Study of the Synergetic Behavior of Surface Active Ionic liquid (SAIL), N-alkyl-N-Carboxyethyl Imidazolium Inner Salts (ACIIS) and Sodium Dodecyl Sulfate (SDDS) in Aqueous Solution

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Abstract

Surface tension and surface pressure were determined and analyzed arising with the interactions of sodium dodecyl sulfate with the ionic liquid having mixed zwitterionic character, (N-C$_{13}$, N'-CO$_2$-Im) (N-alkyl- N'-carboxyethyl imidazolium inner salt), mixing in different molar ratios. It was found that the mixed system possessed relatively reduced CMC values and enhanced surface activity as compared to the individual components indicating the synergistic interactions. NaCl was added to the system which indicated the formation of the cylindrical micelles (CM). The CMs were found to have the stronger network as compared to conventional C$_{13}$ betaine/anionic surfactant mixture (e.g laurylamidopropyl betain/SDDS) and therefore expected to be used in various applications such as synthesis of nano materials, products for personal care and surface and in tertial oil recovery.

Key words: Sodium dodecyl sulfate, CMC, viscosity, surface tension, micelles, surface active ionic liquids.

Introduction

The surface activity of surfactants is due to the structural features of their molecules. The solubility and relative size of polar and non polar part in relation to overall molecular structure determine the surface activity of such substances. CMC is probably the simplest method of characterizing the micellar behaviour of surface active agents (solutes). When surfactant is dissolved in solvent, its hydrophobic part causes distortion of solvent fluid thus increasing the free energy of the system. Surfactants therefore concentrate at the interface while hydrophilic group (carrying a negative or positive charge) opposes this process. The aggregation number for nonionic surfactants is usually large in comparison to other category with about hundreds or thousands molecules constituting a micelle. The hydrophobic part of the aggregate forms the core of micelle while polar head group remains in contact with water. These general tendencies lead these substances surface active i.e. their molecules absorb at air-water or oil-water interfaces and to surfaces of non polar solids or to molecules such as proteins. Hydrophobic interactions are primarily responsible for this phenomenon. The shape of micelle changes with surfactant concentration. Increasing concentration of surfactant changes the spherical micelles to cylindrical micelles or lamellar micelles or enesomorphic structures.

Above all CMC parameters vary according to whether the solute is monomer or aggregation. Since above the CMC, the activity of monomers rises very slowly, so it is also a measure of the concentration at which the thermodynamic activity of the monomers and therefore, its net surface activity and absorbability to various substrates, level off to a nearly constant value.

Like CMC necessary to form micelle, critical temperature is also necessary over which micellar solutions of surfactants can be formed (1,2). In other words, the characteristic solubility behaviour of surfactants is usually observed in aqueous solutions. Very low values of solubility at low temperature show abrupt rise at certain temperature, known as Krafft point (3). The solubility of surfactant at Krafft point is its CMC value at this temperature. For practical purpose, the use of a surfactant is limited to temperature only above the Krafft point. The increase in solubility at high temperature (above Krafft point) is due to the presence of individual surfactant molecules as aggregates i.e. micelles (4). Formation of micelles above Krafft point can be regarded as liquid phase. At the Krafft point, hydrocarbon chain of surfactants passes as they were into liquid state. Adderson and Taylor (5) observed that the CMC of cationic surfactants in water decreases with increase in chain length of alkyl groups and also observed that three factors contribute to the enthalpy changes of micellization, namely those associated with head group aggregation, those with breakdown of hydrocarbon stabilized water structure and changes due to the transfer of the hydrocarbon to micelles. Surface mixed films of cationic surfactants at aqueous solution/air interface has been studied by Paluch and Korchowiec (6).

Mixed surfactants are generally chosen in pharmaceutical and medicinal formulations because of their usefulness in preparing suspensions, dispersions and colloidal solutions (7-10). These surfactant mixtures have superior interfacial properties in comparison to single surfactant such as enhanced surface activity and lower critical micelle concentration (CMC) which is known as the synergistic effect. A number of different combinations of mixed surfactant systems have been studied, including anionic/nonionic (11), nonionic/nonionic (12) cationic/nonionic (13-15), cationic/cationic (16) and surfactant systems. It is well-known that mixtures of anionic and zwitterionic surfactants show significant synergism in aqueous solution (17). Thus, they can self-assemble to form various supra molecular structures above the CMC in aqueous solution, such as spherical micelle, wormlike micelle, vesicle, and laminar structure. However, the studies on the WM solution made of anionic-zwitterionic surfactants are still lacking. Ionic liquids have generated intense scientific and industrial interest due to their special physicochemical properties (18). Ionic liquids with long-chain alkyl groups, emerging as novel surfactants, are of inherent amphiphilic nature and named surface active ionic liquids (SAILs). The great advantage of SAILs is that their physicochemical properties can be designed by reasonable selection of cations, anions, and substituent.

Therefore, the self-aggregation behavior of SAILs in aqueous solution has attracted a considerable amount of attention. A detailed study of the synergetic behavior of zwitterionic SAILs, (N-C_{13}, N'-CO_2-Im) (N-alkyl- N'-carboxyethyl imidazolium inner salt), and anionic surfactant, sodium dodecyl sulfate (SDDS), in aqueous solution is reported. Figure as give below represents their chemical structures.

Fig: -Chemical structure of   (a) N-C_{13},N'-CO_2-Im   (b) SDDS
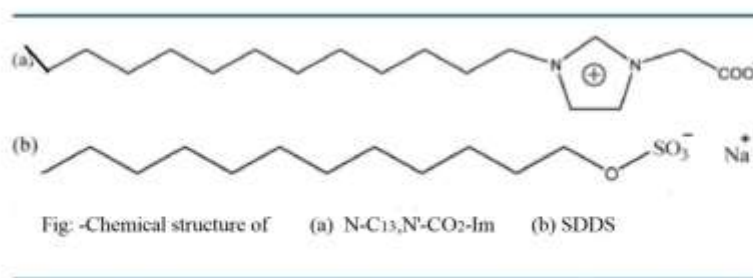
It is found that the WMs could be formed through addition of inorganic salt such as NaCl, KCl to the mixed system. The (N-C_{13}, N'-CO_2-Im)/SDDS mixture was characterized by various measurements, including surface tension, fluorescence, and rheological methods.

Materials and Methods

Materials

The zwitterionic SAILs (N-C$_{13}$, N'-CO$_2$-Im) (N-alkyl- N'-carboxyethyl imidazolium inner salt)] was purchased from ISP Experimental Reagent Co.Ltd. Sodium dodecyl sulfate SDDS (99.9%) and NaCl (AR) was achieved from Alfa. All the reagents were used without further purification. Triply distilled water was used for solution preparation.

Methods

Sample Preparation

The mixed surfactants with desired molar ratios of [N-C$_{13}$, N'-CO$_2$-Im] and SDDS)) were prepared by mixing the individual surfactant solution directly. The samples for surface tension and surface pressure measurements were prepared by diluting the mixed surfactant solution. The samples were induced to form by adding the appropriate quantity of NaCl to the mixed surfactants. After sealing, they were handled by mild heat at 40−50°C for half an hour to ensure the added NaCl solid completely dissolved. The total concentration of surfactants was kept constant. All the samples were prepared and left at the experimental temperature for at least 1 week prior to measurements to keep equilibrium.

Surface Tension Measurements

Surface tension was measured with a tensiometer using the ring method. The temperature was controlled using a thermostatic bath within ±0.1 °C. The surface tension was determined with a single measurement method. All measurements were repeated until the difference between two values was less than 0.2 mN·m^{-1}.

Result and Discussion:

Supporting Information (19) depicts the variation of surface tension (γ) as a function of the concentration for the pure and binary surfactant mixtures (N-C$_{13}$, N'-CO$_2$-Im]/SDDS) in aqueous solution at 25 °C. The break point of curves corresponds to the CMC value. The values of CMC and surface tension at CMC (γcmc) are listed in Table. It is obvious that the γcmc value of the (N-C$_{13}$, N'-CO$_2$-Im]/SDDS) mixed systems is much lower than that of a single surfactant. Surface activity expresses that a compound has the capacity to reduce the surface tension of solution. The lower cmc and γcmc values indicate that the binary surfactant mixture has superior surface activity. Evidently, for the (N-C$_{13}$, N'-CO$_2$-Im]/SDDS) mixed system, the synergistic effects occur easily due to the strong electrostatic attraction between the imidazolium cationic portion of (N-C$_{13}$, N'-CO$_2$-Im) and the SO$_3$ - group of SDDS. Similar behavior has been reported for some other zwitterionic/ anionic surfactant systems (17-18). The Surface Pressure (Πcmc) value decreases upon increasing the mole ratio of (N-C$_{13}$, N'-CO$_2$-Im) reaching a minimum value (24.9 mN·m^{-1}) at M.F. = 0.1. Furthermore, the mixed systems have a much lower CMC value compared with pure SDDS. Generally, the (N-C$_{13}$, N'-CO$_2$-Im]/SDDS) mixed systems exhibit better surface activity than SDDS. As is well known to all, the surfactant mixture usually forms mixed micelles in aqueous medium. The formation of mixed micelles mainly depends on two factors, i.e., the interaction between the charged head groups of individual surfactant and the hydrophobic interaction among hydrocarbon chains.

Table

Values of CMC, Surface Tension at CMC (γcmc) and Surface Pressure at CMC (Πcmc), for different molar fractions (M.F.) of the (N-C$_{13}$, N'-CO$_2$-Im) /SDDS systems in aqueous solution at 25^{0}C.

Mole fraction (M.F.)	CMC mol.litre^{-1}	Surface Tension (γcmc) Nm^{-1}	Surface Pressure (Πcmc) mNm^{-1}
0	7.62	6.55	37.1
0.1	1.52	1.18	24.9
0.3	1.02	0.639	26.1

0.5	0.742	0.514	26.9
0.7	0.598	0.412	26.8
0.9	0.642	0.512	28.4
1.0	1.27	1.01	34.6

For the binary system of (N-C_{13}, N'-CO_2-Im) and SDDS, a pseudo-double chain surfactant is formed due to the strong electrostatic interaction between the imidazolium cationic portion of (N-C_{13}, N'-CO_2-Im) and the SO_3 - group of SDDS. There also exists an enhanced hydrophobic interaction between the hydrocarbon chains, which favors the mixed micelle formation and decreases the CMC. As shown in Table, the CMC value diminishes with the increase of the M.F. value and shows a minimum at M.F. = 0.7. The initial decrease of CMC value with the increase of M.F. can be attributed to the part neutralization of charges on the SO_3 - group of SDDS, which favors the formation of micelles. However, when M.F. is larger than 0.7, the mole ratio of (N-C_{13}, N'-CO_2-Im) substantially exceeds that of SDDS, and the self-interaction of the individual surfactant gradually dominates the formation of micelle and it causes an increase of the CMC.

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