NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2019, 10 (2), P. 176–183

Influence of hexylamine and alcohols as cosurfactants on microemulsion phase behavior and solubilization

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DOI 10.17586/2220-8054-2019-10-2-176-183

This study investigated the influence of cosurfactants on the phase behavior and solubilization capacity of microemulsions. Firstly, we determined the influence of alcohol chain length on the microemulsion solubilization capacity in microemulsion systems containing sodium dodecyl sulfate (SDS), heptane, and water; utilizing n-butanol, n-hexanol, n-octanol and hexylamine as cosurfactants. Then, we compared the effect of the cosurfactant on the solubilization capacity of the microemulsion with SDS. Based on the results, we suggest that hexylamine is a good candidate to produce microemulsions since hexylamine behaved as a cationic surfactant. Secondly, keeping constant the rate of surfactant/cosurfactant and varying the rate of alcohol to hexylamine as cosurfactant, we explain the cosurfactant effect in systems with SDS, alcohol, methylene chloride, and sodium molybdate using the spectrophotometric method. Results showed that the absorbance (ABS) values increased continuously in the systems of n-octanol and n-decanol with increasing amounts of hexylamine. The change in ABS values is considered to be related to microemulsion structure inversion.

Keywords: microemulsion, cosurfactant, microstructure, phase behavior, solubilization.

Received: 18 April 2019

Revised: 21 April 2019

1. Introduction

There is growing interest in investigating phase behavior and the solubilization capacity of microemulsions due to their common use in industrial applications, pharmaceuticals, enhanced oil recovery, consumer products, and drug delivery systems [1–4]. Ever since their introduction, microemulsions have been studied theoretically as well as experimentally by various researchers [5–8]. Understanding the phase behavior and solubilization capacity of microemulsions plays a vital role in designing and developing specific applications.

Microemulsions are thermodynamically stable and optically isotropic mixtures containing water or brine, surfactant, organic solvent, and often a cosurfactant. A microemulsion system comprises four or five components, namely, water, organic solvent, surfactant, cosurfactant, and electrolyte [9]. Structurally, depending on the proportion of the components, they have been classified as either distribution of oil-in-water (O/W) or water-in-oil (W/O) [7, 9–11]. The phase behavior of microemulsion systems is very important, and is shown in the Gibbs triangle diagram [12].

Part of the research on microemulsions is related to the maximum solubility of the organic solvent and/or water with a low amount of surfactant [13, 14]. The use of a cosurfactant, usually a medium-chain-length alkyl alcohol such as n-butanol, increases the stability of the microemulsion [14]. It has been reported that several factors such as the nature of hydrocarbons and alcohols as cosurfactant, concentration of surfactant, temperature and electrolyte influence the properties of the microemulsions, such as solubilization and phase behavior [1, 3, 8, 14–17]. For example, when hydrocarbon levels exceed 50 % or increase the alkyl chain length of the oil, the solubilizing capacity of water decreases in the microemulsion systems, consisting of oil, water, single-surfactant, cosurfactant (alcohol) and electrolyte [18]. Therefore, Li, Wang and Wang suggested that mixed anionic-cationic surfactants were more beneficial for forming W/O microemulsions with low surfactant content than a single surfactant, due to the synergistic effect resulting from strong Coulombic interactions between the cationic and anionic surfactants. They studied the effect of oil and alcohol chain length on the water solubilization and phase behaviors of W/O microemulsions with mixed-surfactant systems containing SDS as an anionic surfactant and tetradecyl trimethyl ammonium bromide (CTAB) as a cationic surfactant. According to their conclusions, the water solubilization capacity in the studied systems: (1) Increases when the cationic surfactant (CTAB) amount is increased in mixed surfactant systems with SDS as a major anionic surfactant, (2) Decreases by increasing the oil chain length at constant ratios of alcohol to the surfactant and anionic to the cationic surfactant, and (3) Increases with an increasing alcohol chain length in the order of n-butanol $<$ n-pentanol $<$ n-hexanol, and as the alcohol concentration increases [18].

Another important argument is that using hexylamine instead of medium-chain-length alcohols as cosurfactant reduces problems with the solubilization of water at high hydrocarbon levels. As cited by Wormuth and Kaler "*the first reference to the use of amines as cosurfactants is by Winsor*" in 1948 [17]. Venable, Elders and Fang indicate that hexylamine is a good candidate to produce microemulsions. Based on previous studies [19], Wormuth and Kaler report that "*pseudoternary-phase diagrams of various amines combined with anionic and cationic surfactants show large one-phase regions and high solubility of water in oil-rich regions*" [17]. Most previous studies on the influence of cosurfactant have been concerned with alcohols. As mentioned above, the selection of cosurfactant is of vital importance. For example, since short-chain alcohols are volatile and flammable substances, medium-chain-length alcohols such as pentanol and hexanol are not suitable for pharmaceuticals due to their high irritation potential, and using long-chain-length alcohols may cause the formation of lamellar liquid crystalline phases instead of microemulsion phases [4, 20]. Therefore, there is a need to better understand the role of hexylamine as a cosurfactant in the behavior of microemulsions. To select the appropriate cosurfactant is crucial to the solubilization capacity of microemulsions, as well as their formation.

Based on the application potential of microemulsions, this study had two aims. Initially, the aim was to investigate the effect of cosurfactants on microemulsion systems with SDS, heptane and water by using n-butanol, n-hexanol, n-octanol and hexylamine as cosurfactant, and then comparing the microemulsion regions in the phase diagrams. The second aim of the study was to explain the structural changes in microemulsions using mixed hexylamine plus alcohol as a cosurfactant with the spectrophotometric method, since the mixtures combining n-alkanol and amine show a variety of different behaviors [21]. Although use of different techniques such as dynamic light scattering (DLS), static light scattering (SLS), and FT-IR, pulse-gradient NMR, and X-ray scattering (SANS, SAXS) [22, 23] give more detailed knowledge of the microemulsion structure, we can also interpret the microemulsion structure by looking at changes in their basic ABS values.

2. Experiment procedure

2.1. Materials

Sodium dodecylsulfate (SDS, Merck, 98 %) was recrystallised twice from hot 99 % ethanol. It was dried in a vacuum oven at 50 °C and stored in a desicator. Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, 99 %), and rubrene 1 (5, 6, 11, 12 tetraphenylnaphthacene, 98 %) were purchased from Aldrich Chemie and were used as received. n-Heptane (Merck, 99 %), n-butanol (Merck, > 99 %), n-hexanol (Merck, 99 %), n-octanol (Aldrich, > 99 %), hexylamine (Merck, > 98 %), methylene chloride (Merck, > 99.5 %), and hydrogen peroxide (Merck, 30 %) were used without further purification. The water was distilled twice.

2.2. Apparatus

A Vortex-Genie 2 Mixer was used for all mixing treatments. The spectra and absorbance measurements were recorded on a Shimadzu UV-1601 spectrophotometer over wavelength ranges of 400 – 600 nm.

2.3. Methods

SDS and heptane were selected as the anionic surfactant and the organic solvent in all systems. We utilized n-butanol, n-hexanol, n-octanol and n-hexylamine as cosurfactants and prepared microemulsion systems of SDS/Heptane/Water at constant pressure and temperature, as previously described [11, 13, 24]. All experiments were carried out at room temperature. A series mixture was prepared consisting of various amounts of surfactant, cosurfactant and organic solvent in 10 mL screw-cap centrifuge tubes. In these microemulsion systems, the weight ratio surfactant/cosurfactant was held constant at 0.5. The contents of the tubes were blended by vortex mixing for several minutes to equilibrate at room temperature. The slurries obtained were titrated with twice-distilled water from a 1 mL micro-burette. After each drop of water was added, the tubes were vigorously stirred in the vortex mixer. The blurred emulsion spontaneously transformed into a clear single-phase environment, indicating the beginning of the microemulsion phase. Then, the titration process continued until permanent turbidity or phase separation was seen visually. Furthermore, samples were equilibrated for at least several days in a thermostatic bath to control the turbidity or phase separation. The procedure used for ternary and quaternary phase diagram determination followed the method introduced by Ezrahi, Aserin, Garti and Berkovic [25]. The surfactant + cosurfactant were considered to be a single component for the ternary phase diagram.

We followed the spectrophotometric method described by Aubry and Bouttemy [26] to investigate the microemulsions' structure with SDS/hexylamine+alcohol/methylene chloride/sodium molybdate (0.2 M). In this part of the experiment, initially, a water-in-oil (W/O) microemulsion with SDS/n-butanol/methylene chloride/sodium molybdate system was adapted from the study of Nardello, Marti, Pierlot and Aubry [27].

3. Results and discussion

3.1. Phase Behavior of SDS/Heptane/Water Systems

We investigated the effects of the cosurfactant on the phase behavior and solubilization capacity of the microemulsions with SDS. The pseudoternary phase diagrams were drawn up at 0.5 of the weight ratio surfactant / cosurfactant, and are presented in Fig. 1. When the systems in which n-butanol, n-hexanol and n-octanol were used as cosurfactant are compared (Fig. 1), it can be seen that the microemulsion region was reduced with increasing alcohol chain length. The interaction energy between the alcohol and oil molecules increases as the alcohol chain length is increased, and hence water solubilization capacity decreases due to the increasing alcohol carbon number [28–30]. As known, phase behavior is correlated with the oil/water interfacial tension, the size of dispersed particles and the solubilization of oil and water in the microemulsion [31]. Depending on the length of the alcohol chain, the distribution of alcohol in the oil and water phases affects microstructure and the extension of microemulsion area. As pointed out by Miyata, Miyamoto and Yonese [32], the second effect of the alcohol is to compete with surfactant for interfacial adsorption by entering the interfacial area and by pulling apart the surfactant molecules, which is caused to decrease of the interfacial surfactant concentration per unit area. The presence of alcohol decreases both the polar head group interaction and the hydrocarbon chain interactions of the surfactant molecules by causing of mutual solubility change of hydrophilic and hydrophobic components.

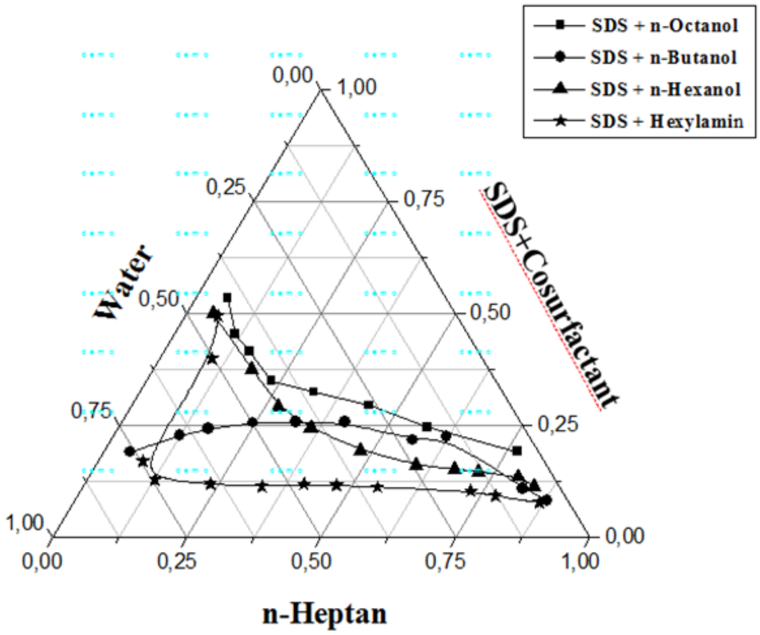

FIG. 1. Pseudoternary phase diagram of the SDS/Cosurfactant/n-Heptan/Water at room temperature. [SDS/Cosurfactant = 0.5 (weight)]

When the phase diagrams (Fig. 1) are examined, it is seen that the microemulsion region in the system with hexylamine as cosurfactant is larger than the others. As can be seen from Fig. 1, hexylamine is an effective cosurfactant for microemulsions, giving rise to high solubilization of heptane and water at the weight ratio surfactant/cosurfactant of 0.5. As pointed out by Venable and Viox [33], medium chain length alkyl amines are more effective cosurfactants for microemulsion formation than are medium chain length alcohols with sodium doecyl sulfate as the surfactant. This observation correlates with the good solubility of water in hexylamine and poor solubility of hexylamine in water [34]. It can also be explained in terms of the hydrophile-lipophile balance (HLB), due to reduction of the strong hydrophilicity of SDS by the amine interaction. This means that the SDS becomes less hydrophilic when hexylamine is added as cosurfactant to the system. A specific ionic interaction between the amine and anionic surfactant occurs in the surfactant-rich interfacial region [17]. The repulsive force in these microemulsions is, in fact, like that in an ionic micelle, resulting from coulombic repulsion between the NH2+ group of the hexylamine head group; which, being directly attached to the alkyl chain, would have to be located close to the hydrophobic core [35].

It is worth noting that hexylamine acts as if positively charged under experimental conditions, thus becoming a cationic surfactant in itself. Due to the role of hexylamine as a cationic cosurfactant, this microemulsion system can be depicted as a mixture of anionic and cationic surfactants. Mixed anionic-cationic surfactant systems often have synergistic effects [2]. As reviewed by Doan, Acosta, Scamehorn and Sabatini, while adding alcohol is not preferred in certain environmental and consumer product formulations, the addition of alcohol is generally necessary to avoid liquid crystal formation in mixed anionic-cationic surfactant systems [2]. Venable, Elders and Fang observed that hexylamine was effective as a cosurfactant with both the aliphatic hydrocarbon heptane and the aromatic hydrocarbon toluene. Similarly, they mention that the superiority of "*hexylamine would be explained with the concept of the hydrophile-lipophile balance (HLB) of surfactant systems, as put forth by Shinoda et al. (1984)*" [19].

3.2. Phase Behavior of SDS/hexylamine + alcohol/methylene chloride/sodium molybdate (0.2 M)

New SDS/methylene chloride/sodium molybdate (aq) systems were prepared to investigate the cosurfactant's effect on structural changes using the spectrophotometric method. In preparation of these systems, the surfactant/cosurfactant ratio was fixed at 0.5 by weight in all of the systems, and combinations of alcohol and hexylamine were used as cosurfactant by changing the ratio of alcohol to hexylamine at 75/25, 50/50, 25/75 by weight. In these media, the resulting microemulsion systems in which both sodium molybdate as an ionic compound and rubrene-1 as an organic compound were dissolved simultaneously were compared. The sodium cations of sodium molybdate decrease repulsion between the negatively-charged head groups of SDS and hence favor the formation of reverse micelles. The water-in-oil microemulsions (W/O) used in the present study are described as roughly spherical water microdroplets coated with an interfacial film of SDS; n-butanol being dispersed in a continuous phase of methylene chloride, as shown by Aubry and Bouttemy [26]. One important feature of these media is their ability to dissolve simultaneously considerable amounts of hydrophilic compounds that are confined in aqueous droplets and hydrophobic organic molecules localized in the continuous organic phase. Structural changes to the microemulsions are interpreted as based on changes to the absorbance. The wavelength (λ) – absorbance (ABS) changes of microemulsions with SDS, alcohol, hexylamine, methylene chloride and sodium molybdate solution are shown in Figs. 2, 3, 4, and 5.

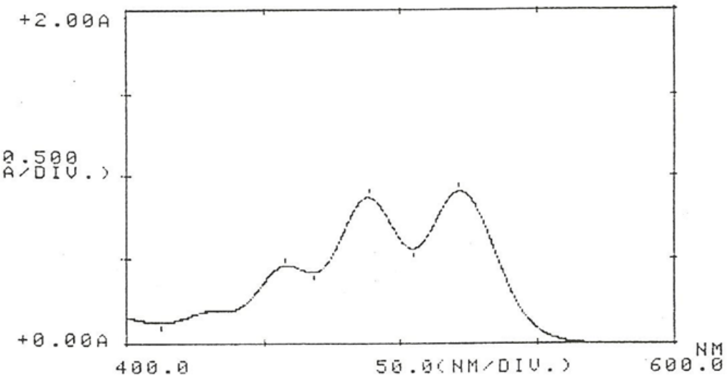

FIG. 2. The wavelength-absorbance change of the system with SDS/Hexylamine/Methylene chloride/Sodium molybdate (aq). SDS/Hexylamine = 0.5

As is seen from Figures 2, 3, 4, and 5, the 0.914 ABS value at 521.8 nm wavelength indicates that hexylamine is also an effective cosurfactant in the SDS/methylene chloride/sodium molybdate (aq) system.

Next, we investigated the more complex effects of changing the ratio of alcohol to hexylamine as cosurfactant by including n-butanol, n-octanol and n-decanol. Alteration in the alcohol-to-hexylamine weight ratio may cause the formation of a wide variety of structures of differing geometry and topology; ranging from oil-in-water spherical droplets, elongated aggregates and bicontinuous systems to water-in-oil droplets [8].

From Figs. 3, 4, and 5 it can be concluded that when the amount of hexylamine is increased in the mixed alcohol plus hexylamine, the solubilization capacity of the microemulsions may increase, decrease, or maximise depending on the structure of the alcohol used. When n-butanol, n-octanol and n-decanol were used, the ABS values increased. Therefore, it was considered that an increase had occurred in the interfacial region; and in each system, the size of water droplets increased relative to the solubility of water in hexylamine on increasing the amount of hexylamine. When the ratio of alcohol to hexylamine was decreased, fading of the red solution was not noticed visually. Thus, we can say that the structure of the microemulsions must have changed from W/O to O/W.

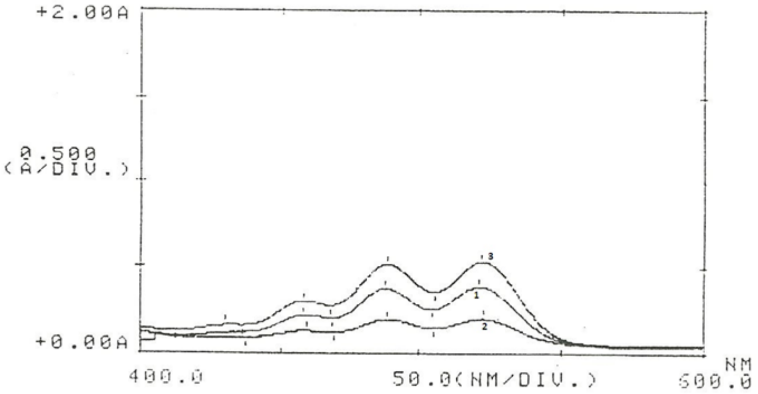

FIG. 3. The wavelength-absorbance change of the system with SDS/n-Butanol + Hexylamine/Methylene chloride/Sodium molybdate (aq). [SDS/(n-Butanol + Hexylamine)] = 0.5

1. n-Butanol + Hexylamine = 75/25 (weight)
2. n-Butanol + Hexylamine = 50/50 (weight)
3. n-Butanol + Hexylamine = 25/75 (weight)

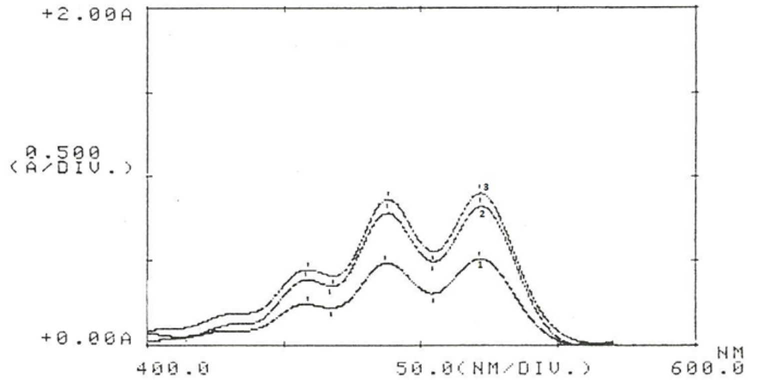

FIG. 4. The wavelength-absorbance change of the system with SDS/n-Octanol + Hexylamine/Methylene chloride/Sodium molybdate (aq). [SDS/(n-Octanol + Hexylamine)] = 0.5

1. n-Octanol + Hexylamine = 75/25 (weight)
2. n-Octanol + Hexylamine = 50/50 (weight)
3. n-Octanol + Hexylamine = 25/75 (weight)

To explain the structural changes, we should consider the cohesive interactions. These interactions are included in the denominator of a modified form of the R-ratio [36,37]:

$$R = \frac{(A_{C_1O} + A_{C_2O}) - A_{OO} - (A_{L_1L_1} + A_{L_1L_2} + A_{L_2L_2})}{(A_{C_1W} + A_{C_2W}) - A_{WW} - (A_{H_1H_1} + A_{H_1H_2} + A_{H_2H_2})},$$

where C_1 is the surfactant and C_2 is the alcohol (cosurfactant). The parameters A stand for cohesive energies per unit area of interface. H and L denote hydrophilic and lipophilic interactions, respectively. Thus, A_{C_1O} (or A_{C_1W}) is the cohesive energy between the lipophilic (or hydrophilic) portions of surfactant molecules and the oil (or water); A_{C_2O} (or A_{C_2W}) is a similar term for the interaction between alcohol and oil (or water) molecules; $A_{L_1L_1}$ (or $A_{H_2H_2}$) are the cohesive energies between the lipophilic (or hydrophilic) moieties of the surfactant and alcohol molecules, respectively; and $A_{L_1L_2}$ (or $A_{H_1H_2}$) denotes the hydrophobic (or hydrophilic) interaction between the surfactant and alcohol. All negative terms promote segregation of the components as separate phases. By definition, A_{C_2O} increases with NA (the alcohol carbon number), tending to increase the R-ratio, and the water solubilization diminishes as NA increases [36,37].

If $R > 1$, the corresponding characteristic system is type II (W/O). If $R < 1$, the characteristic system is type I (O/W). It then follows that there is a correspondence between type III behavior and $R = 1$ [36,37].

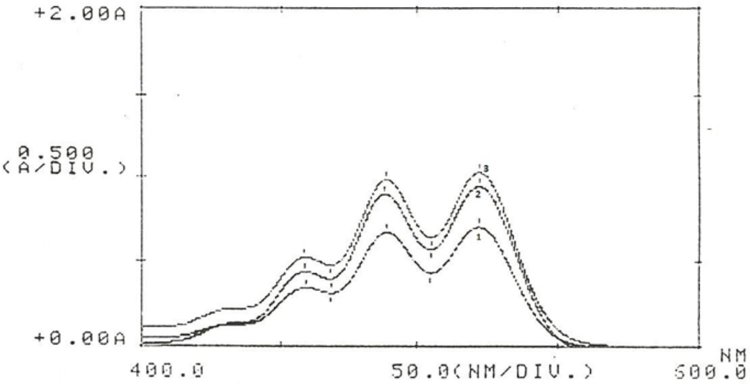

FIG. 5. The wavelength-absorbance change of the system with SDS/n-Decanol + Hexylamine/Methylene chloride/Sodium molybdate (aq). [SDS/(n-Decanol + Hexylamine)] = 0.5

1. n-Decanol + Hexylamine = 75/25 (weight)
2. n-Decanol + Hexylamine = 50/50 (weight)
3. n-Decanol + Hexylamine = 25/75 (weight)

It might be expected that the presence of hexylamine in the aqueous phase would tend to increase the solubility of the surfactants. Thus, with the addition of a low molecular weight alcohol, a microemulsion phase is expected to enrich the proportion of the aqueous phase in the microemulsion. By increasing the amount of hexylamine, which increases the interaction between water molecules and amine groups, it was thought that an increase would occur at A_{CW} and A_{HH}. However, a decrease transpired at A_{CO} and A_{LL}. As the weight ratio of n-butanol/hexylamine was equal (50/50) in the system of n-butanol plus hexylamine, a decrease occurred in the ABS value at 521.8 nm wavelength. The behavior was equally complex compared to that of n-octanol and n-decanol. To explain this disparity, it has been suggested that a breakdown in aggregate structure occurred in the typical microemulsion system. A typical microemulsion system contains neither oil-in-water nor water-in-oil microemulsion particles, but, rapid changes or fluctuations in aggregate size and shape take place. On the other hand, this decrease in the ABS value may be interpreted such that, to a certain extent, the alcohol from the oil phase can partition into the interface to stabilize the additional interfacial area. However, as the alcohol in the oil phase is depleted, further growth of water droplets would increase the interfacial tension at the O/W interface due to an increase in the area per molecule and thus destabilize the microemulsion, and hence prevent further solubilization of water [15]. When the weight ratio of n-butanol/hexylamine was equal to 25/75 in the same system, an increase was observed in the highest hexylamine concentration, as in the other systems. Adding alcohol and hexylamine to the surfactant/water/oil system entails a change in the interaction of energy per unit area of the interface of C layer with the O and W regions. This change is dependent on the nature of the alcohol, the amount of hexylamine, and their interfacial concentrations.

Both from W/O to O/W and from O/W to W/O, trends have been reported in the literature for anionic surfactants [16, 37]. In our study, an inversion from W/O to O/W occurred in the highest additive hexylamine (alcohol/hexylamine = 25/75 (weight)). When the surfactant, alcohol and hexylamine concentrations are decreased by keeping the ratio of surfactant to cosurfactant constant, the interfacial alcohol and hexylamine concentration decreases. The balance of interactions of C with O and W becomes more favorable to W. This tends to in turn microemulsion structure. A_{CW} probably increases due to intermolecular hydrogen bonding, which increases the ability of the -NH_2 group to form hydrogen bonds with water molecules. Finally, the lateral interaction between the surfactant molecules obviously increased. It can be asserted that with addition hexylamine to system with alcohol as a cosurfactant, the change in the cohesion energies accompanying the hydrophilic and hydrophobic interaction between the alcohol, hexylamine and the surfactant (A_{LL} and A_{HH} in the R ratio used as the criterion for the determination of the type of microemulsion) might cause change in the structure of microemulsion. Additionally, it can be suggested that the transition between microemulsion types is mainly caused by changing the HLB values of the water-oil interfacial layer including surfactant and cosurfactant components. It can be stated that n-butanol plus hexylamine equilibrates the interfacial interaction balance of SDS which is a very hydrophilic surfactant.

For further studies, we recommend the use of different techniques such as dynamic light scattering (DLS), static light scattering (SLS), FT-IR *etc.* techniques to design, characterization of microemulsion systems and to examine the effects of cosurfactants on the structure of microemulsion systems as performed in several studies (for example [22,38]).

4. Conclusion

In the first part of the present study, we investigated the effect of hexylamine and three different alcohols as cosurfactants with a SDS/Heptane/Water system on phase behavior and solubilization of microemulsions. According to our results, it can be suggested that hexylamine performed better as a cationic surfactant in the SDS/Heptane/Water system than n-butanol, n-hexanol and n-octanol under experimental conditions. In the second part of the study, we compared the effects of hexylamine only and mixed-cosurfactants (hexylamine+alcohol) with SDS, methylene chloride, and sodium molybdate (0.2 M) systems on the microemulsion structure, based on change in ABS values using the spectroscopic method.

In conclusion, it can be said that the type of cosurfactant used and the ratio of hexylamine to alcohol as cosurfactant have an impact on microemulsion structure due to interactions between the surfactant and organic solvent. This behavior of hexylamine plus alcohol as a cosurfactant may be important for researchers when investigating the appropriate microemulsion medium for industrial applications, pharmaceutical applications, consumer products, and drug delivery systems.

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