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STANDARD THERMODYNAMICS OF TRANSFER. III. SILVER AND SILVER SALT ELECTRODES IN WATER + MONO- AND + DIHYDRIC ALCOHOL MIXTURES *

UPENDRA NATH DASH

Department of Chemistry, Utkal University, Bhubaneswar-4 (India)

BANKA BEHARI DAS, UTTAM KUMAR BISWAL and TAPODHANA PANDA

Department of Chemistry, Bhadrak College, Bhadrak-756100 (India)

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ABSTRACT

The standard thermodynamic quantities of transfer of Ag^+, X^- ($X = N_3$, CNS), Y^{2-} ($Y = SO_4$, CrO_4, Cr_2O_7) and Z^{3-} ($Z = PO_4$ or AsO_4) ions have been evaluated in water + 10 and + 20 mass% methanol, ethanol, 1-propanol and 2-propanol, and in water + 10 and + 30 mass% ethylene glycol. The thermodynamic solubility product constants of silver salts in these solvents have been determined.

INTRODUCTION

In earlier communications [1] we reported the standard thermodynamic quantities 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 aqueous solutions of glycerol and acetone. The present work makes a similar study of Ag^+, N_3^-, CNS^-, SO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, PO_4^{3-} and AsO_4^{3-} in different compositions of water + methanol, + ethanol, + 1-propanol, + 2-propanol and + ethylene glycol mixtures and compares the results between aqueous solutions of mono-, di-, tri- and pentahydric compounds.

As previously [1], cells with liquid-junction potentials:

$$Ag(s), AgCl(s), NaCl(c), NaNO_3(c)//NaNO_3(c), AgNO_3(c), Ag(s) \qquad (A)$$

$$Ag(s), AgCl(s), NaCl(c)//NaN_3(c), AgN_3(s), Ag(s) \qquad (B)$$

$$Ag(s), AgCNS(s), KCNS(c)//KCl(c), AgCl(s), Ag(s) \qquad (C)$$

$$Ag(s), AgCl(s), KCl(c)//K_2Y(c/2), Ag_2Y(s), Ag(s) \qquad (D)$$

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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and

$$\mathrm{Ag(s), AgCl(s), NaCl}(c)//\mathrm{Na_3Z}(c/3), \mathrm{Ag_3Z(s), Ag(s)} \qquad \text{(E)}$$

where s and c represent solid and molarity, respectively, were studied in different compositions of water + methanol, + ethanol, + 1-propanol, + 2-propanol and + ethylene glycol mixtures at temperatures of 5–35 °C.

EXPERIMENTAL

Sodium chloride, sodium nitrate, silver nitrate, potassium chloride, potassium thiocyanate, sodium azide, potassium sulphate, potassium chromate, potassium dichromate, sodium phosphate and sodium arsenate were the samples as used in earlier studies [1]. Methanol, ethanol, 1-propanol and 2-propanol were purified as described earlier [2]. Ethylene glycol (BDH, AnalaR) was treated with 4A molecular sieve and vacuum distilled. The solvent mixtures of various mass percentages were prepared by weight from conductivity water and purified solvents.

Preparation of the electrodes and of the cell solutions, setting up of the cells, EMF and conductance measurements were essentially similar to the procedures described earlier [1,2]. All measurements were made in water baths at the required temperature with a precision of ±0.1 °C. The reproducibility of EMF measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

As usual [1,2], the EMFs, E, of the cells are as follows:
cell (A)

$$E = E^0_{\mathrm{Ag,Ag^+}} - E^0_{\mathrm{Ag,AgCl}} + (RT/F)\ln[\mathrm{Ag^+}][\mathrm{Cl^-}]\gamma^2_{\pm} + E_j \qquad (1)$$

cell (B)

$$E = E^0_{\mathrm{Ag,AgN_3}} - E^0_{\mathrm{Ag,AgCl}} - (RT/F)\ln\left([\mathrm{N_3}]\gamma_{\mathrm{N_3^-}}/[\mathrm{Cl^-}]\gamma_{\mathrm{Cl^-}}\right) + E_j \qquad (2)$$

cell (C)

$$E = E^0_{\mathrm{Ag,AgCl}} - E^0_{\mathrm{Ag,AgCNS}} - (RT/F)\ln([\mathrm{Cl^-}]\gamma_{\mathrm{Cl^-}}/[\mathrm{CNS^-}]\gamma_{\mathrm{CNS^-}}) + E_j \qquad (3)$$

cell (D)

$$E = E^0_{\mathrm{Ag,Ag_2Y}} - E^0_{\mathrm{Ag,AgCl}} + (RT/F)\ln(2c) + (RT/2F)\ln\left(\gamma^2_{\mathrm{Cl^-}}/\gamma_{\mathrm{Y^{2-}}}\right) + E_j \qquad (4)$$

cell (E)

$$E = E^0_{\mathrm{Ag,Ag_3Z}} - E^0_{\mathrm{Ag,AgCl}} + (RT/3F)\ln(3c^2) + (RT/3F)\ln\left(\gamma^3_{\mathrm{Cl^-}}/\gamma_{\mathrm{Z^{3-}}}\right) + E_j \qquad (5)$$

where [ ] and γ represent the molarity and activity coefficient of the species designated, respectively.

Using the molar concentrations of the corresponding electrolyte solutions and expressing the mean molar activity coefficients by the Debye–Hückel expression, the standard molar potentials, E_c^0, of the Ag/Ag^+, $Ag/AgX,X^-$, $Ag/Ag_2Y,Y^{2-}$ and $Ag/Ag_3Z,Z^{3-}$ electrodes were obtained by the method of extrapolating [1,2] the corresponding auxiliary functions to molarity $c = 0$.

As previously [1,2], the values of the liquid-junction potentials, E_j, were calculated from the equivalent conductivity values of the corresponding cell solutions by means of the Lewis–Sargent equation. It was found that the values of E_j varied in the range 0.1–0.3 mV for cells (A)–(C), and 0.2–0.8 mV for cells (D) and (E) in all solvents at all temperatures. The values of $E^0_{Ag,AgCl}$ (molar scale) needed for the calculation of E_c^0 of the electrodes at different temperatures in water + methanol, + ethanol, + 1-propanol, + 2-propanol and + ethylene glycol mixtures were either taken from the literature [3,4] or calculated from the values on the molal scale using the density values of the corresponding mixed solvents at the required temperatures [3,4].

Standard potentials on the molal (E_m^0), mole fraction (E_N^0) and molar (E_c^0) scales (correlated by the usual equation [5]) at various temperatures for any solvent can be expressed as a function of temperature t °C in the following form:

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

The constants a, b and c of eqn. (6) on the molal scale are presented in Table 1. The average deviation between the experimental values and those calculated from eqn. (6) are within ±0.3 mV.

The standard thermodynamic quantities (ΔG^0, ΔH^0 and ΔS^0) on the molal scale for the corresponding electrode reactions at different temperatures in various solvents have been calculated by the usual relationship [5]. These values at 25 °C are presented in Table 1.

The standard thermodynamic quantities (ΔG_t^0, ΔH_t^0 and ΔS_t^0) for the transfer process Ag^+, X^-, Y^{2-} or Z^{3-} (in water) → Ag^+, X^-, Y^{2-} or Z^{3-} (in mixed solvent) were evaluated at different temperatures for various solvent mixtures by the usual relationships [5]. These values of the transfer thermodynamic quantities were obtained on the mole fraction basis, since this eliminates free energy changes due to changes in concentration [6], and are included in Table 2 for 25 °C only. Since the process involves the transfer of charged particles from water to another solvent having a different dielectric constant, the related thermodynamic quantities consist of two parts: electrostatic (el) and non-electrostatic or chemical (ch). Thus for the free energy change,

$$\Delta G_t^0 = \Delta G_{t,el}^0 + \Delta G_{t,ch}^0 \tag{7}$$

TABLE 1

Constants of eqn. (6) and thermodynamic parameters [a] (on the molal scale) (ΔG^0 and ΔH^0 in kJ mol^{-1}; ΔS^0 in J mol^{-1} K^{-1})

Mass% organic solvent	$a = E_m^0$ (at 25 °C)	$-b \times 10^3$	$c \times 10^6$	$-\Delta G_m^0$	$-\Delta S_m^0$	$-\Delta H_m^0$
Methanol: X = N_3						
10	0.2900	0.0933	0.0	27.98	9.08	30.67
20	0.2877	0.1042	−0.75	27.76	10.05	30.76
Y = SO_4						
10	0.6072	1.195	0.5	117.18	230.61	185.9
20	0.5947	1.3142	2.25	114.77	253.62	190.35
Y = CrO_4						
10	0.4418	1.3083	1.5	85.26	252.48	160.50
20	0.4300	1.323	1.0	82.98	255.32	159.07
Y = Cr_2O_7						
10	0.5592	1.2242	−0.75	107.92	236.25	178.32
20	0.5469	1.2817	0.50	105.54	247.35	179.25
Z = PO_4						
10	0.3936	1.1458	−1.25	113.94	331.68	212.78
20	0.3841	1.1808	0.25	111.19	341.81	213.05
Z = AsO_4						
10	0.3468	1.4917	−1.5	100.39	431.81	229.07
20	0.3379	1.4717	0.5	97.81	426.02	224.77
Ethanol: X = N_3						
10	0.2890	0.125	−0.5	27.89	12.06	31.48
20	0.2883	0.0925	0.75	27.82	8.93	30.48
Y = SO_4						
10	0.6059	1.1992	1.75	116.93	231.42	185.89
20	0.5916	1.2475	0.25	114.17	240.75	185.91
Y = CrO_4						
10	0.4338	1.3383	−1.5	83.72	258.27	160.68
20	0.4216	1.3092	−1.25	81.36	252.65	156.65
Y = Cr_2O_7						
10	0.5522	1.22	−1.0	106.57	231.58	176.73
20	0.5404	1.2225	−1.25	104.29	235.92	174.59
Z = PO_4						
10	0.3849	1.3642	0.25	111.42	394.9	229.10
20	0.3764	1.2892	0.75	108.96	373.19	220.17
Z = AsO_4						
10	0.3455	1.3308	1.25	100.01	385.23	214.81
20	0.3365	1.2942	−0.75	97.41	374.64	209.05
1-Propanol: X = N_3						
10	0.2917	0.0881	0.75	28.15	8.50	30.68
20	0.2907	0.0733	1.0	28.05	7.07	30.16
Y = SO_4						
10	0.5878	0.3392	−0.75	113.43	258.44	190.45
20	0.5795	1.2458	1.75	111.83	240.42	183.48

TABLE 1 (continued)

Mass% organic solvent	$a = E_m^0$ (at 25° C)	$-b \times 10^3$	$c \times 10^6$	$-\Delta G_m^0$	$-\Delta S_m^0$	$-\Delta H_m^0$
$Y = CrO_4$						
10	0.4266	1.165	−0.50	82.33	224.82	149.32
20	0.4169	1.1542	1.25	80.45	222.74	146.83
$Y = Cr_2O_7$						
10	0.5436	1.2017	0.50	104.91	231.91	174.01
20	0.5336	1.2292	−1.25	102.98	237.21	173.67
$Z = PO_4$						
10	0.3855	1.2675	1.25	111.59	366.91	220.93
20	0.3763	1.275	0.50	108.93	369.08	218.91
$Z = AsO_4$						
10	0.3440	1.2767	1.0	99.58	369.57	209.71
20	0.3337	1.2733	1.0	96.60	368.59	206.44
2-Propanol: $X = N_3$						
10	0.2913	0.0783	0.50	28.11	7.56	30.16
20	0.2899	0.0892	0.75	27.97	8.61	30.54
$Y = SO_4$						
10	0.5891	1.1925	0.75	113.69	220.13	182.27
20	0.5775	1.1775	1.25	111.45	227.24	179.16
$Y = CrO_4$						
10	0.4233	1.2	1.00	81.69	231.58	150.7
20	0.4120	1.2	1.00	79.51	231.65	148.52
$Y = Cr_2O_7$						
10	0.5437	1.13	1.0	104.92	218.07	169.91
20	0.5319	1.1592	−1.25	102.65	223.71	169.31
$Z = PO_4$						
10	0.3810	1.2575	0.25	110.29	364.01	218.77
20	0.3668	1.2867	0.0	106.76	372.47	217.17
$Z = AsO_4$						
10	0.3424	1.2542	2.25	99.12	363.06	207.31
20	0.3285	1.3367	−1.0	95.09	386.94	210.40
Ethylene glycol: $X = N_3$						
10	0.2874	0.3608	−2.75	27.73	34.81	38.11
30	0.2806	0.3594	−2.25	27.08	34.66	37.40
X = CNS						
10	0.0763	−0.6467	1.0	7.36	−62.4	−11.23
30	0.0735	−0.5592	0.25	7.09	−53.96	−8.99
$Y = SO_4$						
10	0.5933	1.0358	−2.25	114.5	199.9	174.06
30	0.5824	1.2842	0.25	112.4	247.82	186.24
$Y = CrO_4$						
10	0.4550	0.9142	−3.75	87.8	176.52	140.38
30	0.4426	1.075	0.50	85.42	207.46	147.24
$Y = Cr_2O_7$						
10	0.5274	1.4067	0.0	101.78	271.47	182.68
30	0.5239	1.2367	0.0	101.10	238.66	172.22
$Z = PO_4$						
10	0.4025	1.7467	−2.0	116.51	505.62	267.19
30	0.3737	1.6442	1.25	108.18	475.95	250.10

TABLE 1 (continued)

Mass% organic solvent	$a = E_m^0$ (at 25 °C)	$-b \times 10^3$	$c \times 10^6$	$-\Delta G_m^0$	$-\Delta S_m^0$	$-\Delta H_m^0$
$Z = AsO_4$						
10	0.3495	1.780	−1.0	101.17	515.26	254.72
30	0.3295	1.690	1.0	95.38	489.21	241.17
Ag/Ag^+						
10	0.7770	1.2042	−0.75	74.97	116.19	109.6
30	0.7730	1.207	−2.0	74.59	116.46	109.29

[a] Uncertainties in $\Delta G_m^0 = \pm 0.03$ kJ mol^{-1}, $\Delta H_m^0 = \pm 0.04$ kJ mol^{-1} and in $\Delta S_m^0 = \pm 20$ J mol^{-1} K^{-1}.

the same applies for the other thermodynamic quantities, ΔS_t^0 and ΔH_t^0. As usual [1,2], the values of $\Delta G_{t,el}^0$ and $\Delta S_{t,el}^0$ have been evaluated from the Born equations:

$$\Delta G_{t,el}^0 = (Ne^2/2)(\epsilon_s^{-1} - \epsilon_w^{-1})(r_+^{-1} + r_-^{-1}) \quad (8)$$

and

$$\Delta S_{t,el}^0 = (-Ne^2/2)(\epsilon_s^{-1}\theta_s^{-1} - \epsilon_w^{-1}\theta_w^{-1})(r_+^{-1} + r_-^{-1}) \quad (9)$$

where N is Avogadro's number, e is the electric change, ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively, θ_s and θ_w are the temperature coefficients of dielectric constants of the mixed solvent and water, respectively, and r_+ and r_- are the radius of the cation and anion, respectively. Values of the dielectric constants of water and various mixed solvents at the required temperatures were taken from the literature [3,4,7]. Values of θ_s and θ_w were either taken from the literature [2b,4] or computed from dielectric constant values [2b] of the solvents concerned. The ionic radii of Ag^+ ion and different anions were taken from our earlier communication [1b]. 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 these parameters were obtained from the usual relations [1,2]. Values at 25 °C are recorded in Table 2.

Values of the primary medium effect, which is represented by

$$\lim_{N \to 0} (\log {}^s\gamma_w) = (E_N^0)_w - (E_N^0)_s/2.3026(RT/nF)$$

where $(E_N^0)_w$ and $(E_N^0)_s$ are the standard potentials on the mole fraction scale in water and mixed solvent, respectively, and $n = 1$, 2 or 3, in various mixed solvents, are presented in Table 2 for 25 °C only.

The thermodynamic solubility products, K_s^0, of AgX ($X = Cl$, Br, I, N_3, CNS), Ag_2Y ($Y = SO_4$, CrO_4, Cr_2O_7) and Ag_3Z ($Z = PO_4$, AsO_4) in different mixed solvents have been calculated at different temperatures from values of the standard potentials by means of the following equations:

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

$$\ln K_s^0(\mathrm{Ag_2Y}) = [E_c^0(\mathrm{Ag/Ag_2Y}) - E_c^0(\mathrm{Ag/Ag^+})](2F/RT)$$

and

$$\ln K_s^0(\mathrm{Ag_3Z}) = [E_c^0(\mathrm{Ag/Ag_3Z}) - E_c^0(\mathrm{Ag/Ag^+})](3F/RT)$$

where E_c^0 is the standard molar potential of the Ag,AgX; Ag,Ag_2Y; and Ag,Ag_3Z electrodes obtained in the present study or obtained from the literature [2] and $E_c^0(\mathrm{Ag/Ag^+})$ is the standard molar potential of the silver electrode in various mixed solvents determined in the present investigation in water + ethylene glycol or obtained from our earlier work [2b] in water + methanol, + ethanol, + 1-propanol and + 2-propanol mixtures. Data for K_s^m (on the molal scale) were calculated from K_s^c/ρ^2, where ρ is the density of the mixed solvent. The solubility product data in any solvent were fitted by least squares to the equation

$$\log K_s^0(\mathrm{AgX, Ag_2Y\ or\ Ag_3Z}) = A/T + B \tag{10}$$

where T is the temperature in Kelvin. The constants A and B of eqn. (10) in the molal scale are shown in Table 3 along with values of σ, the standard deviation of the least-squares fit. The correlation coefficient for these relations is 0.997, 0.998 and 0.998 for AgX, Ag_2Y and Ag_3Z, respectively, in all solvents.

A comparison of the E_m^0 values of the electrodes in water + methanol, + ethanol, + 1-propanol, + 2-propanol and + ethylene glycol (Table 1) with those in water [1] shows that the E_m^0 values are less in these mixed solvents than in water and decrease with increasing the organic solvent content in the mixed solvents. The lowering of E_m^0 values with increasing proportion of organic co-solvent is in agreement with the electrostatic charging (Born) effect.

It is evident from Table 1 that the standard Gibbs free energy changes for the electrode reactions increase with an increase in the organic co-solvent content in the mixed solvent. The standard enthalpy and entropy changes are all negative (except for the silver–silver thiocyanate electrode in water + ethylene glycol mixtures) but the solvent effect on the magnitudes of these quantities appears to be irregular. The difference in magnitudes of the ΔH^0 and ΔS^0 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 ions from water to the solvent concerned.

TABLE 2

Transfer thermodynamic quantities (mole fraction scales) for X^- (in water) → X^- (in mixed solvent), Y^{2-} (in water) → Y^{2-} (in mixed solvent) and Z^{3-} (in water) → Z^{3-} (in mixed solvent) (where $X = N_3$; $Y = SO_4$, CrO_4 or Cr_2O_7; $Z = PO_4$ or AsO_4) and primary medium effect in water + alcohol and + ethylene glycol mixtures at 25 °C (ΔG^0 and ΔH^0 in kJ mol^{-1}; ΔS^0 in J mol^{-1} K^{-1})

Mass% organic solvent		ΔG^0_t =	$\Delta G^0_{t,el}$ +	$\Delta G^0_{t,ch}$	ΔS^0_t =	$-\Delta S^0_{t,el}$ +	$\Delta S^0_{t,ch}$	ΔH^0_t =	$-\Delta H^0_{t,el}$ +	$\Delta H^0_{t,ch}$	$\lim_{N \to 0}(\log {}^s\gamma_w)$
Methanol											
10	$X = N_3$	0.12	0.13	−0.01	14.53	0.95	15.48	4.43	0.15	4.58	0.0203
20		0.10	0.24	−0.14	14.2	1.65	15.85	4.31	0.25	4.56	0.0169
10	$Y = SO_4$	−0.44	0.08	−0.52	3.28	0.60	3.88	0.53	0.10	0.63	−0.0778
20		1.51	0.15	1.36	−19.49	1.04	−18.45	−4.30	0.16	4.14	0.2637
10	$Y = CrO_4$	0.96	0.08	0.88	−35.66	0.60	−35.06	−9.67	0.10	−9.57	0.1690
20		2.78	0.15	2.63	−38.36	1.04	−37.32	−8.66	0.16	−8.50	0.4868
10	$Y = Cr_2O_7$	−0.79	0.08	−0.87	35.55	0.60	36.15	9.8	0.10	9.90	−0.1386
20		1.12	0.15	0.97	24.61	1.04	25.65	8.45	0.16	8.61	0.1961
10	$Z = PO_4$	16.36	0.10	16.26	121.95	0.70	122.65	52.52	0.11	52.63	2.8652
20		18.41	0.18	18.23	112.08	1.21	118.29	51.63	0.18	51.81	3.2252
10	$Z = AsO_4$	14.99	0.095	14.895	55.37	0.69	56.06	31.62	0.11	31.73	2.6269
20		16.88	0.177	16.703	61.39	1.19	62.58	35.29	0.18	35.47	2.9565
Ethanol											
10	$X = N_3$	0.12	0.16	−0.04	11.88	1.12	13.00	3.64	0.17	3.81	0.0203
20		−0.14	0.30	−0.44	16.54	2.01	18.55	4.77	0.30	5.07	−0.0254
10	$Y = SO_4$	−0.38	0.10	−0.48	2.03	0.71	2.74	0.22	0.11	0.33	−0.0676
20		1.74	0.19	1.55	−4.24	1.27	−2.97	0.48	0.19	0.67	0.3043
10	$Y = CrO_4$	2.32	0.10	2.22	−42.97	0.71	−41.26	−10.2	0.11	−10.09	0.4057
20		4.01	0.19	3.82	−33.29	1.27	−32.02	−5.91	0.19	−5.72	0.7032

10	$Y = Cr_2O_7$	0.38	0.10	0.28	35.88	0.71	36.59	11.08	0.11	11.19	0.0676
20		2.01	0.19	1.82	38.44	1.27	39.71	13.46	0.19	36.65	0.3516
10	$Z = PO_4$	18.58	0.12	18.46	58.03	0.82	58.85	35.88	0.12	36.00	3.2557
20		20.06	0.22	19.84	84.32	1.48	85.80	45.01	0.22	45.23	3.5143
10	$Z = AsO_4$	15.11	0.115	14.995	101.19	0.81	102.00	45.39	0.13	45.52	2.6471
20		16.67	0.217	16.453	116.39	1.46	117.85	51.48	0.22	51.70	2.9210
1-Propanol											
10	$X = N_3$	−0.20	0.18	−0.38	16.46	1.27	17.73	4.69	0.20	4.89	−0.0355
20		−0.49	0.35	−0.84	18.71	2.35	21.06	5.07	0.35	5.42	−0.0862
10	$Y = SO_4$	3.03	0.12	2.91	−23.39	0.81	−22.58	−3.94	0.12	−3.82	0.5308
20		3.84	0.22	3.62	−4.24	1.49	−2.75	2.57	0.22	2.79	0.6728
10	$Y = CrO_4$	3.61	0.12	3.49	−6.91	0.81	−6.10	1.55	0.12	1.67	0.6322
20		4.71	0.22	4.49	−2.08	1.49	−0.59	4.08	0.22	4.30	0.8249
10	$Y = Cr_2O_7$	1.95	0.12	1.88	41.01	0.81	41.82	14.17	0.12	14.29	0.3415
20		3.11	0.22	2.89	37.81	1.49	39.30	14.37	0.22	14.59	0.5443
10	$Z = PO_4$	18.29	0.13	18.16	88.43	0.94	89.37	44.05	0.15	44.20	3.205
20		19.77	0.26	19.51	88.66	1.73	90.39	46.01	0.26	46.27	3.4636
10	$Z = AsO_4$	15.40	0.132	15.268	117.6	0.92	118.52	50.57	0.14	50.71	2.6979
20		17.19	0.257	16.933	122.67	1.71	124.38	53.87	0.25	54.12	3.0123
2-Propanol											
10	$X = N_3$	−0.15	0.19	−0.34	17.18	1.24	18.42	4.95	0.18	5.13	−0.0270
20		−0.41	0.38	−0.79	17.19	2.33	19.82	4.70	0.31	5.01	−0.0710
10	$Y = SO_4$	2.78	0.12	2.66	5.25	0.79	6.04	4.34	0.12	4.46	0.4868
20		4.25	0.24	4.01	9.42	1.48	10.90	7.05	0.20	7.25	0.7438
10	$Y = CrO_4$	4.26	0.12	4.16	−13.33	0.79	−12.54	0.29	0.12	0.41	0.7472
20		5.65	0.24	5.41	−12.06	1.48	−10.58	2.06	0.20	2.26	0.9906
10	$Y = Cr_2O_7$	1.93	0.12	1.81	54.85	0.79	55.64	18.27	0.12	18.39	0.3381
20		3.42	0.24	3.18	50.83	1.48	52.31	18.59	0.20	18.79	0.5984
10	$Z = PO_4$	19.59	0.14	19.45	91.32	0.92	92.24	46.63	0.13	46.76	3.433

TABLE 2 (continued)

Mass% organic solvent		ΔG^0_t =	$\Delta G^0_{t,el}$ +	$\Delta G^0_{t,ch}$	ΔS^0_t =	$-\Delta S^0_{t,el}$ +	$\Delta S^0_{t,ch}$	ΔH^0_t =	$-\Delta H^0_{t,el}$ +	$\Delta H^0_{t,ch}$	$\operatorname{Lim}_{N \to 0}(\log {}^s\gamma_w)$
20		22.55	0.28	22.27	85.3	1.72	87.02	47.81	0.23	48.04	3.9504
10	$Z = AsO_4$	15.86	0.138	15.722	125.8	0.90	126.7	53.47	0.13	53.6	2.7790
20		18.73	0.273	18.457	104.35	1.69	106.04	49.96	0.23	50.19	3.2810
Ethylene glycol											
10	$X = N_3$	0.22	0.06	0.16	−10.56	0.64	−9.92	−2.94	0.13	−2.81	0.0389
30		0.06	0.18	−0.12	−7.51	1.69	−5.82	−2.2	0.32	−1.88	0.0101
10	$X = CNS$	0.78	0.04	0.74	161.93	0.46	162.39	49.15	0.10	49.25	0.1369
30		0.22	0.13	0.09	156.38	1.21	157.59	46.94	0.23	47.17	0.0389
10	$Y = SO_4$	1.96	0.04	1.92	34.2	0.41	34.61	12.15	0.08	12.23	0.3448
30		2.44	0.12	2.32	−7.94	1.07	−6.87	0.07	0.20	0.27	0.4260
10	$Y = CrO_4$	−1.85	0.04	−1.89	40.52	0.41	40.93	10.23	0.08	10.31	−0.3246
30		−1.10	0.12	−1.22	15.28	1.07	16.35	3.45	0.20	3.65	−0.1927
10	$Y = Cr_2O_7$	5.08	0.04	5.04	0.48	0.41	0.89	5.22	0.08	5.30	0.8891
30		4.11	0.12	3.99	39.08	1.07	40.15	15.75	0.20	15.95	0.7201
10	$Z = PO_4$	13.37	0.041	13.329	−51.82	0.47	−51.35	−2.25	0.10	−2.15	2.3429
30		19.24	0.134	19.116	−13.38	1.24	12.14	15.09	0.24	15.33	3.3723
10	$Z = AsO_4$	13.81	0.04	13.77	−26.99	0.47	−26.52	5.89	0.10	5.99	2.4189
30		17.14	0.13	17.01	−6.88	1.23	−5.65	19.31	0.24	19.55	3.0021
10	Ag/Ag^+	1.79	0.03	1.76	−19.71	0.31	−19.40	−4.08	0.06	−4.02	0.3127
30		1.35	0.09	1.26	−17.08	0.81	−16.27	−3.74	0.15	−3.59	0.2367

TABLE 3

Constants of eqn. (10) on the molal (m) scale for different silver salts

Wt.% organic solvent		A	$-B \times 10^3$	σ
Methanol				
10	$X = N_3$	−3876.5205	−4553.6971	0.126
20		−3898.1278	−4725.2987	0.127
10	$Y = SO_4$	−1213.6052	2131.8962	0.048
20		−969.6564	3167.8243	0.031
10	$Y = CrO_4$	−2509.8119	3368.2130	0.081
20		−2315.3814	4176.5264	0.075
10	$Y = Cr_2O_7$	−1648.2282	2300.8559	0.054
20		−1582.7283	2667.7359	0.052
10	$Z = PO_4$	−5338.1002	2244.6342	0.174
20		−5292.0165	2481.3878	0.172
10	$Z = AsO_4$	−4499.2488	7435.0677	0.146
20		−4667.6037	6919.1305	0.152
Ethanol				
10	$X = N_3$	−3889.5073	−4820.3353	0.126
20		−3549.6286	−3362.3810	0.116
10	$Y = SO_4$	−1104.9980	2066.3689	0.036
20		−706.2126	4488.4155	0.023
10	$Y = CrO_4$	−2575.2551	2954.0282	0.084
20		−2138.9546	5450.8003	0.069
10	$Y = Cr_2O_7$	−1722.1426	1813.4664	0.056
20		−1201.6697	4581.9456	0.039
10	$Z = PO_4$	−4402.5692	5100.0190	0.143
20		−3884.8084	8203.4749	0.125
10	$Z = AsO_4$	−5109.8581	4721.0051	0.167
20		−4529.9274	8064.9580	0.147
1-Propanol				
10	$X = N_3$	−3542.8917	−3744.6038	0.115
20		−3784.0582	−4469.4110	0.123
10	$Y = SO_4$	−375.9334	5043.0604	0.012
20		−1097.9258	3038.2897	0.036
10	$Y = CrO_4$	−2501.6944	3357.9585	0.082
20		−3028.5631	2057.6213	0.098
10	$Y = Cr_2O_7$	−1196.4825	3778.6730	0.039
20		−1696.3463	2592.1384	0.055
10	$Z = PO_4$	−3872.0498	6722.8937	0.126
20		−4638.3284	4844.9436	0.151
10	$Z = AsO_4$	−4425.5801	6969.3672	0.144
20		−5266.1689	4893.7347	0.171
2-Propanol				
10	$X = N_3$	−3797.3915	−4449.7343	0.123
20		−3607.4230	−3714.4217	0.118
10	$Y = SO_4$	−1045.5109	3039.6937	0.034
20		−1007.4074	3708.9318	0.032

TABLE 3 (continued)

Wt.% organic solvent		A	$-B \times 10^3$	σ
2-Propanol				
10	$Y = CrO_4$	−2743.9492	2940.1809	0.089
20		−2611.7218	3919.1344	0.085
10	$Y = Cr_2O_7$	−1682.5922	2434.1598	0.054
20		−1592.3100	3294.7593	0.052
10	$Z = PO_4$	−4436.5656	5499.3186	0.144
20		−4247.4213	7086.5640	0.318
10	$Z = AsO_4$	−4256.2428	8147.4136	0.138
20		−4646.3982	7695.3610	0.151
Ethylene glycol				
10	$X = Cl$	−3711.8714	−2942.6479	0.121
30		−3620.4214	−2501.0789	0.118
10	$X = Br$	−4724.9421	3843.8521	0.154
30		−4624.8930	3404.8842	0.151
10	$X = N_3$	−3778.1134	−4390.3416	0.123
30		−3739.5615	−4192.8213	0.122
10	$X = CNS$	−6298.4056	−9284.9781	0.205
30		−6117.3975	−8682.9999	0.199
10	$Y = SO_4$	−2418.9559	−1892.0597	0.078
30		−1586.8379	1145.0571	0.052
10	$Y = CrO_4$	−4216.7358	−3247.4867	0.137
30		−3614.6911	−934.2642	0.117
10	$Y = Cr_2O_7$	−1882.0495	2121.0460	0.061
30		−2324.2092	649.8528	0.075
10	$Z = PO_4$	−3284.3592	7986.8066	0.109
30		−3859.5973	7314.4359	0.126
10	$Z = AsO_4$	−3894.3656	8621.8507	0.127
30		−4332.0809	7973.0224	0.141

As the sign of the ΔG_t^0 values gives an indication of the stabilization of the ions in the solvents concerned, the positive values of ΔG_t^0 (Table 2) signify that the ions in question are more strongly stabilized in water than in mixed solvents, and hence the transfer of those ions from water to the mixed solvents is not favourable. On the other hand, negative ΔG_t^0 values indicate that transfer of the ions concerned from water to the mixed solvent is favourable and the ions interact strongly with the organic co-solvent molecules in the mixed solvents in preference to water molecules. The positive ΔS_t^0 values for the ions (Table 2) indicate that the ions "break the solvent structure" more effectively in the mixed solvents than in water. Consequently the degree of solvent orientation is less in the mixed solvents than in water. Thus the net amount of order created by such ions is less in the mixed solvents than in water, and hence these ions break down more structure in the mixed solvents concerned, whereas, the reverse is the case for the negative values of ΔS_t^0 in the mixed solvents. The positive values of ΔH_t^0 suggest that the transfer process is endothermic because of the dehydration and subsequent resolvation of the ions by the organic co-solvent. The positive and increasing magnitude of the primary medium effect (Table 2) suggests that the escaping tendency of the ions is greater in the mixed solvents than in the aqueous medium. This is in agreement with conclusions based on the fact that the ions with positive ΔG_t^0 values are more strongly stabilized in water than in the mixed solvents.

As expected, the solubility of the silver salts decreases with increasing proportion of organic solvent in the mixed solvents. However, the solvent effect on the solubilities of the silver salts seems to be irregular. It is found that the solubility of the silver salts (except that of silver phosphate and silver arsenate) is greater in the mixed solvents than in water. The higher solubility may be due to the fact that the silver salts are more strongly solvated in the mixed solvents than in water. In any solvent, the solubility of the silver salts follows the order: $Ag_2SO_4 > Ag_2Cr_2O_7 > AgN_3 > AgCl > Ag_2CrO_4 > AgCNS > AgBr > Ag_3PO_4 > Ag_3AsO_4$.

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