J Surfact Deterg (2011) 14:31–35
DOI 10.1007/s11743-010-1212-9

ORIGINAL ARTICLE

# Synthesis, Characterization and Surface Properties of Series Sulfobetaine Surfactants

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Received: 1 March 2010 / Accepted: 6 May 2010 / Published online: 5 June 2010

**Abstract** A series of surface active sulfo-propane betaines and sulfo-butane betaines were synthesized with high yields by the reaction of an appropriate *N*,*N*-dimethyl alkylamine with an excess of 1,3-propane sultone and 1,4-butane sultone. The structures were characterized by $^1$H-NMR spectroscopy and elemental analysis. The micellar properties of these compounds were determined by surface tension methods. Surface tension measurements also provide information about the dependence of the surface tension at the CMC ($\gamma_{cmc}$), p$C_{20}$ (negative logarithm of the surfactant molar concentration $C_{20}$ required to reduce the surface tension by 20 mN/m), the surface excess ($\Gamma_{max}$) at air/solution interface, the minimum area per surfactant molecule at the air solution interface ($A$).

**Keywords** Zwitterionic surfactants · Critical micelle concentration · Surface tension

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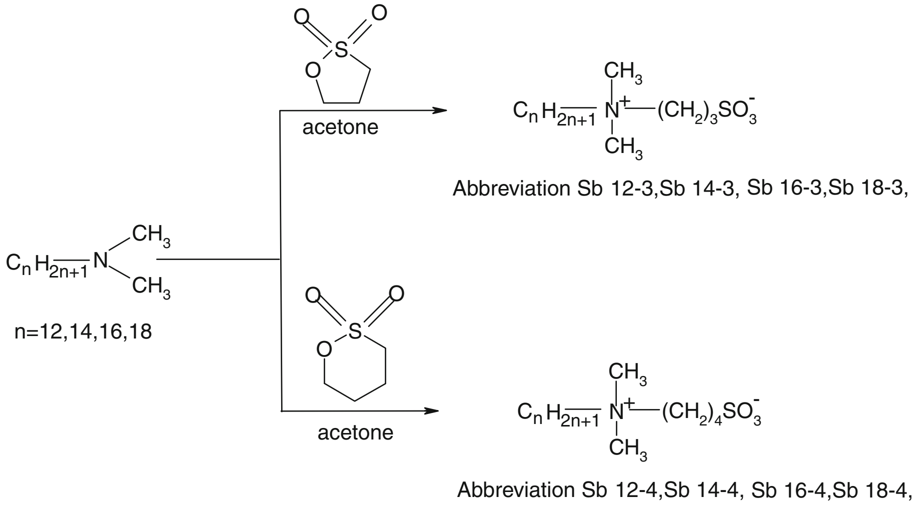
## Introduction

Zwitterionic surfactants, which contain both positively and negatively charged head groups, are interesting molecules because of their many unique properties. In general, they are mild to the skin and eyes, exhibit low toxicity, display excellent water solubility, broad isoelectric ranges, high foam stability, and resistance to hard water and to degradation by oxidizing and reducing agents [1, 2]. Also, changes in temperature, pH, and added electrolyte have been found to have minimal effects on zwitterionic surfactants. Despite these desirable properties, their high production cost, in comparison with other classes of surfactants, limits their industrial use [3].

Betaines are an important kind of zwitterionic surfactants and are widely used as boosters because they stabilize foams against the antifoaming action of the oil droplets contained in commercial hair conditioners or shampoos [4]. Moreover, these surfactants reduce the irritation action of the surfactants on the eyes and skin [5]. In spite of the wide applications of betaine surfactants and their increasing commercial use, it is clear from the literature, that their theoretical aspects have received far less attention than those of nonionic or ionic surfactants, especially on the synthesis and basic air–water interface properties of sulfopropane betaines and sulfo-butane betaines have not been reported systematically.

In the present work, four kinds of sulfo-propane betaines $H\text{-}(CH_2)_mN^+(CH_3)_2(CH_2)_3SO_3^-$ with $m = 12,14,16,18$ and four kinds sulfo-butane betaines $H\text{-}(CH_2)_nN^+(CH_3)_2(CH_2)_4SO_3^-$ with $n = 12,14,16,18$ of high purities were synthesized and their basic air–water interface properties studied. The synthesis route, chemical structures and abbreviations of these surfactants are shown in Scheme 1.



**Scheme 1** Synthesis routes of sulfo-propane betaines and sulfo-butane betaines

## Experimental Procedures

### Materials

Dimethyldodecan-1-amine, dimethyltetradecan-1-amine, dimethylhexadecan-1-amine, dimethyloctadecan-1-amine were from the Kangmanlin Chemical Industry Company (Nanjing Jiangsu Province, China) and used without further purification. 1,3-Propane sultone, 1,4-butane sultone were from the Haiqu Chemical Company (Shanghai China). Acetone and methanol were purchased from the Kemiou Chemicals Company (Tian Jin China). All solvents were distilled prior to use. The synthesis routes of sulfo-propane betaines and sulfo-butane betaines were similar to each other, therefore, we will describe only the synthesis procedure of Sb 12-3.

### Synthesis of Sb 12-3

1,3-Propane sultone (0.25 mol) was dissolved in 50 ml acetone and added to a stirred solution of dimethyldodecan-1-amine (0.05 mol) in 50 ml acetone, and the mixture was refluxed for over 12 h. The end product Sb 12-3 was produced as white solids; the solids were filtered and washed with acetone, and then recrystallized from mixtures of acetone and methanol. The solvent was evaporated under reduced pressure. The yields were analyzed by a Perkin Elmer Series II 2400 instrument with the following results. Sb 12-3 had 89.67%, the yields for Sb 14-3, Sb 16-3 and Sb 18-3 were 92.55, 95.48 and 98.21%; similarly the yields of Sb 12-4, Sb 14-4, Sb 16-4 and Sb 18-4 were 96.96, 96.60, 97.84 and 94.29%, respectively.

### Analytical Methods

$^1$H-NMR spectra were obtained with a Bruker FT-200 spectrometer using $D_2O$ as solvent. Chemical shifts ($\delta$) were reported in ppm related to internal tetramethylsilane.

The surface tension was measured by the drop-volume technique with a water thermostat control with a temperature of 298 ± 0.1 K. The time scale for one drop was 3–50 min depending on the time required to attain equilibrium. The surface tension was then measured three times for each sample within a 3–50 min interval between each reading to ensure equilibrium data. The surface tension ($\gamma$) is given by $\gamma = FV\Delta\rho g/R$, where $R$ is the tip's radius, $\Delta\rho$ the difference of the two phases, $g$ the local gravity acceleration, $V$ the volume of one drop, $F$ $(R/V)^{1/3}\Delta\rho g/R$ is a correction factor which accounts for the nonsphericity of the drop. Each surface tension value was determined from the average at least five measurements. According to the Gibbs law applied to equilibrium systems, the adsorption of surfactant at the gas/liquid interface leads to a reduction in the surface tension of the solution. The surface excess concentration, $\Gamma$ and the surface area $A$, per surfactant was calculated using the Gibbs equation $\Gamma = -(1/nRT)\ (\delta\gamma/\delta \ln C)_T = 1/AN_A$, where $R$ is the gas constant and $T$ the temperature in Kelvin, and $n$ is a constant dependent upon the number of individual ions comprising the surfactant, for zwitterionic surfactants $n$ is taken as 1. $pC_{20}$ is the negative of the logarithm of the surfactant concentration in the bulk phase required to produce a 20 mN/m reduction in the surface tension of the solvent.

## Results and Discussion

### $^1$H-NMR Characterization of the Products

The structures of sulfo-propane betaines and sulfo-butane betaines were confirmed by $^1$H spectral analyses and elemental analysis.

SB 12-3 $^1$H NMR [300 MHz, ($CDCl_3$)] $\delta = 0.754$–$0.842$ (t,3H, –$CH_3$), $\delta = 1.135$–$1.370$ (m,18H, –$(CH_2)_9$–), $\delta = 1.620$–$1.723$ (m,2H, –$\mathit{CH_2}CH_2$–$N^+$), $\delta = 2.060$–$2.158$

(m,2H, $\mathrm{N^+{-}CH_2}\mathit{CH_2}\mathrm{CH_2{-}}$), $\delta = 2.824$–$2.892$ (t,2H, $\mathrm{{-}CH_2}\mathit{CH_2}\mathrm{{-}N^+}$), $\delta = 2.981$–$3.088$ (s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.201$–$3.264$ (t,2H, $\mathrm{N^+{-}}\mathit{CH_2}\mathrm{CH_2CH_2{-}}$), $\delta = 3.352$–$3.441$ (t,2H, $\mathrm{N^+{-}CH_2CH_2}\ \mathit{CH_2}\mathrm{{-}}$);

Elemental analysis for SB 12-3: Calculated C 60.90%, H 11.04%, N 4.17%; Found: C 60.95%, H 11.31%, N 4.21%.

SB 14-3 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.728$–$0.846$ (t,3H, $\mathrm{{-}CH_3}$),$\delta = 1.036$–$1.361$ (m,22H, $\mathrm{{-}(CH_2)_{11}{-}}$), $\delta = 1.598$–$1.732$ (m,2H, $\mathrm{{-}}\mathit{CH_2}\mathrm{CH_2{-}N^+}$), $\delta = 2.049$–$2.168$ (m,2H, $\mathrm{N^+{-}CH_2}\mathit{CH_2}\mathrm{CH_2{-}}$), $\delta = 2.792$–$2.879$ (t,2H, $\mathrm{{-}CH_2}\mathit{CH_2}\mathrm{{-}N^+}$), $\delta = 2.982$–$3.101$ (s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.188$–$3.283$ (t,2H, $\mathrm{N^+{-}}\mathit{CH_2}\mathrm{CH_2CH_2{-}}$), $\delta = 3.362$–$3.465$ (t,2H, $\mathrm{N^+{-}CH_2CH_2}\mathit{CH_2}\mathrm{{-}}$).

Elemental analysis for SB 14-3: Calculated C 62.81% H 11.29% N 3.86%; Found: C 62.85%, H 11.35%, N 3.90%.

SB 16-3 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.704$–$0.835$ (t,3H, $\mathrm{{-}CH_3}$), $\delta = 1.108$–$1.380$ (m,26H, $\mathrm{{-}(CH_2)_{13}{-}}$), $\delta = 1.615$–$1.746$(m,2H, $\mathrm{{-}}\mathit{CH_2}\mathrm{CH_2{-}N^+}$), $\delta = 2.037$–$2.178$ (m,2H, $\mathrm{N^+{-}CH_2}\mathit{CH_2}\mathrm{CH_2{-}}$), $\delta = 2.769$–$2.882$ (t,2H, $\mathrm{{-}CH_2}\mathit{CH_2}\mathrm{{-}N^+}$), $\delta = 2.966$–$3.098$ (s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.173$–$3.314$ (t,2H, $\mathrm{N^+{-}}\mathit{CH_2}\mathrm{CH_2CH_2{-}}$), $\delta = 3.314$–$3.464$ (t,2H, $\mathrm{N^+{-}CH_2CH_2}\ \mathit{CH_2}\mathrm{{-}}$);

Elemental analysis for SB 16-3: Calculated C 64.45% H 11.51% N 3.58%; Found: C 64.55%, H 11.57%, N 3.60%.

SB 18-3 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.757$–$0.865$ (t,3H, $\mathrm{{-}CH_3}$), $\delta = 1.153$–$1.375$(m,30H, $\mathrm{{-}(CH_2)_{15}{-}}$), $\delta = 1.671$–$1.778$ (m,2H, $\mathrm{{-}}\mathit{CH_2}\mathrm{CH_2{-}N^+}$), $\delta = 1.861$–$1.927$(m,2H, $\mathrm{N^+{-}CH_2}\mathit{CH_2}\mathrm{CH_2{-}}$), $\delta = 2.552$–$2.618$ (t,2H, $\mathrm{{-}CH_2}\mathit{CH_2}\mathrm{{-}N^+}$), $\delta = 2.799$–$2.939$ (s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.046$–$3.104$ (t,2H, $\mathrm{N^+{-}}\mathit{CH_2}\mathrm{CH_2CH_2{-}}$), $\delta = 3.219$–$3.326$ (t,2H, $\mathrm{N^+{-}CH_2CH_2}\ \mathit{CH_2}\mathrm{{-}}$).

Elemental analysis for SB 18-3: Calculated C 65.87% H 11.69% N 3.58%; Found: C 65.92%, H 11.71%, N 3.60%.

SB 12-4 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.710$–$0.857$ (t,3H, $\mathrm{{-}CH_3}$), $\delta = 1.094$–$1.388$ (m,18H, $\mathrm{{-}(CH_2)_9{-}}$), $\delta = 1.584$–$1.886$ (m,6H, $\mathrm{{-}(CH_2)_9{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}N^+CH_2(}\mathit{CH_2}\mathrm{)_2\ CH_2{-}}$), $\delta = 2.760$–$2.915$ (t,2H, $\mathrm{{-}(CH_2)_9{-}CH_2{-}}\mathit{CH_2}\mathrm{N^+}$), $\delta = 2.915$–$3.102$ (s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.102$–$3.323$ (t,4H, $\mathrm{{-}N^+CH_2(CH_2)_2}\mathit{CH_2}\mathrm{{-}SO_3{}^-}$).

Elemental analysis for SB 12-4: Calculated C 61.89% H 11.17% N 4.01%; Found: C 61.95%, H 11.75%, N 4.10%.

SB 14-4 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.713$–$1.035$(t,3H, $\mathrm{{-}CH_3}$), $\delta = 1.035$–$1.544$(m,22H, $\mathrm{{-}(CH_2)_{11}{-}}$), $\delta = 1.561$–$1.952$(m,2H + 4H, $\mathrm{{-}(CH_2)_{11}{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}N^+CH_2\ (}\mathit{CH_2}\mathrm{)_2CH_2{-}}$), $\delta = 2.716$–$2.902$ (t,2H, $\mathrm{{-}(CH_2)_{11}{-}CH_2{-}}\mathit{CH_2}\mathrm{N^+}$), $\delta = 2.902$–$3.140$(s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.140$–$3.361$(t,4H, $\mathrm{{-}N^+CH_2(CH_2)_2}\mathit{CH_2}\mathrm{{-}SO_3{}^-}$).

Elemental analysis for SB 14-4: Calculated C 63.66% H 11.41% N 3.71%; Found: C 63.75%, H 11.55%, N 3.80%.

SB 16-4 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.512$–$0.883$ (t,3H, $\mathrm{{-}CH_3}$), $\delta = 0.883$–$1.569$ (m,26H, $\mathrm{{-}(CH_2)_{13}{-}}$), $\delta = 1.569$–$1.916$ (m,2H + 4H, $\mathrm{{-}(CH_2)_{13}{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}N^+CH_2(}\mathit{CH_2}\mathrm{)_2CH_2{-}}$), $\delta = 2.543$–$2.882$ (t,2H, $\mathrm{{-}(CH_2)_{13}{-}CH_2{-}}\mathit{CH_2}\mathrm{N^+}$), $\delta = 2.882$–$3.129$ (s,6H, $\mathrm{{-}(CH_2)_{13}{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}N^+CH_2(}\mathit{CH_2}\mathrm{)_2CH_2{-}}$), $\delta = 3.129$–$3.360$ (t,4H, $\mathrm{{-}N^+CH_2\ (CH_2)_2}\mathit{CH_2}\mathrm{{-}SO_3{}^-}$);

Elemental analysis for SB 16-4: Calculated C 65.19% H 11.60% N 3.46%; Found: C 65.32%, H 11.67%, N 3.56%.

SB 18-4 $^1$H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.769$–$0.830$(t,3H, $\mathrm{{-}CH_3}$), $\delta = 1.128$–$1.337$(m,30H, $\mathrm{{-}(CH_2)_{15}{-}}$), $\delta = 1.626$–$1.862$(m,2H + 4H, $\mathrm{{-}(CH_2)_{15}{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}N^+CH_2\ (}\mathit{CH_2}\mathrm{)_2CH_2{-}}$), $\delta = 2.797$–$2.858$(t,2H, $\mathrm{{-}(CH_2)_{15}{-}CH_2{-}}\ \mathit{CH_2}\mathrm{N^+}$), $\delta = 2.989$–$3.094$(s,6H, $\mathrm{N^+(CH_3)_2}$), $\delta = 3.182$–$3.313$(t,4H, $\mathrm{{-}N^+CH_2(CH_2)_2}\mathit{CH_2}\mathrm{{-}SO_3{}^-}$).

Elemental analysis for SB 18-4: Calculated C 66.51% H 11.78% N 3.23%; Found: C 66.62%, H 11.85%, N 3.26%.

The results of $^1$H NMR and elemental analysis indicated a high level of purity for all products.

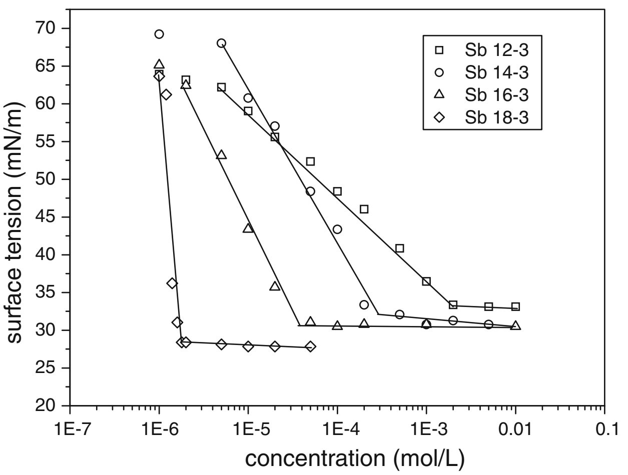


**Fig. 1** Plot of surface tension versus sulfo-propane betaine concentration

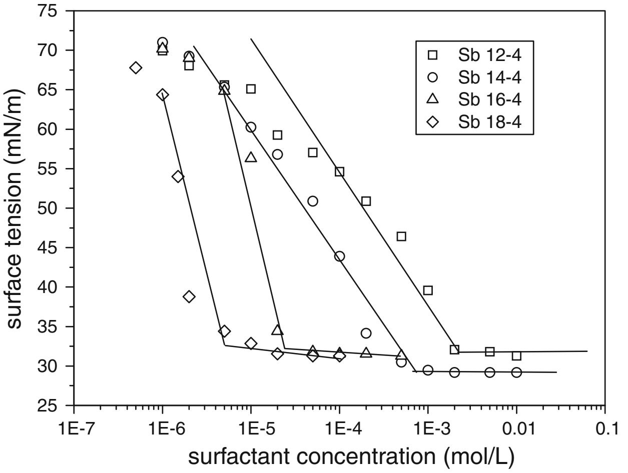


**Fig. 2** Plot of surface tension versus sulfo-butane betaine concentration

**Table 1** Calculated parameters of sulfo-propane betaines and sulfo-butane betaines from equilibrium surface tension

| Surfactant | CMC (M) | $\gamma_{\mathrm{CMC}}$ (mN m$^{-1}$) | $\Gamma$ ($10^{-10}$ mol/cm$^2$) | *A* (nm$^2$) | pC$_{20}$ |
|---|---|---|---|---|---|
| Sb 12-3 | 1.61E−03 | 32.79 | 1.59 | 1.05 | 4.910 |
| Sb 14-3 | 3.77E−04 | 31.84 | 3.32 | 0.50 | 4.485 |
| Sb 16-3 | 2.90E−05 | 30.46 | 3.85 | 0.43 | 5.517 |
| Sb 18-3 | 1.54E−06 | 28.06 | 31.8 | 0.05 | 5.945 |
| Sb 12-4 | 2.20E−03 | 31.48 | 4.17 | 0.40 | 3.518 |
| Sb 14-4 | 2.80E−04 | 29.68 | 3.96 | 0.42 | 4.540 |
| Sb 16-4 | 2.30E−05 | 32.06 | 10.95 | 0.15 | 4.957 |
| Sb 18-4 | 2.15E−06 | 31.83 | 42.02 | 0.04 | 5.752 |

## Equilibrium Surface Tension Measurements of Sulfo-Propane Betaines and Sulfo-Butane Betaines

Surface tension behaviors of sulfo-propane betaine and sulfo-butane betaine surfactants were investigated using the drop-volume technique. All samples were prepared using double distilled water as the solvent. All solutions were clear and homogeneous at the measurement temperature. The variation of the surface tension ($\gamma$) with the surfactant concentration ($c$) was determined and the results are presented in a semi-logarithmic plot, in Figs. 1 and 2.

These figures show that the surface tension values of sulfo-propane betaines and sulfo-butane betaines decrease rapidly when increasing the surfactant concentration before reaching a plateau. A break is shown at a concentration corresponding to the critical micelle concentration (CMC). The parameters obtained from equilibrium surface tension measurements are listed in Table 1. Comparing the sulfo-propane betaines and sulfo-butane betaines, the normal trends of a decreasing CMC with increasing alkyl chain length is observed. The CMC decreases monotonously with the number of hydrocarbon groups because of increased molecular hydrophobic moiety.

The surface excess $\Gamma$ at the air–water interface was calculated by applying the Gibbs adsorption isotherm equation. The area per molecule at the interface was estimated from the corresponding value of $\Gamma$. Table 1 summarized the CMC, $\gamma_{\mathrm{CMC}}$, $\Gamma$, $A$, pC20 values. $\Gamma$ is increased with the hydrophobic length increase, this increases the packing density at the gas–liquid interface. The area per molecule at the interface $A$ decreased (see Table 1) with the increase in the alkyl chain length, while the head group areas of Sb18-3 and Sb18-4 were much smaller, by almost one order of magnitude.

A convenient measurement of the efficiency of adsorption at the gas–liquid interface is the pC$_{20}$ parameter introduced by Rosen [6]. As shown in Table 1, pC$_{20}$ increases as the hydrophobic chain length increases. The results indicate that energetically speaking, the increases in the hydrophobic chain length make the transfer of a surfactant molecule from the bulk to the interface more easily.

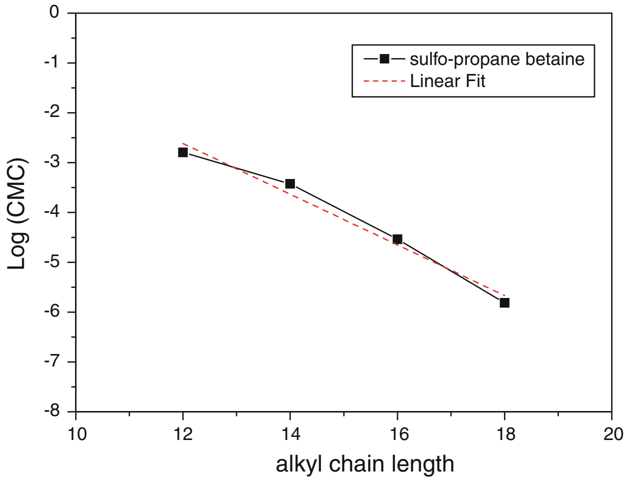


**Fig. 3** Plot of CMC values versus alkyl chain length of sulfo-propane betaines

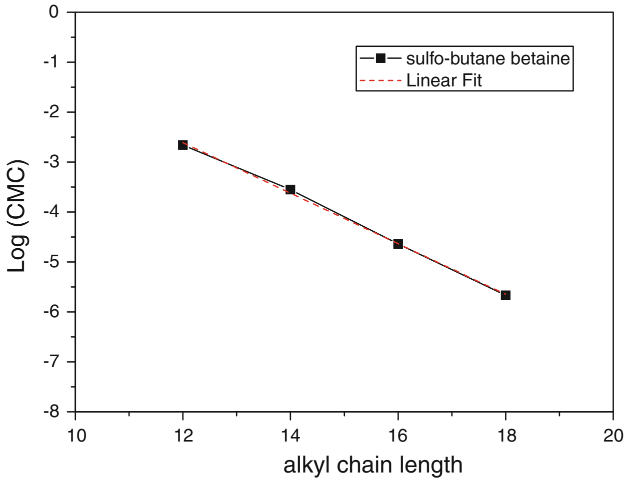


**Fig. 4** Plot of CMC values versus alkyl chain length of sulfo-butane betaines

The CMC is a strong function of the length of the alkyl chain; Rosen [6] reports that the variation of the CMC with the number of carbons in the hydrophobic tail group ($m$) can often be empirically described by the equation $\mathrm{Log(CMC)} = A + B \times m$, where $A$ and $B$ are constants,

$m$ is the carbon number of alkyl chains. For sulfo-propane betaines the equation is $\mathrm{Log(CMC)} = 3.4884 - 0.5087 \times m$, for sulfo-butane betaines the equation is $\mathrm{Log(CMC)} = 3.45773 - 0.5058 \times m$. This means that the CMC decreases roughly one order of magnitude for each addition of two carbons in the surfactant tail group (Figs. 3, 4).

**Acknowledgments** This research has been financially supported by the National Key Basic Research Development Program (2005CB221305).

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