pounds show improved performance with increased hardness. The opposite situation is found for the C_{12} and C_{13} isomers as is evident in Table V.

It is apparent from these data that there will be conflicting factors affecting the performance of mixtures of these isomers. For a given hardness, the 2-phenyl isomers reach maximum performance at C_{11}; then drop off. The internal isomers, however, peak at C_{12}. The overall best performance is found for the internal C_{12} isomer followed by both isomers of C_{11}. It should be noted that while the C_{10} homologs performed very well in a multi-active liquid system, their performance contribution is diminished in a mono-active light-duty powder. From a foam performance viewpoint, an ideal distribution for a straight-chain alkylbenzene sulfonate in this powder system would be a C_{11}–C_{12} mixture with a preponderance of the internal isomers.

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[Received July 26, 1965—Accepted October 22, 1965]

Phase Behavior of the Dimethyldodecyl Amine Oxide-H_2O System

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Abstract

An exploratory study of the aqueous system of dimethyldodecyl amine oxide (DDAO) revealed it to be an interesting and instructive surfactant system showing the unusual occurrence of at least 5 stable phases at room temperature—crystal (100—about 80% DDAO), neat (about 80–70%), viscous isotropic (70–65%), middle (65–35%) and fluid isotropic or nigre (35–0%) in order of decreasing DDAO content. In many respects the system resembles anionic detergent systems such as that of sodium palmitate, in which, however, viscous isotropic is not observed. The maximum temperatures of existence for crystal, neat and middle are, respectively, 116, 145 and 110C. Neat phase is soft and anisotropic, viscous isotropic is somewhat brittle and isotropic, middle is plastic and anisotropic. The mesomorphic phases are particularly well shown microscopically in "dried-down" samples under circular cover glasses. Middle and neat textures under the microscope are typical. At least four crystalline phases were recognized at various degrees of hydration.

Introduction

BECAUSE OF THEIR TECHNOLOGICAL importance and long availability, soaps and other anionic detergents have been subjected to phase study, and the classic aqueous sodium palmitate system is widely known (1). Familiar features of that system are the Krafft melting point near 65C, the two large mesomorphic regions—middle soap at higher and neat soap at lower H_2O contents, middle existing as high as 170C, neat up to 285C, and the curd or crystalline soap which, when anhydrous, passes through several phase states before becoming isotropic at about 300C.

A number of less detailed studies have been carried out on aqueous systems of nonionic detergents and other nonionic surface active compounds, with a wide variety of behavior appearing but normally reminiscent of that of sodium palmitate (2). Mesomorphic states are common. Occasionally middle phase is absent. Phases which are stiff but isotropic have been reported (3,4).

The present work concerns the aqueous system of dimethyldodecyl amine oxide (DDAO), a nonionic detergent of technological interest (5–9).

Experimental

Various preparations of DDAO were used for preliminary phase studies, all samples agreeing qualitatively with the final phase diagram. The principal preparation by A. O. Snoddy of this laboratory, showed the analyses of Table I. The sample which had been freeze-dried was used as such and accepted as 94.0% DDAO, 6.0% H_2O. From it the following main samples were prepared: (94.0), 89.0, 80.0, 75.0, 71.0, 67.0, 66.0, 61.0, 57.0, 47.0, 38.0, 30.0% DDAO. Any sample less than 30.0% DDAO was of fluid nigre phase at 25C and higher temperatures.

It was subsequently found that the DDAO could be dried substantially completely by refluxing in hexane with a Bidwell-Sterling moisture trap. The hexane solution was crystallized at 0C. The highest crystalline melting point obtained was 116C.

The main samples in 3 g amounts were sealed in 15 × 125 mm test tubes with a 2 mm constriction in the middle, through which homogenization was effected by centrifuging the sample back and forth. The samples were then observed between crossed polaroids at room temperature. The tubes were opened and samples introduced into thin-walled Pyrex capillaries for X-ray diffraction at 10 cm sample-to-film distance on a GE XRD-1 unit with CuKα radiation and 0.025 in. pinhole collimating system. Representative diffraction patterns were also recorded on a GE XRD-5 diffractometer with nickel-filtered CuKα radiation.

TABLE I

Analysis of DDAO

	Experiment (Av'ge.)	Theory	
		Anhydrous	(With 6.0% H_2O)
N_2 (Kjeldahl)	5.91%	6.11%	5.74%
H_2O (Karl Fischer)	5.3	0.0	6.0
Purity of alkyl (gas-liquid chromatography)			
C_{12}	94.5%		
C_{14}	3.7		
C_{16}	1.8		

TABLE II

Long-Spacings of Mesomorphic States

	Neat (85–70% DDAO)		Middle (65–35% DDAO)		
	85%	80%	67%	50%	40%
Long-spacing (Å)	31.4	31.4	34.2	35.0	40.5

Other portions were viewed microscopically on a heating stage, equipped with a thermocouple and a movable metal ring which could accommodate sample between a pair of round cover glasses. Moisture loss was reduced by an annular ring of scotch tape sealing metal ring to cover glass but leaving an unobstructed optical path. Samples were run upward (and downward) in temperature twice to observe points of phase change, the average temperature being recorded. Rapid heating rates of 8C per minute were employed to minimize evaporation and might have led to slightly high temperatures of recorded phase change. On a critical sample of 66% DDAO a sealed tube was studied macroscopically between crossed polaroids at a number of temperatures. Data are recorded in Figure 1.

A valuable type of qualitative confirmation of the phase diagram was obtained by a simple but very useful technique commonly used in these laboratories. A drop of fluid nigre of 25–30% DDAO content was placed on a microscope slide and covered with a round cover glass to obtain as nearly perfect coverage as possible, without excess solution extending beyond the cover glass. Upon drying, rings of decreasing H_2O content (and given phase) moved toward the center. At the periphery occurred the phase sequence—fluid nigre, neat, viscous isotropic and middle. The cover glass was photographed between crossed polaroids at intervals of about 2 hr; the resulting prints in Figure 2 are about 1.3 times normal size. It is plain that at room temperature (25C) with decreasing water content there exist regions of fluid nigre, neat, viscous isotropic and middle. Examination of neat and middle, at about 100×, revealed textures typical of those reported by Rosevear (10) for other systems.

The solubility boundary between fluid nigre and middle was obtained by evaporating H_2O from a 30.0% DDAO composition in approximately 2% steps to bracket the boundary between 34.3% (isotropic) and 36.3% (anisotropic) for an accepted boundary of 35.3% DDAO at 25C.

Results and Discussion

Macroscopic Properties of Mesomorphic States

The middle phase (65–35% DDAO at room temperature) is plastic and stringy, not particularly tough. While transparent it is anisotropic and seems never to exist without striations.

TABLE III

Diffraction Date for Crystalline Phases of DDAO

Treatment	Long-Spacings (Å)	Short-Spacings (Å)
Crystd. from hexane, freeze-dried	31.8	5.30W, 4.93W+, 4.42W+, 4.16S, 3.81M
Crystd. from acetone	34(VW), 27.0(VS)	5.23W, 4.52S, 4.21W, 3.96W, 3.90W
Cooled from neat	33.5(S), 27(W)	5.21W, 4.47S, 4.18S-, 3.87M, 3.60M-
Digested weeks in jar	35.8(M), 20.6(M)	Many lines

VW—very weak, W—weak, M—medium, S—strong, VS—very strong.

Four or more phases are involved.

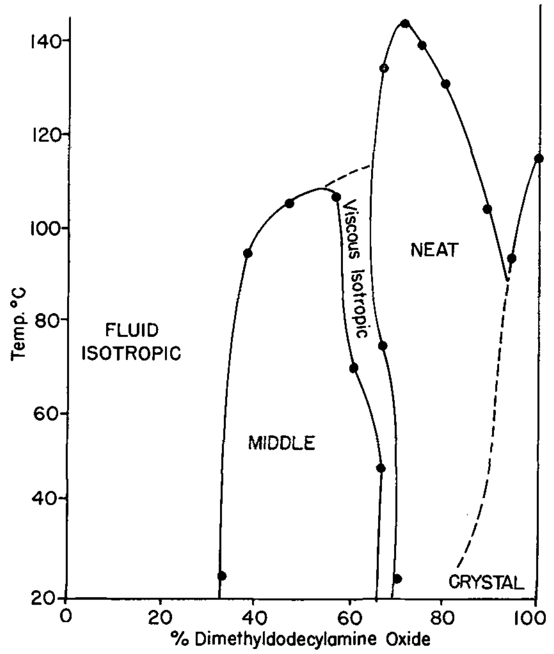

Fig. 1. Aqueous System of Dimethyldodecyl Amine Oxide.

Viscous isotropic (70–65% DDAO) is hard to prepare in substantial quantities because of its narrow (5%) range of existence. It is clear and isotropic but stiff. Unlike middle, it tends to be brittle, not very plastic and not at all stringy.

Neat (80–70% DDAO) is anisotropic, much more fluid but more opaque than middle. Large quantities will pour but not small quantities.

The aqueous DDAO system is a particularly convenient physical chemical system to study because of the several types of phase existing at room temperature.

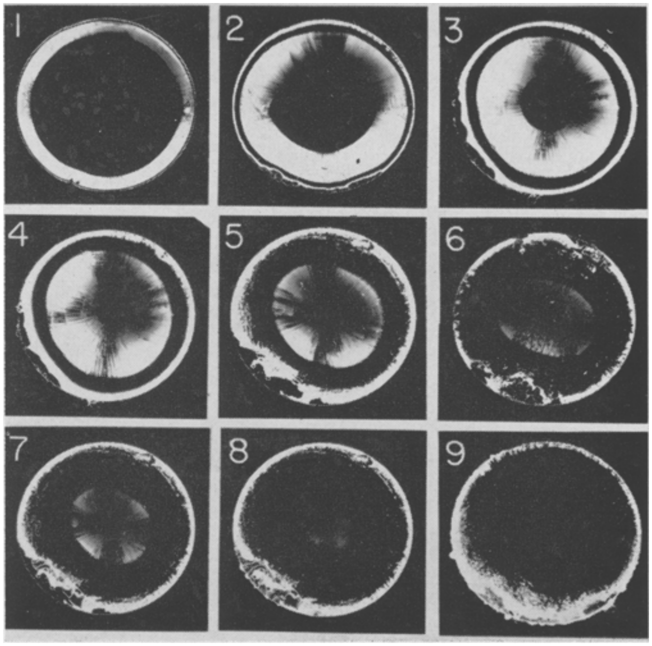

Fig. 2. Course of phase changes in drying DDAO solution: 70% H_2O–30% DDAO on microscope slide under round cover glass between crossed polaroids, approximately 1.3 times normal size (approximately equal time intervals, No. 1 to 9). Phase sequence, from periphery to center—neat, viscous isotropic, middle, fluid isotropic.

Evidences from X-Ray Diffraction

There are serious limitations to use of x-ray diffraction for studying mesomorphic structure, for it is difficult to get enough information on a diffraction pattern, frequently only a first order of long-spacing being obtainable besides the diffuse "liquid" halo. However, on favorable film patterns or diffractometer charts it was possible to obtain 1st, 2nd and 4th orders for a lamellar neat structure. It was also possible to obtain spacings for middle in the ratio $1:\sqrt{3}:\sqrt{4}$ as Luzzati (11) has reported for other middle phases.

No diffraction data reliably attributable to the viscous isotropic phase were obtained. This phase may be identifiable with the "cubic" phase reported by Luzzati et al. (12), but the present author refrains from interpretation.

Experimental 1st order long spacings of neat and middle phases are reported in Table II.

Crystalline States

Efforts to explore the diffraction patterns of crystalline states were only preliminary partly due to prevalence of phase mixtures. Very likely different degrees of crystal hydration were involved. Results obtained are summarized in Table III.

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[Received June 14, 1965—Accepted October 1, 1965]

N-2-Mercaptoethyl Amides of Fatty Acids—A New Class of Derivatives[1]

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Abstract

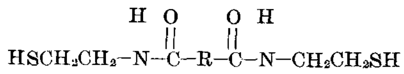
Twelve N-2-mercaptoethyl amides have been prepared by reacting 2-aminoethyl mercaptan with a carboxylic acid in refluxing xylene or toluene. All products were well-defined crystalline compounds except for the dimer acid derivatives. Addition of dithiol amides, prepared from dimer acids and 2-aminoethyl mercaptan, to diolefins gave a new class of potential protective coatings, a polyamide of a dimerized fatty acid with a β-thio linkage. Oxidation of the dithiols gave the corresponding disulfides, another new class of compounds, a polyamide with a β-disulfide structure. Film properties have been obtained with both classes of polymers. Air-dried films were soft and tacky, but baking the films improved hardness. Dry-to-touch times of less than 2 hr at 150C and good alkali resistance were obtained.

Introduction

THE LITERATURE CONTAINS few references to N-2-mercaptoethyl amides (1–5,8,9,11,13,15,17,18). Most of them relate to biochemical studies, but references 2, 5 and 11 concern organic syntheses. In penicillin studies, N-(2-mercaptoethyl)2,2-dimethyl-3-phenyl-3-ketopropionamide was prepared from β-lactam (5). Kuh and Quadbeck (11) prepared N-2-mercaptoethyl acetamide and N-2-mercaptoethyl benzamide by reacting ethylene imine with thioacetic and thiobenzoic acids, respectively. Babichev and Shokol (2) reported on the reaction of 2-aminoethyl mercaptan with the anhydrides of succinic, glutaric and phthalic acids. They obtained the imide or amide depending upon the conditions of the reaction instead of the anticipated ω-(2-thiazoline) alkanoic acids.

We have prepared mercaptoethyl amides of mono- and dibasic acids and studied the addition of dimercaptans to nonconjugated terminal diolefins to give polymers that might serve as a new class of protective coatings. N,N′-Bis(2-mercaptoethyl)-amides were synthesized from 2-aminoethyl mercaptan and dibasic acids, and the reaction can be shown as follows:

$$HOOCRCOOH + H_2NCH_2CH_2SH \longrightarrow$$



$$HSCH_2CH_2{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}CH_2CH_2SH$$

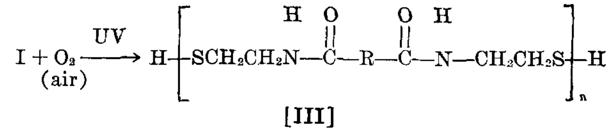
[I]

Biallyl and [I] were reacted in the presence of a persulfate catalyst. A free radical addition gave a new type of polyamide with a β-thio linkage [II] as shown in the following equation, where I is represented as HSR°SH:

$$HSR^{\circ}SH + \left(CH_2{=}CHCH_2\right)_2 \longrightarrow H{-}\left[SR^{\circ}S(CH_2)_6\right]_n{-}H$$

[II]

On oxidation, I gave a new type of polyamide with a β-disulfide structure.



$$I + O_2 \xrightarrow[\text{(air)}]{UV} H{-}\left[SCH_2CH_2\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}CH_2CH_2S\right]_n{-}H$$

[III]

This paper describes the preparation of N-2-mercaptoethyl amides and some polymers obtained therefrom.

Experimental

N,N′-Bis(2-mercaptoethyl)-azelamide

2-Aminoethyl mercaptan was prepared from the hydrochloride (Eastman P8567) by the method of

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[1] Presented at the AOCS Meeting in Chicago, October, 1964.

[2] No. Util. Res. and Dev. Div., ARS, USDA.