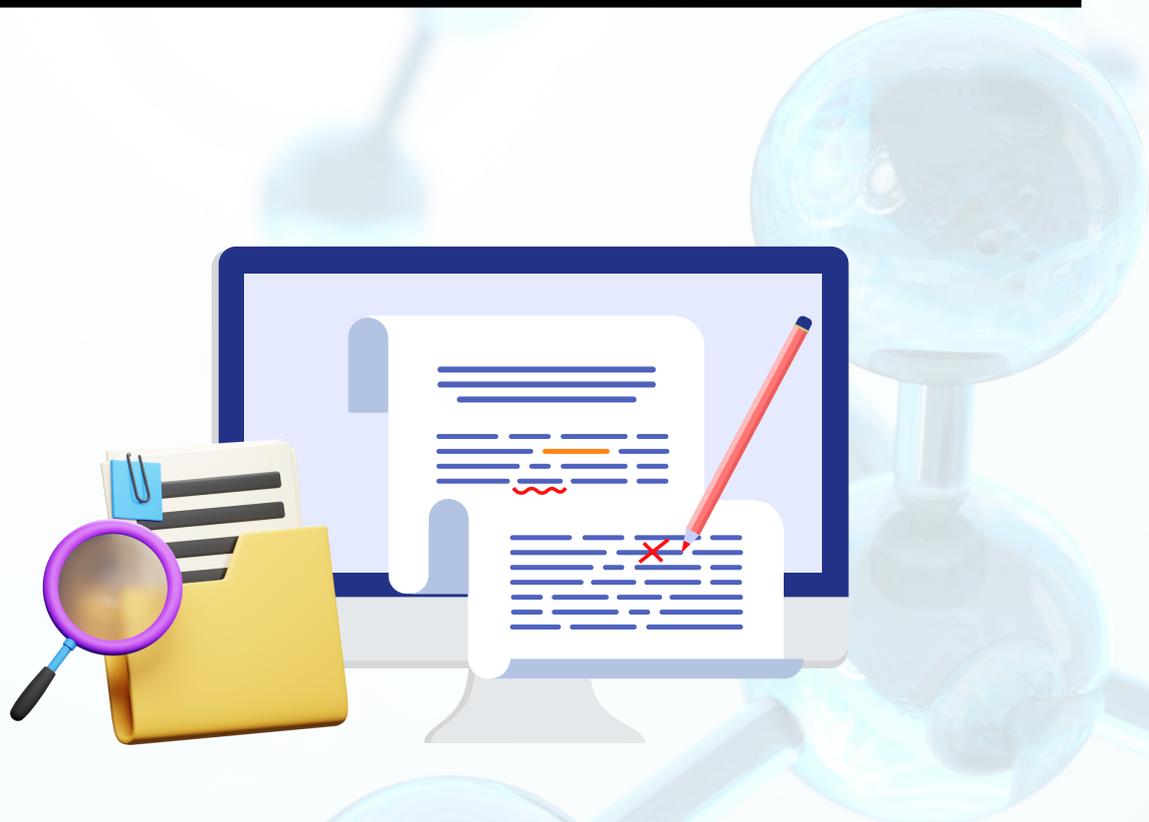

Abstract

ASSOCIATION OF AMPHIPHILIC MOLECULES IN VARIOUS SOLVENT SYSTEMS



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Surfactants are compounds having both parts, hydrophobic and hydrophilic, in the same molecule. Due to this characteristic of surfactant, these molecules associate/accumulate in/at the solution/interface. The charge types (ionic or non-ionic) of the surfactant molecules are decided by the ionic or non-ionic nature of the hydrophilic part of the surfactant molecule. For the above association, various solvent media are utilized such as aqueous solvents, polar nonaqueous solvents, organic solvents, or a mixture of two of the above classes. In recent times, a greener solvent has been introduced which is an analog of ionic liquids (ILs) known as deep eutectic solvents (DESs). DESs have emerged as solvents of the 21st century. DESs are a compositionally diverse range of low-transition-temperature mixtures obtained by mixing hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) in the eutectic molar ratios. The molecular basis of the lowering of melting point originates from various interactions between the constituents. DESs can be divided into five categories (type I-V) depended upon their constituents.

Type III (contains choline chloride (ChCl, HBA) and various HBDs such as urea (reline), glycerol (glyceline), ethylene glycol (ethaline), water (aquoline) or some of their mixtures), and type V (constituted by any mixture of thymol/menthol/camphor) have been synthesized and characterized by FTIR and ^1H NMR. Physical properties (zero shear viscosity, relative viscosity, surface tension, contact angle, pH, specific conductance, density, molar volume, Gordon parameter, micro polarity, apparent dielectric constant) of synthesized DES are measured/computed. Rheological measurements show that all the synthesized DESs are Newtonian in nature like water. Further, density, surface tension, contact angle, pH, conductance, etc. properties show similarity (not in the true value sense) with the characteristics of water. It has also been found that properties can be tuned by either the addition of water or by replacing HBDs in a typical DES.

Solvophobic interactions between surfactant nonpolar groups and DESs together with their H-bonding network are shown to play a decisive role in surfactant aggregation. The association behaviour of various ionic surfactants in different type-III DESs has been studied by spectrofluorometry. Critical micelle concentration (CMC) data were computed using sigmoidal fitting of the fluorescence data. Fluorescence data were also used to compute micelle aggregation number (N_{agg}), micropolarity, and Stern-Volmer binding constant (K_{sv}). In some cases, micellization studies were performed in exclusively water-based DESs (aquoline(s)). In conventional DES (e.g., reline) micellization was observed with only an anionic surfactant namely sodium dodecyl sulphate (SDS). Contrary to this, cationic surfactants show association

behaviour with HBDs such as hydroxy compounds (e.g., glycerol or ethylene glycol). However, aquolines have been found as association media for both anionic and cationic surfactants. To enlarge the spectrum of the study, the effect of salt addition on micellization behaviour in different above-mentioned DESs (whenever possible). The morphology in the surfactant-DES system (with potassium and sodium salt) has been established using polarizing optical microscopy (POM). Salt addition in an aqueous surfactant solution is a successful tool for tuning micellization and micellar morphologies.

In aqueous non-ionic surfactant systems, liquid-liquid phase separation (LLPS) is observed on heating the solution beyond the cloud point (CP). CP is the temperature at which the surfactant solution gets cloudy. However, ionic surfactant solutions are not known to show clouding (or LLPS) in aqueous solution due to the presence of charged micelles. A few ionic surfactant-based systems (with tetra butyl ammonium bromide (TBAB)) have been designed to study clouding phenomena in reline or reline-water mixture (up to eutectic limit). CP data have been compared with pure aqueous medium. It has been noted that CP was more in a reline-water mixture than in pure water. The composition of SDS + TBAB mixture was changed to see the influence on CP data. CP has been found to vary with [SDS] and [TBAB]. Urea as HBD has been partly replaced by other HBDs such as glycerol with different compositions. The above changes have also influenced CP in reline-water mixture. Clouding observed in various DESs (+ water) mixtures may be due to interactions (electrostatic and hydrophobic) between SDS and TBAB.

Above pure and mixed DES systems were used to study their solvent property towards a nearly water-insoluble natural drug i.e., curcumin (CCM). The CCM solubility experiments were performed using spectrophotometry. Solubility data were obtained both in pure DESs (reline, aquolines, or glyceline) and with surfactant + DESs systems, and enhanced CCM solubilities were observed in DESs as well as in surfactant + DESs systems in comparison to pure water. Further, fluorescence spectroscopy was used to study the fluorescence behaviour of CCM in various DESs with and without surfactants. Looking at the green and sustainable nature of DESs, such studies may find potential applications in the pharmacy field as solvent medium. This work may open new avenues for obtaining controllable self-assembly and solvent media for water-insoluble drugs, dyes, and insecticides/pesticides.