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STANDARD THERMODYNAMICS OF TRANSFER.
IV. THE SILVER AND SILVER SALT ELECTRODES IN ACETIC ACID + WATER MIXTURES AT 25 °C

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ABSTRACT

The standard transfer free energy changes for Ag^+, IO_3^- and BrO_3^- ions in 10, 20, 40 and 60 wt% acetic acid mixtures have been evaluated. The thermodynamic solubility product constants of silver halides, pseudo-halides and oxy halides in these solvents have been calculated.

INTRODUCTION

The standard thermodynamic quantities for ions in solvents comprising binary aqueous mixtures depend on the composition of the solvent, as well as on the nature of the organic co-solvent. Although this dependence may appear surprising in the case of few ions, it is often complicated. In recent years, the standard thermodynamic transfer quantities for ions in binary aqueous mixtures containing a protic or an aprotic co-solvent have been reported by different authors [1,2], and the results have been discussed in terms of solvation theory. Although the data in aqueous–basic co-solvent mixtures are quite large [3], relatively few studies [4] have been made on aqueous mixtures containing an acidic co-solvent. However, Samanta and Dash [5] made such studies in binary aqueous mixtures containing acetic acid as the second component. The aim of this investigation is to provide an insight into the solvation of some more simple ions in acetic acid + water mixtures. In this paper we report the standard potentials and the related thermodynamic functions for the silver–silver ion, silver–silver iodate and silver–silver bromate electrodes, and the thermodynamic solubility products of silver halides, pseudo-halides, and oxy halides in acetic acid (10, 20, 40 and 60 wt%) + water mixtures at 25 °C.

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For this purpose, cells of the type [6]

Ag(s), AgCl(s), NaCl(c), $NaNO_3$(c) || $NaNO_3$(c), $AgNO_3$(c), Ag(s) (A)

and

Ag(s), AgCl(s), KCl(c) || KXO_3(c), $AgXO_3$(s), Ag(s) (B)

where XO_3 is IO_3 or BrO_3, have been employed to determine the standard potentials of the silver–silver ion, silver–silver iodate and silver–silver bromate electrodes in different acetic acid + water mixtures.

EXPERIMENTAL

Sodium chloride, potassium chloride, sodium nitrate, silver nitrate, potassium iodate and potassium bromate were either of Merck G.R. grade or B.D.H. AnalaR grade. The salts were dried at 100–120 ° C for 2 h and stored in a vacuum desiccator over calcium chloride until required. Silver iodate and silver bromate were prepared from silver nitrate and the corresponding potassium salts, and the precipitates were repeatedly washed with conductivity water, and kept in conductivity water in amber-coloured bottles until use.

Glacial acetic acid was of G.R. grade. Solvents of various compositions were made up by weight in conductivity water. Stock solutions of the salts were prepared in acetic acid + water mixtures of various compositions on the molar scale.

The silver–silver ion and silver–silver chloride electrodes were prepared as described elsewhere [6]. Preparation of the silver–silver iodate and silver–silver bromate electrodes was similar to that described earlier [7] by applying a paste of the corresponding silver salt to the spongy silver obtained by thermal decomposition of silver oxide [8]. The electrodes thus prepared were stored in 0.05 M aqueous potassium salt solutions for 24 h. Only those which showed a potential difference of 0.1 mV or less, when compared with each other, were used.

Preparation of the cell solutions, setting up of the cells, e.m.f. and conductance measurements were essentially carried out as described earlier [1,5,6]. The measurements were carried out at a constant temperature (25 ± 0.05 ° C). The reproducibility of e.m.f. measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

The results of the e.m.f. measurements for cells (A) and (B) are presented

TABLE 1

E.m.f. data of cells (A) and (B) in various acetic acid+water mixtures at 25 °C

$10^2\,C$ (mol l^{-1})	Wt% acetic acid			
	10	20	40	60
Cell (A)				
0.5	0.3080	0.3250	0.3625	0.4042
1.0	0.3294	0.3427	0.3738	0.4261
2.0	0.3469	0.3759	0.4173	0.4554
4.0	0.3913	0.4099	0.4408	0.4843
5.0	0.4078	0.4280	0.4497	0.4919
6.0	0.4103	0.4311	0.4550	0.5000
8.0	0.4147	0.4343	0.4573	0.5081
10.0	0.4319	0.4477	0.4608	0.5149
Cell (B): $XO_3 = IO_3$				
0.5	0.3757	0.3607	0.3379	0.3228
1.0	0.3113	0.3586	0.3398	0.3249
2.0	0.3822	0.3683	0.3461	0.3216
4.0	0.3784	0.3680	0.3423	0.3235
5.0	0.3847	0.3670	0.3482	0.3225
6.0	0.3744	0.3613	0.3457	0.3178
8.0	0.3646	0.3641	0.3460	0.3228
10.0	0.3824	0.3647	0.3502	0.3205
Cell (B): $XO_3 = BrO_3$				
0.5	0.5942	0.5887	0.5779	0.5649
1.0	0.5952	0.5934	0.5815	0.5687
2.0	0.6000	0.5945	0.5854	0.5719
4.0	0.6079	0.6018	0.5917	0.5820
5.0	0.6113	0.6055	0.5963	0.5849
6.0	0.6124	0.6086	0.6008	0.5868
8.0	0.6196	0.6150	0.6052	0.5921
10.0	0.6259	0.6217	0.6086	0.5995

in Table 1. As usual [6], the e.m.f. of cell (A) is given by the expression

$$E = E^0_{\mathrm{Ag,Ag^+}} - E^0_{\mathrm{Ag,AgCl}} + (RT/F)\ln[\mathrm{Ag^+}][\mathrm{Cl^-}]\gamma_\pm^2 + E_\mathrm{j} \qquad (1)$$

and that of cell (B) is given by [5]

$$E = E^0_{\mathrm{Ag,AgXO_3}} - E^0_{\mathrm{Ag,AgCl}} + (RT/F)\ln\left([\mathrm{XO_3^-}]\gamma_{\mathrm{XO_3^-}}/[\mathrm{Cl^-}]\gamma_{\mathrm{Cl^-}}\right) + E_\mathrm{j} \qquad (2)$$

where the symbols have their usual meanings.

Using the molar concentrations of the corresponding electrolyte solutions and expressing the mean molar activity coefficients by the Debye–Hückel expression, the standard molar potentials, E_c^0, of the Ag/Ag$^+$, Ag/AgIO$_3$ and Ag/AgBrO$_3$ electrodes were obtained by the method of extrapolating [1,6] the corresponding auxiliary functions to the molarity $c = 0$.

The values of liquid junction potential, E_j, were calculated from the equivalent conductances of sodium chloride and silver nitrate for cell (A), and of potassium chloride and the corresponding potassium salt for cell (B) by means of the Lewis–Sargent equation [9]. It was found that the values of E_j varied in the range 0.1–0.3 mV for these cells in all solvents. The values of $E^0_{\mathrm{Ag,AgCl}}$ (molar scale) needed for the calculation of E^0_c of the electrodes in various acetic acid + water mixtures are obtained from E^0_m values [4] using the density values of various solvents [10] at 25 °C. The values of E^0_c of the silver–silver ion, silver–silver iodate and silver–silver bromate electrodes obtained by extrapolating the auxiliary functions to $c = 0$ are listed in Table 2. The average standard deviations in the values of E^0_c are ± 0.3 mV. The standard electrode potentials on the molal (E^0_m) and mole fraction (E^0_N) scales computed from E^0_c by the usual equations are also recorded in Table 2 along with those in water [1c (3),11].

The standard Gibbs free energy change, ΔG^0_m, on the molal scale for the electrode reactions in various solvents has been evaluated at 25 °C by the usual relation [1,12] and is shown in Table 2. The Gibbs free energy change

TABLE 2

Values of the standard potentials of the silver–silver ion, silver–silver iodate and silver–silver bromate electrodes on the molar, molal and mole fraction scales and standard molal Gibbs free energy change, transfer Gibbs free energy change and primary medium effect (mole fraction scale) of Ag^+, IO_3^- and BrO_3^- ions in various acetic acid + water mixtures at 25 °C

Wt% acetic acid	E^0_c (V)	E^0_m (V)	E^0_N (V)	$-\Delta G^0_m$ (kJ mol^{-1})	ΔG^0_t (kJ mol^{-1})	$\lim_{N \to 0} (\log {}^s\gamma_w)$
Silver – silver ion electrode						
0	0.7991	0.7993	0.6507	77.126	–	–
10	0.7865	0.7859	0.5833	75.834	6.506	1.140
20	0.7936	0.7924	0.5938	76.461	5.490	0.962
40	0.7997	0.7975	0.6080	76.949	4.121	0.722
60	0.7927	0.7897	0.6114	76.203	3.795	0.665
Silver – silver iodate electrode						
0	0.3288	0.3290	0.1226	31.746	–	–
10	0.3768	0.3762	0.1736	36.304	−4.919	−0.862
20	0.3629	0.3617	0.1631	34.902	−3.906	−0.684
40	0.3399	0.3377	0.1482	32.586	−2.471	−0.433
60	0.3235	0.3205	0.1421	30.928	−1.885	−0.330
Silver – silver bromate electrode						
0	0.5260	0.5262	0.3198	50.774	–	–
10	0.5930	0.5924	0.3898	57.165	−6.753	−1.183
20	0.5884	0.5872	0.3886	56.661	−6.636	−1.163
40	0.5784	0.5762	0.3867	55.598	−6.454	−1.131
60	0.5653	0.5624	0.3840	54.263	−6.192	−1.085

of transfer, ΔG_t^0, for the Ag^+ and XO_3^- ions is evaluated at 25 °C in different solvents by the usual relationships. The values of ΔG_t^0 were obtained on the mole fraction basis [13] and are presented in Table 2.

An inspection of Table 2 shows that E_m^0 values for the silver–silver ion electrode are less in acetic acid + water mixtures than in water and increase with increasing acetic acid content of the solvent system up to 40 wt% and then decrease at 60 wt%, whereas that for the silver–silver iodate and silver–silver bromate electrodes are higher (except in 60 wt% for the silver–silver iodate electrode) in the mixed solvents than in water and decrease with increasing proportion of acetic acid in the solvent system. It is thus clear that these differences in the E_m^0 values obtained in different solvents are due to the difference in solvation of Ag^+, IO_3^- and BrO_3^- ions in these solvents. As observed, the BrO_3^- ion is more solvated in these solvents than the IO_3^- ion; however, solvation decreases with increasing acetic acid content in water.

The ΔG_m^0 values presented in Table 2 for the electrode reactions show that any change in ΔG_m^0 on passing from water to various solvents will be due to variations of the free energy of solvation. The higher free energy due to solvation of IO_3^- (except at 60 wt%) and BrO_3^- ions in acetic acid + water mixtures may be due to the fact that these ions are more solvated in these mixed solvents than in water and the solvation decreases as the proportion of acetic acid increases. The lower free energy due to solvation of Ag^+ ion in the mixed solvents suggests that Ag^+ ion is less solvated in acetic acid + water mixtures and solvation increases with increasing acetic acid up to 40 wt% and decreased at 60 wt%.

As can be seen from Table 2, the standard Gibbs free energy of transfer for the Ag^+ ion appears to be positive and decreases as the proportion of acetic acid increases. The reverse is the case for the IO_3^- and BrO_3^- ions, where ΔG_t^0 values are negative and increase with increasing acetic acid content in the mixed solvents. The positive values of ΔG_t^0 signify that the transfer of Ag^+ from water to acetic acid + water solvents is not favourable, whereas the negative ΔG_t^0 values indicate that the IO_3^- and BrO_3^- ions are in lower free energy state in the mixed solvents than in water, and, therefore, the transfer process is favourable. The transfer of these ions becomes increasing unfavourable as the proportion of acetic acid increases in the mixed solvents.

The values of the primary medium effect, which is represented by

$$\lim_{N\to 0}(\log {}^{s}\gamma_{w}) = \left[(E_N^0)_w - (E_N^0)_s\right]/2.3026(RT/F)$$

in various acetic acid + water mixtures at 25 °C are presented in Table 2. The sign and magnitude of the primary medium effect could tell us about the stabilization of the ions in the solvent concerned. The positive magnitude of this quantity suggests that the escaping tendency of the Ag^+ ion is greater in acetic acid + water mixtures than in water. This is consistent with conclusions based on the fact that the Ag^+ ion is more strongly stabilized in aqueous medium than in the mixed solvents. The resulting negative magnitude of the primary medium effect indicates that the escaping tendency of the IO_3^- and BrO_3^- ions is less in the mixed solvents than in water. In other words, IO_3^- and BrO_3^- ions are more strongly stabilized in acetic acid + water media than in aqueous medium.

The thermodynamic solubility product, $K^0_{s_0}$, of AgX (X = Cl, Br, I, N_3, CNS, IO_3 or BrO_3) in acetic acid + water mixtures has been calculated at 25 °C from the values of standard potentials by means of the equation

$$\ln K^0_{s_0}(\mathrm{AgX}) = \left[E^0_c(\mathrm{Ag{-}AgX}) - E^0_c(\mathrm{Ag{-}Ag^+})\right]F/RT \tag{3}$$

where $E^0_c(\mathrm{Ag{-}AgX})$ is the standard molar potential of the Ag, AgX, X^- electrode, and $E^0_c(\mathrm{Ag{-}Ag^+})$ is that of the silver electrode obtained in the present study. The values for $K^0_{s_0}$ on the molar scale ($K^c_{s_0}$) are shown in Table 3 at 25 °C, along with those available in water [1c (3),11]. The values of $K^0_{s_0}$ on the molal scale ($K^m_{s_0}$) were calculated from $K^c_{s_0}/\rho^2$, where ρ is the density of the mixed solvent [10]. These values are also included in Table 3. As observed, the silver salts are more soluble in acetic acid + water mixtures than in water and the solubility decreases (except for the silver azide) with increasing acetic acid content in the mixed solvent. The observed decrease in

TABLE 3

Values of thermodynamic solubility products, $K^0_{s_0}$, on the molar ($K^c_{s_0}$) and molal ($K^m_{s_0}$) scales of AgX (X = Cl, Br, I, N_3, CNS, IO_3 and BrO_3) in various acetic acid + water mixtures at 25 °C

X	$K^0_{s_0}$	Wt% acetic acid				
		0	10	20	40	60
Cl	$K^c_{s_0}\times10^9$	0.178	1.216	0.474	0.123	0.0244
	$K^m_{s_0}\times10^9$	0.177	1.022	0.453	0.113	0.0218
Br	$K^c_{s_0}\times10^{13}$	4.898	5.487	2.551	0.571	0.0999
	$K^m_{s_0}\times10^{13}$	4.897	5.370	2.437	0.523	0.0892
I	$K^c_{s_0}\times10^{16}$	0.813	0.989	0.501	0.128	0.0305
	$K^m_{s_0}\times10^{16}$	0.812	0.968	0.479	0.117	0.0272
N_3	$K^c_{s_0}\times10^6$	0.0028	0.853	1.169	1.241	1.640
	$K^m_{s_0}\times10^6$	0.0027	0.835	1.117	1.138	1.464
CNS	$K^c_{s_0}\times10^{12}$	0.955	1.727	0.866	0.346	0.106
	$K^m_{s_0}\times10^{12}$	0.954	1.690	0.827	0.317	0.095
IO_3	$K^c_{s_0}\times10^7$	0.1096	1.189	0.524	0.169	0.117
	$K^m_{s_0}\times10^7$	0.1095	1.164	0.501	0.155	0.104
BrO_3	$K^c_{s_0}\times10^4$	0.240	5.367	3.397	1.818	1.433
	$K^m_{s_0}\times10^4$	0.239	5.253	3.245	1.667	1.279

$K_{s_0}^0$ values with decreasing dielectric constant of the mixed solvents as the proportion of acetic acid increases is in agreement with the electrostatic charging effect of the media. However, the increase in $K_{s_0}^0$ values for the AgN_3 with increasing acetic acid content is surprising. The observed increase in $K_{s_0}^0$ value with increasing composition of the mixed solvent might be due to the preferential solvation of Ag^+ and N_3^- ions by acetic acid in the mixed solvents as compared to the other silver salts. As observed, the solubility of the silver salts in the mixed solvents follows the order $AgBrO_3 > AgN_3 > AgIO_3 > AgCl > AgCNS > AgBr > AgI$, whereas that in aqueous medium is $AgBrO_3 > AgIO_3 > AgN_3 > AgCl > AgCNS > AgBr > AgI$. The sequence $AgN_3 > AgIO_3$ in acetic acid + water mixtures is also expected on account of the preferential solvation of Ag^+ and N_3^- ions by acetic acid in the mixed solvents over the Ag^+ and IO_3^- ions.

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