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Note

THERMODYNAMICS OF THE SILVER—SILVER THIOCYANATE ELECTRODE IN WATER—DIOXANE MIXTURES AT DIFFERENT TEMPERATURES

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In recent years, considerable effort has been devoted to physico-chemical studies in non-aqueous and mixed solvents. Most of these have been concerned with solutions in mixed solvents with a view to explaining the effect of a changing solvent composition of the ion—solvent and electrode—solvent interactions. Several workers [1—6] have presented studies of electrode—solvent interactions in water—dioxane, water—glycol, water—alcohols and water—urea mixtures of various compositions, and have reported the role of the permittivity of the medium towards such interactions.

In previous studies [3,7—9], we have examined the effect of changing the solvent from pure water to 10, 20, 30 and 40 mass % dioxane + water on the dissociation of acids, dissolution of silver salts and standard potentials of the silver—silver chromate electrode. To extend the work, we now report the results of a determination of the standard potentials of the silver—silver thiocyanate electrode and associated thermodynamic parameters for the electrode reaction in these media. However, various thermodynamic quantities for the electrode reaction of this electrode and the dissolution process of silver thiocyanate are known in water [10] and formamide [11].

EXPERIMENTAL

The potassium chloride and potassium thiocyanate were the same samples used in the previous study [11]. Dioxane was purified as described earlier [3]. Silver—silver chloride and silver—silver thiocyanate electrodes were prepared according to the methods available in the literature [11]. The solvent mixtures of various mass percentages were prepared as described in our earlier article [3]. Stock solutions of potassium chloride and potassium thiocyanate were prepared by dissolving the appropriate weighed amounts of these salts in known weights of water—dioxane mixtures of various compositions. Solutions for e.m.f. measurements were prepared from stock solutions by the method of double dilution. The cell vessels were of an all-glass type of the design described earlier [3].

Preparation of the cell solutions, setting up of the cells, e.m.f. and conductance measurements were essentially similar to the methods described earlier [3]. All measurements were made in water baths maintained at appropriate temperatures within ±0.1° C.

Cells of the type

$$\mathrm{Ag{-}AgCNS|KCNS}(m)||\mathrm{KCl}(m)|\mathrm{AgCl{-}Ag} \qquad \text{(A)}$$

were used in the present investigation.

RESULTS AND DISCUSSION

A summary of e.m.f. data of the cell (A) at different temperatures for various water + dioxane mixtures is presented in Table 1. As usual, the e.m.f., E, of cell (A) is given by the expression

$$E = E^0_{\mathrm{Ag-AgCl}} - E^0_{\mathrm{Ag-AgCNS}} - \frac{RT}{F} \ln \frac{m_{\mathrm{Cl^-}}\gamma_{\mathrm{Cl^-}}}{m_{\mathrm{CNS^-}}\gamma_{\mathrm{CNS^-}}} + E_j \qquad (1)$$

where the symbols have their usual significance. The values of the liquid junction potentials, E_j, were calculated from the Lewis and Sargent equation [3] and vary in the range 0.1—0.3 mV at all temperatures in water—dioxane mixtures of different compositions. The logarithmic term is assumed to equal unity since the concentrations in both sides of the cell are identical.

The standard potential, E^0_m, of the Ag(s)|AgCNS(s)|CNS$^-$ electrode was obtained by extrapolating the auxiliary function $E^{0'}$ given by

$$E^{0'} = E^0_{\mathrm{Ag-AgCl}} - E + E_j = E^0_m + f(m) \qquad (2)$$

to the molality $m = 0$, where $E^0_{\mathrm{Ag-AgCl}}$ is the standard molal potential of the Ag(s)|AgCl(s)|Cl$^-$ electrode and is known [2,12] over the temperature range under investigation for various water—dioxane mixtures. The values of E^0_m thus obtained are recorded in Table 2 along with their standard deviations, which were obtained by the method of least squares.

The standard electrode potentials of the silver—silver thiocyanate electrode obtained on the molal scale (E^0_m) are expressed on the molar (E^0_c) and mole fraction (E^0_N) scales, which are interrelated by the equations [1]

$$E^0_c = E^0_m + [2 \times 2.3026(RT/F)] \log d_0$$

and

$$E^0_N = E^0_m - [2 \times (2.3026\, RT/F)] \log (1000/\bar{M}) \qquad (3)$$

where d_0 and $\bar{M}$ are the density and average molecular weight, respectively, of the solvent concerned. These values are expressed as a function of the temperature, t °C, by

$$E^0 = a + b(t - 25) + c(t - 25)^2 \qquad (4)$$

where a, b and c are empirical constants and are shown in Table 3 for different scales in various water—dioxane mixtures along with those computed in water [10].

As usual, the values of the Gibbs energy change, ΔG^0, (on the molal scale) for the electrode reaction

$$\mathrm{AgCNS(s)} + e \rightleftharpoons \mathrm{Ag(s)} + \mathrm{CNS^-}\ \text{(solvated)}$$

TABLE 1

E.m.f. of the cell Ag—AgCNS|KCNS(m)‖KCl(m)|AgCl—Ag from 5 to 35°C in water—dioxane mixtures

10^2 *m* (mole kg^{-1})	*t*(°C)						
	5	10	15	20	25	30	35
Water + 10 mass % dioxane							
1	0.1339	0.1289					0.1164
2	0.1321	0.1296					0.1171
4	0.1316	0.1286					0.1163
5		0.1306	0.1275	0.1246	0.1217	0.1190	0.1161
8	0.1338	0.1306	0.1278	0.1258	0.1233	0.1202	0.1181
10	0.1338	0.1306	0.1288	0.1258	0.1231	0.1200	0.1167
12	0.1348	0.1312	0.1288	0.1258	0.1225	0.1196	0.1179
14	0.1326	0.1296	0.1282	0.1254	0.1222	0.1190	0.1181
16		0.1298	0.1276	0.1250	0.1219	0.1196	0.1171
18	0.1326	0.1296	0.1274	0.1248		0.1192	0.1167
20	0.1328	0.1290		0.1248	0.1221		0.1181
Water + 20 mass % dioxane							
2				0.1089	0.1048	0.1015	0.0977
4	0.1167			0.1089	0.1069	0.1042	0.1015
6	0.1159			0.1087	0.1061	0.1030	0.1007
8	0.1173	0.1142	0.1120	0.1096	0.1075	0.1048	0.1022
10	0.1178	0.1148	0.1125	0.1098	0.1077	0.1048	0.1026
12	0.1189	0.1159	0.1136	0.1108	0.1084	0.1054	0.1031
14		0.1154	0.1131	0.1103	0.1081	0.1051	0.1027
15	0.1185	0.1155	0.1135	0.1109	0.1087	0.1061	0.1040
16		0.1172	0.1153	0.1126	0.1093	0.1068	0.1041
18		0.1162	0.1141	0.1118	0.1091	0.1066	0.1043
19	0.1194	0.1168	0.1142	0.1113	0.1088	0.1064	
20	0.1195	0.1166	0.1140	0.1115	0.1090	0.1065	0.1042
Water + 30 mass % dioxane							
2	0.0984	0.0966	0.0946				0.0854
4	0.1009	0.0987	0.0967				0.0875
5	0.1012	0.0989	0.0970	0.0942	0.0918		0.0870
6	0.1052	0.1020	0.0993	0.0956	0.0925	0.0897	0.0880
8	0.1026	0.0992	0.0976	0.0954	0.0926	0.0896	0.0878
10	0.1037	0.1008	0.0990	0.0971	0.0942	0.0914	0.0890
12	0.1028	0.1005	0.0986	0.0965	0.0937	0.0907	0.0885
14	0.1035	0.1008	0.0988	0.0960	0.0937	0.0908	0.0889
15	0.1036	0.1024	0.0986	0.0964	0.0935	0.0908	0.0888
16	0.1067	0.1031	0.1004	0.0984	0.0951	0.0926	0.0909
18		0.1010	0.0991	0.0971	0.0943	0.0915	0.0894
20		0.1018	0.0996		0.0951	0.0922	
Water + 40 mass % dioxane							
2	0.0839	0.0812	0.0782	0.0764	0.0739	0.0709	0.0684
4	0.0855	0.0830	0.0808	0.0782	0.0745	0.0717	0.0699
6	0.0873	0.0852	0.0819	0.0782	0.0751	0.0725	0.0698
8	0.0864	0.0850	0.0826	0.0784	0.0761	0.0742	0.0697
10	0.0852	0.0828	0.0812	0.0789	0.0769	0.0743	0.0704
15	0.0898	0.0868	0.0849	0.0827	0.0799	0.0780	0.0745
18	0.0888	0.0862	0.0837	0.0810	0.0782	0.0763	0.0742
20	0.0896	0.0873	0.0854	0.0828	0.0803	0.0799	0.0785

TABLE 2

Standard molal potentials (E_m^0 in Abs. volts) for the Ag(s)|AgCNS(s)|CNS$^-$ electrode in water—dioxane mixtures from 5 to 35°C

Mass % diox-ane	t(°C)						
	5	10	15	20	25	30	35
10	0.09062 ±0.0005	0.09048 ±0.0004	0.09037 ±0.0006	0.09032 ±0.0007	0.09021 ±0.0003	0.09015 ±0.0004	0.09008 ±0.0005
20	0.09853 ±0.0007	0.09787 ±0.0006	0.09728 ±0.0004	0.09678 ±0.0004	0.09622 ±0.0005	0.09569 ±0.0006	0.09516 ±0.0007
30	0.10248 ±0.0006	0.10120 ±0.0005	0.09994 ±0.0003	0.09877 ±0.0002	0.09759 ±0.0002	0.09633 ±0.0005	0.09496 ±0.0007
40	0.10403 ±0.0008	0.10245 ±0.0003	0.10099 ±0.0004	0.09955 ±0.0006	0.09787 ±0.0004	0.09650 ±0.0007	0.09486 ±0.0008

have been calculated in Joules from the relation

$$\Delta G^0 = -nFE_m^0 \qquad (5)$$

and can be expressed by the equation [13]

$$\Delta G^0 = AT + B - CT \ln T - \frac{DT^2}{2} \qquad (6)$$

where A, B, C and D are the empirical constants and T is the temperature in degrees Kelvin. The values of ΔH^0, ΔS^0 and ΔC_p^0 for the electrode reaction have been computed by the relations

$$\Delta H^0 = B + CT + \frac{DT^2}{2} \qquad (7)$$

$$\Delta S^0 = -A + C + C \ln T + DT \qquad (8)$$

and

$$\Delta C_p^0 = C + DT \qquad (9)$$

The parameters A, B, C and D of eqns. (6)—(9) are recorded in Table 4 for various water—dioxane mixtures together with those evaluated in water. The values of the various thermodynamic quantites at 25°C are also included in the table for water and for water containing 10, 20, 30 and 40 mass % dioxane.

The thermodynamic quantities, ΔG_t^0, ΔH_t^0, ΔS_t^0 and ΔC_{pt}^0 for the transfer of 1 g ion of CNS$^-$ ions from water (w) to the mixed solvents (s) of various compositions were evaluated by use of the relations [6]

$$\Delta G_t^0 = -\mathrm{F}\,[(E_N^0)_s - (E_N^0)_w] \qquad (10)$$

$$\Delta S_t^0 = F[(b_s - b_w) - (2 \times 2.3026\, R/F) \log(M_w/M_s)] \qquad (11)$$

$$\Delta H_t^0 = \Delta G_t^0 + T\Delta S_t^0 \qquad (12)$$

TABLE 3

Constants of eqn. (4) for molar (c), molal (m) and mole fraction (N) scales in water and water—dioxane mixtures

Mass % dioxane	a			$-10^3\ b$			$10^5\ c$		
	c	m	N	c	m	N	c	m	N
0	0.08732	0.08815	−0.11823	1.143	1.126	1.818	3.644	2.185	2.189
10	0.09051	0.09021	−0.11192	0.0364	0.0214	0.6957	0.0562	0.0264	0.0392
20	0.09692	0.09622	−0.10127	0.1394	0.1121	0.7744	0.0812	0.0321	0.0355
30	0.09869	0.09759	−0.09479	0.2842	0.2504	0.8956	−0.0812	−0.0937	−0.1070
40	0.09933	0.09787	−0.08884	0.3402	0.3055	0.9317	0.1634	0.2264	0.2320

TABLE 4

Constants of eqns. (6)—(9) (on the molal scale), and the thermodynamic quantities at 25°C in water and water—dioxane mixtures

Mass % dioxane	$10^{-3}\ A$	$-10^{-5}\ B$	$10^{-3}\ C$	$-D$	$-10^{-3}\ \Delta G^0$ [a] (J mole^{-1})	$-10^{-3}\ \Delta H^0$ [a] (J mole^{-1})	$-\Delta S^0$ (J mole^{-1} deg^{-1})	ΔC_p^0 [a] (J mole^{-1} deg^{-1})
0	233.476	61.894	40.896	135.929	8.622	37.927	98.34	389.30
10	2.099	0.65183	0.3666	1.1977	8.705	9.109	1.356	9.718
20	6.595	1.8547	1.154	3.847	9.284	12.274	10.034	7.966
30	11.660	3.1371	2.0527	7.0844	9.417	16.564	23.989	−58.430
40	39.476	10.3931	6.938	23.5553	9.444	17.483	26.932	−80.807

[a] Uncertainties in $\Delta G^0 = \pm 5$ J, in $\Delta H^0 = \pm 8$ J, in $\Delta S^0 = \pm 1$ J, and in $\Delta C_p^0 = \pm 4$ J.

TABLE 5

Transfer thermodynamic quantities (on the mole fraction scale) in various water—dioane mixtures at 25°C

Mass % dioxane	$10^{-3}\,\Delta G_t^0$ [a] (J mole^{-1})	$10^{-3}\,\Delta H_t^0$ [a] (J mole^{-1})	ΔS_t^0 [a] (J mole^{-1} deg^{-1})	ΔC_{pt}^0 [a] (J mole^{-1} deg^{-1})
10	—0.4919	28.840	98.429	—381.551
20	—1.5190	25.681	91.274	—384.667
30	—2.1427	21.384	78.948	—449.511
40	—2.7408	20.178	76.907	—527.710

[a] Uncertainties in $\Delta G_t^0 = \pm 2$ J, in $\Delta H_t^0 = \pm 4$ J, in $\Delta S_t^0 = \pm 3$ J, and in $\Delta C_{pt}^0 = \pm 2$ J.

and

$$\Delta C_{pt}^0 = (\Delta C_{pt}^0)_s - (\Delta C_{pt}^0)_w \tag{13}$$

where subscripts w and s refer to water and the mixed solvents, respectively. The values of b_s and b_w were taken from Table 3. As usual, the transfer thermodynamic quantities have been calculated on the mole fraction scale, since that will eliminate effects arising from concentration changes of the CNS$^-$ ion accompanying the transfer process. The values of these transfer quantities at 25° C are given in Table 5.

An inspection of Table 3 shows that the standard electrode potentials of the silver—silver thiocyanate electrode in various water—dioxane mixtures are higher than in water and increase with the increase in dioxane content. Such an observation seems to be contrary to the studies made on the silver—silver halide electrodes [1], e.g. Ag—AgCl, Ag—AgBr, and Ag—AgI in various water—dioxane mixtures. However, the solvent effect on the standard potential of the silver—silver thiocyanate electrode can be examined from the related quantities of free energies of transfer of the CNS$^-$ ion from water to the solvent concerned, since the 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 5, the values of ΔG_t^0 appear to be negative and become more and more negative with increase of mole fraction of dioxane in the water—dioxane mixtures. Thus, the CNS$^-$ ion is more strongly stabilized in the mixed solvents than in water. Moreover, the negative values of ΔG_t^0 for the experimental mixed solvent compositions support the view that water is less basic than the mixed solvents, if it is assumed that the hydration of a larger thiocyanate ion in aqueous solution is negligible [14]. These negative values further indicate that the overall effect of permittivity as well as of chemical nature (which mainly reflects the relative basicity and solvating capacity) of the solvent makes the transfer of CNS$^-$ ions from water to these mixed solvents favourable. Thus, CNS$^-$ ions interact strongly with dioxane molecules in water—dioxane mixtures in preference to water molecules.

It is well known that the values of ΔH_t^0 and ΔS_t^0 give an insight into the structure of the solvents in the transfer process. The positive entropy of

TABLE 6

Primary medium effect, $\lim_{N\to 0} \log {}^{s}\gamma_{w}$ (on the mole fraction scale) of CNS^- ion in various water—dioxane mixtures at 25°C

Mass % dioxane	Lim log ${}^{s}\gamma_{w}$ $N\to 0$
10	—0.1067
20	—0.2867
30	—0.3962
40	—0.4968

transfer of the CNS^- ion from water to the mixed solvents can probably be attributed to more structure breaking by the CNS^- ion in water—dioxane 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^- ion is less in water—dioxane mixtures than in aqueous medium. The CNS^- ion thus "breaks down more structure" in water—dioxane mixtures than in pure water. The positive values of ΔH_t^0 suggest that the transfer process is endothermic because of the dehydration and then resolvation of the CNS^- ion by dioxane. As expected, the transfer heat capacity is negative which reflects the loss of freedom resulting from the interaction of dioxane in water—dioxane mixtures with CNS^- ions.

Further, it is of interest to examine the primary medium effect which results from a difference of the ion—solvent interactions at infinite dilution in each solvent. Thermodynamically, it can be represented by

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

and the limit term indicates the primary medium effect. The values of this quantity at 25°C are given in Table 6. As observed, the value of the primary medium effect is negative, pointing to the fact that the escaping tendency of the CNS^- ion is less in water—dioxane mixtures than in pure water. This is consistent with the conclusions based on the fact that the CNS^- ion is in a lower free energy state in water—dioxane mixtures than in aqueous medium.

REFERENCES

1 T. Mussini, C.M. Formaro and P. Andrigo, J. Electroanal. Chem., 33 (1971) 189.
2 P.K. Das and U.C. Mishra, Electrochim. Acta, 22 (1977) 59.
3 R.C. Das, U.N. Dash and K.N. Panda, Electrochim. Acta. 24 (1979) 99.
4 K.K. Kundu and A.K. Raskhit, Indian J. Chem., 9 (1971) 439.
5 R.N. Roy, R.A. Robinson and R.G. Bates, J. Chem. Thermodyn., 5 (1973) 559.
6 K.K. Kundu and K. Mazumdar, J. Chem. Soc., Faraday Trans., 69 (1973), 806, 1422.
7 R.C. Das, U.N. Dash and K.N. Panda, Thermochim. Acta, 32 (1979) 301.
8 U.N. Dash, D. Satyanarayan, K.N. Panda, S.C. Rath and S.K. Mohanty, Thermochim. Acta, 30 (1979) 217.
9 U.N. Dash, S.C. Rath, S. Supakar and S.K. Nayak, Thermochim. Acta, 33 (1979) 331.

10 U.N. Dash, J. Mohanty and K.N. Panda, Thermochim. Acta, 16 (1976) 55.
11 U.N. Dash, Thermochim. Acta, 30 (1979) 73.
12 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 1967.
13 U.N. Dash and S.K. Nayak, Can. J. Chem., 58 (1980).
14 R.G. Bates, B.R. Staples and R.A. Robinson, Anal. Chem., 42 (1970) 867.