

Research Paper**Thermodynamics of the solvation
of lead nitrate in mixed DMF-H₂O
solvents at 301.15 K.****By****Esam A. Gomaa****Chemistry Department, Faculty of Science,
Mansoura University, 35516-Mansoura, Egypt.****Abstract:**

The Gibbs free energies as very important thermodynamic property were evaluated for $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ in standard gas state to standard state in solution was calculated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid $\text{Pb}(\text{NO}_3)_2$ (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.

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 $\text{Pb}(\text{NO}_3)_2$ 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 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] to 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.

Experimental:

Lead nitrate $\text{Pb}(\text{NO}_3)_2$ GCC-laboratory reagent and N,N-dimethylformamide (DMF) from Merck Co. were used.

Saturated solutions of $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ 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.

Results and Discussion:

The molar solubility (s) for $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ are cited in Table (1). These (s) values in water agreed well with that in literature values [27]. The activity coefficients were calculated by the use of Bebye-Hückel equation [28, 29].

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

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].

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

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].

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

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

(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-H₂O solvents. This is due to more solvation behaviour in the mixed solvents than that of water (see Fig. 1).

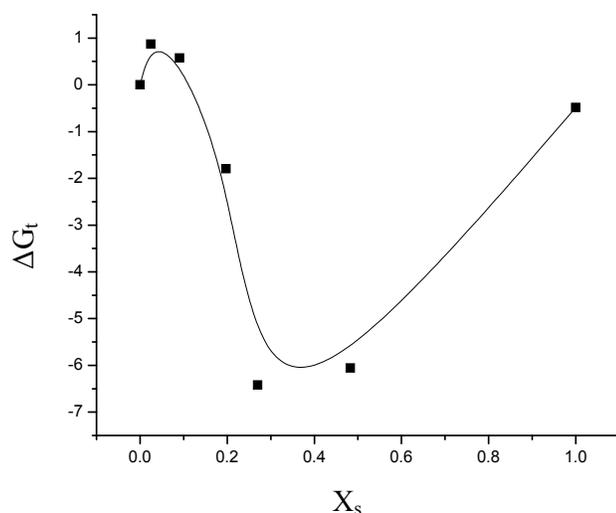


Fig. (1): Gibbs free energies of transfer(G_t) for $Pb(NO_3)_2$ Versus the mole fraction (x_s) of DMF at 301.15 K

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^- were evaluated from exact radii values given in literature [33] and found to be 0.1304. Multiply this ratio by the Gibb 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 we obtain the Gibbs free energy for NO_3^- anion in $Pb(NO_3)_2$.

the obtained values for single ions are presented in Table (2). The conventional Gibbs free energies $\Delta G_s^{*con}(\text{Pb}^{2+})$ for Pb^{2+} ion in solvents are shifted from their absolute values by the absolute free energy of the proton [34] according to equation (5)

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

and for NO_3^- anion is shifted by an equal amount in the opposite direction (equation 6).

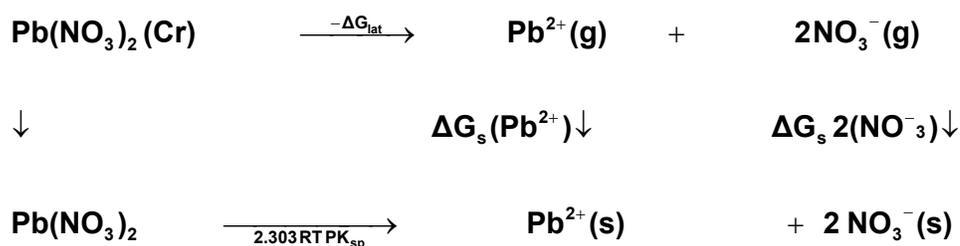
$$\Delta G_s^{*con}(\text{NO}_3^-) = \Delta G_s(\text{NO}_3^-) + 2\Delta G_s(\text{H}^+) \dots \dots \dots (6)$$

Where $\Delta G_s^{*con}(\text{Pb}^{2+})$, $\Delta G_s^{*con}(\text{NO}_3^-)$ and $\Delta G_s(\text{H}^+)$ 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, 35, 36] relation between these values and the diameter for each solvent taken from literature [37], straight line was obtained. 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 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 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(NO₃)₂ in mixed DMF-H₂O solvents:

The libration Gibbs free energies for Pb(NO₃)₂ in mixed DMF-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.



Cycle (1) (thermochemical 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) [38].

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

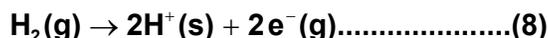
The volume of Pb(NO₃)₂ was calculated by dividing its molecular weight by the density of solid given in literature [3] and apply it in equation (7) to obtain 165.675 KJ/mol as ΔG_{lat} for Pb(NO₃)₂. On the use of equation (8) after cycle (1), the libration free energies for Pb(NO₃)₂ was obtained (82.837 KJ/mol).

$$\Delta G_s(\text{Pb}^{2+}) + 2\Delta G_s(\text{NO}_3^-) = 2.303 \text{ RTPK}_{sp} - \Delta G_{lat} - 2\Delta G^{0 \rightarrow *} \dots\dots\dots(8)$$

The $\Delta G^{0 \rightarrow *}$, the free energy change associated with moving Pb(NO₃)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.



The half cell reaction for the reduction of cation is:



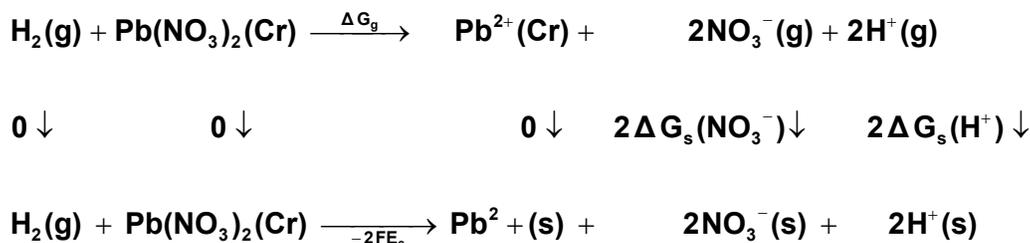
The symbol (Cr) denote the crystalline phase the sum of the two half cells is:



Through the thermo chemical cycle 2 (cycle 2), the conventional free energy for Pb^{2+} can be written as:

$$\Delta G_s^* \text{con}(\text{Pb}^{2+}) = 2\Delta fG(\text{H}^+)g - \Delta fG(\text{Pb}^{2+})g - 2FE_c \dots \dots \dots (11)$$

Where $\Delta fG(\text{H}^+)g$, $\Delta fG(\text{Pb}^{2+})g$ are the gas free energy of formation for H^+ and Pb^{2+} ions. F Favalay constant, equal 23.061 Kcal/mol and E_c is the standard reduction potential of Pb^{2+} $\Delta fG(\text{Pb}^{2+})g$ is difficult to evaluate because of the lack of exact gas $\Delta fG(\text{H}^+)g$ value.



(Cycle 2)

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

$$\Delta G_s^{*con}(\text{NO}_3^-) = -\Delta fG_g - FE_c - 2\Delta G^{0\rightarrow*} \dots\dots\dots(12)$$

Apply last equation the ΔfG_g , 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 ΔG_g value increase by increasing the mole fraction of DMF favouring less solvation.

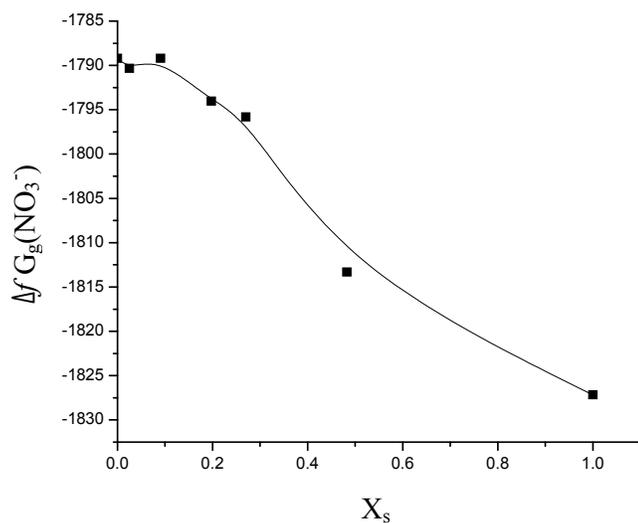


Fig. (2): Relation between $\Delta fG_g(\text{NO}_3^-)$ g against the mole fraction of DMF at 301.15 K.

Table (1): Solubility and Gibbs free energies for $\text{Pb}(\text{NO}_3)_2$ in mixed DMF- H_2O solvents at 301.15 K.

X_s DMF	S g.mol/e	Log γ_{\pm}	pK_{sp}	ΔG KJ/mol	ΔG_t KJ/mol
0	1.78	-1.1697	1.6737	9.6511	0
0.0250	1.70	-1.1476	1.8250	10.5232	0.872
0.0909	1.72	-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	-6.0570
1.0	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 KJ/mol).

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	1531	1523
0.0250	1.3722	9.1504	-1521	1532.15	1523
0.0909	1.3330	8.8893	--1521	1531.88	1523
0.1975	1.0244	6.8312	-1527.97	1535.83	1529
0.2699	0.4214	2.8102	-1551	1536.81	1534
0.4828	0.4686	3.1248	-1551.33	1555.12	1552
1.0	1.1951	7.9703	-1559	1568.97	1561

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
1.0	-1827.18

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