Nano ZnO Catalyzed Synthesis of 2-(4-hydroxynaphthalen-1-yl)-N-methyl-2-phenylacetamide and its Aggregation in Water

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Abstract: A novel organic compound, 2-(4-hydroxynaphthalen-1-yl)-N-methyl-2-phenylacetamide was synthesized by making use of non-toxic recyclable zinc oxide nanoparticles as catalyst and characterized using UV visible, FT-IR and 1H NMR spectral techniques. Using conductometric method, its aggregation property in aqueous medium was studied at various temperatures. The thermodynamic analysis concludes that the driving force of aggregation is not enthalpic in nature.

Keywords: Multi component reactions, ZnO nanoparticles, critical micelle concentration and aggregation

1. Introduction

Nano Science and technology is the pioneering field of 21st century in which an extensive research is going on[1]. Nano particles are characterized by its size below 100 nm and gained considerable importance compared to bulk counterparts. Among different nanoparticles, zinc oxide nanoparticles (ZnO NPs) are very much important due to their utilization in gas sensors, solar cell, cosmetics, drug-delivery systems and so forth[2,3].

Zinc oxide (ZnO) is a colourless, water insoluble inorganic compound used extensively as a catalyst due to its non-toxic recyclable property or an additive for various chemical reactions[4,5]. Multi-component reactions[6] are valuable device for assembling three or more reactants and converting them into higher molecular weight compounds. In recent years, such reactions[7,8] have become a powerful synthetic strategy and the synthetic applications of these protocols are further made more attractive when the reactions are carried out under solvent free conditions.

In the present work an attempt was made to prepare a novel organic compound 2-(4-hydroxynaphthalen-1-yl)-N-methyl-2-phenylacetamide (HNMA) from 1-naphthol, benzaldehyde and N-methylformamide by making use of ZnO NPs as a catalyst. The organic compound HNMA was characterized using UV visible, FT-IR and 1H-NMR and spectroscopic techniques. Additionally the aggregating nature of HNMA in aqueous medium was studied conductometrically at different temperatures in order to study its driving force. In living systems, aggregation of protein is found to be the major cause of a wide variety of disease known as amyloidosis, including Alzheimer's, Parkinson's and prion diseases[9,10]. The mechanism of aggregation is to be studied in order to find drug for the above. In the present work, an attempt is been made to study aggregation of organic molecule which can mimic the aggregation of proteins.

2. Materials and Methods

2.1. Preparation of Zinc Oxide nanoparticles

ZnO NPs were prepared according to the literature method[11] with some modifications. Zinc acetate (0.05 mol) and oxalic acid (0.06 mol) were combined by grinding in a mortar for 2 hr at room temperature. Thus, formed ZnC2O4,2H2O nanoparticles were subjected to microwave (IFB-20BC4) irradiation at 150W microwave power for 30 min to produce ZnO nanoparticles[12].

2.2. Synthesis of 2-(4-hydroxynaphthalen-1-yl)-N-methyl-2-phenylacetamide (HNMA)

In a 50-ml beaker, a mixture of benzaldehyde (3.18 g, 30 mmol), N-Methyl formamide (1.86 g, 30 mmol) and 1-Naphthol (4.32 g, 30 mmol) were subjected to micro wave irradiation for 4 minutes, each pulse was of 30 seconds with intermittent time to avoid overheating. The reaction mixture was stirred with glass rod at regular interval. The progress of reaction was monitored by TLC (n-Hexane: Ethyl acetate (8:2)). After completion of reaction, the reaction mixture was cooled to room temperature and the compound 2-(4-hydroxynaphthalen-1-yl)-N-methyl-2-phenylacetamide (HNMA), was extracted using ethyl acetate as solvent. The insoluble ZnO catalyst was filtered off. The filtrate was collected, dried and the residue HNMA (Molecular formula, C19H17NO3: Molecular Weight, 291.343: colour : Brown) was recrystallized from ethanol.

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2.3 UV-Visible spectrophotometer

To locate the chromophoric absorption, UV visible spectrophotometer instrument SYSTRONICS model type 119 instrument was used at room temperature (302 K). The blank was calibrated using ethanol. The sample was scanned between 270 nm to 700 nm in ethanol medium.

2.4 FT-IR Infrared spectrophotometer

To locate the functional group and to characterize the molecular framework, FT-IR spectrophotometer (ALPHA-BRUKER) was used at air-conditioned temperature (298 K). The method of sample preparation was a direct method without making use of potassium bromide. The presence of OH group will occur at 3402 cm⁻¹. The N-H group will reflect at 3300-3400 cm⁻¹.

2.5. ¹H NMR spectrophotometer

To further characterize the molecular structure, ¹H NMR spectrum was recorded on Bruker FT-NMR spectrophotometer operating at 400 MHz. The solvent used was CDCl₃ and tetramethylsilane (TMS) as an internal reference.

2.6 Conductivity Measurements

The conductance of aqueous solution of HNMA was recorded using Systronics Digital Conductometer (model-304). A Fabricated double walled glass container (70 ml) was used which can circulate water at various temperatures connected with thermostat for thermodynamic work.

3. Results and Discussion

![Scheme 1: Preparation of HNMA from 1-naphthol, N-methyl formamide and benaldehyde](image)

The one pot preparation of HNMA from 1-naphthol, N-methyl formamide and benzaldehyde under solvent from condition using ZnO Nps is shown in scheme 1. It consists of solvophobic aromatic rings and solvophilic hydroxyl group. The UV visible spectrum of HNMA is shown in the figure 1. It exhibits at two characteristic peaks at 310.2 nm and 369 nm. The UV visible spectrum of HNMA is shown in the figure 1. The FT-IR spectrum of HNMA is shown in the figure 2. It shows five major peaks at 1572 cm⁻¹, 1660 cm⁻¹, 3053 cm⁻¹, 3299 cm⁻¹ and 3402 cm⁻¹. The FT-IR spectrum of HNMA supports the structure of HNMA.

To further study about the number and type of protons of HNMA, ¹H NMR is taken in CDCl₃. The ¹H NMR spectrum of HNMA is shown in the figure 3. The chemical shift at 7.0-8.4 is due to the aromatic protons of phenyl and naphthyl rings and 5.8 is due to the C-H methine proton connected to aromatic rings. The peak at 5.5 is due to O-H proton attached to naphthalene ring and the peak at 2.4 is due to methyl group attached to NH of amide.

The aggregate formation of any compound is usually determined by plotting any of its physical property as a function of its concentration and the point of intersection between two straight lines is taken as Critical Micelle Concentration (CMC)\[\text{[13,14]}\]. CMC is defined as the concentration of organic amphiphilic molecules above which micelles formation takes place in true solution\[\text{[15]}\].

In the present study CMC of HNMA was determined by plotting the conductance values at various concentrations measured using digital conductometer versus concentration. As per Arrhenius theory, one should get a straight line, but in the contrary, two lines of different slopes were obtained suggesting aggregation at that particular concentration which is called the critical micelle concentration (CMC) at that particular temperature in water as solvent. The existence of
CMC were determined at different temperatures 306 K, 311 K, 315 K and 319 K (figure 4). From the CMC value obtained from the graph, ln(CMC) was computed. Based on ln (CMC), the thermodynamic parameters (\(\Delta G_m^\circ\), \(\Delta H_m^\circ\), \(\Delta S_m^\circ\)) are obtained using biphasic micellar model\[13,15\]. The standard free energy for aggregate formation, \(\Delta G_m^\circ\) of the HNMA has been calculated from the following equation (1).

\[
\Delta G_m^\circ = RT \ln (CMC) \quad (1)
\]

The standard enthalpy change for micelle formation (\(\Delta H_m^\circ\)) was calculated using the value obtained from the slope of the plot \(\ln (CMC)\) versus temperature. The \(\Delta H_m^\circ\) was calculated using the equation (3).

\[
\Delta H_m^\circ = -RT^2 \left[ \frac{d \ln (CMC)}{dT} \right] \quad (3)
\]

The value of \(\Delta S_m^\circ\) was calculated from \(\Delta G_m^\circ\) and \(\Delta H_m^\circ\), using equation (2). The change in standard heat capacity at constant pressure \(\Delta C_p^\circ\) was obtained from the slope of the plot of \(\Delta H_m^\circ\) versus temperature.

\[
\Delta C_p^\circ = \frac{d \Delta H_m^\circ}{dT} \quad (4)
\]

The values of CMC determined conductometrically for HNMA in aqueous condition at various temperatures and their corresponding thermodynamic parameters determined using equations 1, 2, 3 and 4 are given in table 1. From the table 1, the CMC of the HNMA, increases with decrease in temperature, indicating the micelle formation is less favored with a rise in temperature. The variation of \(\ln (CMC)\) with temperature for the HNMA is shown in figure 5. The thermodynamic parameters (\(\Delta G_m^\circ\), \(\Delta H_m^\circ\), \(\Delta S_m^\circ\)) for the HNMA at various temperatures are also given in table 1. From the values of positive \(\Delta H_m^\circ\), it is clear that the driving

\[\text{Figure 2: FT–IR Spectrum of HNMA}\]
Figure 3: FT-NMR Spectrum of HNMA

Figure 4: Plot of conductivities of various concentrations HNMA at different temperatures.

Figure 5: Plot of ln (CMC) versus temperature for HNMA

Figure 6: Plot of $\Delta H_m^\circ$ versus temperature for HNMA
force for HNMA aggregation is not enthalpic in nature over the temperature range under investigation. When HNMA aggregates, the solvophilic groups (the hydroxyl groups) are 'clustered' together, resulting in a fairly close approach of the hydrophobic groups. This result signifies that the structure of standard heat capacity change for micellization ($\Delta H_{m}^{\circ}$) is not enthalpic in nature. During aggregation less behaviour was observed with water molecules. On increasing the temperature, both $\Delta H_{m}^{\circ}$ and $\Delta S_{m}^{\circ}$ increases, indicating that less solvent molecules are accessible to the complex, resulting in more "structured" HNMA molecules.

The standard heat capacity change for micellization ($\Delta C_{p}^{\circ}$) is obtained from the slope of $\Delta H_{m}^{\circ}$ versus temperature (figure 6; table 1). The positive $\Delta C_{p}^{\circ}$ signifies that the structure of complex is unaffected by the solvent water. Comparing the results of thermodynamic experiments on model organic compounds, it is apparent that the heat capacity changes play a central role in characterizing the solvophobic interactions. The positive heat capacity can be attributed to the ordering of solvent molecules around the exposed solvophilic groups i.e., on increasing the temperature; we get more tightly packed larger micelle like structures. The positive entropic contribution leads to the aggregate stabilization at higher temperature.

4. Conclusion

Using ZnO NPs, a novel organic compound HNMA was prepared using 1-naphthol, N-methyl formamide and benzaldehyde. The compound was characterized using various spectral techniques. In aqueous medium, its aggregation behaviour was studied along with its thermodynamic parameters. The results conclude that the driving force of aggregation is not enthalpic in nature. During aggregation less solvent molecules are accessible which can be inferred from $\Delta H_{m}^{\circ}$ and $\Delta S_{m}^{\circ}$ values at different temperatures. The positive standard heat capacity change for micellization ($\Delta C_{p}^{\circ}$) signifies that the structure of aggregate is unaffected by the solvent water.

References


