

ABSTRACT

The current dissertation entitled "Interaction and Micellization Behavior of Surfactants with Polyelectrolytes in the Presence of Dyes in Aqueous and Binary Solvent Media" is divided into ten chapters. Chapter I describes the surfactant, dye, and polyelectrolyte and their types, micellization, and phase behavior of surfactants, the shape of micelle, critical micelle concentration (CMC), and factors influencing CMC. This chapter also describes the scope and significance of various physicochemical parameters applicable for dye solubilization, and surfactant-polyelectrolyte-dye interactions. This chapter explains the application and objective of the present research work.

Chapter II describes the pertinent literature review of the interaction between different dye-surfactants, dye-polyelectrolytes, and surfactant-polyelectrolytes in various temperatures and solvent compositions. Various techniques like surface tension, UV-visible spectroscopy, and conductivity techniques that allow for the detailed determination of CMC, CAC, binding constant, stability of the complex, binding parameters, surface parameters, and many other physicochemical and thermodynamic properties have been thoroughly reviewed.

Chapter III contains details of the chemicals and instrumentation applied in the current research work. The structure and properties of the various chemicals used in the research work have been described in this chapter. This chapter also provides the details of the process of solvent preparation, solution preparation, and data observed using various techniques like surface tension, UV-visible spectroscopy, and conductivity measurements.

Chapter IV describes the interaction and micellization behavior of CTAB in NaPSS with and without MR in an EtOH-water mixture solvent at varying temperatures. From the conductivity data, various parameters like CAC, α , CMC*, ΔG_b^0 , ΔH_m^0 , ΔG_m^0 , ΔG_{mb}^0 , ΔG_{trans}^0 , and other thermodynamic parameters were anticipated to provide essential information on the interactions taking place in these systems at the molecular levels. Variations of these obtained properties were analyzed and discussed in terms of the varying solvent composition of EtOH-water and temperature. The values of CAC, α , and CMC*, rise as the temperature and ethanol content in volume increase.

Whenever a system is studied at a fixed temperature, its free energy and enthalpy of micellization are both negative. This indicates that as the mixture's ethanol concentration increased, ΔG_m^0 got less negative, signifying that micellization was less spontaneous at higher ethanol contents. Important details about the solvent's structure, polarity, micellization, fluidity, and the degree of interaction between the CTAB and NaPSS in EtOH-water media in the presence and absence of MR were discussed by examining the variation in the ΔG_m^0 with various solvent/solvophobic parameters.

Chapter V explains the interaction and micellization behavior of DTAB in NaCMC with and without MO in EtOH-water mixture solvent at varying temperatures. Based on the acquired data, the α , CAC, and CMC* values calculated from conductivity increased with increasing temperature and volume fraction of ethanol, and also these values dropped for the MO-NaCMC-DTAB system in comparison to the NaCMC-DTAB. Thermodynamic parameters like ΔS_m^0 , ΔH_m^0 , ΔG_{mb}^0 , ΔG_b^0 , and ΔG_m^0 were also evaluated. In comparison to the NaCMC-DTAB system, the MO-NaCMC-DTAB system exhibits more positive ΔS_m^0 values and more negative ΔH_m^0 , ΔG_{mb}^0 , ΔG_b^0 , and ΔG_m^0 values. These findings demonstrate the thermodynamic feasibility and spontaneity tendency of micellization with MO in EtOH-water solvent environments. Whenever a system is studied at a fixed temperature, its free energy and enthalpy of micellization are negative. This indicates that as the mixture's ethanol concentration increased, ΔG_m^0 got less negative, indicating that micellization was less spontaneous at greater ethanol contents.

Chapter VI describes the interaction, spectral, and binding behavior of MR with CTAB in NaPSS in an EtOH-water mixture solvent at room temperature. From the spectroscopic findings, the CMC* value in the mixed solvent increases with increasing volume fraction of ethanol in water. The thermodynamic and spectral parameters like ΔG_m^0 , K_b , and ΔG_b^0 were also obtained at room temperature. The Gibbs micellization energy (ΔG_m^0) has a less negative value $(\Delta G_m^0)_{0.3} > (\Delta G_m^0)_{0.2} > (\Delta G_m^0)_{0.1} > (\Delta G_m^0)_{\text{water}}$ with increasing ethanol content in the solvent mixture, adds more evidence to the idea that raising the ethanol concentration inhibits micellization. The value of K_b varies in the trend: $(K_b)_{\text{water}} < (K_b)_{0.1} < (K_b)_{0.2} < (K_b)_{0.3}$, and ΔG_b^0 drops in the order: $(\Delta G_b^0)_{\text{water}} > (\Delta G_b^0)_{0.1} > (\Delta G_b^0)_{0.2} > (\Delta G_b^0)_{0.3}$. An increased interaction among MR, CTAB, and NaPSS in the after-micellar area is shown by a larger binding constant (K_b) value. This is validated by the feasibility of the processes, as indicated by a drop in the Gibbs

binding energy (ΔG_b^0). The blue spectral shifts indicate that the interaction mechanism was primarily influenced by the solvent composition.

Chapter VII describes the interaction, spectral, and binding activities of MR with CTAB in NaPSS in an EtOH-water mixture solvent at room temperature. The findings show that in the solvent mixture under investigation (water, 0.10, 0.20, and 0.30 V.F. of EtOH-water), the CMC* values derived from spectroscopic data increase with rising volume fraction of ethanol in water as $(\text{CMC}^*)_{\text{water}} > (\text{CMC}^*)_{0.2} > (\text{CMC}^*)_{0.1} > (\text{CMC}^*)_{0.3}$. The Gibbs micellization energy (ΔG_m^0) has a less negative value with increasing ethanol content in the solvent mixture, which adds more evidence to the idea that raising the ethanol concentration inhibits micellization. On the other hand, the overall binding constant value increases with increasing volume fraction of ethanol in water and ΔG_b^0 drops in the order: $(\Delta G_b^0)_{\text{water}} > (\Delta G_b^0)_{0.1} > (\Delta G_b^0)_{0.2} > (\Delta G_b^0)_{0.3}$. An increased MO-DTAB-NaCMC interaction in the after-micellar region is shown by a larger binding constant (K_b) value. This is validated by the spontaneous nature of the processes, as indicated by a drop in the Gibbs binding energy (ΔG_b^0). The blue spectral shifts indicate that the interaction mechanism was primarily influenced by the solvent composition.

Chapter VIII describes the surface, micellization, and thermodynamic behavior of CTAB in NaPSS with and without MR in EtOH-water mixture solvent at varying temperatures. Different surface and thermodynamic parameters like γ_{CMC} , A_{min} , Γ_{max} , Π_{CMC} , pC_{20} , P , N_{agg} , ΔG_m^0 , ΔG_{ads}^0 , ΔG_{eff}^0 , ΔG_{min} , and many other parameters have been determined, comparatively discussed, and analyzed for CTAB/NaPSS and CTAB/NaPSS/MR cases. From the findings of this research work, it is inferred that the values of CMC*, slope ($\frac{d\gamma}{d\ln C}$), and γ_{CMC} calculated from γ versus $\ln [\text{CTAB}]$ for the CTAB/NaPSS/MR case reduced in contrast to the CTAB/NaPSS in the mixture solvent media and the range temperature studied. γ_{CMC} values fall.

Finally, Chapter IX Contains concluding remarks embodied in different chapters (chapters IV to IX) of the current research work.

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