

**Note****THERMODYNAMICS OF THE SILVER/SILVER THIOCYANATE ELECTRODE IN WATER, + METHANOL, + ETHANOL, + 1-PROPANOL, + 2-PROPANOL, AND + GLYCEROL MIXTURES**

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A survey of the literature [1,2] shows that the standard potentials of the silver–silver halide electrodes have been reported either at a single temperature, 25°C, or at different temperatures in various compositions of water + alcohol mixtures. But no work seems to have been done on the determination of the standard potentials of the silver–silver pseudohalide and silver–silver oxyhalide electrodes in these solvents. However, Dash et al. [3] have reported the standard potentials of the Ag–AgCNS, Ag–AgN<sub>3</sub>, Ag–AgBrO<sub>3</sub> and Ag–AgIO<sub>3</sub> electrodes in water + dioxane and water + urea mixtures at different temperatures. With a view to studying the effect of a changing solvent composition on the ion–solvent and electrode–solvent interactions, we now report the standard potentials of the Ag–AgCNS electrode in water + alcohol mixtures at different temperatures.

As before [3,4], the study of cell (A) with liquid junction



has been made in water + alcohol mixtures containing 10 and 20% methanol, ethanol, 1-propanol and 2-propanol, and 50% glycerol by weight at temperatures from 5 to 35°C.

**EXPERIMENTAL**

The preparation of the silver–silver thiocyanate and silver–silver chloride electrodes has been described earlier [3(a)]. Only those electrodes which showed a potential difference of 0.1 mV or less on being compared with another of the same type were used. The cell vessels were of an all-glass type of the design described in our earlier communications [3,4].

Potassium chloride and potassium thiocyanate were the same samples used in the previous study [3(a)]. Methanol, ethanol, 1-propanol and 2-propanol (B.D.H., Laboratory reagents) were dried over magnesium oxide and distilled. The middle fractions of the distillate were similarly treated twice and finally collected in dry containers. Glycerol (B.D.H., Laboratory reagent) was purified by distilling three times under reduced pressure. Solvents of various compositions were made up by weight in conductivity water.

Equimolar solutions of potassium chloride and potassium thiocyanate were prepared from the stock solutions by the double dilution method. The general experimental procedures for setting up of the cells, the e.m.f., and conductance measurements were essentially similar to those described earlier [3,4].

### Results

As usual [3], the standard molar potential,  $E_c^0$  of the silver-silver thiocyanate electrode was obtained by the method of extrapolating [3,4] the auxiliary function,  $E_c^{0'}$  given [3(a)] by

$$\begin{aligned} E_c^{0'} &= E_{\text{Ag,AgCl}}^0 - E - (RT/F) \ln([\text{Cl}^-] \gamma_{\text{Cl}^-} / [\text{CNS}^-] \gamma_{\text{CNS}^-}) + E_j \\ &= E_c^0 + f(c) \end{aligned} \quad (1)$$

where the symbols have their usual significance, to the molarity,  $c = 0$ .

The values of the liquid junction potential  $E_j$ , were calculated from the equivalent conductances of potassium chloride and potassium thiocyanate

TABLE I

Standard molar potentials ( $E_c^0/V$ ) for the silver-silver thiocyanate electrode in water + alcohol mixtures from 5 to 35°C

Alcohol	Wt.% alcohol	$t$ (°C)						
		5	10	15	20	25	30	35
Methanol	10	0.0945	0.0939	0.0933	0.0929	0.0924	0.0917	0.0912
	20	0.0924	0.0918	0.0914	0.0908	0.0904	0.0899	0.0894
Ethanol	10	0.0904	0.0899	0.0892	0.0888	0.0881	0.0876	0.0870
	20	0.0888	0.0885	0.0880	0.0874	0.0868	0.0861	0.0854
1-Propanol	10	0.0967	0.0962	0.0955	0.0948	0.0941	0.0929	0.0920
	20	0.1036	0.1021	0.1008	0.0996	0.0981	0.0969	0.0953
2-Propanol	10	0.0892	0.0886	0.0881	0.0875	0.0868	0.0862	0.0855
	20	0.0918	0.0912	0.0907	0.0903	0.0898	0.0892	0.0886
Glycerol	50	0.0831	0.0825	0.0819	0.0811	0.0803	0.0797	0.0789

TABLE 2

Constants of eqn. (2) for molar (c), molal (m) and mole fraction (N) scales in water + alcohol mixtures

Alcohol	Wt.% alcohol	x	Constants			
			$10^2 A$	$10^4 B$	$10^4 C$	$10^6 D$
Methanol	10	c	11.378	0.49069	-0.17813	-0.13191
		m	16.011	-7.1067	0.74844	0.40471
		N	13.569	-3.2551	-1.1827	1.1598
	20	c	13.573	-2.0022	-0.016194	0.38384
		m	14.052	-5.2427	0.58985	0.17641
		N	11.295	-0.88736	-1.3763	0.85170
Ethanol	10	c	13.739	-8.5077	1.3504	-0.56266
		m	14.830	-8.6459	1.2043	-0.13361
		N	10.116	0.65139	-1.5440	0.62346
	20	c	0.42766	5.0956	0.37118	-2.9803
		m	5.2002	-8.1835	2.4988	-3.2377
		N	3.1462	-0.35586	-0.30703	-1.7968
1-Propanol	10	c	0.21353	-6.4984	3.0772	-5.3364
		m	2.4638	-3.2685	2.0415	-4.0288
		N	2.7334	-1.9044	0.26021	-2.7565
	20	c	16.978	-7.0769	1.0671	-0.94399
		m	16.952	-11.949	2.0967	-1.5818
		N	14.846	-2.5788	-1.0503	0.07379
2-Propanol	10	c	7.3626	2.4516	-0.059409	-1.1206
		m	9.4111	-3.5421	0.92163	-1.2725
		N	9.4149	-3.7961	-0.45054	-0.32715
	20	c	10.781	-5.2645	1.0900	-1.0418
		m	10.372	-0.94783	-0.21351	-0.45581
		N	9.2446	-3.3550	-0.53196	-0.20675
Glycerol	50	c	9.5858	-4.1298	0.96957	-1.2836
		m	11.315	-2.5192	0.3179	-0.39395
		N	11.410	-1.4698	-1.2174	0.70037

by means of the Lewis Sargent equation [4]. It was found that the values of  $E_j$  varied in the range 0.1–0.3 mV in all solvents for all temperatures. The values  $E_{Ag,AgCl}^0$  (molar scale) needed for the calculation of  $E_c^{0'}$  [eqn. (1)] at different temperatures in various compositions of water + alcohol mixtures were taken from the literature [2]. The logarithm term in eqn. (1) tends to zero assuming that the ratio of concentrations and activity coefficients is unity [5], since the concentrations in both sides of the cell are identical. The values of  $E_c^0$  obtained on extrapolating  $E_c^{0'}$  to  $c = 0$  are presented in Table 1. The average standard deviations in the values of  $E_c^0$  are  $\pm 0.3$  mV.

As usual [3(a)], from the  $E_c^0$  values the standard potentials on the molal

TABLE 3

Values of the standard potentials of the silver-silver thiocyanate electrode on the molar, molal and mole fraction scales in water and water+alcohol mixtures at 25°C

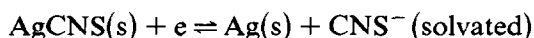
Alcohol	Wt% alcohol	$E_c^0/V$	$E_m^0/V$	$E_N^0/V$
Methanol	0	0.0880	0.0882	-0.1182
	10	0.0924	0.0935	-0.1105
	20	0.0904	0.0923	-0.1093
Ethanol	10	0.0881	0.0892	-0.1139
	20	0.0868	0.0886	-0.1110
1-Propanol	10	0.0941	0.0951	-0.1075
	20	0.0981	0.0991	-0.1035
2-Propanol	10	0.0868	0.0886	-0.1100
	20	0.0898	0.0915	-0.1070
Glycerol	50	0.0803	0.0745	-0.1054

( $E_m^0$ ) and mole fraction ( $E_N^0$ ) scale were calculated. The  $E^0$  values on different scales at various temperatures for any solvent were fitted by the method of least squares, to the equation [3(b)]

$$E_x^0 = A + BT + CT \ln T + \frac{DT^2}{2} \quad (2)$$

where x is c, m or N and  $T(K)$  is any temperature. The constants  $A$ ,  $B$ ,  $C$  and  $D$  of eqn. (2) are presented in Table 2. The average deviation between the experimental values (Table 1) and the values calculated from eqn. (2) is within  $\pm 0.3$  mV. The  $E^0$  values at 25°C are shown in Table 3, along with those in water [3(a), 6].

The standard thermodynamic quantities ( $\Delta G^0$ ,  $\Delta S^0$ , and  $\Delta H^0$ ) for the electrode reaction



and the standard thermodynamic quantities,  $\Delta G_t^0$ ,  $\Delta S_t^0$  and  $\Delta H_t^0$  for the transfer process  $\text{CNS}^-$  (in water)  $\rightarrow$   $\text{CNS}^-$  (in water + alcohol) have been evaluated at different temperatures for various solvents by the usual relations [3,7]. As before [3,8], the transfer thermodynamic quantities were obtained on the mole fraction basis. Table 4 lists these values at 25°C along with the values of the change in electrostatic Gibbs energy ( $\Delta G_{t,\text{el}}^0$ ), the electrostatic entropy ( $\Delta S_{t,\text{el}}^0$ ) and the electrostatic contribution for the change of enthalpy ( $\Delta H_{t,\text{el}}^0$ ).

For the estimation of the  $\Delta G_{t,\text{el}}^0$  and  $\Delta S_{t,\text{el}}^0$  values, the equations [3]

$$\Delta G_{t,\text{el}}^0 = (Ne^2/2)(\epsilon_s^{-1} - \epsilon_w^{-1})(r_+^{-1} + r_-^{-1}) \quad (3)$$

TABLE 4  
Transfer thermodynamic quantities (mole fraction scale) in different water + alcohol mixtures at 25°C

Alcohol	Wt% alcohol	$-\Delta G_t^0$ (kJ mole <sup>-1</sup> )	$\Delta G_{t,el}^0$ (kJ mole <sup>-1</sup> )	$\Delta S_t^0$ (J mole <sup>-1</sup> K <sup>-1</sup> )	$-\Delta S_{t,el}^0$ (J mole <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_t^0$ (kJ mole <sup>-1</sup> )	$-\Delta H_{t,el}^0$ (kJ mole <sup>-1</sup> )
Methanol	10	0.6	1.1	91	27	26.4	6.9
	20	0.7	1.9	92	24	26.7	5.3
Ethanol	10	0.3	1.7	89	26	26.4	6.5
	20	0.6	2.4	90	23	26.3	4.4
1-Propanol	10	0.9	1.5	84	25	24.2	6.1
	20	1.3	2.8	75	22	20.9	3.6
2-Propanol	10	0.7	1.5	90	26	26.1	6.1
	20	1.0	3.0	92	22	26.6	3.5
Glycerol	50	1.1		92		26.4	

and

$$\Delta S_{t,el}^0 = (-Ne^2/2)(\epsilon_s^{-1}\theta_s^{-1} - \epsilon_w^{-1}\theta_w^{-1})(r_+^{-1} + r_-^{-1}) \quad (4)$$

have been employed where the radius of the silver ion ( $r_+$ ) may be taken as 1.26 Å [8] and that of thiocyanate ion ( $r_-$ ) as 2.58 Å [9] assuming the radii of the ions do not change with the change of solvent [8],  $\epsilon_s$  and  $\epsilon_w$  are the dielectric constants of the mixed solvent and water and were taken from the literature [2]. The values of  $\theta_w$  and  $\theta_s$ , the temperature coefficients of the dielectric constants, were obtained from the literature [2]. The values of  $\Delta H_{t,el}^0$  were computed from a knowledge of  $\Delta G_{t,el}^0$  and  $\Delta S_{t,el}^0$ .

## DISCUSSION

An inspection of Table 3 shows that the standard electrode potentials of the silver-silver thiocyanate electrode in various water + alcohol mixtures are, in most cases, higher than in water. Such an observation seems to be contrary to the studies made on the silver-silver halide electrodes [1,2] in various water + alcohol mixtures. However, the solvent effect on the standard potential of the silver-silver thiocyanate electrode can be examined from the related quantities of Gibbs free energies of transfer of the  $CNS^-$  ion from water to the solvent concerned, since the Gibbs free energy of transfer is an important index of the differences in interactions of the ion and the solvent molecules in the two different media.

As can be seen from Table 4, the values of  $\Delta G_t^0$  for HCNS, unlike those for HCl and HBr [1,2,10], appear to be negative and they become increasingly negative as the proportion of alcohol increases. The negative value of  $\Delta G_t^0$  signifies that the transfer of the  $CNS^-$  ion from water to water + alcohol mixtures is favourable. Thus, the  $CNS^-$  ion appears to be in a lower Gibbs energy state and hence more strongly stabilized in these mixed solvents than in water. The positive entropy of transfer of the  $CNS^-$  ion from water to the mixed solvents can probably be attributed to more structure breaking by the

TABLE 5

Primary medium effect  $\lim_{N \rightarrow 0} \log {}^s\gamma_w$  (on the mole fraction scale) of  $CNS^-$  ion in various water + alcohol mixtures at 25°C

Methanol (wt.%)		Ethanol (wt.%)		1-Propanol (wt.%)		2-Propanol (wt.%)		Glycerol (wt.%)
10	20	10	20	10	20	10	20	50
-0.13	-0.15	-0.07	-0.12	-0.18	-0.26	-0.14	-0.19	-0.22

CNS<sup>-</sup> ion in water + alcohol than in water. Consequently, the degree of solvent orientation is less in the mixed solvents than in water. Thus, the net amount of order created by the CNS<sup>-</sup> ion is less in water + alcohol mixtures than in aqueous medium, and hence, the CNS<sup>-</sup> ion "breaks down more structure" in these mixed solvents. The positive  $\Delta H_t^0$  values suggest that the transfer process is endothermic, because of the dehydration and then re-solvation of the CNS<sup>-</sup> ion by alcohols.

The values of the primary medium effect, which is represented [3,8] by

$$\lim_{N \rightarrow 0} (\log {}^s\gamma_w) = \frac{[(E_N^0)_w - (E_N^0)_s]}{2.3026(RT/F)}$$

in various water + alcohol mixtures at 25°C are shown in Table 5. As observed, the value of the primary medium effect is negative, indicating that the escaping tendency of the CNS<sup>-</sup> ion is less in water + alcohol mixtures than in pure water. This is consistent with the conclusions based on the fact that the CNS<sup>-</sup> ion is more strongly stabilized in water + alcohol mixtures than in aqueous medium.

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