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Note

THERMODYNAMICS OF THE SILVER–SILVER ION ELECTRODE IN DIOXANE–WATER MIXTURES

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In continuation of the study on the standard potentials of the silver–silver ion electrode in urea + water mixtures [1], the transfer thermodynamic quantities accompanying the transfer of 1 gram-ion of Ag^+ from the standard state in water to the standard state in urea + water mixtures, and the thermodynamic solubility products of silver halides and silver pseudo-halides have been reported in these media over a range of temperatures. To extend the work in other aqueo–organic solvent systems, we now report the results of a determination of the standard potentials of the silver–silver ion electrode and associated thermodynamic parameters for the electrode reaction in different compositions of dioxane + water mixtures. In the course of these studies, besides obtaining the transfer thermodynamic quantities for the process Ag^+ (in water) → Ag^+ (in dioxane + water), the thermodynamic solubility products of silver halides, silver pseudo-halides and oxyhalides have been evaluated at different temperatures.

As previously [1], the study of cell (A) with liquid junction

$$Ag(s), AgCl(s), NaCl(c), NaNO_3(c)//NaNO_3(c), AgNO_3(c), Ag(s) \qquad (A)$$

has been made in a series of dioxane + water mixtures containing 10, 20, 30 and 40% dioxane by weight at temperatures from 5 to 25°C.

EXPERIMENTAL

The sodium chloride, sodium nitrate and silver nitrate were the same samples used in the previous study [1]. The dioxane was purified as described earlier [2]. Silver–silver chloride and silver electrodes were prepared as described earlier [1]. The solvent mixtures of various mass percentages were prepared as described in our earlier article [2].

Preparation of the cell solutions, setting up of the cells, EMF and conductance measurements were essentially similar to the procedures described earlier [2]. All measurements were made in water baths at the

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required temperature with a precision of ±0.1°C. The reproducibility of EMF measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

As usual [1], the EMF, E, of the cell (A) is given by

$$E = E^0_{\mathrm{Ag,Ag^+}} - E^0_{\mathrm{Ag,AgCl}} + \frac{RT}{F} \ln[\mathrm{Ag^+}][\mathrm{Cl^-}]\gamma^2_{\pm} + E_j \tag{1}$$

where the symbols have their usual significance.

The standard molar potential, E^0_c of the silver–silver ion electrode was obtained by the method of extrapolating [3] the auxiliary function, $E^{0\prime}_c$, given by

$$\begin{aligned} E^{0\prime}_c &= E + E^0_{\mathrm{Ag,AgCl}} - 2k \log c + \frac{2kA(2c)^{1/2}}{1 + (2c)^{1/2}} - E_j \\ &= E^0_{\mathrm{Ag,Ag^+}} + bC \end{aligned} \tag{2}$$

to the molarity $c = 0$, where $E^0_{\mathrm{Ag,AgCl}}$ is the standard molar potential of the silver–silver chloride electrode, and is known [4,5] over the temperature range under investigation for various dioxane–water mixtures.

As previously [1], 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 $E^{0\prime}_c$ to $c = 0$ are presented in Table 1. 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) scales (correlated by the usual equation [3]) at different temperatures for any solvent were fitted, by the least-squares method, to an equation of the form [6,7]

$$E^0_X = A + BT + CT \ln T + \frac{DT^2}{2} \tag{3}$$

TABLE 1

Standard molar potentials for the Ag(s)–Ag$^+$ electrodes in dioxane–water mixtures from 5 to 25°C

Wt % dioxane	E^0_c (abs volts)				
	5°C	10°C	15°C	20°C	25°C
0	0.8186	0.8138	0.8089	0.8031	0.7991
10	0.8003	0.7945	0.7881	0.7822	0.7764
20	0.7982	0.7924	0.7873	0.7815	0.7758
30	0.7957	0.7905	0.7857	0.7810	0.7752
40	0.7942	0.7887	0.7844	0.7786	0.7736

TABLE 2

Constants of eqn (3) for molar (c), molal (m) and mole-fraction (N) scales in dioxane–water mixtures

Wt % dioxane	x	A	B	C	$D\times10^3$
10	c	12.82357	−0.436697	0.07598	−0.2456
	m	110.9715	−4.3071202	0.7598038	−2.6264
	N	94.6542	−3.668765	0.6470588	−2.2371
20	c	−117.30828	4.6386475	−0.8186274	−2.8282
	m	−106.9755	4.2354022	−0.747549	2.5841
	N	−112.9503	4.470533	−0.7892156	2.7293
30	c	33.783736	−1.2910618	0.2279411	−0.7940
	m	37.92766	−1.457037	0.2573529	−0.8980
	N	23.387976	−0.888108	0.1568627	−0.5509
40	c	−259.3450	10.208094	−1.8014705	6.2277
	m	−255.8190	10.04641	−1.7720588	6.1088
	N	−269.75804	10.611183	−1.872549	6.4704

where X is c, m or N, and T is any temperature in degrees Kelvin. The constants A, B, C and D in eqn. (3) for different solvent mixtures are shown in Table 2. The average deviation between the experimental values (Table 1) and values calculated from eqn. (3) is within ±0.3 mV. The E^0 values at 25°C are reported in Table 3 along with those in water [5].

The standard thermodynamic quantities (ΔG^0, ΔS^0 and ΔH^0) on the molal scale for the electrode reaction

$$Ag^+ \text{ (solvated)} + e \rightleftharpoons Ag(s)$$

at different temperatures in various solvents have been evaluated by the usual relations [3,7]. These values for 25°C are included in Table 3. This

TABLE 3

Values of the standard potentials of the silver–silver ion electrode on the molar, molal and mole-fraction scales in dioxane–water mixtures, and thermodynamic quantities on the molal scale at 25°C

	Wt % dioxane			
	10	20	30	40
E^0_c(V)	0.7768	0.7759	0.7752	0.7738
E^0_m(V)	0.7761	0.7751	0.7741	0.7717
E^0_N(V)	0.5635	0.5777	0.5817	0.5854
$-\Delta G^0_m$(J mole^{-1})$\times10^{-3}$	74.89	74.79	74.69	74.46
$-\Delta H^0_m$(J mole^{-1})$\times10^{-3}$	104.9	101.8	107.1	97.6
$-\Delta S^0_m$(J mole^{-1} K^{-1})	127.0	91.0	108.0	77.0

table shows that the Gibbs free energy change increases with increasing dioxane content of the solvent system, i.e. with decreasing the dielectric constant of the solvent. The standard enthalpy and entropy changes are observed to be negative for all the solvents and increase with increase of dioxane content of the solvent system.

The primary medium effect represents the difference in ion–solvent interaction for Ag^+ at infinite dilution in the particular mixed solvent and in water. It measures the change in the escaping tendency of the Ag^+ ion in the transfer from a standard state in one solvent to a standard state in another solvent [3,7]. The values of the primary medium effect (mole-fraction scale) of various dioxane + water mixtures upon the Ag^+ ion at 25°C were computed by eqn. (4).

$$\lim_{N \to 0} (\log {}^{s}\gamma_{w}) = \frac{(E_{N}^{0})_{w} - (E_{N}^{0})_{s}}{2.3026(RT/F)} \tag{4}$$

where the limit term indicates the primary medium effect. These values are also included in Table 3. It is seen that addition of small amounts of dioxane does not appreciably change the behaviour of the solvent medium upon the ions at infinite dilution. However, the medium has a greater effect upon the silver ion as the dioxane content of the solvent system increases. This indicates the fact that the escaping tendency of the Ag^+ ion is greater in dioxane + water solvents than in water medium.

The standard thermodynamic quantities for the transfer of 1 g-ion of Ag^+ from the standard state in water to the standard states of the mixed solvents, Ag^+ (in water) → Ag^+ (in dioxane + water) were calculated from the standard potential of the electrode in water and in the mixed solvent. The standard transfer quantities (ΔG_t^0, ΔS_t^0 and ΔH_t^0) for dioxane + water solvent mixtures were computed by the customary thermodynamic relations

TABLE 4

Transfer thermodynamic quantities and primary medium effect (mole-fraction scale) in different dioxane–water mixtures

	Wt.% dioxane			
	10	20	30	40
ΔG_t^0(J mole^{-1})	2836.85	1466.67	1080.70	723.69
$\Delta G_{t\,el}^0$(J mole^{-1})	88.74	202.31	355.85	573.77
$\Delta G_{t,ch}^0$(J mole^{-1})	2748.11	1264.36	724.85	149.92
$-\Delta S_t^0$(J mole^{-1} K^{-1})	31.75	9.18	6.30	−39.85
$-\Delta S_{t\,el}^0$(J mole^{-1} K^{-1})	0.71	1.45	2.48	3.87
$-\Delta S_{t,ch}^0$(J mole^{-1} K^{-1})	31.04	7.72	3.82	−43.72
ΔH_t^0(J mole^{-1})	−6643.79	4242.73	−1004.76	12609.5
$-\Delta H_{t\,el}^0$(J mole^{-1})	122.28	231.11	382.71	580.35
$\Delta H_{t,ch}^0$(J mole^{-1})	−6521.51	4473.84	−622.05	13189.85
$\lim_{N \to 0} \log {}^{s}\gamma_{w}$	0.4973	0.2573	0.1897	0.1271

[3,6,7] on the mole-fraction basis [8]. The values of these quantities at 25°C are tabulated in Table 4 for various dioxane + water solvent mixtures. A perusal of Table 4 shows that the standard Gibbs free energy of transfer, ΔG_t^0, is positive for all solvents and that the magnitude decreases with increasing proportion of dioxane. The Ag^+ ion thus appears to be in a lower Gibbs energy state in water than in the respective mixed solvent. In other words, water is more basic than the mixed solvents. These conclusions are consistent with those obtained from primary medium effects.

It is known that the ΔH_t^0 and ΔS_t^0 functions are of great significance in examining the structural effects as they contain important contributions from the effects of the ions on the structure of the solvents. As observed, the standard enthalpy and entropy changes appear to be negative for water-rich solvents and positive for the dioxane-rich solvents. The negative ΔS_t^0 value suggests that the amount of order created by the Ag^+ ion in water-rich solvents is greater. Upon further addition of dioxane, the probability of the existence of water molecules around the Ag^+ ion increases considerably and the Ag^+ ion now creates more disorder in the mixed solvent than in water. The increasingly positive values of ΔS_t^0 and ΔH_t^0 point to the fact that upon the addition of dioxane there begins a gradual breakdown of the water structure in the transfer process. The silver ion thus breaks more structure in dioxane-rich solvents than in pure water. This is further supported by the view [9,10] that all structure-breaking processes, including desolvation of ions, are endothermic and are accompanied by gain in entropy.

As usual [3,7], the related thermodynamic quantities are separated into two parts: electrostatic (el), which arises due to the change in the dielectric constant during the transfer of charged particles from water to another solvent, and non-electrostatic or chemical (ch), which takes into account the specific chemical interactions between the ions and the solvent which include solvation as well as the basicity of the solvent. Thus

$$\Delta R_t^0 = \Delta R_{t,el}^0 + \Delta R_{t,ch}^0 \qquad (5)$$

where R is any thermodynamic quantity, e.g. G, H, or S.

Assuming the radius of the Ag^+ ion does not change with the change of solvent [8], the electrostatic parts of the Gibbs free energy change, as well as of the entropy of transfer, can be estimated from the well-known Born equations given by

$$\Delta G_{t,el}^0 = \frac{Ne^2}{2r_+}\left(\epsilon_s^{-1} - \epsilon_w^{-1}\right) \qquad (6)$$

and

$$\Delta S_{t,el}^0 = \frac{-Ne^2}{2r_+}\left[\left(\epsilon_s\theta_s\right)^{-1} - \left(\epsilon_w\theta_w\right)^{-1}\right] \qquad (7)$$

where the radius of the silver ion (r_+) may be taken as 0.126 nm [8], ϵ_s and

TABLE 5

Solubility product constants on the molar (c) and molal (m) scales of AgX (X = Cl, Br, I, N_3, CNS, IO_3 or BrO_3) in dioxane–water mixtures at different temperatures

X	*t*(°C)				
	5	10	15	20	25
10 wt % dioxane					
Cl					
$K_s^c \times 10^{11}$	3 841	6 855	11 810	19 340	30.540
$K_s^m \times 10^{11}$	3 684	6 662	11 540	19.030	30 180
Br					
$K_s^c \times 10^{12}$			7		0 995
$K_s^m \times 10^{12}$					0 943
I					
$K_s^c \times 10^{16}$					1.849
$K_s^m \times 10^{16}$		8			1 828
N_3					
$K_s^c \times 10^{9}$					6 139
$K_s^m \times 10^{9}$					6.067
CNS					
$K_s^c \times 10^{12}$	0.140	0 307	0 648	1 299	2 506
$K_s^m \times 10^{12}$	0 137	0.298	0 633	1.279	2 477
IO_3					
$K_s^c \times 10^{9}$	3 420	6 100	10 530	17.350	27.050
$K_s^m \times 10^{9}$	3.280	5 930	10.248	17.080	26 740
BrO_3					
$K_s^c \times 10^{5}$	1 004	1 564	2.308	3 230	4 353
$K_s^m \times 10^{5}$	1 002	1 519	2 254	3 181	4 302
20 wt % dioxane					
Cl					
$K_s^c \times 10^{11}$	3 073	5 168	8 399	13 700	21 260
$K_s^m \times 10^{11}$	2 911	4 920	8 034	13.220	20 690
Br					
$K_s^c \times 10^{12}$					0 819
$K_s^m \times 10^{12}$					0.797
I					
$K_s^c \times 10^{16}$					1 925
$K_s^m \times 10^{16}$					1 874
N_3					
$K_s^c \times 10^{9}$					5 422
$K_s^m \times 10^{9}$					5 295
CNS					
$K_s^c \times 10^{12}$	0.222	0.451	0.888	1 763	3 242
$K_s^m \times 10^{12}$	0 210	0 429	0.849	1 701	3 154
IO_3					
$K_s^c \times 10^{9}$	2 951	4.052	5 551	7 408	9.754
$K_s^m \times 10^{9}$	2 803	3.858	5 310	7 148	9 493
BrO_3					
$K_s^c \times 10^{5}$	0 945	1 344	1 872	2.578	3 420
$K_s^m \times 10^{5}$	0 895	1 279	1 791	2.488	3 329

TABLE 5 (continued)

X	I(°C)				
	5	10	15	20	25
30 wt % dioxane					
Cl					
$K_s^c \times 10^{11}$	2 208	3 592	5 748	8 982	13 960
$K_s^m \times 10^{11}$	2.047	3 365	5 433	8 570	13 380
N_3					
$K_s^c \times 10^{9}$					4 730
$K_s^m \times 10^{9}$					4 531
CNS					
$K_s^c \times 10^{12}$	0 297	0 569	1 074	1 992	3 667
$K_s^m \times 10^{12}$	0.276	0 533	1 014	1 900	3 514
IO_3					
$K_s^c \times 10^{9}$	1 570	2 035	2 561	3 192	3 491
$K_s^m \times 10^{9}$	1 455	1 905	2 422	3 040	3 345
BrO_3					
$K_s^c \times 10^{5}$	0.765	1.069	1 464	1 938	2 584
$K_s^m \times 10^{5}$	0 710	1 000	1 384	1 849	2 474
40 wt % dioxane					
Cl					
$K_s^c \times 10^{11}$	1 369	2 180	3 307	5 232	7 729
$K_s^m \times 10^{11}$	1.248	2 008	3.087	4 930	7 290
N_3					
$K_s^c \times 10^{9}$					3 559
$K_s^m \times 10^{9}$					3 358
CNS					
$K_s^c \times 10^{12}$	0 341	0 648	1 185	2 260	3 970
$K_s^m \times 10^{12}$	0 311	0 597	1 108	2 130	3 745
IO_3					
$K_s^c \times 10^{9}$	0.798	1 091	1.411	1 839	2 338
$K_s^m \times 10^{9}$	0 728	1 006	1 318	1 733	2 206
BrO_3					
$K_s^c \times 10^{5}$	0.715	0.980	1 351	1 908	2 534
$K_s^m \times 10^{5}$	0 652	0.903	1 261	1 799	2 391

ϵ_w are the dielectric constants of the mixed solvent and water, respectively, and were obtained from the literature [5]. The values of θ_w and θ_s, the temperature coefficients of the dielectric constants, were taken from the literature [5,11].

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 contributions of these quantities were computed from eqn. (5). The values of these quantities at 25°C are presented in Table 4.

An inspection of Table 4 shows that the chemical contribution to the Gibbs free energy change, $\Delta G^0_{t,ch}$, is positive for all solvents and decreasses with increasing dioxane content in the solvent mixture. In so far as $\Delta G^0_{t,ch}$ is a criterion of the changes in the acidity or basicity of the medium, the positive value of $\Delta G^0_{t,ch}$ indicates that the transfer process from water to the respective mixed solvent is not favoured. Thus, as far as chemical reaction or solvation is concerned, the Ag^+ ion is in a lower Gibbs energy state in water than in the mixed solvent. In other words, the mixed solvents possess a smaller solvating capacity toward the Ag^+ ion and are less basic than water. Further, the decreasingly positive values of $\Delta G^0_{t,ch}$ indicate that as the dioxane content in the solvent mixture increases, the solvating capacity as well as the basicity of the mixed solvents decrease. The chemical effects on the entropy and enthalpy of transfer which appear to be negative for solvents of lower dioxane content, increase with increasing the dioxane wt.% in the solvent mixture. For dioxane-rich solvents, the positive value of $\Delta H^0_{t,ch}$ reflects the

TABLE 6

Constants of eqn (4) of AgX for molar (c) and molal (m) scales in dioxane–water mixtures for different silver salts

X	p	Constant	Wt % dioxane			
			10	20	30	40
Cl						
	c	A	−3722 0100	−34 77 5152	−3318 6177	−3113 4282
		B	2 984151	1 999736	1 281319	0 337068
		σ	0 064	0 059	0 057	0 053
	m	A	−3775 3995	−35260 6395	−3376 3150	−3172 6365
		B	3 159073	2 152117	1 456815	0 511507
		σ	0 064	0 060	0 058	0 054
CNS						
	c	A	−5187 0899	−4825 3168	−4525 1191	−4419 1911
		B	5 812802	4 705401	3 74591	3 421584
		σ	0 089	0 082	0 077	0 075
	m	A	−5240 7128	−4874 2498	−4582 7318	−4478 3897
		B	5 988543	4 857088	3 921153	3 602019
		σ	0 089	0 083	0 078	0 076
IO_3						
	c	A	−3709 8323	−2145 0049	−1424 3575	−1929 6102
		B	4 891796	−0 811252	−3 659522	−2 151312
		σ	0 063	0.037	0 024	0 032
	m	A	−3763 5040	−2194 0008	−1481 9805	−1988 7785
		B	5 06771	−0 659306	−3 484284	−1 977046
		σ	0 064	0 037	0 025	0 034
BrO_3						
	c	A	−2560 2380	−2310.5910	−2187 2620	−2278 6327
		B	4.239863	3 29188	2 75474	3 048688
		σ	0 044	0 039	0 037	0 039
	m	A	−2613.4083	−2359 5577	−2244 8746	−2337 8450
		B	4.414032	3 443764	2 929943	3 223148
		σ	0 045	0 040	0 038	0 040

larger enthalpy change involved in breaking down the solvent structure on the transfer process. This view is further supported by the positive value of $\Delta S^0_{t,ch}$, which is associated with an overall disorder created by the Ag^+ ion during the transfer process.

The thermodynamic solubility products, K^0_{so}, of silver halides, silver pseudo-halides and silver oxyhalides in dioxane + water mixtures have been calculated from the values of standard potentials by means of

$$\ln K^0_{so}(AgX) = \left[E^0_{Ag,AgX} - E^0_{Ag,Ag^+}\right]\frac{F}{RT} \tag{8}$$

where $E^0_{Ag,AgX}$ is the standard molar potential of the Ag, AgX (X = Cl, Br, I, N_3, CNS, IO_3 or BrO_3) electrode and is obtained from the literature [3–5,11–13] over the temperature range under investigation. The values for K^0_{so} on the molarity (K^c_{so}) and molality (K^m_{so}) scales at the experimental temperatures are presented in Table 5. The data for K^m_{so} were calculated from K^c_{so}/ρ^2. The solubility data were fitted by least squares to an equation of the type [14,15]

$$\log K^p_{so}(AgX) = \frac{A}{T} + B \tag{9}$$

where p is c or m, and T is any temperature in degrees Kelvin. The constants A and B of eqn. (9) are shown in Table 6, for various silver salts and for all solvents, along with σ, the standard deviation for the precision of the least-squares fit: the correlation coefficient for the relations is within 1.00.

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