Standard Potentials of Silver/Silver Azide and Silver/Silver Thiocyanate Elctrodes in Water + Acetic Acid Mixtures at 25°C.

P.K. SAMANTA
Research & Control Laboratory (Chemical Section)
Steel Authority of India Limited,
Rourkela Steel Plant, Rourkela-769011
and
U.N. DASH
Department of Chemistry, Bhadrak College, Bhadrak-756 100

The standard potentials of the silver/silver azide and silver/silver thiocyanate electrodes in four different compositions of water + acetic acid mixtures at 25°C have been determined from the electromotive force measurments of cells of the type:

Ag (s)/ AgCl (s)/ NaCl (c)//NaN_3(c)/AgN_3(s)/Ag(s)
and
Ag (s)/ AgCNS (s)/ KCNS (c)//KCl (c)/ AgCl (s)/Ag(s)

The results have been discussed in terms of preferential solvation of ions.

No work seems to have been done on the determination of the standard potentials of the silver/silver azide and silver/silver thiocyanate electrodes in water + acetic acid mixtures. However, the standard potentials of the Ag, AgX (X = Cl, Br or I) electrode have been reported[1] in different compositions of water + acetic acid mixtures at 25°C. Dash et al[2] have reported the standard potentials of these electrodes in water + urea, water + dioxane, water + alcohols, water+ glycerol, water + acetone, Water + d-glucose and water + d- fructose solvent systems over a range of temperatures. The present work has been undertaken for the determination of standard potentials of the silver/silver azide and silver/silver thiocyanate electrode in water + acetic acid mixtures containing 10, 20, 40, and 60wt % acetic acid at 25°C. This temperature was selected in the present study since the standard potentials of the reference electrode silver/silver chloride electrode, in four different compositions of water + acetic acid mixtures are known[1] only at 25°C.

As in previous communications[2,3], the cells with liquid junction, viz.

Ag(s)/AgCl(s)/NaCl(c)//NaN_3(c)/ AgN_3(s)/Ag(s) (A)
and
Ag(s)/AgCNS(s)/KCNS(c)//KCl(c)/AgCl(s)/Ag(s) (B)

have been studied in water + acetic acid (10,20,40 and 60 wt%) mixtures for the determination of the standard potentials of the electrode at 25°C.

EXPERIMENTAL

Sodium chloride, sodium azide, potassium chloride and potassium thiocyanate were either of E. Merck G.R., or B.D.H., AnalaR samples. The salts were dried at 100 - 150°C for 2 hrs and stored in a vacuum disiccator over calcium chloride until required.

Glacical 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 water + acetic acid mixtures of various compositions on the molar scale.

The silver/silver chloride, silver/silver azide and silver/silver thiocyanate electrodes were prepared as described earlier[2,3]

Preparation of the cell solutions, setting up of the cells, emf and conductance measurments were essentially similar to that described earlier[2,3]. The measurements were carried out at a constant temperature, 25 ± 0.05° C. The reproducibility of emf measurments was of the order of ± 0.2 mV.

RESULTS AND DISCUSSION

The results of the emf measurements for the cells (A) and (B) are presented in Tables 1 and 2 respectively. As usual[2], the emf of cell (A) is given by the expression

TABLE 1

emf data of cell (A) in various water + acetic acid mixtures at 25°C.

$10^2 c$ mol l^{-1}	wt % acetic acid			
	10	20	40	60
0.5	0.21729	0.24774	0.29085	0.32952
1.0	0.21515	0.24046	0.28185	0.32550
2.0	0.20238	0.22948	0.26982	0.31145
4.0	0.17906	0.21235	0.25368	0.29340
5.0	0.17440	0.20948	0.24530	0.28640
6.0	0.16676	0.19904	0.24014	0.28232
8.0	0.16064	0.19214	0.23224	0.27348
10.0	0.15156	0.18448	1.22558	0.26814

TABLE 2

emf data of cell (B) in various water + acetic acid mixtures at 25°C

10^2 c mol l^{-1}	wt % acetic acid			
	10	20	40	60
0.5	0.11998	0.11795	0.10205	0.08808
1.0	0.12072	0.11806	0.10098	0.08945
2.0	0.12300	0.11842	0.10326	0.09020
4.0	0.12448	0.11898	0.10540	0.09146
5.0	0.12637	0.11830	0.10401	0.09165
6.0	0.12691	0.11870	0.10507	0.09182
8.0	0.12698	0.11922	0.10658	0.09094
10.0	0.12934	0.11940	0.10624	0.09186

$$E = E^\circ_{Ag,AgN_3} - E^\circ_{Ag,AgCl} - (RT/F)\ln([N_3^-]^{\nu}_{N_3^-}/[Cl^-]^{\nu}_{Cl^-}) + E_J \quad \ldots (1)$$

and that of cell (B) is given by

$$E = E^\circ_{Ag,AgCl} - E^\circ_{Ag,AgCNS} - (RT/F)\ln([Cl^-]^{\nu}_{Cl^-}/[CNS^-]^{\nu}_{CNS^-}) + E_J \quad .(2)$$

where the symbols have their usual significance.

By assuming that the ratio of concentrations and activity coefficients equals unity[4], since the concentrations in both sides of the cell are identical, the standard molar potentials, E°_c of the silver/silver azide and silver/silver thiocyanate electrodes were obtained by the method of extrapolating[2,3] respectively, the auxiliary function E^1 given by

$E^1 = E + E^\circ_{Ag,AgCl} - E_j$ for Ag/AgN_3 electrode..(3)

and

$E^1 = E^\circ_{Ag,AgCl} - E + E_J$ for Ag/AgCNS electrode.(4)

to the molarity, c = 0.

The values of the liquid junction potential, E_j were calucalated from the equivalent conductances of sodium azide and sodium chloride, and of potassium chloride and potassium-thiocyanate for the cells (A) and (B), respectively, by means of the Lewis Sargent equation[3(a)]. It was found that the values of E_j varied in the ranges 0.1 - 0.3 mV in all solvents. The values of $E^\circ_{Ag,AgCl}$ (molar scale) needed for the calculation of E^1 (equations (3) and (4))in various compositions of water + acetic acid mixtures are obtained from E°_m values[1] using the density values of various solvents[5] at 25°C. The values of E°_c of the silver/silver azide an silver/silver thiocyanate electrodes obtained on extrapolating E^1 to c = 0 are listed in Table- 3 . The average standard deviations in the values of E°_c are ± 0.3 mV. The standard electrode potentials on the molal (E°_m) and mole - fraction (E°_N) sclaes computed from E°_c by usual equations are also reported in Table-3 along with those in water[2].

The standard Gibbs free energy change, ΔG°_m on the molal scale for the electrode reaction:

$$AgX\ (s) + e \rightleftharpoons Ag\ (s) + X^-\ (solvated)$$

where X is N_3 or CNS, in various solvents has been evaluated at 25°C by the usual relation[6], and is listed in Table- 3 .

For the transfer process, X^- (water) $\rightarrow$ X^- (in water + acetic acid), the gibbs free energy ΔG°_t of transfer is defined by the equation:

$$\Delta G^\circ_t = -F\,(\,{}^sE^\circ_N - {}^wE^\circ_N\,)$$

Where the super scripts w and s donote water and mixed solvent, respectively. ΔG°_t values calculated on the mole - fraction scale[7], are presented in Table- 3

An inspection of Table- 3 shows that E°_m values for the silver/silver azide electrode are higher in water + acetic acid mixed solvents than in water and increase with the increasing acetic acid content of the solvent system upto 40 wt % and then decrease in 60 wt % , whereas that for the silver/silver thiocyanate electrode are smaller (except in 10 wt % acetic acid) in the mixed solvents than in water and decrease with increasing the proportion of acitic acid of the solvent system. It is thus clear that these differences in the E°_m values obtained in different solvents are due to the solvation of

TABLE 3

Values of the standard potentials of the silver/silver azide and silver/silver thiocyanate 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 scales) of N_3^- and CNS^- ions in various water + acetic acid mixtures at 25°C

Wt % acetic acid	E°_C /V	E°_m /V	E°_N /V	$-\Delta G^\circ_m$ / KJmol^{-1}	$-\Delta G^\circ_t$ / KJmol^{-1}	$\lim(\log {}^S\gamma_w)$ N ⟶ 0
			Silver / sliver azide electrode			
0	0.29330	0.29350	0.08710	-	-	-
10	0.42743	0.42688	0.22422	41.2	13.2	-2.32
20	0.44266	0.44149	0.24286	42.6	15.0	-2.63
40	0.45030	0.44807	0.25857	43.3	16.5	-2.90
60	0.45052	0.44750	0.26911	43.2	17.6	-3.08
			Silver / silver thiocyante electrode			
0	0.0880	0.0882	-0.1182	-	-	-
10	0.09061	0.09006	-0.11260	8.7	0.54	-0.095
20	0.07999	0.07881	-0.11982	7.6	-0.16	0.027
40	0.06256	0.06033	-0.12918	5.8	-1.06	0.186
60	0.02518	0.02226	-0.15614	2.2	-3.66	0.641

N_3^- or CNS^- ion in these solvents and any change in E°_m value on passing from water to water + acetic acid mixtures will be due to variation of solvation.

The ΔG°_m value reported in Table-3 for the electrode reactions show that any change in ΔG°_m on passing from water to various solvents will be due to variation of free energy of solvation. The higher free energy due to solvation of N_3^- ion in water + acetic acid solvent systems may be due to the fact that N_3^- ion is more solvated in these mixed solvents rhan in water and the solvation increases as the proportion of acetic acid increases. The lower free energy due to solvation of CNS^- ion in the mixed solvents (except 10 wt% acetic acid) suggests that CNS^- ion is less solvated in water + acetic acid mixed solvents and solvation decreased with increasing acetic acid contents of the solvent system. As the proportion of acetic acid increases, the ΔG°_t value for the N_3^- ion becomes increasingly negative. The negative value of ΔG°_t signifies that the transfer of N_3^- ion from water to water + acetic acid mixtures is increasinly favourable. Thus, the N_3^- ion appears to be in a lower Gibbs energy state and hence more strongly stabilised in these mixed solvents than in water. But, the reverse is the case with CNS^- ion; the increasingly positive values of ΔG°_t signify that the transfer of CNS^- ion from water to water + acetic acid mixtures is not favourable.

At infinite dilution, interionic effects (secondary medium effect) are absent and only ion-solvent ineractions (primary medium effect) are presnet. The primary medium effect is a measure of the change of Gibbs free energy which accompanies the transfer of 1 gm - ion of N_3^- or CNS^- ion from the standard State in water to the standard state in the mixed solvent. The values of the primary effect (mole -fraction scale) of various water + acetic acid mixtures upon N_3^- and CNS^- ions at 25°C were computed by the equation:

$$\lim_{N \to 0} (\log {}^S\gamma_w) = ({}^W E^\circ_N - {}^S E^\circ_N)/2.3026(RT/F) \quad ..(6)$$

Where the limit term indicates the primary medium effect. These values are also shown in Table-3 . It is seen that the medium has a greater effect upon the CNS^- ion as the concentration of acetic acid is gradually increased. The increasingly positive values of the primary medium effect suggest that the escaping tendency of the CNS^- ion is greater in water + acetic acid mixtures than in pure water, whereas the resulting negative magnitudes of this quantity indicates that the escaping tendency of the N_3^- ion is less in the mixed solvents than in the aqueous medium. This is consistent with the conclusions based on the fact that the N_3^- ion is more strongly stabilised in water + acetic acid mixtures than in water medium.

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