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Physico-Chemical Properties of Aqueous Solutions of $C_{n-1}H_{2n-1}OCH_2COONa$

Masakatsu HATO,* Kōzō SHINODA, and Tōru MIYAGAWA
Department of Chemistry, Faculty of Engineering, Yokohama National University, Ooka, Minami-ku, Yokohama 233

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Properties of aqueous solutions of surfactants, $C_{n-1}H_{2n-1}OCH_2COONa$ ($n-1=12$—18), which may be non-toxic, non-allergic and bio-degradable, have been studied. The Krafft points in aqueous solutions of these surfactants are close (+8.5——1.5 °C) to those of the corresponding fatty acid soaps R_nCOONa. The critical micelle concentrations are also close to those of corresponding fatty acid soaps in spite of the introduction of an oxygen atom in the hydrocarbon chain. A study of the effect of water hardness on the solubility revealed that this type of surfactant is, unlike soap, soluble in town water (hardness 4°) in the presence of equal weight of tripolyphosphate.

The majority of ionic surfactants used nowadays are sodium alkyl or alkylaryl sulfonates or sulfates. Great consumption of such substances is undesirable from the viewpoint of environmental preservation and biological recycling. It is expected that compounds composed solely of carbon, hydrogen and oxygen atoms and whose structures resemble fatty acids or their analogues may be easily bio-degradable, non-toxic and non-allergic. However, fatty acid soaps are insoluble in hard water and scum forms in washing process. Thus, surfactants whose ionic groups are carboxyl and are more soluble in hard water could be of some advantage. The present investigation was undertaken to prepare such compounds and study their physico-chemical properties in aqueous solutions.

Experimental

Materials. $R_{n-1}OCH_2COONa(R_{n-1}=C_{n-1}H_{2n-1}$; $n-1=12$—18) were synthesized from respective alcohols, $C_{n-1}H_{2n-1}OH$, and sodium chloroacetate. These acids were purified by vacuum distillation and then neutralized. Their melting points and boiling points and purity determined by gas chromatography are summarized in Table 1.

TABLE 1.

Molecular formula	Mp °C	Bp °C	Purity
$R_{12}OCH_2COOH$	46.0	147(0.06 mmHg)	99.8
$R_{14}OCH_2COOH$	56.2	150(0.025 mmHg)	99.4
$R_{16}OCH_2COOH$	64.3	176(0.025 mmHg)	99.8
$R_{18}OCH_2COOH$	70.8	208.5(0.023 mmHg)	99.2

Procedure. The critical micelle concentration (CMC) was determined by electrical conductivity measurements. The Krafft point was determined from the change in solubility with temperature.[1] It was also confirmed from the color change of pinacyanol chloride since the solubility and the cmc agree at the Krafft point.

Results and Discussion

Critical Micelle Concentration (CMC). The CMC values determined from electrical conductivity *vs.* concentration curves are summarized in Table 2.

TABLE 2.

Molecular formula	CMC mmol/l	Krafft point (°C)
$R_{12}OCH_2COONa$	7.5(55.0 °C)	42
$R_{14}OCH_2COONa$	2.2(64.9 °C)	49
$R_{16}OCH_2COONa$	0.73(75.1 °C)	56
$R_{18}OCH_2COONa$	0.40(75.5 °C)	62

The CMC values of the corresponding fatty acid soaps, R_nCOONa, are close to those of $R_{n-1}OCH_2COONa$. Insertion of oxygen atom in the hydrocarbon chain has little effect on the CMC. Klevens empirically found that the logarithms of the CMC values and the fatal lengths of surfactant molecules from the terminal carbon atom to the atom carrying the charge change linearly.[2] The relation fortuitously holds in several ordinary ionic surfactants. It is evident, however, that the relation will not hold in the case of $C_nH_{2n+1}O(CH_2CH_2O)_mSO_3Me$,[3—5] since the CMC is determined by the free energy change of respective groups at micellization.[6] The ether oxgen atom in R_nOCH_2COONa might increase the hydrophilic property of this surfactant on one hand, but the water and gegenions distributed around polar groups might depress the electrical repulsion on the

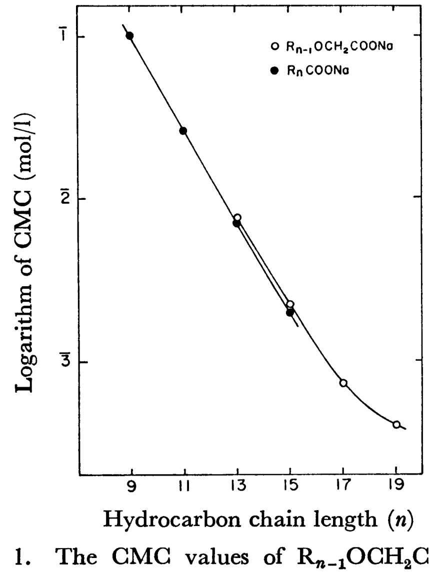

Fig. 1. The CMC values of $R_{n-1}OCH_2COONa$ and R_nCOONa as a function of hydrocarbon chain length of respective surfactants. The CMC values have been determined slightly above respective Krafft points.

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* Address: Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama 221.

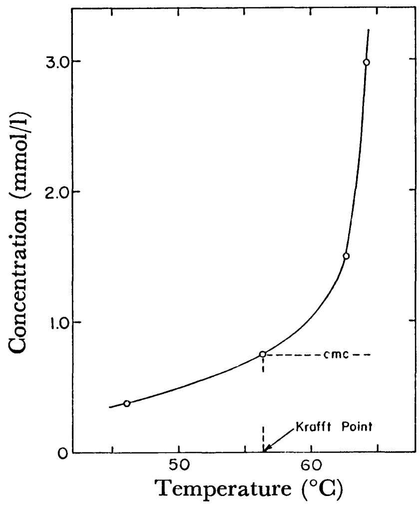
other hand. A comparison of the CMC values of these surfactants with those of fatty acid soaps as a function of hydrocarbon chain length is shown in Fig. 1.[2] Since the change in CMC value with temperature is relatively small over 20—70 °C,[7,8] the CMC values slightly above the Krafft points were plotted.

The logarithms of the CMC values decrease linearly up to 15 carbon atoms, but the slope *vs.* hydrocarbon chain length gradually decreases above 17 carbon atoms. The CMC values as a function of hydrocarbon chain length are expressed as follows:

$$\ln \mathrm{CMC} = -\frac{1}{1+K_g}\frac{m\omega}{kT} - K_0 \qquad (1)$$

where ω is the free energy increase transferring one methylene group from the interior of micelle to aqueous environment, K_g a constant obtained from the change of CMC with the concentration of gegenions, m the number of carbon atoms in hydrocarbon chain and K_0 the experimental constant.[9]

Krafft Point. The Krafft point was determined from the change of solubility of $R_{n-1}OCH_2COONa$ with temperature and the CMC value (Fig. 2).



Solubility of $C_{16}H_{33}OCH_2COONa$ in H_2O

Fig. 2. The change of solubility of $C_{16}H_{33}OCH_2COONa$ in water with temperature and the Krafft point.

The results are summarized in Table 2. The Krafft point is a temperature at which hydrated solid surfactant melts.[1] Thus the Krafft points and melting points of corresponding acids are closely related. The relation is plotted in Fig. 3.

Krafft points of fatty acid soaps are about 20 °C lower than those of the corresponding fatty acids, whereas the Krafft point of $R_{n-1}OCH_2COONa$ is not so low compared with the melting points of $R_{n-1}OCH_2COOH$. The melting points of $R_{n-1}OCH_2COOH$ are merely 3—8 °C lower than those of $R_{n-1}CH_2COOH$. It is evident that the insertion of oxygen atom in the hydrocarbon chain neither depresses the Krafft points nor increases the CMC values. However, the Krafft point of $R_{12}(OCH_2CH_2)OCH_2COONa$ is below 0 °C.

The Change of Krafft Point of $R_{n-1}OCH_2COONa$ as a Function of Water Hardness. Ordinary soaps are salted out by the addition of a very small amount of multi-valent cations. In the case of $R_{n-1}OCH_2COONa$, however, the Krafft point is gradually enhanced with added calcium chloride, particularly in the presence of the chelating agent, tripolyphosphate. The results are plotted in Fig. 4 as a function of the water hardness.

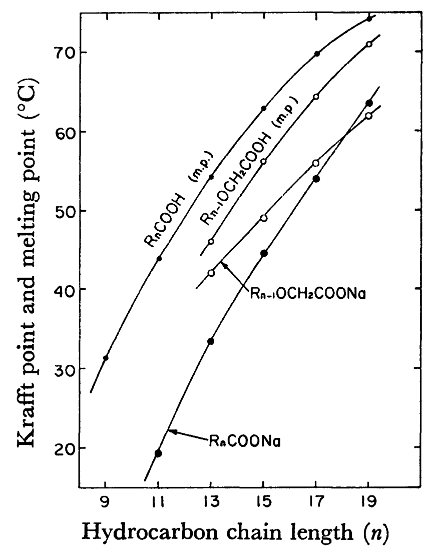


Fig. 3. The comparison among Krafft points of R_{n-1}-OCH_2COONa and R_nCOONa and melting points of corresponding acids.

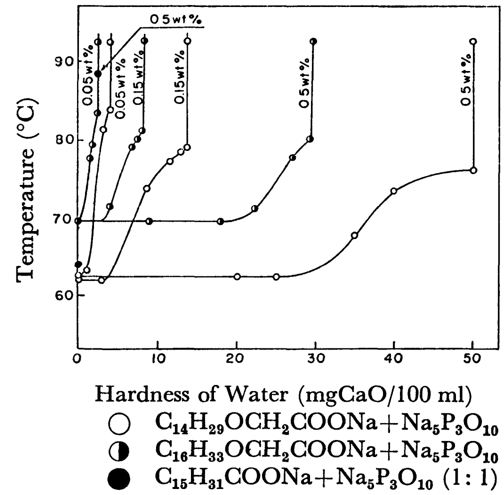


Fig. 4. The change of Krafft point as a function of the concentration of calcium chloride (water hardness).

The solubility gradually decreases with time, because the tripolyphosphate slowly becoming degraded. Since the solutions contained the same weight of tripolyphosphate and surfactants, concentrated solutions were less sensitive to the calcium ions added. Surfactants are usually used at about 0.05 wt % and contain roughly the same weight of tripolyphosphate. It is clear from Fig. 4 that 0.05 wt % solutions of $R_{14}OCH_2COONa$ and $R_{16}OCH_2COONa$ are durable up to about 4° and 2.5°, respectively. Whereas 0.05 wt % $R_{15}COONa$ in the presence of equal weight of tripolyphosphate was salted out at the hardness of 0.3°.

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References

1) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press Inc., New York (1963), p. 7.

2) H. B. Klevens, *J. Am. Oil Chem. Soc.*, **30**, 74 (1953).

3) F. Tokiwa and K. Ohki, *J. Phys. Chem.*, **71**, 1343 (1967).

4) F. Tokiwa, *J. Phys. Chem.*, **72**, 1214 (1968).

5) M. Hato and K. Shinoda, *J. Phys. Chem.*, **77**, 378 (1973).

6) Ref. 1, p. 41.

7) B. D. Flockhart, *J. Colloid Sci.*, **16**, 484 (1961).

8) K. Shinoda, 6th International Congress on Surface Active Substances, Zürich, 1972, Band II, 2, 891, Carl Hanser Verlag, München 1973.

9) Ref. 1, p. 42.