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# THERMODYNAMICS OF THE SILVER–SILVER ION ELECTRODE AND THERMODYNAMIC SOLUBILITY PRODUCTS OF SILVER CHLORIDE IN WATER + D-GLUCOSE AND D-FRUCTOSE MIXTURES AT 25°C

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From the EMF measurements of cells of the type Ag, AgCl, NaCl(c), NaNO$_3$(c)/NaNO$_3$(c), AgNO$_3$(c), Ag, the standard potentials of the silver–silver ion electrode have been determined in water containing 5, 10, 20 and 30 wt. % D-glucose, and in water containing 5 and 10 wt.% D-fructose at 25°C. The standard thermodynamic quantities for the electrode reaction, the primary medium effects of various solvents upon the Ag$^+$ ion and the standard thermodynamic quantities for the transfer of 1 gram-ion of Ag$^+$ in water to the respective mixed solvent have been evaluated and discussed in the light of the ion–solvent interactions as well as the structural changes of the solvents. Using the standard potentials of the silver–silver ion and silver–silver chloride electrodes, the thermodynamic solubility products of silver chloride have been computed at 25°C.

INTRODUCTION

No work seems to have been done on the determination of the standard potentials of the silver–silver ion electrode in binary solvent systems. However, from this laboratory, Dash et al. [1–4] have reported the standard potentials of this electrode in water + urea, water + dioxane and water + alcohols solvent systems over a range of temperatures or at a single temperature, i.e. 25°C. The present work has been undertaken as a part of our programme for the determination of standard potentials of this electrode in different compositions of water + D-glucose and water + D-fructose solvent systems at 25°C. This temperature was selected in the present study since the standard electrode potentials of the silver–silver chloride electrode, which has been used as the reference electrode in this investigation, in D-glucose + water and D-fructose + water mixtures containing 5, 10, 20, and 30, and 5

and 10 wt.% D-glucose and D-fructose, respectively, are known [5,6] only at 25°C.

As in previous communications [1–4,7], the cells with a liquid junction, viz.

Ag, AgCl, NaCl(c), NaNO$_3$(c)/NaNO$_3$(c), AgNO$_3$(c), Ag          (A)
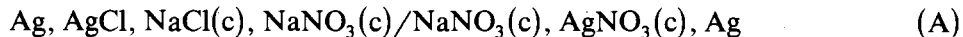
have been studied in water + organic solvent systems for the determination of standard potentials of the silver–silver ion electrode at 25°C.

EXPERIMENTAL

The chemicals, which were obtained in the best grade available and used without further purification, were: sodium chloride (Merck, G.R.), sodium nitrate (BDH, AnalaR), silver nitrate (BDH, AnalaR), D-glucose (Merck) and D-fructose (BDH, AnalaR). The silver and silver–silver chloride electrodes were prepared as described earlier [1,8]. The silver electrodes were of thermal electrolytic type and freshly prepared for each run. The cell vessels were of an all-glass type of the design described earlier [7(a)]. The solvent mixtures of various weight percentages were prepared as described in our earlier article [7(a)].

Solutions for the EMF measurements were freshly prepared for each run by dissolving the appropriate weighed amounts of salts in known volumes of aqueo–organic solvent mixtures.

The setting up of the cells and the EMF and conductance measurements were essentially similar to that described earlier [1,7(a)]. The cells were kept in the water thermostat maintained at ±0.1°C. The reproducibility of the EMF measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

The results of the EMF measurements for the cell (A) are presented in Table 1.

The EMF, $E$, of cell (A) is given by the expression

$$E = E^0_{cell} + \frac{RT}{F} \ln[Ag^+][Cl^-]\gamma_{\pm}^2 + E_j \tag{1}$$

where the symbols have their usual significance.

Using the molar concentration of AgNO$_3$ and NaCl solutions and expressing the mean molar activity coefficients by the Debye–Huckel expression, eqn. (1) becomes

$$E = E^0_{cell} + 2k \log C - \frac{2kA(2C)^{1/2}}{1 + (2C)^{1/2}} + 2k\beta_{\pm}C + E_j \tag{1a}$$

TABLE 1

Summary of EMF data of cell (A) in various water+D-glucose and water+D-fructose mixtures at 25°C

| $C$ (mole dm$^{-3}$) | EMF | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Wt.% D-glucose | | | | Wt.% D-fructose | |
| | 5 | 10 | 20 | 30 | 5 | 10 |
| 0.005 | | | 0.2703 | | | 0.2706 |
| 0.01 | | | 0.3123 | | | |
| 0.02 | | 0.3390 | 0.3450 | | 0.3370 | |
| 0.025 | 0.3460 | 0.3533 | 0.3565 | 0.3569 | | |
| 0.03 | 0.3631 | | | | | 0.3583 |
| 0.035 | 0.3648 | 0.3690 | 0.3745 | 0.3727 | 0.3667 | 0.3684 |
| 0.04 | 0.3725 | 0.3751 | 0.3808 | | 0.3707 | 0.3753 |
| 0.05 | 0.3800 | 0.3881 | | 0.3910 | 0.3813 | 0.3840 |
| 0.07 | 0.4000 | 0.4011 | 0.4030 | 0.4070 | 0.3972 | |
| 0.075 | 0.4022 | 0.4074 | | 0.4100 | 0.3995 | |
| 0.08 | | | | | | 0.4056 |
| 0.085 | | 0.4195 | | 0.4150 | | |

The standard molar potential, $E_c^0$, of the silver–silver ion electrode was obtained by the method of extrapolating [7] the auxiliary function, $E_c^{0'}$, to the molarity $C = 0$. $E_c^{0'}$ is given by

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

$$= E_c^0(\text{Ag/Ag}^+) + bC \qquad (2)$$

where $E_c^0(\text{Ag/AgCl})$ is the standard potential of the silver–silver chloride electrode and is known [5,6] at 25°C in the mixed solvents under investigation, and $A$ is the Debye–Huckel constant calculated by the usual equation [9] from the dielectric constant of the mixed solvents [5] at experimental temperatures. In eqn. (2), $k = (2.3026RT/F)$ and $b = 2k\beta_\pm$ (where $\beta_\pm$ is the usual constant in the Debye–Huckel expression for the activity coefficient i.e.

$$-\log \gamma_i = \frac{Az_i^2\mu^{1/2}}{1 + \mu^{1/2}} - B_i\mu$$

where $i$ is Ag$^+$ or Cl$^-$).

As usual [7(a)], the values of the liquid junction potential, $E_j$, were calculated from the equivalent conductance of silver nitrate and sodium chloride by means of the Henderson equation. The values of $E_j$ were found to be in the range 0.1–0.3 mV in all solvents.

The $E_c^0$ values of the silver–silver ion electrode are presented in Table 2.

TABLE 2

Standard potentials of the silver–silver ion electrode in different scales and the standard thermodynamic quantities in water + D-glucose and water + D-fructose mixtures at 25°C Standard potentials are given in absolute volts.

| | Wt.% D-glucose | | | | | Wt.% D-fructose | |
|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 20 | 30 | 5 | 10 |
| $E_c^0$(V) | 0.7991 | 0.7676 | 0.7646 | 0.7595 | 0.7533 | 0.7684 | 0.7655 |
| $E_m^0$(V) | 0.7991 | 0.7674 | 0.7642 | 0.7587 | 0.7520 | 0.7682 | 0.7651 |
| $E_N^0$(V) | 0.5929 | 0.5634 | 0.5627 | 0.5625 | 0.5618 | 0.5642 | 0.5636 |
| $\Delta G_m^0 \times -10^{-3}$(J mole$^{-1}$) | | 74.05 | 73.74 | 73.21 | 72.56 | 74.12 | 73.83 |
| $\Delta G_t^0 \times 10^{-3}$(J mole$^{-1}$) | | 2.85 | 2.91 | 2.93 | 3.00 | 2.77 | 2.83 |
| $\Delta G_{t,el}^0$(J mole$^{-1}$) | | 11.0 | 22.0 | 48.0 | 79.0 | 11.0 | 22.0 |
| $\Delta G_{t,ch}^0 \times 10^{-3}$(J mole$^{-1}$) | | 2.836 | 2.892 | 2.885 | 2.922 | 2.759 | 2.805 |
| $\lim(\log{}^s\gamma_w)$ $N \to 0$ | | 0.02952 | 0.03022 | 0.03042 | 0.03112 | 0.02872 | 0.02932 |

The average standard deviation in the values of $E_c^0$ is 0.3 mV. From the $E_c^0$ values, the values for the standard potentials on the molal ($E_m^0$) and mole fraction ($E_N^0$) scales have also been calculated at 25°C by the usual equation [10]. These values are also shown in Table 2 along with those in water [11].

The standard Gibbs free energy change, $\Delta G_m^0$, on the molal scale for the electrode reaction, $Ag^+$(solvated) + e ⇌ $Ag$(s) in various solvents has been evaluated at 25°C by the usual relation [7(e)], and is presented in Table 2. As observed, the $\Delta G_m^0$ value increases with increasing D-glucose or D-fructose content in the solvent system, i.e. with decreasing dielectric constant of the solvent. As the dielectric constant decreases, more work is needed to keep the ions apart, and therefore, less work is generated by the electrode reaction and more positive (i.e. less negative) Gibbs free energy changes result.

For the transfer process, $Ag^+$ (in water) → $Ag^+$ (in mixed solvent), the Gibbs free energy of transfer, $\Delta G_t^0$ is defined by the equation

$$\Delta G_t^0 = -F\left({}^s E_N^0 - {}^w E_N^0\right) \qquad (3)$$

where the superscripts w and s denote water and mixed solvent, respectively. $\Delta G_t^0$ values computed on the mole-fraction scale [10] are given in the Table 2.

As usual [1–4,7], the Gibbs free energy of transfer, $\Delta G_t^0$, is regarded as consisting of two parts as given by

$$\Delta G_t^0 = \Delta G_{t,el}^0 + \Delta G_{t,ch}^0 \qquad (4)$$

in which $\Delta G_{t,el}^0$ represents the electrostatic contribution arising from the change in the dielectric constant of the solvents during the transfer of charged particles from water to another solvent, and $\Delta G_{t,ch}^0$ represents the non-electrostatic or chemical contribution which takes into account the specific chemical interactions between the ions and solvent which include solvation as well as the basicity of the solvent. As previously [1–4,7], $\Delta G_{t,el}^0$

was estimated from the well-known Born equation [10] and the values for $\Delta G^0_{t,ch}$ were computed from eqn. (4). These values are listed in Table 2. As observed, the values of $\Delta G^0_t$ and $\Delta G^0_{t,ch}$ are positive for all solvents and the magnitude generally increases with increasing proportions of D-glucose and D-fructose. The Ag$^+$ ion thus appears to be in a lower Gibbs energy state in aqueous medium than in the respective mixed solvent. In other words, the transfer process from aqueous to aqueo–organic solvent system is not favoured. In so far as $\Delta G^0_{t,ch}$ is a measure of solvation as well as the relative basicities of the two solvents, the positive $\Delta G^0_{t,ch}$ value for transfer of the Ag$^+$ ion to all mixed solvents indicates that the mixed solvents possess a smaller solvating capacity towards the Ag$^+$ ion and are weaker bases than water. This is in agreement with the behaviour of the Ag$^+$ ion studied in other aqueous binary solvent systems containing dioxane and alcohols [2–4] lending support to the view that the silver ion, a 'soft' base [12], is less stable in the mixed solvents of enhanced basicity than in water.

The primary medium effect is a measure of the change in Gibbs free energy which accompanies the transfer of 1 gram-ion of Ag$^+$ from the standard state in water to the standard state in the mixed solvent. The values of the primary medium effect (mole-fraction scale) of various water + D-glucose and water + D-fructose mixtures upon the Ag$^+$ ion at 25°C were computed by the equation

$$\lim_{N \to 0} (\log {}^s\gamma_w) = \frac{({}^wE^0_N - {}^sE^0_N)}{2.3026RT/F} \tag{5}$$

where the limit term indicates the primary medium effect. These values are also shown in Table 2. Since the primary medium effect results from a difference of the ion–solvent interactions at infinite dilution in each solvent, the magnitude of this effect should reflect the stabilisation of the Ag$^+$ ion in the solvent concerned. The resulting positive magnitudes of this quantity presumably indicates that the escaping tendency of the Ag$^+$ ion is more in water + D-glucose or water + D-fructose mixtures than in pure water. This is consistent with the conclusions based on the fact that the Ag$^+$ ion is more strongly stabilised in water than in mixed solvents.

TABLE 3

Thermodynamic solubility products on molar ($K^c_s$) and molal ($K^m_s$) scales of AgCl in water + D-glucose and water + D-fructose mixtures at 25°C

| | Ref. | Wt.% D-glucose | | | | Wt.% D-fructose | |
|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 5 | 10 |
| $K^c_s \times 10^{10}$ | 5 | 5.266 | 5.006 | 4.284 | 3.610 | 5.184 | 5.025 |
| | 6 | 5.434 | 5.323 | 4.826 | 4.353 | | |
| $K^m_s \times 10^{10}$ | 5 | 5.234 | 4.937 | 4.150 | 3.436 | 5.153 | 4.956 |
| | 6 | 5.402 | 5.256 | 4.675 | 4.143 | | |

The solubility products, $K_s^0$, of silver chloride in water + D-glucose and water + D-fructose mixtures have been calculated at 25°C from the values of the standard potentials of the silver–silver chloride electrode, and of the silver electrodes by means of the equation

$$\ln K_s^0 = \left[ E_c^0(\text{Ag}/\text{AgCl}) - E_c^0(\text{Ag}/\text{Ag}^+) \right] \frac{F}{RT} \qquad (6)$$

where $E_c^0(\text{Ag}/\text{AgCl})$ is the standard molar potential of the silver–silver chloride electrode and is obtained from the literature [5,6]. The values for $K_s^0$ in the molarity, $K_s^c$, and molality, $K_s^m$, scales are presented in Table 3 at 25°C. The data for $K_s^m$ were calculated from $K_s^c/\rho^2$, where $\rho$ is the density of the mixed solvent.

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