Surface Activity and Some Optical Properties of Na-1-acylaminonaphthalene-5-sulfonates in Solutions

Yoshinori MUSHA, Akio OKAGAWA and Tamotsu KONDO
Faculty of Phamaceutical Sciences, Science University of Tokyo, Funakawara-machi, Shinjuku, Tokyo

and Masuzo NAGAYAMA
Research Laboratory, Lion Fat & Oil Co., Ltd., Hirai, Edogawa-ku, Tokyo

(Received May 19, 1967)

Previous papers[1,2] have reported on the syntheses, properties, and possible applications in basic research and industry of new surface-active agents, which are fluorescent as well as surface-active in aqueous solutions.

There are two ways, in principle, of synthesizing a compound of this kind. First, a strong surface activity can be given to certain fluorescent dyes or intermediates by introducing one or more long-chain alkyl radicals into the dye or intermediate molecules. Secondly, some surface-active agents can be chemically modified to exhibit fluorescence by reaction with appropriate fluorescent reagents.

From the physicochemical point of view, however, the compounds obtained so far are not necessarily suitable for basic research in colloid and interface science, for some of them are subject to light-catalyzed cis-trans isomerization,[1] while others are hardly soluble in water at pH values around 7 or at room temperatures.[2]

In the present study, therefore, an attempt has been made to prepare the compounds by the first method without the shortcomings mentioned above. Thus, a homologous series of Na-1-acylaminonaphthalene-5-sulfonates has been synthesized from 1-naphthylamino-5-sulfonic acid (Laurent's acid) and acyl chlorides. Some properties of these compounds have also been studied.

---

[1] T. Kondo, A. Okagawa and M. Nagayama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sec.)*, **68**, 2125 (1965).

[2] S. Muto, T. Kondo and M. Nagayama, *Yukagaku (J. Japan Oil Chemists' Soc.)*, **15**, 26 (1966).

Experimental

Materials. Acyl chlorides were prepared from thionyl chloride and *n*-fatty acids by the usual method. The purity of all the *n*-fatty acids used was estimated to be more than 99.5% by gas chromatography. Laurent's acid was purchased from K & K Laboratories, Inc., Plainview, N.Y., U.S.A. This material was said to have a purity of about 95%.

Preparation and Purification. The reaction of acyl chloride with Laurent's acid easily gave the desired compound. As an example, the reaction of decanoyl chloride with Laurent's acid will be described below.

9.6 g (0.04 M) of Laurent's acid were dissolved in 150 m*l* of water, with the addition of sodium carbonate to make the resultant solution slightly alkaline. The reaction was initiated by simultaneously dropping 9.5 g (0.05 M) of decanoyl chloride dissolved in 20 m*l* of acetone and of an aqueous 5% sodium carbonate solution into the solution of the sodium salt of Laurent's acid obtained above. An hour was sufficient for the reaction to be completed at room temperature.

The product was purified by dry-column-chromatography[3] as follows. A column made of silica gel (Wako 100—200 mesh) was used. The column was filled with dry packing by slowly pouring in the absorbent while tapping the column. Appropriate quantities of silica gel and a methanolic solution of the product were mixed, and the solvent was evaporated to dryness, thus leaving the silica gel covered with the product. Then the column was loaded by pouring the silica gel on top of the packed column and covering it with a filter paper. The development was done by allowing a chloroform-methanol mixture (2 : 1, v/v) to move down the column. When the solvent reached the bottom of the column, the chromatogram was stopped at this point and the content of the column was extruded. The part exhibiting a violet fluorescence was cut off and treated with the same solvent as had been used in the development. The extracted product was precipitated out of the solution by evaporating the solvent under atmospheric pressure. The precipitate was collected and recrystallized at least two times from methanol, and once from water. The final product was obtained as a white powder; the yield was slightly less than 10%.

The high purity of the compounds thus obtained was checked by thin-layer-chromatography, which gave only one spot on the chromatogram.

In Table 1 are listed the results of the elemental analyses of the homologous compounds. Octanoyl, decanoyl, and dodecanoyl compounds are abbreviated as C_8, C_{10} and C_{12} compounds respectively.

TABLE 1. ELEMENTAL ANALYSES

	C_8		C_{10}		C_{12}	
	Calcd	Found	Calcd	Found	Calcd	Found
C	58.27	59.23	60.13	60.27	61.80	62.39
H	5.97	6.01	6.56	6.51	7.07	7.42
N	3.77	3.74	3.53	3.56	3.27	3.12

Ultraviolet Absorption and Fluorescence Spectra. The ultraviolet absorption spectra were recorded on a Hitachi Model EPA-3A spectrophotometer. The wavelengths in these measurntemes ranged from 210 to 350 mμ.

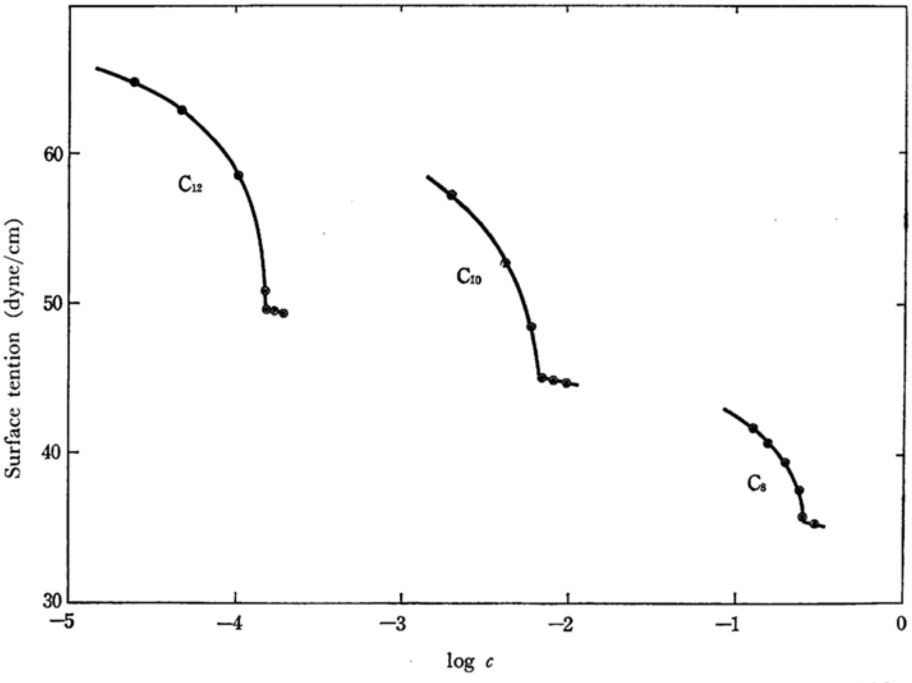

Fig. 1. Surface tension of aqueous solutions of the homologous compounds at 50°C.

---

[3] B. Loev and K. M. Snader, *Chem. & Ind.*, **1965**, 15.

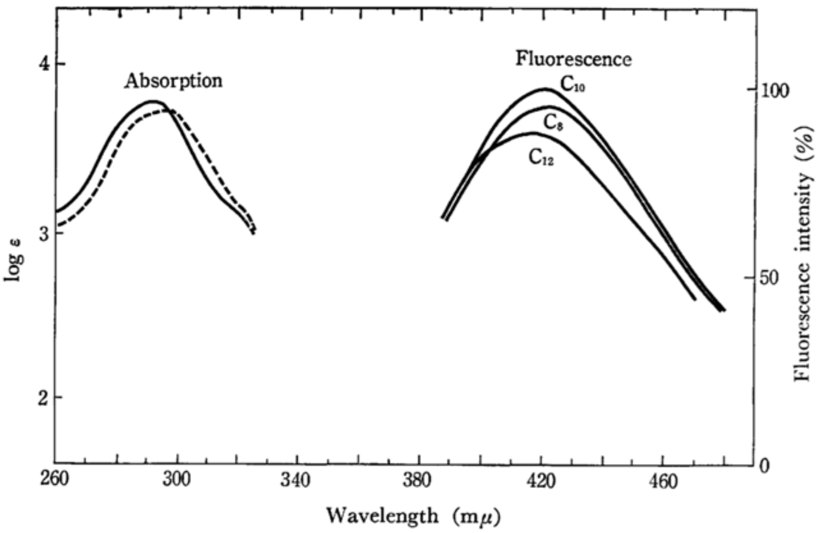

Fig. 2. Ultraviolet absorption and fluorescence spectra of the homologous compounds in water (——) and in methanol (- - -).

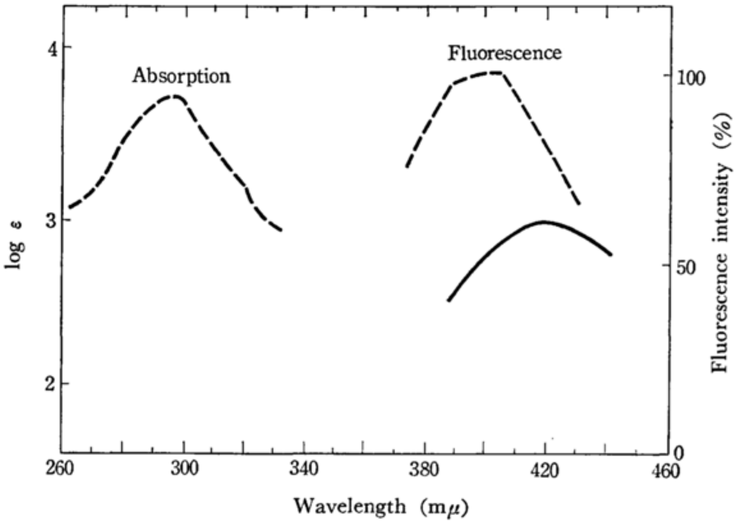

Fig. 3. Ultraviolet absorption and fluorescence spectra of C_{10} compound in methanol (——) and water (- - -)

The fluorescence spectra were obtained with a Hitachi Model ESP-2 spectrophotometer, with attachements for fluorescence measurements. The concentration of all the aqueous and methanolic solutions of the compounds used for the measurements was 5×10^{-5} M.

Surface-tension Measurements. The surface tensions of aqueous solutions of these compounds were measured by the drop-weight method, using a micrometer syringe at 50°C. Necessary precautions were taken to give the equilibrium values in these measurements.

Results and Discussion

Figure 1 gives the sulface tension *vs.* concentration curve for aqueous solutions of the homologous compounds. The concentration at the inflection point on each curve was taken as the CMC. The CMC values for the C_8, C_{10}, and C_{12} compounds were estimated from this figure to be 2.7×10^{-1}, 6.6×10^{-3}, and 1.5×10^{-4} M respectively.

The relation between the CMC and the hydrophobic chain length of the compounds is expressed by the equation: $\log \mathrm{CMC}=5.87-0.80N$, where N is the carbon atom number in a long hydrophobic chain. This means that the CMC of our compounds varies with the hydrophobic chain length in the manner of geometric progression, as does that of many common surface-active agents.

The UV absorption and fluorescence spectra are shown in Figs. 2 and 3. With the exception of fluorescence spectra in water, only one curve is presented in these figures, since the remaining spectra were independent of the chain length. The reason why the fluorescence spectra in water vary with the carbon atom number in an alkyl chain has not been yet established. In the UV absorption spectra, the primary band appeared at about 225 mμ, and for ordinary naphthalene derivatives. The secondary band occured at 290 mμ in water and at 300 mμ in methanol. The peak of the fluorescence spectra was at 420 mμ in water, while it was located at 400 mμ in methanol.

From the experimental results presented above, the homologous compounds may be designated as fluorescent surface-active agents.

Some applications of these compounds in colloid and interface science are now being studied.