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STANDARD THERMODYNAMICS OF TRANSFER. II. SILVER AND SILVER SALT ELECTRODES IN ACETONE + WATER MIXTURES

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ABSTRACT

The standard thermodynamic quantities of transfer of Ag^+, X^-, Y^{2-} and Z^{3-} ions ($X = Cl, Br, I, N_3, CNS, IO_3, BrO_3$: $Y = SO_4, CrO_4, Cr_2O_7, WO_4$; $Z = PO_4, AsO_4$) in water +10, +20, +30 and +40 mass% acetone have been estimated. Thermodynamic solubility products of silver salts in these solvents have been calculated.

INTRODUCTION

In continuation of a study on the determination of the standard thermodynamic quantities of the Ag^+, X^-, Y^{2-} and Z^{3-} ions (X = Cl, Br, I, N_3, CNS, IO_3, BrO_3; Y = SO_4, CrO_4, Cr_2O_7, WO_4; Z = PO_4, AsO_4) in mixed solvent systems [1], we now report the similar thermodynamic quantities of these ions in water +10, +20, +30 and +40 mass% acetone at different temperatures ranging from 5 to 35°C. During the course of these studies, besides obtaining the transfer thermodynamic quantities for the process Ag^+, X^-, Y^{2-}, or Z^{3-} (in water) → Ag^+, X^-, Y^{2-} or Z^{3-} (in acetone + water) (X = Cl, Br, I, N_3, CNS, IO_3, BrO_3: Y = SO_4, CrO_4, Cr_2O_7, WO_4; $Z = PO_4$, AsO_4), the thermodynamic solubility products of AgX, Ag_2Y and Ag_3Z have been evaluated in these solvents.

As before [1], the study of cells with liquid-junction potentials

$$Ag(s), AgBr(s), KBr(c), KNO_3(c) \| KNO_3(c), AgNO_3(c), Ag(s) \qquad (A)$$

$$Ag(s), AgBr(s), NaBr(c) \| NaN_3(c), AgN_3(s), Ag(s) \qquad (B)$$

$$Ag(s), AgBr(s), KBr(c) \| KCl(c), AgCl(s), Ag(s) \qquad (C)$$

$$Ag(s), AgCl(s), KCl(c) \| KX(c), AgX(s), Ag(s) \qquad (D)$$

$$Ag(s), AgCNS(s), KCNS(c) \| KCl(c), AgCl(s), Ag(s) \qquad (E)$$

$$Ag(s), AgCl(s), MCl(c) \| M_2Y(c/2), Ag_2Y(s), Ag(s) \qquad (F)$$

and

$$Ag(s), AgCl(s), MCl(c) \| M_3Z(c/3), Ag_3Z(s), Ag(s) \qquad (G)$$

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where M is K or Na, has been made in 10, 20, 30 and 40 mass% acetone + water mixtures at temperatures from 5 to 35°C.

EXPERIMENTAL

Acetone (BDH, AnalaR) was distilled over $KMnO_4$ thrice and solvents of different compositions were prepared by weight. Potassium or sodium salts were the same samples used in the previous study [1i]. Preparation of the electrodes, and the cell solutions, setting up of the cells, and the EMF and conductance measurements were essentially similar to the procedures described earlier [1b]. All measurements were made in water baths at the required temperature with a precision of ±0.05°C. Constancy of the EMF readings to ±0.2 mV for 1 h was considered the criterion of equilibrium.

RESULTS AND DISCUSSION

The standard molar potentials, E_c^0, were obtained by the method of extrapolating the auxiliary function, $E_c^{0\prime}$, given by

$$E_c^{0\prime} = E + E^0_{\mathrm{Ag,AgBr}} - 2k\log C + 2kA\sqrt{2C}/1 + \sqrt{2C} - E_j \tag{1}$$

for the silver–silver ion electrode

$$\begin{aligned} E_c^{0\prime} &= E + E^0_{\mathrm{Ag,AgBr}} - E_{\mathrm{j}} \\ &= E^0_{\mathrm{Ag,AgX}} + \mathrm{f}(c) \end{aligned} \tag{2}$$

for the silver–silver chloride, silver–silver iodide, silver–silver azide, silver–silver bromate and silver–silver iodate electrodes

$$E_c^{0\prime} = E^0_{\mathrm{Ag,AgCl}} - E + E_{\mathrm{j}} = E^0_{\mathrm{Ag,AgCNS}} + \mathrm{f}(c) \tag{3}$$

for the silver–silver thiocyanate electrode

$$E_c^{0\prime} = E - 1/2k(\log 2C) - 1/2k\left(\frac{4A\sqrt{3C}/2}{1+\sqrt{3C}/2} - \frac{2A\sqrt{C}}{1+\sqrt{C}}\right) + E^0_{\mathrm{Ag,AgCl}} - E_j \tag{4}$$

for the silver–silver sulphate, silver–silver chromate, silver–silver dichromate and silver–silver tungstate electrodes, and

$$\begin{aligned} E_c^{0\prime} &= E - 1/3\ k\ \log\,(3C)^2 - k\left(3A\sqrt{2C}/1 + \sqrt{C} - A\sqrt{C}/1 + \sqrt{C}\right) \\ &\quad + E^0_{\mathrm{Ag,AgCl}} - E_{\mathrm{j}} = E^0_{\mathrm{Ag,Ag_3Z}} + bC \end{aligned} \tag{5}$$

for the silver–silver phosphate and silver–silver arsenate electrodes, to the molarity, $c = 0$.

In the foregoing equations, $E^0_{\mathrm{Ag,AgBr}}$ and $E^0_{\mathrm{Ag,AgCl}}$ are the standard potentials of the silver–silver bromide and silver–silver chloride electrodes, respectively, A is the Debye–Hückel constant, and is known or calculated over the temperature range under investigation for various acetone + water mixtures, E is the observed EMF of the corresponding cells, k is $2.3026(RT/F)$, E_{j} is the liquid-junction potential, b is $\frac{1}{2}k\{2\ \beta_{\mathrm{Cl}^-}-(3/2)\ \beta_{\mathrm{Y}^{2-}}\}$ in eqn. (4) and b is $\frac{1}{2}\{k(\beta_{\mathrm{Cl}^-}-(2/3)\beta_{\mathrm{Z}^{3-}})\}$ in eqn. (5), where β is the usual constant in the Debye–Hückel expression for the activity coefficient [1b,c].

As before [1b], the values of the liquid-junction potential, E_{j}, were calculated. It was found that the values of E_{j} varied in the range 0.1–0.3 mV for cells (A) to (E), 0.1–0.8 mV for cell (F) and 0.1–0.9 mV for cell (G) in all solvents at all temperatures. The values of $E^0_{\mathrm{Ag,AgBr}}$ (molar scale) needed for the calculation of $E^{0\prime}_c$ at different temperatures in various compositions of acetone + water mixtures were taken from the literature.

Standard potentials on the molal (E^0_m), mole-fraction (E^0_N) and molar (E^0_c) scales, by following the usual relationships [1a,c,d] at various temperatures for any solvent, were fitted by the method of least squares, to the equation

$$E^0_p = a + b(t-25) + c(t-25)^2 \tag{6}$$

where p is c, m or N, and t is any temperature (°C). The constants a, b and c of eqn. (6) on the molal scale are presented in Table 1. The average deviations between the experimental values calculated from eqn. (6) are within ± 0.3 mV. The E^0_m values (constant a of eqn. 6) at 25°C are also shown in Table 1.

The standard thermodynamic quantities (ΔG^0, ΔH^0 and ΔS^0), on the molal scale for the corresponding electrode reactions at different temperatures in the mixed solvents, have been evaluated by the usual relationship [1a]. These values at 25°C are presented in Table 2. The standard thermodynamic quantities (ΔG^0_{t}, ΔH^0_{t} and ΔS^0_{t}) for the transfer process, Ag^+, X^-, Y^{2-} or Z^{3-} (in water) $\rightarrow$ Ag^+, X^-, Y^{2-} or Z^{3-} (in acetone + water), were evaluated at different temperatures for the mixed solvents by the usual relationships. These values of the transfer thermodynamic quantities were obtained on a mole-fraction basis [1c]. Table 2 lists these values at 25°C along with the values of the change in electrostatic Gibbs energy ($\Delta G^0_{\mathrm{t,el}}$), the electrostatic entropy ($\Delta S^0_{\mathrm{t,el}}$) and the electrostatic contributions to the change in enthalpy ($\Delta H^0_{\mathrm{t,el}}$).

To estimate the $\Delta G^0_{\mathrm{t,el}}$ and $\Delta S^0_{\mathrm{t,el}}$ values, the equations

$$\Delta G^0_{\mathrm{t,el}} = (Ne^2/2)(\epsilon_{\mathrm{s}}^{-1}-\epsilon_{\mathrm{w}}^{-1})(r_+^{-1}+r_-^{-1}) \tag{7}$$

and

$$\Delta S^0_{\mathrm{t,el}} = (-Ne^2/2)(\epsilon_{\mathrm{s}}^{-1}\theta_{\mathrm{s}}^{-1}-\epsilon_{\mathrm{w}}^{-1}\theta_{\mathrm{w}}^{-1})(r_+^{-1}+r_-^{-1}) \tag{8}$$

were employed, where the radii of various ions were taken as Ag^+ ($r_+ = 0.126$

TABLE 1

Values of E_m^0 at 25°C and constants of eqn. (6) for the molal (m) scale in acetone+water mixtures

Mass% acetone	a (= E_m^0) (V)	$-b \times 10^4$	$c \times 10^6$
X = Cl			
10	0.2154	5.783	−0.25
20	0.2045	8.1	−2.0
30	0.1974	9.633	−3.0
40	0.1911	10.267	−2.0
X = I			
10	−0.1502	2.442	−2.75
20	−0.1513	2.1667	−1.0
30	−0.1523	2.1917	0.75
40	−0.1530	2.3083	−0.75
$X = N_3$			
10	0.2862	2.567	0
20	0.2839	1.7667	2.0
30	0.2818	2.1917	0.75
40	0.2797	2.275	0.25
X = CNS			
10	0.0904	9.025	2.75
20	0.0882	8.683	2.5
30	0.0863	8.675	0.25
40	0.0832	9.2583	−0.25
$X = IO_3$			
10	0.3269	2.86	0
20	0.3151	2.0167	−0.50
30	0.3039	2.175	−0.75
$X = BrO_3$			
10	0.5174	3.192	−0.25
20	0.5135	3.033	1.0
30	0.5095	3.1583	−0.25
Ag/Ag^+			
10	0.7907	9.466	2.0
20	0.7896	8.9417	2.25
30	0.7891	9.2583	0.25
40	0.7883	9.2	0
$Y = SO_4$			
10	0.5918	13.067	0
20	0.5831	13.133	1.00
30	0.5787	13.442	−1.75
$Y = CrO_4$			
10	0.4367	13.533	−1.0
20	0.4247	12.283	−1.50
30	0.4117	12.867	1.0
40	0.4006	11.992	−1.25

TABLE 1 (continued)

Mass% acetone	a (= E_m^0) (V)	$-b\times10^4$	$c\times10^6$
Y = Cr_2O_7			
10	0.4992	12.825	−0.25
20	0.4858	12.5083	1.25
30	0.4748	12.583	−0.50
40	0.4688	12.40	0
Y = WO_4			
10	0.4234	15.95	−1.5
20	0.4077	15.875	−1.75
30	0.3918	15.658	3.75
40	0.3799	16.342	0.25
Z = PO_4			
10	0.3750	16.925	−0.25
20	0.3531	16.9166	0.50
30	0.3367	16.125	−0.25
40	0.3178	15.6833	0.5
Z = AsO_4			
10	0.3402	16.508	−0.75
20	0.3271	16.2083	1.25
30	0.3143	15.767	−2.0
40	0.2967	16.775	0.25

nm), Cl^- (r_- = 0.181 nm). I^- (r_- = 0.219 nm), N_3^- (r_- = 0.117 nm), CNS^- (r_- = 0.258 nm), IO_3^- (r_- = 0.182 nm), BrO_3^- (r_- = 0.191 nm), SO_4^{2-} (r_- = 0.4 nm), CrO_4 (r_- = 0.4 nm), $Cr_2O_7^{2-}$ (r_- = 0.4 nm), WO_4^{2-} (r_- = 0.252 nm), PO_4^{3-} (r_- = 0.238 nm) and AsO_4 (r_- = 0.248 nm) [2]. ϵ_s and ϵ_w are the dielectric constants of the mixed solvents and water, respectively, and were taken from the literature [3]. The values of θ_w and θ_s, the temperature coefficients of the dielectric constants, were taken as 219 for water and 212, 209, 207 and 203 for 10, 20, 30 and 40 mass% acetone, respectively. The values of $\Delta H_{t,el}^0$ were computed from the known values of $\Delta G_{t,el}^0$ and $\Delta S_{t,el}^0$. The chemical contributions of the Gibbs free energy of transfer ($\Delta G_{t,ch}^0$), entropy of transfer ($\Delta S_{t,ch}^0$) and the enthalpy of transfer ($\Delta S_{t,ch}^0$) were obtained from the equation

$$\Delta R_t^0 = \Delta R_{t,el}^0 + \Delta R_{t,ch}^0 \qquad (9)$$

where R is G, S, or H. These values at 25°C are shown in Table 2.

The primary medium effect (log ${}^s\gamma_w$) represents the difference in ion–solvent interaction for Ag^+, X^-, Y^{2-} or Z^{3-} at infinite dilution in the particular mixed solvent and in water. It measures the change in escaping tendency of the Ag^+, X^-, Y^{-2} or Z^{3-} ions in the transfer from a standard state in one solvent to standard state in another. The values of the primary

TABLE 2

Thermodynamic quantities on the molal scale and transfer thermodynamic quantities on the mole-fraction scale in different acetone + water mixtures at 25°C

	Mass% acetone			
	10	20	30	40
Ag^+				
$-10^{-3}\Delta G_m^0$	76.3	76.19	76.14	76.06
$-10^{-3}\Delta H_m^0$	103.53	101.90	102.76	102.52
$-\Delta S_m^0$	91.34	86.27	89.33	88.77
$10^{-3}\Delta G_t^0$	0.48	0.20	−0.16	−0.54
$10^{-3}\Delta G_{t,el}^0$	0.053	0.120	0.199	0.304
$10^{-3}\Delta G_{t,ch}^0$	0.427	0.08	−0.359	−0.844
ΔS_t^0	5.38	11.74	9.75	11.65
$-\Delta S_{t,el}^0$	0.35	0.73	1.15	1.75
$\Delta S_{t,ch}^0$	5.73	12.47	10.90	13.40
$10^{-3}\Delta H_t^0$	2.09	3.7	2.74	2.94
$-10^{-3}\Delta H_{t,el}^0$	0.051	0.098	0.144	0.218
$10^{-3}\Delta H_{t,ch}^0$	2.141	3.798	2.884	3.158
$\lim_{N \to 0} (\log {}^s\gamma_w)$	0.0845	0.0355	−0.0287	−0.0947
$X = Cl$				
$-10^{-3}\Delta G_m^0$	20.78	19.73	19.1	18.44
$-10^{-3}\Delta H_m^0$	37.42	42.92	46.79	47.96
$-\Delta S_m^0$	56.06	78.16	92.92	99.07
$10^{-3}\Delta G_t^0$	0.33	0.98	1.22	1.39
$10^{-3}\Delta G_{t,el}^0$	0.09	0.20	0.34	0.54
$10^{-3}\Delta G_{t,ch}^0$	0.24	0.78	0.88	0.87
$-\Delta S_t^0$	−10.31	11.01	24.53	28.72
$-\Delta S_{t,el}^0$	0.59	1.22	1.94	2.96
$-\Delta S_{t,ch}^0$	−9.72	9.79	22.59	25.76
$-10^{-3}\Delta H_t^0$	−3.39	2.19	6.09	7.25
$-10^{-3}\Delta H_{t,el}^0$	0.09	0.16	0.24	0.36
$-10^{-3}\Delta H_{t,ch}^0$	−3.48	2.03	5.85	6.89
$\lim_{N \to 0} (\log {}^s\gamma_w)$	0.0577	0.1724	0.2129	0.2434
$X = I$				
$10^{-3}\Delta G_m^0$	14.49	14.60	14.70	14.76
$10^{-3}\Delta H_m^0$	7.49	8.37	8.39	8.13
$-\Delta S_m^0$	23.56	20.9	21.15	22.27
$-10^{-3}\Delta G_t^0$	0.57	0.82	1.16	1.54
$10^{-3}\Delta G_{t,el}^0$	0.08	0.19	0.31	0.48
$-10^{-3}\Delta G_{t,ch}^0$	0.65	1.02	1.47	2.02
ΔS_t^0	11.17	15.36	16.12	16.41
$-\Delta S_{t,el}^0$	0.55	1.14	1.79	2.75
$\Delta S_{t,ch}^0$	11.72	16.50	17.91	19.16
$-10^{-3}\Delta H_t^0$	2.76	3.74	3.66	3.34
$-10^{-3}\Delta H_{t,el}^0$	0.08	0.15	0.22	0.34
$-10^{-3}\Delta H_{t,ch}^0$	2.68	3.59	3.44	3.00
$\lim_{N \to 0} (\log {}^s\gamma_w)$	−0.0997	−0.1454	−0.2028	−0.2705

TABLE 2 (continued)

	Mass% acetone			
	10	20	30	40
X = N_3				
$-10^{-3}\Delta G_m^0$	27.62	27.39	27.19	26.99
$-10^{-3}\Delta H_m^0$	34.99	32.57	33.49	33.53
$-\Delta S_m^0$	24.77	17.37	21.13	21.95
$10^{-3}\Delta G_t^0$	0.38	0.19	−0.02	−0.27
$10^{-3}\Delta G_{t,el}^0$	0.11	0.25	0.41	0.63
$10^{-3}\Delta G_{t,ch}^0$	0.24	−0.06	−0.43	−0.90
ΔS_t^0	−0.51	8.74	5.92	6.22
$-\Delta S_{t,el}^0$	0.72	1.50	2.37	3.62
$\Delta S_{t,ch}^0$	0.21	10.24	8.29	9.84
$10^{-3}\Delta H_t^0$	0.18	2.78	1.73	1.57
$-10^{-3}\Delta H_{t,el}^0$	0.11	0.20	0.30	0.45
$10^{-3}\Delta H_{t,ch}^0$	0.29	2.98	2.03	2.02
$\lim_{N\to 0}(\log {}^s\gamma_w)$	0.0609	0.0338	−0.0034	−0.0473
X = CNS				
$-10^{-3}\Delta G_m^0$	8.72	8.51	8.33	8.03
$-10^{-3}\Delta H_m^0$	34.67	33.48	33.27	34.64
$-\Delta S_m^0$	87.08	83.78	83.70	89.33
$-10^{-3}\Delta G_t^0$	0.56	0.73	0.97	1.12
$10^{-3}\Delta G_{t,el}^0$	0.08	0.18	0.30	0.45
$-10^{-3}\Delta G_{t,ch}^0$	0.64	0.91	1.27	1.57
ΔS_t^0	12.44	17.27	18.4	14.14
$-\Delta S_{t,el}^0$	0.53	1.08	1.71	2.6
$\Delta S_{t,ch}^0$	12.97	18.35	20.11	16.74
$10^{-3}\Delta H_t^0$	3.26	4.53	4.63	3.22
$-10^{-3}\Delta H_{t,el}^0$	0.07	0.14	0.21	0.32
$10^{-3}\Delta H_{t,ch}^0$	3.33	4.67	4.84	3.54
$\lim_{N\to 0}(\log {}^s\gamma_w)$	−0.098	−0.1285	−0.1707	−0.1978
X = IO_3				
$-10^{-3}\Delta G_m^0$	31.54	30.40	29.32	
$-10^{-3}\Delta H_m^0$	39.77	36.20	35.58	
$-\Delta S_m^0$	27.60	19.46	20.98	
$10^{-3}\Delta G_t^0$	−0.15	0.61	1.27	
$10^{-3}\Delta G_{t,el}^0$	0.09	0.20	0.34	
$10^{-3}\Delta G_{t,ch}^0$	−0.24	0.41	0.93	
ΔS_t^0	3.79	13.03	13.04	
$-\Delta S_{t,el}^0$	0.59	1.22	1.93	
$\Delta S_{t,ch}^0$	4.38	14.25	14.97	
$10^{-3}\Delta H_t^0$	0.95	4.47	5.14	
$-10^{-3}\Delta H_{t,el}^0$	0.09	0.16	0.24	
$10^{-3}\Delta H_{t,ch}^0$	1.04	4.63	5.38	
$\lim_{N\to 0}(\log {}^s\gamma_w)$	−0.0270	0.1065	0.2231	

TABLE 2 (continued)

	Mass% acetone			
	10	20	30	40
$X = BrO_3$				
$-10^{-3}\Delta G_m^0$	49.92	49.95	49.16	
$-10^{-3}\Delta H_m^0$	59.10	58.27	58.24	
$-\Delta S_m^0$	30.80	29.27	30.47	
$10^{-3}\Delta G_t^0$	0.49	0.48	0.46	
$10^{-3}\Delta G_{t,el}^0$	0.09	0.20	0.33	
$10^{-3}\Delta G_{t,ch}^0$	0.40	0.28	0.13	
ΔS_t^0	−1.37	1.73	1.69	
$-\Delta S_{t,el}^0$	0.58	1.20	1.89	
$\Delta S_{t,ch}^0$	−0.79	2.93	3.58	
$10^{-3}\Delta H_t^0$	0.26	0.95	0.89	
$10^{-3}\Delta H_{t,el}^0$	0.32	0.12	−0.11	
$10^{-3}\Delta H_{t,ch}^0$	−0.06	0.83	1.00	
$\lim_{N\to 0} (\log {}^s\gamma_w)$	0.0862	0.0845	0.0811	
$Y = SO_4$				
$-10^{-3}\Delta G_m^0$	114.20	112.53	111.68	
$-10^{-3}\Delta H_m^0$	189.35	188.05	188.98	
$-\Delta S_m^0$	252.17	253.44	259.41	
$10^{-3}\Delta G_t^0$	2.28	3.18	3.20	
$10^{-3}\Delta G_{t,el}^0$	0.07	0.16	0.26	
$10^{-3}\Delta G_{t,ch}^0$	2.23	3.02	2.94	
$-\Delta S_t^0$	18.08	16.30	20.16	
$-\Delta S_{t,el}^0$	0.47	0.96	1.51	
$-\Delta S_{t,ch}^0$	17.61	15.34	18.65	
$-10^{-3}\Delta H_t^0$	3.1	1.68	2.81	
$-10^{-3}\Delta H_{t,el}^0$	0.07	0.13	0.19	
$-10^{-3}\Delta H_{t,ch}^0$	3.03	1.55	2.62	
$\lim_{N\to 0} (\log {}^s\gamma_w)$	0.3989	0.5578	0.5612	
$Y = CrO_4$				
$-10^{-3}\Delta G_m^0$	84.28	81.96	79.46	77.30
$-10^{-3}\Delta H_m^0$	162.10	152.6	153.45	146.27
$-\Delta S_m^0$	261.16	237.04	248.31	231.42
$10^{-3}\Delta G_t^0$	1.70	3.24	4.94	6.18
$10^{-3}\Delta G_{t,el}^0$	0.07	0.16	0.26	0.40
$10^{-3}\Delta G_{t,ch}^0$	1.63	3.08	4.68	5.78
$-\Delta S_t^0$	44.15	17.14	26.2	6.75
$-\Delta S_{t,el}^0$	0.47	0.96	1.51	2.30
$-\Delta S_{t,ch}^0$	43.68	16.18	24.69	4.45
$10^{-3}\Delta H_t^0$	−11.46	−1.87	−2.87	4.16
$-10^{-3}\Delta H_{t,el}^0$	0.07	0.13	0.19	0.29
$10^{-3}\Delta H_{t,ch}^0$	−11.39	−1.74	−2.68	3.87
$\lim_{N\to 0} (\log {}^s\gamma_w)$	0.2975	0.5679	0.8655	1.0818

TABLE 2 (continued)

	Mass% acetone			
	10	20	30	40
$Y = Cr_2O_7$				
$-10^{-3}\Delta G_m^0$	96.34	93.76	91.62	90.47
$-10^{-3}\Delta H_m^0$	170.09	165.68	163.99	161.78
$-\Delta S_m^0$	247.50	241.38	242.84	239.30
$10^{-3}\Delta G_t^0$	10.52	12.37	13.64	13.91
$10^{-3}\Delta G_{t,el}^0$	0.07	0.16	0.26	0.40
$10^{-3}\Delta G_{t,ch}^0$	10.45	12.21	13.38	13.51
ΔS_t^0	24.45	33.62	34.25	40.53
$-\Delta S_{t,el}^0$	0.47	0.96	1.51	2.3
$\Delta S_{t,ch}^0$	24.92	34.58	35.76	42.83
$10^{-3}\Delta H_t^0$	17.80	22.38	23.85	25.99
$-10^{-3}\Delta H_{t,el}^0$	0.07	0.13	0.19	0.29
$10^{-3}\Delta H_{t,ch}^0$	17.87	22.51	24.04	26.28
$\lim_{N \to 0} (\log {}^s\gamma_w)$	1.8425	2.1670	2.3902	2.4375
$Y = WO_4$				
$-10^{-3}\Delta G_m^0$	81.71	78.68	75.61	73.31
$-10^{-3}\Delta H_m^0$	173.44	169.97	165.66	167.29
$-\Delta S_m^0$	307.80	306.36	302.17	315.37
$10^{-3}\Delta G_t^0$	1.56	3.84	6.08	7.47
$10^{-3}\Delta G_{t,el}^0$	0.08	0.18	0.30	0.45
$10^{-3}\Delta G_{t,ch}^0$	1.48	3.66	5.78	7.02
ΔS_t^0	−0.84	3.18	9.93	0.51
$-\Delta S_{t,el}^0$	0.53	1.08	1.71	2.61
$\Delta S_{t,ch}^0$	−0.31	4.26	11.64	2.10
$10^{-3}\Delta H_t^0$	1.42	4.89	9.15	7.63
$-10^{-3}\Delta H_{t,el}^0$	0.08	0.14	0.21	0.32
$10^{-3}\Delta H_{t,ch}^0$	1.50	5.03	9.36	7.92
$\lim_{N \to 0} (\log {}^s\gamma_w)$	0.2738	0.6728	1.0649	1.3084
$Z = PO_4$				
$-10^{-3}\Delta G_m^0$	108.55	102.21	97.47	91.99
$-10^{-3}\Delta H_m^0$	254.55	248.14	236.56	227.28
$-\Delta S_m^0$	489.94	489.67	466.78	453.98
$10^{-3}\Delta G_t^0$	21.33	26.57	30.08	34.16
$10^{-3}\Delta G_{t,el}^0$	0.08	0.18	0.30	0.47
$10^{-3}\Delta G_{t,ch}^0$	21.25	26.39	29.78	33.69
ΔS_t^0	−26.41	−31.85	−5.16	13.54
$-\Delta S_{t,el}^0$	0.54	1.11	1.75	2.67
$\Delta S_{t,ch}^0$	−25.87	−30.74	3.41	16.21
$10^{-3}\Delta H_t^0$	13.29	16.88	28.38	37.99
$-10^{-3}\Delta H_{t,el}^0$	0.08	0.15	0.22	0.33
$10^{-3}\Delta H_{t,ch}^0$	13.37	17.03	28.60	38.32
$\lim_{N \to 0} (\log {}^s\gamma_w)$	3.7374	4.6553	5.2689	5.9839

TABLE 2 (continued)

	Mass% acetone			
	10	20	30	40
$Z = AsO_4$				
$-10^{-3}\Delta G_m^0$	98.48	94.69	90.98	85.89
$-10^{-3}\Delta H_m^0$	240.88	234.50	226.99	230.59
$-\Delta S_m^0$	477.86	469.18	456.41	485.59
$10^{-3}\Delta G_t^0$	16.53	19.19	21.65	25.39
$10^{-3}\Delta G_{t,el}^0$	0.08	0.18	0.30	0.46
$10^{-3}\Delta G_{t,ch}^0$	16.45	19.01	21.35	24.93
ΔS_t^0	9.54	22.81	38.72	13.63
$-\Delta S_{t,el}^0$	0.53	1.09	1.73	2.64
$\Delta S_{t,ch}^0$	10.07	23.90	40.45	16.27
$10^{-3}\Delta H_t^0$	19.49	26.11	33.31	29.57
$-10^{-3}\Delta H_{t,el}^0$	0.08	0.14	0.22	0.33
$10^{-3}\Delta H_{t,ch}^0$	19.57	26.25	33.53	29.90
$\lim_{N \to 0} (\log {}^s\gamma_w)$	2.8956	3.3621	3.7932	4.4474

medium effect (mole-fraction scale) of various acetone + water mixtures on the Ag^+, X^-, Y^{2-} or Z^{3-} ions at 25°C were computed using the equation

$$\lim_{N \to 0} (\log {}^s\gamma_w) = \left[\left(E_N^0 \right)_w - \left(E_N^0 \right)_s \right] / 2.3026(RT/nF) \qquad (10)$$

where the limit term indicates the primary medium effect and n is 1 for Ag^+ and X^-, 2 for Y^{2-}, and 3 for Z^{3-} ions. These values are also included in Table 2.

An inspection of Table 1 shows that the standard electrode potentials of the electrodes obtained in the present investigation are less in acetone + water mixtures (except for the silver–silver iodide and silver–silver thiocyanate electrodes) than in water, which is in agreement with the behaviour exhibited by these electrodes studied in other mixed solvents [1]. Feakins and French [4] reported the standard potentials of the Ag, AgCl electrode in 10, 20, and 40 mass% acetone + water mixtures at 25°C. Our E_m^0 value in 10 mass% acetone mixture (0.2154 V) is in good agreement with their value (0.2156 V) obtained with this composition. Their other values of E_m^0 in 20 (0.2079 V) and 40 mass% (0.1859 V) are in poor agreement with our values (0.2045 and 0.1911 V) obtained in 20 and 40 mass% acetone mixtures, respectively. Such differences exist even in the values of the standard potentials of the Ag, AgBr electrode in 20 and 40 mass% acetone + water mixtures reported by Bax et al. [5] and Elsemongy [6] at 25°C.

It is seen from Table 2 that, while the standard free energy changes increase, the standard entropy and enthalpy changes which are all negative show an irregular variation with the increase in the acetone content of the solvent. The difference in magnitude of the ΔS^0 and ΔH^0 values may be due to some structural effects. These effects can arise from the solvent properties and/or from the solvation properties of the ions in the different solvent mixtures.

A perusal of Table 2 shows that the standard Gibbs free energy of transfer, ΔG_t^0 for the Ag^+, X^-, Y^{2-} and Z^{3-} ions appears to be positive (except for I^- and CNS^- in all solvents, and Ag^+ in 30 and 40 mass% acetone mixtures) and becomes increasingly positive as the proportion of acetone increases. The positive value of ΔG_t^0 signifies that the transfer of the ions from water to water + acetone solvents is not favourable, whereas the negative ΔG_t^0 values indicate that the I^- and CNS^- ions are in a lower free energy state in the mixed solvents than in water, and, therefore, that the transfer process is favourable as the acetone content increases in the solvent mixtures. Solvent effects on the other thermodynamic parameters (ΔS_t^0 and ΔH_t^0) accompanying the transfer process of ions from water to mixed solvents are highly involved quantities. This is because both parameters are dictated not only by the resulting effects of the transfer process concerned, but each of which also is connected with the building-up and breaking-down of the solvent structure. The positive values of ΔS_t^0, for the Ag^+, I^-, N_3^-, CNS^- IO_3^-, BrO_3^-, $Cr_2O_7^{2-}$, WO_4^{2-} and AsO_4^{3-} ions indicate that the ions break the solvent structure more effectively in the mixed solvent than in water. Thus, the net amount of the order created by these ions is less in acetone + water solvents than in water. The acetone + water solvents are therefore more structured than water. On the other hand, the negative ΔS_t^0 values of the Cl^- (except in 10% acetone), SO_4^{2-}, CrO_4^{2-} and PO_4^{3-} (except in 40% acetone) ions indicate that water is a more structured solvent than the acetone + water solvents. The positive ΔH_t^0 values (except for Cl^-, I^-, SO_4^{2-} and CrO_4^{2-} ions) indicate that the transfer process is endothermic, because of the dehydration and then resolvation of the ions by acetone.

The values of $\Delta G_{t,el}^0$ (Table 2) are all positive and increase with increasing acetone content in the solvent. The chemical part of the free energy ($\Delta G_{t,ch}^0$) which appears to be positive for all solvents (except for Ag^+ and N_3^- ions in acetone-rich solvents, I^- and CNS^- ions in all solvents) mostly increases with increasing acetone concentration in the solvent. As $\Delta G_{t,ch}^0$ points the acid–base properties of mixed solvents, the positive values of $\Delta G_{t,ch}^0$ indicate that the transfer process is unfavourable. The variation of both $\Delta H_{t,ch}^0$ and $\Delta S_{t,ch}^0$ values with solvent composition shows a similar trend to changes observed for ΔH_t^0 and ΔS_t^0, and thus may be explained in the same manner. The sign and magnitude of the primary medium effect (Table 2) could give insight into the stabilization of the ions in the solvent concerned. The positive (except for Ag^+ and N_3^- ions in acetone-rich solvents and I^- and CNS^- ions in all solvents) and increasing magnitude of this quantity suggests that the escaping tendency of the ions is greater in acetone + water solvents than in the aqueous medium.

TABLE 3

Solubility product constants on the molar scales (K_s^c) of AgX (X = Cl, Br, I, N_3, CNS, IO_3, BrO_3), Ag_2Y (Y = SO_4, CrO_4, Cr_2O_7, WO_4) and Ag_3Z (Z = PO_4, AsO_4) in acetone + water mixtures at 25°C

	Mass% acetone			
	10	20	30	40
X = Cl				
$K_s^c \times 10^{11}$	18.84	12.23	11.77	8.32
X = Br				
$K_s^c \times 10^{13}$	6.28	5.80	5.02	4.03
X = N_3				
$K_s^c \times 10^{10}$	29.88	28.29	26.38	24.98
X = I				
$K_s^c \times 10^{17}$	12.45	12.30	12.11	12.02
X = CNS				
$K_s^c \times 10^{13}$	14.41	13.75	13.08	11.87
X = IO_3				
$K_s^c \times 10^{9}$	14.45	9.45	6.23	–
X = BrO_3				
$K_s^c \times 10^{6}$	24.09	21.43	18.63	–
Y = SO_4				
$K_s^c \times 10^{8}$	18.88	10.35	7.58	–
Y = CrO_4				
$K_s^c \times 10^{13}$	10.93	4.57	1.71	0.77
Y = Cr_2O_7				
$K_s^c \times 10^{11}$	14.07	5.27	2.33	1.54
Y = WO_4				
$K_s^c \times 10^{13}$	3.82	1.20	0.37	0.15
Z = PO_4				
$K_s^c \times 10^{22}$	8.30	0.72	0.11	0.013
Z = AsO_4				
$K_s^c \times 10^{24}$	14.27	3.43	0.82	0.12

The thermodynamic solubility products (on the molar scale), K_{so}^c, of AgX (X = Cl, Br, I, N_3, CNS, IO_3, BrO_3), Ag_2Y (Y = SO_4, CrO_4, Cr_2O_7, or WO_4) and Ag_3Z (Z = PO_4, AsO_4) in acetone + water mixtures have been calculated at different temperatures from the values of standard potentials by means of the usual relationships [1i]. These values at 25°C are presented in Table 3. The data for K_{so}^m (on the molal scale) were calculated from K_{so}^c/ρ^2, where ρ is the density of the mixed solvents. The solubility product in any solvent were fitted by least squares to the equation

$$\log K_{so}^m(\mathrm{AgX\ or\ Ag_2Y\ or\ Ag_3Z}) = A/T + B \tag{11}$$

The constants A and B of eqn. (11) (on the molal scale) are presented in Table 4 along with the values of σ, the standard deviation of the least-squares fit: the correlation coefficient for these relations is 0.996, 0.998 and 0.999 for AgX, Ag_2Y and Ag_3Z, respectively.

TABLE 4

Constants of eqn. (11) for molal (m) scale in acetone + water mixtures for different silver salts

	Mass% acetone			
	10	20	30	40
X = Cl				
A	−3523.0661	3205.9839	−2990.4359	−2889.8762
$B\times10^3$	2109.3328	881.0525	92.8099	−324.9031
σ	0.114	0.104	0.098	0.096
X = Br				
A	−4363.0005	−4233.3825	−4097.2861	−4059.6611
$B\times10^3$	2443.9858	1988.2013	1486.0239	1289.4915
σ	0.142	0.134	0.133	0.123
X = I				
A	−5907.96	−5888.4723	−5831.822	−5816.094
$B\times10^3$	3928.157	3878.0477	3700.167	3659.659
σ	0.191	0.192	0.190	0.190
X = N_3				
A	−3647.831	−3690.4596	−3642.3703	−3597.3606
$B\times10^3$	3725.536	3862.9905	3691.121	3529.7782
σ	0.185	0.120	0.118	0.117
X = CNS				
A	−3627.2646	−3631.9549	−3661.6356	−3563.7665
$B\times10^3$	349.99	359.2719	450.4803	95.4539
σ	0.118	0.118	0.119	0.116
X = IO_3				
A	−3397.1492	−3533.8726	−3556.9122	
$B\times10^3$	3571.6953	3861.0265	3774.5257	
σ	0.108	0.112	0.113	
X = BrO_3				
A	−2390.8261	−2358.1384	−2366.441	
$B\times10^3$	3415.8436	3271.8669	3255.9954	
σ	0.076	0.076	0.076	
Y = SO_4				
A	−1028.108	−919.16482	−1003.2363	
$B\times10^3$	−3265.9269	−3872.5446	−3706.6883	
σ	0.031	0.027	0.028	
Y = CrO_4				
A	−2575.8304	−2841.4479	−2769.6904	−3115.1321
$B\times10^3$	−3303.8116	−2782.9312	−3422.1983	−2603.9785
σ	0.081	0.090	0.090	0.099
Y = Cr_2O_7				
A	−2036.1527	−2083.1315	−2214.8466	−2270.5292
$B\times10^3$	−3012.1801	−3257.3365	−3152.1544	−3129.8313
σ	0.066	0.067	0.072	0.076
Y = WO_4				
A	−1901.5194	−1946.5346	−2050.9378	−1973.0369
$B\times10^3$	−6032.8569	−6336.7995	−6495.6447	−7130.41
σ	0.061	0.064	0.066	0.063

TABLE 4 (continued)

	Mass% acetone			
	10	20	30	40
$Z = PO_4$				
A	−3069.8967	−3147.5441	−3784.7513	−4172.571
$B \times 10^2$	−1077.6843	−1155.719	−1020.321	−980.2152
σ	0.098	0.102	0.123	0.136
$Z = AsO_4$				
A	−3805.1874	−384.778	−4359.49	−3996.372
$B \times 10^2$	−1007.537	−1059.84	−941.8012	−1146.614
σ	0.121	0.12	0.196	0.130

A comparison of the solubility data of the silver salts obtained in the present study with that in water reported elsewhere [1h,i] shows that these silver salts are less soluble in acetone + water mixtures than in water and solubility decreases with increasing acetone content, i.e., with a decrease in the dielectric constant of the solvent.

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