

# EFFECT OF 1-ALKANOLS ON THE CRITICAL MICELLE CONCENTRATION OF SODIUM DODECYL BENZENE SULFONATE

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الخلاصة :

تستخدم طريقة الموصلية عند درجة حرارة قدرها (٢٥°م) لتعيين التركيز الجزئي الحرج (CMC) لصوديوم دودسيل بنزين سلفونيت (SDBS) ويوجد كميات قليلة من ألكانولات -١ (C<sub>1</sub>-C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>)؛ وجدنا أن CMC تتناقص خطياً مع ازدياد ألكانولات -١ المضافة (C<sub>a</sub>) وذلك عند تركيزات قليلة. ثم قمنا بتقدير قيم الميل الحدية (-ΔCMC/ΔC<sub>a</sub>) لكل غُول (كحول) مستخدم. واستخدمت قيم الميل هذه لحساب التغير في الطاقة الحرة ΔG°(CH<sub>2</sub>) للتحويل لكل مجموعة ميثيلين (CH<sub>2</sub>) من الماء إلى جزئيات (SDBS). كما قمنا بمناقشة تَدَوُّبِ ألكانولات -١ بواسطة SDBS من خلال الجزئيات المضافة وتفاعلها.

## ABSTRACT

The critical micelle concentration (CMC) of sodium dodecyl benzene sulfonate (SDBS) in the presence of small amounts of 1-alkanols (C<sub>1</sub>-C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>) was determined by the conductivity method at 25°C. The CMC decreases linearly with an increase in the concentration (C<sub>a</sub>) of the added 1-alkanols, within their low concentration ranges. The limiting slopes (-ΔCMC/ΔC<sub>a</sub>) were estimated from the straight lines for each alcohol. Using these slopes the standard free energy change of transfer per methylene (CH<sub>2</sub>) group, ΔG°(CH<sub>2</sub>), from water to SDBS micelles has been calculated. Solubilization of 1-alkanols by SDBS has been discussed in terms of additive-micelle hydrophobic interaction.

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### INTRODUCTION

The aqueous micellar solutions of surfactants are used as solvents for many oil soluble, water-insoluble, or sparingly soluble compounds. Micelle formation by the self-association of surfactant molecules, is an important phenomenon because a number of important interfacial phenomena, such as detergency and solubilization depend on the existence of micelles in solution [1]. The presence of micelle is reflected by the critical micelle concentration (*CMC*) of the surfactant. It is well-known that *CMC* is affected by the presence of organic additives in solution at a constant temperature [1].

Alcohols are interesting additives because their hydrophobicity is continuously changeable with their chain-length; also they are well-known to depress the *CMC* of surfactant solutions [2–6]. The ability of an additive to depress *CMC* depends upon the size and nature of the hydrocarbon portion of their molecules [5]. The alcohols are considered as co-surfactants and strengthen the hydrophobic bonding in the surfactant solution.

Previously, we reported the depression of *CMC* of cetyltrimethyl-ammonium bromide (CTAB) solutions by phenol and benzyl alcohol [7] and 1-alkanols [8]. Sodium dodecyl benzene sulfonate (SDBS) is the least studied anionic surfactant. The only reported *CMC* value of this surfactant in the literature is  $12 \times 10^{-4} \text{ mol dm}^{-3}$  at  $60^\circ\text{C}$  [9]. The temperature has a disaggregation effect on self-association of ionic surfactants, for temperature increase causes disruption of the structured water surrounding the hydrophobic groups, an effect that disfavor micellization and hence relatively higher reported value at  $60^\circ\text{C}$  would be understandable. The objective of the present work is to estimate the effect of 1-alkanols ( $C_1$ – $C_4$ ,  $C_6$ ,  $C_8$ ) on the *CMC* of SDBS at room temperature. The rate of decrease of *CMC* with additive concentration ( $-\Delta CMC/\Delta C_a$ ) has been used for the determination of the standard free energy change of transfer per methylene group,  $\Delta G^\circ(\text{CH}_2)$ , for 1-alkanols from water to SDBS micelles at  $25^\circ\text{C}$ .

### EXPERIMENTAL

#### Materials

Sodium dodecyl benzene sulfonate (SDBS) was the product of Fluka, whereas the additives, *i.e.*, methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol, and 1-octanol were obtained from E-Merck, Germany. All the compounds were of analytical grade and were used without further purification. Water was distilled three times and was doubly deionized.

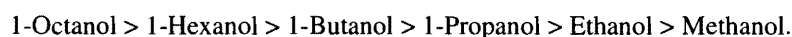
#### Conductance Measurements

The specific conductance of the SDBS solutions with and without additives (1-alkanols) were measured on a Microprocessor Conductivity Meter of WTW, model LF 2000/C at  $25 \pm 0.01^\circ\text{C}$ . During an experimental run the concentration of each additive was kept constant. The *CMCs* of the SDBS solutions were determined from plots of specific conductance *versus* the surfactant concentration ( $C_s$ ). The break point in the curve gives the *CMC* as shown in the Figure 1. Conductivity of the solutions changes markedly with change of temperature. Therefore, the temperature was kept constant at  $25^\circ\text{C}$  using a water thermostat to control the temperature to within  $\pm 0.1^\circ\text{C}$ . The solutions were stirred with a magnetic stirrer during the experiment.

An aqueous solution with a given concentration of alkanols was prepared and a portion of it was used for the preparation of surfactant solution ( $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ). A known amount of aqueous solution of additive was kept into the beaker placed in the water thermostat. From burette the surfactant solution already prepared using additive solution as solvent was successively added into the beaker. Conductivity cell was dipped into that beaker for the measurement of specific conductance. By this method the concentration of additives was kept constant while the concentration of surfactant was increased successively throughout the experiment.

### RESULTS AND DISCUSSION

The effect of various 1-alkanols is demonstrated by the depression in the *CMC* of SDBS solutions as a function of 1-alkanol concentration  $C_a$ , as shown in Figure 2. It is obvious that *CMC* reduces almost linearly with increasing  $C_a$  and the order of *CMC* depression is:



Shirahama [10] proposed that added alcohol molecules are partitioned between the bulk aqueous phase and the micellar phase due to the hydrophobic interaction between the solubilized alcohol molecules and the hydrocarbon part of the micelle. The straight chain alcohols are preferentially adsorbed at the interfacial region of the micelle. Adsorption of alcohols decrease the work required for micellization, by decreasing the mutual repulsions of the ionic heads of surfactant molecules. The long chain alcohols, most effective in reducing the *CMC*, when adsorbed at the surface are subjected to the lateral pressure tending to force them to inner portion of the core [11]. The straight chain alcohols, having smaller cross-sectional area, decrease the *CMC* of sodium dodecyl sulfate (SDS) more effectively than their branched chain analogs [12]. The *CMC* lowering is generally attributed to two factors: an increase in entropy of mixing of surfactant with the solubilized alkanols in micelles, and the decrease in the electrical work of micellization of the surfactant ion due to the decrease in the surface charge density caused by the solubilized alkanols [10, 13].

An obvious depression in the *CMC* in the case of more hydrophobic 1-alkanols, *i.e.*, 1-butanol, 1-hexanol, 1-octanol rather than that of less hydrophobic alcohols, *i.e.*, 1-propanol, ethanol, methanol, suggests that short chain alcohols are adsorbed mainly in the outer portion of the micelle close to the water micelle interface [5]. On the other hand, long chain alcohols may penetrate deeper into the interior of the micelle mainly due to the hydrophobic forces in operation [5,8,14]. Therefore, long chain alcohols induce micellization at lower SDBS concentration due to hydrocarbon–hydrocarbon interaction between the alcohol molecules and the surfactant molecules inside the micelles. Consequently, the hydrophobic interaction caused marked depression in *CMC* of SDBS.

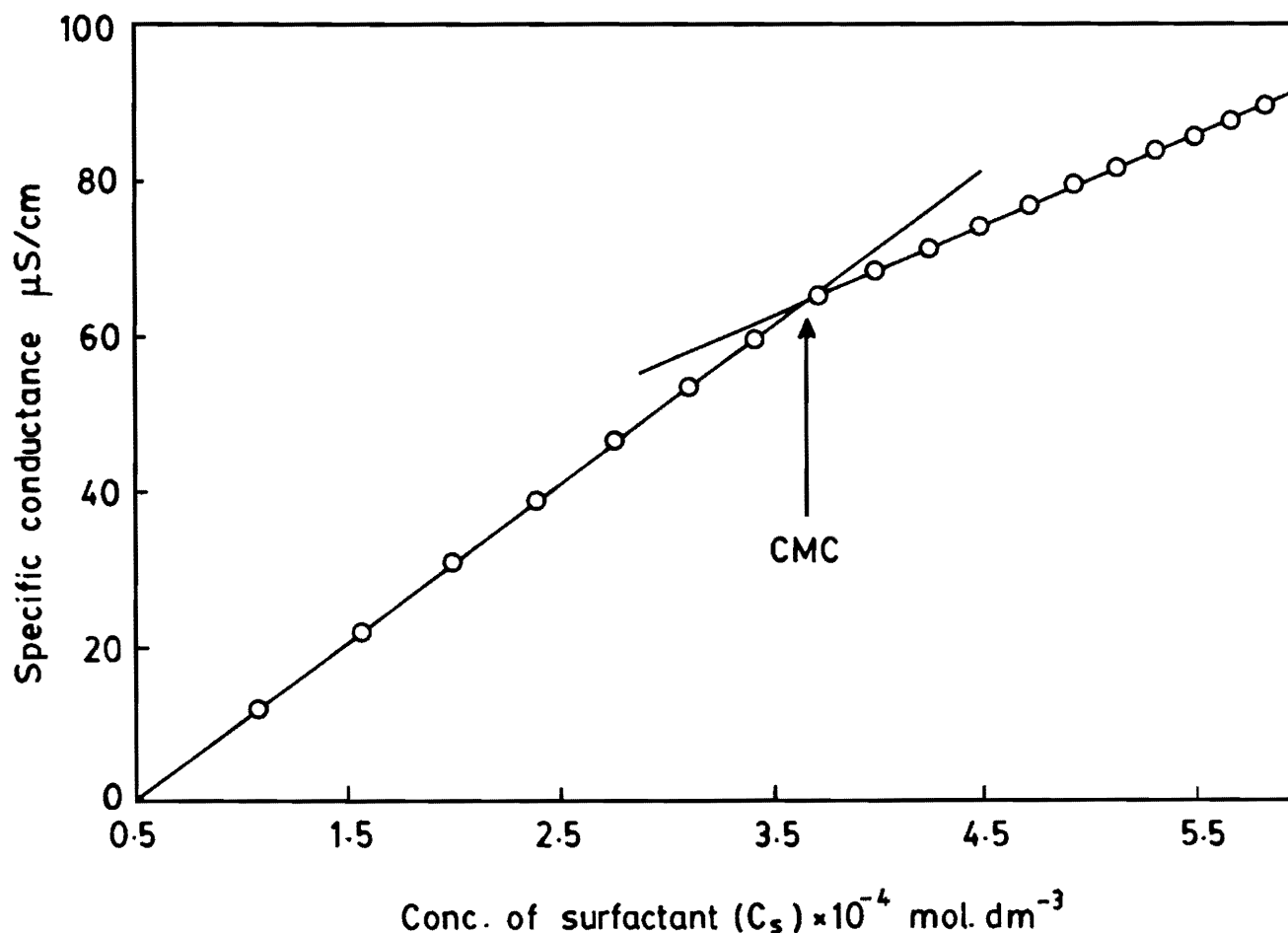


Figure 1. The Relationship Between Specific Conductance and Concentration of SDBS at 25°C.

The rate of CMC decrease versus concentration of each alcohol at limiting dilution, provides the slope  $(-\Delta CMC/\Delta C_a)$ . Table 1 lists  $\ln(-\Delta CMC/\Delta C_a)$  values, which show monotonic increases from methanol to 1-octanol. The standard free energy change of transfer per methylene ( $\text{CH}_2$ ) group,  $\Delta G^\circ(\text{CH}_2)$ , for 1-alkanols, from aqueous environment to micelle of SDBS is calculated by using a relationship proposed by Manabe and co-workers [15]:

$$\Delta G^\circ(\text{CH}_2) = -RT \, d \ln \left( -\frac{\Delta CMC}{\Delta C_a} \right) / dm$$

where  $R$  is the gas constant and  $T$  is absolute temperature. Figure 3 shows the plot of  $\ln(-\Delta CMC/\Delta C_a)$  versus  $m$  ( $m$  is the number of carbon atoms in the straight chain of 1-alkanol molecules), the slope of which provides the values of  $d \ln(-\Delta CMC/\Delta C_a)/dm$ . The value of  $\Delta G^\circ(\text{CH}_2)$  thus calculated from the above equation for the 1-alkanol-SDBS system is  $-2.36 \pm 0.05$  kJ/mol at 25°C. This is in good agreement with the reported value, *i.e.*,  $-2.51$  kJ/mol for the 1-alkanol-SDS system [15, 16].

The negative value of  $\Delta G^\circ(\text{CH}_2)$  indicates that the solubilization of 1-alkanols into micelles is a spontaneous phenomenon. The  $\Delta G^\circ(\text{CH}_2)$  value actually suggests that each methylene ( $\text{CH}_2$ ) group in a molecule of an alcohol contributes  $-2.36$  kJ/mol energy during the process of its solubilization in SDBS micelles. The energetic considerations may lead us to conclude that the shorter chain alcohols are located at micelle surface region but the longer chain alcohols may penetrate deeper and are incorporated into the inner core of the micelle. Consequently, the hydrocarbon part of the alcohol molecules plays a significant role in the solubilization process.

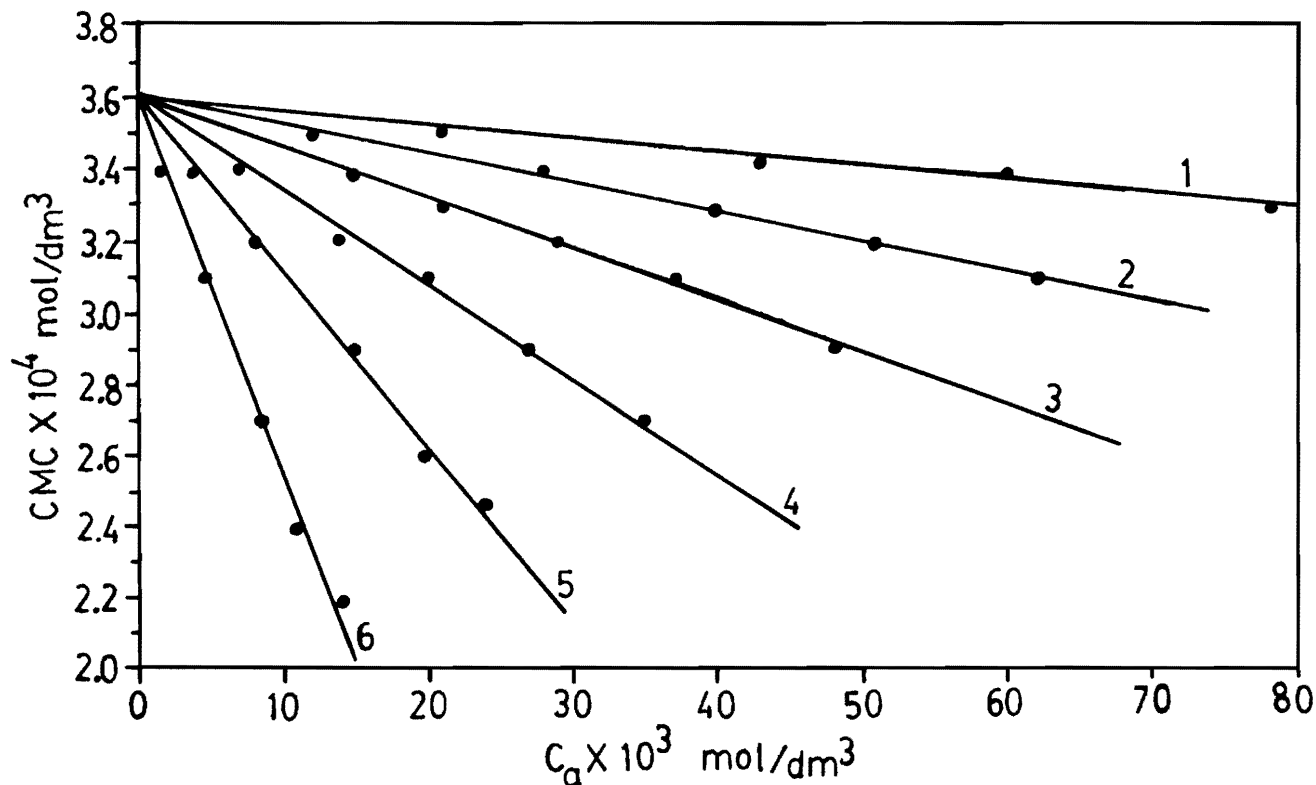
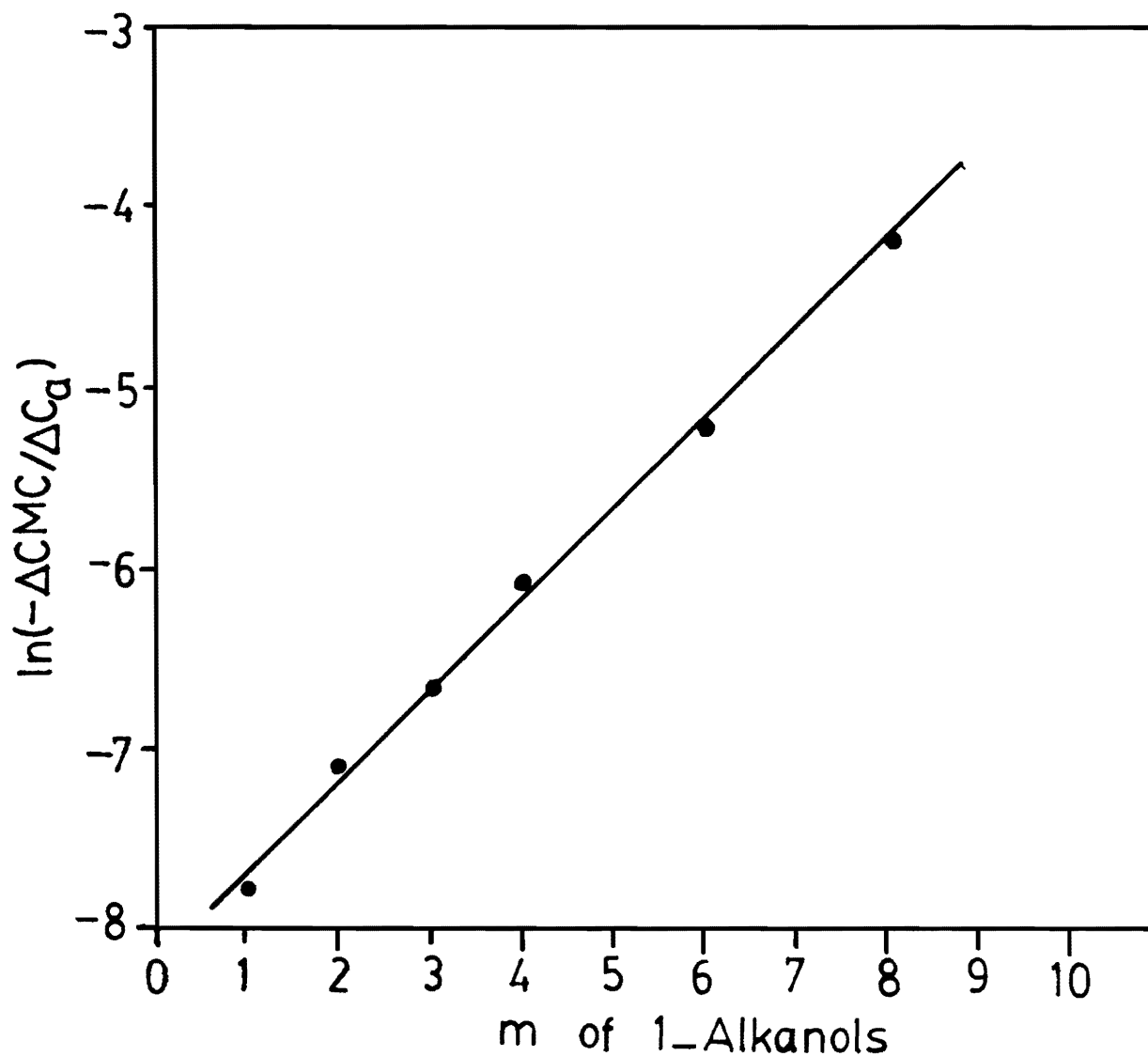


Figure 2. The Relationship Between CMC of SDBS and Concentration of 1-Alkanols ( $C_a$ ), at 25°C: (1) Methanol, (2) Ethanol, (3) 1-Propanol, (4) 1-Butanol, (5) 1-Hexanol, (6) 1-Octanol.

**Table 1. The Rate of CMC Depression of SDBS by 1-Alkanols of Varying Number of Carbon Atoms ( $m$ ) at 25°C.**

Additive	$m$	$\ln\left(-\frac{\Delta CMC}{\Delta C_a}\right)$
Methanol	1	-7.78
Ethanol	2	-7.11
1-Propanol	3	-6.03
1-Butanol	4	-6.03
1-Hexanol	6	-5.21
1-Octanol	8	-4.16

Figure 3. The Dependence of  $\ln(-\Delta CMC/\Delta C_a)$  on the Number ( $m$ ) of Carbon Atoms in 1-Alkanol Molecules at 25°C.

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