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Thermodynamics of the Solvation of Lead Nitrate in Mixed Propanol-H$_2$O Solvents at Different Temperature.

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Research Article

ABSTRACT

The aim of this study was to determine the thermodynamics of the solvation of Pb(NO$_3$)$_2$ in mixed propanol-H$_2$O solvents , which is very toxic heavy metal salt at different temperatures. The Gibbs free energies as very important thermodynamic property were evaluated for Pb(NO$_3$)$_2$ in mixed propanol-H$_2$O solvents at different temperature from the experimental solubility measurements. The ratio of the ionic radii 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 the moving Pb(NO$_3$)$_2$ in standard gas state to standard state in solution was evaluated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for Pb(NO$_3$)$_2$(cr) was also calculated and used for further evaluation (the symbol (cr) denotes the crystalline phase). The conventional Gibbs free energies for the cation (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 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].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 [18-22] for partition the salt Gibbs free energies into single ion contribution. The aim of this work is to estimate the single ion Gibbs free energies for Pb^{2+} & NO$_3^-$ ions in mixed propanol-H$_2$O solvents at different temperature.

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 [23]. 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. 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 of NO_3^- ion, to explain the ionic behavior.

MATERIALS AND METHODS

Lead nitrate $Pb(NO_3)_2$ GCC-laboratory reagent and propanol (Pr-OH) from Merck Co. were used. Saturated solutions of $Pb(NO_3)_2$ were prepared by dissolving different amounts in closed test tubes containing different Propanol-H_2O mixtures. These mixtures were then saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking thermostat (ModelDW101S) 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 293.15K, 303.15K and 315.15K.

RESULTS AND DISCUSSION

The molar solubility (S) for $Pb(NO_3)_2$ at 293.15K, 303.15K and 315.15K were measured gravimetrically with average of the second number after comma in water, propanol and their mixtures. The solubility values for $Pb(NO_3)_2$ are cited in Table 1, Table 2 and Table 3 . The mean activity coefficient ($\log \gamma_\pm$) of ions which can be estimated from the Debye-Hückel limiting law, as modified by Robinson and Stokes [24 - 80].

$$\log \gamma_\pm = -\frac{AZ_+ Z_- \sqrt{I}}{I + Br^o \sqrt{I}} \qquad \ldots\ldots\ldots(2)$$

Where Z_+ and Z_- are the charges of ions in solutions, A= 1.823 ×10⁶(ε.T)$^{-3/2}$,   B = 50.29 (ε.T)$^{-½}$, r°is the solvated radius, εis the dielectric constant of the solvents and S is the molar solubility. The values of ε for propanol-water mixtures were taken from previous publication [26]. These data ($\log \gamma_\pm$) were tabulated also in Table 1, Table 2 and Table 3. The solubility product was calculated by the use of equation (2) [27-90].

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

The solubility product (pK$_{sp}$) data are given in Table 1, Table 2 and Table 3 from these solubility products, the Gibbs free energies of solvation and the transfer Gibbs free energies from water to organic solvent and mixed solvents were calculated by using equations (3) and (4) [29- 96]. Their values are tabulated also in Table 1, Table 2 and Table 3.

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

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

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

It was concluded that the Gibbs free energies of transfer ($\Delta \mathbf{G_t}$) increase in negativity by increasing the mole fraction of propanol in the mixed Propanol-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. Positive Gibbs free energy values indicate disfavorable conditions. (Figs. 1-3).

Table 1: Solubility, activity coefficient, solubility product, Gibbs free energies change and transfer Gibbs free energies change for $Pb(NO_3)_2$ in mixed propanol-H_2O solvents at 293.15 K.

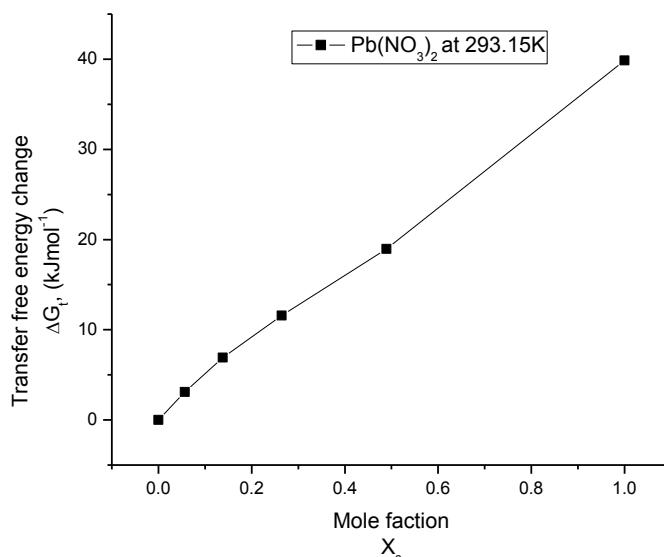| X_s, propanol	S, mol/L	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s, KJ/mol	ΔG_t, kJ/mol
0	1.4095	-0.379	0.0889	0.4992	0
0.0565	0.9237	-0.381	0.6408	3.5969	3.098
0.1378	0.5494	-0.483	1.6179	7.4085	6.909
0.2645	0.295	-0.396	2.1525	12.082	11.583
0.4895	0.1167	-0.438	3.4682	19.467	18.968
1.0	0.015	-0.823	7.1886	40.349	39.850

Figure 1. Transfer Gibbs free energies changes of (ΔG_t) for $Pb(NO_3)_2$ versus the mole fraction (X_s) of propanol at 293.15K.

Table 2: Solubility, activity coefficient, solubility product, Gibbs free energies change and transfer Gibbs free energies change for $Pb(NO_3)_2$ in mixed propanol-H_2O solvents at 303.15 K.

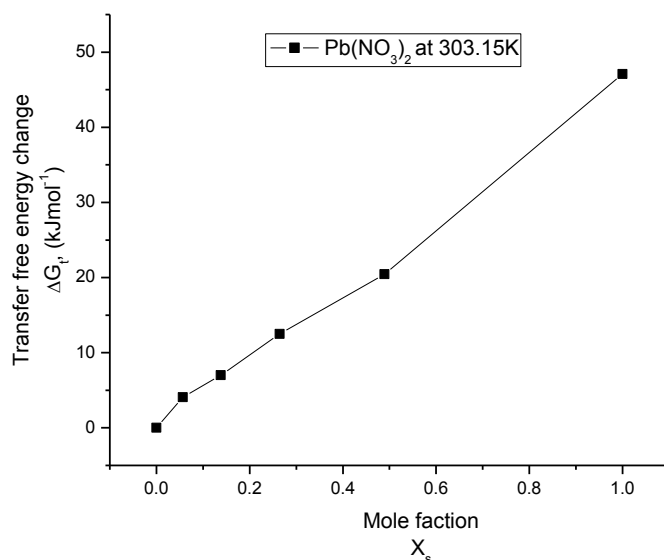| X_s, propanol	S, mol/L	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s, kJ/mol	ΔG_t, kJ/mol
0	1.4355	-0.387	0.0890	0.5166	0
0.0565	0.8254	-0.382	0.7907	4.5896	4.073
0.1378	0.572	-0.392	1.2937	7.5093	6.993
0.2645	0.277	-0.399	2.2411	13.008	12.492
0.4895	0.1036	-0.436	3.6134	20.974	20.457
1.0	0.0038	-0.558	8.2029	47.613	47.097

Figure 2: Transfer Gibbs free energies changes of (ΔG_t) for $Pb(NO_3)_2$ versus the mole fraction (X_s) of propanol at 303.15K.

Table 3: Solubility, activity coefficient, solubility product, Gibbs free energies change and transfer Gibbs free energies change for $Pb(NO_3)_2$ in mixed propanol-H_2O solvents at 313.15 K.

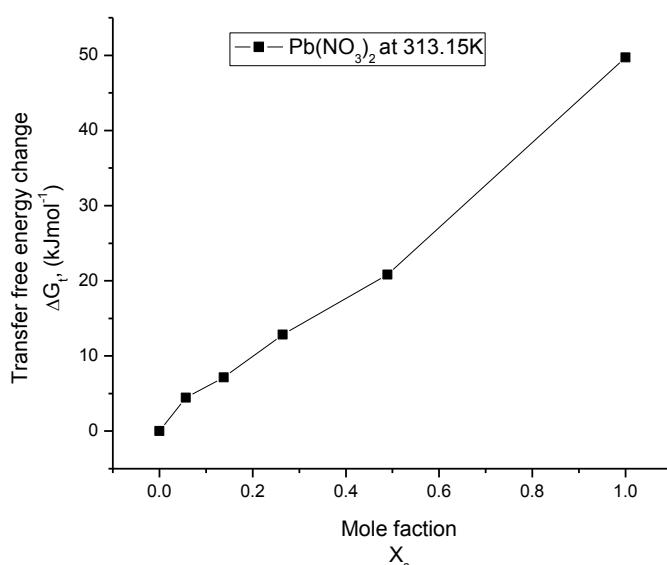| X_s, propanol	S, mol/L	$\log \gamma_\pm$	pK_{sp}	ΔG_s, kJ/mol	ΔG_t, kJ/mol
0	1.5188	-0.3871	0.0137	0.0823	0
0.0565	0.8448	-0.3815	0.7578	4.5438	4.461
0.1378	0.6174	-0.3955	1.2037	7.2170	7.135
0.2645	0.3003	-0.4055	2.1552	12.923	12.840
0.4895	0.1191	-0.4557	3.4879	20.913	20.831
1.0	0.0038	-0.6007	8.3045	49.793	49.711

Figure 3: Transfer Gibbs free energies changes of (ΔG_t) for $Pb(NO_3)_2$ versus the mole fraction (X_s) of propanol at 313.15K.

Single Ion Gibbs Free Energies and Convention Gibbs 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 [30-32] and found to be (132 nm/179 nm= 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 4. The conventional Gibbs free energies $(\Delta G_s)^{*con}(Pb^{2+})$ for Pb^{2+} ion in solvents are shifted from their absolute values by the absolute free energy of the proton [45-47] according to equation (5)

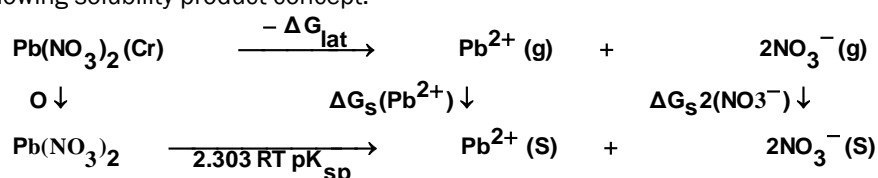$$\Delta G_S^{*con}\,(Pb^{2+}) \;=\; \Delta G_S\,(Pb^{2+}) \;-\; 2\,\Delta G_S\,(H^+)\;\;.......(5)$$

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

$$\Delta G_S^{*con}\,(NO_3^-) \;=\; \Delta G_S\,(NO_3^-) \;+\; 2\Delta G_S\,(H^+).......(6)$$

Where $\Delta G_s\,(Pb^{2+}),\,\Delta G_s\,(NO_3^-)\text{ and }\Delta G_s\,(H^+)$ 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 [12,35,36] relation between these values and the diameter for each solvent taken from literature [37-40], a straight line was obtained. From this line the proton solvation free energies in pure water and propanol were obtained. 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 4. 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 4. 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 propanol 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 Propanol-H_2O Solvents

The libration Gibbs free energies for $Pb(NO_3)_2$ in mixed propanol-H_2O solvents at 293.15K, 303.15K and 313.15K were calculated following cycle 1 (thermochemical cycle 1) as done before [12] for silver salts following solubility product concept.

$$Pb(NO_3)_2\,(Cr) \xrightarrow{\;-\Delta G_{lat}\;} Pb^{2+}\,(g) \;+\; 2NO_3^-\,(g)$$

$$O\downarrow \qquad\qquad \Delta G_S(Pb^{2+})\downarrow \qquad\qquad \Delta G_S 2(NO_3^-)\downarrow$$

$$Pb(NO_3)_2 \xrightarrow{\;2.303\,RT\,pK_{sp}\;} Pb^{2+}\,(S) \;+\; 2NO_3^-\,(S)$$

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) [30-50].

$$\Delta G_{lat} = \frac{232.8}{\sqrt[3]{V}} \;+\; 110 \;\;K\;J/mol.......(7)$$

The volume of $Pb(NO_3)_2$ was calculated by dividing its molecular weight by the density of solid given in literature [40-96] and apply it in equation (7) to obtain 165.675 kJ mol^{-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}).

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

The $2\Delta G^{0} \rightarrow *$, the free energy change associated with moving Pb(NO₃)₂ from standard gas phase of one 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.

$$H_2(g) \rightarrow 2H^+(s) + 2e^-(g)\ldots\ldots(9)$$
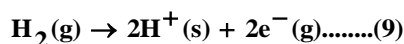
The half-cell reaction for the reduction of cation is:

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

The symbol (cr) denotes the crystalline phase the sum of the two half cells are:

$$H_2(g)\ +\ \ Pb^{2+}(s) \rightarrow Pb(cr)\ +\ 2H^+(s) \quad \ldots\ldots(\ 11)$$
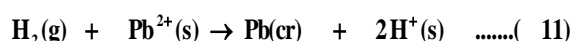
Through the use of thermochemical cycle 2, the conventional free energy for Pb²⁺ can be written as:

$$\Delta G_s^{*con}(Pb^{2+})\ = 2\ \Delta f G(H^+)_g - \Delta f G(Pb^{2+})_g - 2\ FEc\ldots\ldots(1\ 2)$$

Where $\Delta f G(H^+)_g$ and $\Delta f G(Pb^{2+})_g$ are the gas free energy of formation for H⁺ and Pb²⁺ ions, F (faraday constant) = 96.485 kJ per volt gram equivalent and Ec is the standard reduction potential of Pb²⁺, $\Delta f G(Pb^{2+})_g$ is difficult to evaluate because of the lack of exact $\Delta f G(H^+)_g$ value.

$$
\begin{array}{llllll}
H_2(g) & + Pb(NO_3)_2(cr) & \xrightarrow{\Delta Gg} Pb^{2+}(cr) & + 2NO_3^-(g) & + 2H^+(g) \\
\downarrow 0 & \downarrow 0 & 0\downarrow & 2\Delta G_s(NO_3^-)\downarrow & 2\Delta G_s(H^+)\downarrow \\
H_2(g) & + Pb(NO_3)_2(cr) & \xrightarrow{-2FEc} Pb^{2+}(s) & + 2NO_3^-(g) & + 2H^+(g)
\end{array}
$$
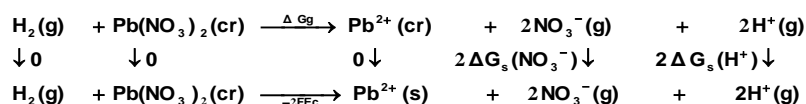
(Cycle 2)

Also the conventional free energy of the nitrate anion NO₃⁻ can be written following Truhlar [41] explanation as:

$$\Delta G_s *con(NO_3^-) = -\ \Delta f Gg - FEc - 2\Delta G^{0\rightarrow}\ldots\ldots(13)$$

Applying equation (13) the ΔfG_g, the gas free energies of formation for the anion NO₃⁻was estimated in the mixed propanol-H₂O solvents and their values are given in Table 4, 5 and Fig. 4. the ΔfG_g,value increase by increasing the mole fraction of propanol that favouring less solvation.

Table 4: Single ion Gibbs free energies for Pb²⁺ and NO₃⁻¹ and their half conventional free energies at 293.15K in mixed propanol-H₂O solvents (kJmol⁻¹).

Xs, propanol	$\Delta G(Pb^{2+})$	$\Delta G(NO_3^-)$	$\frac{1}{2}\Delta G_s^{*con}(Pb^{2+})$	$\frac{1}{2}\Delta G_s^{*con}(NO_3^-)$	$-\Delta G_s*(H^+)$
0	0.3679	0.1312	-1523.24	1523.74	1523.61
0.0679	2.6509	0.9459	-1533.89	1537.29	1536.35
0.1595	5.4598	1.9486	-1548.80	1556.20	1554.26
0.2873	8.9044	3.1775	-1570.40	1582.48	1579.31
0.4886	14.3471	5.1198	-1604.41	1623.87	1618.76
1.0	29.7372	10.6117	-1689.96	1730.31	1719.70

Table 5. Gas formation free for NO_3^- anion in mixed Propanol-H2O solvents at 293.15 K

$X_s,$ propanol	$\frac{1}{2}\Delta fG_g$
0	-1727.51
0.0679	-1818.01
0.1595	-1820.23
0.2873	-1832.45
0.4886	-1840.11
1.0	-1844.33

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 propanol-H2O solvents at 293.15K, 303.15K and 313.15K from the experimental solubility. 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 $Pb(NO_3)_2$ was also calculated and used for further evaluation. These conventional solvation free energies were then combined with experimental and calculated gas-phase 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 standard against which the absolute solvation free energies of other single ions can be derived. For example, Table 4 shows the absolute single-ion solvation free energies of the ions considered in this work.

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