

Effect of 1-Alkanols on the Critical Micelle Concentration of Cetyltrimethyl Ammonium Bromide

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(Received 11th July, 1996, revised 21st October, 1996)

Summary: The interaction of 1-alkanols (C_1 - C_4 , C_5 and C_6) with cetyltrimethyl ammonium bromide (CTAB), a cationic surfactant, was studied by a conductivity method at 25.0°C. The critical micelle concentration (CMC) of CTAB decreased linearly with an increase in the concentration of added 1-alkanols within their low concentration regions. The water-micelle partition coefficient, K_x , and the standard free energy change of solubilization, ΔG° , of each alcohol from water to micelle were calculated from the limiting slopes, $\Delta CMC/\Delta C_a$. The free energy of transfer per methylene group, ΔG° (CH_2) has also been estimated. For 1-alkanols, K_x values increased linearly with the increase in the number of carbon atoms, m_n , in the alkyl chain of respective alcohols.

Introduction

Surfactants are characterized by a hydrophilic charged 'head' and a hydrophobic hydrocarbon 'tail.' The most outstanding property of the surfactants is their tendency to form large aggregates, the micelles, at sharply defined critical micelle concentration (CMC). The surfactant molecules associate themselves into micelles in such a manner that their hydrophobic tails tend to congregate and their hydrophilic head provide protection [1]. The physical behaviour of the surfactant micelles can be viewed as the construction of a model membrane system to mimic a biological system like a living cell. This experimental model is useful for studying the interaction of biological surfaces with the additive molecules. The presence of micelle is reflected by

the CMC, which is affected by organic additives in solution at a constant temperature [1-4].

Alcohols are amphiphilic in nature and their hydrophobicity is continuously changeable with chain length [1]. These hydrophobic portions of alcohol molecules are responsible for their distribution between the micelles of a surfactant and the surrounding aqueous solutions. It is known that the CMC lowering ability of the alcohols can be linked to the partition coefficient of the additive between the micelle and water [5-6].

The aim of the present work was to estimate the effect of various 1-alkanols i.e. Methanol, Ethanol, 1-Propanol, 1-Butanol, 1-Hexanol and 1-

Octanol on the CMC of CTAB and then utilizing CMC-depression data for the determination of water-micelle partition coefficient K_x , standard free energy change of solubilization ΔG° and the free energy change of transfer per methylene group $\Delta G^\circ(\text{CH}_2)$.

Results and Discussion

The values of CMC for CTAB obtained at 25°C in the presence of each of the six 1-alkanols are listed in Table-1. These are calculated by a break in specific conductivity vs surfactant concentration plots. The change in CMC of CTAB is shown as a function of 1-alkanol concentration (C_a), in Figure 1. The addition of 1-alkanols to both anionic and cationic micellar solutions is well known to depress CMC [6,8-12]. In the present study the order of CMC-depression is as follow: 1-Octanol > 1-Hexanol > 1-Butanol > 1-Propanol > Ethanol > Methanol.

Table-1: CMC of CTAB in presence of various concentration of 1-alkanols at 25.00°C.

$C_a \times 10^3$ mol/dm ³	CMC $\times 10^4$ mol/dm ³ (± 0.1)	$C_a \times 10^3$ mol/d m ³	CMC $\times 10^4$ mol/dm ³ (± 0.1)
Methanol		1-Butanol	
0	9.1	0	9.1
35	9.0	8	8.7
49	8.9	15	8.5
59	8.8	24	8.1
78	8.7	32	7.9
88	8.6	40	7.6
Ethanol		1-Hexanol	
0	9.1	0	9.1
20	8.9	5	8.4
30	8.8	10	7.8
41	8.7	15	7.1
50	8.6	20	6.6
65	8.4	25	6.2
1-Propanol		1-Octanol	
0	9.1	0	9.1
15	8.7	0.35	8.1
22	8.6	0.65	7.3
30	8.4	0.95	6.7
40	8.2	1.30	6.4
45	8.1	1.65	6.1

As the hydrophobicity of added 1-alkanol increases, the more marked depression on CMC is observed. The additive molecules are solubilized (partitioned) into the micellar phase of CTAB due to the hydrophobic interaction between the solubilized additive molecules and the hydrocarbon part of the micelle exposed to water which causes a

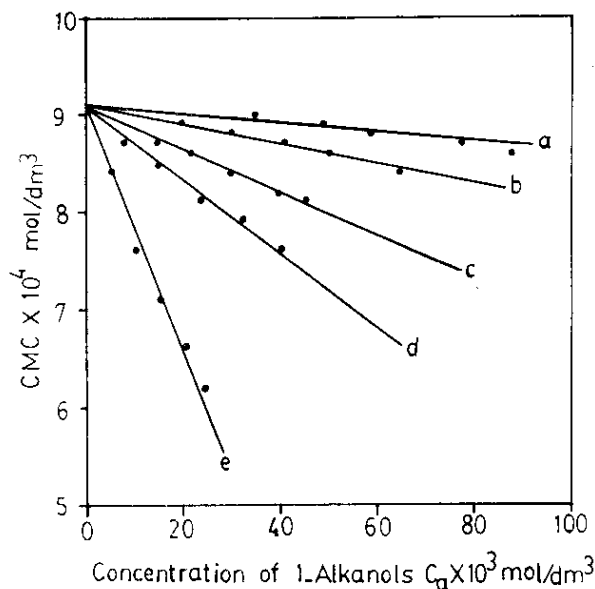


Fig. 1: Relation between CMC of CTAB and concentration of added 1-alkanols, (a)-Methanol, (b) Ethanol, (c) 1-Propanol (d) 1-Butanol, (e) 1-Hexanol at 25.00°C.

reduction of the free energy of the micelle, hence CMC decreases [1].

Fig. 1 also gives information about the standard free energy change of transfer per methylene group $\Delta G^\circ(\text{CH}_2)$. The slopes of the straight lines ($-\Delta\text{CMC}/\Delta C_a$) provides values for each alcohol, indicating a monotonous increase in the values of these slopes from methanol to 1-Octanol as given in Table-2. The $\Delta G^\circ(\text{CH}_2)$ from aqueous environment to CTAB micelle is calculated from the slope of the plot $\ln(-\Delta\text{CMC}/\Delta C_a)$ vs m_n where m_n is number of carbon atoms in alkyl chain of 1-alkanol molecule as illustrated in Fig. 2. The value of $\Delta G^\circ(\text{CH}_2)$ is determined by the Manabe and Koda equation [8]:

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

where R is the gas constant and T is absolute temperature. In our case $\Delta G^\circ(\text{CH}_2) = -2.25$ kJ/mol in CTAB system which shows a good agreement with the reported value i.e. -2.58 kJ/mol [12].

Table-2: The values of $\ln(-\Delta\text{CMC}/\Delta\text{Ca})$, m_n , K_x , and ΔG° of added 1-alkanols in CTAB solutions at $25.00^\circ\text{C} \pm 0.01$.

No.	Additive	m_n	$\ln(-\Delta\text{CMC}/\Delta\text{Ca})$	K_x	ΔG° kJ/mol
1.	Methanol	1	-8.17	28	-8.20
2.	Ethanol	2	-6.98	92	-11.12
3.	1-Propanol	3	-6.12	216	-13.26
4.	1-Butanol	4	-5.62	354	-14.55
5.	1-Hexanol	6	-4.20	1477	-18.09
6.	1-Octanol	8	-1.99	13378	-23.55

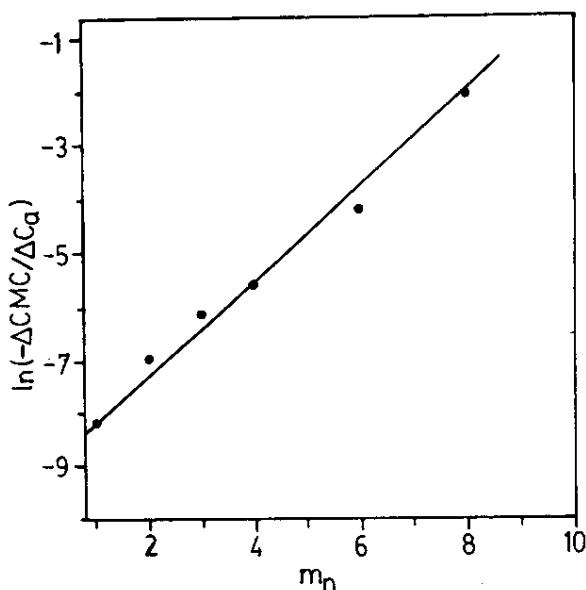


Fig. 2: Dependence of $\ln(-\Delta\text{CMC}/\Delta\text{Ca})$ on the chain length (m_n) of 1-alkanols hydrocarbon at 25.00°C .

Hayase and Hayano [6] suggested that 1-alkanols are solubilized and hence partitioned between surfactant micelles and bulk water phases, obeying the partition law. Shirahama and Kashiwabara [13] suggested a relation between the limiting slope ($-\Delta\text{CMC}/\Delta\text{Ca}$) and the partition coefficient, K , of additive between aqueous and micellar phases as:

$$K = \left(\frac{-\Delta\text{CMC}}{\Delta\text{Ca}} \right) / \theta \cdot \text{CMC}_0$$

where θ represents the interaction of the surfactant with the additive. Abu-Hamdiyyah [12] estimated θ value as 0.62 using conductivity method for CTAB-alkanols system. CMC_0 is the CMC of a surfactant

without additive, which was $9.1 \times 10^{-4} \text{ mol/dm}^3$. The ΔG° from bulk water micelle is given by

$$\Delta G^\circ = -RT \ln K_x$$

The K_x is represented as $K_x = K \cdot n_w$, where n_w is the number of moles of water per dm^3 (55.5 mol/dm^3). The values of K_x and ΔG° of 1-alkanols are given in Table-2. The K_x tends to increase with the hydrophobicity (m_n) of the 1-alkanols in the following order:

Methanol < Ethanol < 1-Propanol < 1-Butanol < 1-Hexanol < 1-Octanol. K_x values suggest that shorter chain alcohols are adsorbed mainly in the outer portion of the micelle close to the water-micelle interface. Similar behaviour has also been observed for CTAB-Phenol system [14] at 25.0°C . The longer chain alcohols (C_6 , C_8) may penetrate deeper into the interior of the micelle mainly due to the hydrophobic forces in operation. Similar type of hydrophobic interactions between sodium dodecyl benzene sulphonate (SDBS) micelles and hemicyanine dye has been found to be responsible for the dye's solubilization into SDBS micelles [15]. The deeper penetration of long chain alcohols (C_6 , C_8) into inner hydrocarbon core of the micelle, thus contribute not only to the decrease of the hydrocarbon-water contact region, but also to the increase of the hydrophobic interactions in the micellar core [16].

The standard free energy change of solubilization, ΔG° decreases linearly with an increase in the hydrophobicity (m_n) of 1-alkanols as illustrated in Fig. 3. The negative values of ΔG° indicate that these additives are solubilized preferably in the micelles of CTAB.

Experimental

Materials and equipments

The cetyltrimethyl ammonium bromide (CTAB) was the product of Fluka, Switzerland. Whereas, 1-alkanols (C_1 - C_4 , C_6 and C_8) were the products of E-Merck, Germany. All these compounds were of analytical grade and were used without further purification. A Microprocessor based conductivity meter of WTW model LF 2000/C, Germany and a Thermostat of Japan Coda Co. were used for experimental measurements.

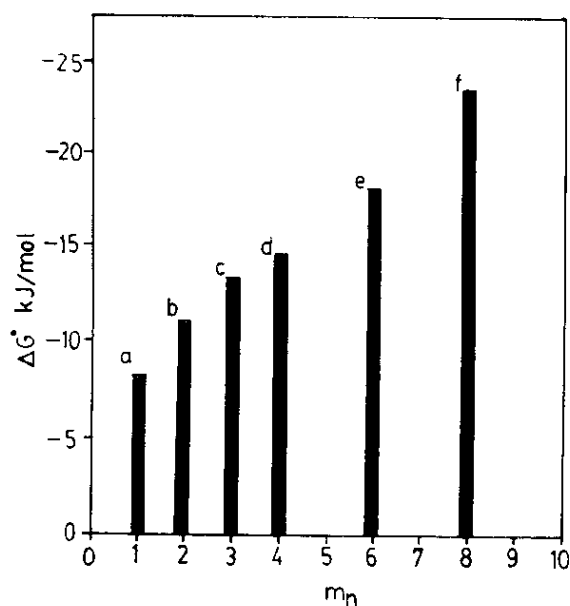


Fig. 3: The calculated values of standard free energy change of solubilization for added 1-alkanols in terms of chain length (m_n) at 25.00°C; (a) Methanol, (b) Ethanol, (c) 1-Propanol (d) 1-Butanol, (e) 1-Hexanol, (f) 1-Octanol.

Conductance measurements

The cell of Conductivity Meter was calibrated following the method of Fuoss and co-workers [7] using aqueous KCl solution in concentration range $2-30 \times 10^{-4}$ mol/dm³. Specific conductance of 18 (CTAB) solutions of concentration range from 1.4×10^{-4} to 14.2×10^{-4} mole/dm³ with and without additives was measured at $25.00 \pm 0.01^\circ\text{C}$. During each experimental run, concentration of the additive (alcohol) was kept constant. The CMC was determined from the plot of specific conductivity against concentration of the surfactant solutions.

Thermostat was used to control the temperature within $\pm 0.01^\circ\text{C}$.

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