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SHORT COMMUNICATION

INVESTIGATION OF 1-ALKANOLS IN ORGANISED SOLUTIONS

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ABSTRACT. Conductometric behaviour of 1-alkanols (C_5-C_{10}) in organised solutions of sodium dodecylbenzenesulfonate (SDBS) is investigated. Interaction of each alkanol with anionic surfactant is reflected in terms of association constants, K_c. It is observed that self-assembly of SDBS is induced by the alkanol addition. The depression in critical micelle concentration (CMC) of SDBS caused by each alkanol is translated to partition coefficient, K_c by using interaction coefficient. The dimensionless partition coefficient, K_x is utilized to highlight the energy efficiency of the solubilization process. The results indicate that even longer chain alkanols prefer interfacial area for their residence. The relative solubility of each alkanol is enhanced with increasing SDBS concentration. Such basic information could be vital for development of nano-scale assemblies for specific delivery of water soluble drugs.

KEY WORDS: SDBS, Alcohols, Partition coefficient, Relative solubility, Conductometry

INTRODUCTION

Surfactants possess a peculiar property of self-assembly at certain concentration, termed as the critical micelle concentration (CMC). Owing to this unique property, they are assumed to have played a significant role in the origin of life [1]. The presence of water soluble surfactants affects the self aggregation of amphiphiles and hence limits their capability as drug-delivery systems [2].

Organic additives in small amount might produce significant alterations in the aggregation of surfactant monomers, and hence the information regarding the effect of organic additives has significance for theoretical as well as practical purposes. The change in critical micelle concentration of surfactant is either due to incorporation of additives into micelles or as result of modification of solvent-micelle or solvent-surfactant interactions. This causes change in water structure [3]. A physical model based on the distribution of non-ionic amphiphiles such as alkanols, between water and micellar phase may provide an insight into bioaccumulation, toxicity and distribution among environmental compartments [4]. Additionally, it could allow mimicking protein folding, which has certain significance for protein conformational diseases such as Alzheimer's [5]. The change in CMC caused by an additive can be utilized for determination of partition coefficient of solute [6, 7]. Our previous work includes the investigation of surfactant-dye aggregates by conductometry and spectroscopic analysis [8-11]. The present study describes the interaction of 1-alkanol with SDBS, relatively less focused area of the widely studied surfactant-alkanol interaction [12-20]. The involvement of each alkanol in the formation of mixed aggregates is reflected in terms of relative solubility *(S_r/S_o).* The basic information obtained from the interaction of alcohols with surfactant allows for development of assemblies on small scale for specific delivery of drugs.

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EXPERIMENTAL

Chemicals. Sodium dodecylbenzenesulfonate (> 85%) was obtained from Fluka (Switzerland). 1-Alkanols were the product of MP Biomedicals (China). All chemicals were used as received. Water was distilled twice and deionized prior to measurements.

Methods and measurements. The specific conductance of SDBS solution with and without 1-alkanol was measured on a Microprocessor conductivity meter of WTW, Model LF/2000C (Germany) at 25 ^{o}C. The conductivity meter was calibrated by a method reported by Lind *et al.* [21]. The concentration of each alkanol was kept constant during an experimental run. The specific conductance was recorded as a function of surfactant concentration. A thermostat of Koda Co. (Japan) was used to allow for temperature fluctuations in the range of mere ±0.01 ^{o}C. The critical micelle concentration of each batch was determined by plotting specific conductance against the surfactant concentration, C_s (Figure 1).

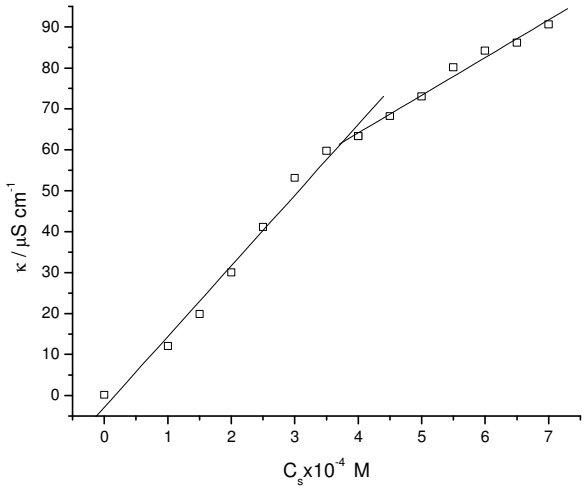

Figure 1. Specific conductance as a function of SDBS concentration.

RESULTS AND DISCUSSION

The binding affinity between Alkanol (A) and surfactant (S) in micellar solution can be represented by association equilibrium

$$nA + S_m \rightleftarrows A_nS_m$$

where "n" alcohols molecules are associated with a micelle comprising "m" surfactant monomers.

The critical micelle concentration of SDBS was obtained by plotting specific conductance of surfactant solution as a function of SDBS concentration. The CMC was found to be 3.77 x 10^{-4} M at 25 ^{o}C (Figure 1). A comparative analysis of CMCs of SDBS is given in Table 1 [22-25]. In each case the alkanol addition induced self-assembly of the surfactant earlier than the critical

micelle concentration. The linear relationship between CMC of SDBS and additive concentration gives $\Delta CMC/\Delta C_a$. The depression of CMC of surfactant caused by alkanol, determined as a ratio of change in CMC of SDBS (ΔCMC) to change in additive concentration (ΔC_a) is shown in Table 2 (i.e., -*k*). The negative value of *k* reflects a decrease in CMC. This is due to reduction in electric work of micellization as a result of decrease in repulsion between the surfactant head group caused by alkanols' presence. The small change in CMC can be understood keeping in view the fact that small amount of additive is not likely to significantly alter the macroscopic physical property of the surfactant system.

Table 1. Critical micelle concentration of sodium dodecylbenzenesulfonate at different temperatures.

Temperature (^oC)	CMC x 10^{-4} M	Reference
25	3.77	This work
25	3.60	22
25	6.30	23
60	12.0	24
25	4.10	25

The depression in CMC can be translated to micelle-water partition coefficient, K_c through an interaction parameter, I_s as [26]

$$K_c = k / I_s.CMC_o \quad (1)$$

where CMC_o is the critical micelle concentration of surfactant in the absence of alkanols.

The interaction parameter is independent of the chain length of alkanol in the case of sodium dodecyl sulfate [27] and we assume the same is true in our case. Shah *et al.* reported I_s for SDBS equal to 0.84 [23], which is considered valid for alkanol-SDBS systems investigated in the present study. The interpretation of I_s has been given by Manabe *et al.* [28] and Abu-Hamdiyaah *et al.* [29].

It is apparent from the values of micelle water partition coefficients, K_c given in Table 2 that higher alkanols are more efficiently involved in formation of mixed aggregates with the surfactant. There is steep increase in K_c for 1-octanol, 1-nonanol and 1-decanol. This is due to self aggregation tendency of these alkanol, which allow them to align along the polarity gradient offered by anionic micelles of SDBS. Owing to their lower hydrophobicity, smaller chain alkanols get adsorbed in the interfacial area. Electrical conductivity and isentropic conductivity of 1-hexanol in NaDS reported elsewhere [30] identifies an initial increase in conductivity as well as compressibility with the hexanol content. This is due to alignment of hexanol into anionic micelles along a polarity gradient. The existence of polar head group of alkanols in the interfacial area causes the release of counter ions, hence the conductivity of solution continues to increase [31, 32]. Alkanols are more compressible in hydrocarbon like environment than in bulk water, hence the increased compressibility also reflects an increased solubilization into hydrocarbon like interior of the micelles, however during such process, there is no further change in charge density at the micellar surface with upon alkanol addition, i.e. the value is conductivity becomes constant [33, 34]. The phenomenon is expected to be more prominent with higher alkanols. Though the longer chain alkanols are expected to make their way deeper into the micelles, they also caused an enhancement in conductivity, showing their presence at the micellar surface. As the chain length increases, the disruption of water structure occurs and there is spontaneous transfer of alkanols to micellar phase. In order to ascertain the energy efficiency of the process, free energy change of transfer of alkanol from bulk aqueous to micellar phase is computed by using dimensionless partition coefficient, K_x.

$$\Delta G^o = - RTlnK_x \quad (2)$$

where $K_x = K_c n_W$ and n_W is the no of moles of water present per cubic decimeter of solution.

Table. 2. Quantitative-parameters for SDBS-alkanol interaction.

Additive	-*k*	ln(dCMC/dC$_a$)	K_c (M^{-1})	K_x	K_x[b]
1-Pentanol	0.0048	-5.34	15.1	839	944
1-Hexanol	0.0055	-5.21[a]	17.7	981	2440
1-Heptanol	0.0076	-4.88	24.0	1330	6440
1-Octanol	0.0156	-4.16[a]	49.3	2730	16300
1-Nonanol	0.0240	-3.73	75.7	4200	n.a.
1-Decanol	0.0441	-3.12	139	7740	n.a.

[a]Ref. [22]. [b]values for SDS [38]. n.a. : not available.

The comparison between ΔG^o for 1-alkanols is portrayed as Figure 2. The negative values of ΔG^o are indicative of the spontaneity of the solubilization process, where the transfer of higher analogues is more energy efficient.

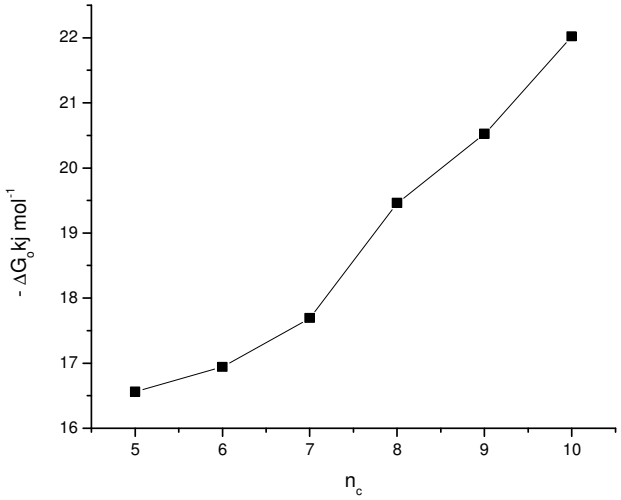

Figure 2. Dependence of free energy change of transfer of alkanols to SDBS micelles on number of carbon atoms in 1-alkanol (n_C).

Figure 3 shows the effect of micellar concentration of sodium dodecylbenzenesulfonate on relative solubility of 1-alkanols. Greater amount of each alkanol is solubilized at higher micellar concentration, [M]. Since relative solubility is dependent on partition equilibrium constant, K_x, the alkanol with higher K_x apparently shows a greater value for S_t/S_o [35]

$$S_t/S_o = 1 + K_x \nu[M] \quad (3)$$

where [M] is micellar concentration, and ν is the partial molal volume computed from the following relationship

$$\nu = N_A (N_{agg} A)^{1.5} (1/6\pi^{0.5}) \quad (4)$$

where N_A is the Avogardro's constant, N_{agg} is the micellar aggregation number [36] and A is the area per molecule of surfactant at surface saturation [37].

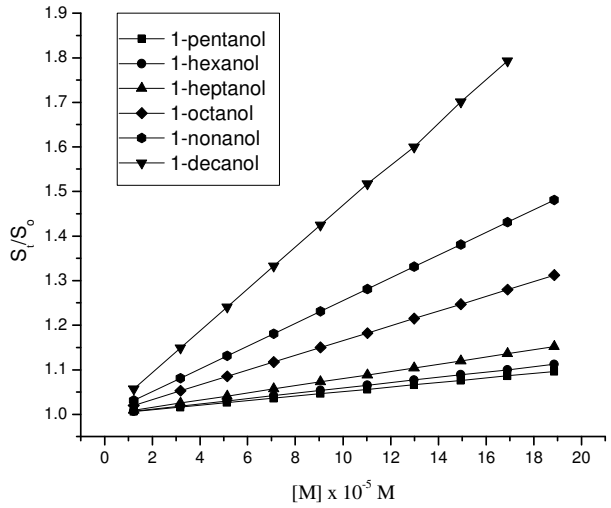

Figure 3. Relative solubility of 1-alkanols as a function of micellar concentration.

The extent of partitioning of 1-alkanols depends upon their hydrophobicity. At low additive concentration, the more hydrophobic members of the series are likely to orient in a way that their polar head groups are present in the palisade layer, while their hydrophobic tails interact with the non-polar core of the surfactant. Due to congestion, some coiling might also occur at higher alkanol concentration, since the volume of micellar core is smaller compared to surface. The change in conductivity upon alkanol addition suggests that all the additives spend most of their residence time in the interfacial area. The K_x values for 1-alkanols in SDS [38] are significantly high for equally hydrophobic members investigated in the present study showing a more efficient formation of mixed aggregates with SDS that lacks aromatic moiety. It is possible to control the size of these mixed aggregates and utilize them for delivery of water soluble drugs [39].

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