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ISSN 2455-6378

Interactions of polyvinyl alcohol with sodium dodecyl sulphate and their characterization and electrochemical applications

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Abstract

This study looked at the hydrophilic poly (vinyl alcohol) (PVA) when it was combined with the organic surfactant sodium dodecyl sulphate (SDS). Using a magnetic stirrer, the aqueous solution was made with various surfactant and polymer concentrations. Fourier transform infrared (FTIR) was used to determine structural characteristics. It shown that PVA included exclusively anionic surfactants. The optical properties in the (200-800 nm) wavelength band were measured at room temperature. The optical band gap (Eg) for the allowed transition increases as surfactant concentration rises. The absorption band in the UVvisible spectrum was found to be at 272 nm. The solubility of the polymer, as seen in the UV-vis spectra, caused the absorbance of PVA/SDS to increase at a lower concentration. Due to the interaction between PVA and SDS at the interface, AFM investigations demonstrated that the anionic surfactant was present and homogenously mixed with PVA. This suggests that PVA and SDS are compatible with one another. Cyclic voltammetry was used to investigate electrochemical behaviour and corrosion resistance.

Keywords: Polymers, Surfactants, solubility, interaction, electrochemical studies

1. Introduction

Material corrosion has remained a topic of attention in the technological world. In the field of corrosion inhibition, scientists are tenacious in their search for better and more practical methods to prevent metal corrosion. The addition of corrosion inhibitors to the corrosive environment has been utilized as an alternative to traditional corrosion inhibition techniques. [1] The pace of metal corrosion has been slowed down by the use of several approaches. One of the most useful strategies for preventing corrosion in acidic conditions is the use of inhibitors. There are three different types of inhibitors that prevent corrosion on metallic materials: surfactant inhibitors [2], organic inhibitors [3], and inorganic inhibitors [4]. Heterocyclic inhibitors have a number of benefits, including strong inhibitory effectiveness [5-8], low cost, and simplicity in manufacture. Based on their mode of action and ability to donate electrons, effective inhibitors are chosen.Additionally, the presence of heterocyclic rings containing Sulphur, phosphorus, and/or nitrogen atoms oxvgen. strengthens the inhibitory ability of adsorption active sites with lone pair and or orbitals [9-11]. Physisorption is a result of electrostatic interaction between the charged hydrophilic groups and the charged active centers on the metal surface. By pushing water molecules away from the metal surface and generating a dense barrier film, several authors demonstrated that the majority of inhibitors were adsorbed there [12].

A synthetic polymer with outstanding film-forming, emulsifying, and adhesive capabilities is polyvinyl alcohol, which is water soluble. This versatile polymer provides exceptional resistance to solvents, grease, and oil in addition to having excellent tensile strength, flexibility, and oxygen barrier. The characteristics of polyvinyl alcohol define many of the appropriate applications for it. Most commonly, aqueous solutions are utilized with polyvinyl alcohol. Its degree of hydrolysis and degree of polymerization both influences how soluble it is in water, with the latter element having a particularly large impact [13– 18]. The interaction between a polymer and surfactant has undergone substantial research because to its numerous industrial applications. The

ISSN 2455-6378

fundamental ideas governing interactions between polymers and surfactants are presented.[19] Due to the complexity of the behavior of surfactant-polymer systems in aqueous solutions, there are still many debates and doubts regarding these systems' behavior. The chemical makeup of the two substances and the net charges on either one or both of their molecules determine how well surfactant and polymer interact with one another. [20-22] explored how the functional group and chain length of the surfactant affect interactions between polymers and surfactants. When compared to other types of polymers, anionic surfactants are observed to interact with nonionic polymers more strongly [23, 24].

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Due to its relative affordability, accessibility, abundance of volatile functional groups, hydrophilic characteristics, superior charge storage capacity, and high dielectric strength, PVA is of tremendous importance. These features, particularly their optical properties like the energy gap and refractive index, improve their industrial and technological uses as surfactants, adhesives, drug delivery, coating material, a supercapacitor component, a solar cell component, optical sensors, and nonlinear optical devices [25-26]. One of the most widely used anionic surfactants, sodium dodecyl sulphate (SDS), is produced in excess of 3.8 million tons annually for applications in the fields of cosmetics, apparel, food, fuel, and medicine. The benefits of completing this determination utilizing the micellar characteristics of various surfactants, such as sodium dodecyl sulphate, or SDS, on an electrode made of glassy carbon have been investigated by Wen et al. [27]. This is due to the surfactant's adsorption on the electrode and the solubilization of electroactive substances on micellar aggregates, both of which may cause changes in the redox potential, the energy transfer coefficients, and the diffusion coefficients of the species present close to the electrode, as was observed by Wen et al. for ascorbic acid and its lipophilic derivatives in the presence of CTAB and SDS micelles.

This work focuses on solubility and other Spectroscopic features of sodium dodecyl sulphate solutions in poly vinyl alcohol at different concentration. Studies on the optical characteristics of polymers have many applications in electronic and optical devices such as solid-state batteries, fuel cells, solar cells, and other favorable medical technology. PVA is an ideal polymer for the microelectronic sector due to its high dielectric strength (strong insulating material), good charge storage capacity, low electrical conductivity, and high flexibility. In order to understand the nature of charge transport in these materials, electrical conduction in polymers has been the subject of substantial research in current years..

2. Materials and Methods

Polyvinyl alcohol (PVA) and sodium dodecyl sulphate (SDS) are the compounds employed in the current experiments. Without further refining, the materials used in this investigation were of analytical quality. Double distilled water was used as a solvent for the entire experiment. The entire inventory of chemicals used in this study was obtained from Sigma Aldrich Chemicals Ltd.

A magnetic stirrer was used to produce the fresh aqueous solutions with varying surfactant and polymer concentrations for a period of 8 to 10 hours, forming a continuous, homogenous solution at a low rotation per minute to prevent mechanical deterioration. In the distilled water, a proper quantity of a anionic surfactant and the polymer solution was properly dissolved for 15 minutes. For this investigation, a wide range of concentrations (0.1–0.7 wt%) that approximate the SDS were used. The polymer was employed in concentrations of 100 ppm, 500 ppm, 1000 ppm, and 1500 ppm. These chemical substances were selected to correspond to those used in industrial settings. [28-33]

FTIR spectrometer(Shimadzu's IR Affinity) was used to analyze the PVA with SDS FTIR spectroscopy in the transmittance mode and in the wavenumber range 400-4000cm⁻¹. PVA/SDS solution's ultraviolet visible (UV-vis) absorption spectrum was determined in the 200–800 nm range using a computer-controlled Jasco V-530 UV–Vis Spectrophotometer. With the Nanosurf Easy2scan BT02218 profiler, atomic force microscopy was completed. A sharp cantilever tip interacts with the sample surface to sense the local forces between the molecules and the tip. CH-instrument Inc., TX, USA, investigated the electrochemical behavior.

3. Results and Discussion

3.1. UV-vis spectroscopy

The absorbance, transmittance, and reflectance of polymeric materials are crucially revealed by UV-vis spectroscopy, making it an intriguing analytical research approach. The evaluation of the optical properties of PVA with SDS and the recording of the spectrum data were performed using a Jasco UV-Visible Spectrometer. The optical properties of PVA with SDS were evaluated and the spectral data were recorded using a Jasco UV-Visible Spectrometer [34]. Because it has exceptional optical properties, including outstanding transparency and sensing capabilities, PVA is also a major watersolublepolymer. The UV absorbance spectra of PVA, SDS, and PVA/SDS dispersion are depicted in Figures 1-5. SDS was linked to strong energy absorption and had a characteristic absorbance band at 272 nm. Electronic transitions π - π^* (K-band) are attributed to these absorbance bands.[35, 36].

International Journal of Advanced Scientific Research and Management, Special Issue 4, ICAMA-18, Apr 2019

<u>www.ijasrm.com</u>

ISSN 2455-6378

UV–Vis absorption spectra were noted in the wavelength range of 200–800nm. In the presence of anionic surfactants SDS the absorbance maxima conforming to the π – π * band is blue-shifted by 272 nm along with the Concomitant increase in absorbance. The increase in absorbance with the addition of surfactant is possibly due to the improved solubility of the polymer in the micelle. Figure 1 represents UV–visible absorption spectra of PVA with SDS, absorption maximum (λ_{max}) of PVA was found to be 364 nm [37].

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Fig.2 UV –Vis Spectra of PVA 100 ppm with SDS (a) 0.1 wt% SDS (b) 0.3 wt % SDS (c) 0.5 wt % SDS (d) 0.7 wt %SDS







Fig.4 UV –Vis Spectra of PVA 1000 ppm with SDS (a) 0.1 wt% SDS (b) 0.3 wt % SDS (c) 0.5 wt % SDS (d) 0.7 wt % SDS



Fig. 5 UV –Vis Spectra of PVA 1500 ppm with SDS (a) 0.1 wt% SDS (b) 0.3 wt % SDS (c) 0.5 wt % SDS (d) 0.7 wt % SDS

3.1.1. Band gap energy

The optical band gap energy of Polymer-surfactant at different concentrations has been determined using the equation Eg=hC/max. Band gap energies for PVA, SDS, and PVA with SDS at various concentrations are 4.1 eV, 5.0 eV, and 4.2 eV, 4.3 eV, 4.4 eV, and 4.5 eV, respectively. The optical band gap energy was determined using the tauc relation and is shown in table 1.

Table 1. I	Band gap	energy	values	of	PVA	with	differe	nt
	co	oncentra	ation of	SI	DS			

Sl. No	Samples	Band
		gap(eV)
1	PVA	5.0
2	SDS	4.1
3	PVA+0.1%SDS	4.2
4	PVA+0.3%SDS	4.3
5	PVA+0.5%SDS	4.4
6	PVA+0.7%SDS	4.5





Fig 6. Band gap value of PVA 1000 ppm with SDS (a) SDS b) PVA c) 0.1 wt% SDS +PVA d)0.3 wt % SDS+PVA(e) 0.5 wt % SDS+PVA (f) 0.7 wt %SDS+PVA

3.2. FTIR Analysis

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The main peaks of PVA (Fig.7) were noticed at 3280cm⁻¹, 2917cm⁻¹, 1690cm⁻¹, 1425cm⁻¹, 1324cm⁻¹, 1081cm⁻¹, and 839cm⁻¹. These peaks are assigned to the O-H stretching vibration of the hydroxyl group, CH₂asymmetric stretching vibration, C=O carbonyl stretch, C-H bending vibration of CH2,C-H deformation vibration, C-O stretching of acetyl groups and C-C stretching vibration [38-41]. The surfactant SDS exhibits four distinct bands (in the range of 900-1600 cm⁻¹) in which 993, 1219, and 1278 cm⁻¹ are related with the vibrational modes of sulphate group and 1472 cm⁻¹ corresponds to the scissoring of methylene group.[42]. When increasing the concentration of SDS, the peak reduced (c=o)and a peak 2917 disappear(fig.8) when increasing the These results indicate that the concentration. interaction of polymer with surfactant.

3.3 AFM

AFM is a highly effective analytical research technique for characterizing heterogeneous systems. AFM images were also used for roughness, porosity and fractal dimension [43]. Atomic force microscopy (AFM) tapping mode was used to further study the surface morphology of PVA with SDS.AFM topographical images of PVA with SDS were observed using the instrument "Nanosurf easy 2 Scan". The results are displayed in Figures 9-10. It can be seen that different concentrations of SDS with PVA. It has a significant effect on thesurface topography of the samples. Due to the strong interfacial adhesion and good compatibility between PVA and SDS, the surface of the polymer with surfactant clearly showed that the surface was coarse at higher concentrations.

From the 3-D image, at a lower concentration a folded mountain structure was observed. It may be due to the PVA with SDS binding. Measurements were achieved with PVA-SDS samples were scanned to ensure that the morphology of the examined materials is the representative one.



Fig 7. FTIR spectra of a) PVA b) SDS



Fig.8 FTIR spectra of (a) 500 ppm PVA (b) 0.1wt%SDS+500 ppm PVA, (c) 0.3 wt% SDS+500 ppm PVA(d) 0.5 wt% SDS+500 ppm PVA (e) 0.7 wt% SDS+500 ppm PVA



Fig. 9 AFM topographic images of PVA and SDS 3.4. Cyclicvoltammetric Studies

Cyclic voltametric behavior of PVA with surfactant at different concentration. Fig.11 displays voltammogram recorded at different concentration. Samples were coated on glassy carbon electrode

ISSN 2455-6378

(GCE), AgCl/AgCl and platinum wire electrode were used as working electrode, reference electrode and counter electrode respectively. An increase in peak separation with increase in scan rate proves the quasi-reversibility of the electron transfer process. Current value increases when increase in scan rate. Cyclic Voltammograms of PVA with surfactant were recorded in the potential range from -1 to 1.2 at 100mV/s.

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The polymer surfactant was recorded in the potential range from -1 to 1.0 at 100mV/s. Fig. 11 shows two peaks are visible in anodic and cathodic side, which are due to redox reactions.CV curves are gradually enlarged with increasing concentration of surfactant. The synthesis of polymer with surfactant is confirmed by its good reversible redox activity.



Fig. 10 AFM topographic images of PVA 1500 ppm with SDS (a) 0.1 wt% SDS (b) 0.3 wt % SDS (c) 0.5 wt % SDS (d) 0.7 wt % SDS



Fig. 11 Cyclic voltammetric behavior of a) Bare b) 0.1 %SDS with PVA c) 0.3 %SDS with PVA d) 0.5% SDS with PVA e) 0.7 %SDS with PVA

3.4.1Electrochemical impedance measurements

Electrochemical impedance spectroscopy is used to determine the Equivalent circuit parameters such as charge transfer resistance and ohmic resistance. EIS is a two -part Nyquist curve; that is a semicircle in the high frequency region and a straight line in the low frequency region [44]. Internal charge transfer resistance is represented by the semicircle in the high frequency region (Rs). The larger the diameter of the semicircle improved the charge transfer resistance. Fig. 12 is an EIS diagram in the high frequency region, and it can be seen that the PVA with SDS the appearance of a semi-circular arc indicates that there is a certain charge transfer resistance. This figure indicates that the highest resistance in terms of coating strength was demonstrated because of higher impedance, it was more protected. It also illustrates that the impedance curve of PVA with 0.5% SDS exhibits a very high resistance and higher capacitance property. Polymersurfactant has capacitance and has shown substantial potential in charge-discharge behavior. Polymeric coating showed a higher coating capacitance represented by lower impedance because of the two properties are inversely proportional. It would be observed that polymeric coating with higher capacitance can store higher charge [45].

Fig.12 shows the EIS curves of PVA, SDS, PVA with SDS. Generally, if the semicircle of EIS curves has larger diameter, it refers to slower rate of corrosion, we can take from the diameter of the curves forming semicircle as the indicate of the anticorrosive performance [45]. From Fig. 12, it can be seen that EIS curves of all samples show similar semicircles. However, the diameter of EIS curves of PVA with 0.5% SDS is the largest than the diameter of EIS curves of PVA, which indicates the anticorrosive performance of PVA with 0.5% SDS is best. Thus, it can be seen that the PVA with 0.5% SDS can form not only a great barrier but also the protection of anode and the passivation of the metal surface [46-48].



Figure12 EIS diagram of a) PVA b) SDS c) 0.1%SDS with PVA d) 0.3%SDS with PVA e) 0.5% SDS with PVA f) 0.7% SDS with PVA

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3.4.2 Tafel Polarization Studies

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The Tafel Polarization behavior of PVA with SDS in 0.1 M H₂SO₄ are studied. The corrosion of bare, PVA, SDS and PVA with SDS modified electrodes were studied by potentiodynamic polarization curves which shown in figs. 13 and 14. The electrochemical parameters (I corr and Ecorr) associated with polarization measurements are listed in Table 2, where I_{corr} and E corr are the corrosion current density and the corrosion potentials, it is observed that, in addition of SDS, cathodic curves show increase current density. With the increase in SDS concentration increases the current value. This behavior indicates that SDS introduced into the PVA effects on both cathodic and anodic reactions of corrosion process, since the corrosion rate is directly related to the corrosion current density (I_{corr}). The corrosion rate is higher for 0.5%SDS with PVA when compared to bare solution.

It can be seen that the Polyvinyl-Alcohol with increase in concentration of surfactant gives a left side shift to a cathodic inhibition (protection) until the addition of 0.1-0.5% concentration, then right side shift to anodic side when increasing the concentration of 0.7%. 0.5% addition indicating that the Polyvinyl-Alcohol-surfactant acts as incubator. However, the inhibitor addition does not change the hydrogen evolution reaction mechanism such as indicated by the slight changes in the cathodic side. This indicates that hydrogen evolution is activation controlled [49, 50]. Tafel curves fig (14) shows that the protective action of the SDS promotes a change of the corrosion potential to more positive values for PVA. Further it inferred that PVA with SDS improve the corrosion resistance property. It makes the coating more corrosion resistance at lower concentration.

Table 2. The polarization data from different concentration of PVA with SDS at different concentration

Samples	E _{corr} (V)	βc (1/V)	Ba (1/V/)	I _{corr} (A)	Rate (mil/year)			
0.1%SDS with PVA	-0.1603	6.269	4.621	2.018	33.08			
0.3%SDS with PVA	-0.1653	6.403	4.679	1.625	0.2663			
0.5%SDS with PVA	-0.1854	6.137	4.350	4.331	0.7100 F			
0.7%SDS with PVA	-0.2846	15.985	10.207	3.351	0.5493 0			
PVA	-0.0535	7.582	4.560	1.901	0.3117 A			
Bare	-0.6202	4.899	2.139	317.1	519.7]			

4. Conclusions

In this present work, there are few findings can be deduced after completely performing the characterization tests. polyvinyl alcohol with different concentrations of SDS was prepared and characterized to show the effect of their structural, optical, and electrical properties. The FTIR results suggested a strong interaction between PVA and

SDS. PVA/SDS dispersion shows good optical properties observed by UV-Vis Spectroscopy. Microscopic studies reveal that SDS was homogeneously mixed with PVA due to interfacial interaction. This indicates that PVA and SDS have a good compatibility with each other. PVA with SDS showed relatively higher impedance indicating greater protection. It also illustrates that the impedance curve of PVA with SDS surfactant exhibits very high resistance and greater capacitance EIS confirms PVA with 0.5%SDS property. concentrations is used as high resistance due to its anticorrosive activity. Concluding the experimental part, it was clearly demonstrated that all techniques used, are able to characterize and to follow the promoted corrosion inhibition process the concentration of surfactant with polymer. Polyvinyl-Alcohol with SDS exhibited good inhibiting properties in 1 M H₂SO₄solution and increased with increasing the concentration of inhibitor.



g.14 Polarization curves for PVA with SDS a) bare b) 0.1%SDS ith PVA c) 0.3%SDS with PVA d) 0.5 %SDS with PVA d) 7%SDS with PVA

Potential / V

cknowledgments

The authors are grateful to the Department of Science and Technology (FAST TRACK and FIST) in New Delhi, India for using the CHI Electro Chemical workstation and Jasco UV-VISIBLE Spectrophotometer at V.O. Chidambaram College, Thoothukudi-8.

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ISSN 2455-6378

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