

# STUDY OF SOLVATOCHROMATIC, PHOTOLUMINESCENCE, ELECTROCHEMICAL AND ANTIBACTERIAL PROPERTY OF A SODIUM VANILLIN POLYMERIC COMPLEX

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**Abstract:** Solvatochromatic, electrochemical and photoluminescence properties of a sodium vanillin polymeric complex was studied in five different polar solvents like ethanol, methanol, DMF, DMSO and water. Solvatochromatic study show that due to the difference in the dielectric constant values of the solvent, the shifting of  $\lambda_{\max}$  at 310 nm in the UV-visible spectra for n- $\pi^*$  transition of the complex in ethanol, DMF and DMSO is more than that obtained for the complex in water and methanol. Fluorescence emission spectra of the complex were taken which shows that excepting methanol,  $\lambda_{\max}$  values of the polymeric complex in ethanol, DMF, DMSO and water shifted to the longer wave length with the increase in the polarity of the solvent which can stabilize the excited state of the polymeric complex.  $\Delta E$  of the complex in different solvents were calculated from their respective  $E_{pa}$  and  $E_{pc}$  values of the complex obtained from respective voltammograms which indicates the highest reversibility of the complex in methanol because of the lowest calculated  $\Delta E$  value. The calculated  $E_{1/2}$  values of the polymeric complex in different solvents showed that the oxidizing power of the complex in ethanol and water is maximum as the  $E_{1/2}$  values of the complex in those solvents are highest and equal. The ligand vanillin and its sodium complex were tested against the bacteria *E. coli* and *B. subtilis* by using the disc diffusion method. Ampicillin was used as a standard. It was observed that the Na-Vanillin complex was more toxic than its parent ligand and the toxicity increased with increase in concentration of the solution of the test components.

**Keywords:** solvatochromatic; photoluminescence; electrochemical; antibacterial; polymer

## 1. Introduction:

Vanillin is a phenolic aldehyde, an organic compound with the molecular formula  $C_8H_8O_3$ . Its functional groups include aldehyde, ether and phenol. 3-Methoxy-4-hydroxybenzaldehyde (vanillin) is an important compound used in the food industry, perfumery and cosmetics, animal-feed, manufacture of pharmaceutical, agrochemical products, as a synthesis intermediate, etc.[1-3]. The bioactivity of vanillin and its non-linear optical properties [4, 5] are an area of growing interest in the recent years. However, the bioactivities are dependent on their mode of chelation with metal ions. These features include short intramolecular hydrogen bonds and packing configurations. Therefore, studies of the metal complexes of such ligands are important to explore potential new compounds. Vanillin can coordinate with many metal ions and some of its complexes have important material properties [6-9]. The coordination chemistry of alkali metals finds tremendous applications in biology, chemistry [10,11] and biotechnology[12,13] due to their interesting properties. In addition, recently, an increasing interest is focussed on formation of dinuclear, multinuclear and polymeric coordination compounds[14-16] created by self-assembly of the components [17-19]. We have also reported a polymeric complex of sodium with vanillin, the structure of which has been established by single crystal X-ray diffraction [20]. The complex crystallizes in orthorhombic system with space group  $P_{na21}$ . The data exhibit that the crystal contains polymeric Na complex of vanillin and coordinated water molecules. The polymeric structure shows two different types of sodium metals and each one is six coordinated, where one of the Na metals is bonded to one methoxy, one phenoxy of the same vanillin and four water molecules. The other Na metal is bonded to aldehyde of one vanillin, methoxy oxygen of another vanillin and four water molecules. The two sodium atoms are bridged by vanillin and aqua ligands, which further extend intermolecular oxygen-oxygen interactions to strengthen the polymeric structure.

This paper intend to present the solvatochromatic, photoluminescence, electrochemical and antibacterial property of the polymeric complex under study.

## 2. Experimental:

### 2.1. General:

Analytical grade chemicals were purchased from different commercial sources and used as received. All solvents were distilled under  $N_2$  prior to use.

#### 2.1.1. Solvatochromic Method:

To study the effect of solvent having different polarities, standard solutions ( $1 \times 10^{-4} M$ ) were prepared in spectrophotometric grade solvents such as ethanol, methanol, DMF, DMSO, water and analyzed in a Shimadzu UV-1700 spectrophotometer (Japan). Vanillin in ethanol of same concentration was used as standard to determine the shifting of  $\lambda_{max}$  of the polymeric solution in five different solvents.

#### 2.2.2. Fluorescence spectroscopic Method:

Fluorescence emission spectra of the complex in five different solvents having different polarity were recorded on F-2500 FL spectrophotometer (Japan) with scan speed 1500 nm/min.. All the solutions were prepared in spectrophotometric grade solvents. The solution concentration of the polymeric complex in ethanol, methanol, DMF, DMSO and water were  $5 \times 10^{-5} molL^{-1}$ . The emission intensity of each solution of the complex in different solvents was also determined from the respective spectra.

#### 2.2.3. Cyclic voltametric studies

Cyclic voltametric studies of the complex was done on a CHI-660B electrochemical analyser (USA) to examine the electrochemical property of the polymeric complex in five different solvents with different polarity (ethanol, methanol, DMF, DMSO and water). The electrochemical cell was equipped with a glassy carbon working electrode, a platinum wire auxiliary electrode and Ag/AgCl reference electrode filled with 1M NaCl solution. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte. The concentration of the polymeric complex in ethanol, methanol, DMF, DMSO and water was  $1 \times 10^{-5} molL^{-1}$ . All the measurements were done at scan rate 0.1 V/s.

#### 2.2.4. Antibacterial Activity:

The bacteria were cultured in nutrient agar medium in petri dishes and used as inoculums for the study. The components to be tested were dissolved in DMSO giving 0.5 and 1% solutions and filter paper discs of 5 mm diameter and 1 mm thickness soaked into them. These discs were placed on the previously seeded plates and incubated at  $35 \pm 2 ^\circ C$  for 24 h. The diameter (mm) of the inhibitory zone around each disc was measured after 24 h.

## 3. Results and Discussion:

### 3.1. Solvatochromism:

Solvatochromic study of the polymeric complex was performed in five different solvents (water, DMSO, DMF, methanol, and ethanol) and was compared with UV- visible spectrum of the ligand in ethanol having same solution concentration ( $1 \times 10^{-4} M$ ). The obtained spectra were given in Fig.1, which represents the shifting in wavelength ( $\lambda_{max}$ ) of the complex in ethanol with respect to the ligand (vanillin) in the same solvent. The figure also represents the shifting of the  $\lambda_{max}$  values of the polymeric complex in water, DMSO, DMF and methanol having different polarity. At room temperature, the polymeric complex in different solvents exhibits similar absorption spectra in the UV-visible region. The  $\lambda_{max}$  values of the ligand and polymer in the two different regions in the UV-visible spectra are summerised in the Table 1.

Table1: UV-visible spectral data of complex and ligand.

Compound	Solvent	$\lambda_{max}$ (nm)			
		Polymeric complex		Vanillin	
		$\pi$ - $\pi^*$	n- $\pi^*$	$\pi$ - $\pi^*$	n- $\pi^*$
Sodium vanillin Polymer	Ethanol	285	355	280	310
	Methanol	281	350	-	-
	DMF	305	366	-	-
	DMSO	306	371	-	-
	Water	292	349	-	-

The absorption at 280nm can be assigned to  $\pi$ -  $\pi^*$  transition and that at 310nm can be attributed to the n-  $\pi^*$  transition of the ligand [21]. It is observed that both the  $\pi$ -  $\pi^*$  and n-  $\pi^*$  absorption peaks for the ligand in ethanol was red shifted to the longer wavelength at 285nm and 355nm respectively for the complex in the same solvent which undoubtedly indicates the formation of polymeric complex. The effect of polarity of the solvent on the polymeric complex is also exhibited by the Fig. 1. It is found that the shifting of  $\lambda_{max}$  for n-  $\pi^*$  transition of the complex in ethanol, DMF and DMSO is more than that obtained for the complex in water and methanol. This may be due to the difference in the dielectric constant values of the solvent under study.

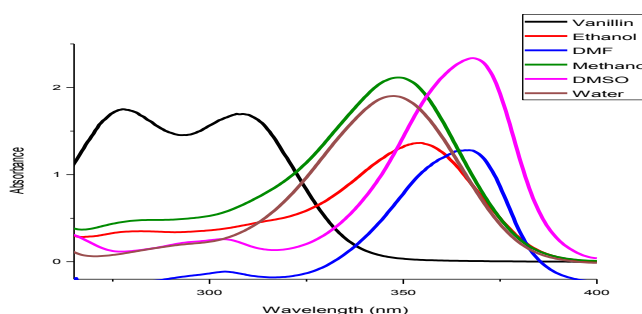


Figure 1: UV- visible spectra of the polymer complex and ligand for solvatochromatic study.

### 3.2. Fluorescence emission spectra:

The emission spectra of the polymeric complex in five different solvents with different polarities are shown in the Fig. 2. which clearly represent that the newly synthesized polymeric complex shows single peak emission spectra in five different solvents under study. Similar to the absorption UV-visible spectra recorded for the solvatochromic study of the complex, the emission spectra of the complex are also strongly dependent on the polarity of the solvent. It is observed from the figure that excepting methanol,  $\lambda_{max}$  values of the polymeric complex in ethanol, DMF, DMSO and water shifted to the longer wave length with the increase in the polarity of the solvent.

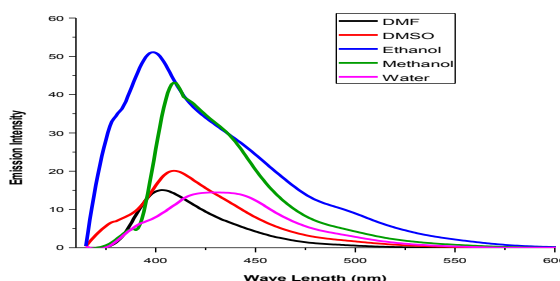


Figure 2: Fluorescence emission spectra of the polymeric complex in the different solvents

This may be due to the fact that excited state ( $S_1$ ) of the complex is polar which is better stabilized by the more polar solvent and as a result energy gap between the ground ( $S_0$ ) and excited state ( $S_1$ ) of the complex decreases with the increase in the solvent polarity. Emission frequency and  $\lambda_{max}$  values of the emission spectra are listed in

the Table 2, which reflects that emission intensity of the complex in ethanol and methanol is much more than that for the other solvents. This may be due to the lower dielectric constant of the two solvents which destabilizes the excited state ( $S_1$ ) causing more number of molecules to come down to the ground state during emission process.

Table 2: Fluorescence emission spectral data of the polymeric complex in the different solvents

Compound	Solvent	$\lambda_{max}$ (nm)		Emission Intensity
		Excitation	Emission	
Sodium vanillin polymer	Ethanol	355	398	51.87
	Methanol	385	410	40.80
	DMF	355	403	15.07
	DMSO	380	408.5	20.29
	Water	385	426.5	14.46

### 3.3. Cyclic voltametric studies:

The data obtained from the electrochemical studies are summarised in the Table 3. The electrochemical curves obtained for the newly synthesized complex in ethanol, methanol, DMF, DMSO and water are presented in the Fig.3.

Table 3: Electrochemical data of the complex in different solvents.

Compound	Solvent	Scan Rate (V/s)	$E_{pa}(V)$	$E_{pc}(V)$	$\Delta E(V)$	$E_{1/2}(V)$
Sodium Vanillin Polymer	Ethanol		+ 0.80, -0.12	+0.41, -0.45	0.29	0.15
	Methanol		+0.70	+0.43, -0.68	0.02	0.01
	DMF	0.1	+0.74	+0.36, -0.54	0.20	0.10
	DMSO		+0.87, +0.62	-	-	-
	Water		+0.58	-0.28	0.30	0.15

$$\Delta E(V) = (E_{pa} - E_{pc}) \quad E_{1/2}(V) = (E_{pa} + E_{pc})/2$$

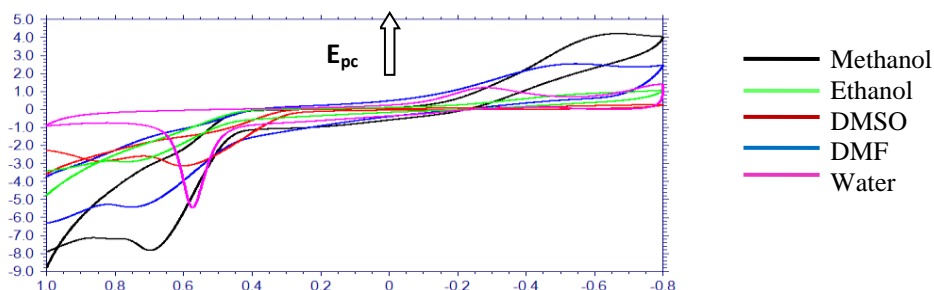


Figure 3: Cyclic voltammogram of the complex in different solvents

It is observed from the table that except DMSO where an irreversible electrochemical process was observed, in other four solvents the complex showed reversible redox processes. This may be due to the lesser stability of the complex in DMSO which made the electrochemical process irreversible. It is also noticeable from the figure that unlike in other solvents, the complex in water showed a very sharp anodic peak in the voltammogram. The facts may be explained by the adsorption of the complex on the surface of the electrode which accelerated the process of direct electron transfer between the complex and the electrode very fast in the absence of solvent.  $\Delta E$  of the complex in different solvents were calculated from their respective  $E_{pa}$  and  $E_{pc}$  values of the complex. The value indicated the highest reversibility of the complex in methanol because of the lowest calculated  $\Delta E$  value.  $E_{1/2}$  value of the complex is an indicator of its oxidizing power. More positive the  $E_{1/2}$  value more will be the oxidizing power of the complex. The calculated  $E_{1/2}$  values of the polymeric complex in different solvents showed that the oxidizing power of the complex in ethanol and water is maximum as the  $E_{1/2}$  values of the complex in those solvents are highest and equal.

### 3.4. Antibacterial activity:

The ligand vanillin and its sodium complex were tested for the in vitro growth inhibitory activity against the bacteria *E. coli* and *B. subtilis* by using the disc diffusion method. Ampicillin was used as a standard. From the results (Table 4), it was observed that the Na-Vanillin complex was more toxic than its parent ligand and the toxicity increased with increase in concentration of the solution of the test components. However, the moderate activity was observed for the test components compared to the standard ampicillin.

Table 4: Antibacterial activity of Na-vanillin complex.

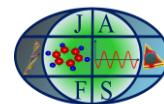
Test components	Zone of Inhibition (mm)			
	<i>E. Coli</i>		<i>B. Subtilis</i>	
	0.5%	1%	0.5%	1%
Ligand, Vanillin	6	9	5	8
Na-Vanillin complex	12	18	10	13
Ampicillin	25	25	20	20

### 4. Conclusion:

The solvatochromatic study indicates that the shifting of  $\lambda_{max}$  for  $n \rightarrow \pi^*$  transition of the complex in ethanol, DMF and DMSO is more than that obtained for the complex in water and methanol. It is observed from the luminescence study that excepting methanol,  $\lambda_{max}$  values of the polymeric complex in ethanol, DMF, DMSO and water shifted to the longer wave length with the increase in the polarity of the solvent. The electrochemical study of the complex in different solvents indicates that except DMSO where an irreversible electrochemical process was observed, in other four solvents the complex showed reversible redox processes. From the antibacterial study it can also be concluded that the polymeric complex has the potential to show moderate inhibition activity against the micro organisms *E. coli* and *B. subtilis* compared to the standard ampicillin.

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