

THERMODYNAMIC PROPERTIES OF THE SILVER ION IN ALCOHOL + WATER SOLVENT MIXTURES FROM ELECTROMOTIVE FORCE MEASUREMENTS AND THERMODYNAMIC SOLUBILITY PRODUCT CONSTANTS OF AgX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or CNS) AT DIFFERENT TEMPERATURES

UPENDRA NATH DASH, BANKA BEHARI DAS, UTTAM KUMAR BISWAL, TAPODHAN PANDA, NARENDRA KUMAR PUROHIT, DUSHMANTA KUMAR RATH and SHUBHANKAR BHATTACHARYA

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

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ABSTRACT

The standard potentials of the silver–silver ion electrode in alcohol+water solvent mixtures containing 10 and 20 wt% methanol, ethanol, 1-propanol and 2-propanol have been determined from the electromotive force measurements of the cell $\text{Ag(s)}, \text{AgCl(s)}, \text{NaCl(c)}, \text{NaNO}_3(\text{c})// \text{NaNO}_3(\text{c}), \text{AgNO}_3(\text{c}), \text{Ag(s)}$ at seven different temperatures in the range 5–35°C. The standard potentials in each solvent have been represented as a function of temperature. The standard thermodynamic functions for the electrode reaction, the primary medium effects of various solvents upon Ag^+ , and the standard thermodynamic quantities for the transfer of 1 g-ion of Ag^+ from water to the respective alcohol+water media have been evaluated and discussed in the light of ion–solvent interactions as well as the structural changes of the solvents. From the values of the standard potentials of the Ag/Ag^+ and $\text{Ag}/\text{AgX}, \text{X}^-$ electrodes, the thermodynamic solubility product constants of silver chloride, silver bromide, silver iodide and silver thiocyanate have been determined in alcohol+water solvent mixtures at different temperatures.

INTRODUCTION

Until quite recently no exhaustive studies on the behaviour of silver–silver ion electrode in binary solvent systems had been made. Dash et al. [1] first reported the standard potentials of the silver–silver ion electrode in various compositions of urea + water and dioxane + water mixtures at different temperatures ranging from 5 to 35°C from a study of the cell



The present work deals with similar studies made on cell (A) in the temperature range 5–35°C with a view to determining the standard potentials of the Ag/Ag^+ electrode and the relevant thermodynamic functions for

the Ag^+ ion in alcohol + water solvent mixtures containing 10 and 20 wt% methanol, ethanol, 1-propanol and 2-propanol at these temperatures. In addition, the thermodynamic solubility product constants of AgX (X is Cl, Br, I or CNS) have been evaluated in these solvent mixtures at different temperatures.

EXPERIMENTAL

Sodium chloride, sodium nitrate, and silver nitrate were the same samples as used in earlier studies [1]. Methanol, ethanol, 1-propanol and 2-propanol were purified as described earlier [2]. Silver and silver-silver chloride electrodes were prepared as described earlier [1]. The solvent mixtures of various mass percentages were prepared as described previously [2].

Preparation of the cell solutions, setting up of the cells, EMF and conductance measurements were essentially similar to the procedures described earlier [3]. All measurements were made in water baths at the required temperature with a precision of $\pm 0.1^\circ\text{C}$. The reproducibility of EMF measurements was of the order of ± 0.2 mV.

RESULTS AND DISCUSSION

As previously [1], the EMF, E , of cell (A) is given by the expression

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

where the symbols have their usual meanings.

The standard molar potential E_c^0 of the silver-silver ion electrode was obtained by the method of extrapolating [4] the auxiliary function $E_c^{0'}$ given by

$$\begin{aligned} E_c^{0'} &= E + E_c^0(\text{Ag}, \text{AgCl}) - 2k \log C + 2kA(2C)^{1/2}/1 + (2C)^{1/2} - E_j \\ &= E_c^0(\text{Ag}, \text{Ag}^+) + bC \end{aligned} \quad (2)$$

to the molarity $C = 0$, where $E_c^0(\text{Ag}, \text{AgCl})$ is the standard molar potential of the silver-silver chloride electrode, and are calculated from the molal potential [5] using the density values [5] over the temperature range under investigation for various alcohol + water solvent mixtures.

As in earlier communications [1], the values of the liquid junction potentials E_j were calculated and found to vary in the range 0.1–0.3 mV in all solvents for all temperatures. The values of E_c^0 obtained on extrapolating $E_c^{0'}$ to $C=0$ are presented in Table 1. The average standard deviation in the values of E_c^0 is ± 0.3 mV.

Standard potentials on the molar (E_c^0), molal (E_m^0) and mole fraction

TABLE 1

Standard molar potentials (E_c^0 in abs. volts) for the Ag(s)-Ag⁺ electrodes in alcohol + water mixtures from 5 to 35°C

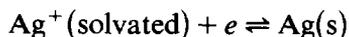
| Wt. % | Organic solvent | $t(^{\circ}\text{C})$ | | | | | | |
|-------|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|
| | | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| 0 | | 0.8186 | 0.8138 | 0.8089 | 0.8031 | 0.7991 | 0.7950 | 0.7891 |
| 10 | Methanol | 0.8102 | 0.8047 | 0.7999 | 0.7954 | 0.7904 | 0.7850 | 0.7803 |
| 20 | | 0.8029 | 0.7972 | 0.7917 | 0.7870 | 0.7820 | 0.7766 | 0.7719 |
| 10 | Ethanol | 0.7967 | 0.7918 | 0.7868 | 0.7819 | 0.7762 | 0.7710 | |
| 20 | | 0.8092 | 0.8055 | 0.8020 | 0.7988 | 0.7943 | 0.7895 | 0.7849 |
| 10 | 1-Propanol | 0.7902 | 0.7864 | 0.7821 | 0.7774 | 0.7739 | 0.7696 | 0.7652 |
| 20 | | 0.7970 | 0.7922 | 0.7871 | 0.7827 | 0.7779 | 0.7726 | 0.7679 |
| 10 | 2-Propanol | 0.8008 | 0.7958 | 0.7908 | 0.7861 | 0.7822 | 0.7776 | 0.7736 |
| 20 | | 0.8032 | 0.7992 | 0.7943 | 0.7910 | 0.7865 | 0.7825 | 0.7782 |

(E_N^0) scales (correlated by the usual equation [4]) at different temperatures for any solvent were fitted, by the method of least-squares, to an equation of the form [6]

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

where x is C, m or N and T is any temperature in kelvins. The constants A , B , C and D of eqn. (3) for different solvent mixtures are shown in Table 2. The average deviation between the experimental values (Table 1) and values calculated from eqn. (3) is within ± 0.3 mV. The E^0 values at 25°C are reported in Table 3 along with those in water [5].

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



at different temperatures in various solvents have been evaluated by the usual relations [4]. These values for 25°C are presented in Table 3, which shows that Gibbs free energy change decreases with increasing alcohol (except methanol) contents of the solvent system, i.e., with decreasing the dielectric constant of the solvent. The lowering of Gibbs free energy change with increase of ethanol, 1-propanol and 2-propanol contents of the solvent systems may be due to the fact that the Ag⁺ is more solvated in the solvents containing the increased proportion of ethanol, 1-propanol and 2-propanol. The standard enthalpy and entropy changes are found to be negative for all

TABLE 2

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

| wt. % | Organic solvent | x | A | B | C | D × 10 ⁴ |
|-------|-----------------|---|-------------|------------|------------|---------------------|
| 10 | Methanol | c | -41.15215 | 1.6469052 | -0.2904725 | 9.979 |
| | | m | -32.316925 | 1.3039053 | -0.230077 | 7.917 |
| | | N | -36.8588901 | 1.4793817 | -0.26109 | 8.975 |
| 20 | | c | 1.4970167 | -0.0058629 | 0.0004377 | 0.06505 |
| | | m | -1.513724 | 0.11223 | -0.020397 | 0.7843 |
| | | N | 12.741505 | -0.44084 | 0.076824 | -2.5264 |
| 10 | Ethanol | c | 77.743608 | -2.9944922 | 0.52777 | 18.157 |
| | | m | 21.88068 | -0.83068 | 0.1469331 | 5.183 |
| | | N | -18.7227 | 0.7659045 | -0.135118 | 4.606 |
| 20 | | c | -10.26658 | 0.427705 | -0.0750691 | 2.489 |
| | | m | -13.28942 | 0.5458456 | -0.0959024 | 3.207 |
| | | N | -26.153998 | 1.0456831 | -0.184074 | 6.226 |
| 10 | 1-Propanol | c | -2.731181 | 0.138501 | -0.024289 | 0.781 |
| | | m | 2.493284 | -0.0635393 | 0.0112493 | 0.424 |
| | | N | -31.79637 | 1.267543 | -0.223272 | 7.589 |
| 20 | | c | 41.506558 | -1.569233 | 0.276081 | -9.416 |
| | | m | 5.8068247 | -0.1827603 | 0.0319255 | -1.0734 |
| | | N | 8.744291 | -0.2973118 | 0.0519733 | -1.757 |
| 10 | 2-propanol | C | -10.85268 | 0.4720166 | -0.083678 | 2.936 |
| | | m | -0.496413 | 0.0709852 | -0.013103 | 0.534 |
| | | N | -11.34739 | 0.5057399 | -0.090309 | 3.274 |
| 20 | | c | 122.0988 | -4.7022575 | 0.8278971 | 28.284 |
| | | m | 114.5435 | -4.4080102 | 0.7760494 | 26.506 |
| | | N | 117.4748 | -4.5225206 | 0.7960972 | 27.191 |

the solvents and increase with increase of alcohol contents (except for 1-propanol) of the solvent systems.

The primary medium effect represents the difference in ion-solvent interaction for Ag^+ at infinite dilution in the particular mixed solvent and in water. It measures the change in escaping tendency of the Ag^+ ion in the transfer from a standard state in one solvent to a standard state in another. The values of the primary medium effect (mole fraction scale) of various alcohol + water mixtures upon the Ag^+ ion at 25°C were computed using eqn. (4)

$$\lim_{N \rightarrow 0} (\log {}^s\gamma_w) = [(E_N^0)_w - (E_N^0)_s] / 2.3026(RT/F) \quad (4)$$

$N \rightarrow 0$

where the limit term indicates the primary medium effect. These values are also included in Table 3. The medium has a greater effect upon the silver ion

TABLE 3

Values of the standard potentials of the silver-silver ion electrode on the molar (E_c^0), molal (E_m^0), and mole fraction (E_N^0) scales in alcohol + water mixtures and thermodynamic quantities on the molal scale at 25°C

| | Wt. % organic solvent | | | | | | | | | | | |
|--|-----------------------|--------|--------|---------|--------|--------|------------|--------|--------|------------|----|----|
| | Methanol | | | Ethanol | | | 1-Propanol | | | 2-Propanol | | |
| | 10 | 20 | 20 | 10 | 10 | 20 | 10 | 10 | 20 | 10 | 10 | 20 |
| E_c^0 (V) | 0.7896 | 0.7820 | 0.7820 | 0.7767 | 0.7939 | 0.7737 | 0.7780 | 0.7818 | 0.7874 | | | |
| E_m^0 (V) | 0.7910 | 0.7833 | 0.7833 | 0.7776 | 0.7956 | 0.7743 | 0.7791 | 0.7829 | 0.7890 | | | |
| E_N^0 (V) | 0.5866 | 0.5819 | 0.5819 | 0.5741 | 0.5958 | 0.5719 | 0.5807 | 0.5798 | 0.5905 | | | |
| $-10^3 \Delta G_m^0$ (J mole ⁻¹) | 76.32 | 75.6 | 75.6 | 75.0 | 76.8 | 74.7 | 75.2 | 75.5 | 76.1 | | | |
| $-10^3 \Delta H_m^0$ (J mole ⁻¹) | 105.5 | 104.4 | 104.4 | 106.9 | 101.3 | 98.8 | 102.0 | 100.1 | 93.9 | | | |
| $-\Delta S_m^0$ (J mole ⁻¹ K ⁻¹) | 99.0 | 96.0 | 96.0 | 107.0 | 82.0 | 81.0 | 89.0 | 82.0 | 59.0 | | | |

as the alcohol content of the solvent systems increases. This suggests that the escaping tendency of the Ag^+ ion is greater in alcohol + water solvents than in water medium.

The standard changes of Gibbs free energy (ΔG_t^0), entropy (ΔS_t^0) and enthalpy (ΔH_t^0) for the transfer of 1 g-ion of Ag^+ from the standard state in water to the standard states of the mixed solvents were calculated by the usual thermodynamic relations [4,6,7] on the mole fraction scale [8]. The values of these quantities at 25°C are given in Table 4 for various alcohol + water solvent mixtures. The standard Gibbs free energies of transfer are positive for all the solvent compositions (except for 20 wt.% ethanol) and decrease with increasing alcohol content, except methanol, in the solvent mixture. The positive ΔG_t^0 values indicate that the Ag^+ ion is in a higher free energy state in alcohol + water solvent mixtures than in water, suggesting that water has more affinity for the Ag^+ ion than alcohol + water solvent mixtures have. The values of ΔS_t^0 and ΔH_t^0 are positive except for methanol (in 10 wt.% ethanol only ΔS_t^0 is negative) mixtures, so the entropy in alcohol + water mixtures is more than in pure water, and hence the net amount of order created by the Ag^+ ion in alcohol + water mixtures, except in methanol and 10 wt.% ethanol, is less than in pure water. The Ag^+ ion thus breaks more structure in the mixed solvent than in water. This is further supported with the view [9] that all structure-breaking processes, including desolvation of ions, are endothermic and are accompanied by a gain in entropy.

As previously [1,3,7], the transfer Gibbs free energy change is divided into two parts as

$$\Delta G_t^0 = \Delta G_{t,el}^0 + \Delta G_{t,ch}^0 \quad (5)$$

The electrostatic contribution to the Gibbs free energy of transfer ($\Delta G_{t,el}^0$) may be computed from the Born expression

$$\Delta G_{t,el}^0 = (Ne^2/2r_+) (\epsilon_s^{-1} - \epsilon_w^{-1}) \quad (6)$$

where the radius of the silver ion (r_+) may be taken as 0.126 nm [8], ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively, and were obtained from the literature [10]. The electrostatic part of the entropy of transfer can be calculated from

$$\Delta S_{t,el}^0 = (-Ne^2/2r_+) (\epsilon_s^{-1}\theta_s^{-1} - \epsilon_w^{-1}\theta_w^{-1}) \quad (7)$$

The values of θ_w and θ_s can be evaluated [11] from the slopes of the linear plots of $\ln \epsilon$ vs. T for water and the alcohol + water mixtures, using a simple empirical equation [5] in which θ is a constant, characteristic of the medium [5,8].

$$d \ln \epsilon / dT = -1/\theta \quad (8)$$

From a knowledge of $\Delta G_{t,el}^0$ and $\Delta S_{t,el}^0$ the electrostatic part of the enthalpy

TABLE 4
Transfer thermodynamic quantities and primary medium effect (mole fraction scale) in different alcohol + water mixtures at 25°C

| | Wt. % organic solvent | | | | | | | | | | | |
|--|-----------------------|-----------|----------|----------|----------|----------|------------|----------|----|------------|----|----|
| | Methanol | | | Ethanol | | | 1-Propanol | | | 2-Propanol | | |
| | 10 | 20 | 20 | 10 | 10 | 20 | 10 | 10 | 20 | 10 | 10 | 20 |
| ΔG^0 (J mole ⁻¹) | 607.896 | 1061.405 | 1814.038 | -279.825 | 2026.319 | 1177.195 | 1264.037 | 231.579 | | | | |
| ΔG_{cat}^0 (J mole ⁻¹) | 62.64 | 116.57 | 75.58 | 143.09 | 86.94 | 170.04 | 90.99 | 180.30 | | | | |
| ΔG_{ch}^0 (J mole ⁻¹) | 545.25 | 944.84 | 1738.463 | -422.92 | 1939.38 | 1007.18 | 1173.05 | 51.28 | | | | |
| ΔS_t^0 (J mole ⁻¹ K ⁻¹) | -2.56 | -5.45 | 5.16 | 12.83 | 9.94 | 7.72 | 17.18 | 38.89 | | | | |
| $-\Delta S_{\text{rel}}^0$ (J mole ⁻¹ K ⁻¹) | 0.458 | 0.79 | 0.534 | 0.861 | 0.610 | 1.13 | 0.594 | 1.12 | | | | |
| ΔS_{ch}^0 (J mole ⁻¹ K ⁻¹) | -2.10 | -50.66 | -4.63 | 13.69 | 10.55 | 8.85 | 17.77 | 40.01 | | | | |
| ΔH_t^0 (J mole ⁻¹) | -153.9 | -57311.17 | 254.45 | 3683.17 | 4972.31 | 3460.31 | 6374.42 | 11794.15 | | | | |
| $-\Delta H_{\text{cat}}^0$ (J mole ⁻¹) | 73.69 | 118.79 | 83.50 | 113.37 | 94.87 | 165.95 | 85.93 | 154.09 | | | | |
| ΔH_{ch}^0 (J mole ⁻¹) | -80.2083 | -57192.37 | 337.95 | 3796.54 | 5046.00 | 3626.26 | 6460.35 | 11948.24 | | | | |
| $\lim_{N \rightarrow 0} (\log^* \gamma_w)$ | 0.1068 | 0.1863 | 0.3181 | -0.0487 | 0.3553 | 0.2066 | 0.2218 | 0.0409 | | | | |

TABLE 5

Solubility product constants, on the molar(c) and molal(m) scales, of AgX (X = Cl, Br, I or CNS) in various alcohol + water mixtures at different temperatures

| X | Ref. | (°C) | | | | | | |
|--------------------------|------|-------|-------|-------|-------|-------|-------|-------|
| | | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| <i>10 wt. % methanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.245 | 0.420 | 0.704 | 1.168 | 1.877 | 2.899 | 4.251 |
| | 12 | | | | | 2.044 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.253 | 0.435 | 0.730 | 1.213 | 1.955 | 3.027 | 4.455 |
| | 12 | | | | | 2.129 | | |
| Br | | | | | | | | |
| $K_s^c \times 10^{13}$ | 17 | | | | | 5.755 | | |
| $K_s^m \times 10^{13}$ | | | | | | 5.993 | | |
| I | | | | | | | | |
| $K_s^c \times 10^{16}$ | 17 | | | | | 1.083 | | |
| $K_s^m \times 10^{16}$ | | | | | | 1.128 | | |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.107 | 0.217 | 0.429 | 0.849 | 1.639 | 3.010 | 5.302 |
| $K_s^m \times 10^{12}$ | | 0.105 | 0.224 | 0.445 | 0.883 | 1.707 | 3.144 | 5.556 |
| <i>20 wt. % methanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.239 | 0.425 | 0.729 | 1.207 | 1.925 | 2.982 | 4.498 |
| | 12 | | | | | 2.237 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.255 | 0.455 | 0.781 | 1.292 | 2.070 | 3.215 | 4.866 |
| | 12 | | | | | 2.405 | | |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.133 | 0.278 | 0.559 | 1.090 | 2.070 | 3.817 | 6.875 |
| $K_s^m \times 10^{12}$ | | 0.142 | 0.296 | 0.599 | 1.666 | 2.226 | 4.116 | 7.438 |
| <i>10 wt. % ethanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.427 | 0.745 | 1.271 | 2.051 | 3.234 | 5.222 | 8.623 |
| | 12 | | | | | 3.255 | | |
| | 13 | | | | 2.047 | 3.033 | 5.263 | 8.785 |
| | 15 | | | | | 3.015 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.441 | 0.772 | 1.317 | 2.129 | 3.374 | 5.449 | 9.026 |
| | 12 | | | | | 3.393 | | |
| | 13 | | | | 2.124 | 3.163 | 5.491 | 9.196 |
| | 15 | | | | | 3.142 | | |
| Br | | | | | | | | |
| $K_s^c \times 10^{12}$ | 21 | | | 0.313 | 0.571 | 1.023 | 1.836 | 3.386 |
| | 23 | | | 0.306 | 0.560 | 1.001 | 1.802 | 3.316 |
| $K_s^m \times 10^{12}$ | 21 | | | 0.325 | 0.593 | 1.066 | 1.916 | 3.544 |
| | 23 | | | 0.317 | 0.581 | 1.043 | 1.881 | 3.471 |

TABLE 5 (continued)

| X | Ref. | (°C) | | | | | | |
|----------------------------|------|-------|-------|-------|-------|-------|-------|--------|
| | | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.156 | 0.321 | 0.641 | 1.228 | 2.291 | 4.315 | 8.586 |
| $K_s^m \times 10^{12}$ | | 0.161 | 0.332 | 0.665 | 1.274 | 2.388 | 4.502 | 8.988 |
| <i>20 wt. % ethanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.161 | 0.272 | 0.449 | 0.779 | 1.168 | 1.814 | 2.750 |
| | 12 | | | | | 1.303 | | |
| | 13 | | | | 0.723 | 1.141 | 1.837 | 2.759 |
| | 15 | | | | | 1.140 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.171 | 0.290 | 0.479 | 0.832 | 1.250 | 1.947 | 2.970 |
| | 12 | | | | | 1.395 | | |
| | 13 | | | | 0.772 | 1.222 | 1.973 | 2.973 |
| | 15 | | | | | 1.220 | | |
| Br | | | | | | | | |
| $K_s^c \times 10^{12}$ | 21 | | | 0.134 | 0.245 | 0.435 | 0.751 | 1.278 |
| | 23 | | | 0.136 | 0.247 | 0.438 | 0.759 | 1.276 |
| $K_s^m \times 10^{12}$ | 21 | | | 0.143 | 0.262 | 0.466 | 0.807 | 1.377 |
| | 23 | | | 0.145 | 0.263 | 0.469 | 0.815 | 1.375 |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.088 | 0.170 | 0.322 | 0.602 | 1.115 | 2.021 | 3.597 |
| $K_s^m \times 10^{12}$ | | 0.933 | 0.181 | 0.343 | 0.643 | 1.194 | 2.171 | 3.876 |
| <i>10 wt. % 1-propanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.520 | 0.854 | 1.378 | 2.179 | 3.383 | 5.151 | 7.711 |
| | 16 | | | | | 3.342 | | |
| | 18 | | | | | 3.346 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.537 | 0.882 | 1.426 | 2.259 | 3.514 | 5.367 | 8.061 |
| | 16 | | | | | 3.472 | | |
| | 18 | | | | | 3.476 | | |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.269 | 0.517 | 0.967 | 1.788 | 3.252 | 5.705 | 9.982 |
| $K_s^m \times 10^{12}$ | | 0.278 | 0.534 | 1.001 | 1.853 | 3.378 | 5.944 | 10.433 |
| <i>20 wt. % 1-propanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.296 | 0.506 | 0.883 | 1.416 | 2.235 | 3.474 | 5.634 |
| | 16 | | | | | 2.051 | | |
| | 18 | | | | | 2.150 | | |
| $K_s^m \times 10^{10}$ | 5 | 0.314 | 0.538 | 0.940 | 1.510 | 2.390 | 3.726 | 6.063 |
| | 16 | | | | | 2.193 | | |
| | 18 | | | | | 2.299 | | |
| | 18 | | | | | 2.277 | | |

TABLE 5 (continued)

| X | Ref. | (°C) | | | | | | |
|----------------------------|------|-------|-------|-------|-------|-------|-------|-------|
| | | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| <i>10 wt. % 2-propanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.326 | 0.562 | 0.934 | 1.498 | 2.316 | 3.479 | 5.056 |
| | 15 | | | | | 2.399 | | |
| | 19 | | | | | 2.326 | | |
| | 22 | | | 0.957 | 1.522 | 2.326 | 3.483 | 4.996 |
| $K_s^m \times 10^{10}$ | 5 | 0.336 | 0.581 | 0.966 | 1.552 | 2.406 | 3.625 | 5.284 |
| | 15 | | | | | 2.492 | | |
| | 19 | | | | | 2.417 | | |
| | 22 | | | 0.990 | 1.578 | 2.417 | 3.629 | 5.222 |
| Br | | | | | | | | |
| $K_s^c \times 10^{12}$ | 20 | | | 0.222 | 0.407 | 0.717 | 1.221 | 2.002 |
| | 21 | 0.059 | 0.116 | 0.221 | 0.408 | 0.719 | 1.221 | 2.016 |
| $K_s^m \times 10^{12}$ | 20 | | | 0.229 | 0.422 | 0.745 | 1.272 | 2.092 |
| | 21 | 0.061 | 0.120 | 0.229 | 0.423 | 0.745 | 1.272 | 2.107 |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.128 | 0.257 | 0.506 | 0.964 | 1.786 | 3.225 | 5.568 |
| $K_s^m \times 10^{12}$ | | 0.132 | 0.266 | 0.523 | 0.999 | 1.855 | 3.360 | 5.820 |
| <i>20 wt. % 2-propanol</i> | | | | | | | | |
| Cl | | | | | | | | |
| $K_s^c \times 10^{10}$ | 5 | 0.194 | 0.343 | 0.576 | 0.887 | 1.328 | 1.979 | 3.028 |
| | 8 | 0.194 | 0.344 | 0.577 | 0.891 | 1.325 | 1.975 | 3.032 |
| | 15 | | | | | 1.391 | | |
| | 19 | | | | | 1.343 | | |
| | 22 | | | 0.579 | 0.873 | 1.277 | 1.857 | 2.808 |
| $K_s^m \times 10^{10}$ | 5 | 0.206 | 0.365 | 0.613 | 0.946 | 1.420 | 2.122 | 3.258 |
| | 8 | 0.206 | 0.366 | 0.615 | 0.950 | 1.417 | 2.118 | 3.263 |
| | 15 | | | | | 1.487 | | |
| | 19 | | | | | 1.436 | | |
| | 22 | | | 0.617 | 0.932 | 1.366 | 1.992 | 3.021 |
| Br | | | | | | | | |
| $K_s^c \times 10^{12}$ | 21 | 0.040 | 0.082 | 0.158 | 0.276 | 0.466 | 0.785 | 1.359 |
| $K_s^m \times 10^{12}$ | | 0.043 | 0.087 | 0.168 | 0.294 | 0.498 | 0.842 | 1.462 |
| CNS | | | | | | | | |
| $K_s^c \times 10^{12}$ | 2 | 0.128 | 0.261 | 0.510 | 0.920 | 1.614 | 2.853 | 5.282 |
| $K_s^m \times 10^{12}$ | | 0.136 | 0.277 | 0.543 | 0.981 | 1.726 | 3.060 | 5.684 |

change $\Delta H_{t,el}^0$ has been evaluated. The chemical contribution of the Gibbs free energy of transfer ($\Delta G_{t,ch}^0$), entropy of transfer ($\Delta S_{t,ch}^0$) and enthalpy of transfer ($\Delta H_{t,ch}^0$) can then be obtained by subtracting the respective electrostatic contribution values from the molar quantities. These values so obtained at 25°C are shown in Table 4.

The chemical contribution to the Gibbs free energy of transfer, $\Delta G_{t,ch}^0$ is positive for all solvents (except for 20 wt.% ethanol) and decreases with increasing alcohol content, except for methanol, in the solvent mixture. In so far as $\Delta G_{t,ch}^0$ is a criterion of the changes in the acidity or basicity of the medium, the positive value of $\Delta G_{t,ch}^0$ indicates that the transfer process from water to the respective mixed solvent is not favoured. Thus, as far as chemical reaction or solvation is concerned, the Ag^+ ion is in a lower Gibbs energy state in water than in the mixed solvent. In other words, the mixed solvents possess a smaller solvating capacity toward Ag^+ and are less basic (i.e., more acidic) than water. The positive values of $\Delta H_{t,ch}^0$ for ethanol, 1-propanol and 2-propanol contents of solvent mixtures reflect the larger enthalpy change involved in breaking down the solvent structure on the transfer process. This view is further supported by the positive value of $\Delta S_{t,ch}^0$ for these solvent mixtures (except for 10 wt.% ethanol), which is associated with an overall disorder created by the Ag^+ ion during the transfer process.

The thermodynamic solubility products K_{so}^0 of silver chloride, silver bromide, silver iodide and silver thiocyanate in alcohol + water mixtures have been calculated from the values of standard potentials by means of the equation

$$\ln K_{so}^0(AgX) = [E^0(Ag, AgX) - E^0(Ag, Ag^+)](F/RT) \quad (9)$$

where $E^0(Ag, AgX)$ is the standard molar potential of the Ag, AgX (X is Cl, Br, I or CNS) electrode and is either obtained from the literature [4] or calculated from the standard molal potentials [5,8,12–23] using the density data of the mixed solvents, over the temperature range under investigation. The values for K_{so}^0 on the molarity (K_{so}^c) and molality (K_{so}^m) scales at the experimental temperatures are listed in table 5. The data for K_{so}^m were calculated from K_{so}^c/ρ^2 . The solubility data were fitted by least squares to the usual equation [24,25]

$$\log K_{so}^p(AgX) = A/(T/K) + B \quad (10)$$

where p is c or m, and T is any temperature in kelvins.

The constants A and B of eqn. (10) are shown in Table 6 for various silver salts for all solvents, along with σ , the standard deviation for the precision of the least-squares fit; the correlation coefficient for the relations is within 1.00.

TABLE 6

Constants of eqn. (10) on molar (c) and molal (m) scales in alcohol+water mixtures for different silver salts

| AgX X≡ | Ref. | p | Wt.% organic solvent | | | | |
|-----------|------|---|----------------------|------------|-------------|------------|--|
| | | | Methanol | | Ethanol | | |
| | | | 10 | 20 | 10 | 20 | |
| Cl | | | | | | | |
| A | 5 | c | -3527.05925 | -3625.9316 | -3728.7328 | -3516.4834 | |
| B | | | 2.093326 | 2.44145 | 3.038288 | 1.865708 | |
| σ | | | 0.059 | 0.060 | 0.062 | 0.059 | |
| A | | m | -3542.8360 | -3641.7980 | -37724.5946 | -3532.0941 | |
| B | | | 2.164311 | 2.52642 | 3.211737 | 1.948162 | |
| σ | | | 0.059 | 0.061 | 0.063 | 0.059 | |
| A | 13 | c | | | -3819.4586 | -3497.5733 | |
| B | | | | | 3.329045 | 1.798446 | |
| σ | | | | | 0.059 | 0.054 | |
| A | | m | | | -3841.6543 | -3520.532 | |
| B | | | | | 3.421078 | 1.949799 | |
| σ | | | | | 0.059 | 0.054 | |
| A | 22 | c | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| A | | m | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| A | 8 | c | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| A | | m | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| Br | | | | | | | |
| A | 20 | c | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| A | | m | | | | | |
| B | | | | | | | |
| σ | | | | | | | |
| A | 21 | c | | | -4590.3827 | -4341.719 | |
| B | | | | | 3.423705 | 2.205182 | |
| σ | | | | | 0.073 | 0.053 | |
| A | | m | | | -4610.4252 | -4362.2953 | |

| 1-Propanol | | 2-Propanol | |
|-------------|-------------|-------------|-------------|
| 10 | 20 | 10 | 20 |
| - 3339.9236 | - 3651.2373 | - 3385.1529 | - 3394.0311 |
| 1.734118 | 2.606279 | 1.712248 | 1.515927 |
| 0.082 | 0.061 | 0.056 | 0.057 |
| - 3355.5134 | - 3668.3038 | - 3400.454 | - 3410.4857 |
| 1.803415 | 2.693208 | 1.780531 | 1.600722 |
| 0.056 | 0.061 | 0.057 | 0.057 |
| | | - 3177.3182 | - 3043.3793 |
| | | 1.022116 | 0.323848 |
| | | 0.051 | 0.049 |
| | | - 3197.473 | - 3063.9855 |
| | | 1.106605 | 0.422395 |
| | | 0.051 | 0.049 |
| | | | - 3397.7521 |
| | | | 1.528956 |
| | | | 0.057 |
| | | | - 3473.3631 |
| | | | 1.815926 |
| | | | 0.058 |
| | | - 4232.835 | |
| | | 2.051777 | |
| | | 0.067 | |
| | | - 4252.5375 | |
| | | 2.134709 | |
| | | 0.068 | |
| | | - 4372.8131 | - 4350.4784 |
| | | 2.518184 | 2.272454 |
| | | 0.073 | 0.073 |
| | | - 4388.1032 | - 4366.3519 |

TABLE 6 (continued)

| AgX X≡ | Ref. | p | Wt.% organic solvent | | | |
|-----------|------|---|----------------------|------------|------------|------------|
| | | | Methanol | | Ethanol | |
| | | | 10 | 20 | 10 | 20 |
| <i>B</i> | | | | | 3.508578 | 2.304168 |
| <i>σ</i> | | | | | 0.074 | 0.070 |
| <i>A</i> | 23 | c | | | -4597.9972 | -4316.0135 |
| <i>B</i> | | | | | 3.440111 | 2.121754 |
| <i>σ</i> | | | | | 0.073 | 0.073 |
| <i>A</i> | | m | | | -4615.3867 | -4336.1685 |
| <i>B</i> | | | | | 3.515858 | 2.219454 |
| <i>σ</i> | | | | | 0.074 | 0.069 |
| CNS | | | | | | |
| <i>A</i> | 2 | c | -4836.7948 | -4888.7420 | -4976.8888 | -4606.6265 |
| <i>B</i> | | | 4.43307 | 4.716555 | 5.080573 | 3.507676 |
| <i>σ</i> | | | 0.081 | 0.081 | 0.083 | 0.077 |
| <i>A</i> | | m | -4852.0997 | -4904.4766 | -4992.0848 | -4622.4995 |
| <i>B</i> | | | 4.502451 | 4.801062 | 5.149254 | 3.591013 |
| <i>σ</i> | | | 0.081 | 0.082 | 0.083 | 0.077 |

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