STANDARD POTENTIALS OF SILVER/SILVER AZIDE AND SILVER/SILVER THIOCYANATE ELECTRODES IN WATER + D-GLUCOSE AND WATER + D-FRUCTOSE MIXTURES AT 25 C

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The standard potentials of the silver/silver azide and silver/silver thiocyanate electrodes in different compositions of water + D-glucose and water + D-fructose mixtures at 25 C have been determined from the emf measurements of cells of the type :

$$Ag(s)/AgCl/NaCl(c) \parallel NaN_3\ (c)/AgN_3\ (s)/Ag(s) \quad \text{and}$$
$$Ag(s)/AgCNS(s)/KCNS(c) \parallel KCl(c)/AgCl(s)/Ag(s)$$

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

In a potentiometric determination of standard potentials of the electrodes of the second kind, Dash and Samanta reported the standard potentials of silver/silver azide and silver/silver thiocyanate electrodes in water + acetic acid mixtures at 25°C <1>. Dash et al have reported the standard potentials of these electrodes in aqueous, non-aqueous and various aquo-organic solvent systems over a range of temperatures <2>. In continuation of such studies, the present work reports the standard potentials of these two electrodes in water + D-glucose and water + D-fructose mixtures at 25°C. This temperature was chosen in the present work since the standard potentails of the reference electrodes, silver/silver chloride, in different compositions of water + D-glucose and water + D-fructose mixtures are known <3> only at 25°C.

As in the previous communications , the cells with liquid junction viz.

$Ag(s)/AgCl(s)/NaCl(c) \parallel NaN_3(c)/AgN_3(s)/Ag(s)$ .....(A)

and

$Ag(s)/AgCNS(s)/KCNS(c) \parallel KCl(c)/AgCl(s)/Ag(s)$ .....(B)

are set up

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 desiccator over calcium chloride until required.

D-Glucose and D-fructose were of G.R. samples and used without further purification. Solvents of various compositions were made up by weight in conductivity water. Stock solutions of the salts were prepared in water + D-glucose and water + D-fructose mixtures of specified compositions on the molar scale.

The silver/silver chloride, silver/silver azide and silver/silver thiocyanate electrodes were prepared as described earlier <2>. Cells A and B are set up.

Preparations of cell solutions, setting up of the cells, e.m.f and conductance measurements were essentially similar to that described earlier 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 the cells (A) and (B) are presented in the Table 1 and 2, respectively. The e.m.f. of cell A is given by the expression <1>

$$E^\circ_{cell} = E^\circ_{Ag,AgCl_3} - E^\circ_{Ag,AgCl}$$
$$-(RT/F)\ \ln([N_3^-]\ \gamma_{N_3^-} / [Cl^-]\gamma_{Cl^-}) + E_j \quad ...(1)$$

and that of cell (B) is given by

$$E^\circ_{cell} = E^\circ_{Ag,AgCl} - E^\circ_{Ag,AgCNS}$$
$$-(RT/F)\ \ln([Cl^-]-\gamma Cl^- [CNS]\ \gamma CNS^-) + E_j \quad (2)$$

where the symbols have their usual significance.

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TABLE 1

EMF DATA OF CELL(A) IN VARIOUS SUGAR SOLUTIONS AT 25°C

10^2C mol/L	% of D glucose				% of D fructose	
	5	10	20	30	5	10
0.5	0.0680	0.0673	0.0695	0.0730	-	0.0690
1.0	0.0668	0.0682	0.0697	0.0710	-	-
2.0	-	0.0699	0.0690	0.0720	0.0674	0.0672
2.5	0.0656	0.0651	0.0679	-	-	-
3.0	0.0669	0.0671	0.0674	0.0704	0.0671	0.0669
4.0	0.0652	0.0668	0.0681	0.0700	0.0687	0.0660
5.0	0.0656	0.0663	0.0676	0.0701	0.0671	0.0666
6.0	0.0655	0.0659	0.0661	0.0695	0.0665	0.0669
7.0	-	-	-	0.0697	0.0667	0.0665

TABLE 2

EMF DATA OF CELL(B) IN VARIOUS SUGAR SOLUTIONS AT 25°C

10^2C mol/L	% of D glucose				% of D fructose	
	5	10	20	30	5	10
0.5	-	0.1270	0.1290	0.1250	-	0.1279
1.0	0.1298	0.1250	0.1260	0.1259	0.1299	0.1290
2.0	0.1315	0.1329	0.1316	-	0.1300	0.1282
2.5	0.1312	-	-	0.1260	0.1293	0.1274
3.0	-	0.1342	0.1284	-	0.1293	0.1300
4.0	0.1304	0.1310	0.1350	0.1261	0.1313	0.1290
5.0	0.1339	0.1335	0.1360	-	0.1302	-
6.0	-	0.1289	0.1359	-	0.1319	-
7.0	0.1334	0.1332	-	0.1267	0.1323	-
8.0	-	0.1353	-		-	-

Since the concentrations in both half cells are equal and one could assume that the ratio of the activity coefficients is unity, the third term on the right hand side of equations (1) and (2) becomes 0. The standard molar potentials, E°_c of the silver/silver azide and silver/silver thiocyanate elecrodes were obtained by extraprolating , the auxiliary function, E′ given by

$$E' = E_{cell} + E^\circ_{AgN_3,AgCl} - E_j \text{ for } Ag/AgN_3 \text{ electrode} \quad (3)$$

and

$$E' = E^\circ_{AgN_3,AgCl} - E_{cell} + E_j \text{ for } Ag/AgCNS \text{ electrode} \quad (4)$$

to the molarity, c=0.

The value of the liquid junction potential E_j were calculated from the equivalent conductances of sodium azide and sodium chloride, for cell A and of potassium chloride and potassium thiocyanate for the cell (B), by means of the Lewis-sargent equation <2d>. It was found that the values of E_j varied in the ranges 0.1 - - 0.3 mV in all solvents. The value of $E^\circ_{AgN_3,AgCl}$ (molar scale) needed for the calculation of E′ in equations (3) and (4) in various compositions of the mixtures are obtained from E°_m values <3> using the density values of the particular medium at 25°C. The auxiliary function E′ given by equation (3) and (4) are calculated and these E′ values are extracpolated to C=0. The values E°_c the silver/silver azide and silver/siler· thiocynate electrodes obtained on extrapolating E′ to C=0 are presented 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 molefraction (E°_N) scales computed from E°_c by usual relations also

shown in Table 3.

The standard Gibbs free energy change, on the molal scale, ΔG°_{m}, 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 and is listed in Table 3.

For the transfer process,
X^{-} (water) ⟶ X^{-} (in mixed solvent) the Gibb's free energy, of transfer ΔG°_{t} is defined by the equation:

$$\Delta G^{\circ}_{t} = -F({}^{s}E^{\circ}_{N} - {}^{w}E^{\circ}_{N}) \text{ ---------->} \quad (5)$$

where the super scripts s and w refer to water and mixed solvent, respectively. G°_{t} values evaluated in the mole-fraction scale ⟨2d⟩, are listed in Table 3. This value is regarded as consisting of two parts as given by

$$\Delta G^{\circ}_{t} = \Delta G^{\circ}_{t,el} + \Delta G^{\circ}_{t,ch} \text{ --------->} \quad (6)$$

In which $\Delta G^{\circ}_{t,el}$ respresnts the electrostatic contribution arising from the change in the dielectric constant of the solvents during the transfer of charged particles from water to another solvent and $\Delta G^{\circ}_{t,ch}$ represents the non-electrostatic or chemical contribution which takes into account the specific chemical interactions between the ions and solvent which include solvation as well as the basicity of the solvent. As in earlier communications ⟨2d⟩ $\Delta G^{\circ}_{t,el}$ was estimated from the Born equation ⟨5⟩ and the values of $\Delta G^{\circ}_{t,ch}$ were computed from equation (6). These values are presented in Table - 3.

A perusal of Table 3 shows that E°_{m} values for the sliver/silver azide electrode decrease with increasing D - glucose or D-fructose content of the solvent system, but that for the silver/silver thiocyanate electrode are higher in 5 wt% D-glucose

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 THERMODYNAMIC QUANTITIES, AND PRIMARY MEDIUM EFFECT (MOLE-FRACTION SCALES) OF N_3^- AND CNS^- IONS IN DIFFERENT MEDIA AT 25°C

	% of D glucose				% of D fructose	
	5	10	20	30	5	10
			Silver/Silver azide electrode			
E°_{c} /V	0.2862	0.2826	0.2752	0.2672	0.2872	0.2837
E°_{m} /V	0.2860	0.2822	0.2744	0.2659	0.2870	0.2833
E°_{N} /V	0.0820	0.0807	0.0782	0.0757	0.0830	0.0818
$-\Delta G^{\circ}_{m}$ /KJmol^{-1}	27.60	27.23	26.48	25.66	27.69	27.34
ΔG°_{t} /KJmol^{-1}	0.49	0.62	0.86	1.10	0.39	0.51
$\Delta G^{\circ}_{t,el}$/KJmol^{-1}	0.024	0.05	0.10	0.17	0.024	0.05
$\Delta G^{\circ}_{t,ch}$/KJmol^{-1}	0.047	0.57	0.76	0.93	0.37	0.46
lim(log γ_w) N --> 0	0.086	0.108	0.150	0.193	0.069	0.09
K^{c}_{s} x 10^{9} (molar)	7.24	7.11	6.31	6.07	7.34	7.18
K_s x 10^{9} (molal)	7.20	7.00	6.11	5.78	7.53	7.08
			Silver/silver thiocyanate electrode			
E°_{c} /V	0.0889	0.0853	0.0788	0.0694	0.0907	0.0874
E°_{m} /V	0.0887	0.0849	0.0780	0.0681	0.0905	0.0870
E°_{N} /V	-0.1153	-0.1166	-0.1183	-0.1221	-0.1135	-0.1145
$-\Delta G^{\circ}_{m}$/KJmol^{-1}	8.56	8.19	7.53	6.57	8.73	8.39
ΔG°_{t} / "	-0.28	-0.15	0.01	0.38	-0.45	-0.36
$\Delta G^{\circ}_{t,el}$ "	0.02	0.03	0.07	0.12	0.02	0.03
$\Delta G^{\circ}_{t,ch}$ "	-0.30	-0.18	-0.06	0.26	-0.47	-0.39
lim(log ${}^{s}\gamma_w$) N --> 0	-0.049	-0.027	0.002	0.066	-0.079	-0.063
K_s x 10^{12} (molar)	3.37	3.29	3.12	2.75	3.50	3.45
K_s x 10^{12}(molal)	3.35	3.24	3.02	2.62	3.48	3.39

and D - fructose mixtures but lower in higher compositions. In both the cases, the E°_{m} values are higher in water + D-fructose mixtures than in water +D glucose mixed solvents. It is thus clear that these differences in the E°_{m} values are due to the difference in solvation of N_3^- or CNS^- ions in these media.

Any change in ΔG°_{m} on passing from water to various solvents will be due to variation of free energy of solvation. The lower free energy due to solvation of N_3^- and CNS^- ions in the mixed solvents (expect 5 wt% each of D - Glucose and D - fructose for CNS^- ion) suggests that N_3^- and CNS^- ions are less solvated in the mixed solvents and solvation decreases with increasing D - glucose or D - fructose cntents of the solvent system. As observed, the values of ΔG°_{t} and $\Delta G^{\circ}_{t,sh}$ for the N_3^- ion are positive for all solvents and the magnitude generally increases with increasing proportions of D - glucose and D - fructose. The transfer of N_3^- ion from aqueous to sugar solution system is not favoured. In so far as $\Delta G^{\circ}_{t,sh}$ is a measure of solvation as well as the relative basicities of the two solvents, the positive $\Delta G^{\circ}_{t,sh}$ value for the transfer of N_3^- ion to all mixed solvents possess a smaller solvating capacity towards the N_3^- ion. But the reverse is the case with CNS^- ion (except in 30 wt% D - glucose). However, the decreasingly negative values of ΔG°_{t} and $\Delta G^{\circ}_{t,sh}$ with increasing proportions of D - glucose and d - fructose suggest that the transfer process from aqueous to mixed solvents gradully becomes less favoured as the sugar content increases.

The primary medium effect is a measure of the change of Gibb's 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 medium effect (mole - fraction scale of various media upon the N_3^- and CNS^- ions at 25°C were calculated by the equation:

$$\lim_{N \to 0} (\log {}^{s}\gamma_{w}) = ({}^{\circ w}E^{\circ}_{N} - {}^{s}E_{N})/2.3026(RT/F) \quad \text{---------- (7)}$$

these values are also shown in Table 3. It is seen that the medium has a greater effect upon the N_3^- and CNS^- ions as the concentrations of D - glucose and D - fructose is gradually increased. The increasingly positive values of the primary medium effect auggest that the escaping tendency of the N_3^- and CNS^- ions is greater in water + D glucose and water + D fructose mixtures (excepting 5 and 10 wt% each of D glucose and D fructose for the CNS^- ions) than in pure water. This is consistent with the conclusions based on the fact that the N_3^- ion is more strongly stabilised in water than in mixed solvents whereas the CNS^- ion is less stabilised in water than in lower compositions of D glucose and D fructose mixtures.

The soluility products, K°_{s} of silver azide and silver thiocyanate in different media have been calculated at 25°C from the values of the standard potentials of the silver/silver azide and silver/silver thiocyanate electrodes, and of the silver electrode by means of the equation:

$$\ln K^{\circ}_{s}(AgX) = [E^{\circ}_{c}(Ag/Ag^{x}) - E^{\circ}_{c}(Ag/Ag^{+})] (F/RT) \quad \text{---------- (8)}$$

where X is N_3^- or CNS^- and E°_{c} (Ag/Ag$^+$) is the standard molar potential of the silver/silver ion electrode and is obtained from our earlier work [6]. The values for K°_{s} in the molarity scale (K^{c}_{s}) and molality scale (K^{m}_{s}) were calculated (Table 3) at 25°C. The data for K^{m}_{s} were calculated from K^{c}_{s}/ρ^2, where ρ is the density of the mixed solvent. As observed, the solubility of silver azide and silver thiocynate decreases with increasing proportion of sugars.

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