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Thermodynamics of Hydrobromic Acid in 10 wt. Per Cent 2-Propanol-Water Mixture from Electromotive Force Measurements

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The e. m. f.'s of the cell: Pt, $H_2(g)$ | HBr(m), 10 wt-% 2-propanol, 90 wt-% water | AgBr, Ag at temperatures 15, 25 and 35 °C for hydrobromic acid solutions in the range from 0.003 to 0.1 mol kg^{-1} have been measured. The data have been used to derive a) the equation of standard potential of Ag/AgBr electrode as a function of temperature, b) the standard thermodynamic quantities for the cell reaction and the reaction of HBr formation, c) the mean activity coefficients of HBr, d) the primary medium effect, and e) the standard quantities for transfer of HBr from water to the mixed solvent of the 10 wt-% 2-propanol. According to values for e), it can be stated that the transfer process of HBr is not spontaneous, and that the mixed solvent is a stronger base than water and has a more developed structure than water.

INTRODUCTION

Aqueous-organic mixed solvents are of great importance as reaction media. These solvents have an influnce on the chemical equilibria as well as on the rates and mechanisms of reactions in solution. Therefore, the study of the effect of the solvent on the properties of electrolytes in mixed solvents is very interesting.

In our research we have taken hydrobromic acid as electrolyte and water-2-propanol as mixed solvent. Investigations have been made on the cell of the following type

Pt,$H_2(g)$ | HBr(m), 10 wt-% 2-propanol, 90 wt-% water | AgBr,Ag

with measurements of e. m. f. at different temperatures and different concentrations of HBr. From these data it is possible to determine some thermodynamic properties of the hydrobromic acid in this solvent and to deduce the acid-base properties and the structure of the mixed solvent.

EXPERIMENTAL

The solutions of hydrobromic acid were prepared by weighing the water stock solution of HBr, 2-propanol and redistilled water. The stock solution was prepared from HBr of *p. a.* purity (»Kemika«), distilled before the use, and then the middle part of the distillate was taken. The concentration of the stock solution was determined gravimetrically by weighing silver bromide. The 2-propanol was of *p. a.* purity (»Kemika). The molalities of the HBr solutions ranged from 0.003 to 0.1 mol kg^{-1}.

The Ag/AgBr electrodes were of an electrolytic type[1]. A Pt foil of 0.8 × 1 cm dimension was plated with silver for 24 hours from a solution 0.05 M $KAg(CN)_2$

and 0.005 M KCN at a current density of 1.2—1.4 mA/cm^2, with an Ag anode. The electrodes were then held for 2—3 hours in concentrated NH_4OH and thorougly washed with water. The electrodes were bromidized in 0.1 M KBr at a current density of 2 mA/cm^2 for such a period of time until about 8—10% of the Ag has passed into AgBr. The electrodes were then conditioned in 0.1 M KBr for two days before the bias potential was measured. The electrodes which had a bias potential of < 0.035 mV were used.

The hydrogen electrodes were of similar dimensions as the Ag/AgBr electrodes and were prepared by platinizing in 2% chloroplatinic acid solution, 1 M in HCl and 0.02% in lead acetate for 3 minutes at a current density of 0.1 A/cm^2. The platinization was also made in a solution without lead acetate for 4 minutes at the same current density. The electrodes thus obtained were of a less intensive colour. Both kinds of electrodes gave satisfactory results which were verified by changing the electrodes during the experiment.

The experimental cell was a modification of the one used by Feakins and co-workers[2], which consists of two compartments (each of a 10 ml volume) linked by a tap, each compartment being provided with a gas saturator. Hydrogen was obtained by electrolysis, purified by passing through two vessels with a solution containing 5% pyrogallol and 14% NaOH, then passed first through a vessel with 10 wt-% 2-propanol, and then through the cell saturator. In the Ag/AgBr compartment argon was purified and saturated in the same way as the hydrogen.

E. m. f.' s were measured by a Feussner precision compensator in conjunction with a galvanometer (sensitivity 4×10^{-9} A/mm scale) and a standard cell. The cells were thermostated to ± 0.02 K in a water bath. The measurements were made at 25 °C, then at 15, at 35 and again at 25 °C with the tap open. The equilibrium was reached in about 3—5 hours after the initiation of hydrogen bubbling, and the criterion for equilibrium was a constant e. m. f. stable to ± 0.05 mV for one hour. At lower concentrations of HBr, before putting it into the cell, the Ag/AgBr electrode was held in the mentioned solution overnight.

RESULTS

The observed values of the e. m. f. corrected to 1 atm pressure of hydrogen are given in Table I. These corrections were made by means of data for vapour pressure of the mixed solvent at different temperatures[3]. The results in the table are the mean values of two parallel measurements for each molality of HBr. The accuracy of the e. m. f. measurement was about ± 0.05 mV, and the values at 25 °C at the beginning and at the end also agree within ± 0.05 mV.

TABLE I.

Electromotive force E/V of the cell Pt,H_2 (g, 1 atm) | HBr(*m*) in 10 wt-% 2-propanol | AgBr,Ag *from* 15 *to* 35 °C

m / mol kg^{-1}	*t*/°C 15	25	35
0.003	0.36095	0.36737	0.37284
0.005	0.33615	0.34186	0.34652
0.009	0.30839	0.31285	0.31648
0.015	0.28505	0,28863	0.29146
0.025	0.25985	0.26288	0.26508
0.040	0.23849	0.24069	0.24208
0.060	0.21943	0.22106	0.22165
0.080	0.20528	0.20674	0.20703
0.100	0.19579	0.19598	0.19597

Standard electrode potential

For the cell reaction

$$0.5\,H_2\,(g, 1\,atm) + AgBr(s) = Ag(s) + (H^+ + Br^-)\ (m) \tag{1}$$

Nernst's equation reads as follows:

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

where E^o_m is the standard potential of the Ag/AgBr electrode on the molal scale, k is 2.3026 RT/F, and $\gamma_\pm$ is the mean activity coefficient of HBr at the molality m. The mean activity coefficient is given by equation (3)

$$\log \gamma_\pm = -\frac{A\,(dm)^{1/2}}{1 + \mathring{a}\,B\,(dm)^{1/2}} + b\,m - \log (1 + 0.002\,M_{xy}m) \tag{3}$$

in which A and B are the Debye-Hückel constants, d is the solvent density, $\mathring{a}$ is the ion-size parameter, b is the parameter of interaction and M_{xy} is the mean molecular weight of the solvent. Equations (2) and (3) lead to equation (4)

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

If the terms on the left-hand side of equation (4) are expressed by E', we obtain equation (5)

$$E' = E^o_m - 2\,k\,b\,m \tag{5}$$

Values of E' were plotted against molalities of HBr and the curve was extrapolated to $m = 0$ to get the standard potential E^o_m. (Figure 1).

Values for the dielectric constant of the solvent were taken from Åkerlöf's data[4], and for the solvent densities from Moore and Felsing's data[3], while the mean molecular weight of the solvent was calculated by the equation

$$M_{xy} = 100/(x_1/M_1 + x_2/M_2) \tag{6}$$

In this equation x_1 and x_2 are the weight percentages of each solvent and M_1 and M_2 are their molecular weights. For $\mathring{a}$ the value 5 Å was taken.[5] Use of the value 4 Å for $\mathring{a}$ gave different slopes but had no appreciable influence on E^o_m (Figure 1).

To get more precise value for E^o_m the method of least squares (with $\mathring{a} = 5$ Å) was used. The data are given in Table II together with the values for the standard potential on the concentration scale E^o_c and on the mole fraction scale E^o_N which were calculated according to the equations

$$E^o_c = E^o_m + 2\,k \log d \tag{7}$$

$$E^o_N = E^o_m - 2\,k \log (1000/M_{xy}) \tag{8}$$

The standard deviation was computed from deviations of the experimental data for the values E' at each molality and the corresponding values of E' calculated by equation (5). On the average, the standard deviations were 0.33, 0.20 and

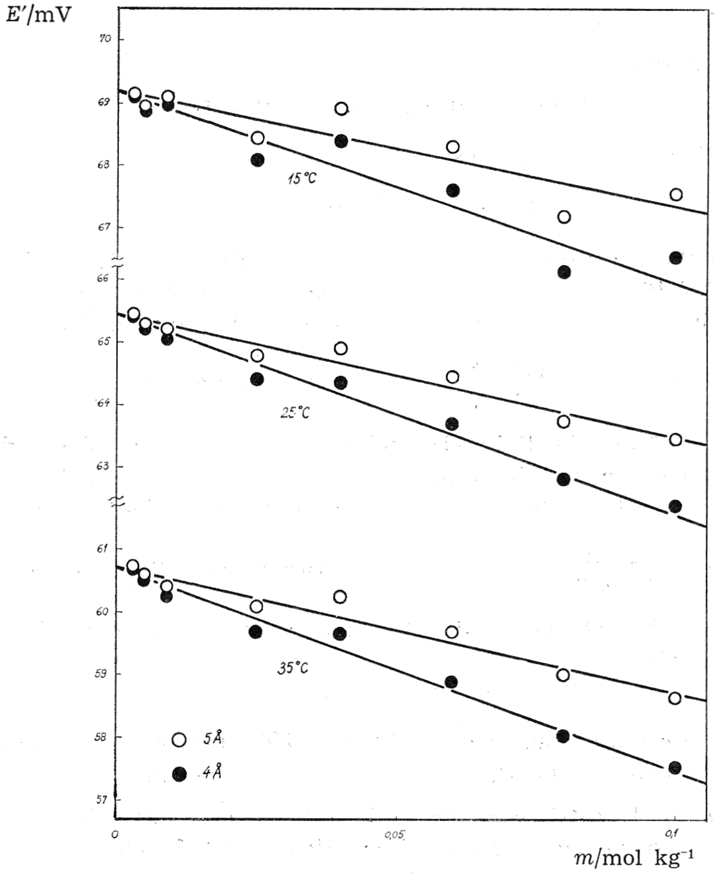


Fig. 1. Determination of the standard potential E^{o}_{m} of Ag/AgBr electrode by ex
$m_{HBr} = 0$ of the function E' in 10 wt-% 2-propanol-water mixture at different te

TABLE II.

Standard potential of the Ag/AgBr *electrode in 10 wt-% 2-propan*
15 to 35 °C

	t/°C		
	15	25	35
E^{o}_{m} /V	0.06915	0.06544	0.06071
E^{o}_{C} /V	0.06833	0.06445	0.05949
E^{o}_{N} /V	—0.12671	—0.13721	—0.14874

0.17 mV at 15, 25 and 35 °C respectively. The greatest difference b
two values for E^{o}_{m} was 0.06 mV at 15 °C.

The values of E^{o}_{m} in Table II can be represented as a functio
rature in the range from 15 to 35 °C by the following equation

$$E^{o}_{m} = 0.06544 - 4.22 \times 10^{-4}\,(t - 25) - 5.10 \times 10^{-6}\,(t - 25)^2 \tag{9}$$

$$E^{o}_{m} = -0.26206 + 2.619 \times 10^{-3}\,T - 5.10 \times 10^{-6}\,T^2 \tag{10}$$

Standard thermodynamic quantities for the cell reaction and for the reaction of formation of hydrobromic acid

The standard thermodynamic quantities ΔG^o, ΔH^o and ΔS^o for reaction (11) can be obtained from the value E^{o}_{m} and the temperature coefficient $\mathrm{d}E^{o}_{m}/\mathrm{d}T$ [derived from equation (10)]

$$0.5\,H_2\,(g, 1\,atm) + AgBr(s) = Ag(s) + (H^+ + Br^-)\ \text{(std. state, } m = 1, \text{ in 10 wt-\% 2-propanol)} \tag{11}$$

The mentioned quantities were obtained by means of the Gibbs-Helmholtz equation.

Further, taking the data from the literature[6] for $\Delta_f G^o$ and $\Delta_f H^o$ of AgBr formation from elements and S^o for AgBr, H_2 and Br_2 we can obtain $\Delta_f G^o$ and $\Delta_f H^o$ for the reaction of HBr formation:

$$0.5\,H_2\,(g, 1\,atm) + 0.5\,Br_2\,(l) = (H^+ + Br^-)\ \text{(std. state, } m = 1 \text{ in 10 wt-\% 2-propanol)} \tag{12}$$

and S^o for hydrobromic acid. The values are given in Table III.

TABLE III.

Standard thermodynamic quantities at 25 °C: ΔG^o, ΔH^o, ΔS^o for reaction (11); $\Delta_f G^o$, $\Delta_f H^o$ for reaction (12), and standard entropy S^{o}_{HBr}

$(\Delta G^o)_{11}$/J mol^{-1}	$(\Delta H^o)_{11}$/J mol^{-1}	$(\Delta S^o)_{11}$/J K^{-1} mol^{-1}	$(\Delta_f G^o)_{12}$/J mol^{-1}	$(\Delta_f H^o)_{12}$/J mol^{-1}	S^{o}_{HBr} /J K^{-1} mol^{-1}
—6314	—18457	—40.73	—103215	—118831	89.02

Mean activity coefficients of HBr

The mean activity coefficients of hydrobromic acid can be calculated by using the value E^{o}_{m} for the cell and e. m. f. values for corresponding molality according to the equation (13)

$$\log \gamma_{\pm} = (E^{o}_{m} - E)/2\,k - \log m \tag{13}$$

The values of E are obtained by equations (4) and (5), and values of E^{o}_{m} from equation (9).

The mean activity coefficients refer to a unit value for the infinitely dilute solution in the mixed solvent. An error of ± 0.05 mV in e. m. f. measurement corresponds to an error of ± 0.001 in the value of $\gamma_{\pm}$. The data of the activity coefficients are given in Table IV.

TABLE IV.

Mean activity coefficients ($\gamma_{\pm}$) of hydrobromic acid in 10 wt-% 2-propanol at different temperatures

$t/^{\circ}C$	$m/\text{mol kg}^{-1}$						
	0.003	0.005	0.009	0.015	0.04	0.06	0.1
15	0.937	0.922	0.901	0.879	0.832	0.811	0.787
25	0.936	0.921	0.899	0.878	0.831	0.811	0.787
35	0.935	0.919	0.897	0.875	0.827	0.807	0.783

Primary medium effect

According to Owen[7] the primary medium effect ($\log {}_{w}^{s}\gamma_{\pm}^{o}$) represents the difference in ion-solvent interaction for HBr in mixed solvent and in water. It can be obtained according to the equation (14)

$$\log {}_{w}^{s}\gamma_{\pm}^{o} = ({}^{w}E_{m}^{o} - {}^{s}E_{m}^{o})/2\,k \qquad (14)$$

where ${}^{s}E_{m}^{o}$ is the E_{m}^{o} of the cell in 10 wt-% 2-propanol, and ${}^{w}E_{m}^{o}$ in water[8]. In fact, ${}_{w}^{s}\gamma_{\pm}^{o}$ represents the mean activity coefficient of HBr at infinite dilution in the mixed solvent refering to the unit value at infinite dilution in water. The values for different temperatures are given in Table V.

TABLE V.

Primary medium effect, $\log {}_{w}^{s}\gamma_{\pm}^{o}$ (molal scale) of 10 wt-% 2-propanol on hydrobromic acid at 15, 25 *and* 35 °C

	$t/^{\circ}C$		
	15	25	35
$\log {}_{w}^{s}\gamma_{\pm}^{o}$	0.05649	0.04725	0.04122
${}_{w}^{s}\gamma_{\pm}^{o}$	1.139	1.115	1.100

Standard thermodynamic quantities for transfer of HBr from water to mixed solvent

For the transfer process

$$\text{HBr (in } H_2O) = \text{HBr (in 10 wt-\% 2-propanol)}$$

the standard Gibbs free energy change is

$$\Delta_t G^o = \Delta G_s^o - \Delta G_w^o = F({}^{w}E_N^o - {}^{s}E_N^o) = F\,\Delta E_N^o \qquad (15)$$

where E_N^o is the standard electrode potential on the mole fraction scale; the superscripts s and w refer to the mixed solvent and pure water, respectively. The calculation is made on the mole fraction scale, since that will eliminate free energy deviation due to concentration changes.

The following relation for the temperature dependence of ΔE°_{N} in the range from 15 to 35 °C was obtained from the data for 10 wt-% 2-propanol and for water solutions[8], respectively

$$\Delta E^{\circ}_{N} = 0.17343 - 1.0674 \times 10^{-3}\, T + 1.65 \times 10^{-6}\, T^{2} \tag{16}$$

where T is in K. For $\Delta_t G^{\circ}$ we find

$$\Delta_t\ G^{\circ} = 16734 - 102.99\, T + 0.1592\, T^{2} \tag{17}$$

The values of the other thermodynamic functions can be obtained by using the usual relations, namely

$$\Delta_t\ S^{\circ} = 102.99 - 0.3184\, T \tag{18}$$

$$\Delta_t\ H^{\circ} = 16734 - 0.1592\, T^{2} \tag{19}$$

The values of these quantities are summarized in Table VI.

TABLE VI.

Standard thermodynamic quantities accompanying the transfer of HBr *from water to 10 wt-% 2-propanol at different temperatures*

t/°C	$\Delta_t G^{\circ}$/J mol^{-1}	$\Delta_t H^{\circ}$/J mol^{-1}	$\Delta_t S^{\circ}$/J K^{-1} mol^{-1}
15	275	3516	11.24
25	180	2582	8.06
35	115	1617	4.88

DISCUSSION

We have restricted our discussion on the thermodynamic quantities for the transfer process of HBr from water to the mixed solvent.

The positive values for $\Delta_t G^{\circ}$ in the investigated temperature range show that HBr has a lower free energy in water than in mixture water-2-propanol (10 wt-%) and therefore the transfer process is not spontaneous. This can also be found by inspecting the values for the primary medium effect.

However, it is convenient to consider $\Delta_t G^{\circ}$ as summary quantity[9] composed of a electrostatic part [$\Delta_t G^{\circ}$ (el)], caused by the change in the dielectric constant of the medium and a chemical part [$\Delta_t G^{0}$ (chem)] due to the difference in solvation and other ion-solvent interactions, namely

$$\Delta_t\ G^{\circ} = \Delta_t\ G^{\circ}\,(\mathrm{el}) + \Delta_t\ G^{\circ}\,(\mathrm{chem}) \tag{20}$$

The electrostatic part of the free energy change can be computed from Born's equation (21)

$$\Delta_t\ G^{\circ}\,(\mathrm{el}) = \frac{1}{2}\, N_A\, e^{2}\, (D_s^{-1} - D_w^{-1})\, (r_{+}^{-1} + r_{-}^{-1}) \tag{21}$$

where N_A is Avogadro's constant, e the unit of charge, D_s and D_w are the dielectric constants of the mixed solvent and water, respectively, r_+ and r_-

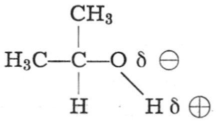
are the effective radii of the cation taken as 2.8 Å[10] and that of the anion taken as 1.95 Å[11]. Although the application of this equation involves some uncertainties especially due to the choice of effective ionic radii, it is possible to derive some qualitative conclusions. From equations (20) and (21) we obtained the quantities in Table VII.

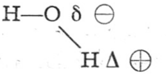
TABLE VII.

Gibbs free energies of transfer of HBr from water to 10 wt-% 2-propanol at different temperatures

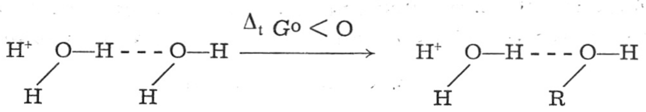
$t/{}^{\circ}C$	$\Delta_t G^{\circ}/J\ mol^{-1}$	$\Delta_t G^{\circ}(el)/J\ mol^{-1}$	$\Delta_t G^{\circ}(chem)/J\ mol^{-1}$
15	275	723	—448
25	180	776	—596
35	115	827	—712

From Table VII, it is evident that the values $\Delta_t G^{\circ}$ (chem) are negative, and that the chemical part in the transfer process of HBr is a spontaneous reaction, although it cannot be expected for both ions. In this case we would use the Feakins's interpretation[12], given for the mixture methanol-water. Because of the inductive effect of the methyl groups in the 2-propanol molecule the negative charge on the oxygen atom is somewhat higher than in the water molecule $(\delta \ominus_{\text{2-propanol}} > \delta \ominus_{\text{water}})$, while the positive charge of the hydrogen atom in the hydroxylic group is lower in 2-propanol than in water $(\delta \oplus_{\text{water}} > \delta \oplus_{\text{2-propanol}})$. In other words 2-propanol is more »basic« than water and less »acidic«.

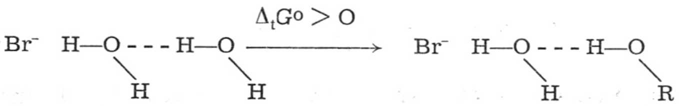




Further, in a 2-propanol-water mixture, which is extensively hydrogen bonded, one might expect that a 2-propanol molecule induces a change in charge density in a water molecule adjacent to it as well as in other molecules of water at some distance. Due to these changes the water molecules in the mixture are also more »basic« (or less »acidic«) than the ones in pure water. Therefore the transfer process of the hydrogen ion can be expressed as follows



and similarly for the bromide ion



where R is $(CH_3)_2CH$.

As already mentioned, $\Delta_t G^0$ (chem) is negative for HBr, and we can conclude that $\Delta_t G^0$ (chem) for the transfer of hydrogen ion is more negative than the positive value for the transfer of bromide ion. Therefore it can be stated that the mixture 2-propanol-water (10 wt-%) acts as a stronger base than water.

The changes in enthalpy and entropy are positive and decrease as the temperature increase (Table VI.). These effects can be connected with the structure-breaking process, which is endothermic and leads to an increase in entropy[13]. The process of transfer of ions from water to another solvent involves desolvation of ions in water and resolvation in the mixed solvent, and leads to structure changes. The fact that the values for $\Delta_t H^0$ and $\Delta_t S^0$ are positive, shows that the ions break more structure in the mixed solvent than in water; that is, the mixture of 2-propanol-water (10 wt-%) is a more highly structured solvent than water. This agrees to other data[12,14,15] which show that the addition of relatively small amounts of alcohols into water promotes its »three-dimensional structure«.

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SAŽETAK

Termodinamička svojstva bromovodične kiseline u 10%-tnoj smjesi 2-propanol—voda na osnovi mjerenja elektromotorne sile članka

I. Mekjavić i I. Tominić

Mjerena je EMS članka: Pt,H_2(g) | HBr(m), 10 tež.% 2-propanol, 90 tež.% voda | AgBr,Ag pri temperaturama 15, 25 i 35 °C u području koncentracija HBr od 0,003 do 0,1 mol kg^{-1}. Iz dobivenih vrijednosti nađena je temperaturna ovisnost standardnog potencijala elektrode Ag/AgBr, zatim su određene a) standardne termodinamičke veličine za reakciju članka i za reakciju nastajanja bromovodične kiseline, b) srednji koeficijenti aktiviteta HBr, c) primarni efekt medija i d) standardne termodinamičke veličine prijenosa HBr iz vode u 10 tež.% 2-propanol. Na osnovi podataka za d) može se zaključiti da je proces prijenosa HBr nespontan, da je miješano otapalo jača baza od vode i da ima više razvijenu strukturu nego li voda.

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