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Note

THERMODYNAMICS OF THE SILVER–SILVER IODATE AND SILVER–SILVER BROMATE ELECTRODES IN DIOXANE–WATER MIXTURES

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A survey of the literature [1–3] shows that the standard potentials of the silver–silver iodate and silver–silver bromate electrodes are known in aqueous medium from the solubility data at a single temperature, 25°C, or at different temperatures. Recently, Dash [4–6] has reported the standard potentials of these electrodes at different temperatures in formamide from both the electromotive force measurements of cells involving these electrodes and solubility measurements of the corresponding silver salt. Dash and co-workers [7,8] have also determined the solubility product of these silver salts in dioxane–water and urea–water mixtures at different temperatures.

In continuation of the study on ion–solvent interactions in binary solvent systems [9–11], we now report the standard potentials of the silver–silver iodate and silver–silver bromate electrodes in water and dioxane–water mixtures at different temperatures with a view to examining the role the permittivity of the medium towards ion–solvent interactions. As previously [5,10a,11], the following cell with a liquid junction

$$Ag(s),AgCl(s),KCl(c)||KXO_3(c),AgXO_3(s),Ag(s)$$

has been employed for the determination of the standard potentials of the $Ag(s)–AgXO_3(s), XO_3^-$ electrode, where XO_3 is IO_3 or BrO_3.

EXPERIMENTAL

The potassium chloride, potassium iodate and potassium bromate (B.D.H. Analar reagents) were dried at 100–120°C for 2 h and stored in a vacuum desiccator over calcium chloride until required. Dioxane was purified as described earlier [10a]. Conductivity water was used. Silver–silver chloride, silver–silver iodate and silver–silver bromate electrodes were prepared according to the methods available in the literature [5,11]. Solvents of

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various compositions were made up by weight in conductivity water. Stock solutions of potassium chloride, potassium iodate and potassium bromate were prepared in dioxane–water mixtures of various compositions on the molar scale. The cell vessels were of an all-glass type of design described elsewhere [5,10a].

Equimolar solutions of potassium chloride and potassium iodate or bromate were prepared from the stock solutions by the double-dilution method. The general experimental procedures for setting up the cells, the E.M.F., and conductance measurements were essentially similar to those described earlier [10a,11]. All measurements were made in water baths maintained at appropriate temperatures within ±0.1°C.

RESULTS AND DISCUSSION

The standard molar potentials, E_c^0 of the silver–silver iodate and silver–silver bromate electrodes were obtained by the method of extrapolating [10a,11] the auxiliary function, $E_c^{0'}$, given by ref. 11b

$$\begin{aligned} E_c^{0'} &= E + E^0_{\mathrm{Ag,AgCl}} + (RT/F)\ln([\mathrm{XO_3^-}]\gamma_{\mathrm{XO_3}}/[\mathrm{Cl^-}]\gamma_{\mathrm{Cl^-}}) - E_j \\ &= E + E^0_{\mathrm{Ag,AgCl}} - E_j \qquad (1) \end{aligned}$$

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

As before, the values of the liquid junction potential, E_j were calculated. It is found that the E_j values varied in the range 0.1–0.3 mV in all solvents for all temperatures. The values of $E^0_{\mathrm{Ag,AgCl}}$ (molar scale) needed for the calculation of $E_c^{0'}$ [eqn. (1)] at different temperatures in various compositions of dioxane–water mixtures are taken from the literature [12,13]. 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 is ±0.3 mV.

By following the usual relations [11], standard potentials on the molal (E_m^0) and mole fraction (E_N^0) scale were calculated from that on the molar scale (E_c^0) using the density and average molecular weight of the solvent concerned at different temperatures. The values of the standard potentials are expressed as a function of temperature, T (Kelvin), by ref. 14

$$E_p^0 = A + BT + CT\ln T + DT^2/2 \qquad (2)$$

where p is c, m or N, and A, B, C and D are empirical constants and are shown in Table 2 for different scales in various dioxane–water mixtures along with those in water. The average deviation between the experimental values (Table 1) and the values calculated from eqn. (2) is within ±0.2 mV. The E^0 values at 25°C are listed in Table 3.

As before [11,14], the standard thermodynamic quantities (ΔG^0, ΔH^0, and

TABLE 1

Standard molar potentials (E_c^0 in abs. volts) for the $Ag(s)|AgXO_3(s)|\ XO_3^-$ electrode (XO_3 is IO_3 or BrO_3) in water and dioxane–water mixtures from 5 to 35°C

Mass percent dioxane	XO_3	*t* (°C)						
		5	10	15	20	25	30	35
0	IO_3	0.3334	0.3324	0.3313	0.3301	0.3288	0.3269	0.3248
	BrO_3	0.5308	0.5293	0.5287	0.5271	0.5260	0.5241	0.5224
10	IO_3	0.3335	0.3326	0.3317	0.3307	0.3291	0.3278	0.3259
	BrO_3	0.5258	0.5241	0.5227	0.5209	0.5188	0.5163	0.5143
20	IO_3	0.3275	0.3212	0.3154	0.3084	0.3020	0.2954	0.2893
	BrO_3	0.5209	0.5190	0.5171	0.5144	0.5117	0.5096	0.5059
30	IO_3	0.3098	0.3025	0.2945	0.2864	0.2749	0.2668	0.2605
	BrO_3	0.5135	0.5115	0.5093	0.5065	0.5038	0.5007	0.4979
40	IO_3	0.2922	0.2857	0.2786	0.2704	0.2632	0.2559	0.2485
	BrO_3	0.5103	0.5078	0.5062	0.5040	0.5019	0.4998	0.4959

TABLE 2

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

Constants	p	Mass percent dioxane					XO_3^-
		0	10	20	30	40	
A	c	0.10188	0.15528	0.63481	0.59774	0.54387	IO_3
	m	0.12335	0.15072	0.61233	0.56949	0.48715	
	N	0.096934	0.14982	0.58376	0.59188	0.50762	
	c	0.35593	0.37659	0.35657	0.32375	0.35972	BrO_3
	m	0.42104	0.34110	0.27585	0.34439	0.32668	
	N	0.44644	0.41142	0.33843	0.34532	0.34518	
10^3 B	c	−0.91621	−2.0219	−1.7146	2.5919	0.11054	IO_3
	m	−1.1951	−1.0075	−1.1780	1.7651	0.073168	
	N	−0.46041	−0.5179	−0.066083	0.87753	−0.7091	
	c	0.97488	−0.34105	−1.8302	1.7056	−1.8995	BrO_3
	m	−1.0082	1.2113	1.1315	−0.36226	−2.3346	
	N	−2.2696	−0.94967	−1.3445	−0.79327	−3.4225	
10^4 C	c	5.886	7.4060	1.6460	−6.4504	−1.0731	IO_3
	m	6.1471	5.2559	0.75309	−4.3539	−0.25922	
	N	3.4849	2.7635	−2.6235	−4.1682	−0.22882	
	c	0.99964	3.6554	7.2704	0.14959	7.1336	BrO_3
	m	4.2655	0.80284	2.0415	4.1801	8.4458	
	N	5.1150	2.9397	5.0016	3.7051	9.1596	
-10^5 D	c	1.1250	1.0829	0.22788	−0.003575	0.2955	IO_3
	m	1.0856	0.93213	0.19771	0.18196	0.45709	
	N	0.96622	0.76093	0.032394	0.14102	0.41035	
	c	0.65399	0.84862	1.2015	0.79640	1.1328	BrO_3
	m	0.71806	0.72055	1.0098	0.99853	1.2712	
	N	0.71843	0.70078	1.0655	0.96304	1.2763	

TABLE 3

Values of the E^0 (in abs. volts) of the Ag(s)|$AgXO_3$(s)|XO_3^- electrode (XO_3 is IO_3 or BrO_3) on the molar, molal and mole-fraction scale in water and dioxane–water mixtures at 25°C

E^0	XO_3	Mass percent dioxane				
	≡	0	10	20	30	40
E_c^0	IO_3	0.3288	0.3291	0.3020	0.2749	0.2632
	BrO_3	0.5260	0.5188	0.5117	0.5038	0.5019
E_m^0	IO_3	0.3290	0.3288	0.3013	0.2738	0.2617
	BrO_3	0.5262	0.5181	0.5110	0.5027	0.5005
E_N^0	IO_3	0.1226	0.1267	0.1038	0.0814	0.0750
	BrO_3	0.3198	0.3164	0.3135	0.3103	0.3138

ΔS^0) for the electrode reaction

$$AgXO_3(s) + e \rightleftharpoons Ag(s) + XO_3^- \text{ (solvated)}$$

and the standard transfer thermodynamic quantities (ΔG_t^0, ΔH_t^0, and ΔS_t^0) for the process

$$XO_3^- \text{ (in water)} \rightarrow XO_3^- \text{ (in dioxane–water)}$$

have been evaluated at different temperatures for various solvents. The transfer thermodynamic quantities on the mole fraction basis [9,11] at 25°C are listed in Table 4 along with the changes in electrostatic (el) and chemical (ch) contributions to these transfer thermodynamic quantities [11].

Assuming the radii of the ions do not change with the change of solvent [15], the values of $\Delta G_{t,el}^0$ and $\Delta S_{t,el}^0$ have been estimated by the well-known Born equations

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

and

$$\Delta S_{t,el}^0 = (-Ne^2/2)(\epsilon_s^{-1}\theta_s^{-1} - \epsilon_w^{-1}\theta_w^{-1})(r_+^{-1} + r_-^{-1}) \tag{5}$$

where the radius of the silver ion (r_+) may be taken as 1.26 Å [15] and that of iodate ion (r_-) as 1.82 Å and the bromate ion (r_-) as 1.91 Å [16], ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, and were taken from the literature [13]. The values of θ_w and θ_s, the temperature coefficients of dielectric constants, were obtained from the literature [13].

The values of $\Delta H_{t,el}^0$ were computed from a knowledge of $\Delta G_{t,el}^0$ and $\Delta S_{t,el}^0$. The chemical parts of these quantities have been evaluated from the relation

$$\Delta R_t^0 = \Delta R_{t,el}^0 + \Delta R_{t,ch}^0$$

where R is G, S or H.

As far as we know, no measurements have been made on the concentra-

TABLE 4

Transfer thermodynamic quantities * for the process, XO_3^- (in water)→XO_3^- (in dioxane-water). (XO_3 is IO_3 or BrO_3) at 25°C

	Mass percent dioxane							
	10		20		30		40	
	a	b	a	b	a	b	a	b
ΔG_t^0	−0.43	0.30	1.79	0.55	3.79	0.88	4.54	0.57
$\Delta G_{t,el}^0$	1.52	1.49	3.47	3.40	6.09	5.98	9.82	9.63
$\Delta G_{t,ch}^0$	−1.95	−1.19	−1.68	−2.85	−2.31	−5.09	−5.28	−9.07
ΔS_t^0	7	−8	−89	−18	−128	−19	−104	−10
$\Delta S_{t,el}^0$	−12	−12	−25	−24	−42	−42	−66	−65
$\Delta S_{t,ch}^0$	19	4	−64	7	−86	23	−38	55
ΔH_t^0	1.6	−2.1	−24.6	−4.8	−34.4	−4.8	−26.5	−2.5
$\Delta H_{t,el}^0$	−2.1	−2.0	−3.9	−3.9	−6.5	−6.4	−9.9	−9.8
$\Delta H_{t,ch}^0$	3.7	−0.08	−20.6	−0.9	−27.9	1.6	−16.6	7.3

a is IO_3; b is BrO_3.

* ΔG^0 in kJ $mole^{-1}$, ΔS^0 in J $mole^{-1}K^{-1}$, and ΔH^0 in kJ $mole^{-1}$.

tion cells for the determination of the standard potentials of the silver–silver iodate and silver–silver bromate electrodes in water over a range of temperature. However, the standard molal potentials of these electrodes are available in water at a single temperature, 25°C, or at three different temperatures, 25, 30 and 35°C, which are calculated from the solubility data of the corresponding silver salt and the standard molal potentials of the silver electrode in water. A comparison of our E_m^0 values in water at 25°C (0.3290 V), 30° (0.3271 V) and 35°C (0.3251 V) with those reported by Li and Tulo [1] at 25° (0.3551 V), 30° (0.3525 V) and 35°C (0.3499 V) in water for the silver–silver iodate electrode, and those at 25° (0.5262 V), 30° (0.5243 V) and 35°C (0.5227 V) with the E_m^0 values available in water at 25°C (0.5500 V) [2], and at 25° (0.5528 V), 30° (0.5512 V) and 35°C (0.5506 V) [3] for the silver–silver bromate electrode, shows that the present set of data obtained in water from the study of the concentration cell are found to be widely discrepant from the E_m^0 values reported earlier. This discrepancy might be due to the much lower solubility of $AgIO_3$ or $AgBrO_3$ in presence of KIO_3 or $KBrO_3$ (used in the concentration cells) than in presence of KNO_3 or in water only. Since the concentration cells of the type used in the present study have been widely employed for the determination of the standard potentials of the electrodes of the second kind in different solvents [5,10a,11,17], it seems fairly certain that the present set of E_m^0 values obtained in water over a range of temperature are more promising.

An inspection of Table 1 shows that the standard potentials of the silver–silver iodate and silver–silver bromate electrodes in various dioxane–water mixtures are less (except in water + 10 mass % dioxane for the former) than that in water, and decrease with the increase in dioxane content in water. Such an observation seems to be similar to the studies made on the silver–silver halide electrodes in various dioxane–water mixtures [18]. The observed decrease in the E^0 values with increase in dioxane content in water is consistent with the conclusions based on purely electrostatic considerations by Feakins and French [19] using Born's equation. However, any change in E^0 values of the silver–silver iodate electrode on passing from water to water + 10 mass % dioxane will be due to the variation of the free energy of solvation of the IO_3^- ion in the solvent concerned.

A perusal of Table 4 shows that the values of ΔG_t^0 for the transfer of XO_3^- ions from water to dioxane–water mixtures are positive (except for IO_3^- ion in water + 10 mass % dioxane) which indicates 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 XO_3^- ions from water to these mixed solvents unfavourable. Thus, XO_3^- ions appear to be in a lower free energy state in water than in mixed solvents. However, the negative ΔG_t^0 value for IO_3^- ion in water + 10 mass % dioxane signifies that the IO_3^- ion is more strongly stabilized in this solvent than in pure water and other mixed solvents.

TABLE 5

Primary medium effect $\lim_{N \to 0} \log {}^{s}\gamma_{w}$ (on the mole-fraction scale) of IO_3^- and BrO_3^- ions in various dioxane–water mixtures at 25°C

Ion	Mass percent dioxane			
	10	20	30	40
IO_3^-	−0.069	0.318	0.696	0.805
BrO_3^-	0.058	0.107	0.161	0.101

As chemical contribution to the Gibbs energy of transfer of an ion in solution is attributed to the solvation of the ion, $\Delta G^0_{t,ch}$ of XO_3^- ions should reflect the solvating capacities of the solvent concerned and water towards XO_3^- ion. However, it is found that the chemical contribution to the Gibbs energy of transfer is negative and appears to be a solvent parameter that measures the increase in basicity of the mixed solvent. Thus, the negative values of $\Delta G^0_{t,ch}$ suggest that the mixed solvent is more basic than water, but the electrostatic factors predominate over the chemical interaction or solvation resulting in an overall unfavourable effect on the transfer process from water to the mixed solvent. The negative values of ΔS_t^0 and ΔH_t^0 for XO_3^- ions (except in 10 mass % dioxane for IO_3^- ion) lend support to the view that for a transfer from water to a more ordered mixture of low dioxane content, the amount of disorder created by XO_3^- ions in the mixed solvent is less and hence gives negative values of ΔS_t^0 and ΔH_t^0 (Table 4).

The primary medium effect is a measure of the change of Gibbs energy upon transfer of one gram ion of XO_3^- from infinite dilution in water to infinite dilution in the mixed solvent, resulting from a difference in the ion–solvent interactions at infinite dilutions and is independent of concentration. The resulting positive magnitudes of this quantity as can be seen from Table 5 (except in 10 mass % dioxane for IO_3^- ion) and presumably indicate that the escaping tendency of the XO_3^- ions is more in dioxane–water mixtures than in pure water. This is consistent with the conclusions based on the fact that the XO_3^- ions are less stabilized (but the IO_3^- ion is more stabilized in water + 10 mass % dioxane) in dioxane–water mixtures than in pure water.

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