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THERMODYNAMICS OF THE SILVER—SILVER THIOCYANATE ELECTRODE IN UREA—WATER MIXTURES

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ABSTRACT

E.m.f. measurements on cells of the type Ag(s), AgCNS(s), KCNS(c)//KCl(c), AgCl(s), Ag(s) in four different compositions of urea—water mixtures at seven different temperatures from 5 to 35°C have been made to determine the standard potentials of the silver—silver thiocyanate electrode in these media. These values have been used to evaluate the transfer thermodynamic quantities accompanying the transfer of 1 g ion of CNS^- ion from the standard state in water to the standard state in urea—water mixtures.

INTRODUCTION

As part of our studies on ion—solvent interactions [1], we have recently reported [2] the standard potentials of the Ag—AgCNS electrode at different temperatures in various compositions of water—dioxane mixtures and the related transfer properties, ΔG_t^0, ΔS_t^0, ΔH_t^0 and ΔC_{pt}^0, of the CNS^- ion. In the present work, we present data on the standard potentials of this electrode in urea—water mixtures at different temperatures, the primary medium effect and the related transfer thermodymanic quantities of the CNS^- ion.

As before [2,3], the study of cell (A) with liquid junction

Ag(s), AgCNS(s), KCNS(c)//KCl(c), AgCl(s), Ag(s) (A)

has been made in a series of urea—water mixtures containing 11.52, 20.31, 29.64 and 36.83 mass % urea at temperatures from 5 to 35°C.

EXPERIMENTAL

Urea (BDH, Analar) was used without further purification. Solvents of various compositions were made up by weight in conductivity water. The stock solvents as well as potassium chloride and potassium thiocyanate solutions were kept at low temperature (~5°C) [4]. Equimolar solutions of potassium chloride and potassium thiocyanate were prepared from the stock solutions by double dilution method.

Preparation of the silver—silver chloride and the silver—silver thiocyanate electrodes, preparation of the cell solutions, setting up of the cells, the e.m.f.

TABLE 1

E.m.f. data of cell (A) in various urea—water mixtures at different temperatures

$10^2 C$ (mol l^{-1})	t (°C)						
	5	10	15	20	25	30	35
Water—11.52 wt.% urea							
2	0.1430	0.1401	0.1368	0.1342	0.1318	0.1289	0.1260
4	0.1415	0.1393	0.1368	0.1341	0.1315	0.1289	0.1260
5	0.1415	0.1390	0.1368	0.1356	0.1323	0.1298	0.1266
6	0.1402	0.1378	0.1350	0.1321	0.1292	0.1261	0.1236
8	0.1398	0.1370	0.1347	0.1314	0.1294	0.1272	0.1248
10	0.1387	0.1366	0.1340	0.1316	0.1290	0.1264	0.1236
12	0.1390	0.1372	0.1348	0.1317	0.1288	0.1258	0.1228
14	0.1390	0.1360	0.1336	0.1315	0.1292	0.1268	0.1238
15	0.1389	0.1366	0.1333	0.1306	0.1292	0.1262	0.1236
16	0.1391	0.1364	0.1336	0.1305	0.1282	0.1257	0.1231
18	0.1388	0.1368	0.1336	0.1305	0.1282	0.1256	0.1238
20	0.1380	0.1360	0.1336	0.1307	0.1291	0.1260	0.1230
Water—20.31 wt.% urea							
2	0.1401	0.1367	0.1337	0.1306	0.1284	0.1263	0.1250
4	0.1400	0.1365	0.1337	0.1301	0.1283	0.1260	0.1245
5	0.1390	0.1350	0.1322	0.1299	0.1270	0.1258	0.1237
6	0.1390	0.1360	0.1321	0.1300	0.1270	0.1253	0.1234
12	0.1392	0.1348	0.1326	0.1303	0.1275	0.1254	0.1232
14	0.1390	0.1356	0.1332	0.1306	0.1288	0.1260	0.1235
15	0.1388	0.1346	0.1315	0.1286	0.1264	0.1245	0.1228
16	0.1380	0.1340	0.1312	0.1283	0.1261	0.1243	0.1224
18	0.1378	0.1343	0.1318	0.1286	0.1267	0.1247	0.1225
20	0.1374	0.1340	0.1309	0.1282	0.1265	0.1245	0.1223
Water—29.64 wt.% urea							
2	0.1350	0.1325	0.1295	0.1271	0.1250	0.1225	0.1200
4	0.1342	0.1317	0.1290	0.1270	0.1240	0.1224	0.1200
5	0.1360	0.1330	0.1300	0.1270	0.1251	0.1224	0.1200
6	0.1335	0.1315	0.1295	0.1274	0.1248	0.1220	0.1198
8	0.1350	0.1326	0.1300	0.1271	0.1250	0.1222	0.1200
10	0.1350	0.1325	0.1300	0.1270	0.1259	0.1232	0.1205
12	0.1340	0.1315	0.1296	0.1276	0.1255	0.1225	0.1199
14	0.1346	0.1318	0.1294	0.1272	0.1245	0.1218	0.1196
15	0.1343	0.1327	0.1296	0.1265	0.1240	0.1220	0.1195
16	0.1346	0.1326	0.1295	0.1270	0.1250	0.1220	0.1195
18	0.1350	0.1325	0.1298	0.1272	0.1253	0.1224	0.1200
20	0.1342	0.1320	0.1295	0.1270	0.1251	0.1226	0.1200
Water—36.83 wt.% urea							
2	0.1340	0.1320	0.1295	0.1270	0.1240	0.1210	0.1190
4	0.1345	0.1315	0.1290	0.1261	0.1240	0.1210	0.1188
5	0.1335	0.1310	0.1285	0.1260	0.1233	0.1209	0.1178
6	0.1340	0.1310	0.1285	0.1258	0.1231	0.1209	0.1180
8	0.1340	0.1308	0.1285	0.1260	0.1233	0.1206	0.1177
10	0.1340	0.1310	0.1284	0.1262	0.1233	0.1209	0.1190
12	0.1340	0.1310	0.1282	0.1260	0.1235	0.1208	0.1186
14	0.1292	0.1265	0.1253	0.1228	0.1206	0.1183	0.1162
15	0.1347	0.1317	0.1294	0.1265	0.1243	0.1214	0.1192
16	0.1340	0.1312	0.1295	0.1268	0.1237	0.1210	0.1190
18	0.1337	0.1305	0.1284	0.1257	0.1236	0.1207	0.1188
20	0.1335	0.1310	0.1290	0.1265	0.1237	0.1214	0.1196

and the conductance measurements were essentially similar to the procedures described earlier [2].

RESULTS AND DISCUSSION

A summary of the e.m.f. data of cell (A) at different temperatures is given in Table 1. As usual, the e.m.f., E, of cell (A) is given by the expression [2]

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

where the symbols have their usual significance.

The standard molar potential, E^0_{c}, of the silver—silver thiocyanate electrode was obtained by the method of extrapolating [2] the auxiliary function, $E^{0\prime}_{\mathrm{c}}$, given by

$$E^{0\prime}_{\mathrm{c}} = E^0_{\mathrm{Ag,AgCl}} - E + E_{\mathrm{j}} = E^0_{\mathrm{c}} + \mathrm{f}(c) \qquad (2)$$

to the molarity, $c = 0$, where $E^0_{\mathrm{Ag,AgCl}}$ is the standard potential of the silver—silver chloride electrode, and is known [4] over the temperature range under investigation for various urea—water mixtures.

As usual [2,3], the values of the liquid junction potentials, E_{j}, were calculated and found to vary in the range 0.1—0.3 mV in all solvents for all temperatures. The values of E^0_{c} obtained on extrapolating $E^{0\prime}_{\mathrm{c}}$ to $c = 0$ are presented in Table 2. The average standard deviation in the values of E^0_{c} is ±0.3 mV.

Standard potentials on the molal (E^0_{m}), mole fraction (E^0_{N}) and molar (E^0_{c}) scale (correlated by the usual equation [5]) at various temperatures for any solvent were fitted, by the method of least-squares, to an equation of the form [6]

$$E^0_{\mathrm{p}} = A + BT + CT\ln T + DT^2/2 \qquad (3)$$

where p is c, m or N, and T is any temperature in Kelvin. The constants A, B, C, and D of eqn. (3) for the different solvent mixtures are shown in Table 3. The average deviation between the experimental values (Table 2) and values calculated from eqn. (3) is within ±0.2 mV. The values of the

TABLE 2

Standard molar potentials (E^0_{c} in abs. volts) for the Ag(s)—AgCNS(s) CNS$^-$ electrodes in urea—water mixtures from 5 to 35°C

Wt.% urea	t (°C)						
	5	10	15	20	25	30	35
0	0.12468	0.11260	0.10210	0.09280	0.08800	0.08400	0.07930
11.52	0.13238	0.13174	0.13104	0.13032	0.12969	0.12907	0.12849
20.31	0.15572	0.15462	0.15329	0.15213	0.15111	0.15010	0.14905
29.64	0.17344	0.17293	0.17213	0.17142	0.17071	0.17009	0.16942
36.83	0.18332	0.18274	0.18220	0.18165	0.18106	0.18054	0.18000

TABLE 3

Constants of eqn. (3) for molar (c), molal (m) and mole fraction (N) scales in urea—water mixtures

Mass % urea		A	B	C	$10^5 D$
11.52	c	−2.48122	0.10306	−0.018181	6.22834
	m	−3.25472	0.13385	−0.02364	8.16010
	N	−2.98953	0.12285	−0.02182	7.53920
20.31	c	−4.81692	0.19584	−0.034545	11.83700
	m	−5.31725	0.216243	−0.038181	13.16700
	N	−5.051446	0.205253	−0.036363	12.54600
29.64	c	−0.873584	0.041309	−0.007273	2.43570
	m	−1.398462	0.061875	−0.010909	3.70960
	N	−1.398576	0.061223	−0.010909	3.70960
36.83	c	1.828433	−0.062157	0.010909	−3.69360
	m	0.765807	−0.020940	0.003636	−1.17780
	N	1.553461	−0.052488	0.009091	−3.06466

standard potentials on the different scales in different solvents at 25°C are presented in Table 4.

As before [2,6], the standard thermodynamic quantities (ΔG^0, ΔH^0 and ΔS^0) for the electrode reaction

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

at different temperatures in various solvent mixtures have been calculated. These values may be expressed as function of temperature in the equations

$$\Delta G^0 = A' + B'T + C'T \ln T + D'T^2/2 \tag{4}$$

$$\Delta S^0 = -B' - C' - C' \ln T - D'T \tag{5}$$

and

$$\Delta H^0 = A' - C'T - D'T^2/2 \tag{6}$$

TABLE 4

Values of the standard potentials of the silver—silver thiocyanate electrode on the molar, molal and mole fraction scales in different urea—water mixtures and thermodynamic quantities on the molal scale at 25°C

	Wt.%			
	11.52	20.31	29.64	36.83
E_c^0(V)	0.12969	0.15111	0.17071	0.18106
E_m^0(V)	0.12825	0.14848	0.16680	0.17618
E_N^0(V)	−0.07380	−0.05000	−0.02761	−0.01484
$-10^{-4}\ \Delta G_m^0$(J mole^{-1})	1.2370	1.4320	1.6099	1.7001
$-10^{-4}\ \Delta H_m^0$(J mole^{-1})	1.5975	2.0676	1.9809	1.9796
$-\Delta S_m^0$(J mole^{-1} K^{-1})	12.0998	21.3291	12.4454	9.3796

Decomposition in nitrogen resulted in a combined heat effect of 174 ± 17 kJ mole^{-1} for the two decomposition steps. This agrees well with results from some exploratory experiments performed in the DSC equipment, also under nitrogen, which resulted in a mean total heat effect of about 165 kJ mole^{-1}. Such a change of atmosphere apparently has no or only a very small influence of the magnitude of the heat effect. The heat effect of decomposition of anhydrous $Mn(NO_3)_2$ was 155 ± 12 kJ mole^{-1}.

X-ray diffraction patterns of some of the DTA products obtained by decomposing the solution showed lines which corresponded well with the pattern of the standard γ-MnO_2 samples (ICS Nos. 1, 2, 3 and 9). In some patterns the strongest line of Mn_2O_3 was faintly visible. X-Ray diffraction photographs of products of the decomposition of anhydrous $Mn(NO_3)_2$ revealed the presence of much more Mn_2O_3 besides γ-MnO_2.

Other experiments also showed that an appreciable percentage of Mn_2O_3 must be present in the product prepared by decomposing anhydrous $Mn(NO_3)_2$. This follows from the heat effects determined on product and reference samples, as shown in Table 6. The heats of reaction given in the Table refer to decomposition to Mn_2O_3 in an air flow of 100 ml min^{-1}. The weight of the aqueous $Mn(NO_3)_2$ sample did not affect the heat of decomposition to Mn_2O_3 of the MnO_2 formed as the primary product.

DISCUSSION

From thermobalance experiments it is known that an equimolar solution of water and $Mn(NO_3)_2$ can be obtained relatively easily. Further removal of water is very difficult, although a reasonable evaporation rate can still be obtained by applying vacuum [1,11].

When the results given in Fig. 2 are considered, it is seen that these experimental facts tie in with the results of the thermodynamic calculations: if the partial pressure of water above a solution of manganese nitrate is low enough water evaporates until anhydrous $Mn(NO_3)_2$ is obtained.

It is concluded from Fig. 3 that decomposition to MnO_2 and NO_2 is thermodynamically more likely than decomposition to MnO_2 and N_2O_4; the temperature at which ΔG_r^0 is zero for the decomposition to NO_2 being $\simeq 95°C$ as against $\simeq 140°C$ for decomposition to N_2O_4. In this connection it should be borne in mind that the thermodynamic data apply to the formation of β-MnO_2. However, from X-ray data it was concluded that γ-MnO_2 was formed in the two-step decomposition. The difference in the heat of reaction, ΔH_r^0, between the decomposition of γ-MnO_2 to Mn_2O_3 and that of β-MnO_2 to Mn_2O_3 is estimated as 15 kJ mole^{-1}. This value can be deduced from the heats of reaction obtained for the IC samples (Table 6). Because ΔH_r^0 for the decomposition of β-MnO_2 does not change much with temperature, the difference in ΔH_r^0 between γ-MnO_2 and β-MnO_2 is also believed not to vary much with temperature. If the entropy for γ-MnO_2 is not much higher than the entropy for β-MnO_2, the free energy change for decomposition of $Mn(NO_3)_2$ to γ-MnO_2 will be higher than for decomposition to β-MnO_2 by at most 15 kJ mole^{-1}. This implies that the lines in Fig. 3 will shift to higher the CNS$^-$ ion (r_-) as 2.58 Å [1], ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively. The values of ϵ_s for various compositions of urea—water mixtures and that of ϵ_w' at different temperatures were obtained from the literature [4,8]. The values of θ_w and θ_s, the temperature coefficients of the dielectric constants, were taken from the literature [4].

The values of $\Delta H^0_{t,el}$ were computed from a knowledge of $\Delta G^0_{t,el}$ and $\Delta S^0_{t,el}$. The chemical parts of these quantities were evaluated using eqn. (7). The values of these quantities at 25°C are presented in Table 5.

It should be noted, however, that although the Gibbs energy and entropy calculations from the Born equation may involve uncertainties, it may still be worthwhile interpreting some general conclusions of a quantitative nature from these derived thermodynamic quantities (Table 5). It is found that as the proportion of urea increases, ΔG^0_t values for the CNS$^-$ ion become increasingly negative and increase with increase in temperature. The negative value of ΔG^0_t signifies that the transfer of the CNS$^-$ ion from water to urea—water mixtures is increasingly favourable. Thus, the CNS$^-$ ion appears to be in a lower Gibbs energy state and hence, more strongly stabilized in mixed solvents than in water, a behaviour similar to that found for HCl, HBr and HI studied in these solvents [4]. As the chemical contribution to the Gibbs energy of transfer of an ion in solution is attributed to the solvation of ions, $\Delta G^0_{t,ch}$ of the CNS$^-$ ion should reflect the solvating capacities of the solvent concerned and water towards the CNS$^-$ ion. The negative values of $\Delta G^0_{t,ch}$ thus suggest that mixed solvents possess a larger solvating capacity towards CNS$^-$ ion and are more basic than water. Further, the increasingly negative values of $\Delta G^0_{t,ch}$ indicate that as the proportion of urea increases, the solvating capacity as well as the basicity of the mixed solvents increase. It is, however, interesting to check whether the chemical effects on the entropy and enthalpy of transfer of the CNS$^-$ ion should influence the solvation of the ion. It is known that all structure-forming processes including solvation of ions are exothermic and accompanied by a decrease in entropy, and the structure-breaking processes, including desolvation of ions, are endothermic and accompanied by gain of entropy. The positive values of ΔS^0_t and ΔH^0_t indicate that for a transfer process the amount of disorder created by the CNS$^-$ ion in the mixed solvent is more. When electrostatic effects are taken into account for both $\Delta H^0_{t,el}$ and $\Delta S^0_{t,el}$, the contribution of the relative structural aspects of the solvent from the chemical interaction ($\Delta S^0_{t,ch}$ and $\Delta H^0_{t,ch}$) is positive.

Table 6 shows the primary medium effect values of CNS$^-$ ion in various urea—water mixtures at four different temperatures. Since the primary medium effect, which is represented by [5]

$$\lim_{N\to 0}(\log {}^{S}\gamma_w) = [(E^0_N)_w - (E^0_N)_S]/2.3026(RT/F)$$

where the limit term indicates the primary medium effect, results from a difference of the ion—solvent interactions at infinite dilution in each solvent, the magnitude of this effect should reflect the stabilization of the ion in the solvent concerned. The resulting negative magnitudes of this quantity presumably indicate that the escaping tendency of the CNS$^-$ ion is less in

TABLE 6

Primary medium effect, $\lim_{N \to 0} \log {}^{s}\gamma_{w}$ (on the mole fraction scale), of the CNS^- ion in various urea—water mixtures at 5, 15, 25 and 35°C

Wt.% urea	t(°C)			
	5	15	25	35
11.52	−0.2779	−0.5604	−0.7511	−0.8605
20.31	−0.7410	−0.9896	−1.1529	−1.2373
29.64	−1.1074	−1.3660	−1.5319	−1.6179
36.83	−1.3261	−1.6474	−1.7477	−1.8320

urea—water mixtures than in pure water. This is consistent with the conclusions based on the fact that the CNS^- ion is more strongly stabilized in urea—water mixtures than in water medium.

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