

Thermodynamics of the Solvation of Potassium Thiocyanate in Mixed EtOH-H₂O Solvents at 301.15 K

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Abstract The Gibbs free energies as very important thermodynamic property were evaluated for potassium thiocyanate (KSCN) in mixed ethanol (EtOH-H₂O) solvents at 301.15 K from the experimental solubility measurements. The ratio of the ionic radii between potassium and thiocyanate ions was used to divide the total Gibbs free energy of the salt into its individual contribution in the mixtures used. Libration Gibbs free energy associated with moving KSCN in standard gas state to standard state in solution was evaluated according to specific cycle for the solvation process using the solubility products. Also the lattice energy for solid KSCN (Cr) was calculated and used for further evaluation. The conventional Gibbs free energies for the cation (K⁺) and anion (SCN⁻) were estimated theoretically and also the Gibbs free energy of (SCN⁻) gas was evaluated and all values were discussed. The present work is concerned with relative (conventional) and absolute Gibbs free energies of the solvation of ions used.

Keywords Gibbs Free Energies, potassium Thiocyanate, conventional Free Energies, solubility Measurements, thermodynamic Solvation Energies

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 solvents [7, 8]. 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 KSCN is important than that of neutral solutes. Understanding the partition 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⁺ & SCN⁻ ions in mixed EtOH-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. Single ion thermodynamics is important for studying the experimental and theoretical behavior of different salts in various solvents. Single ion thermodynamics are necessary for studying ionic conduction, solvent rotation solvent reorientation, solvent geometric distortion, solvent electronic polarization and electronic conduction [6]. The aim of this work is to provide the theoretical and experimental researchers with different ions data which help in explanation of different electrical properties.

1.1. Relative and Conventional Solvation Free Energies of Ions

The Gibbs solvation free energies of ions are often tabulated as relative free energies by setting the free energy 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 that are shifted by equal amount in the opposite direction.

1.2. Conventional Gibbs Free Energies from Reduction Potentials

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In the present article relative (conventional) solvation free energies of ions and ion-solvent interaction have been determined using combination of experimental and theoretical free energy of formation. When the convention for the absolute Gibbs free energy of the proton is followed, the solution phase 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 illustrated through the use of thermochemical cycle[12]. This last procedure can be used to estimate the gas free energy of formation for SCN^- ion, to explain the ionic behaviour.

2. Experimental

Potassium thiocyanate (KSCN) from Griffin & George Co. and ethanol (EtOH) from Merck Co. were used. Saturated solutions of KSCN were prepared by dissolving different amounts in closed test tubes containing different EtOH-H₂O 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 KSCN in each mixture was measured gravimetrically by evaporating 1 ml of the saturated solution in small cups using I. R. lamp. The

measurements were done by three readings for each solution at 301.15 K.

3. Results and Discussion

The molar solubility (s) for KSCN at 301.15 K was measured gravimetrically with average of the second number after common in water, ethanol (EtOH) and their mixtures.

The solubility values for KSCN at cited in Table (1). The (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. Their data ($\log \gamma_{\pm}$) were tabulated also in Table (1). The solubility product was calculated by the use of equation (2)[30].

$$\text{p}K_{\text{sp}} = -\log S^2 + \log \gamma_{\pm}^2 \quad (2)$$

The solubility product ($\text{p}K_{\text{sp}}$) data are given in Table (1). From these 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].

$$\Delta G = 2.303 RT \text{p}K_{\text{sp}} \quad (3)$$

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

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

X _s EtOH	S g.mol/e	Log γ_{\pm}	pK _{sp}	ΔG KJ/mol	ΔG_t KJ/mol
0	4.320	-1.0508	0.8326	4.8011	0
0.0333	4.013	-1.0140	0.8211	4.7313	-0.6677
0.0718	2.984	-0.8744	0.7992	4.6082	-0.1928
0.1171	2.573	-0.8119	0.8028	4.6297	-0.1717
0.1711	2.051	-0.7249	0.8258	4.7620	-0.0391
0.2241	1.515	-0.6238	0.8868	5.1132	0.3121
0.3171	1.255	-0.5460	0.9359	5.3965	0.5954
0.4194	0.720	-0.4295	1.1443	6.5983	1.7972
0.5332	0.412	-0.3249	1.4200	6.7183	3.3868
0.7359	0.206	-0.2297	1.8316	10.5615	5.7604
1.0	0.206	-0.2297	1.8316	10.5615	5.7604

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

X _s EtOH	$\Delta G(\text{K}^+)$	$\Delta G(\text{SCN}^-)$	$\Delta G_s^{*con}(\text{K}^+)$	$\Delta G_s^{*con}(\text{SCN}^-)$	$\Delta G_s^*(\text{H}^+)$
0	2.222	2.5784	-1520.42	1525.59	1523
0.0333	2.1872	2.5471	-1519.9	1524.33	1521.7
0.0718	2.1289	2.4792	-1518.28	1522.89	1520.41
0.1171	2.1389	2.4907	-1518.28	1521.25	1518.6
0.1711	2.2000	2.5619	-1514.67	1519.38	1516.82
0.2241	2.3622	2.7509	-1512.55	1517.66	1514.91
0.3171	2.4931	2.9033	-1509.04	1514.44	1511.54
0.4194	3.0114	3.5068	-1504.84	1511.37	1507.86
0.5332	3.7827	4.4050	-1499.24	1507.44	1503.03
0.7359	4.8794	5.6821	-1431.56	1442.12	1436.44
1.0	4.8794	5.6821	-1482.03	1492.59	1486.91

It was concluded that the Gibbs free energies of transfer (ΔG_t) increase in negativity by increasing the mole fraction of EtOH in the mixed EtOH-H₂O solvents. This is due to more solvation behaviour in the mixed solvents than that in water (see Fig. 1).

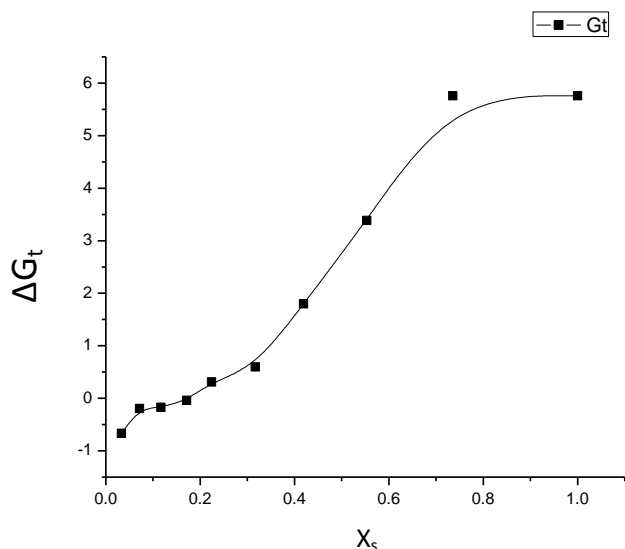


Figure 1. Gibbs free energies of transfer for KSCN (ΔG_t) versus the mole fraction of EtOH (X_s) at 301.15 K

The evaluated single ion free energies for K^+ ion in pure water and ethanol solvents agreed well with the data estimated by using both Ph_4AsBPh_4 and Ph_4SbBPh_4 assumptions given in literature[28]. Therefore the evaluation of single ion values as given here is simple and good method.

Single ion Gibbs free energies and conventional Gibbs free energies for K^+ and SCN^- ions:

Single ion solvation free energies are well defined in statistical mechanics and determining their values is an important step in understanding the structure of solutions.

The real free energy of difference upon moving a single ion from the gas phase into a solution includes a contribution from the difference between the electrical potential of a medium and that of the vacuum.

It is of interest to consider absolute solvation free energy (also called intrinsic solvation free energy) from which the absolute free energy differs from the real one by the charge on the ion times the potential of the phase.

It was well known that the preferential single ion thermodynamic (intrinsic) parameters depend on the ionic radii of the two ions (cation and anion). Therefore, the ionic radii ratio between K^+ and SCN^- were evaluated from exact given radii in literature[33] and found to be 0.462.

Multiply this ratio by the Gibbs free energies of KSCN we get the ionic Gibbs free energies for K^+ ions. This last value was subtracted from the KSCN Gibbs free energy we obtain the Gibbs free energy for SCN^- anion. The obtained values for single ions are presented in Table (2). The conventional Gibbs free energies $\Delta G_s^{*con}(K^+)$ for K^+ ion in solvents are shifted from their absolute values by the absolute free energy of the proton[34] according to equation (5).

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

And for (SCN^-) anion is shifted by an equal amount in the opposite direction.

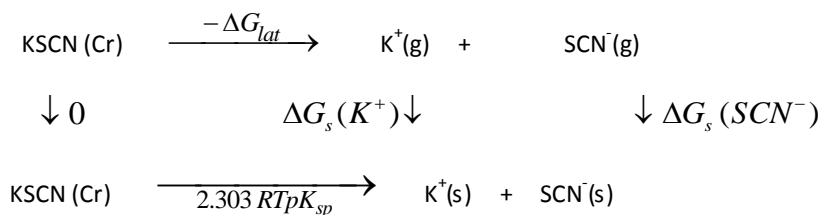
$$\Delta G_s^{*con}(SCN^-) = \Delta G_s(SCN^-) + \Delta G_s(H^+) \quad (6)$$

Where $\Delta G_s(K^+)$, $\Delta G_s(SCN^-)$ and $\Delta G_s(H^+)$ are the Gibbs free energies of solvation for potassium, thiocyanate and proton in solvents.

From the mean values of proton solvation free energies in water and other solvents in literature[12, 35, 36], relation between these values and the diameter for each solvent taken from Kim work[37] straight line was obtained. From this line the proton solvation free energies in pure water and EtOH were obtained and found to be 1523 and 1486.91 KJ/mol, respectively multiplying each value by its mole fraction in the mixture and then sum the results. The mixed solvent proton free energies were obtained and their values are given in Table (2). Apply equation (5) and (6) we get the conventional Gibbs free energies for the cation and the anion, 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 increase with increase in the mole fraction of EtOH due to more solvation and the sum of them gives the values for the neutral salt.

3.1. Libration Gibbs Free Energies for KSCN in Mixed EtOH-H₂O Solvents

The libration Gibbs free energies for KSCN in mixed EtOH-H₂O solvents at 301.15 K were calculated following cycle 1 (thermochemical cycle 1) as done before[12] for silver salts following solubility product concept.



The thermochemical cycle 1. (cycle 1)

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, equation (7)[38].

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

The volume of KSCN was calculated by dividing its molecular weight by the density of solid given in literature[4] and applies it in equation (7) to obtain 172.49 KJ/mol. On the use of equation (8) after cycle (2), the libration free energy for KSCN was obtained (86.245 KJ/mol).

$$\begin{aligned} \Delta G_s(K^+) + \Delta G_s(SCN^-) \\ = 2.303 RT pK_{sp} - \Delta G_{lat} - 2\Delta G^{0 \rightarrow *} \end{aligned} \quad (8)$$

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

3.2. Conventional Free Energies from Reduction Potentials

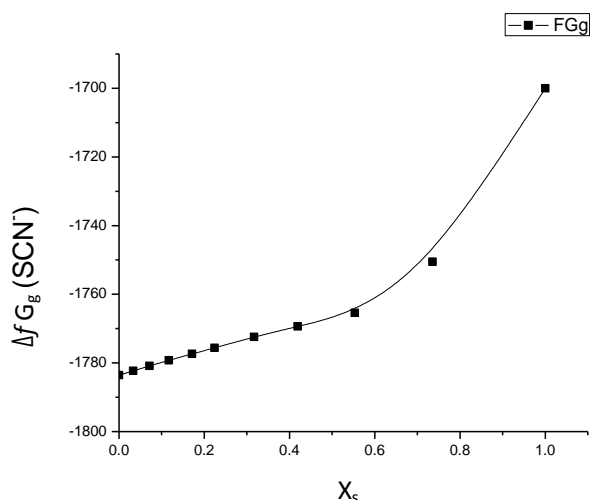
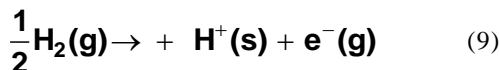


Figure 2. Relation between $\Delta f G_g$ (SCN⁻) against the mole fraction of EtOH (X_s) at 301.15 K

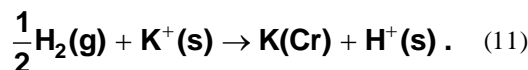
The absolute Gibbs free energy of the proton is followed solution phase free energy change associated with the following half cell.



The half cell reaction for the reduction cation is:



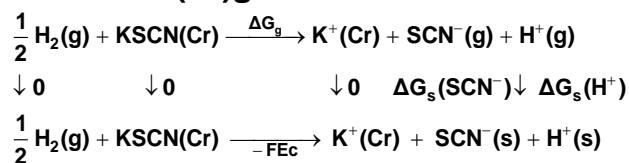
The symbol (Cr) denotes the crystalline phase. The sum of the two half cells is:



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

$$\Delta G_s^{*con}(K^+) = \Delta f G(H^+)g - \Delta f G(K^+) - FE_c \quad (12)$$

Where $\Delta f G(H^+)g$, $\Delta f G(K^+)$ are the gas free energy of formation for H⁺ and K⁺ ions. Faraday's constant = 23.061 Kcal/mol and Ec is the standard reduction potential of K⁺. $\Delta f G(K^+)$ is difficult to evaluate because of the lack of exact $\Delta f G(H^+)g$ value.



Thermochemical cycle 2. (cycle 2)

Also the conventional free energy of the thiocyanate anion SCN⁻ can be written following Truhlar[12] explanation as:

$$\Delta G_s^{*con}(SCN^-) = -\Delta f G_g - FE_c - 2\Delta G^{0 \rightarrow *} \quad (13)$$

Apply last equation the $\Delta f G_g$, gas free energies for the anion SCN⁻ were estimated in the mixed EtOH-H₂O solvents and their values are given in Table (5) and Fig. (2). The $\Delta f G_g$ values increase by increasing the mole fraction of EtOH favoring less solvation.

Table (3). Gas formation free energy for SCN⁻ anion in mixed EtOH-H₂O solvents at 301.15 K (in KJ/mol)

X _s EtOH	ΔfG _g
0	-1783.56
0.0333	-1782.30
0.0718	-1780.86
0.1171	-1779.22
0.1711	-1777.35
0.2241	-1775.63
0.3171	-1772.41
0.4194	-1769.34
0.5332	-1765.41
0.7359	-1700.03
1.0	-1750.56

4. Conclusions

This work gives a lot of data for single ion thermodynamic free energies for potassium and thiocyanate ions in mixed ethanol water solvents which help in discussing the preferential solvation in the used solvents. Also the data can help for studying other salts having the same common ions used.

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