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Facile Solubilization of Organochalcogen Compounds in Mixed Micelle Formation of Binary and Ternary Cationic-Nonionic Surfactant Mixtures

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This study investigated the water solubility enhancements of organochalcogen compounds, viz. bis(diphenylmethyl)diselenide [(C₆H₅)₂CHSe]₂ and 3,3'-dibromo-4,4'-dimethyl-2-dipyridyl diselenide [C₁₂H₁₀N₂Se₂Br₂] in micellar media. Two cationic and one nonionic surfactants possessing the same hydrocarbon tail, namely hexadecyltrimethylammonium bromide ($C_{16}Br$), hexadecyltrimethylammonium chloride ($C_{16}Cl$), and polyoxyethylene(20)mono-n-hexadecyl ether (Brij 58), in their single as well as equimolar binary and ternary mixed states have been used. Solubilization capacity has been evaluated in terms of the molar solubilization ratio and the micelle water partition coefficients. The association constants between the solubilizate molecules and that of micelle and the average number of solubilizate molecules per micelle have also been quantified. The results showed that cationic surfactants exhibit less solubilization as compared to nonionic surfactant. The mixing effects of surfactants on micelle formation and solubilization efficiencies have also been discussed. It has been observed that cationic-nonionic binary combinations showed better solubilization capacity as compared to pure cationic, nonionic, or cationic-cationic binary mixtures. An equimolar cationic-cationicnonionic ternary surfactant system provides higher solubilization than cationic-cationic but lowers than their cationic-nonionic counterpart. In addition, Fourier transform infrared has been employed with fair success to predict the information regarding the aggregates and the mechanism of docking of the surfactant and the chalcogenides in the system. The analysis has provided valuable information for the selection of mixed surfactants for solubilizing water-insoluble compounds. Certainly the solubilization ability of these surfactants is not simply related to molar capacity. The results give sufficient encouragement to warrant more detailed investigation of the features of surfactant properties that affect solubilization.

Introduction

Micelles are dynamic nanoscopic aggregates of surfactant molecules having a specific capability to solubilize a wide variety of organic molecules with different polarities and hydrophobicities. They are the host structures used in several types of organic reactions, catalysis, polymerization, and transport of drugs and dyes. In these applications, the size and stability of the micelles are important features that determine and explain their role in a variety of chemical processes. The tailoring of micelle properties may be achieved by adding salts, organic solutes or a second type of surfactant forming the so-called mixed micellar system.

Mixed micelles of ionic with nonionic surfactants have been a topic of several investigations owing to their extended use in technical, pharmaceutical and biological fields, since they work better than pure micelles. ^{14,15} In an aqueous medium, surfactants in pure and mixed states self-assemble to form micelles. The threshold concentration (cmc) is an important criterion for understanding the fundamentals of the self-organizing process. The mixtures of the surfactant types, nonionic/nonionic, ¹⁶ anionic/nonionic, ¹⁷ cationic/nonionic, ¹⁸ anionic/biosurfactant, ¹⁹ anionic/anionic, ²⁰ cationic/cationic²¹ and cationic/anionic²² have been reported. The theories of Clint, ²³ Motomura, ²⁴ Rosen, ²⁵ Blankschtein, ²⁶ and Rubingh²⁷ have been used to analyze and compare the experimental results to understand the synergism

and antagonism of the binary compounds. The larger size and the thermodynamic stability of mixed micelles would enhance the incorporation capability of solutes into the micellar phase, which is an important issue in many of the applications of micellar solutions.

An enhanced aqueous solubility of otherwise slightly soluble organic substances brought about by the presence of surfactant micelle is well documented in literature. 28–30 Treiner et al. 31 used the framework of the regular solution approach to evaluate partition coefficients of neutral organic solutes between micellar and aqueous phases. However, Zhou and Zhu 32 have reported a positive deviation of solubilization from the ideal value in number of mixed SDS-nonionic systems. It would be fruitful to investigate this point further to gain insight into the solubilization phenomena.

In the present study, efforts have been made to solubilize the water-insoluble organic derivative of chalcogen, that is, bis(diphenylmethyl)diselenide [(C₆H₅)₂CHSe]₂ and 3,3'-dibromo-4,4'-dimethyl-2-dipyridyl diselenide [C₁₂H₁₀N₂Se₂Br₂] in single, binary, and ternary surfactant mixtures of hexadecyl (C₁₆) chain length surfactant having cationic and nonionic head groups. These chalcogenides are rigid nonplanar moieties having bulky selenium bridge and find potential applications in synthesis of various Se compounds.^{33–35} The evaluation of solubilization capabilities of equimolar cationic—nonionic, cationic—cationic, and cationic—cationic—nonionic mixed systems have also been investigated. The systems were investigated using static fluorescence and UV—visible spectroscopy, surface tension, and

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SCHEME 1: Structures of Surfactants and Solubilizate Molecules^a

 a (a) Hexadecyltrimethylammonium bromide ($C_{16}Br$), (b) hexadecyltrimethylammonium chloride ($C_{16}Cl$), (c) polyoxyethylene(20)mono-n-hexadecyl ether (Brij 58), (d) bis(diphenylmethyl)diselenide [(C_6H_5)₂CHSe]₂, and (e) 3,3'-dibromo-4,4'-dimethyl-2-dipyridyl diselenide [$C_{12}H_{10}N_2Se_2Br_2$].

conductivity. Fourier transform infrared (FTIR) studies were also carried out to investigate the additive association with surfactant. The interaction parameters for mixed micelle formation were also correlated with the solubilization interaction parameters for finding out synergism in solubilization capabilities of multi component surfactant system. The experimental results of this study will be useful to understand and predict the solubilization properties of mixed surfactant systems.

Experimental Section

Materials. The cationic surfactants, hexadecyltrimethylammonium bromide (C₁₆Br) and hexadecyltrimethylammonium chloride (C₁₆Cl), and the nonionic surfactant, polyoxyethylene-(20)mono-n-hexadecyl ether (Brij 58), were purchased from Fluka with purity >99%. The molecular structures of surfactants are shown in Scheme 1. Organochalcogens, that is, bis(diphenylmethyl)diselenide [(C₆H₅)₂CHSe]₂ and 3,3'-dibromo-4,4'dimethyl-2-dipyridyl diselenide (C₁₂H₁₀N₂Se₂Br₂) used as hydrophobic solutes in the present study, were synthesized in the laboratory and characterized using spectroscopic techniques (Scheme 1). Acridine orange dye from Himedia (>97%) was used to determine the cmc using dye micellization method. Pyrene was obtained from Fluka (>98%) and N-hexadecylpyridinium chloride (CPyCl, > 97.5%) was from Fluka. Surfactant solutions were prepared in triply distilled water having conductivity lower than 3 μ S.

Methods. Critical Micelle Concentration Determination. The cmc values of all the surfactants studied were determined using spectroscopic, conductivity, and surface tension techniques. Dye micellization method using Acridine Orange (AO) dye was applied to determine the cmc from UV (Jasco V 530) and fluorescence (Shimadzu RF-540, Japan) technique (Supporting Information, Figure S1-S3 and Table 1). The concentration of the AO was kept at 2.5×10^{-5} M in sample cell. The specific conductivity was measured using a Pico digital conductivity meter from Laboratory India instruments with an absolute accuracy of $\pm 3\%$ and precision of $\pm 0.1\%$ (Supporting Information, Figure S4). Surface tension measurements were done with a calibrated du Noüy tensiometer (Krüss, Germany) by the ring detachment technique (Figure 1). The γ values were accurate within $\pm 0.1 \text{ mNm}^{-1}$. The Gibbs surface excess at cmc (Γ_{max}) of all surfactant solutions were calculated from the surface tension (γ) versus logarithm of surfactant concentration (log C_t) (Supporting Information, Table 2). An automatic thermostatted bath from Julabo was used for maintaining the temperature within ± 0.01 °C.

FTIR Spectroscopy. To get more insight into the interaction between the chalcogenides and the surfactant, the system was further characterized by Fourier transform infrared spectroscopy (FTIR) in the frequency range of 4400–350 cm⁻¹ with the help of Perkin-Elmer FTIR spectrophotometer using AgCl plates.

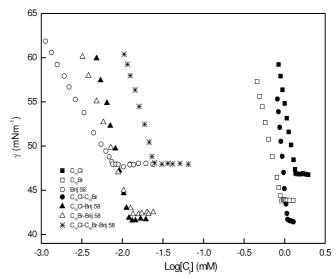


Figure 1. Plot of the surface tension (γ) vs the total surfactant concentration (C_l) of single, binary, and ternary surfactant combinations.

Results and Discussion

Critical Micelle Concentration and Surfactant Interaction in Mixed Micellar Media. The cmc values of single as well as mixed surfactant systems are listed in Table 1. The values for pure surfactants are comparable with the literature values, given in parentheses in Table 1. The ideal cmc values, cmc_{ideal} calculated using the Clint²³ equation for mixed surfactant systems are also presented in the Table 1 for equimolar binary and ternary systems. All the obtained cmc values were initiated to be lesser than the cmcideal, indicative of negative deviation from ideal behavior for mixed micelles formation. Rubingh's equation²⁷ (eq A Supporting Information) based on regular solution theory has also been used to estimate negative deviation of experimental cmc values from cmc_{ideal}. The interaction parameter, β (indicator of the degree of interaction between two surfactants in mixed micelles) along with the micellar mole fraction, X_{i}^{m} , and activity coefficient, f_{i} of the ith surfactant within mixed micelles calculated using Rubingh²⁷ treatment have also been presented in Table 1 for the chosen equimolar binary and ternary mixed surfactant systems. The negative value of β signifies attractive interactions. This synergism would result in part from the charge screening and reduction of the repulsion between cationic head groups caused by intercalating the nonionic surfactant between cationic monomers.³⁶ A minor negative value of β and minute deviation of f_i values from unity in the cationic-cationic mixed micellar system designate their ideal behavior in the mixed micelle formation. However, their negative deviation from ideal behavior is comparable with the

TABLE 1: Experimental Critical Micelle Concentration (cmc_{exp}), cmc_{ideal}, Interaction Parameter (β), and Activity Coefficients (f_i) Values of Equimolar Binary and Ternary Surfactant Mixtures at 298.15 K^a

surfactant system	cmc _{exp} (mM)	cmc _{ideal} (mM)	β	$X_1^{\mathrm{M}}/X_2^{\mathrm{M}}/X_3^{\mathrm{M}}$	$f_1/f_2/f_3$
C ₁₆ Br	$0.92 (0.89)^{44}$				
$C_{16}Cl$	$1.38 (1.4)^{44}$				
Brij58	$0.0077 (0.0081)^{45}$				
$C_{16}Br-C_{16}Cl$	1.09	1.17	-0.16	0.68/0.32/	0.96/0.92
C ₁₆ Br-Brij58	0.013	0.015	-3.09	0.10/0.90/	0.46/0.47
C ₁₆ Cl-Brij58	0.012	0.016	-2.98	0.14/0.86/	0.47/0.48
$C_{16}Br-C_{16}Cl-Brij58$	0.025	0.026	-2.89	0.11/0.05/0.84	0.27/0.04/0.88

^a Error limits of cm c_{exp} , β , and f_i are $\pm 2\%$.

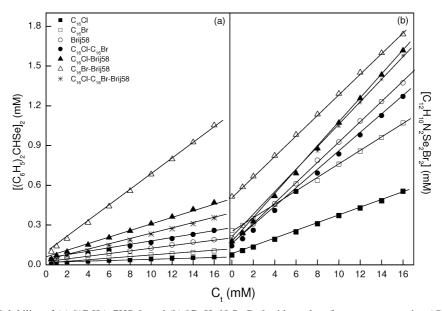


Figure 2. Variation of Solubility of (a) $[(C_6H_5)_2CHSe]_2$ and (b) $[C_{12}H_{10}N_2Se_2Br_2]$ with total surfactant concentration (C_t) of single and equimolar binary and ternary surfactant combinations.

earlier results for cationic—cationic and cationic—nonionic mixed binary system.³⁷ It is well documented in literature^{38,39} that for ionic—nonionic mixed surfactant systems, momentous electrostatic self-repulsion of ionics and weak steric self-repulsion (depending on the headgroup size) of nonionic before mixing and the electrostatic self-repulsion of the ionic surfactant is reinstated by the ion-dipole interaction between the hydrophilic groups of cationic and nonionic surfactants. The above parameters in ternary mixtures viz., C₁₆Br—C₁₆Cl—Brij 58 have also been assessed (Table 2) using a multicomponent nonideal mixed micelle model based on a pseudophase separation approach developed by Holland and Rubingh.⁴⁰ The model makes an effective use of net interactions on binary systems.

Molar Solubilization Ratio (χ) and Micelle/Aqueous phase partitioning of organochalcogens. Solubilization of a substance can be estimated using two parameters, the molar solubilization ratio (χ) and the micelle—water partition coefficient (K). The χ value is characterized as the amount of solute (organochalcogen) that can be solubilized by one mole of micellar surfactant. It illustrates the ability of the surfactant to solubilize the organochalcogen and is given by^{41,42}

$$\chi = \frac{\{[S_{\rm t}] - [S_{\rm emc}]\}}{[C_{\rm t} - {\rm cmc}]} \tag{1}$$

where $[S_t]$ is the total apparent solubility of the solubilizate, $[S_{cmc}]$ is the apparent solubility of the additive at cmc, which is taken as their water solubility, [S], because it changes only very slightly up to the cmc of the surfactant. C_t is the molar concentration of surfactant in solution and cmc is the critical micelle concentration.

 χ is equal to the ratio of organochalcogen concentration solubilized in micelles to the surfactant concentration in the micellar form and is obtained from the slope of the curves that results when solubilizate concentration is plotted against the surfactant concentration. The variation of solubilities of $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$ in single and equimolar mixed surfactant systems are plotted in Figure 2. The aqueous solubilities of organochalcogen compounds amplify linearly with surfactant concentration, demonstrating their solubility enrichment over that in water. This phenomenon is presumably associated to the micellar solubilization. The χ values from the above plots are tabulated in Table 2 for all systems studied herein. To further examine the efficiency of solubilization, the micelle—water partition coefficient, K, of the solubilizate flanked by the micelle and aqueous phases has also been evaluated⁴³ via eq 2

$$K = \frac{\{[S_t] - [S]\}}{[S]}$$
 (2)

The value of K in term of χ can also be written as $K = \chi[C_t - \text{cmc}]/[S]$. In order to eliminate the dependence of K on the surfactant concentration, a molar micelle—water partition coefficient, K_m , can be defined as follows

$$K_{\rm m} = \frac{\chi[1 - \text{cmc}]}{[\text{cmc}]} \tag{3}$$

The estimated $K_{\rm m}$ values are presented in Table 2 for various organochalcogenides in the selected surfactant systems. In accordance with earlier findings, ^{44,45} χ and $K_{\rm m}$ values are found to be higher for nonionic than for cationic surfactants indicating

TABLE 2: Aggregation Number (N_{agg}) , Molar Solubilization Ratio (χ) , log K_m , Association Constant (K_1) , and Average Number of Solubilizate Molecules Per Micelle (S^M) of Organochalcogenides in Various Single and Equimolar Mixed Micellar Systems at 298.15 Ka

			$[(C_6H_5)_2CHSe]_2$			$[C_{12}H_{10}N_2Se_2Br_2]$			
surfactant system	$N_{ m agg}$	χ	log K _m	$K_1 \text{ (mMdm}^{-3}\text{)}$	$S^{M} \times 10^{-3}$	χ	log K _m	$K_1 \text{ (mMdm}^{-3}\text{)}$	$S^{\rm M} \times 10^{-2}$
C ₁₆ Br	66	0.0057	1.27	0.311	4.61	0.068	2.15	3.491	8.73
C ₁₆ Cl	59	0.0028	0.97	0.149	2.21	0.034	1.86	1.833	4.58
Brij58	67	0.015	1.69	0.977	14.46	0.077	2.37	4.99	12.48
$C_{16}Br-C_{16}Cl$	61	0.012	1.59	0.601	8.89	0.089	2.26	4.806	12.02
C ₁₆ Br-Brij58	65	0.065	2.31	3.959	58.59	0.107	2.33	5.211	13.03
C ₁₆ Cl-Brij58	61	0.028	1.96	1.644	24.33	0.099	2.30	5.784	14.46
$C_{16}Br-C_{16}Cl-Brij58$	65	0.021	1.84	1.338	19.81	0.097	2.29	5.939	14.85

^a Error limits in the measurement of N_{agg} , χ , $\log K_{\text{m}}$, K_{1} , and S^{M} are ± 1.8 , ± 3.5 , ± 1.5 , ± 1.9 , and $\pm 2.8\%$, respectively.

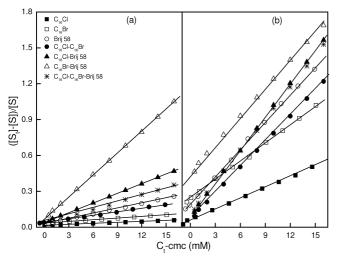


Figure 3. Plot of $(\{[S_t] - [S]\})/[S]$ of (a) $[(C_6H_5)_2CHSe]_2$ and (b) $[C_{12}H_{10}N_2Se_2Br_2]$ against surfactant concentration in micellar form $(C_t - cmc)$ of single and equimolar bi- and ternary surfactant combinations.

that for the same hydrophobic chain length nonionic has higher solubilizing power for the given organochalcogen compounds. The case of $C_{16}Br$ and $C_{16}Cl$ is also comparable where the former reveals considerable larger values of χ and $K_{\rm m}$ in contrast with the latter. Here, the aggregation numbers also diverge in addition to lower counterion (Cl⁻) polarizability. Assuming that the inner nonpolar core of the micelle is accountable for organochalcogen solubilization, $K_{\rm m}$ should be roughly comparative to the nonpolar content of the surfactant. This has been demonstrated by Kile and Chiou⁴⁶ for solubilization of DDT in nonionic surfactant where the major contributor to solubilization was the nonpolar part of the surfactant. Additionally, their solubilization studies for cationic, anionic, and nonionic surfactants pointed out that $K_{\rm m}$ values could be better related to nonpolar part of the surfactant moderately than with the micelle size, leading to the conclusion that micellar size may not be a prime factor for observed variations in $K_{\rm m}$ values for ionic and nonionic surfactants.

However, the equimolar binary surfactant mixtures of cationic—nonionic mixed surfactants demonstrate higher γ and $K_{\rm m}$ values than cationic—cationic mixed system. The values are still elevated than those of single nonionic surfactant demonstrating synergism in organochalcogen solubility improvement over the single surfactant system (Table 2). Moreover, χ and $K_{\rm m}$ values of cationic—cationic systems are appreciably amplified when adding nonionic surfactant as observed in the case of ternary system. This might be interrelated to higher micellar core solubilization characterstatic of nonionic surfactant in addition to the micelle-water interface.

To better understand the mechanism involved in the process of micellization, the understanding of the thermodynamic parameters controlling solubilization is very constructive. From the thermodynamic approach, solubilization can be considered as a usual partitioning of the solute flanked by the two phases, micelle and aqueous; consequently the standard free energy of solubilization, ΔG°_{s} can be expressed by the following expression⁴⁷

$$\Delta G^{\circ}_{s} = -RT \ln K_{m} \tag{4}$$

where R, T, and $K_{\rm m}$ are the gas constant, absolute temperature, and the molar partition coefficients between the micelle and the aqueous phase respectively. The ΔG°_{s} values thus computed are tabulated in the Table 3 (Supporting Information). For all the systems, ΔG°_{s} is negative, demonstrating spontaneous solubilization. The largest negative value was observed for the C₁₆Br-Brij 58 micellar system showing that the solubilizations of organochalcogen are energetically more complementary in cationic-nonionic system, due to additional micelle-water interface adsorption.

Evaluation of Binding Constants of Organochalcogenides with Single and Mixed Micelles. The binding constant (K_1) serves the interaction parameter between solubilizate incorporated into micelles. K_1 is related to the total surfactant concentration, $[C_t]$, cmc, and aggregation number, N_{agg} , of micelles through the equation

$$\frac{\{[S_t] - [S]\}}{[S]} = \frac{K_1}{N_{\text{arg}}} (C_t - \text{cmc})$$
 (5)

The value of K_1/N_{agg} can be evaluated from the slope of ({[S_t] -[S])/([S]) against $(C_t - \text{cmc})$. The aggregation number was determined by utilizing external fluorophore (Pyrene) using steady-state fluorescence measurements. The formulation can also be used to evaluate average number of solubilizate molecules per micelle, S^M, according to the following equation⁴⁸

$$S^{M} = \frac{\{[S_{t}] - [S]\}}{[C_{t}]} = K_{1}[S]$$
 (6)

The value of [S] can be taken as water solubility of organochalcogenides, which changes only very slightly up to cmc of the surfactant. Figure 3 shows the representative plots of $(\{[S_t] - [S]\})/([S])$ against $(C_t - \text{cmc})$ for single, binary, and ternary systems studied herein.

The value of K_1 for $[(C_6H_5)_2CHSe]_2$ has been found to be lower than $[C_{12}H_{10}N_2Se_2Br_2]$. This may be an indication of the different solubilization capacity of two compounds. Among the cationic and nonionic surfactants, the latter shows a greater magnitude of K_1 values compared to former. A substantial increase in K_1 in surfactants when a nonionic surfactant is mixed

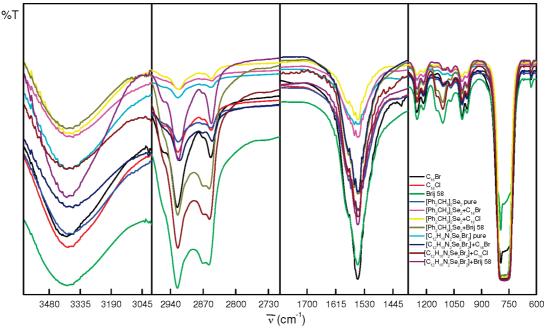
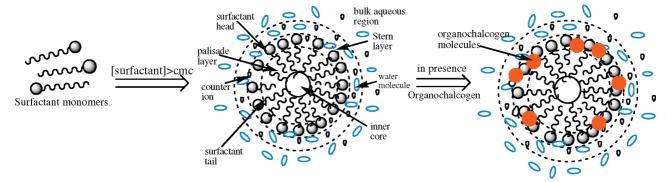


Figure 4. FTIR spectra of pure $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$ in presence and absence of hexadecyl surfactants $(C_{16}Br, C_{16}Cl)$ and Brij 58).

SCHEME 2: The Packing of Organochalcogen Derivative in Micellar Media



with the cationic indicates increased stability of the solubilizate in the mixed cationic-nonionic surfactant systems relative to pure cationic. It has been observed⁴⁹ that in addition to the micellar core solubilization organochalcogens are adsorbed at the cationic micelle-water interface due to electrostatic interactions between π -electrons of organochalcogenides and the positive charges. In the case of cationic surfactant, lower values of binding constant can therefore be attributed to the limited solubilization at micelle-water interface and micellar core. On the other hand, in nonionic surfactant due to weak interaction of oxygen of polyoxyethylene glycol with π -electrons of organochalcogens, more of micellar core solubilization would be prevalent. This is responsible for comparatively larger values of K_1 , χ , and K_m for nonionic surfactant. Only a small mole fraction of cationic surfactant has been used in solubilization in case of cationic—nonionic mixed micelles (Table 1). A slight positive charge developed on mixed micelles due to presence of cationic surfactant facilitates micelle-water interface adsorption in addition to the micellar core solubilization characteristic of nonionic's. A similar explanation can be furnished for mixed ternary systems, wherein these values are higher than the cationic surfactants.

FTIR Analysis. To get additional insight into the interaction between the solubilizate and the surfactant, the system was further characterized by FTIR. The typical FTIR spectra of $C_{16}Br$, $C_{16}Cl$, and Brij 58 are shown in Figure 4. The symmetric

and antisymmetric CH₂ stretching [$\nu_{\text{sym}}(\text{C-H})$ and $\nu_{\text{asym}}(\text{C-H})$] vibrations of C₁₆Br occurs at 2845 and 2925 cm⁻¹, and that of C₁₆Cl and Brij 58 occur at 2853, 2926 cm⁻¹ and 2854, 2920 cm⁻¹, respectively. The band in the region 1500–1400 cm⁻¹ is ascribed to the methylene (CH₂) scissoring mode in pure hexadecyl hydrocarbon chain surfactants of the studied system. The N⁺-CH₃ stretching band resonates at 1550 and 1557 cm⁻¹ in the case of C₁₆Br and C₁₆Cl, respectively. The peaks in the region between 1250 and 1000 \mbox{cm}^{-1} correspond to the $C{-}N^{+}$ stretching mode in $C_{16}Br$ and $C_{16}Cl$. The rocking (ρ_r) $(CH_2)_n$ mode of Brij 58 is at 793 cm⁻¹. The spectra of $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$ show peaks in the region 3200-3300 cm⁻¹ that correspond to C-H stretching vibrations in the aromatic compounds. The peak at 1558 cm⁻¹ is for C=C, C=N stretching vibrations of pyridine ring. The peak in region 2900–2800 cm⁻¹ is ascribed to methylene antisymmetric and symmetric vibrations, respectively. The peak at 1252 cm⁻¹ is due to the C-H deformation mode of methyl group. The presence of organochalcogen compounds in micellar solution shows conspicuous peak shifts. The methylene symmetric vibrations are now observed at 2850 cm⁻¹. The band at 1557 cm⁻¹ due to N⁺-CH₃ stretching vibration in the C₁₆Cl molecules is shifted to 1547 and 1549 cm⁻¹ in the presence of $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$, respectively The rocking (ρ_r) (CH₂)_n mode in case of Brij 58 is now at 786 and 778 cm⁻¹ in the presence of $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$. These observed changes indicate that organochalcogenides interact strongly with surfactant molecules. Thus on the basis of above FTIR analysis, we propose a mechanism of surfactant docking with solubilizate molecules as shown in Scheme 2. The mechanism indicates that organochalcogen compounds, i.e., $[(C_6H_5)_2CHSe]_2$ and $[C_{12}H_{10}N_2Se_2Br_2]$, are interacting electrostatically through their π -electron clouds with the headgroup of surfactant molecules.

The spectroscopic and conductivity analysis have yielded fair results and indicate that the organochalcogen compounds are expected to stay at micellar surface, where π -electrons of organochalcogenides electrostatically interact with headgroup of micelles.

Conclusion

The present study represents a systematic investigation on the effects of cationic as well as nonionic surfactants with hexadecyl chain length on the solubilization of organochalcogen compounds. The solubilization capacity has been evaluated in terms of molar solubilization ratio and micellar-water partition coefficient values. An increase in solubility of the organochalcogenides in nonionic surfactant of same hydrophobic chain length has been observed as compared to cationic surfactant. Among equimolar binary combinations in cationic-nonionic mixtures indicate better solubilization than pure cationic, nonionic, or cationic-cationic mixtures. The study also gives information regarding the interaction between the surfactant and additive aggregates and the mechanism of docking of the surfactant and the solubilizate molecules in the system. The analysis has yielded interesting results and provides valuable information for the selection of mixed surfactants for solubilizing water-insoluble compounds. Certainly the solubilization ability of these surfactants is not simply related to molar capacity, but these results give sufficient encouragement to warrant more detailed investigation of the features of surfactant properties that affect solubilization.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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