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# Mixed Micelles of Binary Mixtures of Sodium Dodecylbenzene Sulfate and Tween 80 Surfactants in Aqueous Solutions

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## Abstract:

In the present work, the surface properties of mixed binary surfactants containing sodium dodecylbenzene sulfate (SDBS) and Tween 80 (TW80) surfactants in aqueous solutions were studied at temperature 293 K using surface tension measurements. The critical micelle concentration (cmc) magnitude for both individual surfactants and their mixtures were established the obtained results revealed that the magnitude of cmc of the mixtures are less than the magnitude of individual surfactants and decrease with the increase in Tween 80 percent in solution which indicate the nonideal mixing of the two surfactants. The values of molecular interaction parameters $\beta^m$ and the mole fraction of surfactants in the micelle (X1) were calculated on the basis of Rubingh's model and showed that the interaction parameter is always negative but at 0.9 mole fraction of TW80 surfactant ($\alpha_1$) is positive.

**Key words:** Binary mixture, Mixed micelles, Surface tension, Tween 80.

## Introduction:

Tweens are nontoxic nonionic surfactants and are widely used in various scientific and industrial applications (1). Their compatible set of physical properties allows them to blend with many other surfactants. The bulk and interfacial behaviors of binary mixtures of Triton X-100 and TW-80 and ternary mixtures of Triton X-100, TW-80 and CTAB (cetyl trimethyl ammonium bromide) were studied using four techniques; conductometric, spectrophotometric, fluorimetric and tensiometric (2). Some parameters such as, micelle formation, counter-ion binding, adsorption at interface, mixed micelle composition and molecular interaction in mixed micelles have been estimated using equations of Rubing, Motomura and Clint models.

The mixtures of n-dodecyl-β-D-maltoside and one of anionic sodium dodecyl sulfate, cationic dodecyltrimethyl ammonium bromide, and nonionic pentaethyleneglycol monododecyl ether in water solution have been studied using tensiometer and fluorescence spectroscopy (3). $\beta^\sigma$, $\beta^m$ , and $X_1$ parameters were calculated and the values of interactions followed the order anionic/nonionic > cationic/nonionic > nonionic/nonionic mixtures.

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The cmc of five binary mixture systems was measured by performing conductivity technique. These systems are sodium dodecyl sulfate with one of five surfactants with nonionic charge, Triton X-100, TW 20, TW 60, TW 80 or TW 85 (4). The β parameter was calculated and the results show that SDS- anionic surfactant system has synergism effects and the nonionic surfactant has longer hydrocarbon chain that shows interactions with the head of SDS greater than the others which show stronger synergism.

Cyclic voltammetry, conductivity and surface tension techniques were used to investigate the mixed systems of anionic surfactant having negative charge on the head sodium dodecyl sulfate and nonionic surfactants tween 20 /tween 40/tween 60 /tween 80(5). The β parameter was estimated using regular solution theory and their negative values suggest the synergistic behavior of the systems studied. $\Delta G^\circ_m$ (Gibbs free energy of micellization) was computed for all systems studied of tween series.

The surface properties of film adsorbed of mixed surfactants of Tween 20 and Tween 80 on water – Air have been investigated by surface tension measurements at 298 K (6). cmc, $\Gamma_{max}$ (maximum surface excess), $A_{min}$ (minimum surface area per molecule), $P^{C20}$ (the negative log C20 where C20 is the molarity of surfactant required to decrease the surface tension of the solvent 20 mN/m), and CMC/C20 have been determined. The results have been analyzed in the light of Rosen's theory to evaluate the composition of the mixed film adsorbed and the corresponding interaction parameters ($X_1^{\sigma}$and $\beta^{\sigma}$ respectively). The negative sign of interaction parameters $\beta^{\sigma}$ indicate the attractive interaction for certain systems. The synergism effect at the adsorbed film was examined.

Binary mixture of surfactants is always used in practical applications, such as detergents, emulsions, wetting, foaming and defoaming, and pharmaceutical field, to enhance the properties of individual surfactant, therefore, the aim of this work is to investigate adsorption properties of anionic-nonionic mixed systems that consist of binary mixture systems of sodium dodecylbenzene sulfate and Tween 80 surfactants in water solutions by surface tension measurements to understand the nature of interaction among the surfactants in mixed micelles.

## Materials and Methods:

Tween 80 (polyoxyethylene sorbitan monooleate) as nonionic surfactant was obtained from Sigma Chemical Co., Soduimdodecylbenzyl sulfate (SDBS) as anionic surfactant is BDH product and has 80% active constituent, the remainder additive is sodium sulfate and free from commercial detergent additive. The individual and mixtures of surfactant solution were prepared in deionized water and were kept for at least 30 minutes for equilibrium at certain temperature before measuring surface tension. The solutions of surfactant that have different concentration and percentage of mixture were prepared by diluting certain amounts of stock solution in 50 ml volumetric flask with deionized water.

### Surface Tension Measurements

Du Noüy's ring platinum tension meter from S.E.O. Co. Ltd, (Korea) was used to measure the surface tension (γ). Platinum ring was thoroughly cleaned using 5M $HNO_3$ solution before each measurement and the results were the average of three measurements. The cmc magnitude was determined corresponding to the intersection of the lines of the pre- and post- micelle regions of the concentration in the plots of γ vs. natural logarithm of surfactant concentration.

## Results and Discussion:

The surface tension for the individual surfactant (SDBS and TW-80) and their mixture at the temperature 293K were measured as a function of their concentration to determine the critical micelle concentration (cmc).Their cmc was then considered as the point of intersection between two continuous lines obtained from the point of discontinuity in a γ versus ln C plot. The decrease in surface tension versus the natural logarithm of the total surfactant concentration for the SDBS and TW-80 surfactants and typical mixed surfactant systems are shown in Fig. 1.

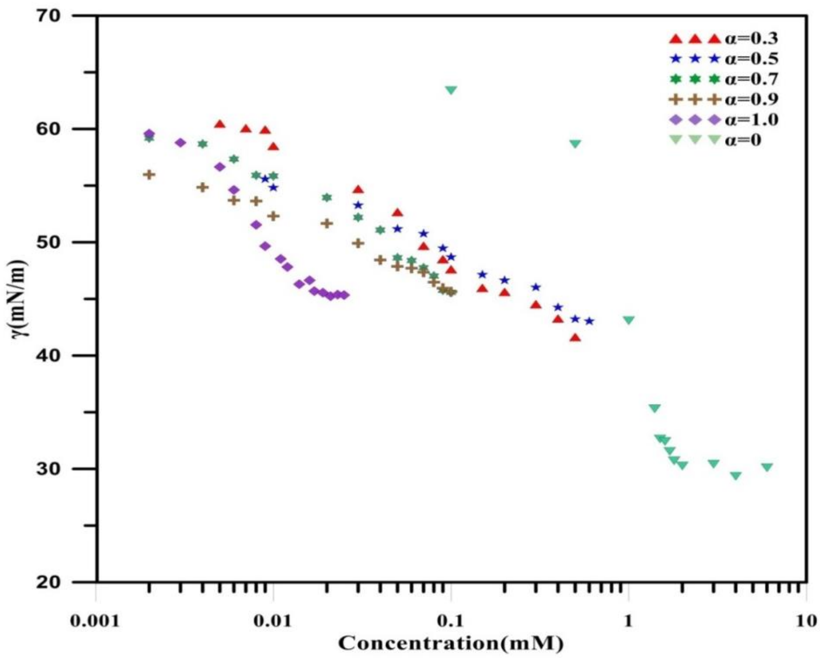


**Figure 1. Surface tensions (γ) versus ln[C] for individual and typical binary mixed surfactant systems**

The ideal mixed micelles ($cmc_{id}$) for any binary surfactant system, as proposed by Clint (7, 8), is given by the following equation:

$$\frac{1}{cmc_{id}} = \frac{\alpha_1}{cmc_1} + \frac{\alpha_2}{cmc_2} \quad ... \ (1)$$

where $\alpha_1$and $\alpha_2$ are the mole fraction of surfactant 1(TW80) and surfactant 2 (SDBS)in the total mixed solute respectively, and $cmc_1$, $cmc_2$ and $cmc_{id}$ are critical micelle concentrations for components 1, 2, and mixture respectively. The cmc was obtained experimentally ($cmc_{exp}$) at 293 K and their calculation from equation (1) are listed in Table 1. Figure 2 shows the deviation of cmc values of nonideal mixture from ideal mixture as a function of mole fraction of surfactant1.

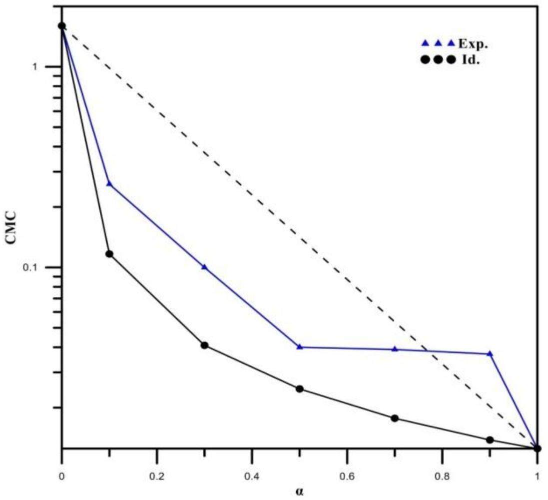


**Figure 2. The values of ideal and experimental cmc as a function of $\alpha_1$**

The results in Table 1 show that the magnitudes of cmc of Tween 80 are smaller than SDBS because of the electrostatic repulsions which are present in head groups. For mixed system, cmc of all mixtures is smaller than the cmc of anionic surfactant (SDBS) and greater than the cmc of nonionic surfactant (TW 80) and it decreases as the mole fraction of nonionic surfactant increases. This behavior indicates that there is a synergistic effect of mixed micelles in the solution formed.

Figure 2 shows that the mixed cmc values measured experimentally different from mixed cmc values calculated theoretically in the whole mixing range which show an attractive interaction present in the mixed micelle except the mixture of$\alpha_1$ = shows 0.9 which repulsion interaction (9), (The dot line in Fig. 3.2 means the behavior of ideal solutions).

The measured mixed cmc values experimentally are different from than those calculated assuming ideal mixture. These deviations have been analyzed by using Rubingh model (10, 11) which is allowed to calculate the micelle mole fraction ($X_1$) and interaction parameter ($\beta^m$) (a measure of the interactions between surfactants in the mixed micellar system) by using the following equations:

$$\frac{[X_1{}^2 \ln(cmc_{exp}\alpha_1 / cmc_1 \ X_1)]}{(1-X_1)^2 \ \ln[cmc_{exp}(1-\alpha_1) \ / \ cmc_2(1-X_1)]} = 1 \quad ... \ (2)$$

$$\beta = \frac{[\ln(cmc_{exp} \ \alpha_1 \ / \ cmc_1 \ X_1)]}{(1-X_1)^2} \quad .... \ (3)$$

Where $X_1$ is the surfactant1 mole fraction in the mixed surfactants micelles and $\beta^m$ is the parameter measure the extent of interaction between the two surfactants in the mixed micelle. $X_1$ values can be calculated from solution Equation 2 while the values of $\beta^m$ can be calculated by substituting $X_1$ in equation 3. The values of $X_1$and $\beta^m$ calculated are listed in Table 1.

The activity coefficients of the two surfactants ($f_1$ and $f_2$) in the micelle of mixed surfactants were calculated by substituting $\beta^m$ in equations 4 and 5.

$$f_1 = \exp[\beta^m \ (1-X_1)^2] \ \ ... \ (4)$$

$$f_2 = \exp[\beta^m \ (X_1)^2] \quad ....(5)$$

The activity coefficients ($f_1$ and $f_2$) were substituted in equation 6 to estimate excess Gibbs free energy of mixing ($\Delta G_{ex}$) (12):

$$\Delta G_{ex} = [X_1 \ lnf_1 + (1-X_1) lnf_2]RT \quad ... \ (6)$$

The values of $f_1$, $f_1$ and $\Delta G_{ex}$ calculated from the equations above are listed in Table 1.

**Table 1. The interaction parameters values for SDBS / Tween 80 mixed surfactant systems at 293 K.**

| $\alpha_1$ | $cmc_{ideal}$ | $cmc_{exp}$ | $X_1$ | $\beta^m$ | $f_1$ | $f_2$ | $\Delta G_{ex}$ |
|---|---|---|---|---|---|---|---|
| 0 | 1.60 | 1.60 | ---- | ---- | ---- | ---- | ---- |
| 0.1 | 0.117 | 0.26 | ---- | ---- | ---- | ---- | ---- |
| 0.3 | 0.041 | 0.10 | ---- | ---- | ---- | ---- | ---- |
| 0.5 | 0.025 | 0.040 | 0. 220 | - 0.5649 | 0.7052 | 0.9725 | - 0.246 |
| 0.7 | 0.018 | 0.039 | 0.2862 | - 0.2222 | 0.89292 | 0.9819 | - 0.113 |
| 0.9 | 0.015 | 0.037 | 0.3466 | + 0.0599 | 1.0259 | 1.0072 | + 0.033 |
| 1.0 | 0.0125 | 0.0125 | ---- | ---- | ---- | ---- | ---- |

The Rubingh model is insolvable up to a$\alpha_1$= 0.3 due to the large divergence in the values of cmc of the two surfactants (13).

The results show that $X_1$ values of $\alpha_1$ = 0.5 to $\alpha_1$ = 0.9 is very small and little increases with increasing $\alpha$ of surfactant 1which indicates that the interaction between the two surfactants is small. When $\beta^m$ value is equal to zero the mixture is ideal, when the value is positive the interaction between the molecules of the two surfactants in the micelle is repulsion, but when the value is negative the interaction is attraction (5). The obtained values of $\beta^m$ indicate the interactions inside the micelle between two surfactants which lead to deviation from ideal behavior. The $\beta^m$ values of systems $\alpha_1$ = 0.5 and $\alpha_1$ = 0.7 are negative which means that the attractive interaction between the head groups of the two surfactants leads to stabilization due to electrostatic factor (10), but for system $\alpha_1$ = 0.9 the $\beta^m$ value is positive which indicates a repulsive interaction, Maeda (14) suggested that the interaction between the chains of the two surfactants may play major role in addition to the interaction between the heads of surfactants in the formation of mixed micelles, especially for the dissimilar chain lengths. The values of activity coefficients, $f_1$ and $f_2$ obtained from equations 4 and 5 are less than 1 which meaning the non-ideal behavior of the studied binary systems except for $\alpha_1$ system which shows a value greater than unity (15).

The table also shows that the calculated $\Delta G_{ex}$ values for $\alpha_1$= 0.5 and 0.7 are negative which means that the micelles of mixed surfactants studied are more stable than the micelles of SDBS and TW 80 in individual forms and the maximum value are observed in case of $\alpha_1$ = 0.5system. For $\alpha_1$ = 0.9 system the value of $\Delta G_{ex}$ is positive which suggests the micelles of individual surfactants are more stable than the mixed micelles.

## Conclusions:

Binary mixture of SDBS and Tween 20 surfactants system gives better micelles properties than individual surfactant solution. The evaluated parameters show that an attractive interaction in the mixed system of $\alpha_1$ = 0.5 and 0.7 but the mixture system of $\alpha_1$ = 0.9 shows repulsive interaction. $\Delta G_{ex}$ values obtained suggest that the mixed micelles for $\alpha_1$ = 0.5 and 0.7 are more stable than the micelles of individual components but for $\alpha_1$ = 0.9 is in opposite direction.

## Conflicts of Interest: None.

## References:

1. Rosen M J. Surfactant and interfacial phenomenon. 3rd ed., chapter 1. John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.
2. 2-Moulik SP , Soumen G. Surface chemical and micellization behaviours of binary and ternary mixtures of amphiphiles (Triton X-100, Tween-80 and CTAB) in aqueous medium. J. Mol. Liq., 1997; 72(1–3): 145-161.
3. Zhang R, Zhang L, Somasundaran P. Study of mixtures of n-dodecyl-β-d-maltoside with anionic, cationic, and nonionic surfactant in aqueous solutions using surface tension and fluorescence techniques. JCIS. 2004 Oct 15;278(2):453-60.
4. Ćirin DM, Poša MM, Krstonošić VS, Milanović ML. Conductometric study of sodium dodecyl sulfate-nonionic surfactant (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85) mixed micelles in aqueous solution. Hem. Ind.. 2012;66(1):21-28.
5. Manisha B, Dixit SG. Study of mixed micelles of Sodium dodecyl sulfate and nonionic surfactants polysorbates tween series: Their interaction and thermodynamic parameter using cyclic voltammetry. Int. J. Chem. Stud. 2015; 3(3): 22-25.
6. Sameer H K , Ban A. Surface Properties of Mixed Adsorbed Surfactants Film of Tween 20 and Tween 80 on Liquid – Air Interfacial. IJSR. 2017; 6 (7) ,936-939.
7. Clint, JH. Micellization of Mixed Nonionic Surface-Active Agents .J. Chem. Soc. Faraday Trans. 1975; 1:73: 1327.
8. Sachin K M, Sameer A K, Man S, Ajaya B. Study on surface properties of sodiumdodecyl sulfate and dodecyltrimethylammonium bromide mixed surfactants and their interaction with dyes. J .Heliyon. 2019; 5: 1510.
9. Sameer H K, Bahar S. Adsorption Properties for Aqueous Solution of Binary Mixture of Cocamidopropyl betaine- Sodiumdodecyl sulfate Surfactants on Air-Liquid Interface. IJSBAR. 2015; 24(3): 50.
10. Rubingh DN. In Solution Chemistry of surfactants. edited by K.L. Mittal Plenum, New York., 1979; 337.
11. Sachin K M, Sameer A, Karpe M S, Ajaya B. Self-assembly of sodium dodecylsulfate and dodecyltrimethylammonium bromide mixed surfactants with dyes in https://dx.doi.org/10.6084/m9.figshare.
12. Motomura K, Aratono M, Ogino I K, Abe M. Mixed Surfactant System. Dekker, New York, 1993; 99.
13. Chanchal D, Tanushree C, Soumen G, Bijan D. Mixed micellization of anionic–nonionic surfactants in aqueous media: a physicochemical study with theoretical consideration. . Colloid Polym Sci .2008; 286:1143–1155. DOI 10.1007/s00396-008-1876-0
14. Maeda H. A Thermodynamic Analysis of Charged Mixed Micelles in Water. J. Phys. Chem. B. 2005; 109: 15933.
15. Patel R, Khan AB, Dohare N, Ali MM, Rajor HK. Mixed micellization and interfacial properties of ionic liquid-type imidazolium gemini surfactant with

amphiphilic drug amitriptyline hydrochloride and its thermodynamics. J. Surfactants Deterg. 2015;18: 719–728. doi:10.1007/s11743-015-1709-3.

# مايسيلات مختلطة من مخاليط ثنائية من الصوديوم دوديسيل بنزين سلفونات و توين 80 الفعالة سطحيا في المحاليل المائية

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**الخلاصة:**

في هذا البحث تم دراسة الصفات السطحية لمزيج ثنائي من المواد الفعالة سطحيا sodium dodecylbenzene sulfate (SDBS) و Tween 80 (TW80) في المحلول المائي عند 293 كلفن باستخدام قياسات الشد السطحي. تم الحصول على التركيز الحرج لتكوين المايسل (cmc) لكلا المادتين الفعالة سطحيا منفردة ولمزيجهما. وكانت النتائج تدل على ان قيمة cmc للمزيج هي اقل من قيمتها للمواد الفعالة سطحيا منفردة وتقل هذه القيمة مع زيادة تركيز المادة الفعالة سطحيا TW 80 مما يدل على ان المزيج كان غير مثاليا. حسبت قيمة التاثر بين المادتين داخل المايسل $\beta^m$ والكسر المولي للمادة الفعالة سطحيا TW 80 ($X_1$) داخل المايسل باستخدام نموذج Rubingh وبينت النتائج ان جميع قيم $\beta^m$ كانت سالبة ماعدا القيمة عند الكسر المولي للمادة الفعالة سطحيا TW 80 ( $\alpha$0.9 =1) فكانت موجبة.

**الكلمات المفتاحية:** خليط ثنائي، مايسيلات مختلطة، الشد السطحي، توين 80.