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Thermodynamics of Solvation for Nano Zinc Oxide in 2 MNH_4Cl+ Mixed DMF – H_2O Solvents at Different Temperatures

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Keywords

Molalsolubility, Nano Zinc Oxide, Free Energies, Enthalpies, Entropies, Mixed DMF – H_2O Solvents

The molal solubilities for nano zinc oxide (ZnO) in 2 MNH_4Cl plus different percentages of dimethylformamide (DMF) and water solvents were measured at 294.15 K , 303.15 K , 309.15 K and 313 K .From the molalsolubilities for nanoZnO , the salvation parameters , activity coefficients, solubility products , free energies of solvation , transfer free energies for interaction , enthalpy of solution and entropy of solvation in 2 M NH_4Cl plus mixed DMF – H_2O solvents were evaluated . All these solvation parameters were discussed.

Introduction

The solubility of solutes in mixed solvents has great importance in many industrial processes as well as laboratory uses. The solubility of solutes in mixed solvents depends primarily on solvation of solutes or their constituent ions by the components of solvent mixtures [1].

Studying the thermodynamics of different salts, is important for evaluating the single ion thermodynamic parameters which help in explanation of the preferential salvation of ions [2].

Thermodynamic study helps in the removal of heavy elements using solvent extraction which is necessary to get rid of the hard ions [3].

Experimental

Materials

Zinc nitrate hexa hydrate $Zn(NO_3)_2$. 6 H_2O 98% and ammonium chloride from Aldrich were used. Dimethyl formamide (DMF) from Adwic was used.

Synthesis of Nano Zinc Oxide

To 100 ml of 1 M $Zn(NO_3)_2$. 6 H_2O dilute ammonia was slowly added with stirring till pH value of 8. The solution was

sealed in autoclave and heated at 353 K for 2 days. After that time the produced precipitate was filtered, washed several times by distilled water and then dried at 383 K.

Preparation of Saturated Solutions and Solubility Measurements

The saturated solutions of nano ZnO were prepared by dissolving solid amount in closed test tubes containing 2 M NH_4Cl + different DMF – H_2O mixtures. The tubes were placed in water thermostat for a period of three days till equilibrium reached.

The solubility of ZnO in each mixture was measured by taking 1 ml of each saturated solution putting in a small weighed beaker (10 ml) and evaporate under I.R lamp till dryness and then reweight [4 & 5].

The blank material was measured by evaporation of saturated NH_4Cl alone samples in mixed DMF – H_2O solvents without adding ZnO.

The molal solubilities for nano ZnO samples were calculated by subtracting the evaporated weights of samples minus that of pure NH_4Cl ones.

The same procedures were repeated at different temperatures.

Results and Discussion

TEM Images

The TEM images of ZnO sample in pure DMF were measured using electron microscope model Joel 2010 and shown in Fig. (1). The images show almost deformed spherical particle shapes with an average size of 21 and 41 nm ,respectively . Also, they show different voids between the particle grains .Fig. 2 f shows the diffraction of ZnO sample in which the measured interplane spacing (0.52nm) matches well with the literature reported value for nano forms Wurtzite ZnO [6].

Zeta Potential Measurement

The Zeta potential for nano ZnO in pure DMF was measured and found to be – 11.3 mv indicating low solubility of the nano ZnO and moderate association of the particles. Also low conductivity value 0.507 m s / cm indicate also low ability for ionization in the solvent. Three peaks reported at -120, -10.5 and -75.3 m v.

Size Distribution in DMF Solution

The size distribution for nano ZnO in pure DMF was measured in Zeta apparatus and found to have average diameter value of 529.6 nm (Fig .2). This value indicates that the nano ZnO material is very slightly solvated in DMF and the diameter increases to reach 529.6 nm as maximum value.

Gibbs Free Energies of Solvation

Since the solubility (S_m) of nano ZnO is very small in pure solvents, therefore all the measurements can be done in presence of 2 M NH_4Cl. The molal solubility for ZnO in 2 M NH_4Cl + DMF – H_2O mixtures at 294.15 K , 303,15 K , 309.15 K & 313.15 K were measured gravimetrically by taking the mean values for three readings for each solution . The S_m values are cited in Table 1as example at 294.14K.

The activity coefficients were calculated by the use of Debye – Hückel equation (1) [7-20] and their values are given also in Table 1 also.

$$\log \gamma_{\pm} = - 0.5062 \times (Sm)^{0.5} \quad (1)$$

Where S_m is the molal solubility. The solubility product was calculated by the use of the equation (2) [8].

$$pKsp = - 2 (\log Sm + \log \gamma_{\pm}) \quad (2)$$

From these 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&4 .

$$\Delta G = 2.303\ RTpK_{sp} \quad (3)$$

$$\Delta G_t = \Delta G_S - \Delta G_w \quad (4)$$

All the data are tabulated in Tables 1.

It was calculated from the tables that the Gibbs free energies of transfer ΔG_t increase in positivity by increasing the mole fraction of DMF in the mixtures. This is due to more difficult salvation in the mixed solvents than that of pure water.

Enthalpies and Entropies of Solvation

From the linear plots of ΔG vs T of nano ZnO, the entropy of solvation could be obtained from the slopes for each solution percentage. We can also determine the enthalpy change Δ H at 303.15K as example by using equation (5) [9-55].

$$\Delta G_s = \Delta H_s - T\Delta S_s \quad (5)$$

These data are given in Table (2).

Table (1). *Molal solubility S_m, log activity coefficient (log γ), solubility product (pK_{sp}) , Gibbs free energy of salvation (Δ G) and transfer Gibbs free energy for nano zinc oxide at different mole fractions (X_s) of DMF in 2 M NH_4Cl + DMF – H_2O mixtures at 294.15 K.*

X_sDMF	S_m	log $\gamma_\pm$	pK_{sp}	Δ GkJ/mol	Δ G_tkJ/mol
0	1.2464	- 0.5651	0.9389	5.1714	0
0.0252	0.5610	- 0.3791	1.2602	6.9415	1.7781
0.0718	0.0487	- 0.1117	2.8483	15.6886	10.5172
0.0909	0.0234	- 0.0774	3.4152	18.8109	13.6395
0.1346	0.0679	- 0.1319	2.5994	14.3174	9.1460
0.1894	0.1634	- 0.5459	0.9603	5.2893	0.1179

Table (2). *Enthalpies and entropies of solvation parameters and Gibbs free energies for nano zinc oxide in 2 M NH_4Cl + DMF – H_2O mixtures at 303.15 K.*

X_s DMF	Δ HkJ/mol	Δ SkJ/mol
0	66.5730	0
0.0253	291.302	0.2383
0.0718	183.105	0.9942
0.0909	1331.670	0.6359
0.1346	2153.560	4.4247
0.1894	4330.529	14.3216

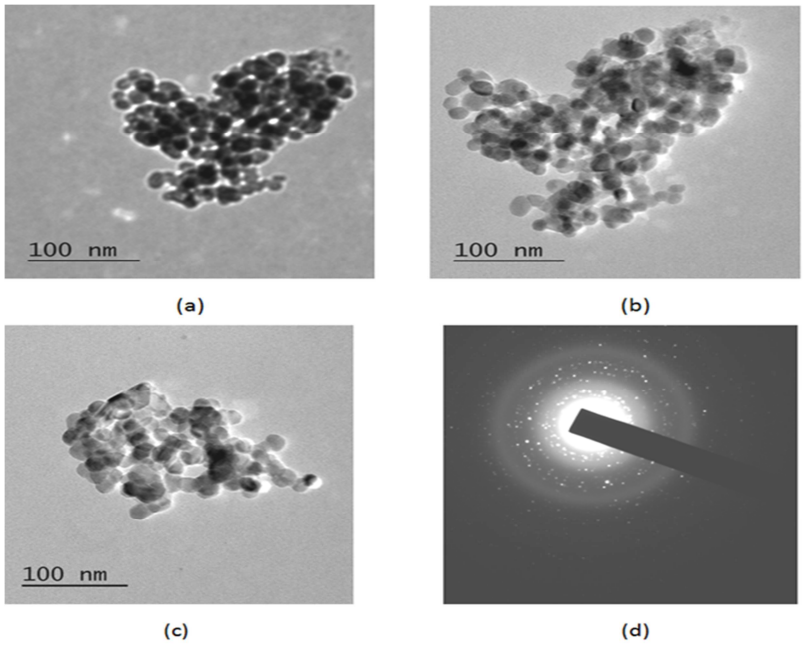


Fig (1). *TEM images for nano zinc oxide, (d) is electron diffraction image.*

Size Distribution Report by Intensity

v2.2

Malvern

Sample Details

Sample Name: dmf 2 1
SOP Name: mansettings.nano
General Notes:

File Name: Dr. Esam A. Gomaa
Record Number: 32
Material RI: 1.59
Material Absorbtion: 0.010
Dispersant Name: dmf
Dispersant RI: 1.320
Viscosity (cP): 0.7690
Measurement Date and Time: 04

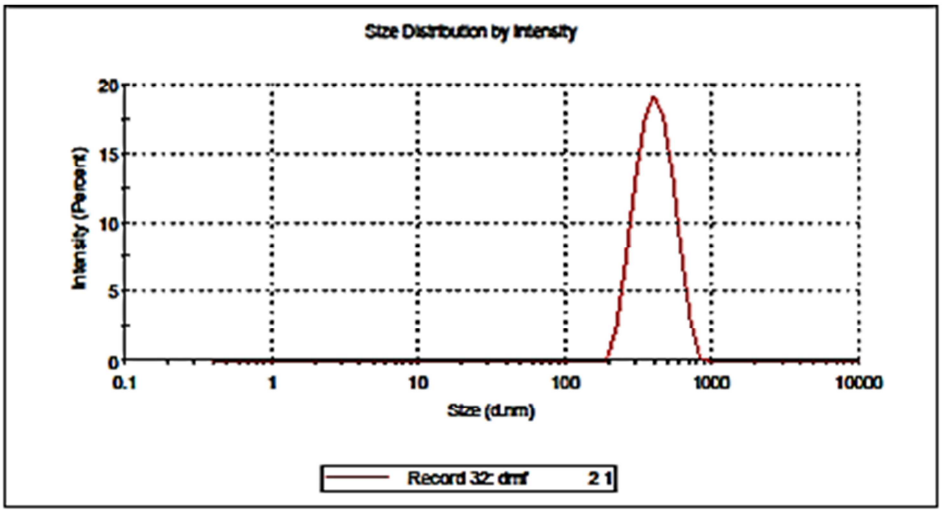
System

Temperature (°C): 25.0
Count Rate (kcps): 279.4
Cell Description: Disposable sizing cuvette
Duration Used (s): 50
Measurement Position (mm): 4.65
Attenuator: 10

Results

		Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 529.6	Peak 1:	416.1	100.0	115.9
PdI: 0.464	Peak 2:	0.000	0.0	0.000
Intercept: 0.891	Peak 3:	0.000	0.0	0.000

Result quality: Refer to quality report



Malvern Instruments Ltd
www.malvern.com

Zetasizer Ver. 7.01
Serial Number : MAL1062067

File name: dr elham.dts
Record Number: 32
04

Fig (2). Size distribution for nano zinc oxide.

Conclusion

It was concluded that the solubility of ZnO decreases by increase of DMF percentages in 2 M NH_4Cl due to the positive values of Gibbs free energies.

Also the solubility is endothermic ones having positive values for both enthalpies and entropies. All the thermodynamic parameters were supported by the Zeta potential which shows very small value of nano ZnO solution.■

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