Thermodynamics of the solvation of lead nitrate in mixed DMF-H_2O solvents at 301.15 K.

Esam A. Gomaa[1*], Elsayed M. Abou Elleef [2]

** Corresponding Author: Esam A. Gomaa eahgomaa65@yahoo.com*

[1] Chemistry Department, Faculty of Science, Mansoura University, 35516-Mansoura, Egypt.

[2] Basic Science Department, Delta Higher Institute for Engineering & Technology, 35681-Dalkha,Mansoura,Egypt

ABSTRACT

Aims: The aim of this study was to determine Thermodynamics of the solvation of lead nitrate in mixed DMF-H_2O solvents at 301.15 K. The Gibbs free energies as a very important thermodynamic property were evaluated for $Pb(NO_3)_2$ in mixed dimethylformamide DMF - H_2O solvents at 301.15 K from the experimental solubility measurements. The ratio of the ionic between lead and nitrate 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 $Pb(NO_3)_2$ in standard gas state to standard stat in solution was evaluated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid $Pb(NO_3)_2$ (cr) was also calculated and used for further evaluation.

The conventional Gibbs free energies for the cation (Pb^{2+}) and anion (NO_3^-) were estimated theoretically and also the Gibbs free energy of NO_3^- gas was evaluated and all values were discussed.

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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-1) [9]. Determining accurate values for the Gibbs free energies of ionic solutes like $Pb(NO_3)_2$ is important than that of neutral solutes. 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. 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 (sodium and potassium) 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 Pb^{2+} & NO_3^- ions in mixed DMF-H_2O 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.

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 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.

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 reaction of hydrogen gas is equal to zero. Reduction potentials following this convention for hydrogen electrode are referred as standard reduction potentials. Form 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 of NO_3^- ion, to explain the ionic behaviour.

2. MATERIAL AND METHODS

Lead nitrate $Pb(NO_3)_2$ GCC-laboratory reagert and N-N-dimethylformamide (DMF) from Merck Co. were used.

Saturated solutions of $Pb(NO_3)_2$ were prepared by dissolving different amounts in closed test tubes containing different DMF-H_2O mixtures. These mixtures were then saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility of $Pb(NO_3)_2$ in each mixture was measured gravimetrically by evaporating 1 ml of the saturated solution in small beaker 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 $Pb(NO_3)_2$ at 301.15 K were measured gravimetrically with average of the second number after comma in water, dimethylformamide (DMF) and their mixtures. The solubility values for $Pb(NO_3)_2$ are cited in Table (1). The mean activity coefficient ($\gamma\pm$) of the ions which can be estimated from the Debye-Hückel limiting law, as modified by Robinson and Stokes [27, 28].

$$\log \gamma_{\pm} = -\frac{A Z_{+} Z_{-} \sqrt{S}}{1 + B r^{\circ} \sqrt{S}} \qquad \text{..........(1)}$$

Where Z_+ and Z_- are the charges of ions in solutions, **A= 1.823 ×106(ε.T)**$^{-3/2}$**,** **B = 50.29 (ε.T)**$^{-1/2}$ **, r°** is the solvated radius , ε is the dielectric constant of the solvents and S is the molar solubility. The values of ε for DMF-water mixtures were taken from previous publications [29]. These data ($\log \gamma_\pm$) were tabulated also in Table (1). The solubility product was calculated by the use of equation 2 [30].

$$pK_{sp} = -4(\log S^3 + \log \gamma_\pm{}^3) \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The solubility product (pKsp) 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) [31- 34]. Their values are tabulated also in Table (1).

$$\Delta G = 2.303\ RT\ pK_{sp} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

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

Where (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 indicating the spontaneous nature of $Pb(NO_3)_2$ solubilization. This is due to more solvation behaviour in the mixed solvents than that of water where the Gibbs free energy values provide information on whether the process conditions favor or disfavor $Pb(NO_3)_2$ solubilization in the aqueous carrier solution. Negative Gibbs free energy values indicate favorable conditions. (See Fig.1).

Single ion Gibbs free energies and conventional free energies for Pb^{2+} and NO_3^- 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 Pb^{2+} and NO_3^- was evaluated from exact radii values given in literature [35] and found to be (132/179= 0.737). Multiplying this ratio by the Gibbs free energies of $Pb(NO_3)_2$ we get the ionic Gibbs free energies of Pb^{2+} ion. This last value was subtracted from the $Pb(NO_3)_2$ Gibbs free energy and we obtain the Gibbs free energy for NO_3^- anion. The obtained values for single ions are presented in Table (2). The conventional Gibbs free energies ΔG_s^{*con} (Pb^{2+}) for Pb^{2+} ion in solvents are shifted from their absolute values by the absolute free energy of the proton [26] according to equation (5)

$$\Delta G_s^{*con}(Pb^{2+}) = \Delta G_s(Pb^{2+}) - 2\Delta G_s(H^+) \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and for NO3- anion is shifted by an equal amount in the opposite direction (equation 6).

$$\Delta G_s^{*con}(NO_3^-) = \Delta G_s(NO_3^-) + \Delta G_s(H^+) \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where ΔG_s^{*con} (Pb^{2+}), ΔG_s^{*con} (NO_3^-) and ΔG_s(H^+) are the Gibbs free energies of solvation for lead, nitrate and proton in solvents.

From the mean values of proton solvation free energies in water and other solvents in literature [12, 36, and 37] relation between these values and the diameter for each solvent taken from literature [38-40 and 41], a straight line was obtained. From this line the proton solvation free energies in pure water and DMF were obtained and found to be -252 to -263 kcal/mol ,(this is about -1053 and -1099 KJmol-1), respectively. Multiplying each value by its mole fraction in the mixture and then summing the results. The mixed solvent proton free energies were obtained and their values are given in Table (2). With equations (5) and (6) we get the conventional Gibbs free energies for the cation and anion and 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 DMF due to more solvation and the sum of them gives the values for the neutral salt.

Libration Gibbs free energies for $Pb(NO_3)_2$ in mixed DMF-H_2O solvents:

The libration Gibbs free energies for $Pb(NO_3)_2$ in mixed DMF-H_2O solvents at 301.15 K were calculated following cycle 1 (thermochemical cycle 1) as done before [12] for silver salts following solubility product concept.

$$\begin{array}{ccccc} Pb(NO_3)_2\,(Cr) & \xrightarrow{-\Delta G_{lat}} & Pb^{2+}(g) & + & 2NO_3^-(g) \\ O\downarrow & & \Delta G_s(Pb^{2+})\downarrow & & \Delta G_s\,2(NO_3^-)\downarrow \\ Pb(NO_3)_2 & \xrightarrow[2.303RTpK_{sp}]{} & Pb^{2+}(s) & + & 2\,NO_3^-(s) \end{array}$$

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 following equation (7) [42].

$$\Delta G_{lat} = \frac{232.8}{\sqrt[3]{V}} + 110\ \text{KJ mol}^{-1}\ldots\ldots\ldots\ldots(7)$$

The volume of $Pb(NO_3)_2$ was calculated by dividing its molecular weight by the density of solid given in literature [3] and apply it in equation (7) to obtain 165.675 $kJmol^{-1}$ as ΔG_{lat} for $Pb(NO_3)_2$. On the use of equation (8) after cycle (1), the libration free energies for $Pb(NO_3)_2$ was obtained (82.837 kJmol-1).

$$\Delta G_s\ (Pb^{2+}) + 2\Delta G_s\,(NO_3^-) = 2.303\ RT\,pK_{sp} - \Delta G_{lat} - 2\Delta G^{0\to *}\ldots\ldots(8)$$

The $\Delta G^{0\to *}$, the free energy change associated with moving $Pb(NO_3)_2$ from standard gas phase of 1 atmosphere to solution phase. This free energy change has been referred as "compression" work of the gas or libration 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.

$$H_2(g) \rightarrow 2H^+(s) + 2e^-(g)\ldots\ldots\ldots\ldots(9)$$

The half cell reaction for the reduction of cation is:

$$Pb^{2+}(s) + 2e^- \rightarrow Pb(Cr)\ldots\ldots\ldots\ldots(10)$$

The symbol (cr) denote the crystalline phase the sum of the two half cells is:

$$H_2(g) + Pb^{2+}(s) \rightarrow Pb(Cr) + 2H^+(s)\ldots\ldots\ldots(11)$$

Through the use of thermochemical cycle 2, the conventional free energy for Pb^{2+} can be written as:

$$\Delta G_s\,{*}\,con\,(Pb^{2+}) = 2\Delta f\,G(H^+)g - \Delta f\,G(Pb^{2+})g - 2FE_C\ldots\ldots\ldots(12)$$

Where $\Delta f\,G(H^+)g$, $\Delta f\,G(Pb^{2+})g$ are the gas free energy of formation for H^+ and Pb^{2+} ions. F is Faraday constant, equal 96.485 kJ per volt gram equivalent and Ec is the standard reduction potential of Pb^{2+} $\Delta f\,G(Pb^{2+})g$ is difficult to evaluate because of the lack of exact gas $\Delta f\,G(H^+)g$ value.

$$\mathbf{H_2(g) + Pb(NO_3)_2(Cr) \xrightarrow{\Delta G_g} Pb^{2+}(Cr) \quad + \quad 2NO_3^-(g) \quad + 2H^+(g)}$$

$$\mathbf{0\downarrow \qquad 0\downarrow \qquad 0\downarrow \qquad 2\Delta G_s(NO_3^-)\downarrow \quad 2\Delta G_s(H^+)\downarrow}$$

$$\mathbf{H_2(g) + Pb(NO_3)_2(Cr) \xrightarrow[-2FE_c]{} Pb^{2+}(s) \quad + \quad 2NO_3^-(s) \quad + 2H^+(s)}$$

(Cycle 2)

Also the conventional free energy of the nitrate anion NO_3^- can be written following Truhlar [43] explanation as:

$$\Delta G_s^{*con}(NO_3^-) = -\Delta f G_g - FE_c - 2\Delta G^{0\rightarrow *} \text{..................(13)}$$

Applying last equation the $\Delta f\, G_g$, the gas free energies of formation for the anion NO_3^- was estimated in the mixed DMF-H_2O solvents and their values are given in Table.3. and Fig. (2). the $\Delta f\, G_g$ value increase by increasing the mole fraction of DMF favouring less solvation.

Table 1. Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed DMF-H_2O solvents at 301.15 K.

X_s , DMF	S, mol/L	Log $\gamma\pm$	pK_{sp}	Δ G , $kJmol^{-1}$	ΔG_t , $kJmol^{-1}$
0	1.780	-1.1697	1.6737	9.6511	0
0.0250	1.700	-1.1476	1.8250	10.5232	0.8720
0.0909	1.720	-1.1498	1.7728	10.2225	0.5715
0.1975	1.989	-1.2365	1.3623	7.8556	-1.7954
0.2699	2.350	-1.3440	0.9232	3.2316	-6.4192
0.4828	2.730	-1.4486	0.5604	3.5934	-6.0577
0.7213	2.620	-1.4486	0.9431	5.4381	-4.2130
0.8921	2.103	-1.4486	1.2210	7.0409	-2.6102
1.0000	2.657	-1.4291	0.6237	9.1655	-0.4856

Table 2. Single ion Gibbs free energies for Pb^{2+} and nitrate and their half conventional energies at 301.15 K. in mixed DMF-H_2O solvents (in $kJmol^{-1}$).

X_s , DMF	$\Delta G(Pb^{2+})$	$\Delta G(NO_3^-)$	$\frac{1}{2}\Delta G_s^{*con}(Pb^{2+})$	$\frac{1}{2}2\Delta G_s^{*con}(NO_3^-)$	$\Delta G_s^*(H^+)$
0	1.2585	8.3923	-1521.00	1531	-1052.3
0.0250	1.3722	9.1504	-1521.21	1532.15	-1052.3
0.0909	1.3330	8.8893	-1521.34	1531.88	-1052.3
0.1975	1.3244	6.8312	-1527.97	1535.83	-1052.9
0.2699	1.4214	2.8102	-1544.08	1536.81	-1053.4
0.4828	1.4686	3.1248	-1550.33	1555.12	-1055.2
0.7213	1.3802	3.5624	-1551.71	1559.56	-1055.2
0.8321	1.2686	3. 4561	-1553.33	1561.32	-1055.2
1.0	1.2195	3.3703	-1559.05	1568.97	-1056.1

Table 3. Gas formation free for NO_3^- anion in mixed DMF-H_2O solvents at 301.15 K.

X_s , DMF	ΔfG_g
0	-1789.21
0.0250	-1790.36
0.0909	-1789.21
0.1975	-1794.04
0.2699	-1795.82
0.4828	-1813.33
0.7213	-1817.14
0.8321	-1820.56
1.0	-1827.18

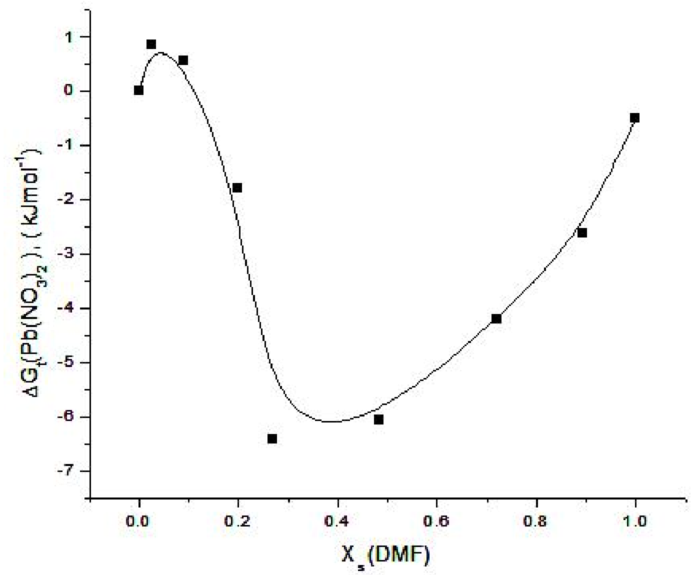

Fig. 1. Gibbs free energies of transfer (ΔG_t) for $Pb(NO_3)_2$ versus the mole fraction (X_s) of DMF at 301.15 K.

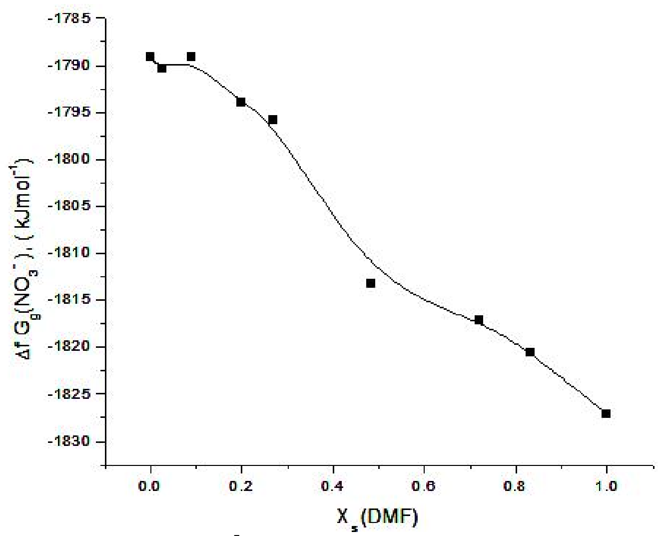

Fig. (2): Relation between $\Delta f G_g(NO_3^-)$ against the mole fraction (X_s) of DMF at 301.15 K.

4. CONCLUSION

Using a combination of experimental gas-phase free energies of formation and solution-phase reduction potentials, we determined conventional solvation free energies of $Pb(NO_3)_2$ in mixed DMF-H_2O solvents at 301.15 K from the experimental solubility measurements. Libration Gibbs free energy associated with moving $Pb(NO_3)_2$ in standard gas state to standard stat in solution was evaluated according to thermochemical cycle for the solvation process using the solubility product. Also the lattice energy for solid $Pb(NO_3)_2$ (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. For example, Table 2 shows the absolute single-ion solvation free energies of the ions considered in this work.

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