C} - 25) - 6{,}15 \times 10^{-6}\,(t/^{0}\mathrm{C} - 25)^2$$

b) 50 tež.% 2-propanol

$$E^{\circ}_{m}\ /\mathrm{V} = 0{,}04023 - 8{,}49 \times 10^{-4}\,(t/^{0}\mathrm{C} - 25) - 4{,}50 \times 10^{-6}\,(t/^{0}\mathrm{C} - 25)^2$$

c) 70 tež.% 2-propanol

$$E^{\circ}_{m}\ /\mathrm{V} = 0{,}00575 - 12{,}37 \times 10^{-4}\,(t/^{0}\mathrm{C} - 25) - 5{,}95 \times 10^{-6}\,(t^{0}/\mathrm{C} - 25)^2$$

d) 90 tež.% 2-propanol

$$E^{\circ}_{m}\ /\mathrm{V} = -\,0{,}0764 - 20{,}55 \times 10^{-4}\,(t/^{0}\mathrm{C} - 25) - 13{,}5 \times 10^{-6}\,(t^{0}/\mathrm{C} - 25)^2$$

Dobivene vrijednosti za standardne potencijale upotrebljene su za izračunavanje 1) standardnih termodinamičkih veličina za reakciju članka i za reakciju nastajanja bromovodične kiseline, 2) srednjih koeficijenata aktiviteta HBr, 3) primarnog efekta medija i 4) standardnih termodinamičkih veličina prijenosa HBr iz vode u pojedino miješano otapalo. Na osnovi rezultata za 4) raspravlja se o kiselinsko-baznim svojstvima otapala i o njegovoj strukturi.

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