

# 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 (DMSO), N-methyl-pyrrolidone (NMePy) and ethanol (ETOH) were estimated from the experimental solubility measurements at 298.15K. The macroscopic free energies  $\Delta G(\text{Ma})$  and free energy of transfer  $\Delta G_t(\text{Ma})$  for  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  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 unsymmetrical 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 coulombic interactions 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

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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

$\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  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- methyle-pyrrolidone (NMePy) were obtained from Merck (zur analyse). The solubilities of  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  in the organic solvents, AN, NMFA, DMFA, PC, DMSO, NMePy and EtOH as explained in Ref. (8) are listed in Tables (1 and 2).

Prediction of electrolyte activity coefficients is one of the classical problems in physical chemistry and is outlined in classical work[13]. The defining characteristic of ions is that they carry a net charge and so the principle interaction between ions are largest contribution to the activity coefficients are coulombic. Debye and Hückel solved the problem for system purely electrostatic interactions between point charges surrounded by a dielectric continuum. Therefore the extended Debye-Huckel equation was applied taking account of the ion size[14]

From the activity coefficients  $\gamma_{\pm}$ , calculated using Debye Hückel equation and from the molar solubility data. Values of  $\text{pK}_{\text{sp}}$   $\text{Ag}_2\text{CrO}_4$  were estimated by use of equation (1).

$$\text{pK}_{\text{sp}} = -\log 4 S^3 + 4 (\log \gamma_{\pm})^3 \quad (1)$$

The solvated radius of the  $\text{Ag}_2\text{CrO}_4$  electrolyte were calculated by summing the ionic radii of the salt[15] to the solvent radius for each organic solvent taken from ref. 13. The log activity coefficients ( $\log \gamma_{\pm}$ ) and the solubility products ( $\text{pK}_{\text{sp}}$ ) calculated for  $\text{Ag}_2\text{CrO}_4$  in the solvents under consideration are represented in Table 1 also.

The measured solubilities for  $\text{Ag}_3\text{PO}_4$  as explained also in ref. 12 in the organic solvents, AN, NMFA, DMFA, PC, DMSO, NMePy and EtOH are listed in Table 2, from the activity coefficients  $\gamma_{\pm}$ , calculated using Debye Hückel equation as explained in ref. 12 and from the molal solubility data. Values of  $\text{pK}_{\text{sp}}$  were estimated by use of equation (2).

$$\text{pK}_{\text{sp}} = [-\log (27S^4) + 27 (10 \log \gamma_{\pm})^4] \quad (2)$$

The experimental macroscopic free energies of solvation of  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  in the organic solvents at 298.15K

were evaluated by the use of equation (3).

$$\Delta G (\text{Ma}) = 2.303 RT \text{pK}_{\text{sp}} \quad (3)$$

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

$$\Delta G_t (\text{Ma}) = \Delta G_s (\text{Ma}) - \Delta G_{\text{EtOH}} (\text{Ma}) \quad (4)$$

The macroscopic free energies  $\Delta G (\text{Ma})$  and free energy of transfer  $\Delta G_t (\text{Ma})$  for  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  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.

$$\Delta G_t (\text{Ma}) = \Delta G_t (\text{N}) + \Delta G_t (\text{el}) \quad (5)$$

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

**Table 1.** Molal solubilities, log activity coefficients ( $\log \gamma_{\pm}$ ) and solubility products of  $\text{Ag}_2\text{CrO}_4$  in different solvents at 298.15 K

Solvent	m molal	$\log \gamma_{\pm}$	$\text{pK}_{\text{sp}}$
AN	$1.5737 \times 10^{-4}$	-0.0063	10.8072
NMFA	$2.5495 \times 10^{-3}$	-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

**Table 2.** Molal solubilities, log activity coefficients ( $\log \gamma_{\pm}$ ) and solubility products of  $\text{Ag}_3\text{PO}_4$  in different solvents at 298.15K

Solvent	m molal	$\log \gamma_{\pm}$	$\text{pK}_{\text{sp}}$
AN	$1.6237 \times 10^{-5}$	-0.0020	17.7245
NMFA	$1.3788 \times 10^{-3}$	-0.0187	9.9918
DMFA	$1.8699 \times 10^{-4}$	-0.0069	13.5116
PC	$6.7755 \times 10^{-5}$	-0.0041	15.2406
DMSO	$1.3346 \times 10^{-4}$	-0.0058	14.0613
NMePY	$1.5699 \times 10^{-3}$	-0.0200	9.7651
EtOH	$3.5986 \times 10^{-4}$	-0.0096	12.3345

**Table 3.** Macroscopic experimental, electrostatic and neutral free energies for  $\text{Ag}_2\text{CrO}_4$  in different solvents at 298.15 K (in kJ/mole)

Solvent	$\Delta G (\text{exp})$ Mac	$\Delta G_t (\text{exp})$ Mac	$\Delta G_t (\text{el})$	$\Delta G_t (\text{N})$
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

**Table 4.** Macroscopic experimental, electrostatic and neutral free energies for  $\text{Ag}_3\text{PO}_4$  in different solvents at 298.15 K (in kJ/mole)

Solvent	$\Delta G (\text{exp})$ Mac	$\Delta G_t (\text{exp})$ Mac	$\Delta G_t (\text{el})$	$\Delta G_t (\text{N})$
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

$$\Delta G_t(\text{el}) = \left( \frac{694.1}{r} - \frac{0.0235}{\epsilon} \right) \quad (6)$$

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



For the calculation of the microscopic free energies for  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  in the organic solvents under consideration at 298.15K, the Pierotti theory[5-7] was applies.

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.

$$G = G_c + G_i \quad (7)$$

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  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Ag}_3\text{PO}_4$  data are given in Table (3).

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

$$G_i = G_L + G_{\text{ind}} + G_v + G_{\text{dip}} \quad (8)$$

All the microscopic free energies for  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  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 solvation of  $\text{Ag}_2\text{CrO}_4$  in some organic solvents at 298.15K (in kJ/mole)

Solvent	$G_c$	$G_L$	$G_{\text{ind}}$	$G_v$	$G_{\text{dip}}$
AN	88.9629	71.6309	1.8219	18.0307	-161.0510
NMFA	93.9556	75.4451	1.9245	15.5678	-100.6469
DMFA	84.4032	83.99.07	2.1421	14.1245	-
PC	81.287	87.2097	2.2223	11.8677	-103.0410
DMSO	87.2097	81.2873	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 solvation of  $\text{Ag}_3\text{PO}_4$  in some organic solvents at 298.15K (in kJ/mole)

Solvent	$G_c$	$G_L$	$G_{\text{ind}}$	$G_v$	$G_{\text{dip}}$
AN	99.1491	79.8326	2.0305	20.0952	-179.4913
NMFA	104.7135	84.0835	2.1448	17.3503	-112.1709
DMFA	94.0673	93.6076	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  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$ . 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  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  are the microscopic free energies, which can be theoretically calculated. These microscopic free energies are novel and new for explaining the solvation behaviours of these important salts ( $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$ ) 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  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  necessary in electroplating and photographic technology.

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