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Micellization behavior of mixed surfactants in pure water and methanol-water mixed solvent media by density methods

Ajaya Bhattarai*, Kavita Pathak, Bikash Dev
Department of Chemistry, M.M.A.M.C., Tribhuvan University, Biratnagar, Nepal
* E-mail: bkajaya@yahoo.com

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Abstract

The properties of anionic-rich and cationic-rich mixtures of dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS) in pure water and methanol-water mixed solvent media were studied using density measurements at room temperature. The results showed that density increases with increasing concentration of surfactant mixture over the entire concentration range investigated in pure water and in the given mixed solvent media and which are found to decrease with an increase in the volume fraction of methanol in the solvent composition. The critical micelle concentration increases with the increase in volume fraction of methanol for both the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) systems.

Keywords: Mixed solvent; Dodecyltrimethylammonium bromide; Sodium dodecylsulfate; Density; Critical micelle concentration.

1. Introduction

Mixed surfactant systems are much favored from the view point of economy and performance. They are less expensive than isomerically pure surfactants. The latter often arises from the deliberate formulation of mixtures of different surfactant type to exploit the synergistic behavior in mixed systems or to provide qualitatively different types of performance in a single formulation. The performance of mixed surfactant systems is often superior to that of a single surfactant system. The practical formulations often require the addition of surfactant additives to help control the physical properties of the product or improve its stability. Different surfactants are often deliberately mixed to provide enhanced performance [1]. The optimization of mixtures of surfactants in aqueous solution is an important part of the formulation of many commercial cleaning products [2]. Hence, it is essential to understand how surfactants interact in mixtures [3]. The mixed surfactant systems often show synergistic behavior, resulting in reduction of the total amount of surfactant used in a particular application, which in turn reduces both cost and environmental impact.

It was reported that the physical properties of the mixed surfactant systems such as critical micelle concentration (cmc) are often substantially lower than that expected based on the properties of pure components due to the synergistic behavior [4]. Especially mixing of the two surfactant ions of opposite charge, cationic/anionic surfactant mixtures exhibits largest synergistic effects while it seems to be negligible for mixtures of nonionic surfactants. There is physically simple explanation for enhanced synergism in such mixed charge systems. The basic idea is the hydrophobicity of the salts formed by the strong interactions between two different surfactants with opposite charge [5-6]. Since the properties of surfactant solutions change markedly when micelle formation occurs, many investigations have been focused on determining the values of the cmc in various systems and many studies have been carried out to elucidate the factors that determine the cmc value at which micelle formation becomes significant, especially in aqueous media. The most important factor known to affect the cmc in aqueous solution is the structure of the surfactant [7].

There is little work in the literature dealing with the solution properties of binary mixtures of anionic (sodium dodceylsulfate) and cationic (dodecyltrimethylammonium bromide) surfactants and few works has been done on the effect of medium [8-9]. Among various physical parameters, densities have been recognized as the quantities that are sensitive to structural changes occurring in solution [10]. In this article, the results are reported for density measurements and critical micelle concentration have been calculated for anionic-rich (SDS in the presence of DTAB) and cationic-rich (DTAB in the presence of SDS) mixtures in pure water and methanol-water mixed solvent media at room temperature (20 ^{0}C).

The aim of this research work is to analyze the influence of concentration and solvent composition on the micellization behavior of mixed surfactants in pure water and methanol-water mixed solvent media.

2. Experimental

Methanol (E. Merck, India, 99% pure) was first distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g.cm^{-3} and a coefficient of viscosity of 0.4742 mPa.s at 308.15 K. These values are in good agreement with those found in the literature [11].Triply distilled water with a specific conductance lower than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents. DTAB was purchased from Loba Chemie Private Limited, Mumbai, India. DTAB was recrystallized several times until no minimum in the surface tension-concentration plot was observed and its critical micellar concentration (cmc) agreed with the literature value [12].

Sodium dodecylsulfate was purchased from Merck Specialties Private Limited, India. It was recrystallized several times for purification. A minimum in the surface tension-concentration plot was observed. The aqueous solutions of the purified and unpurified samples of sodium dodecylsulfate exhibited a minimum in the surface tension versus log c plot (where c is the concentration of sodium dodecylsulfate). The minimum in the γ versus log c plot for sodium dodecylsulfate is considered to be due to the presence of highly surface-active dodecyl alcohol molecules [13]. Dodecyl alcohol may be present as an impurity in the supplied sample of sodium dodecylsulfate or may be produced in the sodium dodecylsulfate solution by hydrolysis. The cmc of sodium dodecylsulfate is taken to be the concentration of sodium dodecylsulfate corresponding to the minimum in the γ versus log c plot and is equal to 8.10 mmol.kg^{-1} in the absence of any added electrolyte at 25 °C. This value is in good agreement with the cmc of sodium dodecylsulfate obtained from conductance measurements (8.10 mmol.kg^{-1}) previously [14].

For the measurement of density in cases of both anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) solution, was performed using a Kruss K20S Force tensiometer purchased from Germany, which was funded by Third World Academy of Sciences(TWAS), Italy at room temperature (20 °C). The tensiometer was calibrated against distilled water, the holder for the density probe and the probe itself was thoroughly cleaned with distilled water, acetone and kept for a while to natural dry before each measurement. To measure the density, holder was hung vertically; the clean density body (i.e. probe) was attached to the holder and waited until the holder along with the density body no longer moved. The weight of the density body was determined in air, immediately after that the density body was removed from the holder. Again, the vertically hung holder was dipped into the solution up to the yoke and pressed the tare to tare the weight of the holder in the liquid. The sample stage was moved downward and the weight to the holder was attached with the help of tweezers. Then the holder with the density body was dipped in the solution to exactly the same depth as during the taring process and the liquid had come to rest. Finally, the density of the solution was measured and noted. For every measurement, sample solution was stirred with a magnetic stirrer and then the stirring of the sample was continued for 3 minutes in order to make the homogenous solution.

Similar procedures were followed for the measurement of densities for both anionic and cationic rich mixtures having different concentrations and several readings were noted.

3. Results and Discussion

The densities for anionic-rich (SDS in the presence of DTAB) and cationic-rich (DTAB in the presence of SDS) mixtures in pure water and in three different methanol-water mixtures (containing 0.10, 0.20 and 0.30 volume fraction of methanol) at room temperature (20 °C) are depicted in figures 1-2. It is evident that density exhibits almost increase with increasing concentration of anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) solutions as shown in Figs 1A and 1B. In fact, the variation of density with mixed surfactant concentrations is always found to be linear in higher concentration range and such trend was also observed previously [9] whereas in the lower concentration range, a break can be seen with the decreasing pattern in densities. It is also observed that densities decreases gradually with the increase of methanol content for the studied methanol-water mixed solvent system.

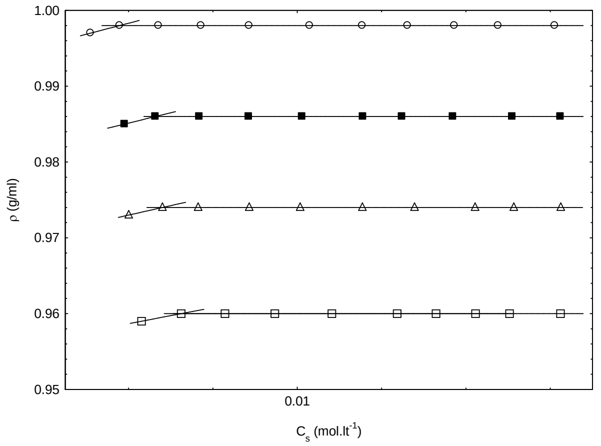


Fig. 1A: Concentration dependence of density for anionic-rich mixtures (SDS in the presence of DTAB) at room temperature, in pure water (open circles) and different methanol-water mixtures (closed squares, 0.10 volume fraction of methanol; open triangles, 0.20 volume fraction of methanol; open squares, 0.30 volume fraction of methanol).

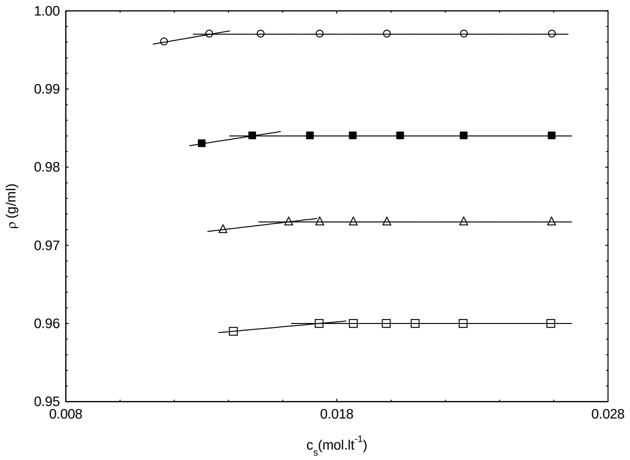


Fig. 1B: Concentration dependence of density for cationic-rich mixtures (DTAB in the presence of SDS) at room temperature, in pure water (open circles) and different methanol-water mixtures (closed squares, 0.10 volume fraction of methanol; open triangles, 0.20 volume fraction of methanol; open squares, 0.30 volume fraction of methanol).

Estimation of the slope leads to an important insight as to the solution behavior of anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) mixtures. However, below the cmc, concentration of the mixed surfactants decreases along with the density having slopes, intercepts and correlation coefficients as shown in Tables 1 and 2:

Table 1: The experimental slopes, intercepts and correlation coefficients of fits (as r^2) of anionic-rich system (SDS in the presence of DTAB) from figure (1A) in pure water and methanol-water mixtures.

Volume fraction of methanol	Slope	Intercept	r^2
0	1.45	0.990	1.00
0.1	1.37	0.977	1.00
0.2	1.25	0.965	1.00
0.3	1.06	0.952	1.00

Table 2: The experimental slopes, intercepts and correlation coefficients of fits (as r^2) of cationic-rich system (DTAB in the presence of SDS) from figure (1B) in pure water and methanol-water mixtures.

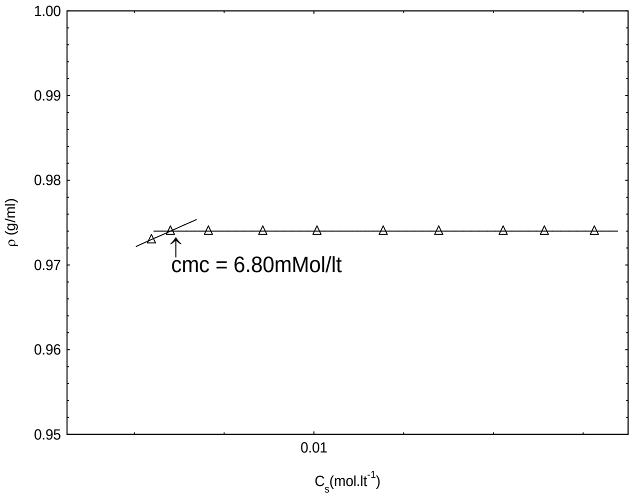
Volume fraction of methanol	Slope	Intercept	r^2
0	0.601	0.989	1.00
0.1	0.537	0.976	1.00
0.2	0.412	0.966	1.00
0.3	0.316	0.955	1.00

The possible explanation for the positive slopes in the present mixed solvent media may be that the counterion binding would become quite appreciable in these media as the concentration of the surfactant is increased, thereby weaker ion-solvent interactions. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the surfactant, resulting in a net positive volume change per mole of the added surfactant.

There are several methods to obtain the critical micelle concentration. We found very less literature [7, 15-16] regarding the calculation of the cmc from the density measurement. The intersection between the two straight lines gives the cmc. Bhattarai et. al [9] only measured densities at a higher concentration range of CTAB and SDS system in pure water and methanol water mixed solvent media but the cmc has not been calculated. While here, in our case new improvement has been done by measuring density in both higher and lower concentration range of mixed surfactants and the cmc has been calculated (fig 2) and the cmcs are found to be increased for both the anionic-rich and cationic-rich mixtures by the addition of methanol in pure water.

Harkot and Janczuk [7] carried out density measurement and calculated the cmc of two cationic surfactants: (dodecylethyldimethylammonium bromide and benzyldimethyldodecylammonium bromide) in aqueous solutions. Gonzalez-Perez et. al [16] studied the micellar properties of octyldimethylbenzylammonium bromide in aqueous solution by density measurement at different temperatures. As alcohol is added to a surfactant mixture solution, the dielectric constant and degree of structuring of the solvent is lowered. As more alcohol is added, this process continues and the micelles expand, hence leading to an increased cmc.

It can also be seen that cmc increases with the increasing methanol content for both the anionic-rich and cationic-rich mixtures of water and methanol-water mixed solvent media as tabulated in Table 3.



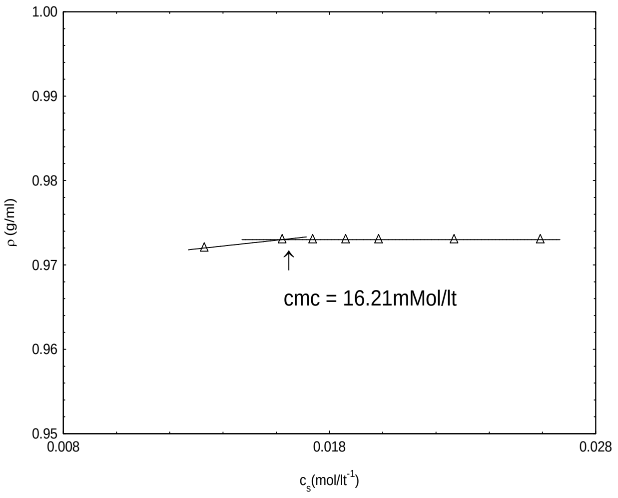


Fig. 2A : Representative figure of concentration dependence of density for anionic-rich surfactant mixture (SDS in the presence of DTAB) in 0.20 volume fraction of methanol at room temperature: for critical micelle concentration (cmc) calculation.

Fig. 2B: Representative figure of concentration dependence of density for cationic-rich surfactant mixture (DTAB in the presence of SDS) in 0.20 volume fraction of methanol at room temperature: for critical micelle concentration (cmc) calculation.

Table 3: The critical micelle concentration (cmc) for both the anionic-rich (SDS-DTAB) system and cationic-rich (DTAB-SDS) system obtained from density measurements in pure water and in methanol-water mixed solvent media containing 0.10, 0.20 and 0.30 volume fractions of methanol.

	Anionic-rich (SDS in the presence of DTAB)	Cationic-rich (DTAB in the presence of SDS)
Volume fraction of methanol	cmc(mMol/lt)	cmc(mMol/lt)
0	5.79	13.31
0.1	6.63	14.89
0.2	6.80	16.21
0.3	7.24	17.34

4. Conclusions

The experimental results of the density of anionic-rich (SDS in the presence of DTAB) and cationic-rich (DTAB in the presence of SDS) mixtures of pure water and methanol-water mixed solvent media have been presented as a function of the concentration of surfactants. The densities are found to be almost linear in higher concentration range while, a break is seen in the lower concentration range which results decrease in densities. Also, densities gradually decrease with an increase in the volume fraction of methanol for both the anionic-rich and cationic-rich mixtures in a given mixed solvent medium. After cmc, visible slopes were observed and they followed the decreasing trend for both the SDS/DTAB and DTAB/SDS systems. Estimation of slopes and intercepts provides a pertinent view regarding the solution behavior of mixed surfactants in methanol-water mixtures. The cmcs are found to be increased with the increase in volume fraction of methanol for both the anionic-rich (SDS-DTAB) and cationic-rich (DTAB-SDS) systems.

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