Surface-Active Properties and Thermal Behavior of S-Alkylthio-Carboxylic Acids and Their Potassium Salts

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ABSTRACT: S-Alkylthiocarboxylic acids and their potassium salts were prepared by photoaddition of α-olefins (C_{10}, C_{12}, and C_{14}) with mercapto carboxylic acids such as thiomalic acid, thiopropionic acid, and thioglycolic acid. The physicochemical solution properties and thermal stabilities for three series of thiosurfactants were evaluated. S-Alkylthiocarboxylic acids that contain bridged S-bonds provide excellent thermally stable surfactants, and their alkaline salts exhibit good surface activity. *JAOCS 72*, 805–809 (1995).

KEY WORDS: α-Olefin, mercapto carboxylic acid, photoaddition, S-alkylthiocarboxylic acid, S-alkylthioglycolic acid, S-alkylthiomalic acid, S-alkylthioproprionic acid, surface activity, thermal stability.
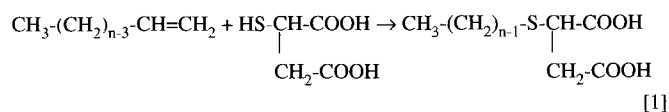
Syntheses of anionic (1–4), cationic (5,6), nonionic (7–9), and amphoteric (10,11) surfactants with a thioether moiety have been reported in many papers or patents. In general, these thioether surfactants provide good antimicrobial properties and effective antifungal or disinfectant activities (11). An S-dodecylthiopropionate surfactant has been prepared (12,13) and exhibits good heat stability, which is useful for specific purpose, such as high-temperature lubrication or boiler washing at high temperatures. Both the thioether and carbonyl groups in $C_{12}H_{25}$-S-CH_2-CH_2-COOH inhibit iron corrosion in cooling water *via* chelate–complex formation of [($C_{12}H_{25}$-S-$CH_2CH_2COO)_3$Fe(III)] (14). Thioether surfactants could also be employed in the industrial fields of plastics, rubber, textile, leather, petroleum, etc. However, scarcely any work on this type of surfactants, except for S-dodecylthiopropionate, has been published. Moreover, fundamental studies on the surface activity and heat-stability of S-dodecylthiopropionate have not been carried out in detail.

In this paper, three series of S-alkylthiomalic acids, S-alkylthiopropionic acids, and S-alkylthioglycolic acids have been synthesized. The surface activities and thermal behavior of these derivatives have been evaluated. In particular, the effect of alkyl chainlength on these properties has been investigated.

EXPERIMENTAL PROCEDURES

Preparation. S-alkylthiomalic acid homologues (Cn-TMA) were prepared as follows:

$$CH_3\text{-}(CH_2)_{n-3}\text{-}CH=CH_2 + HS\text{-}\underset{|}{C}H\text{-}COOH \rightarrow CH_3\text{-}(CH_2)_{n-1}\text{-}S\text{-}\underset{|}{C}H\text{-}COOH$$
$$CH_2\text{-}COOH \qquad\qquad CH_2\text{-}COOH$$

[1]

In a 1000-mL internally illuminated photoreactor, equipped with a reflux condenser, thiomalic acid (TMA) (97.6 g, 0.65 mole; Tokyo Kasei Ind. Ltd., Tokyo, Japan) was placed in 4-methyl-2-pentanone (456.6 g) and homogeneously dissolved under stirring at 60°C for 0.5 h. Subsequently, the photoaddition of α-olefins (0.65 mole) was carried out under ultraviolet (UV) illumination (250–400 nm) from a high-pressure mercury lamp (200 W; Toshiba Lighting & Tech. Co. Ltd., Tokyo, Japan). The α-olefins employed as starting materials (1-hexene, 1-decene, 1-dodecene, or 1-tetradecene) were obtained from Mitsubishi Kasei Ind. Ltd. (Tokyo, Japan). The end point of the reaction was monitored by iodometric titration to check the residual amount of mercapto groups as well as by disappearance of the 910 and 990 cm^{-1} bands (double-bond absorption of α-olefins). The solvent was removed under reduced pressure (20 mmHg at 100°C) to obtain the crude product (149.7 g). After dissolving the product in tetrahydrofuran (10 mL), distilled water (1000 mL) was added, and the resulting precipitate was filtered off. This treatment was repeated three times to remove the unchanged TMA. Purified product yields were: C_6-TMA, 66.0% (98.9 g); C_{10}-TMA, 70.5%, 133.0 g; C_{12}-TMA, 72.8%, 150.6 g; and C_{14}-TMA, 78.9%, 175.5 g.

The potassium salts of Cn-TMA were prepared by neutralization of TMA with KOH as follows: An ethanol solution of TMA was neutralized under reflux (about 78°C) for 0.5 h with an equivalent amount of aqueous potassium hydroxide, and

the crystals were precipitated in a large volume of ethanol (fifty times). They were separated and dried in a vacuum oven under reduced pressure. ^{1}H Nuclear magnetic resonance (NMR) spectra in D_2O solution with sodium 3-(trimethylsilyl)-1-propanesulfonate as a reference were recorded with a JEOL NMR (500 MHz) spectrometer (Tokyo, Japan). The following peaks of TMA homologues were observed: δ = 0.88 ppm (t, 3H, -CH$_3$); 1.2–1.3 ppm [-(CH$_2$)$_n$-: n = 10, 12, 14]; 1.6 ppm (q, 2H, -CH$_2$-C-S); 3.0 ppm (2H, -CH$_2$-S-), 3.2 and 3.6 ppm (2H, -C-CH$_2$-COOK), 4.3 ppm (H, -S-CH-COOK); the Fourier transform infrared (FT–IR) spectra were measured with a JASCO FT–IR-5000 spectrophotometer (Tokyo, Japan); -COOK salt (1574 and 1470 cm^{-1}), -COOH (1680 cm^{-1}), -S- (2852 and 1412 cm^{-1}), -S-CH$_2$- (1199 and 1174 cm^{-1}), -OH (br, 3500 cm^{-1}). The elemental analyses of TMA homologues for C, H, and S were within 1.7% of the calculated values.

S-Alkylthiopropionic acid (Cn-TPA) homologues were prepared according to the same procedure described above:

CH$_3$-(CH$_2$)$_{n-3}$CH=CH$_2$ + HS-CH$_2$CH$_2$-COOH

$\rightarrow$ CH$_3$-(CH$_2$)n-1-S-CH$_2$CH$_2$-COOH

[2]
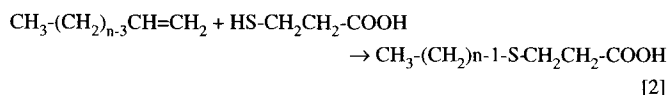
Thiopropionic acid (TPA) (0.65 mole, 68.9 g, reagent grade; Tokyo Kasei Ind. Ltd.) was added to an equimolar amount of α-olefins (0.65 mole) in a threefold molar excess of solvent (4-methyl-2-pentanone). The purification and preparation of potassium salts of TPA were the same as described above. The yields for the alkyl homologues were as follows: C$_{10}$-TPA, 62.2%, 99.6 g; C$_{12}$-TPA, 71.5%, 127.7 g; and C$_{14}$-TPA, 75.5%, 146.6 g. The elemental analyses for C, H, and S were within 0.68% of the calculated values. ^{1}H NMR; δ = 0.88 ppm (t, 3H, -CH$_3$), 1.2–1.3 ppm [-(CH$_3$)n-; n = 7, 9, 11], 1.6 ppm (q, 2H, -CH$_2$-C-S-), 2.6 ppm (t, 2H, -CH$_2$-S-), 2.9 ppm (t, 2H, -S-CH$_2$-C), 3.1 pm (t, 2H, -S-C-CH$_2$-COOH); FT–IR, -COOK salt (1564 and 1468 cm^{-1}), -S- (2854 and 1419 cm^{-1}) and -S-CH$_2$- (1189 cm^{-1}).

S-Alkylthioglycolic acid (Cn-TGA) was synthesized by the addition of thioglycolic acid (TGA) (0.65 mole, 59.8 g; Tokyo Kasei Ind. Ltd.) to 1-alkene (1 mole) in 2-butanone under air-bubbling and UV irradiation (250–400 nm) at 80°C for 10 h. The reaction is the following:

CH$_3$-(CH$_2$)$_{n-3}$CH=CH$_2$ + HS-CH$_2$-COOH $\rightarrow$ CH$_3$-(CH$_2$)$_{n-1}$-S-CH$_2$-COOH

[3]
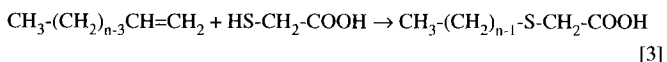
The end point of the reaction was also determined by iodometric titration to check the residual amount of mercapto groups. After washing with distilled water and subsequent recrystallization with hexane, the purified products were obtained. The yields for each homologue were as follows: C$_{10}$-TGA, 54.5%, 82.3 g; C$_{12}$-TGA, 60.9%, 103.0 g; and C$_{14}$-TGA, 64.8%, 119.6 g. The photoaddition followed predominantly an anti-Markovnikov rule. Each potassium salt of TGA was prepared by neutralization of TGA with equimolar alcoholic KOH solution under reflux. The elemental analyses for C, H, and S were within 1.3% of the theoretical values. ^{1}HNMR, δ

= 0.88 ppm (t, 3H, -CH$_3$), 1.2–1.3 ppm [-(CH$_2$)$_n$-], 2.8 ppm (t, 2H, -CH$_2$-S-) and 3.55 ppm (s, 2H, -S-CH$_2$-COO); FT–IR, -COOK salt (1591 and 1468 cm^{-1}), -S- (2904, 2852 and 1406 cm^{-1}), -S-CH$_2$- (1209 cm^{-1}).

Experimental methods. The surface tension of each surfactant was measured in 0.1% KOH solution at 25°C by the Wilhelmy vertical plate method with a Shimadzu ST-1 tensiometer (Tokyo, Japan). Foam height was measured for each surfactant solution in soft water at 35°C according to the Ross-Miles procedure. The thermal stability for each sample (5 mg) was evaluated by a thermal gravity (TG) measurement at 5°C/min under a nitrogen atmosphere.

The mean micellar aggregation number (n) of the K-TPA series was determined according to the Turro and Yekta equation (15) by using a photoluminescent probe procedure, based on the quenching of a donor [Ru(bipy)$_3$$^{2+}$] by a hydrophobic luminescent quencher, 9-methylanthracene ([Q] = quencher concentration). The instruments used were a JASCO-660 UV-VIS spectrophotometer and a JASCO-FP-770 fluorescence spectrophotometer. The ratio of luminescence intensities (I/I_0) in the presence and absence of [Q] is related by the following expression:

$$I/I_0 = \exp\{-[Q]/(M)\} \quad [4]$$

where

$$(M) = \frac{(Det)-(\text{free monomer})}{n} \quad [5]$$

and hence,

$$[\ln(I/I_0)]^{-1} = \frac{(Det)}{[Q]\,n} - \frac{(\text{free monomer})}{[Q]n} \quad [6]$$

(M) is the micelle concentration, and (Det) the surfactant concentration. The aggregation number (n) can be calculated from the slope of $[\ln(I/I_0)]^{-1}$ vs. (Det) plot according to Equation 6.

RESULTS AND DISCUSSION

The surface tension vs. concentration profiles for two series of K-TGA and K-TPA homologues are shown in Figure 1. The surface tension decreased with increasing concentration to reach a definite value of critical micelle concentration (CMC). The effect of alkyl chainlength (C$_{10}$, C$_{12}$, and C$_{14}$) of K-TGA on the surface tension is shown by the regular drop of 3 mN/m at the CMC for a difference of two methylene groups. The drop of surface tension at the CMC for the K-TPA homologues had the constant value of 4 mN/m for a difference of two methylene groups. All these TGA and TPA homologues exhibited excellent surface activities. In particular, the C$_{14}$ homologues of K-TPA has a surface tension of 24 mN/m at the CMC. The CMC values determined from the
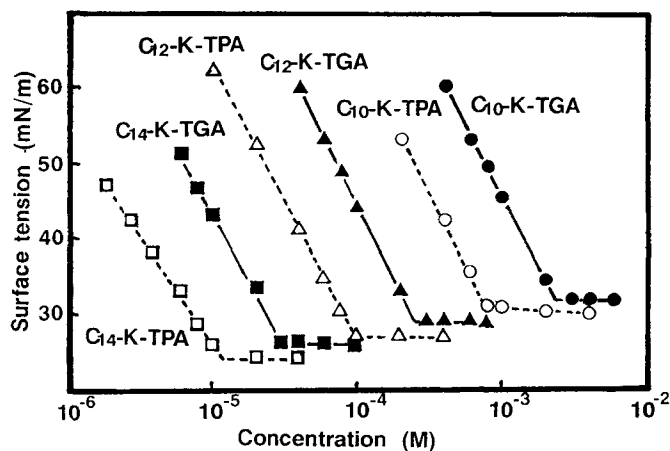
FIG. 1. Surface tension vs. concentration profiles for each potassium salt or alkyl-(Cn-) thioglycolic acid (TGA) and alkyl-(Cn-) thiopropionic acid (TPA) homologues at 25°C.

FIG. 3. Effect of alkyl chainlength of Cn-K-TPA on the mean micelle aggregation number. Inset: variation of $[\ln(I_o/I)]^{-1}$ with surfactant concentration. See Figure 1 for abbreviation.

breakpoint of the surface vs. concentration plots are as follows: C_{10}-TGA, 2.6 mM; C_{12}-TGA, 0.25 mM; C_{14}-TGA, 0.03 mM; and C_{10}-TPA, 0.83 mM; C_{12}-TPA, 0.09 mM; C_{14}-TPA, 0.013 mM. The TGA series have higher CMC values than those of the TPA series due to their having one less CH_2 group. Because TPA is more hydrophobic than TGA, it forms larger micelles than TGA.

The effect of alkyl chainlength on log CMC is depicted in Figure 2: the C_{10}, C_{12}, and C_{14} homologues of K-TGA and K-TPA gave a straight line. These CMC values are lower than those of K-fatty acid salts: The sulfur moiety containing the alkyl chain plays a hydrophobic role. The following experimental expressions were obtained: log CMC = 2.24−0.48N for the K-TGA homologues and log CMC = 1.41−0.45N for the K-TPA homologues, where N is the alkyl chainlength. One sulfur molecule corresponds to the hydrophobicity of three or four methylene groups.
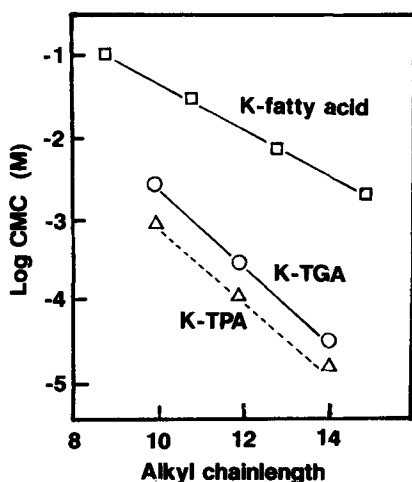
With respect to the K-TPA series, the mean aggregation number (n) increased with increasing alkyl chainlength as shown in Figure 3. The concentration dependence of $[\ln(I_o/I)]^{-1}$ (see inset) is linear, in agreement with the Turro and Yekta equation (15). The micelle aggregation number of C_{10}-K-TPA is n = 58, that of C_{12}-K-TPA is n = 76, and that of C_{14}-K-TPA is n = 100. The aggregation number is inversely related to the CMC. The aggregation number for the TPA series could not be assayed because of their poor solubility in aqueous solution under the same conditions as above.

Figure 4 shows the foam height against the alkyl chainlength of TGA and TPA potassium salts. Foaming power is dependent upon the carbon number. The C_{12}-homologue of both K-TGA and K-TPA provides the greatest foaming power compared with the other alkyl homologues. This relative superiority is maintained after 5 min. However, the foaming power of C_{12}-K-TPA and C_{12}-K-TGA is lower than that of

FIG. 2. Relationship between log critical micelle concentration (CMC) and carbon number of Cn-TGA, Cn-TPA, and potassium salts of fatty acids (K-fatty acid) at 25°C in aqueous KOH solution (0.1%). See Figure 1 for abbreviations.
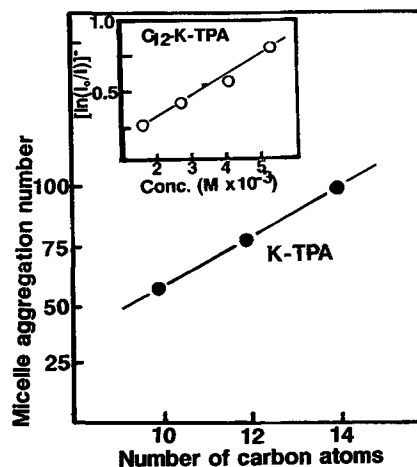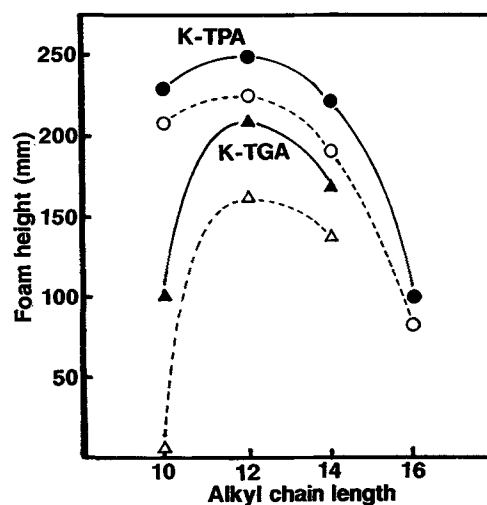

FIG. 4. Effect of alkyl chainlength on foaming power. The foam height was measured at 35°C: ● Cn-K-TPA immediately after dropping; ▲ Cn-K-TGA immediately after dropping; ○ Cn-K-TPA 5 min after dropping; △ Cn-K-TGA 5 min after dropping. See Figure 1 for abbreviations.

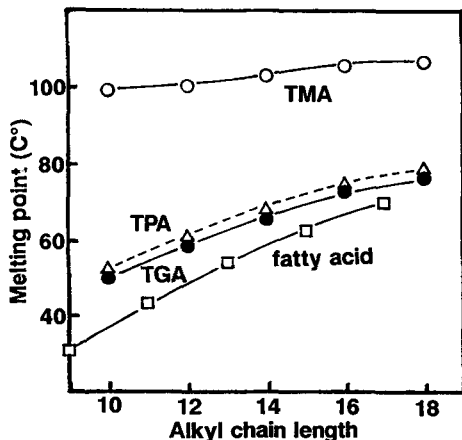FIG. 5. Effect of alkyl chainlength on the melting point. Cn-TMA, alkylthiomalic acid. See Figure 1 for other abbreviations.

FIG. 7. Effect of alkyl chainlength on the thermal decomposition temperature. See Figures 1 and 5 for abbreviations.

potassium tetradecanoate, employed as a standard sample, for which the foam height, immediately after dropping, is 302 mm, and after 5 min, 257 mm.

The dependence of chainlength on melting point is shown in Figure 5. The melting points of TMA, TPA, and TGA increased with increasing alkyl chainlength. Comparing the melting points of the same alkyl homologues, they increased in the order of fatty acid < TGA < TPA < TMA. TMA, with two carboxyl groups, had the highest melting point (about 100°C), due to hydrogen bonding.

Thermal weight loss is depicted in Figure 6. Both C_{12}-TPA and C_{12}-TGA are thermally more stable than the corresponding fatty acids with the same alkyl chain. No decomposition occurs for C_{12}-TPA and C_{12}-TGA, even at about 200°C. The decomposition temperature for dodecanoic acid is 187°C (determined by extrapolating the thermal curve).

The effect of alkyl chainlength on decomposition temper-

ature is shown in Figure 7. The temperature for TPA and TGA increases with alkyl chainlength. TMA exhibits an ultimate decomposition temperature (270°C) for the homologue with the 14-carbon chain. The thio-surfactants TGA and TPA are more stable by *ca.* 40°C compared with the fatty acid. Evidence for hydrogen bonding between the sulfur atom in the thioether and a proton in the -OH or -COOH moiety was assessed by IR spectroscopy. We selected a simplified system as mentioned below: The comparison was made by examining IR spectra of three component systems comprising dipentyl thioether (a proton acceptor), phenol (a proton donor), and carbon tetrachloride (a solvent). When only phenol is dissolved into carbon tetrachloride, there is one bond-stretching band, corresponding to the free O-H group, at 3616 cm^{-1}. On adding a proton acceptor (dipentyl thioether) to the solution, the intensity of the free O-H band is lowered, and a new band appears at a lower frequency (3460 cm^{-1}), which is assigned to a hydrogen-bonded O-H stretching vibration. The thioether moiety plays the role of a proton acceptor for the hydrogen-bond formation. It may be supposed to form a dimeric complex between -S- and -COOH through mutual intermolecular hydrogen bonding, as in the case of dodecyl-thiopropionic acid. For these reasons, thioether surfactants possess highly heat-resistant characteristics.
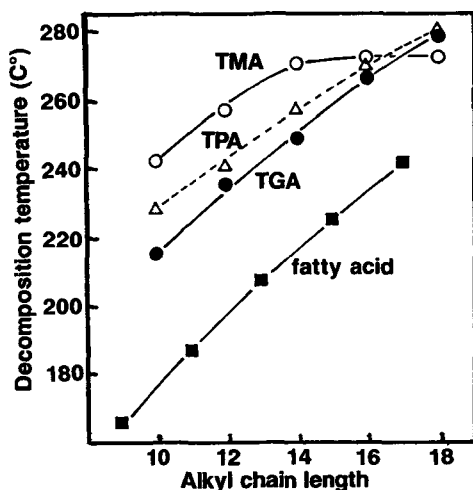
ACKNOWLEDGMENT

FIG. 6. Weight loss vs. temperature curves, showing the extrapolation procedure used to determine the thermal decomposition temperature. See Figure 1 for abbreviations.
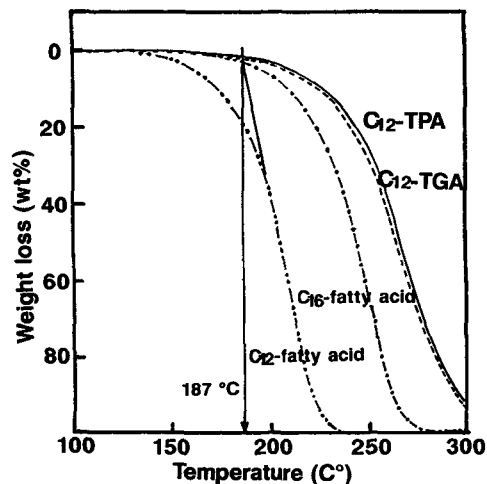
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