

Thermodynamics of the Solvation of Potassium Chromate in Mixed DMF-H₂O Solvents at 301.15 K

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Abstract The Gibbs free energies for K₂CrO₄ were evaluated in mixed dimethylformamide (DMF)-H₂O solvents at 301.15 K from the experimental solubility measurements. From the experimental solubility data also the ionic radii of potassium and chromate ions are evaluated. The total free energy of the salt is divided into its individual contribution in the mixtures used. Libration Gibbs free energy for moving K₂CrO₄ from standard gas state to standard solution state was calculated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid K₂CrO₄ (cr) was also calculated and used for further evaluation. The conventional Gibbs free energies for the cation (K⁺) and the anion (CrO₄²⁻) were estimated theoretically and also the Gibbs free energy of CrO₄²⁻ gas was evaluated and all values were discussed.

Keywords Thermodynamics, Gibbs Free Energies, Potassium Chromate, Solvation, Solubility, Aqueous and Dimethylformamide Mixtures

1. Introduction

For neutral species experimental solvation Gibbs free energies have been tabulated large number of solutes in both aqueous[1-7] and non-aqueous[7, 8] solvents. Typically, these solvation free energies are determined experimentally [8] and their uncertainty is relatively low (~ 0.8 KJ/mol)[9].

Determining accurate values for the Gibbs free energies of ionic solutes like K₂CrO₄ is important than that of neutral solutes. Understanding the partitioning of single ions between different liquid phases is important in many areas of biology. For example, the electrical signals sent by nerve cells are activated by changes in cell potential that are caused by the movement of various ions across the neuronal membrane[10]. The division of thermodynamic Gibbs free energies of solvation of electrolytes into ionic constituents is conventionally accomplished by using the single ion solvation Gibbs free energy of one reference ion, conventionally, the proton, to set the single ion scales[11, 12]. The aim of this work is to estimate the single ion Gibbs free energies for K⁺ & CrO₄²⁻ ions in mixed DMF H₂O solvents at 301.15 K.

Sums of solvation free energies of cations and anions are well defined through the use of thermochemical cycles involving calorimetric or electrochemical measurements [13-17]. A number of different extra thermodynamic

approximations have been used[18-25] for partition the sums of cation and anion Gibbs free energies into single ion contribution. Solvation Gibbs free energies for single ions are necessary for theoretical calculations.

2. Relative and Conventional Solvation Free Energies of Ions

The Gibbs solvation free energies of ions as relative free energies by settling the free energy of solvation of some reference ion equal zero[26]. Proton was chosen as reference ion. For ions, this result in a set of conventional free energies of solvation that the cations are shifted from their absolute values by the value for the absolute Gibbs solvation free energy of the proton.

The conventional Gibbs free energies of solvation for anions are shifted by an equal amount in the opposite direction.

3. Conventional Gibbs Free Energies from Reduction Potentials

When the convention for the absolute Gibbs free energy of the proton is followed, the solution-phase free energy change associated with the half cell for reduction of hydrogen gas is equal to zero. Reduction potentials following this convention for hydrogen electrode are referred as standard reduction potentials. From the half cell reaction for the reduction of metal cation to crystalline phase and the half reduction reaction of hydrogen gas, the redox reaction can be

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illustrated through the use of thermochemical cycle[12]. This last procedure can be used to estimate the gas free energy of formation for CrO_4^{2-} ion, to explain the ionic behaviour.

4. Experimental

Potassium chromate K_2CrO_4 Griffinkamp and N-N, dimethylformamide (DMF) from Merck Co, were used.

Saturated solutions of K_2CrO_4 were prepared by dissolving different amounts of the salt in closed test tubes containing different DMF- H_2O mixtures. These mixtures were then saturated with nitrogen gas as inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility of K_2CrO_4 in each mixture was measured gravimetrically by evaporating 1 ml of the saturated solution in small cup using I. R. lamp. The measurements were done by three readings for each solution at 301.15 K.

5. Results and Discussion

The molar solubility (S) for K_2CrO_4 was measured gravimetrically in mixed DMF- H_2O solvent at 301.15 K. The solubility values with an average number of the second number after comma are cited in Table (1). These (S) value in water agreed well with that in literature values[27]. The

activity coefficients were calculated by the use of Debye-Hückel equation[28, 29].

$$(\log \gamma_{\pm}) = -0.5062 \sqrt{I} \quad (1)$$

Where I is the ionic strength calculated from S values. These data $(\log \gamma_{\pm})$ were tabulated also in Table (1).

The solubility product was calculated by the use of equation 2[30].

$$\text{pK}_{\text{sp}} = -4(\log S^3 + \log \gamma_{\pm}^3) \quad (2)$$

The solubility product (pK_{sp}) data are given in Table (1). From solubility products the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations (3) and (4). Their values are tabulated also in Table (1)[31, 32].

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

$$\Delta G_t = \Delta G_s - \Delta G_w \quad (4)$$

s, w denote solvent and water respectively.

It was concluded that the Gibbs free energies of transfer (ΔG_t) increase in negativity by increasing the mole fraction of DMF in the mixed DMF- H_2O solvents. This is due to more solvation behaviour in the mixed solvents than that of water (see Fig. 1).

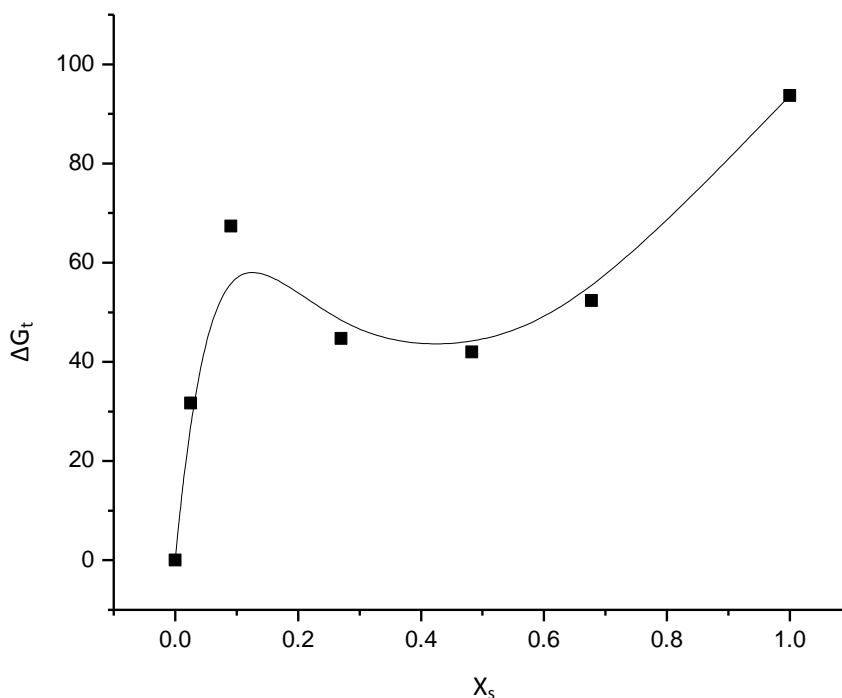


Figure 1. Gibbs free energies of transfer for K_2CrO_4 versus the mole fraction of DMF at 301.15 K

Table (1). Solubility and Gibbs free energies for K₂CrO₄ in mixed DMF-H₂O solvents at 301.15 K

| X _s DMF | S g.mol/l | log γ_{\pm} | pK _{sp} | ΔG KJ/mol | ΔG_i KJ/mol |
|--------------------|-----------|--------------------|------------------|-------------------|---------------------|
| 0 | 3.218 | -0.4984 | -0.6469 | -3.7301 | 0 |
| 0.0253 | 2.245 | -1.3136 | 4.8523 | 27.7788 | 31.700 |
| 0.0909 | 1.416 | -1.4754 | 11.0342 | 63.6244 | 67.354 |
| 0.2699 | 0.910 | -1.1828 | 7.1106 | 41.0056 | 44.7357 |
| 0.4828 | 0.411 | -0.7939 | 6.6359 | 38.2633 | 41.9934 |
| 0.6773 | 0.340 | -0.7014 | 8.4280 | 48.5960 | 52.3261 |
| 1.0 | 0.051 | -0.2800 | 15.5970 | 89.9333 | 93.6642 |

Single ion Gibbs free energies and convention free energies for K⁺ and CrO₄²⁻ ions.

It was well known that the preferential single ion thermodynamic parameters depend on the ionic radii of two ions (cation and anion). Therefore the ionic radii ratio between K⁺ and CrO₄²⁻ were evaluated from exact radii values given in literature[35] and found to be 0.4399.

Multiply the ionic radii ratio for K⁺ / CrO₄²⁻ by the Gibbs free energies of K₂CrO₄ we get the ionic Gibbs free energies for K⁺ ion. Then subtract K⁺ Gibbs free energies from K₂CrO₄ Gibbs free energy we obtain the Gibbs free energies for CrO₄²⁻ anion in K₂CrO₄. The obtained values for single ions are presented in Table (2). The conventional Gibbs free energies (ΔG_s^{con}) (K⁺) for potassium ion in solvents are shifted from their absolute values by the absolute free energy of the proton[34] according to equation (5).

$$2\Delta G_s^{\text{con}}(\text{K}^+) = 2\Delta G_s(\text{K}^+) - 2\Delta G_s(\text{H}^+) \quad (5)$$

and for (CrO₄²⁻) anion is shifted by an equal amount in the opposite direction (equation 6).

$$\Delta G_s^{\text{con}}(\text{CrO}_4^{2-}) = \Delta G_s(\text{CrO}_4^{2-}) + 2\Delta G_s(\text{H}^+) \quad (6)$$

Where $\Delta G_s(\text{K}^+)$, $\Delta G_s(\text{CrO}_4^{2-})$ and $\Delta G_s(\text{H}^+)$ are the Gibbs free energies of solvation for potassium, chromate and proton in solvents.

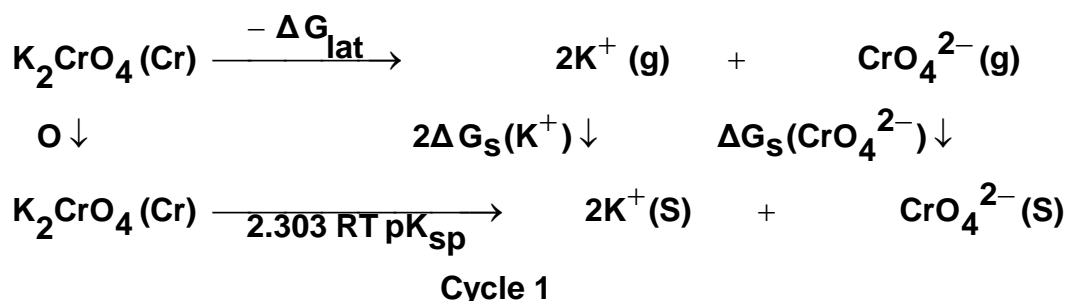
From the mean values of Gibbs free energies for the proton in water and other solvents given in literature[12, 35, 36], a straight line was drawn between these mean proton values and the diameter for each solvent taken from[37]. From this line the proton solvation free energies in pure water and DMF were obtained and found to be 1523 and 1561 KJ/mol, respectively. Multiplying these values by the mole fraction of each solvent and then sum the results. The mixed solvent proton free energies in DMF-H₂O mixtures were obtained and their values are given in Table (2). Apply equations (5) and (6) we get the conventional Gibbs free energies for the cation K⁺ and the anion CrO₄²⁻, their values are given also in Table (2). Cation conventional free energy values are negative indicating exothermic character and anion values are positive indicating endothermic character. Both values conventional Gibbs free energies for potassium and chromate ions increase with increase of the mole fraction of DMF due to more solvation and the sum of them gives the values for the neutral salt.

Table (2). Single ion Gibbs free energies for K⁺, chromate CrO₄²⁻ and their half conventional energies at 301.15 K. in mixed DMF-H₂O solvents (in KJ/mol)

| X _s DMF | $\Delta G(\text{K}^+)$ | $\Delta G(\text{CrO}_4^{2-})$ | $\frac{1}{2}(2\Delta G_s^{\text{con}})(\text{K}^+)$ | $\frac{1}{2}\Delta G_s^{\text{con}}(\text{CrO}_4^{2-})$ | $\Delta G_s^*(\text{H}^+)$ |
|--------------------|------------------------|-------------------------------|---|---|----------------------------|
| 0 | 1.6408 | 2.089 | -1524 | 1520.91 | 1523 |
| 0.0253 | 12.3078 | 15.6701 | -1510.68 | 1538.67 | 1523 |
| 0.0909 | 27.9884 | 35.6366 | -1495.01 | 1558.63 | 1523 |
| 0.2699 | 18.0386 | 22.9672 | -1515.96 | 1556.96 | 1534 |
| 0.4828 | 16.8320 | 21.4312 | -1524.16 | 1562.43 | 1541 |
| 0.6773 | 21.3774 | 27.2186 | -1530.62 | 1579.21 | 1552 |
| 1.0 | 39.5616 | 50.3716 | -1521.43 | 1611.37 | 1561 |

Libration Gibbs free energies for K₂CrO₄ in mixed DMF-H₂O solvents:

The libration Gibbs free energies for K₂CrO₄ in mixed DMF/H₂O solvents at 301.15 K were calculated following thermochemical cycle 1 (cycle 1) as applied in literature[12] for silver salts following solubility product concept.



Where ΔG_{lat} is the lattice free energy, (g) and (s) denote the gas and solution cases. The lattice energy was calculated following Bartlett's relationship following equation (7)[38-41].

$$\Delta G_{\text{late}} = \frac{232.8}{\sqrt[3]{V}} + 110 \text{ KJ/mol} \quad (7)$$

The volumes for solid K_2CrO_4 was calculated by dividing its molecular weight by the density of solid given in literature[4] and apply it in equation (7) to obtain 198.938 KJ/mol as ΔG_{lat} for K_2CrO_4 .

On the use of equation (8) cycle (1), the liberation free energy for K_2CrO_4 was obtained (99.468 KJ/mol).

$$2\Delta G_{\text{S}}(\text{K}^+) = \Delta G_{\text{S}}(\text{CrO}_4^{2-}) = 2.303 \text{ RT pK}_{\text{sp}} - \Delta G_{\text{lat}} - 2\Delta G^{0 \rightarrow *} \quad (8)$$

The $2\Delta G^{0 \rightarrow *}$, the free energy change associated with moving K_2CrO_4 from standard gas phase at 1 atmosphere to solution phase. This free energy change has been referred as “compression” work of the gas or liberation free energy.

Conventional free energies from reduction potentials:

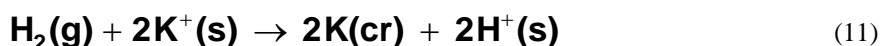
The absolute Gibbs free energy of the proton is followed solution phase free energy change associated with the following half cell.



The half cell reaction for the reduction of cation is:



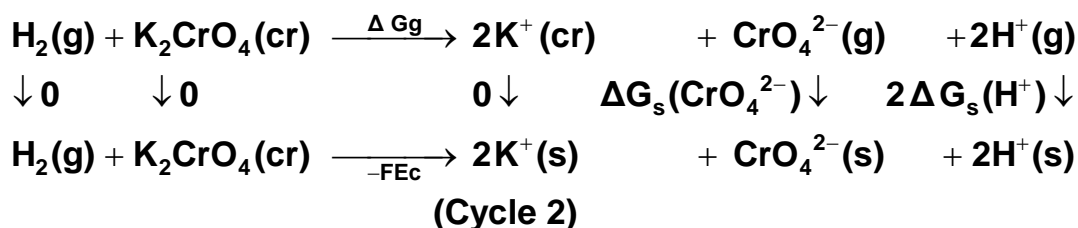
The symbol (cr) is the crystal phase. The sum of the two half cells is:



Through the thermochemical cycle 2, the conventional free energy of K^+ can be written as:

$$2\Delta G_{\text{S}}^{*\text{con}}(\text{K}^+) = 2\Delta fG(\text{H}^+)\text{g} - 2\Delta fG(\text{K}^+) - 2\text{FEc} \quad (12)$$

Where $\Delta fG(\text{H}^+)\text{g}$, $\Delta fG(\text{K}^+)$ are the gas free energy of formation for H^+ and K^+ ions. F faraday's constant, equal = 23.061 Kcal/mol and E_c is the standard reduction potential of K^+ .



Also the conventional free energy of the chromate ion can be written following Truhlar[12] explanation as:

$$\Delta G_{\text{S}}^{*\text{con}}(\text{CrO}_4^{2-}) = -2\Delta fG_{\text{g}} - 2\text{FEc} - 2\Delta G^{0 \rightarrow *} \quad (13)$$

Apply last equation the ΔG_g , gas free energies of formation for the anion CrO_4^{2-} and K^+ estimated in the mixed DMF-H₂O solvents and their values are given in Table (3) and Fig. (2). The $\Delta f G_g$ values increase by increase of the mole fraction of DMF favoring less solvation.

Table (3). Gas formation free energy for CrO_4^{2-} anion and K^+ cation in mixed DMF-H₂O solvents at 301.15 K (in KJ/mol)

| X_s DMF | $\Delta f G_g (\text{CrO}_4^{2-})$ | $\Delta f G_g (\text{K}^+)$ |
|-----------|------------------------------------|-----------------------------|
| 0 | -1835.31 | 2760.40 |
| 0.0253 | -1853.07 | 2746.58 |
| 0.0909 | -1873.07 | 2731.41 |
| 0.2699 | -1871.38 | 2752.36 |
| 0.4828 | -1876.83 | 2760.56 |
| 0.6773 | -1893.61 | 2766.61 |
| 1.0 | -1925.77 | 2750.11 |

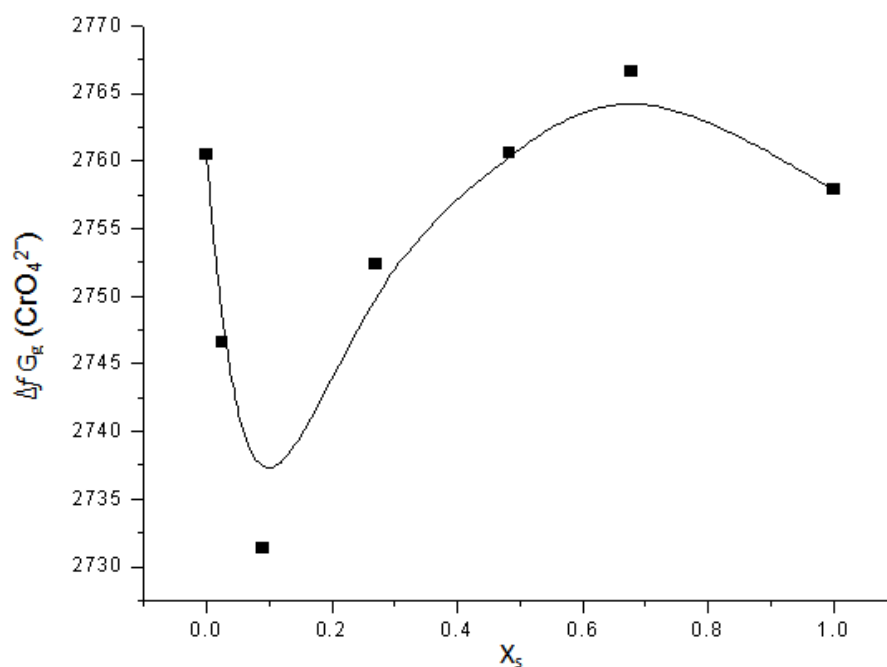


Figure 2. Relation between $\Delta f G_g (\text{CrO}_4^{2-})$ against the mole fraction of DMF at 301.15 K

6. Conclusions

By the use of combination of experimental gas-phase free energies of formation and solution-phase reduction potentials, we determined conventional solvation free energies of K_2CrO_4 in mixed DMF-H₂O solvents at 301.15 K from the experimental solubility measurements. Libration Gibbs free energy associated with moving K_2CrO_4 in standard gas state to standard state in solution was evaluated according to thermochemical cycle for the solvation process using the solubility product. Also the lattice energy for solid K_2CrO_4 (cr) was also calculated and used for further evaluation. These conventional solvation free energies were then combined with experimental and calculated gas-phase clustering free energies to determine conventional solvation free energies of ion-solvent clusters containing up to solvent molecules. The values for the absolute solvation free energy

of the proton obtained in this work should be useful as standards against which the absolute solvation free energies of other single ions can be derived.

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