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# STANDARD THERMODYNAMICS OF TRANSFER. I. SILVER AND SILVER SALT ELECTRODES IN GLYCEROL + WATER MIXTURES

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## ABSTRACT

The standard thermodynamic quantities of transfer of $Ag^+$, $X^-$, $Y^{2-}$ and $Z^{3-}$ ions ($X = N_3$, CNS, $IO_3$, $BrO_3$, $VO_4$; $Y = SO_4$, $CrO_4$, $Cr_2O_7$, $WO_4$; $Z = PO_4$, $AsO_4$) in water plus 5, 10, 20 or 30 wt% glycerol have been evaluated. The thermodynamic solubility product constants of silver salts in these solvents have been calculated.

## INTRODUCTION

As a continuation of our investigations on the determination of the standard thermodynamic quantities of $Ag^+$, $X^-$, $Y^{2-}$ and $Z^{3-}$ ions ($X = Cl$, Br, I, $N_3$, CNS, $IO_3$, $BrO_3$; $Y = CrO_4$, $WO_4$; $Z = PO_4$, $AsO_4$) in aqueous and aqueo–organic solvents, and the standard transfer thermodynamic quantities of these ions in aqueo–organic solvents [1], we now report the similar thermodynamic quantities of $Ag^+$, $X^-$, $Y^{2-}$ and $Z^{3-}$ ions ($X = VO_3$, $N_3$, CNS, $IO_3$, $BrO_3$; $Y = SO_4$, $CrO_4$, $Cr_2O_7$, $WO_4$; $Z = PO_4$, $AsO_4$) in water or water plus 5, 10, 20 or 30 wt% glycerol at different temperatures ranging from 5 to 35°C.

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

$$\mathrm{Ag(s), AgCl(s), NaCl(c), NaNO_3(c)//NaNO_3(c), AgNO_3(c), Ag(s)} \qquad \text{(A)}$$

$$\mathrm{Ag(s), AgCl(s), MCl(c)//MX(c), AgX(s), Ag(s)} \qquad \text{(B)}$$

$$\mathrm{Ag(s), AgCNS(s), KCNS(c)//KCl(c), AgCl(s), Ag(s)} \qquad \text{(C)}$$

$$\mathrm{Ag(s), AgCl(s), MCl(c)//M_2Y(c/2), Ag_2Y(s), Ag(s)} \qquad \text{(D)}$$

and

$$\mathrm{Ag(s), AgCl(s), MCl(c)//M_3Z(c/3), Ag_3Z(s), Ag(s)} \qquad \text{(E)}$$

where M = K, Na, has been made either in water or in a series of water + glycerol mixtures containing 5, 10, 20 and 30% (w/w) glycerol at temperatures from 5 to 35°C.

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## EXPERIMENTAL

The following chemicals were obtained in the best grade available and were used without further purification: sodium chloride, potassium chloride, sodium nitrate (Merck, G.R.), silver nitrate, sodium azide, potassium thiocyanate, sodium metavanadate, potassium bromate, potassium iodate, potassium sulphate, potassium chromate, potassium dichromate, sodium tungstate, sodium phosphate and sodium arsenate (BDH, AnalaR). Glycerol (BDH, AnalaR) was vacuum distilled as described earlier [1g]. Silver salts were prepared from silver nitrate (Guaranteed reagent) and the corresponding sodium or potassium salts, and the precipitates were repeatedly washed with conductivity water, and were kept in conductvity water in amber-coloured bottles before use.

The Ag–AgX electrodes (X = Cl, $N_3$, CNS) were prepared electrolytically as described earlier [1]. Preparation of the Ag–AgX, Ag–$Ag_2Y$ and Ag–$Ag_3Z$ electrodes (X = $BrO_3$, $IO_3$, $VO_3$; Y = $SO_4$, $CrO_4$, $Cr_2O_7$, $WO_4$; Z = $PO_4$, $AsO_4$) was similar to that described elsewhere [1b,2] by applying a paste of the corresponding silver salts to the spongy silver obtained by the thermal decomposition of silver oxide [3]. The silver electrode was prepared as described in an earlier article [1g]. The electrodes thus prepared were stored in 0.05 M aqueous sodium or potassium salt solutions for 24 h. Only those which showed a potential difference of 0.1 mV or less on being mutually compared with each other were used.

Preparation of the solvent mixtures of various mass percentages, preparation of the cell solutions, setting up of the cells, and EMF and conductance measurements were carried out essentially similarly to the procedures described earlier [1b]. All measurements were made in water baths maintained at the appropriate temperature ($\pm 0.05$°C). The reproducibility of EMF measurements was of the order of $\pm 0.2$ mV.

## RESULTS AND DISCUSSION

As usual, the EMF, $E$, of the cell (A) is given by [1e]

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

of cell (B) [1c]

$$E = E^0_{\mathrm{Ag,AgX}} - E^0_{\mathrm{Ag,AgCl}} - (RT/F)\ln([X^-]\gamma_{\mathrm{x^-}}/[\mathrm{Cl^-}]\gamma_{\mathrm{Cl^-}}) + E_{\mathrm{j}} \qquad (2)$$

of cell (C) [1d]

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

of cell (D) [1d]

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

and of cell (E) [1d,4]

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

where the symbols have their usual meanings.

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, $E^0_c$, of the $\mathrm{Ag/Ag^+}$, $\mathrm{Ag/AgX,X^-}$, $\mathrm{Ag/Ag_2Y,Y^{2-}}$ and $\mathrm{Ag/Ag_3Z,Z^{3-}}$ electrodes were obtained by the method of extrapolating [1,4] the corresponding auxiliary functions [1,4] to the molarity, $c = 0$.

The values of the liquid-junction potential, $E_{\mathrm{j}}$, were calculated from the equivalent conductances of potassium or sodium chloride and the corresponding sodium or potassium salts by means of the Lewis and Sargent equation [1b]. It was found that the values of $E_{\mathrm{j}}$ varied in the range 0.1–0.3 mV for the cells (A), (B) and (C), and 0.1–0.6 mV for the cells (D) and (E) in all solvents for all temperatures. The values of $E^0_{\mathrm{Ag,AgCl}}$ (molar scale) needed for the calculation of $E^0_c$ of the electrodes at different temperatures and in water and various glycerol + water mixtures were taken from the literature [5].

Standard potentials on the molal ($E^0_m$), mole fraction ($E^0_N$) and molar ($E^0_c$) scales (correlated by the usual equation [1a] 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 $p = c$, $m$ or $N$ and $t$ is any temperature (°C). The constants $a$, $b$, and $c$ of eqn. (6) are presented in Table 1. The average deviations between the experimental values and those calculated from eqn. (6) are within $\pm 0.3$ mV. The $E^0_p$ values (V) (constant $a$ of eqn. 6) at 25°C are also shown in Table 1.

The standard thermodynamic quantities ($\Delta G^0$, $\Delta H^0$ and $\Delta S^0$) on the molal scale for the corresponding electrode reactions [1,4] at different temperatures in various solvents have been calculated by the usual relationship [1,4]. These values for 25°C are presented in Table 2.

The standard thermodynamic quantities ($\Delta G^0_{\mathrm{t}}$, $\Delta H^0_{\mathrm{t}}$ and $\Delta S^0_{\mathrm{t}}$) for the transfer process $\mathrm{Ag^+}$, $\mathrm{X^-}$, $\mathrm{Y^{2-}}$ or $\mathrm{Z^{3-}}$ (in water) $\rightarrow$ $\mathrm{Ag^+}$, $\mathrm{X^-}$, $\mathrm{Y^{2-}}$ or $\mathrm{Z^{3-}}$ (in glycerol + water) were evaluated at different temperatures for various solvent mixtures by the usual relationships. These values of the transfer thermodynamic quantities were obtained on the mole fraction basis [1] and are included in Table 2 for 25°C only.

An inspection of Table 1 shows that the standard electrode potentials of the $\mathrm{Ag/Ag^+}$, $\mathrm{Ag/AgX}$, $\mathrm{X^-}$, $\mathrm{Ag/Ag_2Y}$, $\mathrm{Y^{2-}}$ and $\mathrm{Ag/Ag_3Z}$, $\mathrm{Z^{3-}}$ electrodes in various glycerol + water mixtures are less than in water (except in 5 and 10 wt% for the Ag/AgCNS, $\mathrm{CNS^-}$ and 5 wt% for the $\mathrm{Ag/AgIO_3}$, $\mathrm{IO_3^-}$

TABLE 1

Values of $E_p^0$ at 25°C and constants of eqn. (6) for molar ($c$) molal ($m$) and mole fraction ($N$) scales in glycerol + water mixtures

| Wt% glycerol | $p$ | Constants | | |
|---|---|---|---|---|
| | | $a$ ( = $E_p^0$(V)) | $-b \times 10^3$ | $c \times 10^6$ |
| $X = VO_3$ | | | | |
| 0 | $c$ | 0.3188 | 1.332 | −1.2 |
| | $m$ | 0.3189 | 1.31 | 0 |
| | $N$ | 0.1125 | 2.001 | 0.25 |
| $X = N_3$ | | | | |
| 5 | $c$ | 0.2899 | 0.3633 | 0 |
| | $m$ | 0.2891 | 0.336 | 0.4 |
| | $N$ | 0.0849 | 1.0233 | 0 |
| 10 | $c$ | 0.2866 | 0.5015 | 0.5 |
| | $m$ | 0.2853 | 0.496 | 0 |
| | $N$ | 0.0832 | 1.162 | 2.0 |
| 20 | $c$ | 0.2802 | 0.396 | 0 |
| | $m$ | 0.2778 | 0.4025 | −0.5 |
| | $N$ | 0.0804 | 1.0665 | −0.5 |
| 30 | $c$ | 0.2747 | 0.4333 | 2.67 |
| | $m$ | 0.2712 | 0.345 | 2.0 |
| | $N$ | 0.0789 | 0.99 | 2.0 |
| $X = CNS$ | | | | |
| 5 | $c$ | 0.0932 | 0.1933 | 2.0 |
| | $m$ | 0.0926 | 0.19 | 0 |
| | $N$ | −0.1117 | 0.873 | 0 |
| 10 | $c$ | 0.0912 | 0.3267 | −10.0 |
| | $m$ | 0.0909 | 0.34 | −12.0 |
| | $N$ | −0.1121 | 1.196 | −10.0 |
| 20 | $c$ | 0.0861 | 0.1 | 10.0 |
| | $m$ | 0.0833 | 0.115 | 12.0 |
| | $N$ | −0.1131 | 0.68 | 12.0 |
| 30 | $c$ | 0.0820 | 0.145 | 2.0 |
| | $m$ | 0.0784 | 0.1367 | 2.67 |
| | $N$ | −0.1138 | 0.7817 | 2.667 |
| $X = IO_3$ | | | | |
| 5 | $c$ | 0.3293 | 0.285 | 1.5 |
| | $m$ | 0.3285 | 0.2592 | 1.75 |
| | $N$ | 0.1243 | 0.943 | 1.75 |
| 10 | $c$ | 0.3265 | 0.3192 | 0.75 |
| | $m$ | 0.3253 | 0.3125 | 0.75 |
| | $N$ | 0.1232 | 0.9925 | 0.75 |
| 20 | $c$ | 0.3223 | 0.3075 | −0.75 |
| | $m$ | 0.3198 | 0.3142 | −0.75 |
| | $N$ | 0.1224 | 0.975 | −0.50 |
| 30 | $c$ | 0.3163 | 0.2917 | 0.50 |
| | $m$ | 0.3126 | 0.295 | 0.50 |
| | $N$ | 0.1204 | 0.9417 | 0.50 |

TABLE 1 (continued)

| Wt% glycerol | $p$ | Constants | | |
|---|---|---|---|---|
| | | $a$ ( $= E_p^0$(V)) | $-b \times 10^3$ | $c \times 10^6$ |
| X = $BrO_3$ | | | | |
| 5 | $c$ | 0.5202 | 0.4075 | −2.75 |
| | $m$ | 0.5194 | 0.3817 | −2.50 |
| | $N$ | 0.3151 | 1.065 | −2.50 |
| 10 | $c$ | 0.5181 | 0.35 | 2.0 |
| | $m$ | 0.5170 | 0.3683 | −0.50 |
| | $N$ | 0.3149 | 1.0483 | −0.50 |
| 20 | $c$ | 0.5151 | 0.3517 | −1.5 |
| | $m$ | 0.5127 | 0.3575 | −1.75 |
| | $N$ | 0.3152 | 1.0183 | −1.5 |
| 30 | $c$ | 0.5112 | 0.36 | 0 |
| | $m$ | 0.5076 | 0.35667 | 0 |
| | $N$ | 0.3153 | 1.0042 | 0.25 |
| $Ag/Ag^+$ | | | | |
| 5 | $c$ | 0.7747 | 0.91 | 2.0 |
| | $m$ | 0.7738 | 0.88 | 2.0 |
| | $N$ | 0.5697 | 1.605 | −0.8 |
| 10 | $c$ | 0.7718 | 0.8273 | 1.6 |
| | $m$ | 0.7705 | 0.8207 | 1.6 |
| | $N$ | 0.5684 | 1.493 | 2.0 |
| 20 | $c$ | 0.7661 | 0.87 | 0 |
| | $m$ | 0.7637 | 0.8693 | 0.4 |
| | $N$ | 0.5663 | 1.533 | 0.4 |
| 30 | $c$ | 0.7617 | 0.8283 | 1.333 |
| | $m$ | 0.7581 | 0.82 | 2.0 |
| | $N$ | 0.5659 | 1.465 | 2.0 |
| Y = $SO_4$ | | | | |
| 0 | $c$ | 0.6073 | 1.229 | −1.2 |
| | $m$ | 0.6074 | 1.202 | −0.5 |
| | $N$ | 0.4009 | 1.893 | −0.75 |
| 5 | $c$ | 0.6046 | 1.2367 | 0 |
| | $m$ | 0.6037 | 1.1933 | 2 |
| | $N$ | 0.3996 | 1.9 | 0 |
| 10 | $c$ | 0.5999 | 1.2167 | 3.0 |
| | $m$ | 0.5982 | 1.2753 | 0.8 |
| | $N$ | 0.3961 | 1.9446 | 1.2 |
| 20 | $c$ | 0.5916 | 1.298 | −0.8 |
| | $m$ | 0.5892 | 1.3046 | −0.8 |
| | $N$ | 0.3918 | 1.968 | −0.8 |
| 30 | $c$ | 0.5857 | 1.2893 | −1.6 |
| | $m$ | 0.5820 | 1.292 | −1.2 |
| | $N$ | 0.3898 | 1.9353 | −1.2 |
| Y = $CrO_4$ | | | | |
| 5 | $c$ | 0.4484 | 0.959 | 0.8 |
| | $m$ | 0.4476 | 0.9353 | 0.8 |
| | $N$ | 0.2436 | 1.6187 | 0.8 |

TABLE 1 (continued)

| Wt% glycerol | $p$ | Constants | | |
|---|---|---|---|---|
| | | $a$ ( $= E_p^0$(V)) | $-b \times 10^3$ | $c \times 10^6$ |
| 10 | $c$ | 0.4470 | 0.99 | −2.0 |
| | $m$ | 0.4454 | 1.004 | 4.0 |
| | $N$ | 0.2433 | 1.6775 | 4.5 |
| 20 | $c$ | 0.4438 | 0.976 | 0.4 |
| | $m$ | 0.4415 | 0.9827 | 0.4 |
| | $N$ | 0.2441 | 1.6387 | 0.8 |
| 30 | $c$ | 0.4410 | 0.9805 | −2.5 |
| | $m$ | 0.4374 | 0.9845 | −2.5 |
| | $N$ | 0.2451 | 1.626 | −2.0 |
| Y = $Cr_2O_7$ | | | | |
| 0 | $c$ | 0.5574 | 1.4093 | −1.6 |
| | $m$ | 0.5575 | 1.3983 | −1.5 |
| | $N$ | 0.3511 | 2.0892 | −1.25 |
| 5 | $c$ | 0.5279 | 1.3592 | −2.25 |
| | $m$ | 0.5271 | 1.3392 | −2.25 |
| | $N$ | 0.3229 | 2.0225 | −2.25 |
| 10 | $c$ | 0.5167 | 1.3375 | 0.25 |
| | $m$ | 0.5155 | 1.3308 | 0.25 |
| | $N$ | 0.3134 | 2.0108 | 0.25 |
| 20 | $c$ | 0.4963 | 1.26916 | 1.75 |
| | $m$ | 0.4939 | 1.2725 | 1.75 |
| | $N$ | 0.2965 | 1.92666 | 2.0 |
| 30 | $c$ | 0.4754 | 1.30667 | 2.0 |
| | $m$ | 0.4717 | 1.31 | 2.0 |
| | $N$ | 0.2795 | 1.95083 | 2.25 |
| Y = $WO_4$ | | | | |
| 5 | $c$ | 0.4348 | 1.5983 | 3.5 |
| | $m$ | 0.4343 | 1.5725 | 3.75 |
| | $N$ | 0.2301 | 2.2558 | 3.75 |
| 10 | $c$ | 0.4210 | 1.705 | 2.5 |
| | $m$ | 0.4197 | 1.6983 | 2.5 |
| | $N$ | 0.2177 | 2.3725 | 2.75 |
| 20 | $c$ | 0.4065 | 1.65 | 0 |
| | $m$ | 0.4041 | 1.6567 | 0 |
| | $N$ | 0.2067 | 2.32 | 0 |
| 30 | $c$ | 0.3838 | 1.7567 | −3.0 |
| | $m$ | 0.3799 | 1.7867 | −3.0 |
| | $N$ | 0.1877 | 2.4275 | −2.75 |
| Z = $PO_4$ | | | | |
| 5 | $c$ | 0.3859 | 1.5167 | 2.0 |
| | $m$ | 0.3851 | 1.4967 | 2.0 |
| | $N$ | 0.1808 | 2.18 | 2.0 |
| 10 | $c$ | 0.3717 | 1.5808 | 2.25 |
| | $m$ | 0.3804 | 1.5742 | 2.25 |
| | $N$ | 0.1783 | 2.2483 | 2.5 |

TABLE 1 (continued)

| Wt% glycerol | $p$ | Constants | | |
|---|---|---|---|---|
| | | $a\ (=E_p^0(\mathrm{V}))$ | $-b\times10^3$ | $c\times10^6$ |
| 20 | $c$ | 0.3732 | 1.6075 | 0.25 |
| | $m$ | 0.3703 | 1.61416 | 0.25 |
| | $N$ | 0.1734 | 2.2775 | 0.25 |
| 30 | $c$ | 0.3663 | 1.5033 | 1.0 |
| | $m$ | 0.3627 | 1.50667 | 1.0 |
| | $N$ | 0.1708 | 2.15 | 1.0 |
| Z = $AsO_4$ | | | | |
| 5 | $c$ | 0.3518 | 1.48166 | 4.5 |
| | $m$ | 0.3510 | 1.4583 | 4.5 |
| | $N$ | 0.1468 | 2.1417 | 4.5 |
| 10 | $c$ | 0.3497 | 1.4658 | 0.75 |
| | $m$ | 0.3489 | 1.4592 | 0.75 |
| | $N$ | 0.1465 | 2.1 | 1.0 |
| 20 | $c$ | 0.3419 | 1.5617 | 2.5 |
| | $m$ | 0.3394 | 1.5683 | 2.5 |
| | $N$ | 0.1421 | 2.2317 | 2.5 |
| 30 | $c$ | 0.3331 | 1.54666 | 1.0 |
| | $m$ | 0.3294 | 1.5525 | 0.75 |
| | $N$ | 0.1373 | 2.1958 | 0.75 |

electrodes), which is in agreement with the behaviour exhibited by the silver–silver halide electrodes studied in glycerol + water mixtures [1h].

It is evident from Table 2 that the standard Gibbs free energy changes for the electrode reactions increase with an increase in the glycerol content of the solvent mixture. The standard enthalpy and entropy changes are all negative, but the solvent effect on the magnitude of these quantities appears to be irregular. The difference in magnitude of the $\Delta H^0$ and $\Delta S^0$ 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 $Ag^+$, $X^-$, $Y^{2-}$ or $Z^{3-}$ ions from water to the solvent concerned, since the Gibbs free energy of transfer is an important index of the differences in interactions of the ion and the solvent molecules in the two different media.

As can be seen from Table 2, the standard Gibbs free energy of transfer, $\Delta G_t^0$, for the $Ag^+$, $X^-$, $Y^{2-}$ and $Z^{3-}$ ions appears to be positive (except for $CNS^-$ in all solvents and $IO_3^-$ in 5 and 10 wt% glycerol) and becomes increasingly positive as the proportions of glycerol increase. The positive values of $\Delta G_t^0$ signify that the transfer of the ions from water to water + glycerol solvents is not favourable, whereas the negative $\Delta G_t^0$ values indicate that the $CNS^-$ ion is in a lower free energy state in the mixed solvents than in water, and, therefore, the transfer process is favourable. The transfer of the $IO_3^-$ ion becomes increasingly unfavourable as the proportions of glycerol increases in the solvent mixtures. The positive values of $\Delta G_t^0$

TABLE 2

Thermodynamic quantities on the molal scale and transfer thermodynamic quantities on the mole fraction scale in different glycerol + water mixtures at 25°C ($\Delta G^0$ and $\Delta H^0$, J mol$^{-1}$, and $\Delta S^0$ J mol$^{-1}$ K$^{-1}$)

| | Wt% glycerol | | | | |
|---|---|---|---|---|---|
| | 0 | 5 | 10 | 20 | 30 |
| $Ag^+$ | | | | | |
| $-10^{-3}\,\Delta G_m^0$ | 77.13 | 74.67 | 74.35 | 73.69 | 73.15 |
| $-10^{-3}\,\Delta H_m^0$ | 105.95 | 99.97 | 97.95 | 98.69 | 96.73 |
| $-\Delta S_m^0$ | 96.60 | 84.91 | 79.19 | 83.88 | 79.12 |
| $10^{-3}\Delta G_t^0$ | | 2.24 | 2.36 | 2.57 | 2.61 |
| $10^{-3}\Delta H_t^0$ | | 4.4 | 7.74 | 6.8 | 8.79 |
| $\Delta S_t^0$ | | 7.23 | 18.04 | 14.18 | 20.74 |
| $X = VO_3$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 30.77 | | | | |
| $-10^{-3}\Delta H_m^0$ | 68.44 | | | | |
| $-\Delta S_m^0$ | 126.40 | | | | |
| $X = N_3$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 28.32 | 27.90 | 27.53 | 26.81 | 26.17 |
| $-10^{-3}\Delta H_m^0$ | 35.77 | 37.56 | 41.79 | 38.38 | 36.09 |
| $-\Delta S_m^0$ | 25.01 | 32.42 | 47.86 | 38.84 | 33.29 |
| $10^{-3}\Delta G_t^0$ | | 0.21 | 0.38 | 0.65 | 0.79 |
| $-10^{-3}\Delta H_t^0$ | | 2.45 | 6.27 | 3.25 | 0.91 |
| $-\Delta S_t^0$ | | 8.87 | 22.25 | 13.04 | 5.66 |
| $X = CNS$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 8.62 | 8.94 | 8.77 | 8.04 | 7.56 |
| $-10^{-3}\Delta H_m^0$ | 37.93 | 14.4 | 18.55 | 11.34 | 11.50 |
| $-\Delta S_m^0$ | 98.35 | 18.33 | 32.81 | 11.10 | 13.19 |
| $-10^{-3}\Delta G_t^0$ | | 0.63 | 0.59 | 0.49 | 0.42 |
| $10^{-3}\Delta H_t^0$ | | 23.6 | 14.35 | 29.28 | 26.42 |
| $\Delta S_t^0$ | | 80.9 | 49.74 | 99.53 | 89.71 |
| $X = IO_3$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 31.72 | 31.7 | 31.39 | 30.86 | 30.16 |
| $-10^{-3}\Delta H_m^0$ | 40.74 | 39.15 | 40.37 | 39.89 | 38.65 |
| $-\Delta S_m^0$ | 30.27 | 25.01 | 30.15 | 30.32 | 28.47 |
| $10^{-3}\Delta G_t^0$ | | −0.16 | −0.06 | 0.02 | 0.21 |
| $10^{-3}\Delta H_t^0$ | | 1.62 | 0.3 | 0.88 | 2.03 |
| $\Delta S_t^0$ | | 6.07 | 1.29 | 2.98 | 6.19 |
| $X = BrO_3$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 50.75 | 50.12 | 49.89 | 49.47 | 48.98 |
| $-10^{-3}\Delta H_m^0$ | 59.13 | 61.09 | 60.48 | 59.75 | 59.23 |
| $-\Delta S_m^0$ | 28.12 | 36.83 | 35.54 | 34.50 | 34.41 |
| $10^{-3}\Delta G_t^0$ | | 0.45 | 0.47 | 0.44 | 0.43 |
| $-10^{-3}\Delta H_t^0$ | | 1.88 | 1.38 | 0.54 | 0.15 |
| $-\Delta S_t^0$ | | 7.72 | 6.11 | 3.22 | 1.86 |

TABLE 2 (continued)

| | Wt% glycerol | | | | |
|---|---|---|---|---|---|
| | 0 | 5 | 10 | 20 | 30 |
| $Y = SO_4$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 117.22 | 116.5 | 115.44 | 113.71 | 112.32 |
| $-10^{-3}\Delta H_m^0$ | 186.34 | 185.13 | 188.78 | 188.73 | 186.62 |
| $-\Delta S_m^0$ | 231.97 | 230.29 | 246.11 | 251.77 | 249.33 |
| $10^{-3}\Delta G_t^0$ | | 0.25 | 0.93 | 1.76 | 2.14 |
| $-10^{-3}\Delta H_t^0$ | | 0.15 | 2.04 | 2.56 | 0.29 |
| $-\Delta S_t^0$ | | 1.38 | 9.98 | 14.48 | 8.18 |
| $Y = CrO_4$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 86.69 | 86.38 | 85.95 | 85.20 | 84.41 |
| $-10^{-3}\Delta H_m^0$ | 151.75 | 140.17 | 143.69 | 141.72 | 141.03 |
| $-\Delta S_m^0$ | 219.3 | 180.5 | 193.75 | 189.64 | 189.99 |
| $-10^{-3}\Delta G_t^0$ | | 0.12 | 0.10 | 0.25 | 0.44 |
| $10^{-3}\Delta H_t^0$ | | 10.74 | 7.19 | 9.26 | 9.8 |
| $\Delta S_t^0$ | | 35.8 | 24.45 | 31.94 | 34.39 |
| $Y = Cr_2O_7$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 107.59 | 101.72 | 99.48 | 95.3 | 91.03 |
| $-10^{-3}\Delta H_m^0$ | 188.0 | 178.74 | 176.02 | 168.48 | 166.37 |
| $-\Delta S_m^0$ | 269.85 | 258.4 | 256.8 | 332.9 | 252.8 |
| $10^{-3}\Delta G_t^0$ | | 5.4 | 7.28 | 10.54 | 13.82 |
| $10^{-3}\Delta H_t^0$ | | 9.27 | 11.78 | 19.88 | 21.77 |
| $\Delta S_t^0$ | | 12.88 | 15.13 | 31.38 | 26.68 |
| $Y = WO_4$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 84.1 | 83.91 | 80.99 | 77.98 | 73.31 |
| $-10^{-3}\Delta H_m^0$ | 174.86 | 174.25 | 178.66 | 173.26 | 176.06 |
| $-\Delta S_m^0$ | 304.6 | 303.47 | 327.74 | 319.71 | 344.80 |
| $10^{-3}\Delta G_t^0$ | | −1.41 | 2.14 | 4.26 | 7.93 |
| $10^{-3}\Delta H_t^0$ | | 0.71 | −3.61 | 1.53 | −0.99 |
| $\Delta S_t^0$ | | 2.87 | −19.65 | −9.52 | −30.27 |
| $Z = PO_4$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 130.8 | 111.48 | 110.12 | 107.31 | 104.99 |
| $-10^{-3}\Delta H_m^0$ | 264.94 | 240.59 | 246.34 | 246.55 | 234.99 |
| $-\Delta S_m^0$ | 450.13 | 433.26 | 457.14 | 467.24 | 437.10 |
| $10^{-3}\Delta G_t^0$ | | 18.9 | 19.63 | 21.04 | 21.80 |
| $10^{-3}\Delta H_t^0$ | | 24.59 | 19.42 | 18.28 | 30.07 |
| $\Delta S_t^0$ | | 19.68 | −0.09 | −8.69 | 28.36 |
| $Z = AsO_4$ | | | | | |
| $-10^{-3}\Delta G_m^0$ | 116.2 | 101.61 | 101.0 | 98.25 | 95.35 |
| $-10^{-3}\Delta H_m^0$ | 260.22 | 227.4 | 226.87 | 229.09 | 229.28 |
| $-\Delta S_m^0$ | 483.27 | 422.14 | 422.4 | 439.07 | 449.41 |
| $10^{-3}\Delta G_t^0$ | | 13.84 | 13.92 | 15.20 | 16.59 |
| $10^{-3}\Delta H_t^0$ | | 33.11 | 36.8 | 26.71 | 31.2 |
| $\Delta S_t^0$ | | 64.28 | 76.35 | 38.23 | 48.62 |

support the view that the $Ag^+$, $X^-$ (except for $CNS^-$ for all solvents and $IO_3^-$ for water-rich solvents), $Y^{2-}$ and $Z^{3-}$ ions are more strongly stabilised in water than in the mixed solvents.

TABLE 3

Primary medium effect, $\lim_{N\to 0} \log^s \gamma_w$ (on the mole fraction scale) of the $Ag^+$, $X^-$, $Y^{2-}$ and $Z^{3-}$ ions in various glycerol + water mixtures at 25°C

| | Wt% glycerol | | | |
|---|---|---|---|---|
| | 5 | 10 | 20 | 30 |
| $Ag^+$ | 0.3922 | 0.4141 | 0.4496 | 0.4564 |
| $X = N_3$ | 0.0372 | 0.0659 | 0.1133 | 0.1386 |
| CNS | −0.1099 | −0.1031 | −0.0862 | −0.0744 |
| $IO_3$ | −0.0287 | −0.0101 | 0.0034 | 0.0372 |
| $BrO_3$ | 0.0794 | 0.0828 | 0.0778 | 0.0761 |
| $Y = SO_4$ | 0.0439 | 0.1623 | 0.3077 | 0.3753 |
| $CrO_4$ | −0.0203 | −0.0169 | −0.0439 | −0.0778 |
| $Cr_2O_7$ | 0.9534 | 1.2746 | 1.8459 | 2.4206 |
| $WO_4$ | −0.0439 | 0.3753 | 0.7472 | 1.3895 |
| $Z = PO_4$ | 3.3115 | 3.4383 | 3.6867 | 3.8186 |
| $AsO_4$ | 2.4240 | 2.4392 | 2.6624 | 2.9058 |

The positive values of the standard transfer entropy, $\Delta S_t^0$, for the $Ag^+$, $CNS^-$, $IO_3^-$, $CrO_4^{2-}$, $Cr_2O_7^{2-}$ and $AsO_4^{3-}$ ions 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 these ions is less in glycerol + water mixtures than in water, and, hence, these ions break down more structure in these mixed solvents, which are more structured than water. On the other hand, the negative $\Delta S_t^0$ values of the $N_3^-$, $BrO_3^-$, $SO_4^{2-}$, $WO_4^{2-}$ and $PO_4^{3-}$ ions indicate that the net amount of order created by these ions is more in glycerol + water mixtures than in water and assume that these ions are more effectively breaking the water structure than in the mixed solvents. The positive $\Delta H_t^0$ values (except for $N_3^-$, $BrO_3^-$ and $SO_4^{2-}$ ions) suggest that the transfer process is endothermic, because of the dehydration and then solvation of the ions by glycerol.

The 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 $n$ is 1, 2, or 3 in various glycerol + water mixtures at 25°C are shown in Table 3. The sign and magnitude of the primary medium effect could give us an insight into the stabilization of the ions in the solvent concerned. The positive and increasing magnitude of this quantity suggests that the escaping tendency of the ions is greater in glycerol + water mixtures than in the aqueous medium.

The thermodynamic solubility products, $K_s^0$, of AgX ($X = N_3$, CNS, $IO_3$, $BrO_3$, $VO_3$), $Ag_2Y$ ($Y = SO_4$, $CrO_4$, $Cr_2O_7$, $WO_4$) and $Ag_3Z$ ($Z = PO_4$, $AsO_4$) in water or glycerol + water mixtures have been calculated at different temperatures from the values of standard potentials by means of the equations

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

TABLE 4

Solubility product constants on the molar scale ($K_s^c$) of AgX (X = $VO_3$, $N_3$, 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 glycerol + water mixtures at 25°C

| | Wt% glycerol | | | | |
|---|---|---|---|---|---|
| | 0 | 5 | 10 | 20 | 30 |
| X = $VO_3$ | | | | | |
| $K_s^c \times 10^9$ | 7.69 | | | | |
| X = $N_3$ | | | | | |
| $K_s^c \times 10^9$ | 2.82 | 6.41 | 6.21 | 6.12 | 5.86 |
| X = CNS | | | | | |
| $K_s^c \times 10^{13}$ | 9.55 | 29.62 | 31.39 | 32.14 | 32.39 |
| X = $IO_3$ | | | | | |
| $K_s^c \times 10^9$ | 10.96 | 29.58 | 29.69 | 31.48 | 29.58 |
| X = $BrO_3$ | | | | | |
| $K_s^c \times 10^5$ | 2.40 | 4.98 | 5.15 | 5.69 | 5.83 |
| Y = $SO_4$ | | | | | |
| $K_s^c \times 10^6$ | 0.34 | 1.78 | 1.54 | 1.26 | 1.12 |
| Y = $CrO_4$ | | | | | |
| $K_s^c \times 10^{12}$ | 1.41 | 9.30 | 10.45 | 12.69 | 14.38 |
| Y = $Cr_2O_7$ | | | | | |
| $K_s^c \times 10^9$ | 6.9 | 4.53 | 2.38 | 0.76 | 0.21 |
| Y = $WO_4$ | | | | | |
| $K_s^c \times 10^{12}$ | 0.49 | 3.30 | 1.38 | 0.70 | 0.17 |
| Z = $PO_4$ | | | | | |
| $K_s^c \times 10^{20}$ | 234.4 | 1.91 | 1.66 | 1.17 | 0.89 |
| Z = $AsO_4$ | | | | | |
| $K_s^c \times 10^{22}$ | 61.65 | 3.58 | 3.94 | 3.08 | 1.82 |

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

and

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

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 and $E_c^0(Ag/Ag^+)$ is the standard molar potential of the silver electrode in water obtained from the literature [1e] or in the mixed solvents determined from the present investigation. The values for $K_s^c$ (on the molar scale) are given in Table 4 for 25°C only. The data for $K_s^m$ (on the molal scale) were calculated from $K_s^c/\rho^2$, where $\rho$ is the density of the mixed solvent. The solubility product data in any solvent were fitted by least squares to the equation

$$\log K_s^q(\text{AgX or } Ag_2Y \text{ or } Ag_3Z) = A/T + B \qquad (7)$$

where $q = c$ or $m$ and $T$ is any temperature (K). The constants $A$ and $B$ of eqn. (7) are shown in Table 5 along with the values of $\sigma$, the standard deviation of the least-squares fit: the correlation coefficient for these rela-

TABLE 5

Constants of eqn. (7) for molar (*c*) and molal (*m*) scales in glycerol + water mixtures for different silver salts

| | $q$ | Wt% glycerol | | | |
|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 |
| X = $N_3$ | | | | | |
| $A$ | $c$ | −3305.5831 | −2946.5956 | −3175.5966 | −3164.6827 |
| $B \times 10^3$ | | 2882.0362 | 1684.6642 | 2440.8557 | 2388.9138 |
| $\sigma$ | | 0.055 | 0.066 | 0.053 | 0.054 |
| $A$ | $m$ | −3341.6835 | −2961.4961 | −3181.8965 | −3175.8918 |
| $B \times 10^3$ | | 2990.6596 | 1713.3641 | 2422.4676 | 2364.8974 |
| $\sigma$ | | 0.056 | 0.049 | 0.053 | 0.054 |
| X = CNS | | | | | |
| $A$ | $c$ | −4553.3137 | −4348.6673 | −4359.1964 | −4360.6197 |
| $B \times 10^3$ | | 3746.9112 | 3087.538 | 3130.008 | 3151.7923 |
| $\sigma$ | | 0.076 | 0.073 | 0.074 | 0.073 |
| $A$ | $m$ | −4589.4189 | −4430.5617 | −4365.4251 | −4439.9412 |
| $B \times 10^3$ | | 3855.5653 | 3345.164 | 3110.0891 | 3360.513 |
| $\sigma$ | | 0.076 | 0.074 | 0.075 | 0.074 |
| X = $IO_3$ | | | | | |
| $A$ | $c$ | −3190.0023 | −3018.0472 | −3091.5334 | −3064.0415 |
| $B \times 10^3$ | | 3174.6885 | 2599.209 | 2867.3791 | 2751.11642 |
| $\sigma$ | | 0.099 | 0.098 | 0.10 | 0.10 |
| $A$ | $m$ | −3224.3549 | −3032.1654 | −3097.2558 | −3075.6878 |
| $B \times 10^3$ | | 3277.1032 | 2625.2138 | 2845.938 | 2728.7202 |
| $\sigma$ | | 0.10 | 0.099 | 0.100 | 0.10 |
| X = $BrO_3$ | | | | | |
| $A$ | $c$ | −2105.3645 | −1985.8294 | −2066.7447 | −1984.4691 |
| $B \times 10^3$ | | 2753.728 | 2374.9159 | 2686.4784 | 2423.0165 |
| $\sigma$ | | 0.069 | 0.065 | 0.067 | 0.065 |
| $A$ | $m$ | −2142.7752 | −1999.9476 | −2072.6641 | −1996.1153 |
| $B \times 10^3$ | | 2866.8448 | 2391.9211 | 2665.4605 | 2403.0676 |
| $\sigma$ | | 0.070 | 0.062 | 0.068 | 0.065 |
| X = $SO_4$ | | | | | |
| $A$ | $c$ | −801.66485 | −490.19216 | −507.65364 | −485.72285 |
| $B \times 10^3$ | | −3064.4942 | −4166.484 | −4200.5411 | −4329.7107 |
| $\sigma$ | | 0.013 | 0.007 | 0.008 | 0.008 |
| $A$ | $m$ | −893.0365 | −538.35506 | −562.3176 | −497.37017 |
| $B \times 10^3$ | | 2951.5128 | −4024.2012 | −4054.7518 | −4352.3859 |
| $\sigma$ | | 0.014 | 0.009 | 0.009 | 0.008 |
| Y = $CrO_4$ | | | | | |
| $A$ | $c$ | −3457.2798 | −2886.2037 | −2908.3925 | −2897.2792 |
| $B \times 10^3$ | | 583.5144 | −1305.8035 | −1140.558 | −1128.3882 |
| $\sigma$ | | 0.058 | 0.048 | 0.048 | 0.048 |
| $A$ | $m$ | −3213.6957 | −2897.7564 | −2914.3146 | −2908.9265 |
| $B \times 10^3$ | | −263.6485 | −1288.472 | −1160.4842 | −1150.876 |
| $\sigma$ | | 0.053 | 0.048 | 0.048 | 0.048 |

TABLE 5 (continued)

| | $q$ | Wt% glycerol | | | |
|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 |
| $Y = Cr_2O_7$ | | | | | |
| $A$ | $c$ | −1249.4697 | −1074.5248 | −1469.7509 | −1431.6859 |
| $B \times 10^3$ | | −4150.155 | −5021.6045 | −4187.7515 | −4872.8547 |
| $\sigma$ | | 0.042 | 0.036 | 0.048 | 0.047 |
| $A$ | $m$ | −1286.8803 | −1088.6429 | −1475.6703 | −1433.3322 |
| $B \times 10^3$ | | −4037.039 | −4995.6 | −4208.7692 | −4895.335 |
| $\sigma$ | | 0.042 | 0.036 | 0.048 | 0.047 |
| $Y = WO_4$ | | | | | |
| $A$ | $c$ | −1307.4926 | −872.5469 | −1282.449 | −1150.7255 |
| $B \times 10^3$ | | −7086.5853 | −8928.4501 | −7858.6853 | −8930.9064 |
| $\sigma$ | | 0.043 | 0.028 | 0.042 | 0.038 |
| $A$ | $m$ | −1344.9033 | −886.4682 | −1288.3684 | −1159.703 |
| $B \times 10^3$ | | −6973.4714 | −8902.8682 | −7879.7035 | −8962.4723 |
| $\sigma$ | | 0.044 | 0.029 | 0.042 | 0.038 |
| $Z = PO_4$ | | | | | |
| $A$ | $c$ | −3049.2485 | −2456.0854 | −2605.0087 | −2938.8682 |
| $B \times 10^3$ | | −9484.6472 | −8834.7847 | −1119.1276 | −1018.7656 |
| $\sigma$ | | 0.099 | 0.080 | 0.085 | 0.096 |
| $A$ | $m$ | −3166.3339 | −2470.5929 | −2610.7356 | −2949.9283 |
| $B \times 10^3$ | | −9106.208 | −1151.0011 | −1121.2702 | −1021.1366 |
| $\sigma$ | | 0.100 | 0.086 | 0.085 | 0.096 |
| $Z = AsO_4$ | | | | | |
| $A$ | $c$ | −3702.9786 | −3261.9669 | −3534.5831 | −3186.6248 |
| $B \times 10^3$ | | −9008.747 | −1079.2342 | −9549.5603 | −1081.4855 |
| $\sigma$ | | 0.100 | 0.100 | 0.100 | 0.104 |
| $A$ | $m$ | −3740.00 | −3273.2238 | −3549.0905 | −3192.1549 |
| $B \times 10^3$ | | −8896.4605 | −1081.5636 | −9521.7248 | −1083.6704 |
| $\sigma$ | | 0.100 | 0.100 | 0.100 | 0.104 |

tions is 0.995, 0.997 and 0.999 for AgX, $Ag_2Y$ and $Ag_3Z$, respectively. The thermodynamic molar solubility product data for $AgVO_3$, $Ag_2SO_4$ and $Ag_2Cr_2O_7$ in aqueous medium were fitted by least squares to the following equations

$$\log K_s^c(AgVO_3) = -1935.5393/T - 1.61817;\ \sigma = 0.032$$

$$\log K_s^c(Ag_2SO_4) = -1225.0018/T - 2.375874;\ \sigma = 0.02$$

and

$$\log K_s^c(Ag_2Cr_2O_7) = -1205.1741/T - 4.131809;\ \sigma = 0.021$$

the correlation coefficient for these relations is 0.990.

A perusal of Table 4 shows that $AgN_3$, AgCNS, $AgIO_3$, $AgBrO_3$, $Ag_2SO_4$, $Ag_2CrO_4$ and $Ag_2WO_4$ are less soluble in water than in mixed solvents. The higher solubility of these silver salts in the mixed solvents may be due to the fact that these salts are more strongly solvated in the mixed solvents than in water. The reverse is the case, however, in the cases of $Ag_2Cr_2O_7$, $Ag_3PO_4$ and $Ag_3AsO_4$, where these silver salts are more strongly solvated in water than in mixed solvents. Unfortunately, it is not possible at present to compare the solubility of $AgVO_3$ in water with that in glycerol + water mixtures because of lack of data in the mixed solvents. Since $NaVO_3$ is sparingly soluble in glycerol + water mixtures for preparing the cell solutions for determining the standard potentials of the $Ag/AgVO_3$ electrode, it was not possible in the present study to evaluate the solubility of $AgVO_3$ in the mixed solvents.

A comparison of the solubility product data of $Ag_2SO_4$ in water, available from the literature or calculated from the literature solubility values, $2.19 \times 10^{-5}$ M at 18°C [6], $2.43 \times 10^{-5}$ and $3.69 \times 10^{-5}$ M at 0 and 100°C, respectively [7], $7.0 \times 10^{-5}$ M at room temperature [8] and $7.943 \times 10^{-5}$ M at 25°C [9], with the present value ($3.4 \times 10^{-7}$ M at 25°C) shows a poor agreement. The solubility data of $Ag_2Cr_2O_7$ available in water [8] at room temperature ($2.0 \times 10^{-7}$ M) is also widely different from our value ($6.9 \times 10^{-9}$ M) obtained in water at 25°C. Such differences might be due to the use of different physical methods [10] for the determination of solubility values. However, the fair reproducibility of the present result and the smooth linear variation of solubility with temperature in both water and glycerol + water solvents suggest that the present set of data obtained at a number of temperatures is more reliable.

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