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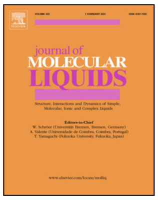

Composition triggered Aggregation/Solubilization behaviour of mixed counter charged gemini Surfactants: A Multi-technique investigations

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ABSTRACT

Aqueous association behaviour of counter charged gemini surfactants has been studied by fluorometry, dynamic light scattering (DLS), Zeta(ζ)-potential and SANS measurements at 303 K. For the purpose, P, P’-1,4-butanedieyl, P, P’-didodecylester, disodium salt, anionic surfactant(12–4-12A) and cationic gemini surfactants: Butanediyl-1,4-bis (N, N-dimethyl-N-tetradecyl-ammonium) dibromide (14–4–14); Ethane-1,2-diyl bis (N, N-dimethyl-N-tetradecyl-ammonium acetoxy) dichloride (14-Eg-14) and (D-isosorbate-1,4-diyl bis (N, N-dimethyl-N-tetradecylammonium acetoxy) dichloride (14-Isb-14) were mixed for varying mole fraction range (x = 0–1). Fluorescence data using pyrene as a probe are used to obtain CMC values which were theoretically treated using regular solution theories. It has been observed that mixing causes non spherical micelles and even vesicle formation was observed in one of the combinations (12–4-12A + 14–4–14) at x = 0.4. Various compositions are used to solubilize polycyclic aromatic hydrocarbon (pyrene, anthracene and phenanthrene) in order to have an idea of solubility enhancement efficacy. Micellar morphology/environment has been used to draw a correlation between apparent dielectric constant (D_{exp}) - composition - solubilization potential. Findings can be used for loading various hydrophobic materials in an appropriate amphiphilic mixture for various applications such as dye solubilization, drug solubilization, drug delivery or drug targeting.

1. Introduction

Organised assemblies resulted from amphiphilic molecules (surfactants, ionic liquids, polymers, drugs, biomolecules etc.,) play an important part in physical and life sciences [1]. To achieve the requirement of the application, different strategies are adopted to search an optimal system with or without (single) combination of more than one component [2–4]. Such strategies are namely architectural changes (chain length, nature of spacer, nature of charge of amphiphile/counter ion etc.),experimental conditions (temperature, pH, additives etc.,) and mixing components/composition [5–13]. Mixing of components (surfactants), in place of single surfactant seems an effect mode to regulate/boost synergistic properties of aqueous organised assemblies. Among the above procedures, mixing of surfactant components is an effective and easy way to get morphologies of desired architecture only by varying the mixing ratio [14–17]. Special effort has been directed towards the obtaining vesicles, since mixing of amphiphiles of counter charges resulted in thermodynamically stable aggregates [2,18].

Gemini surfactant (represented as m-s-m, m and s are carbon numbers in hydrocarbon chain and spacer groups) has been introduced as having potential to work as the surfactant of the 21st century [5,13,19,20]. In last decade, positively charged gemini surfactant has been continuously utilise as one of the members of the mixture, which resulted in mixed micellization and boosted solubilisation efficacies [21–23]. Recently, even mixing of block copolymers(non-ionic components) modifies association phenomenon and drug solubilisation [24]. However, the full potential of mixing gemini surfactants at the application front is yet to be fully exploited [25–28]. Gemini surfactants provide rich functionality due to the presence of spacer group which could be solvophilic or solvophobic, rigid or semi-rigid, lengthy or smaller [29]. The simultaneous presence of gemini surfactants of counter-charges has only been investigated scarcely, and data available are not sufficient to have a good database for full utilisation in the field of bio-

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Micro-Environment mapping of mole fraction inspired contrasting charged aqueous gemini micelles: A drug solubilization/release study

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ABSTRACT

Data on aggregation/morphological behaviour of contrasting charge aqueous gemini mixtures at 303 K have been acquired in this study. Anionic and cationic components of the mixture were phosphoric acid, *P*, *P*' −1,4-butanedieyl, *P*, *P*' didodecylester, disodium salt (12–4-12A) and (ethane-1,2-diyl bis (*N*, *N*-dimethyl-*N*-alkylammoniumacetoamide) dichloride) (12-Eda-12 or 14-Eda-14), respectively. Fluorescence data are used to acquire critical micelle concentration (CMC) value and micro-environmental information (micro-polarity and dielectric constant). DLS, SANS and TEM confirm the presence of ellipsoidal, rod-shaped or vesicles at different compositions of the mixture(s). Further, zeta-potential (ζ) data reveal the charge reversal on the aggregate by mole fraction (x) variation (0–1) of the mixture. Solubilization of an anti-cancer drug (raloxifene hydrochloride, RLX) has been seen in various morphologies (spectrophotometrically) and it has been found that vesicles (formed at $x = 0.4$ or 0.6) solubilize more RLX than the any other morphology. RLX release profile follows *Higuchi model* which confirms the diffusional release mechanism. RLX solubilised in 12–4-12A + 14-Eda-14 mixture ($x = 0.6$ and $x = 0.4$, respectively) showed good cell proliferation behaviour (9.06 µg/mL) over pure RLX (21.75 µg/mL) towards MCF-7.

1. Introduction:

Vesicle is the most important surfactant morphology among various structures formed in aqueous solution [1–4]. This tag may be due to the applications of vesicles in broad span of scientific fields ranging from biology to nanotechnology [5–11]. Various strategies are adopted to get surfactant vesicles in aqueous solution. These methodologies are based on mixing cationic surfactants with amphiphilic molecule, medium-chain alcohol, selection of molecular architecture through tedious organic synthesis, additive induced structural modification or by adulterating with counter charged amphiphilic molecules (e.g., oppositely charged surfactants) [2,12–16]. Recently, a new trend of combining a dimeric (gemini) amphiphile and counter charged monomeric surfactants has been immerged which provides a potential method of obtaining rich variety of surfactant aggregates and their inter-changes [17–21]. Geminis are denoted like *m*-*s*-*m*, where *m* and *s* are carbon numbers in hydrocarbon chain and the head group connecting moiety (spacer), respectively [22,23].

Later, surfactant mixtures and inherent morphologies are used to modify the solubilization efficacies of otherwise water-insoluble compounds (e.g., polycyclic aromatic hydrocarbons, PAHs) [19,24,25]. The magnitude of solubilization has been found to be dependent on the site of solubilization and micro-environment provided by the aggregate morphology [26–31]. Therefore, morphology and micro-environment are key factors and should be investigated with this point of view. The mixing of surfactants (anionic-non-ionic or cationic-non-ionic) has been shown to change micro-polarity (with composition) of the resulting aggregate experienced by pyrene (as the probe) [32–36]. This micro-environment can be tuned and exploited for the incorporation of various water-insoluble organic material [35,37–39].

In the above context, studies have been initiated involving the mixing of contrasting charge gemini surfactants in order to see the interaction, morphologies and solubilization efficacies (of PAHs) [24,40–42]. In these studies, composition inspired morphological changes (e.g., micelle-vesicle) were observed with contribution from the nature of the spacer. Further, zeta (ζ)-potential data

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