Standard Electrode Potentials of the Silver-Silver Sulphate and Silver-Silver Dichromate Electrodes in Water+Dioxane Mixtures at Different Temperatures

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The standard electrode potentials of the silver-silver sulphate and silver-silver dichromate electrodes in different compositions of water + dioxane mixtures at 5°, 15°, 25° and 35°C have been determined using cells with liquid junction potentials. From the values of the standard electrode potentials, the standard thermodynamic quantities (ΔG°, ΔH° and ΔS°) for the electrode processes and the transfer thermodynamic quantities (ΔG°_t, ΔH°_t and ΔS°_t) for the process, $X^=$(in water) ---- $X^=$ (in water + dioxane), where X is SO_4 or Cr_2O_7, have been evaluated. The thermodynamic solubility products, K°_{so} of Ag_2X have also been calculated in different compositions of water + dioxane mixtures at the experienced temperatures.

The standard electrode potential of silver, silver sulphate electrode has been reported in water(1) at a single temperature, 25°C from solubility measurements. Quite recently, Dash et al (2) have reported the standard electrode potentials of silver, silver sulphate and silver, silver dichromate electrodes along with other electrodes of the second kind in water and in different composition of water + glycerol, + acetone, + urea and + alcohol mixtures. In earlier communications (3), the standard electrode potentials of the silver-silver chromate and silver-silver tungstate electrodes in various compositions of water + dioxane mixtures have been determined at different temperatures ranging from 5° TO 35°C. With a view to comparing the standard electrode potentials between these electrodes, the present work aims at determining the standard electrode potentials of the silver-silver sulphate and silver-silver dichromate electrodes in these mixed solvents.

EXPERIMENTAL

MATERIALS

Dioxane was of BDH (Analar) sample and purified further by the method described earlier (3). Solvents of various compositions were made up by weight in conductivity water. The dioxane contents of the solution are accurate to within + 0.02%.

Potassium chloride, potassium sulphate, potassium dichromate and silver nitrate were either of G.R. or BDH (Analar) grade. The potassium salts were dried at 100-120°C for 2 hrs. and stored in vacuum desiccator over calcium chloride until required. Stock solutions ($\simeq 10^{-1}$ C) of the potassium salts were prepared in water + dioxane mixtures of specified compositions. Solutions of appropriate concentrations (= 2.5 X 10^{-3} C to 7 X 10^{-3} C correct to within ±0.05%) for e.m.f. measurements were prepared from stock solutions.

The silver-silver chloride electrodes were of the thermal electrolytic type, and were made by anodizing the silver electrodes prepared by the method described earlier (4) in a 0.1 C hydrochloric acid (G.R.) solution. The silver-silver sulphate and silver-silver dichromate electrodes were of the paste type, and were prepared (5) by giving the paste of silver sulphate or silver dichromate on the silver electrodes. After preparation, the electrodes were stored in the corresponding 0.05 C acqueous solution of potassium chloride, potassium sulphate or potassium dichromate for about 24-48 h and then mixed with the corresponding potassium salt solutions of appropriate concentrations prepared in water + dioxane mixed solvents for e.m.f. measurements, as needed before use. Only those electrodes were used which showed a potential difference of 0.1 m V, or less, on being compared with another of the same type.

MEASUREMENTS

The cell vessels were of an all-glass type of the design described earlier (3). Preparation of the cell solutions and setting up of the cells were essentially similar to procedure described elsewhere (3).

Measurements of the e.m.f. of the cell of the type(A) were made

$$Ag(s),AgCl(s),KCl(c)//K_2X(c/2),Ag_2X(s),Ag(s) \quad ....A$$

at 5°, 15°, 25° and 35°C with a Bajaj (India) potentiometer in conjunction with a d.c. galvanometer (Elfo, India) and a Weston standard

cell (Muirhead and Co., England). The equilibrium was reached in 2-3 h after immersing the cells in the thermostat maintained at appropriate temperature within ± 0.05°C. Constant e.m.f. values of ± 0.08 mV for a period of 1/2 hr were considered adquate and regarded as the criterion for equilibrium.

Conductance measurements were made on a digital direct reading conductivity meter (Systronics, Type 304) with a sensitivity of 0.1% and giving a conductance value of three digits. The conductances of the different concentrations of the potassium salts were measured making appropriate corrections for the conductances of the solvents. Measurements were carried out at a temperature maintained constant within ± 0.05°C

RESULTS AND DISCUSSION

The e.m.f., E of the cell (A) is given by the expression (3).

$$E = E^\circ + (RT/2F)\ln(2C) + (RT/2F)\ln(\nu_{Cl^-}^2/\nu_{X^{2-}}) + E_j \quad --(1)$$

Where the symbols have their usual significance.

Using the molar concentrations of the corresponding electrolyte solutions and expressing the mean molar activity coefficients by the Debye-Huckel expression, the standard molar potentials E_c° of the Ag, Ag_2SO_4, SO_4^{2-} and Ag, $Ag_2Cr_2O_7$ $Cr_2O_7^{2-}$, electrodes were obtained by the method of extrapolating the corresponding auxiliary functions $E_C^{o'}$ given by (3)

$$E_C^{o'} = E - 1/2\ K\log(2C) - 1/2\ K\left(\frac{4A\sqrt{3C/2}}{1+\sqrt{3C/2}} - \frac{2A\sqrt{C}}{1+\sqrt{C}}\right) + E^\circ_{Ag,AgCl} - E_j = E^\circ_{Ag,Ag_2X} + bc \quad --(2)$$

to the molarity C = 0, where $E^\circ_{Ag,AgCl}$ is the standard molar potential of the silver-silver chloride electrode and A is the Debye-Huckel constant, and are known(6-7) over the temperature range under investigation for various water + dioxane mixtures. In equation (2), k = 2.3026 (RT/F) and b = k/2 $[(2\beta_{Cl^-}) - (3/2\ \beta_{X^{2-}})]$ where β is the usual constant in the Debye-Huckel expression for the activity coefficient, i.e.,

$$-\log\gamma_i = \frac{Az_i^2\sqrt{\mu}}{1\pm\sqrt{\mu}} - \beta_i\mu$$

where i is Cl^- or X_2^-.

The values of the liquid - junction potential, E_j were calculated from the equivalent conductances of potassium chloride and potassium sulphate or potassium dichromate solutions by means of the Lewis and Sargent equation(2). It was found that values of E_j varied in the range 0.001 - 0.008 V in all solvents for all temperatures.

Substituting the numerical values of $E_{j(3a)}$ in equation(2) and extra polating the $E_C^{o'}$ values to C = 0, the values of E_C° for the Ag, Ag_2 X, X^{2-} electrode were obtained in various water + dioxane mixtures. These values of E_C° are given in Table.1. The average standard deviation in the values of E_C° is ± 0.4 mV.

TABLE 1

STANDARD MOLAR POTENTIALS (E_C° in abs. Volts) FOR THE Ag, Ag_2 X, X^{2-} ELECTRODES (X = SO_4, CrO_4, Cr_2O_7 or WO_4) IN WATER + DIOXANE MIXTURES AT 25°C

X	mass% dioxane		
	10	20	30
SO_4	0.5985	0.5888	0.5797
CrO_4	0.4325	0.4133	0.3868
Cr_2O_7	0.5158	0.4944	0.4742
WO_4	0.4708	0.4617	0.4422

Standard potentials on the molal (E_m°), molefraction (E_N°) and molar (E_C°) scale (correlated by the usual equation (9)) at various temperatures for any solvent were fitted by the method of least-squares, to the equation,

$$E_p^\circ = a + b\ (t - 25) + c\ (t - 25)^2 \quad --(3)$$

Where p is C, m or N and t is any temperature (°C). The constants a, b and c of equation (3) on the molal scale (p = m) are recorded in Table 2 along with those for the silver-silver chromate and silver-silver tungstate electrodes(3) for the sake of comparison. The average deviations between the E_m° values calculated from the experimental E_C° values and the E_m° values calculated from equation (3) are within ± 0.3 mV. The standard thermodynamic quantities (ΔG°, ΔH° and ΔS°) on the molal scale for the electrode reaction, Ag_2 X (s) + 2e ⇌ 2 Ag(s) + X^{2-}(solvated) at different temperatures in various solvents have been calculated by the usual relation(3). These values at 25°C are presented in Table 2 alongwith those for the silver-silver chromate and silver-silver tungstate electrode reactions(3) for the sake of comparison.

The standard transfer thermodynamic quantities, ΔG_t°, ΔH_t° and ΔS_t° for the process, X^{2-} (in water)→X^{2-} (in water + dioxane) were evaluated at different temperatures for various solvent mixtures by the usual relations. The values of the transfer thermodynamic quantities were obtained on the mole-fraction basis since that will eliminate free energy changes due to concentration changes(2,3). These values at 25°C

TABLE 2

(CONSTANTS OF EQUATION (3) ON MOLAL SCALE AND VALUES OF ΔG°_m , ΔH°_m (in kJ mole/1), ΔS°_m (J/° k/mole) IN WATER + DIOXANE MIXTURES.

Mass% dioxane	X	a	-10^3 b	10^7C	$-\Delta G^\circ_m$	$-\Delta H^\circ_m$	$-\Delta S^\circ_m$
10	SO_4	0.5981	1.2975	7.5	115.4	190.0	250.4
20		0.5881	1.3942	2.5	113.5	192.1	263.9
30		0.5787	1.3292	-12.3	111.68	191.7	256.5
10	CrO_4	0.4322	0.9279	-30.9	83.4	136.65	179.13
20		0.4126	1.085	-17.7	79.62	141.95	209.43
30		0.3858	1.1024	-57.1	74.47	137.62	212.73
10	Cr_2O_7	0.5155	1.2717	5.0	99.48	172.6	245.4
20		0.4936	1.2942	12.5	95.26	169.7	249.8
30		0.4731	1.3158	-12.5	91.3	167.0	253.9
10	WO_4	0.4710	1.837	20.0	90.99	19.97	364.6
20		0.4611	2.023	20.0	88.93	19.13	343.6
30		0.4416	1.67	-140.0	85.27	18.69	341.1

* Uncertainties $\Delta G^\circ = \pm 6$J $\Delta H^\circ = \pm 6$J $\Delta S^\circ = \pm 3$J

TABLE 3

VALUES OF ΔG°_t , ΔH°_t AND ΔS°_t FOR THE TRANSFER PROCESS IN WATER + DIOXANE MIXTURES AT 25°C (ΔG°'s IN kJ/MOLE/L, ΔH°'s IN kJ MOLE/1 AND ΔS°'s IN KJ °K/L MOLE/L)

Parameter	X = SO_4			X = CrO_4		
	mass% dioxane			mass% dioxane		
	10	20	30	10	20	30
ΔG°_t	0.93	2.01	2.80	2.43	5.35	9.59
$\Delta G^\circ_{t,el}$	0.12	0.27	0.47	1.37	3.12	5.49
$\Delta G^\circ_{t,Ch}$	0.81	1.74	2.33	1.06	2.23	4.10
ΔS°_t	-12.93	-26.11	-15.34	46.7	19.9	12.2
$\Delta S^\circ_{t,el}$	0.92	1.91	3.25	0.92	1.91	3.25
$\Delta S^\circ_{t,Ch}$	-12.01	-24.20	-12.09	47.62	21.81	15.45
ΔH°_t	- 2.93	- 5.78	- 1.77	16.35	11.28	13.23
$\Delta H^\circ_{t,el}$	0.15	0.30	0.50	0.15	0.30	0.50
$\Delta H^\circ_{t,Ch}$	- 2.78	- 5.48	- 1.27	16.50	11.58	13.73
$\lim_{N\to 0} \log_{S\to W}$	0.1623	0.3516	0.4902	0.4260	0.9364	1.6804
		X = Cr_2O_7		X = WOw		
ΔG°_t	7.28	10.61	13.59	- 7.72	- 6.55	- 3.88
$\Delta G^\circ_{t,el}$	0.12	0.27	0.47	0.12	0.27	0.47
$\Delta G^\circ_{t,Ch}$	7.16	10.34	13.12	- 7.84	- 6.82	- 4.35
ΔS°_t	28.95	25.90	25.09	-56.5	-33.5	-27.5
$\Delta S^\circ_{t,el}$	0.92	1.91	3.25	0.92	1.91	3.25
$\Delta S^\circ_{t,Ch}$	29.87	28. 27.81 55	28.34	-55.58	-24.25	-31.59
ΔH°_t	15.9	18.33	21.06	-24.56	-16.53	-12.06
$\Delta H^\circ_{t,el}$	0.15	0.30	0.50	0.15	0.30	0.50
$\Delta H^\circ_{t,Ch}$	16.05	18.63	21.56	-24.41	-16.23	-11.56
$\lim_{N\to 0} \log_{S\to W}$	1.2746	1.8594	2.3801	- 1.3388	- 1.1731	- 0.6728

* Uncertainties in $\Delta G^\circ_t = \pm 5$J ; in $\Delta H^\circ = \pm 6$J ; in $\Delta S^\circ = \pm 3$J

are recorded in Table 3 .

It is evident from Table-2 that the standard Gibbs free energy changes for the electrode reactions increase with an increase in the dioxane content in the solvent mixture. The standard enthalpy and entropy changes are all negative, but the solvent effect on the magnitude of these quantities appears to be irregular. The difference in magnitude of the ΔH° and ΔS° values may be due to some structural effects. These effects can arise from either the combined effect of the solvent properties and solvation properties of the ions or the latter property alone in the different solvent mixtures. However, the solvent effect on the standard potentials of the electrodes can be examined from the related quantities of Gibbs free energy of transfer of the X^{2-} ions from water to the solvent concerned, since this is an important index of the differences in interactions of the ion and the solvent molecules in the two different media.

A perusal of Table-3 shows that the ΔG_t° value for the SO_4^{2-} and $Cr_2O_7^{2-}$ ions appears to be positive and becomes increasingly positive as the proportion of dioxane increases, wheras the ΔG_t° value for the WO_4^{2-} ion is negative and increases with increase of the dioxane content in the mixture. The positive values of ΔG_t° signify that the transfer of the SO_4^{2-}, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions from water to water + dioxane solvents is not favourable. Thus, these ions appear to be in lower Gibbs energy state and hence, more strongly stabilized in water than in water + dioxane solvents. The negative ΔG_t° value indicates that the WO_4^{2-} ion is in a lower Gibbs energy state in the mixed solvents than in water, and therfore, the transfer process is favourable.

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 entropy gain. The positive values of ΔS_t° and ΔH_t° of the CrO_4^{2-} and $Cr_2O_7^{2-}$ ions and the negative values for the SO_4^{2-} and WO_4^{2-} ions substantiate the view.

As the chemical contribution to the Gibbs energy of transfer of an ion in solution is attributed to the solvation of ions, $\Delta G_{t,ch}^\circ$ of the SO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$ and WO_4^{2-} ions, should reflect the solvating capacities of the solvent concerned and water towards these ions. The positive values of $\Delta G_{t,ch}^\circ$ for the SO_4^{2-}, CrO_4^{2-} and $Cr_2O_7^{2-}$ of ions (Table 3) thus suggest that mixed solvents possess a smaller solvating capacity towards the ion concerned than water, and the solvating capacity decreases as the dioxane content in water increases. However, the negative $\Delta G_{t,ch}^\circ$ values for the WO_4^{2-} ion suggest a stronger affinity of the ion towards mixed solvent than water.

The values of the primary medium effect, which is represented by

$$\lim_{N \to 0} (\log_{S/W}) = [(E^\circ_N)_W - (E^\circ_N)_S]/2.3026\ (RT/2F) \quad (7)$$

in various water + dioxane mixtures at 25°C are recorded in Table-3. . The sign and magnitude of this effect could give us an insight into the stabilization of the SO_4^{2-}, CrO_4^{2-} $Cr_2O_7^{2-}$ and WO_4^{2-} ions in the solvent concerned. The positive and increasing magnitude of this quantity for the SO_4^{2-} CrO_4^{2-} and $Cr_2O_7^{2-}$ ions suggests that the escaping tendency of the ions is greater in water dioxane mixtures than in the aqueous medium. This is consistent with the conclusions based on the fact that the SO_4^{2-}, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions are more strongly stabilized in water than in mixed media. But the reverse is the case with the WO_4^{2-} ion where the primary medium effect values appear to be negative.

TABLE 4

SOLUBILITY PRODUCT CONSTANTS ON THE MOLAR SCALE ($K^c_{SO_4}$) OF Ag_2X AND Ag_3Y (X = SO_4, CrO_4, Cr_2O_7 or WO_4 & Y = PO_4 or AsO_4) IN WATER + DIOXANE MIXTURES AT 25°C

	Water % dioxane		
	10	20	30
X = SO_4 10^6 K^c_{so}	0.97	0.48	0.25
X = CrO_4 10^{13} K^c_{so}	23.45	5.51	0.72
X = Cr_2O_7 10^9 K^c_{so}	1.55	0.31	0.07
X = WO_4 10^{11} K^c_{so}	4.66	2.4	0.55
Y = PO_4 10^{19} K^c_{so}	10.54	0.34	0.18
Y = ASO_4 10^{21} K^c_{so}	22.35	1.22	0.11

As before(2), the thermodynamic solubility products, K°_{so} of Ag_2 x (X is SO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$ or WO_4^{2-}) and Ag_3Y (Y is PO_4^{3-} or AsO_4^{3-}) in water + dioxane mixtures have been calculated at different temperatures from the values of the standard potentials by means of the equation

$$\ln K^\circ_{so}\ (Ag_2X) = [E^\circ\ (Ag\text{-}Ag_2X) - E^\circ\ (Ag\text{-}Ag^+)]\ (2F/RT)$$

and

$$\ln K^\circ_{so}\ (Ag_3Y) = [E^\circ\ (Ag\text{-}Ag_3Y) - E^\circ\ (Ag\text{-}Ag^+)]\ (3F/RT) \quad \ldots 8$$

TABLE 5

CONSTANTS OF EQUATION (9) FOR MOLAL (m) SCALE IN DIOXANE + WATER MIXTURES FOR DIFFERENT SILVER SALTS

	Water % dioxane		
	10	20	30
SO_4 A	-1429.0157	-1148.2246	-1177.7334
10^3.B	-1224.3743	-2474.6183	-2657.2572
σ	0.047	0.037	0.038
CrO_4 A	-4117.4458	-3727.2026	-3688.4783
10^3.B	2178.4297	249.5784	748.0311
σ	0.134	.121	0.124
Cr_2O_7 A	-2267.5695	-2294.7436	-2288.2417
10^3.B	1216.6973	-1816.8162	-2501.2899
σ	0.073	0.075	0.075
WO_4 A	-922.33892	-1551.8629	-2546.4102
10^3.B	-7194.6956	-5489.2326	-5378.6199
σ	0.030	0.054	0.050
PO_4 A	-1642.6492	- 150.8425	- 6.0501
10 .B	-1246.6675	-1893.267	-1970.2814
σ	0.053	0.005	0.038
AsO_4 A	-2912.3889	175.60751	-2713.8745
10^2.B	- 992.9205	-2150.0976	-1282.2477
σ	0.097	0.006	0.089

E°_S 's are the standard molar potentials of the Ag, Ag_2X, X^{2-},Ag,Ag_3Y, Y^{3} and $Ag\text{-}Ag^{+}$ electrodes obtained in the present study or reported elesewhere (2,3,9) are used in the calculation. The values for K°_{so} (on the molar scale K^c_{so}) are presented in Table 4 for 25°C only. The solubility product data in any temperature were fitted by least-squares to the equation(2)

$$\text{Log } K^c_{so} (Ag_2 X \text{ or } Ag_3 Y) = A/T + B \qquad \text{------(9)}$$

Where T is any temperature in degree Kelvin and A and B are the constants. These constants are shown in Table-5 along with the values of σ , the standard deviation of the least squares fit . the correlation coefficient for these relations is 0.998 and 0.999 for Ag_2X and Ag_3Y.

As observed in Table-4, the solubility of the silver salts decreases with increase in dioxane content of the mixed solvents. This is in agreement with the fact that the solubility of the salts decreases with decrease in dielectric constant of the solvents concerned the relative solubilities of these salts in any solvent is in the order : $Ag_2SO_4 > Ag_2Cr_2O_7 > Ag_2WO_4 > Ag_2CrO_4 > Ag_3PO_4 > Ag_3AsO_4$.

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