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Thermodynamics of the Solvation of Lead Nitrate in Mixed Acetone-H_2O Solvents at Different Temperatures.

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Research Article

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ABSTRACT

The Gibbs free energies as very important thermodynamic property were evaluated for $Pb(NO_3)_2$ in mixed Acetone-H2O solvents at different temperature 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. 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 their 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 uncentainity is relatively low ($\approx$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 understanding the partitioning of single ions between different liquid phases is important in many areas of biology. For example, the electrical singles 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 acetone (Ac)-H_2O solvents at different temperatures. A number of different extra thermodynamic approximations have been used [13-25] 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 polvaiton of some reference ion equal zero [26]. Proton was chosen as reference ion. For ions, this result in a set of convertional 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 $Pb(NO_3)_2$ GCC-laboratory reagert and n-propanol from Merck Co. were used.

Saturated solutions of Pb(NO3)2 were prepared by dissolving different amounts in closed testtubes containing different Acetone-H_2O mixtures. These mixtures were then saturated withnitrogen 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 smallbeaker using I. R. lamp. The measurements were done by three readings for each solutionat 293.15 K, 298.15K,303.15K and 308.15 K.

Results and Discussion:

The molar solubility (S) for $Pb(NO_3)_2$ at 293.15 K,298.15 K,303.15 K and 308.15 K were measured gravimetrically with average of the second number after comma in water, acetone and their mixtures. The solubility values for $Pb(NO_3)_2$ are cited in Table 1,Table 2, Table 3 and Table 4. The mean activity coefficient $(\log \gamma_{\pm})$ of ions which can be estimated from the Debye-Hückel limiting law, asmodified by Robinson and Stokes [28, 29- 80]].

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

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 [30-99].

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

The solbility 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].

$$\Delta G = 2.303 \; RT \, pK_{sp} \text{.......... ....(3)}$$

$$\Delta G_t = \Delta G_s - \Delta G_w \text{.......... .... (4)}$$

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

It was concluded that the Gibbs free energies of transfer (ΔG_t) increase in negativity byincreasing the mole fraction of acetone in the mixed acetone-H_2O solvents indicating thespontaneous nature of $Pb(NO_3)_2$ solubilization. This is due to more solvation behaviour inthe mixed solvents than that of water where the Gibbs free energy values provideinformation 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. (Fig. 1 - 4)

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Table 1: Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed acetone-H_2O solvents at 293.15 K.

X_s, Ac	S, mol/L	log $\gamma_\pm$	pK_{sp}	ΔG_s,KJ/mol	ΔG_t, kJ/mol
0	1.4095	-0.38	0.0922	0.5173	0
0.071	1.0237	-0.39	0.5366	3.0118	2.494
0.1667	0.5351	-0.393	1.3855	7.777	7.260
0.3044	0.2465	-0.401	2.4133	13.546	13.029
0.5255	0.1012	-0.447	3.6912	20.719	20.201
1.0	0.069	-1.124	6.1023	34.252	33.735

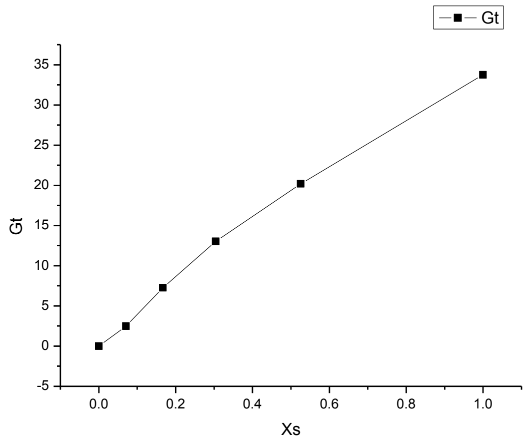

Figure 1: Gibbs free energies of transfer (ΔGt) for Pb(NO3)2 versus the mole fraction (Xs) of acetone at 293.15 K

Table 2: Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed acetone-H_2O solvents at 298.15 K.

X_s, Ac	S, mol/L	log $\gamma_\pm$	pK_{sp}	ΔG_s,KJ/mol	ΔG_t, kJ/mol
0	1.4355	-0.384	0.0774	0.4417	0
0.071	0.9627	-0.39	0.6159	3.5158	3.074
0.1667	0.5899	-0.401	1.2822	7.3199	6.878
0.3044	0.3853	-0.434	1.9308	11.023	10.581
0.5255	0.1793	-0.504	3.1186	17.803	17.362
1.0	0.1038	-1.229	5.8916	33.633	33.192

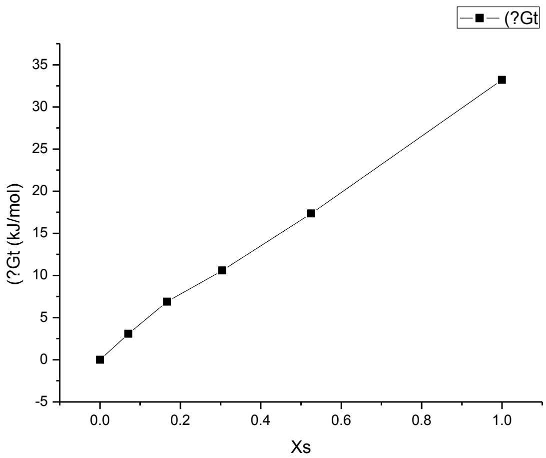

Figure 2: Gibbs free energies of transfer (ΔGt) for Pb(NO3)2 versus the mole fraction (Xs) of acetone at 298.15 K

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Table 3: Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed acetone-H_2O solvents at 303.15 K.

X_s, Ac	S, mol/L	log $\gamma_\pm$	pK_{sp}	ΔG_s,KJ/mol	ΔG_t, kJ/mol
0	1.3909	-0.385	0.1222	0.7093	0
0.0710	0.9532	-0.392	0.6350	3.6858	2.976
0.1667	0.5793	-0.402	1.3109	7.6088	6.900
0.3044	0.3545	-0.432	2.0318	11.793	11.084
0.5255	0.1903	-0.513	3.0675	17.805	17.096
1.0	0.0697	-1.159	6.1851	35.901	35.192

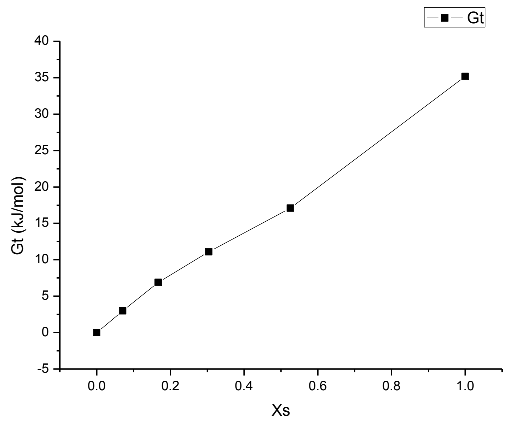

Figure 3. Gibbs free energies of transfer (ΔGt) for Pb(NO3)2 versus the mole fraction (Xs) of Acetone at 303.15 K

Table 4: Solubility and Gibbs free energies for $Pb(NO_3)_2$ in mixed acetone-H_2O solvents at 308.15 K.

X_s, Ac	S, mol/L	log $\gamma_\pm$	pK_{sp}	ΔG_s,KJ/mol	ΔG_t, kJ/mol
0	1.4865	-0.39	0.051	0.3007	0
0.0710	1.0180	-0.398	0.5668	3.3443	3.044
0.1667	0.7068	-0.416	1.0932	6.4504	6.150
0.3044	0.4173	-0.447	1.8643	11.000	10.699
0.5255	0.2287	-0.537	2.8991	17.105	16.804
1.0	1.6917	-1.693	3.7229	21.966	21.665

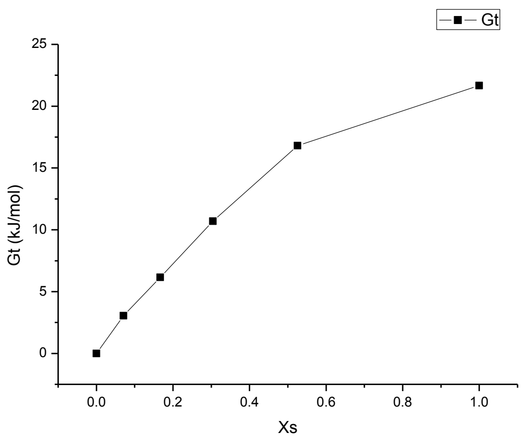

Figure 4: Gibbs free energies of transfer (ΔGt) for Pb(NO3)2 versus the mole fraction (Xs) of acetone at 308.15 K

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Single ion Gibbs free energies and conventional free energies for Pb^{2+} and NO_3^- ions:

It was well known that the preferrentional 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 substracted 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 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 [34] according to equation (5)

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

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

$$\Delta G_s^{*con}(NO_3^-) = \Delta G_s(NO_3^-) + 2\Delta G_s(H^+) \quad (6)$$

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, 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 acetone were obtained and found to be 1523 and 1633.61 KJ/mol, respectivity 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 (4). 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 enxothermic character. Both values increase with increase in the mole fraction of acetone due to more solvation and the sum of them gives the values for the neutral salt.

Table 4: Single ion Gibbs free energies for Pb^{2+} and nitrate and their half conventional free energies at 298.15 K. in mixed acetone-H_2O solvents (in kJmol-1)

X_s Ac	Δ G(Pb^{2+})	Δ 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	0.0925	0.6168	-1522.91	1523.91	1523
0.0710	0.4806	3.2051	-1528.19	1531.88	1528.68
0.1667	0.9921	6.6199	-1535.34	1542.85	1536.33
0.3044	1.5378	10.2551	-1545.81	1557.61	1547.35
0.5255	2.2293	14.8666	-1562.81	1579.91	1565.04
1.0	4.589	30.6029	-1598.41	1633.41	1603

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