

THERMODYNAMICS OF SILVER–SILVER BROMATE, SILVER–SILVER IODATE, SILVER–SILVER SULPHATE, SILVER–SILVER CHROMATE AND SILVER–SILVER DICHROMATE ELECTRODES IN WATER + UREA MIXTURES AND RELATED THERMODYNAMIC SOLUBILITY PRODUCTS

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ABSTRACT

The standard potentials of the silver–silver bromate, silver–silver iodate, silver–silver sulphate, silver–silver chromate and silver–silver dichromate electrodes in four different compositions of water+urea mixtures at four different temperatures from 5 to 35°C have been determined from EMF studies of the cell: $\text{Ag(s), AgCl(s), KCl(c) // K}_x\text{Z(c/x), Ag}_x\text{Z(s), Ag(s)}$ where x is 1 or 2, and Z is BrO_3 , IO_3 , SO_4 , CrO_4 or Cr_2O_7 . These values have been used to evaluate the transfer thermodynamic quantities accompanying the transfer of 1 g-ion of BrO_3^- , IO_3^- , SO_4^{2-} , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ from the standard state in water to the standard state in water+urea mixtures. From the standard electrode potential values, the thermodynamic solubility products of Ag_xZ have also been computed in these solvents.

INTRODUCTION

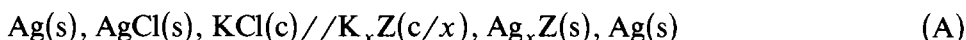
In continuation of a study on the standard potentials of the electrodes of the first kind and second kind in aqueous, non-aqueous and mixed solvent systems [1–11], we now report the results of a determination of the standard potentials of the silver–silver bromate, silver–silver iodate, silver–silver sulphate, silver–silver chromate and silver–silver dichromate electrodes and associated thermodynamic parameters for the electrode reactions in different compositions of water + urea mixtures. During the course of these studies, besides obtaining the transfer thermodynamic quantities for the process, Z^{x-} (in water) \rightarrow Z^{x-} (in water + urea), the thermodynamic solubility products of Ag_xZ have been evaluated in these solvents.

EXPERIMENTAL

The preparation of the solvents and the electrodes has been described earlier [5]. Potassium salts were the same samples as those used in a previous

study [11]. Stock solutions of various potassium salts were prepared by dissolving the appropriate weighed amounts of the potassium salts in known volumes of water + urea mixtures of various compositions. Solutions for EMF measurements were prepared from stock solutions by the double-dilution method. Stock solvents as well as the solutions were preserved at low temperatures ($\sim 5^\circ\text{C}$).

Preparations of the cell solutions, setting up of the cells, EMF and conductance measurements were essentially similar to the procedures described earlier [4]. All measurements were made over water baths at the required temperature with a precision of $\pm 0.1^\circ\text{C}$. Constancy of the EMF readings to ± 0.2 mV for 1 h was considered the criterion of equilibrium. As previously, the study of cell (A) with a liquid junction was made.



RESULTS AND DISCUSSION

The standard molar potentials, E_c^0 , were obtained by the method of extrapolating [1] the auxiliary function, E_c^0 , given by [1,3]

$$\begin{aligned} E_c^0 &= E + E_{\text{Ag,AgCl}}^0 + (RT/F) \ln([\text{Z}^-] \gamma_{\text{Z}^-} / [\text{Cl}^-] \gamma_{\text{Cl}^-}) - E_j \\ &= E + E_{\text{Ag,AgCl}}^0 - E_j \\ &= E_{\text{Ag,AgZ}}^0 + f(c) \end{aligned} \quad (1)$$

for the silver–silver bromate and silver–silver iodate electrodes and

$$\begin{aligned} E_c^0 &= E - \frac{1}{2}k(\log 2c) - \frac{1}{2}k(4A\sqrt{3c}/2/1 + \sqrt{3c}/2) - (2A\sqrt{c}/1 + \sqrt{c}) \\ &\quad + E_{\text{Ag,AgCl}}^0 - E_j = E_{\text{Ag,Ag}_2\text{Z}}^0 + bc \end{aligned} \quad (2)$$

for the silver–silver sulphate, silver–silver chromate and silver–silver dichromate, to the molarity, $c=0$. In the foregoing equations, $E_{\text{Ag,AgCl}}^0$ is the standard potential of the silver–silver chloride electrode, A is the Debye–Hückel constant, and is known over the temperature range under investigation for various water + urea mixtures [12], E is the observed EMF of the cell (A), k is $2.3026(RT/F)$, E_j is the liquid-junction potential, and b is $\frac{1}{2}k[2\beta_{\text{Cl}^-} - (3/2)\beta_{\text{Z}^{2-}}]$ in eqn. (2), where β is the usual constant in the Debye–Hückel expression for the activity coefficient, i.e., $-\log \gamma_i = Az_i^2\sqrt{\mu}/1 + \sqrt{\mu} - \beta_i\mu$, where i is Cl^- , SO_4^{2-} , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$.

As before [1], the values of the liquid-junction potential, E_j , were calculated. It is found that E_j varied in the ranges 0.1–0.3 and 0.1–0.6 mV for the silver–silver bromate and silver–silver iodate, and silver–silver sulphate, silver–silver chromate and silver–silver dichromate electrodes, respectively, in all solvents for all temperatures. The values of $E_{\text{Ag- AgCl}}^0$ (molar

TABLE 1

Constants of eqn. (3) in water + urea mixtures

Mass % urea	Z	a	-10^3b	10^7c
11.52	BrO ₃	0.5597	0.9375	2.5
	IO ₃	0.3834	1.4108	-27.5
	SO ₄	0.6169	1.9633	-10.0
	CrO ₄	0.4995	0.8275	-37.5
	Cr ₂ O ₇	0.5867	1.6117	65.0
20.31	BrO ₃	0.5687	0.5708	12.5
	IO ₃	0.3928	1.4142	22.5
	SO ₄	0.6305	1.6875	52.5
	CrO ₄	0.5174	0.7133	-30.0
	Cr ₂ O ₇	0.6017	1.5525	47.5
29.64	BrO ₃	0.5776	0.5340	2.5
	IO ₃	0.4063	1.3425	-2.5
	SO ₄	0.6376	1.7817	5.0
	CrO ₄	0.5304	0.69	-10.0
	Cr ₂ O ₇	0.6160	1.6717	35.0
36.83	BrO ₃	0.5817	0.4525	7.5
	IO ₃	0.4149	1.3408	2.5
	SO ₄	0.6457	1.705	15.0
	CrO ₄	0.5443	0.6683	-55.0
	Cr ₂ O ₇	0.6246	1.5525	17.5

scale), needed for the calculation of E_c^0 in eqns. (1) and (2) at different temperatures in various compositions of water + urea mixtures, are taken from the literature [12].

By following the usual relations [1,3], standard potentials on the molal (E_m^0) and the 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 ($^{\circ}\text{C}$)

$$E_m^0 = a + b(t - 25) + c(t - 25)^2 \quad (3)$$

where a , b and c are empirical constants and are given in Table 1 for molal scale in various compositions of water + urea mixtures. The average deviation between the experimental values and those calculated from eqn. (3) is within ± 0.2 mV. The E^0 values at 25°C are listed in Table 2 along with those available in water [1,3].

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

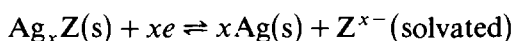


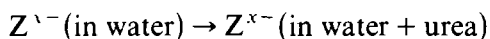
TABLE 2

E^0 values for the $\text{Ag}(s)$, $\text{Ag}_x\text{Z}(s)$, Z^{x-} electrodes on different scales in water and water + urea mixtures at 25°C

E^0	Z	Mass % urea				
		0	11.52	20.31	29.64	36.83
E_c^0	BrO_3	0.5260 ^a	0.5611	0.5713	0.5815	0.5920
	IO_3	0.3288 ^a	0.3848	0.3955	0.4102	0.4198
	SO_4	0.6036 ^b	0.6182	0.6334	0.6415	0.6507
	CrO_4	0.4491 ^b	0.5008	0.5200	0.5343	0.5494
	Cr_2O_7	0.5574 ^b	0.5881	0.6043	0.6199	0.6295
E_m^0	BrO_3	0.5262 ^a	0.5597	0.5687	0.5776	0.5871
	IO_3	0.3290 ^a	0.3834	0.3928	0.4063	0.4149
	SO_4	0.6037 ^b	0.6169	0.6305	0.6376	0.6457
	CrO_4	0.4492 ^b	0.4995	0.5174	0.5304	0.5443
	Cr_2O_7	0.5575 ^b	0.5867	0.6017	0.6160	0.6246
E_N^0	BrO_3	0.3198 ^a	0.3576	0.3702	0.3832	0.3961
	IO_3	0.1226 ^a	0.1813	0.1944	0.2119	0.2239
	SO_4	0.3996 ^b	0.4147	0.4321	0.4432	0.4548
	CrO_4	0.2428 ^b	0.2974	0.3189	0.3360	0.3535
	Cr_2O_7	0.3511 ^b	0.3846	0.4032	0.4216	0.4334

^a From refs. 1 and 3. ^b From ref. 11.

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



have been evaluated at different temperatures for various solvents. The transfer thermodynamic quantities on a mole-fraction basis at 25°C are shown in Table 3 along with the standard thermodynamic quantities on the molal scale.

An inspection of Table 2 shows that the values of the standard potentials of the $\text{Ag}-\text{Ag}_x\text{Z}$ electrodes are higher in various compositions of water + urea mixtures and increase with the increase in urea content in water lending support to the linear correlation between E^0 and the reciprocal of the dielectric constant of the solvent concerned. The observed increase in the E^0 values of these electrodes with the increase in dielectric constant of the water + urea mixtures as the proportion of urea increases, is in agreement with the electrostatic charging (Born) effect of the media. The higher values of E^0 in various compositions of water + urea mixtures than in water may also be explained by the higher basicity of the water + urea mixtures which decreases the Gibbs free energy of the electrode reaction, by decreasing the free energy of Z^{x-} (solvated), where Z is SO_4 , CrO_4 and Cr_2O_7 and x is 2, in these solvents.

TABLE 3

Values of ΔG_m^0 , ΔH_m^0 and ΔS_m^0 for the electrode reaction and ΔG_t^0 , ΔH_t^0 and ΔS_t^0 for the transfer process in water+urea mixtures at 25°C (ΔG^0 and ΔH^0 values in kJ mol⁻¹, ΔS^0 values in J K⁻¹mol⁻¹)

Z	Parameter ^a	Mass % urea				
		0	11.52	20.31	29.64	36.83
BrO ₃	$-\Delta G_m^0$	50.75	54.01	54.87	55.73	56.65
	$-\Delta H_m^0$	59.13	80.96	71.29	71.09	69.66
	$-\Delta S_m^0$	28.12	90.46	55.08	51.55	43.66
	$-\Delta G_t^0$		3.65	4.86	6.12	7.36
	$-\Delta H_t^0$		21.71	12.06	11.87	10.48
	$-\Delta S_t^0$		60.50	24.05	19.23	10.38
	$\lim_{N \rightarrow 0} \log(^s\gamma_w)$		-0.639	-0.852	-1.072	-1.289
IO ₃	$-\Delta G_m^0$	31.72	36.99	37.90	39.20	40.03
	$-\Delta H_m^0$	40.74	77.56	78.57	77.81	78.59
	$-\Delta S_m^0$	30.27	136.13	136.46	129.54	129.38
	$-\Delta G_t^0$		5.66	7.41	8.62	9.77
	$-\Delta H_t^0$		36.72	37.73	37.01	37.49
	$-\Delta S_t^0$		104.12	103.28	95.2	92.95
	$\lim_{N \rightarrow 0} \log(^s\gamma_w)$		-0.992	-1.214	-1.509	-1.712
SO ₄	$-\Delta G_m^0$	117.22	119.05	121.68	123.05	124.61
	$-\Delta H_m^0$	186.34	231.96	218.72	225.5	222.66
	$-\Delta S_m^0$	231.97	378.88	325.66	343.84	329.04
	$-\Delta G_t^0$		2.66	6.02	8.16	10.4
	$-\Delta H_t^0$		45.86	32.35	39.15	36.39
	$-\Delta S_t^0$		144.97	88.34	103.96	87.22
	$\lim_{N \rightarrow 0} \log(^s\gamma_w)$		-0.4665	-1.0548	-1.4301	-1.822
CrO ₄	$-\Delta G_m^0$	86.69	96.39	99.85	102.36	105.04
	$-\Delta H_m^0$	151.75	143.98	140.87	142.04	143.47
	$-\Delta S_m^0$	219.3	159.69	137.66	133.16	129.03
	$-\Delta G_t^0$		10.54	14.67	17.99	21.36
	$-\Delta H_t^0$		6.85	9.89	8.71	7.29
	$-\Delta S_t^0$		58.38	82.5	89.58	96.19
	$\lim_{N \rightarrow 0} \log(^s\gamma_w)$		-1.846	-2.573	-3.151	-3.743
Cr ₂ O ₇	$-\Delta G_m^0$	107.50	113.22	116.12	118.88	120.54
	$-\Delta H_m^0$	188.01	205.91	205.4	215.02	209.82
	$-\Delta S_m^0$	269.85	311.04	299.6	322.61	299.61
	$-\Delta G_t^0$		6.46	10.05	13.61	15.88
	$-\Delta H_t^0$		17.77	17.34	26.98	22.34
	$-\Delta S_t^0$		37.94	24.44	44.86	21.64
	$\lim_{N \rightarrow 0} \log(^s\gamma_w)$		-1.133	-1.761	-2.383	-2.782

^a Uncertainties in the values of ΔG^0 , ΔH^0 and ΔS^0 at 25°C are of the order of ± 0.03 and ± 0.5 kJ mol⁻¹ and ± 2 J K⁻¹ mol⁻¹, respectively.

A perusal of Table 2 shows that the E^0 values of the Ag, Ag_xZ , Z^{x-} electrodes at 25°C follow the order: $\text{SO}_4 > \text{Cr}_2\text{O}_7 > \text{BrO}_3 > \text{CrO}_4 > \text{IO}_3$ in both water and water + urea mixtures, where SO_4 , Cr_2O_7 , etc., are the anion of the corresponding electrode material to which the electrode is reversible and these represent corresponding electrodes of the second kind. It can be concluded that the strength of solvation of the anion (irrespective of its size) to which the electrode is reversible (since the cation of the electrode material is the same) is the deciding factor in explaining the relative values of the standard potentials of the electrodes of the second kind.

It is known that the Gibbs free energy of transfer is an important index of the differences in interactions of the ions and solvent molecules in the two different media. As can be seen from Table 3 the values of ΔG_t^0 for the transfer of Z^{x-} ions from water to water + urea mixtures appear to be negative and become increasingly negative with increasing urea content in water + urea mixtures. The negative values of ΔG_t^0 indicate that the transfer of Z^{x-} ions from water to water + urea mixtures is favourable. Thus, Z^{x-} ions appear to be in a lower Gibbs energy state and, hence, more strongly stabilised in water + urea mixtures. It is known that all structure-forming processes, including solvation of ions, are exothermic and accompanied by a decrease in entropy, whereas the structure breaking processes, including desolvation of ions, are endothermic and accompanied by entropy gain. The negative values of ΔH_t^0 and ΔS_t^0 for BrO_3^- , IO_3^- , SO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ and the positive values of ΔH_t^0 and ΔS_t^0 for CrO_4^{2-} ion in the mixed solvents substantiate this view.

The primary medium effect which results from a difference of the ion-solvent interactions at infinite dilution in each solvent can be represented by

$$\lim_{N \rightarrow 0} (\log {}^s\gamma_w) = x \left[(E_N^0)_w - (E_N^0)_s \right] / 2.3026(RT/F)$$

TABLE 4

Solubility product constants on the molar scale (K_{so}^c) of Ag_xZ in water and water + urea mixtures at 25°C

	Mass % urea				
	0	11.52	20.31	29.64	36.83
$\text{Z} = \text{BrO}_3$					
$10^5 K_{so}^c$	2.40	10.2	10.3	13.6	14.3
$\text{Z} = \text{IO}_3$					
$10^8 K_{so}^c$	1.096	10.73	10.95	17.25	17.52
$\text{Z} = \text{SO}_4$					
$10^6 K_{so}^c$	0.34	0.89	1.32	1.96	1.97
$\text{Z} = \text{CrO}_4$					
$10^{11} K_{so}^c$	0.14	9.84	19.52	47.04	73.88
$\text{Z} = \text{Cr}_2\text{O}_7$					
$10^8 K_{so}^c$	0.69	8.59	13.7	36.5	37.7

where the limit term indicates the primary medium effect and $x = 1$ for BrO_3 or IO_3 and $x = 2$ for SO_4 , CrO_4 or Cr_2O_7 ions. As the magnitude of this effect indicates the stabilisation of the ion in the solvent concerned, the resulting negative magnitude of this quantity (Table 3) suggests that the escaping tendency of the ions is lower in water + urea mixtures than in pure water. This is consistent with the conclusions based on the fact that the Z^{x-}

TABLE 5

Constants of eqn. (5) for the molar (c) and molal (m) scales in water + urea mixtures for different silver salts

	q	Wt% urea			
		11.52	20.31	29.64	36.83
BrO₃					
A	c	-1447.3761	-1928.9661	-2271.2833	-2049.8242
10^3B		872.471	2493.96	3756.3812	3036.2997
σ		0.047	0.062	0.074	0.067
A	m	-1470.2105	-1955.1526	-2304.3433	-2087.2757
10^3B		926.1043	2536.2116	3801.645	3069.1217
σ		0.048	0.063	0.075	0.065
IO₃					
A	c	-1668.9855	-1541.5161	-1850.6464	-1592.2064
10^3B		-1367.884	-1777.5977	-563.74	-1410.288
σ		0.054	0.050	0.060	0.052
A	m	-1694.9874	-1568.1828	-1883.727	-1629.6579
10^3B		-1304.0327	-1732.4257	-518.5707	-1366.8287
σ		0.055	0.051	0.061	0.053
SO₄					
A	c	737.3833	286.76051	-179.8338	281.95908
10^3B		-8515.1257	-6827.647	-5091.906	-6640.9857
σ		0.024	0.009	0.006	0.009
A	m	711.3814	260.57408	214.22714	241.84097
10^3B		-8452.0012	-6784.142	-5051.5212	-6588.862
σ		0.023	0.009	0.007	0.008
CrO₄					
A	c	-3951.3814	-4088.228	-4587.3252	-4063.4848
10^3B		3238.8217	4010.0633	6061.478	4491.5509
σ		0.093	0.098	0.095	0.098
A	m	-3977.5679	-4116.8966	-4621.7187	-4100.9352
10^3B		3302.3269	4062.0524	6111.0344	4535.2499
σ		0.093	0.099	0.096	0.099
Cr₂O₇					
A	c	-411.57733	-489.53136	-642.40683	-384.52325
10^3B		-5650.978	-5189.5312	-4268.253	-5121.6996
σ		0.013	0.016	0.021	0.012
A	m	-437.76376	-515.53326	-676.80017	-393.23906
10^3B		-5587.473	-5146.4067	-4218.697	-5176.6589
σ		0.014	0.014	0.022	0.013

ions are more strongly stabilised in water + urea mixtures than in aqueous medium.

The thermodynamic solubility product, K_{so}^0 , of Ag_xZ ($Z = BrO_3, IO_3$ and $x = 1$; or $Z = SO_4, CrO_4, Cr_2O_7$ and $x = 2$) in water + urea mixtures have been calculated at different temperatures from the values of standard potentials by means of the equation

$$\ln K_{so}^0(Ag_xZ) = [E_c^0(Ag-Ag_xZ) - E_c^0(Ag-Ag^+)] xF/RT \quad (4)$$

where $E_c^0(Ag-Ag_xZ)$ is the standard molar potential of the Ag, Ag_xZ, Z^{x-} electrode and $E_c^0(Ag-Ag^+)$ is that of the silver electrode obtained from the literature [5]. The values for K_{so}^0 on the molar (K_{so}^c) scale are shown in Table 4 at 25°C only, along with those available in water for the sake of comparison. The values of K_{so}^0 on the molal scale (K_{so}^m) were calculated from K_{so}^c/ρ^2 , where ρ is the density of the mixed solvent. The solubility product data in any solvent were fitted by the method of least-squares to the equation

$$\log K_{so}^q(Ag_xZ) = A/T + B \quad (5)$$

where q is c or m and T (K) is any temperature. The constants A and B in eqn. (5) 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 0.997.

An inspection of Table 5 shows that these silver salts are more soluble in water + urea mixtures than in water and the solubility increases with increasing urea content in the mixed solvent. The observed increase in K_{so}^0 values with the increase in dielectric constant of the mixed solvents as the proportion of urea increases is in agreement with the electrostatic charging effect of the media.

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