Studies on surface and micellization properties of binary and ternary mixtures of sodium dodecyl sulfate, cethylpyridinium chloride and polyethylene glycol hexadecyl ether in aqueous media

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ABSTRACT

Binary and ternary mixtures of sodium dodecyl sulfate (SDS), cethylpyridinium chloride (CPC) and polyethylene glycol hexadecyl ether (BRIJ-58) were mixed in different mole ratios to prepare aqueous homogeneous solutions. Their surface tensions were measured and studied in details. Accordingly critical micelle concentration (CMC), activity coefficients, interfacial adsorption, minimum area per molecule and energy related parameters for binary and ternary systems were assessed.

KEYWORDS: Dodecyl sulfate (SDS), cethylpyridinium chloride (CPC) polyethylene glycol hexadecyl ether (BRIJ-58) ,CMC, specific conductivity, ternary combinations etc.

Introduction

Surface active agents are multifunctional chemical compounds which have found a number of applications in various industries such as pharmaceuticals, detergents, petroleum and automobiles etc. They have also great utility in electronic printing, magnetic recording, biomedical research. Therefore, scientific community is highly interested in the study of the unusual properties, physical attributes, and phase behavior of these chemicals [1-3]. It has also been observed that most of the times, mixtures of surfactants is more useful and effective in comparison to the single surfactant, in terms of micellization, dispersion, emulsification, drug delivery, corrosion inhibition and oil recovery related applications [4, 5].

Therefore, the mixed micelle systems make an extensive contribution to the field of both academic and commercial applications of surfactants as well as the surfactant-containing systems [6]. During mixed micellization, in some cases clouding phenomenon also takes place whichn is very common in case of non-ionic surfactants [7] while under special circumstances, ionic surfactants undergo phase separation [8].A number of binary systems have been explored in the literature [9-15] and their physicochemical and thermodynamic properties have been analyzed in detail. In comparison to binary systems, ternary systems have been less studied and a limited work is available on them [16-22].

In the present piece of research work a detail surface and micellization properties of CPC, SDS and BRIJ-58 (Polyoxyethylene (20) cetyl ether) in binary and ternary mixtures in an aqueous medium. The different theoretical models have been used to understand the interaction among the components in mixed micelles.

Experimental

Materials

Cetylpyridinium chloride (CPC), Sodium dodecyl sulfate (SDS) and BRIJ-58 were purchased from Merck, BDH and Sigma with 90% purity. The solutions were prepared in double distilled deionized water having specific conductivity 1 to 2 μS cm^{-1}.

Surface tension measurements

Surface tension measurements were made with stalagmometer. The different concentrations of the surfactant solutions were prepared from the stock solutions by adding adequate amount of the solvent. . The measured surface tension values were plotted as a function of the logarithm of surfactant concentration (Fig. 1). The accuracy of the measurements was within ±0.1 m Nm^{-1}.

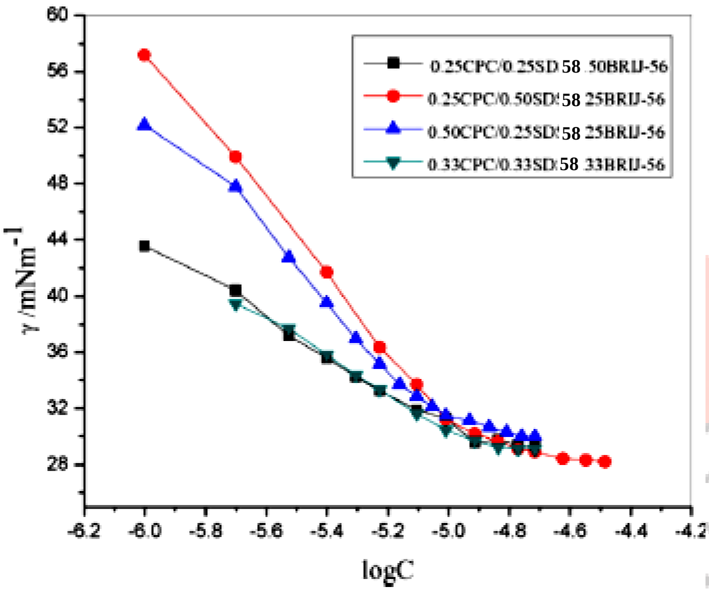

Fig. 1:-Determination of the CMC of ternary combinations of CPC, SDS and BRIJ-58 at different mole ratios at 298 K.

Results and Discussion:-

Interaction of surfactants in micelles:-

For ideal mixtures, where the individual components are non-interacting, CMC of a mixture can be predicted using the following equation [23],

$$\left(\frac{1}{\mathrm{CMC}_{ideal}}\right)=\sum_{i=1}^{n}\left(\frac{\alpha_i}{f_1 CMC_i}\right) \qquad (1)$$

where α_i is the stoichiometric mole fraction of the i^{th} component in the mixture, CMC_i is the critical micellar concentration of the pure i^{th} component and f_i is its activity coefficient. P.M. Holland, D.N. Rubingh, gave the Clint equation (24) for ideal conditions, $f_i = 1$,

$$\left(\frac{1}{\mathrm{CMC}_{ideal}}\right)=\sum_{i=1}^{n}\left(\frac{\alpha_i}{CMC_i}\right) \qquad (2)$$

The Clint's model is straightforward to predict ideal CMC from the knowledge of the CMC's of the individual surfactants in the mixture, and it is useful for comparison between ideal and nonideal mixtures. A lower experimental value of observed CMC (CMCexp) for the binary mixture as reported in Table 1 and Fig. 2 signifies synergistic interaction among the components in the mixture.

Table 1:-Experimental CMC (CMC_{exp}), Ideal CMC (CMC_{ideal}) and other miceller parameters of pure and binary mixtures at 298 K.

System	10^4 CMC_{exp} (M)	10^4 CMC_{ideal} (M)	χ	χ_{ideal}	β	f_1	f_2
CPC	08.260	-	-	-	-	-	-
SDS	23.300	-	-	-	-	-	-
BRIJ 58	00.116	-	-	-	-	-	-
CPC+SDS	01.040	9.930	0.59	0.889	−11.01	0.157	0.022
SDS+BRIJ-58	00.072	0.231	0.29	0.005	−10.39	0.005	0.417
CPC+BRIJ-58	00.080	0.229	0.30	0.014	−08.41	0.016	0.468

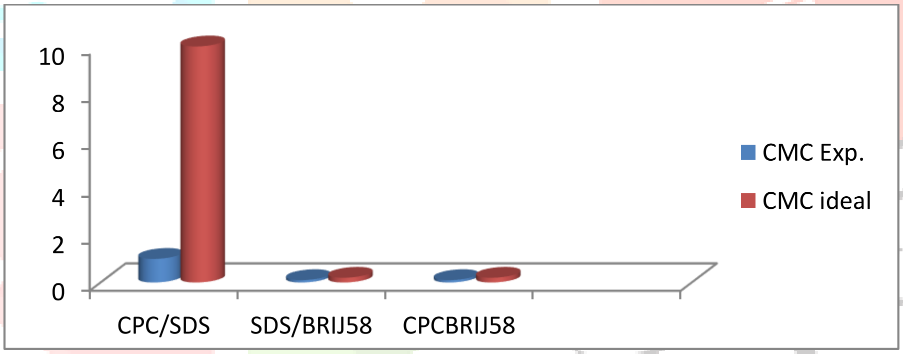

Fig. 2:- Experimental CMC (CMC_{Exp}), ideal CMC (CMC_{Ideal}) of CPC/SDS/BRIJ-58 binary system at 298 K.

The ERSA treatment for ternary mixed systems

Holland and Rubingh have extended the RSA (regular solution approximation) for binary mixed micelle formation to nonideal multicomponent systems by considering only the pair interaction parameters. It has been successfully applied in case of ternary surfactant systems for evaluation of micellar composition, activity coefficients.

In a ternary component mixture, activity coefficients fi, fj, and fk, of mixed micelle forming amphiphilic species i, j, the following expression is obtained

$$\ln f_i = \sum_{\substack{i=1 \\ (j\neq 1)}}^{3} \beta_{ij} \chi_j^{s2} + \sum_{\substack{j=1 \\ (i\neq j\neq k)}}^{3} \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) \chi_j^s \chi_k^s \qquad (3)$$

Where βij represents the net pairwise interaction between components i and j, and Xj s is the molefraction of jth component in the micelles. At CMC, the relation holds, Xsi ¼ αiCMC j f jXs j α jCMCi f I andΣXsi ¼ 1, where the terms CMCi and CMCj are CMC values of ith and jth components in the pure state.

The CMC values evaluated by the Rubingh–Holland method were lower than the experimental values except one. The CMC values obtained by Clint's have higher values from both obtained by experiment and by Rubingh–Holland method, indicating the synergistic nonideal nature of the mixed ternary micellar system (Fig. 3).

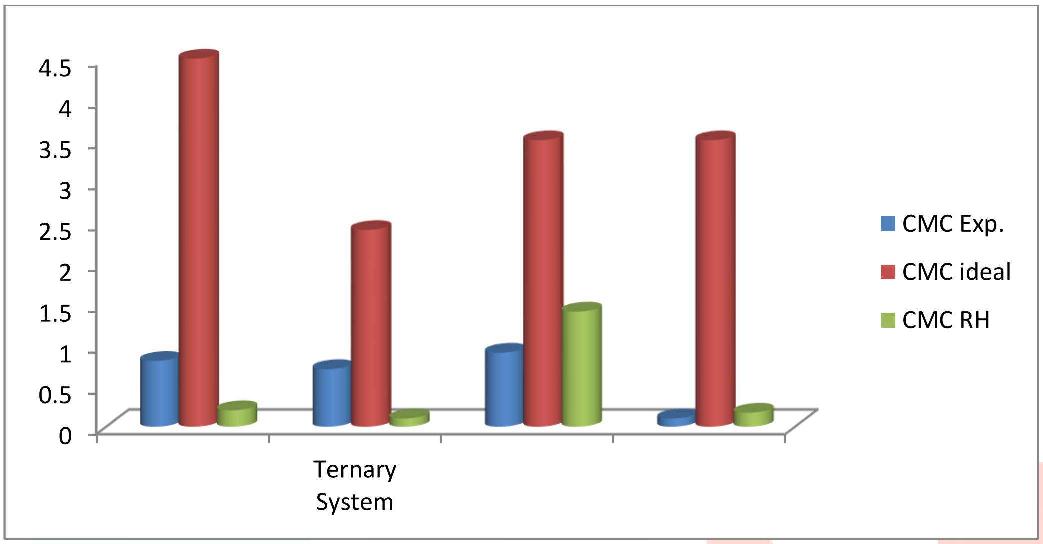

Fig. 3:- Experimental CMC (CMC_{Exp}), ideal CMC (CMC_{Ideal}) and Rubingh–Holland CMC (CMC_{RH}) of CPC/ SDS/ BRIJ-58 ternary system at different mole ratios.

4. Conclusions

The following conclusions can be drawn from this study.

(i) The micellar parameters like ΔGm, β values are negative, suggesting synergism in mixed micelle formation.

(ii) The results of our study show that the experimental CMC values of binary combinations are smaller than the ideal CMC determined from the Clint equation, an indication of negative deviation from ideal behavior in the mixed micelle formation.

(iii) Mixed micelle formation by ternary mixtures has been analyzed in light of the Rubingh–Holland model. The CMCRH values were lower than CMCexp and CMCClint. An overall nonideal by way of synergistic interaction among the components resulted.

(iv) The ternary surfactant micelle was mainly composed of nonionic components, so the nonionic surfactant suppressed the activity of ionic surfactant in the mixed micelles.

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