

**Note****THERMODYNAMICS OF THE SILVER–SILVER ION ELECTRODE AND THERMODYNAMIC SOLUBILITY PRODUCT CONSTANTS OF SILVER HALIDES AND PSEUDO-HALIDES IN UREA–WATER MIXTURES**

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Recently the energetics of ion-solvation in aquo-organic solvents have received increased attention. These are of much importance as they constitute the basis of theories of ion–solvent interactions and provide an insight into the structural aspects of the solvents. Several workers [1–22] have presented studies on the behaviour of electrolytes in aqueous organic solvent mixtures employing electromotive force measurements of galvanic cells using the silver–silver halide electrodes in conjunction with a reference electrode. No work seems to have been done on the study of the behaviour of the  $\text{Ag}/\text{Ag}^+$  electrode in binary water–organic solvent mixtures. However, the standard potentials of this electrode are known in water [23] and formamide [24]. This paper reports the results obtained for the potentiometric measurements of cells involving the  $\text{Ag}/\text{Ag}^+$  electrode in conjunction with the  $\text{Ag}/\text{AgCl}$  electrode in urea + water solvents at different temperatures ranging from 5 to 35°C, and the transfer thermodynamic quantities accompanying the process  $\text{Ag}^+$  (in water)  $\rightarrow$   $\text{Ag}^+$  (in urea + water)

**EXPERIMENTAL**

Sodium nitrate, sodium chloride, silver nitrate and urea were of analytical grade or guaranteed reagents and used without further purification. Solvents of various compositions were made up by weight in conductivity water. The stock solvents as well as sodium nitrate, sodium chloride and silver nitrate solutions were kept at a low temperature ( $\sim 5^\circ\text{C}$ ) [17]. Equimolar solutions of sodium nitrate, sodium chloride and silver nitrate were prepared from the stock solutions by double dilution method.

Silver–silver chloride electrodes were prepared according to the method described in the literature [25]. Silver electrodes were of thermal electrolytic

TABLE 1

Standard molar potentials ( $E_c^0$  in abs. volts) for the Ag(s)-Ag<sup>+</sup> electrodes in urea-water mixtures from 5 to 35°C

Wt. % urea	$t(^{\circ}\text{C})$						
	5	10	15	20	25	30	35
0	0.8186	0.8138	0.8089	0.8031	0.7991	0.7950	0.7891
11.52	0.8194	0.8136	0.8075	0.8021	0.7971	0.7919	0.7856
20.31	0.8288	0.8230	0.8172	0.8122	0.8073	0.8018	0.7960
29.64	0.8359	0.8298	0.8234	0.8165	0.8103		
36.83	0.8404	0.8353	0.8303	0.8248	0.8195	0.8136	0.8084

type and freshly prepared for each run. The cell vessels were of an all-glass type as described earlier [19].

The general experimental details, such as preparation of the cell solutions, setting up of the cells, EMF and conductance measurements, were essentially similar to those described earlier [19,21]. All measurements were made in water baths maintained at appropriate temperatures within  $\pm 0.1^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

The EMF,  $E$ , of cell (A)

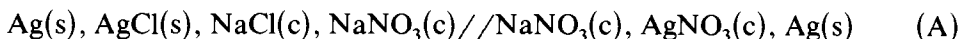


TABLE 2

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

Wt.% urea	x	A	B	C	$10^3D$
11.52	c	63.94461	-2.444104	0.430336	-1.4729
	m	94.31183	-3.622856	0.637883	-2.18142
	N	99.901957	-3.831718	0.674208	-2.29902
20.31	c	48.09698	-1.828624	0.32089	-1.09534
	m	48.010389	-1.819383	0.320104	-1.09186
	N	43.470444	-1.643898	0.28909	-0.986
29.64	c	-62.000492	2.471987	-0.436274	1.505233
	m	-61.11766	2.408676	-0.4240195	1.4416
	N	-62.008654	2.471349	-0.436274	1.505233
36.83	c	-62.591	2.4709608	-0.4352061	1.48478
	m	-67.2179	2.651346	-0.467006	1.59412
	N	-94.2851	3.70337	-0.652432	2.2287

TABLE 3

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

	Wt. % urea			
	11.52	20.31	29.64	36.83
$E_c^0(\text{V})$	0.7975	0.8072	0.8103	0.8189
$E_m^0(\text{V})$	0.7952	0.8046	0.8059	0.8139
$E_N^0(\text{V})$	0.5940	0.6061	0.6120	0.6227
$-10^{-3} \Delta G_m^0 (\text{J mole}^{-1})$	76.73	77.64	77.76	78.53
$-10^{-3} \Delta H_m^0 (\text{J mole}^{-1})$	104.0	106.2	118.7	112.8
$-\Delta S_m^0 (\text{J mole}^{-1} \text{K}^{-1})$	93.0	97.0	137.0	114.0

can be expressed as

$$E = E_{\text{Ag,Ag}^+}^0 - E_{\text{Ag,AgCl}}^0 + (RT/F) \ln[Ag^+][Cl^-] \gamma_{\pm}^2 + E_j \quad (1)$$

where the symbols have their usual meaning

Using the molar concentrations of  $\text{AgNO}_3$  and  $\text{NaCl}$  solutions and expressing the mean molar activity coefficients by the Debye-Hückel expressions, eqn. (1) becomes

$$E = E_{\text{Ag,Ag}^+}^0 - E_{\text{Ag,AgCl}}^0 + 2k \log C - \frac{2kA(2C)^{1/2}}{1 + (2C)^{1/2}} + 2k\beta_{\pm} C + E_j$$

TABLE 4

Transfer thermodynamic quantities and primary medium effect (mole fraction scale) in different urea-water mixtures at 25°C

	Wt. % urea			
	11.52	20.31	29.64	36.83
$-\Delta G_t^0 (\text{J mole}^{-1})$	106.14	1273.69	1842.99	3792.11
$-\Delta G_{t,\text{el}}^0 (\text{J mole}^{-1})$	44.66	74.56	100.27	117.06
$-\Delta G_{t,\text{ch}}^0 (\text{J mole}^{-1})$	61.48	1199.13	1742.71	3675.05
$\Delta S_t^0 (\text{J mole}^{-1} \text{K}^{-1})$	8.0	2.0	-17.0	-19.0
$\Delta S_{t,\text{el}}^0 (\text{J mole}^{-1} \text{K}^{-1})$	0.27	0.45	0.66	0.75
$\Delta S_{t,\text{ch}}^0 (\text{J mole}^{-1} \text{K}^{-1})$	8.00	1.09	-17.77	-19.37
$\Delta H_t^0 (\text{J mole}^{-1})$	2363.0	-816.0	-6958.0	-8429.0
$\Delta H_{t,\text{el}}^0 (\text{J mole}^{-1})$	35.0	60.0	98.0	107.0
$\Delta H_{t,\text{ch}}^0 (\text{J mole}^{-1})$	2328.0	-876.0	-7055.0	-8536.0
$\lim_{N \rightarrow 0} \log^s \gamma_w$	-0.0183	-0.2228	-0.3225	-0.5034

TABLE 5

Solubility product constants, on the molar ( $K_s^c$ ) and molal ( $K_s^m$ ) scales of AgX (X = Cl, Br, I, N<sub>3</sub> or CNS) in urea – water mixtures at different temperatures

AgX	$t(^{\circ}\text{C})$						
	5	10	15	20	25	30	35
11.52 wt. % urea							
X = Cl							
$K_s^c \times 10^{10}$	1.356	2.264	3.623	5.678	8.647	13.295	20.833
$K_s^m \times 10^{10}$	1.265	2.119	3.399	5.341	8.175	12.612	19.851
X = Br							
$K_s^c \times 10^{12}$	0.234	0.455	0.850	1.508	2.615	4.569	8.054
$K_s^m \times 10^{12}$	0.220	0.418	0.798	1.419	2.472	4.444	7.652
X = I							
$K_s^c \times 10^{16}$	0.194	0.457	1.036	2.211	4.587	9.528	19.934
$K_s^m \times 10^{16}$	0.181	0.428	0.971	2.080	4.336	8.915	18.993
X = N <sub>3</sub>							
$K_s^c \times 10^9$	1.403	2.428	4.070	6.604	10.505	16.888	27.466
$K_s^m \times 10^9$	1.308	2.271	3.819	6.212	9.931	16.021	26.168
X = CNS							
$K_s^c \times 10^{12}$	0.359	0.742	1.473	2.777	6.246	9.554	18.026
$K_s^m \times 10^{12}$	0.335	0.694	1.382	2.612	5.905	9.064	17.174
20.31 wt. % urea							
X = Cl							
$K_s^c \times 10^{10}$	2.213	3.432	5.288	7.919	11.985	18.364	28.812
$K_s^m \times 10^{10}$	1.941	3.062	4.733	7.111	10.819	16.630	26.236
X = Br							
$K_s^c \times 10^{12}$	0.354	0.674	1.252	2.197	3.814	6.574	11.344
$K_s^m \times 10^{12}$	0.309	0.602	1.120	1.973	3.444	5.953	10.330
X = I							
$K_s^c \times 10^{16}$	0.291	0.686	1.556	3.298	6.875	14.079	28.727
$K_s^m \times 10^{16}$	0.255	0.612	1.390	2.961	6.222	12.749	26.157
X = N <sub>3</sub>							
$K_s^c \times 10^9$	2.343	3.874	6.263	9.772	15.146	23.474	36.291
$K_s^m \times 10^9$	2.055	3.456	5.606	8.777	13.672	21.255	33.042
X = CNS							
$K_s^c \times 10^{12}$	0.637	1.274	2.441	4.468	8.119	14.574	26.574
$K_s^m \times 10^{12}$	0.557	1.138	2.185	4.011	7.329	13.200	23.880
29.64 wt. % urea							
X = Cl							
$K_s^c \times 10^{10}$	2.745	4.589	7.530	12.374	19.860	30.384	43.894
$K_s^m \times 10^{10}$	2.318	3.889	6.408	10.575	17.060	26.212	38.054
X = Br							
$K_s^c \times 10^{12}$	0.510	0.987	1.865	3.407	6.352	11.894	17.559
$K_s^m \times 10^{12}$	0.431	0.837	1.587	2.996	5.456	9.397	15.223

TABLE 5 (continued)

AgX	<i>t</i> (°C)						
	5	10	15	20	25	30	35
<b>X = I</b>							
$K_s^c \times 10^{16}$	0.468	1.099	2.502	5.649	12.229	24.814	47.043
$K_s^m \times 10^{16}$	0.396	0.932	2.129	4.828	10.505	21.404	40.785
<b>X = N<sub>3</sub></b>							
$K_s^c \times 10^9$	3.084	5.310	8.892	15.045	24.445	38.176	55.962
$K_s^m \times 10^9$	2.605	4.501	7.567	12.860	20.997	32.931	48.516
<b>X = CNS</b>							
$K_s^c \times 10^{12}$	0.992	2.049	4.062	8.054	15.431	28.035	47.676
$K_s^m \times 10^{12}$	0.838	1.738	3.457	6.885	13.255	24.182	41.333
36.83 wt. % urea							
<b>X = Cl</b>							
$K_s^c \times 10^{10}$	3.324	5.203	8.235	12.896	20.229	30.865	44.916
$K_s^m \times 10^{10}$	2.696	4.237	8.111	10.597	20.323	30.881	44.936
<b>X = Br</b>							
$K_s^c \times 10^{12}$	0.658	1.192	2.200	3.916	6.973	12.036	19.660
$K_s^m \times 10^{12}$	0.534	0.971	1.801	3.217	5.836	9.994	16.417
<b>X = I</b>							
$K_s^c \times 10^{16}$	0.633	1.483	3.073	6.619	14.125	29.026	56.156
$K_s^m \times 10^{16}$	0.513	1.208	2.515	5.439	11.681	24.104	46.892
<b>X = N<sub>3</sub></b>							
$K_s^c \times 10^9$	3.496	5.646	9.294	15.104	24.637	39.057	58.992
$K_s^m \times 10^9$	2.841	4.599	7.607	12.410	20.372	32.431	49.263
<b>X = CNS</b>							
$K_s^c \times 10^{12}$	1.237	2.377	4.597	8.728	16.519	30.206	52.541
$K_s^m \times 10^{12}$	1.002	1.936	3.762	7.171	13.661	25.084	43.873

or

$$E_c^0 = E + E_{\text{Ag,AgCl}}^0 - 2k \log C + \frac{2kA(2C)^{1/2}}{1 + (2C)^{1/2}} - E_j = E_{\text{Ag,Ag}^+}^0 + bC \quad (2)$$

where  $k = 2.3026(RT/F)$  and  $b = 2k\beta_{\pm}$  (here  $\beta_{\pm}$  is the usual constant in the Debye-Hückel expression for the activity coefficient, i.e.,  $\log \gamma_i = -Az_i^2 \mu^{1/2} / 1 + \mu^{1/2} + \beta_i \mu$ , where  $i$  is  $\text{Ag}^+$  or  $\text{Cl}^-$ ).

The values of the liquid junction potentials,  $E_j$ , were calculated from Lewis and Sargent's equation [21] and vary in the range 0.1–0.2 mV at all temperatures in different solvents. Linear extrapolations of  $E_c^{0'}$  against  $C$  can be made to obtain values of  $E_{\text{Ag,Ag}^+}^0$ .

The values of  $E_{\text{Ag,AgCl}}^0$  (molar scale) needed for calculation of  $E_c^{0'}$  [eqn. (2)] at different temperatures in urea + water solvents were calculated using the density, etc., of the mixed solvent from the values on the molal scale available in the literature [17] and that of  $A$ , the Debye-Hückel constant,

were also taken from the literature [17]. The values of  $E_c^0$  obtained on extrapolating  $E_c^{0'}$  to  $C=0$  are listed in Table I. The average standard deviations in the values of  $E_c^0$  is  $\pm 0.4$  mV.

As usual (21,22), standard potentials on the molal ( $E_m^0$ ) and mole fraction

TABLE 6

Constants of eqn. (4) for molar (c) and molal (m) scales, in urea-water mixtures for different silver salts

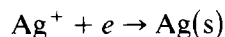
AgX $p$	Wt. % urea			
	11.52	20.31	29.64	36.83
X = Cl				
A c	-3388.3625	-3193.21806	-3557.3659	-3227.8324
B	2.31908	1.8115805	3.2397	2.130926
$\sigma$	0.056	0.053	0.059	0.054
A m	-3414.4198	-3238.4358	-3456.9672	-3264.3353
B	2.380822	1.919028	2.819517	2.1708104
$\sigma$	0.057	0.054	0.058	0.054
X = Br				
A c	-4377.3368	-4303.4905	-4374.4235	-4209.7279
B	3.117256	3.028729	3.461901	2.961936
$\sigma$	0.073	0.072	0.073	0.070
A m	-4430.1128	-4348.7078	-4407.2344	-4246.2309
B	3.179387	3.136161	3.50577	3.002335
$\sigma$	0.073	0.073	0.074	0.071
X = I				
A c	-5740.7416	-5688.5635	-5701.4851	-5557.7618
B	3.93685	3.93089	4.198171	3.79651
$\sigma$	0.096	0.095	0.095	0.093
A m	-5767.4245	-5733.7599	-5734.3063	-5594.2666
B	4.002295	4.03828	4.242361	3.836401
$\sigma$	0.096	0.096	0.096	0.093
X = N <sub>3</sub>				
A c	-3690.1000	-3398.0552	-3582.0049	-3504.7705
B	4.415784	3.590191	4.390632	4.143768
$\sigma$	0.062	0.057	0.060	0.063
A m	-3716.2120	-3443.2729	-3614.8159	-3538.9149
B	4.479063	3.697625	4.434801	4.178425
$\sigma$	0.062	0.064	0.061	0.059
X = CNS				
A c	-4848.2296	-4608.1187	-4789.0403	-4648.5498
B	5.004289	4.37966	5.240511	4.810867
$\sigma$	0.081	0.077	0.080	0.078
A m	-4874.3065	-4653.3364	-4821.8512	-4685.0528
B	5.067587	4.487094	5.28468	4.850752
$\sigma$	0.081	0.078	0.082	0.078

( $E_N^0$ ) scales were calculated from that on the molar scale ( $E_c^0$ ). The standard potentials ( $E^0$ ) on different scales at various temperatures for any solvent were fitted, by the method of least-squares, to an equation of the form [26]

$$E_x^0 = A + BT + CT \ln T + DT^2/2 \quad (3)$$

where  $x$  is  $c$ ,  $m$  or  $N$  and  $T$  is any temperature in kelvins. The constants  $A$ ,  $B$ ,  $C$  and  $D$  of eqn. (3) are shown in Table 2. The average deviation between the experimental values (Table 1) and the values calculated from eqn. (3) is within  $\pm 0.4$  mV. The  $E^0$  values at  $25^\circ\text{C}$  are listed in Table 3, along with those in water [23].

The standard thermodynamic quantities ( $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$ ) on the molal scale for the electrode reaction



at different temperatures in various solvents have been calculated by the usual relations [21]. These values for  $25^\circ\text{C}$  are included in Table 3.

As reported previously [21,22], the standard thermodynamic quantities,  $\Delta G_t^0$ ,  $\Delta S_t^0$  and  $\Delta H_t^0$ , for the transfer process



have been evaluated at different temperatures for various solvents. The values of these quantities at  $25^\circ\text{C}$  are presented in Table 4 which also includes the change in electrostatic Gibbs energy ( $\Delta G_{t,\text{el}}^0$ ), the electrostatic entropy ( $\Delta S_{t,\text{el}}^0$ ) and the electrostatic contribution for the change of enthalpy ( $\Delta H_{t,\text{el}}^0$ ). These values of the transfer quantities were obtained by the usual equations [21] on the mole fraction basis [21,22].

Inspection of Table 4 shows that as the proportion of urea increases, the  $\Delta G_t^0$  value for the  $\text{Ag}^+$  ion becomes increasingly negative. The negative value of  $\Delta G_t^0$  signifies that the transfer of the  $\text{Ag}^+$  ion from water to urea + water mixtures is increasingly favourable. Thus, the  $\text{Ag}^+$  ion appears to be in a lower Gibbs energy state and hence, more strongly stabilized in mixed solvents than in water. 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 decrease in values of  $\Delta S_t^0$  and  $\Delta H_t^0$  indicates that for a transfer process the amount of order created by the  $\text{Ag}^+$  ion in the mixed solvent is more.

Table 4 shows the primary medium effect values of the  $\text{Ag}^+$  ion in various urea + water mixtures at  $25^\circ\text{C}$ . Since the primary medium effect which is represented by [21]

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

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  $\text{Ag}^+$  ion is less in urea + water mixtures than in pure water. This is consistent with the conclusions based on the fact that the  $\text{Ag}^+$  ion is more strongly stabilized in mixed solvents than in water medium.

The thermodynamic solubility products,  $K_s^0$ , of silver halides and silver pseudo-halides in various compositions of urea + water mixtures have been calculated from the values of standard potentials by means of the equation

$$\ln K_s^0 = [E_{\text{Ag,AgX}}^0 - E_{\text{Ag,Ag}^+}^0] / (F/RT)$$

where  $E_{\text{Ag,AgX}}^0$  is the standard molar potential of  $\text{Ag,AgX}$  ( $X = \text{Cl, Br, I, N}_3$ , or  $\text{CNS}$ ) electrode and is obtained from the literature [17,21,22] over the temperature range under investigation. The values for  $K_s^0$  on the molarity ( $K_s^c$ ) and molality ( $K_s^m$ ) scales at the experimental temperatures are shown in Table 5. The data for  $K_s^m$  were calculated from  $K_s^c/\rho^2$ . The solubility product data were fitted by least-squares to an equation of the form [27]

$$\log K_s^p(\text{AgX}) = A/(T/K) + B \quad (4)$$

where  $p$  is  $c$  or  $m$ ,  $X$  is  $\text{Cl, Br, I, N}_3$  or  $\text{CNS}$ ,  $A$  and  $B$  are the empirical constants, and  $T$  is any temperature in kelvins. The constants  $A$  and  $B$  of eqn. (4) are reported in Table 6 along with the standard deviation,  $\sigma$ , for the precision of the least-squares fit; the correlation coefficient for the relations is within 1.00.

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