



## SOLVATION PARAMETERS OF LEAD ACETATE IN MIXED WATER-N,N-DIMETHYLFORMAMIDE MIXTURES AT 298.15 K

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**abstract:** The molar solubility of lead acetate (LA) in mixed DMF-H<sub>2</sub>O solvents was measured at 298.15 K. From the molar solubilities the solvation parameters, Debye Huckel constants A, B, activity coefficient, solubility products, free energies of solvation and transfer free energies for the interaction of (LA) from water as reference solvent to mixed (DMF-H<sub>2</sub>O) solvents were evaluated. All the solvation parameters were discussed.

**key words:** molar solubility; lead acetate; free energies of solvation; water; DMF.

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### Introduction

Many publications have reported on the behaviour of salts in anhydrous solvents [1,2]. Solubility studies for some silver 1:1 salts were also studied in literature [3]. Thermodynamic parameters were also calculated for 1:1 symmetric electrolytes from solubilities [4]. Solubilities of some divalent and trivalent electrolytes were experimentally studied [5,6].

Lead acetate has very wide applications in inorganic and biochemistry, because of its toxicity [7]. For example (LA) affects the heart muscle cells in rabbits [8]. Lead acetate influenced on soil microbial biomass and structure of soil [9]. Also lead acetate can be used for electrolytic coloring of Aluminium [10].

The aim of this work is to evaluate the solubilities and study the solvation behaviour of divalent lead acetate salt in mixed DMF-H<sub>2</sub>O solvents for discussing the salt-solvent and ion-ion interactions [11-14].

### Experimental

The used lead acetate and N,N-dimethylformamide (DMF) were supplied from Merck Co. The saturated solution of lead acetate (LA) was prepared by dissolving it in closed test

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tubes containing different H<sub>2</sub>O-DMF mixtures. The mixtures were then saturated with N<sub>2</sub> gas as inert atmosphere. The tubes were placed in a shaking thermostat (Model GFL) for a period of four days, followed by another two days without shaking to reach the necessary equilibrium at room temperature (298.15 K).

The solubility of lead acetate in each mixture was determined gravimetrically (at least four measurements for each) by taking 1 ml of the saturated solution and subjecting it to complete evaporation using a small aluminium disks heated by an infrared lamp and weighing the residue by using four digital Mettler AE 240 balance. The accuracy of the solubility data is in the average values of 0.01 mole/l plus or minus as cited in such methods in previous work [11]

## Results and Discussion

The molar solubilities for lead acetate (LA) at 298.15 K were measured and their values are cited in Table 1 in water, N,N-dimethylformamide and their mixtures. The solubility of (LA) in water was agreed well with that of Apelblat data [15].

**Table 1** Mixed solvents radii ( $r$ ), dielectric constants of solvents ( $\epsilon$ ), solvation radii ( $r_s$ ), solubilities ( $S$ ), Debye Huckel constants  $A$ ,  $B$  and log activity coefficients ( $\gamma_{\pm}$ ) for lead acetate in different DMF-H<sub>2</sub>O solvents at 298.15 K.

Mole fraction of DMF ( $X_S$ )	$r$ solvent in A°	$\epsilon$	$r_s$ (A°)	$S$	$A$	$B$ ( $\times 10^{-5}$ )	Log $\gamma_{\pm}$
0	1.360	78.30	12.440	0.184	0.512	329	0.216
0.025	1.477	66.26	12.557	0.214	0.522	331	0.193
0.055	1.584	76.01	12.664	0.229	0.535	334	0.183
0.090	1.696	74.55	12.776	0.238	0.551	337	0.183
0.134	1.808	72.72	12.888	0.209	0.572	342	0.208
0.189	1.920	70.43	13.000	0.158	0.600	347	0.270
0.259	2.032	67.52	13.112	0.079	0.639	355	0.493
0.352	2.144	63.65	13.424	0.065	0.699	365	0.614
0.482	2.256	58.24	13.334	0.050	0.798	382	0.835
0.677	2.368	50.13	13.448	0.037	1.000	411	-1.259
1.0	2.480	36.70	13.560	0.028	1.596	481	2.412

The activity coefficients were calculated by the use of the modified Debye-Huckel equation [8]:

$$\log \gamma_{\pm} = -\frac{A Z_1 Z_2 \sqrt{S}}{1 + B r_{\text{solv}} \sqrt{S}} \quad (1)$$

Where  $A$ ,  $B$  are constants of Debye Huckel equation given by:

$$A = 1.825 \times 10^6 / (T \cdot \epsilon)^{3/2} \quad (2)$$

$$B = 50.29 \times 10^8 (T \cdot \epsilon)^{1/2} \quad (3)$$

$Z_1, Z_2$  are charges of cation and anion,  $S$  is the molar solubility and  $\epsilon$  is the dielectric constant of the solvent.

$r_{\text{solv}}$  is the solvated lead acetate radius in mixed solvents under consideration. It was calculated by adding the van der Waals volumes of acetate ion to the crystal radius of lead and finally adding the radii of DMF-H<sub>2</sub>O solvents.

The Van der Waals radius of acetate were calculated theoretically by using Bondi method [16] and found to be 2.61 Å, where the crystal radius of Pb is 2.02 Å [16]. The final (LA) solvated radii in the mixed solvents were also given in Table (1). The dielectric constants for the mixtures of solvent used were calculated from the dielectric constants of pure solvents [17] and apply equation (4) and their values are given in Table (1) also

$$\epsilon_{\text{mixed}} = X_{\text{S(DMF)}} \epsilon_{\text{DMP}} + X_{\text{S(H}_2\text{O)}} \epsilon_{\text{H}_2\text{O}} \quad (4)$$

Where  $X_{\text{S(DMF)}}$  and  $X_{\text{S(H}_2\text{O)}}$  are the mole fraction of dimethylformamide and water respectively.

The solubility product was calculated by the use of equation (5).

$$pK_{\text{SP}} = \left[ -\log 4S^3 + 4(\log \gamma_{\pm})^3 \right] \quad (5)$$

Where  $S$  is the molar solubility of Pb(H<sub>3</sub>COO)<sub>2</sub> in mixed DMF-H<sub>2</sub>O solvents  $pK_{\text{SP}}$  data are given in Table 2. From these solubility products the Gibbs are energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations (6) and (7) and their values are tabulated in Table (2)

$$\Delta G = 2.303 RT pK_{\text{SP}} \quad (6)$$

$$\Delta G_t = \Delta G_S - \Delta G_W \quad (7)$$

**Table 2** Solubility product  $PK_s$ , Gibbs free energies of salvation ( $\Delta G$ ) and Gibbs free energies of transfer ( $\Delta G_t$ ) from mixed solvents to water for lead acetate in mixed DMF-H<sub>2</sub>O solvents at 298.15 K.

$X_s$	$pK_{\text{SP}}$	$\Delta G$ (kJ/mole)	$\Delta G_t$ (kJ/mole)
0.0	1.563	8.8443	0
0.025	1.378	7.7950	-1.0451
0.055	1.293	7.3161	-1.5281
0.090	1.249	7.0704	-1.7738
0.134	1.402	7.9324	-0.9119
0.189	1.723	9.7479	0.9035
0.259	2.225	12.5919	3.7476
0.352	2.033	11.5509	2.6566
0.482	0.975	5.5173	-3.3270
0.677	-4.281	-24.2219	-33.0662
1.0	-9.926	-56.1640	-65.0083

It was concluded that the Gibbs free energies of salvation  $\Delta G$  increase on more adding DMF in the mixtures. This is due to the ease of solvation i.e., the reaction is more spontaneous in case of solvents rich with DMF. Also the Gibbs free energies of transfer increase rapidly by increasing the mole fraction of DMF in the mixtures. At more fractions of DMF between 0.189-0.352 non systematic values are obtained (Table 2), which may be due to solvent-solvent interaction.

It was concluded the activity coefficient for (LA) has greater values in mixed solvent than both of pure solvents indicating bigger ion-ion interaction of both acetate and lead ions in the mixtures than in pure solvents.

It also resulted that the solubilities of (LA) decrease by increasing DMF portions, due to the salt-solvent interactions. Therefore when we need less concentrated solutions of (LA) and more effective in its applications we can use it in mixed DMF-H<sub>2</sub>O solvents.

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