The Macroscopic and Microscopic Free Energies of Solvation of Silver Chromate and Silver Phosphate in Some Organic Solvents at 298.15K

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Abstract  The macroscopic free energies of solvation of silver chromate and silver phosphate in different solvents, acetonitrile (AN), N-methylformamide (NMFA), N-N, dimethylformamide (DMFA), propylene carbonate (PC), dimethyl sulphoxide (DMSD), N-methyl-pyrrolidone (NMePy) and ethanol (ETOH) were estimated from the experimental solubility measurements at 298.15K. The macroscopic free energies ∆G(Ma) and free energy of transfer ∆ G

t (Ma) for Ag 2CrO4 and Ag3PO4 in the organic solvents represent the macroscopic part of the free energies. The macroscopic free energies for both electrolytes were evaluated experimentally and compared with the microscopic free energies which calculated theoretically. The microscopic free energies of solvation of silver chromate and silver phosphate in the used solvents were theoretically calculated, which are the cavity, the lennard Jones, the induced, the volume and the dipole-dipole free energies and not only electrostatic energy as explained before. The macroscopic and microscopic free energies were compared and discussed.

Keywords  Macroscopic, Microscopic, Cavity, Lennard Jones, Induced, Volume and Dipole-Dipole Energies -Silver Chromate –Silver Phosphate

1. Introduction

The solubility of an electrolyte is influenced by a wide range of factors, including ion association, variation in ionic activity coefficients, complexation and temperature. Solubility is an equilibrium property enable to thermodynamic parameters through the standard state free energy. Ion pairing can occur in dilute solutions for many electrolytes, particularly these with multivalent ions and for all electrolytes in concentrated solutions. Ion pairing is generally more pronounced in non-aqueous solvents which have lower dielectric constants than water. In effect, the ion pairs represent a reservoir of electrolyte in the solution and increase the solubility. The complexity of the system increases for usymmetrical electrolytes or for mixed electrolyte systems[1]. Bjerrum[2] proposed, that the motion of ions would be coupled when the energy of attraction between them exceeded the thermal energy. For solely columbic interaction theory predicts a distance within which the electrostatic attraction between ions is greater than 2kT. Which will be sufficient to couple the motions of the ions. The treatment takes account of only electrostatic interactions and neglects molecularity of solvent. Nevertheless, in low concentration, strong interactions between ions and solvent molecules resulting in ion pair configuration. The three commonly assumed structures are, the first in which the ion retains their individual solvation shells, and so is separated by two solvent molecules. The second in which the ions share some part of their solvation shells so are separated by one molecule and the third where the ions are in contact and share a common solvation shell.

The presence of species such creates an experimental difficulty, the different techniques will have different sensitivities to the species present. Thus the conductance will see on the dissociated ions and the presence of ion pairs is determined by difference from experimental molar conductance and that expected for strong electrolyte[3].

The formation of complexes (complexation) provides a route to increased solubility. Several equivalent representations of the speciation in these systems have been used[4]. Pierotti theory[5] applies the scaled particle theory[6] to estimate solubilities, heats, entropies and molar capacities of solutions.

Good agreement between theory and experiment for evaluating the thermodynamic parameters has been obtained for a number of neutral compounds and gases in a variety of solvents[7-11].

Many authors like Bjerrum and others reported that the electrostatic energy plays important role in the solvation energy. In this work more work (novel) was done to explain the different types of electrostatic coulombic energy[11].

The aim of the present work is to extend the applicability
of the scaled particle theory (especially applied for noble gases) as novel method for discussing the solvation of the electrolyte, silver chromate and silver phosphate in different organic solvents. Knowing the other factors affecting the solubility is very important here. Is the electrostatic energy play important role in the solubility or not.

2. Experimental

Ag₂CrO₄ and Ag₃PO₄ are of the type Riedel-de-Häen AG, Seelze- Hannover was used. acetonitrile (AN), N-N, dimethylformamide (DMFA), dimethylsulphoxide (DMSO) and ethanol (EtOH) were obtained from BDH. N- methylformamide (NMFA), propylene carbonate (PC) and N- methyl-pyrrolidone (NMePy) were obtained from Merck (zur analyse). The solubilities of Ag₂CrO₄ and Ag₃PO₄ in the organic solvents under consideration were done gravimetrically with at least three measurements as explained in previous works.[12-14].

3. Results and Discussion

The measured molar solubilities for Ag₂CrO₄ and Ag₃PO₄ in the organic solvents, AN, NMFA, DMFA, PC, DMSO, NMePY and EtOH as explained in Table 2, from the molar solubility data. Values of pKsp were estimated by use of equation (2).

\[ \Delta G(\text{Ma}) = 2.303 \times 10^{-3} \, \text{RT} \, pK_{sp} \]  (3)

The macroscopic free energies of transfer \( \Delta G_i(\text{Ma}) \) from ethanol (EtOH) as reference solvent to the organic solvent (s) could be calculated by using equation (4).

\[ \Delta G_i(\text{Ma}) = \Delta G_i(\text{N}) - \Delta G_i(\text{el}) \]  (4)

The macroscopic free energies \( \Delta G(\text{Ma}) \) and free energy of transfer \( \Delta G_i(\text{Ma}) \) for Ag₂CrO₄ and Ag₃PO₄ in the organic solvents, expressed the total solvation energies and represented in Tables (2 and 3). The values of the last macroscopic energies of transfer are divided into neutral (non-electrostatic) and electrostatic free energy of solvation.

\[ \Delta G_i(\text{Ma}) = \Delta G_i(\text{N}) + \Delta G_i(\text{el}) \]  (5)

The electrostatic free energy can be calculated by using Born equation as follows[14].

\[
\text{Solvent} & \quad \text{m molal} & \log \gamma_+ & \log \gamma_- & pK_{sp} \\
AN & 1.5373 \times 10^{-4} & -0.0063 & 10.8072 \\
NMFA & 2.5495 \times 10^{-4} & -0.0504 & 7.1938 \\
DMFA & 1.7446 \times 10^{-4} & -0.0132 & 3.1489 \\
PC & 1.8331 \times 10^{-4} & -0.0135 & 10.6074 \\
DMSO & 3.0444 \times 10^{-4} & -0.0174 & 9.9474 \\
NMePY & 3.7168 \times 10^{-4} & -0.0609 & 6.6894 \\
EtOH & 1.8325 \times 10^{-4} & -0.0135 & 3.1349 \\
\]

\[
\text{Solvent} & \quad \text{m molal} & \log \gamma_+ & \log \gamma_- & pK_{sp} \\
AN & 1.6237 \times 10^{-4} & -0.0020 & 17.7245 \\
NMFA & 1.3788 \times 10^{-4} & -0.0187 & 9.9918 \\
DMFA & 1.8699 \times 10^{-4} & -0.0069 & 13.5116 \\
PC & 6.7755 \times 10^{-4} & -0.0041 & 15.2406 \\
DMSO & 1.3346 \times 10^{-4} & -0.0058 & 14.0613 \\
NMePY & 1.5699 \times 10^{-4} & -0.0200 & 9.7651 \\
EtOH & 3.5986 \times 10^{-4} & -0.0096 & 12.3345 \\
\]

\[
\text{Solvent} & \quad \Delta G(\text{exp}) & \Delta G(\text{Mac}) & \Delta G(\text{el}) & \Delta G(\text{N}) \\
AN & 61.4748 & 43.6423 & 1.1725 & 42.4698 \\
NMFA & 40.9159 & 23.0834 & -6.3430 & 39.4264 \\
DMFA & 17.9118 & 0.0793 & 1.4640 & -1.3847 \\
PC & 60.3381 & 42.5056 & 0.9238 & 41.5808 \\
DMSO & 56.5837 & 38.7512 & -0.5530 & 39.3042 \\
NMePY & 38.0513 & 20.2183 & 2.0055 & 18.2133 \\
EtOH & 17.8325 & 0 & 0 & 0 \\
\]

\[
\text{Solvent} & \quad \Delta G(\text{exp}) & \Delta G(\text{Mac}) & \Delta G(\text{el}) & \Delta G(\text{N}) \\
AN & 100.8222 & 30.6599 & 1.0737 & 29.5862 \\
NMFA & 32.3567 & -37.8056 & -4.4626 & -33.34 \\
DMFA & 76.8580 & 6.6957 & 0.9104 & 5.785 \\
PC & 86.6931 & 16.5308 & -1.9366 & 18.4671 \\
DMSO & 79.9848 & 9.8225 & -0.4046 & 10.22 \\
NMePY & 55.5468 & -14.6155 & 1.4905 & 13.125 \\
EtOH & 70.1623 & 0 & 0 & 0 \\
\]
and Ag$_2$CrO$_4$, Ag$_3$PO$_4$ data are given in Table (3).

Therefore two difference types of free energies are present, cavity and interaction energy. Therefore two difference types of free energies are present, cavity and interaction energy. Therefore two difference types of free energies are present, cavity and interaction energy.

$$
AG_i(\text{el}) = \left(\frac{694.1}{r} - 0.0235\right) \varepsilon
$$

Where $r$ is the solvated radius for Ag$_2$CrO$_4$ and for Ag$_3$PO$_4$, which is the sum of both electrolyte radius and solvent radix$[15,16]$. $\varepsilon$ is solvent dielectric constant$[13]$. The calculated values of $AG_i(N)$ and $AG_i(\text{el})$ for Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ in the organic solvents are also given in Table (2). It was shown from Table (2) that all the three types of free energies, $AG_i(Ma)$, $AG_i(\text{el})$ and $AG_i(N)$ for Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ have the following order:

AN > PC > DMSO > NMFA > NMePy > DMFA

For the calculation of the microscopic free energies for Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ in the organic solvents under consideration at 298.15K, the Pierotti theory$[5-7]$ was applied. This model explains the solvation process through the creation of solute in the solvent followed by interaction. Therefore two difference types of free energies are present, cavity and interaction energy.

$$
G = G_c + G_i
$$

Where $G_c$ is the cavity free energy and $G_i$ is the microscopic interaction free energy the cavity free energy, necessary to form cavity of electrolyte size in solution was calculated by using Pierotti's theory based on Reiss model$[13]$ and Ag$_2$CrO$_4$, Ag$_3$PO$_4$ data are given in Table (3).

The interaction free energy ($G_i$) is a composite of Lennard Jones energy ($G_i$), the induced free energy ($G_{\text{ind}}$), the volume free energy ($G_v$), and the dipole-dipole free energy ($G_{\text{dip}}$).

$$
G_i = G_i + G_{\text{ind}} + G_v + G_{\text{dip}}
$$

All the microscopic free energies for Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ solutions were calculated as explained in ref. 13 and the evaluated data are presented in Tables (5 and 6).

**Table 5.** The microscopic free energies of solution of Ag$_2$CrO$_4$ in some organic solvents at 298.15K (in kJ/mole)

| Solvent | $G_c$ | $G_i$ | $G_{\text{ind}}$ | $G_v$ | $G_{\text{dip}}$ |
|---------|-------|-------|------------------|-------|------------------|
| AN      | 88.9629 | 71.6309 | 1.8219          | 18.0307 | -161.0510       |
| NMFA    | 93.9556 | 75.4451 | 1.9245          | 15.5678 | -100.6469       |
| DMFA    | 84.0342 | 83.9997 | 2.1421          | 14.2121 | -                |
| PC      | 81.287   | 81.287  | 2.2223          | 11.8677 | -103.0410       |
| DMSO    | 87.2097  | 87.2097 | 2.0734          | 13.6777 | -80.1303        |
| NMePy   | 33.3810  | 81.3217 | 2.3484          | 12.0739 | -                |
| EtOH    | 95.3545  | 37.3149 | 1.7870          | 17.2518 | -216.77         |

**Table 6.** The microscopic free energies of solution of Ag$_3$PO$_4$ in some organic solvents at 298.15K (in kJ/mole)

| Solvent | $G_c$ | $G_i$ | $G_{\text{ind}}$ | $G_v$ | $G_{\text{dip}}$ |
|---------|-------|-------|------------------|-------|------------------|
| AN      | 99.1491 | 79.8326 | 2.0305          | 20.0952 | -79.4913        |
| NMFA    | 104.7135 | 84.0835 | 2.1448          | 17.3503 | -112.1709       |
| DMFA    | 94.0673  | 93.8076 | 2.3873          | 15.7417 | -                |
| PC      | 90.5943  | 97.1952 | 2.4767          | 13.2265 | -114.8391       |
| DMSO    | 97.1952  | 90.5946 | 2.3109          | 15.2430 | -89.3052        |
| NMePy   | 86.2411  | 90.6330 | 2.6173          | 13.4564 | -                |
| EtOH    | 106.2725 | 81.7095 | 2.0461          | 19.2271 | -241.5901       |

It was concluded that the neutral free energy is the major part (big part) in the macroscopic experimental free energies for both electrolytes Ag$_2$CrO$_4$ and Ag$_3$PO$_4$. Also it is concluded that cavity formation free energy is the major energy in the microscopic free energy$[17-20]$. Summing all the microscopic free energies give values in the same order as that of the macroscopic free energy values. Also it was concluded that the electrostatic coulombic energies for Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ are the microscopic free energies, which can be theoretically calculated. These microscopic free energies are noble and new for explaining the solvation behaviours of these important salts (Ag$_2$CrO$_4$ and Ag$_3$PO$_4$) in industry. The data were compared with that of the total macroscopic free energies evaluated from the experimental solubility data giving good results. This work gives a lot of data about the solubilities of the two used salts Ag$_2$CrO$_4$ and Ag$_3$PO$_4$ necessary in electroplating and photographic technology.

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