

Thermodynamics of the solvation of lead nitrate in mixed DMF-H₂O solvents at 301.15 K.

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ABSTRACT

Aims: The aim of this study was to determine Thermodynamics of the solvation of lead nitrate in mixed DMF-H₂O solvents at 301.15 K. The Gibbs free energies as a very important thermodynamic property were evaluated for Pb(NO₃)₂ in mixed dimethylformamide DMF - H₂O 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(NO₃)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(NO₃)₂ (cr) was also calculated and used for further evaluation (the symbol (cr) denotes the crystalline phase).

The conventional Gibbs free energies for the cation (Pb²⁺) and anion (NO₃⁻) were estimated theoretically and also the Gibbs free energy of NO₃⁻ gas was evaluated and all values were discussed.

Place and Duration of Study: Chemistry Department, Faculty of Science, Mansoura University and Basic Science Department, Delta Higher Institute for Engineering and Technology, Dalkha , Mansoura, Egypt, between June 2012 and July 2013.

Keywords: Thermodynamics; Gibbs free energies; lead nitrate; solubility; solvation; aqueous and dimethylformamide.

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(NO₃)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

32 electrolytes into ionic constituents is conventionally accomplished by using the single ion
33 solvation Gibbs free energy of one reference ion, conventionally, the proton, to set the
34 single ion scales [11, 12].

35 Sums of solvation free energies of cations and anions are well defined through the use of
36 thermochemical cycles involving calorimetric or electrochemical measurements [13-17]. A
37 number of different extra thermodynamic approximations have been used [18-25] for
38 partition the sums of cation and anion Gibbs free energies into single ion contribution.

39 The aim of this work is to estimate the single ion Gibbs free energies for Pb^{2+} & NO_3^- ions in
40 mixed DMF- H_2O solvents at 301.15 K.

41

42 **1.1 Relative and conventional solvation free energies of ions:**

43 The Gibbs solvation free energies of ions are often tabulated as relative free energies by
44 setting the free energy of solvation of some reference ion equal zero [26]. Proton was
45 chosen as reference ion. For ions, this result in a set of conventional free energies of
46 solvation that the cations are shifted from their absolute values by the value for the absolute
47 Gibbs solvation free energy of the proton. The conventional Gibbs free energies of solvation
48 for anions are shifted by an equal amount in the opposite direction.

49 **1.2 Conventional Gibbs free energies from reduction potentials:**

50 When the convention for the absolute Gibbs free energy of the proton is followed, the
51 solution-phase free energy change associated with the half cell for reaction of hydrogen gas
52 is equal to zero. Reduction potentials following this convention for hydrogen electrode are
53 referred as standard reduction potentials. From the half cell reaction for the reduction of
54 metal cation to crystalline phase and the half reduction reaction of hydrogen gas, the redox
55 reaction can be illustrated through the use of thermochemical cycle [12]. This last procedure
56 can be used to estimate the gas free energy of formation of NO_3^- ion, to explain the ionic
57 behaviour.

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60 **2. MATERIAL AND METHODS**

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

64 Saturated solutions of $\text{Pb}(\text{NO}_3)_2$ were prepared by dissolving different amounts in
65 closed test tubes containing different DMF- H_2O mixtures. These mixtures were then
66 saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking
67 thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility of
68 $\text{Pb}(\text{NO}_3)_2$ in each mixture was measured gravimetrically by evaporating 1 ml of the saturated
69 solution in small beaker using I. R. lamp. The measurements were done by three readings
70 for each solution at 301.15 K.

71

72 **3. RESULTS AND DISCUSSION**

73

74 The molar solubility (S) for $\text{Pb}(\text{NO}_3)_2$ at 301.15 K were measured gravimetrically with
75 average of the second number after comma in water, dimethylformamide (DMF) and their
76 mixtures. The solubility values for $\text{Pb}(\text{NO}_3)_2$ are cited in Table (1). The mean activity
77 coefficient (γ_{\pm}) of the ions which can be estimated from the Debye-Hückel limiting law, as
78 modified by Robinson and Stokes [27, 28].

79

$$\log \gamma_{\pm} = - \frac{AZ_+Z_- \sqrt{S}}{1 + Br^o \sqrt{S}} \dots\dots\dots(1)$$

80

Where Z_+ and Z_- are the charges of ions in solutions, $A = 1.823 \times 10^6 (\epsilon.T)^{-3/2}$,
 81 $B = 50.29 (\epsilon.T)^{-1/2}$, r^o is the solvated radius, ϵ is the dielectric constant of the solvents and
 82 S is the molar solubility. The values of ϵ for DMF-water mixtures were taken from previous
 83 publications [29]. These data ($\log \gamma_{\pm}$) were tabulated also in Table (1). The solubility product
 84 was calculated by the use of equation 2 [30].

85

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

86

The solubility product (pK_{sp}) data are given in Table (1) from these solubility
 87 products, the Gibbs free energies of solvation and the transfer Gibbs free energies from
 88 water to mixed solvents were calculated by using equations (3) and (4) [31- 34]. Their values
 89 are tabulated also in Table (1).

90

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

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

91

Where (s), (w) denote solvent and water, respectively.

92

It was concluded that the Gibbs free energies of transfer (ΔG_t) increase in
 93 negativity by increasing the mole fraction of DMF in the mixed DMF-H₂O solvents indicating
 94 the spontaneous nature of Pb(NO₃)₂ solubilization. This is due to more solvation behaviour
 95 in the mixed solvents than that of water where the Gibbs free energy values provide
 96 information on whether the process conditions favor or disfavor Pb(NO₃)₂ solubilization in the
 97 aqueous carrier solution. Negative Gibbs free energy values indicate favorable conditions.
 98 (See Fig.1).

99

100 **3.1 Single ion Gibbs free energies and conventional free energies for Pb²⁺ and NO₃⁻**
 101 **ions:**

102

It was well known that the preferential single ion thermodynamic parameters depend on the
 103 ionic radii of two ions (cation and anion). Therefore the ionic radii ratio between Pb²⁺ and
 104 NO₃⁻ was evaluated from exact radii values given in literature [35] and found to be (132/179=
 105 0.737). Multiplying this ratio by the Gibbs free energies of Pb(NO₃)₂ we get the ionic Gibbs
 106 free energies of Pb²⁺ ion. This last value was subtracted from the Pb(NO₃)₂ Gibbs free
 107 energy and we obtain the Gibbs free energy for NO₃⁻ anion. The obtained values for single
 108 ions are presented in Table (2).

109

The conventional Gibbs free energies ΔG_s^{*con} (Pb²⁺) for
 110 Pb²⁺ ion in solvents are shifted from their absolute values by the absolute free energy of the
 111 proton [26] according to equation (5)

112

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

113

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

114

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

115

Where ΔG_s^{*con} (Pb²⁺), ΔG_s^{*con} (NO₃⁻) and $\Delta G_s(H^+)$ are the Gibbs free energies of
 116 solvation for lead, nitrate and proton in solvents.

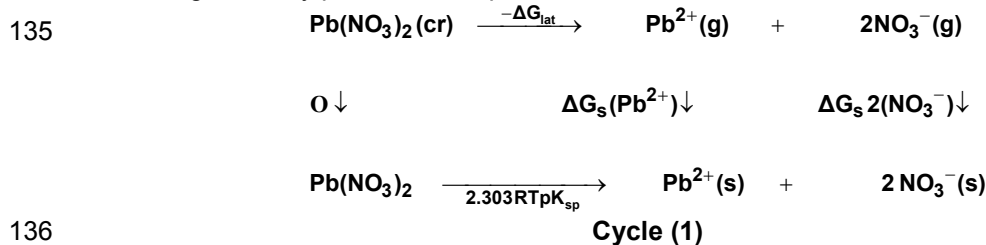
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From the mean values of proton solvation free energies in water and other solvents
 118 in literature [12, 36, and 37] relation between these values and the diameter for each solvent
 119 taken from literature [38-40 and 41], a straight line was obtained.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

124 we get the conventional Gibbs free energies for the cation and anion and their values are
 125 given also in Table (2). Cation conventional free energy values are negative indicating
 126 exothermic character and anion values are positive indicating **endothermic** character. Both
 127 values increase with increase in the mole fraction of DMF due to more solvation and the sum
 128 of them gives the values for the neutral salt.
 129

130 **3.2 Libration Gibbs free energies for Pb(NO₃)₂ in mixed DMF-H₂O solvents:**
 131

132 The libration Gibbs free energies for Pb(NO₃)₂ in mixed DMF-H₂O solvents at 301.15 K were
 133 calculated following cycle 1 (**thermochemical** cycle 1) as done before [12] for silver salts
 134 following solubility product concept.



137 Where ΔG_{lat} is the lattice free energy, (g) and (s) denote the gas and solution cases. The
 138 lattice energy was calculated following Bartlett's relationship following equation (7) [42].

139

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

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

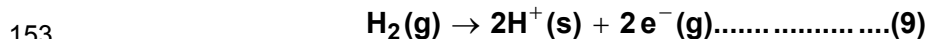
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$$\Delta G_s(\text{Pb}^{2+}) + 2\Delta G_s(\text{NO}_3^-) = 2.303 RTpK_{\text{sp}} - \Delta G_{\text{lat}} - 2\Delta G^{0 \rightarrow *} \dots\dots\dots(8)$$

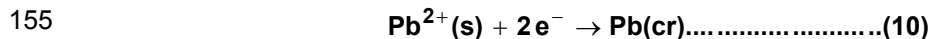
145 The $\Delta G^{0 \rightarrow *}$, the free energy change associated with moving Pb(NO₃)₂ from
 146 standard gas phase of 1 atmosphere to solution phase. This free energy change has been
 147 referred as "compression" work of the gas or libration free energy.
 148

149 **3.3 Conventional free energies from reduction potentials:**
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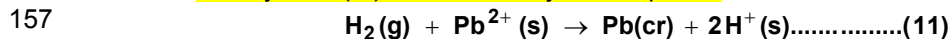
151 The absolute Gibbs free energy of the proton is followed solution phase free energy change
 152 associated with the following half cell.



154 The half cell reaction for the reduction of cation is:



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

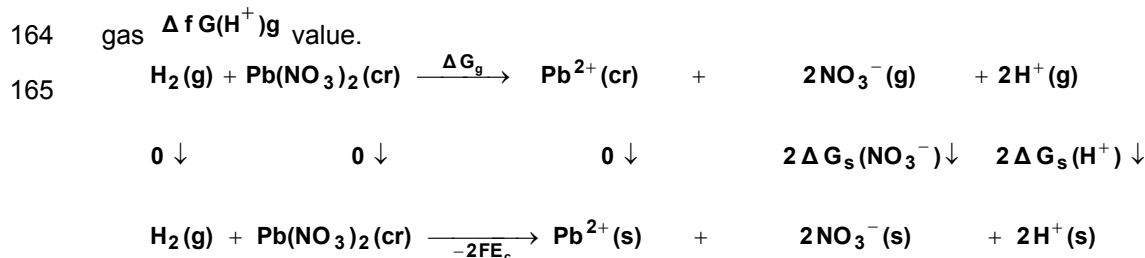


158 Through the use of thermochemical cycle 2, the conventional free energy for Pb²⁺
 159 can be written as:

160

$$\Delta G_s^* \text{con}(\text{Pb}^{2+}) = 2\Delta fG(\text{H}^+)_{\text{g}} - \Delta fG(\text{Pb}^{2+})_{\text{g}} - 2FE_c \dots\dots\dots(12)$$

161 Where $\Delta fG(\text{H}^+)_{\text{g}}$, $\Delta fG(\text{Pb}^{2+})_{\text{g}}$ are the gas free energy of formation for H⁺ and Pb²⁺
 162 ions. F is Faraday constant, equal 96.485 kJ per volt gram equivalent and Ec is the standard
 163 reduction potential of Pb²⁺ $\Delta fG(\text{Pb}^{2+})_{\text{g}}$ is difficult to evaluate because of the lack of exact



(Cycle 2)

167 Also the conventional free energy of the nitrate anion NO_3^- can be written following

168 Truhlar [43] explanation as:

169 $\Delta G_s^{*con}(NO_3^-) = -\Delta f G_g - FE_c - 2\Delta G^{0 \rightarrow *}$ (13)

170 Applying last equation the $\Delta f G_g$, the gas free energies of formation for the anion NO_3^- was

171 estimated in the mixed DMF-H₂O solvents and their values are given in Table.3. and Fig. (2).

172 the $\Delta f G_g$ value increase by increasing the mole fraction of DMF favouring less solvation.

173

174

175 Table 1. Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed DMF-H₂O solvents at

176 301.15 K.

X_s , DMF	S, mol/L	Log $\gamma \pm$	pK_{sp}	ΔG , 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

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180 Table 2. Single ion Gibbs free energies for Pb^{2+} and nitrate and their half conventional

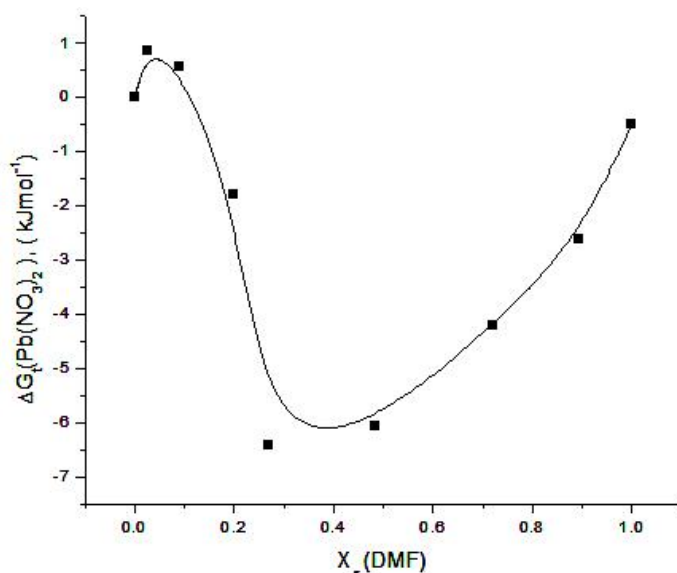
181 energies at 301.15 K. in mixed DMF-H₂O solvents (in kJmol⁻¹).

X_s , DMF	$\Delta G(Pb^{2+})$	$\Delta G(NO_3^-)$	$\frac{1}{2} \Delta G_s^{*con}(Pb^{2+})$	$\frac{1}{2} \Delta G_s^{*con}(NO_3^-)$	$\Delta G_s^*(H^+)$
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

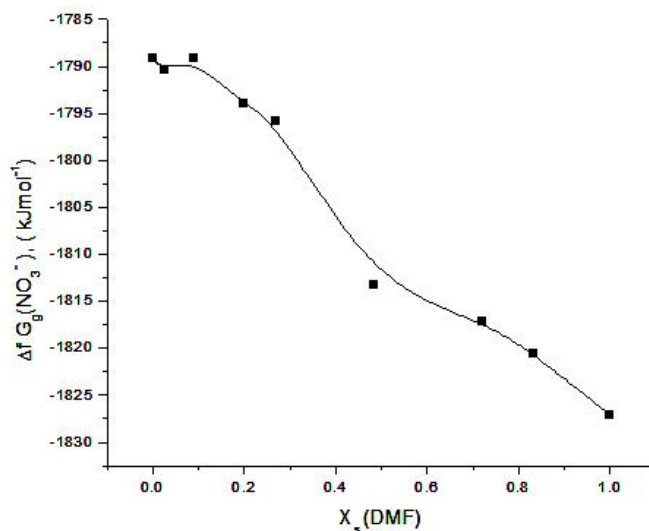
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183 Table 3. Gas formation free for NO_3^- anion in mixed DMF- H_2O solvents at 301.15 K.

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



184 Fig. 1. Gibbs free energies of transfer (ΔG_t) for $\text{Pb}(\text{NO}_3)_2$ versus the mole fraction (X_s)
 185 of DMF at 301.15 K.
 186



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

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Using a combination of experimental gas-phase free energies of formation and solution-phase reduction potentials, we determined conventional solvation free energies of $\text{Pb}(\text{NO}_3)_2$ in mixed DMF- H_2O solvents at 301.15 K from the experimental solubility measurements. Libration Gibbs free energy associated with moving $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ (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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ACKNOWLEDGEMENTS

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This work was supported by Chemistry Department, Faculty of Science, Mansoura University and Basic Science Department, Delta Higher Institute for Engineering and Technology, Mansoura, Egypt.

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