SYNTHESIS OF SURFACE-ACTIVE SUBSTANCES FROM ω -Chloro

CARBOXYLIC ACIDS

S. A. Dmitriev, N. M. Karavaev and A. V. Smirnova

Institute of Mineral Fuels, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Otedelenie Khimicheskikh Nauk, No. 10, pp. 1800-1803, October 1961 Original article submitted April 19, 1961

Nesmeyanov and Freidlina with co-workers [1-6] showed that the CCl₃ group of α , α , α , ω -tetrachloroalkanes which they obtained by the telomerization of ethylene with carbon tetrachloride is hydrolyzed by sulfuric or nitric acid with formation of normal ω -chloro carboxylic acids having chains of odd numbers of carbon atoms. From some ω -chloro carboxylic acids (9-chlorononanoic, 11-chloroundecanoic, and 13-chlorotridecanoic acids) we have synthesized some surface-active substances of different types: anionic, cationic, and nonionic. As Rebinder and Taubman showed [7-9], one condition for high surface activity in organic substances is an optimum balance in the characters of the hydrophobic and hydrophilic parts of the molecule.

To increase the length of the hydrocarbon chain and change the physical and chemical properties, in particular to remove the dipolarity of the ω -chloro carboxylic acid, the halogen was replaced by an aromatic group (phenyl*, tolyl, naphthyl, phenoxy). This replacement was effected by alkylating the corresponding aromatic compound with the ω -chloro carboxylic acids by the Friedel-Crafts method. As a result we obtained the following aryl carboxylic acids: 9-phenylnonanoic, 9-tolylnonanoic, 9-naphthylnonanoic, 9-phenoxynonanoic, 11-phenylundecanoic, 11 tolylundecanoic, 11-phenoxyundecanoic, and 13-phenyltridecanoic. The characteristics of these are given in Table 1.

Acid	М.р.	B,p, in °C			C. %		H, %	
		(pinmm)	d ²⁰ 4	n ²⁰ _D	found	calc.	found	calc.
9-Phenylnonanoic		177-179	0,993	1,5030	76,58	76,90	9,44	9,43
9-Phenoxynonanoic	6768	195-197			71,72	71,93	8,75	8,86
9-Naphthylnonanoic	-	(3) 222 -225			79,78	80,24	8,57	8,51
11-Phenylundecanoic		(3) 191–193	0,976	1,4985	76,86	77,84	9,88	9,98
11-Phenoxyundecanoic	72—73	(3) 217–222			72,81	73,36	9,44	9,42
13-Phenyltridecanoic		(3) 205–211	_				: ;	i
11-Tolylundecanoic		(3) 204—208	0,9 7 3	1,5012	78,64	78,21	10,28	10,21
9-Tolylnonanoic		(4) 194—198 (4)	0,989	1,5038	77,85	77,38	9,80	9,74

TABLE 1.

It should be noted that the replacement of chlorine in ω -chloro carboxylic acids by aryl (phenyl, tolyl, naphthyl) results in the acid becoming a liquid at room temperature (m.p. below 0). These acids have the advantage over un-saturated fatty acids in that they are stable to keeping. It is known that in most cases surface-active substances pre-

^{*} A benzene ring included in the straight chain of the hydrophobic part of a surface-active substance is equivalent to the lengthening of this chain by four carbon atoms.

pared from liquid acids have better technological properties than those derived from higher-melting acids (40-60) for a given length of hydrophobic chain.

EXPERIMENTAL

By condensing the acid chlorides of the above acids with taurines we obtained some anionic surface-active substances that differed among themselves only in the structure and composition of the hydrophobic part, which made it possible to determine the effect of the structure of the acid on the surface-activity properties of the product. To compare the physicochemical properties of the products we took the sodium salt of N-methyl-N-oleoyltaurine, which is widely used here and abroad under the trade name "Igepon T"; it has the formula:

$$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 CO(CH_3)NCH_2 - CH_2 - SO_3Na$$

The right-hand hydrophilic part of the substances synthesized (residue of N-methyltaurine sodium salt) remained unchanged in the first group of syntheses. The above-indicated aryl carboxylic acids were converted by the action of a 5-6 fold amount of thionyl chloride into their acid chlorides, which were condensed with the sodium salt of N-methyltaurine in a weakly alkaline medium with formation of the N-(arylalkanoyl) N-methyltaurine sodium salt:

$$RCOCI + CH_3NHC_2H_4SO_3Na \xrightarrow[-NaCI]{} RCON (CH_3) C_2H_4SO_3Na$$

TABLE 2.

Surface-active substance *	Surface tension (erg/sq. cm)		Fc	Crit.concn.					
	107-	0.10		1% soln.		0.1% soln.			formation
	soln.	soln.	0	30 sec	3 min	0	30 sec	3 min	(moles/liter)
N-Methyl-N-(9-phenylnonanoyl)									
taurine Na salt	35.6	-	450	200	0	-	-	-	1.8 . 10 - 3
N-Methyl-N-(11-phenylundecanoyl)									
taurine Na Salt	34.5	38.0	500	500	200	500	250	0	1.3 . 10-3
N-Methyl-N-(13-phenyltridecanoyl)							1		
taurine Na salt	32.8	-	620	620	600	550	550	550	-
N-Methyl-N-(9-phenoxynonanoyl)							1		
taurine Na salt	44.8	48.4	380	200	0	250	50	0	1.3 . 10-3
N-Methyl-N-(11-phenoxyun-									
decanoyl) taurine Na salt	44.2	47.2	350	250	0	300	50	0	1.2 . 10-3
N-Methyl-N-(9-naphthylnonanoyl)									
taurine Na salt	37.7	-	400	250	0	400	250	0	$1.4 \cdot 10^{-3}$
N-Methyl-N-(9-tolylundecanoyl)									
taurine Na salt	32.9	-	500	350	250	-	-	-	-
N -Methyl-N-(11-tolyundecanoyl)									
taurine Na salt	33.0	37.7	520	500	200	480	200	0	$1.4 \cdot 10^{-3}$
N-Methyl-N-oleoyltaurine Na									
salt (for comparison)	32.2	35.4	600	600	600	450	450	450	1.2 · 10-3

*All determinations were carried out at pH 7.

As a result we obtained the anionic surface-active preparations listed in Table 2, from which it will be seen that with increase in the length of the chain in the hydrophobic part of the molecule the surface-activity properties of the substance improve and attain the level of the standard (N-methyl-N-oleoyltaurine sodium salt) at N-methyl-N-(13-phenyltridecanoyl)taurine sodium salt. The sodium salts of N-methyl-N-(11-tolylundecanoyl)taurine and of N-methyl-N-(11-phenylundecanoyl)taurine were close in properties to Igepon T. The introduction of an electronegative element (e.g., oxygen in the phenoxy carboxylic acid) in the hydrophobic chain, as would be expected,

Surface-active substance	Surface tension (erg/sq. cm)		Foa	Crit.concn.					
	1%	0.1% soln.	1% soln.			0.1% soln.			for micelle
	soln.								(moles/liter)
N-Methyl-N-(9-phenylnonanoyl)									
taurine Na salt	35.6	-	450	200	0	-	-	-	1.8 . 10-3
N-(9-Phenylnonanoyl)									
taurine Na salt	34.2	-	470	450	0	-	-	-	1.9 . 10-3
N-Methyl-N-(11-phenylundecanoyl)								
taurine Na salt	34.6	38.0	500	500	200	500	250	0	1.3 . 10-3
N-(11-Phenylundecanoyl)									
taurine Na salt	33.6	37.3	550	550	350	550	550	100	_

greatly reduces the surface activity of the substance, which may be explained by the reduction in the hydrophobic character of the chain due to the presence of the ether oxygen, which is capable of forming hydrogen bonds in an aqueous solution.

The lowering of the stability of the foam, i.e., of the elastoviscous properties of the adsorption film on introduction of the naphthyl group at the end of the hydrocarbon chain of the saturated aliphatic acid may be explained by the large transverse size of the naphthalene nucleus, which probably hinders the compact packing of the unimolecular adsorption layer at the interface of the phases. The investigation showed also that the products obtained do not lose their surface activity either in alkaline or in acid media; they are good dispersing agents for calcium soaps and are stable toward calcium and magnesium salts, i.e., may be used in hard water and in sea water, which is particularly valuable for many technological processes. The critical concentration for micelle formation is an important index of the properties of surface-active substance in various processes (emulsification, dispersion, solubilization, detergency, etc.). The fairly low values of the critical concentrations for micelle formation (c_{crit} was determined by the electrical conductivity method) in the snythesized products indicate their great tendency for micelle formation and consequently the possibility of utilizing them in the above-indicated technological processes.

To determine the effect of the structure and composition of the hydrophilic part on the surface-activity properties of the same preparations we snythesized two further substances, in which, unlike the first group of syntheses, only the hydrophilic part was changed. In this case, instead of N-methyltaurine sodium salt, we took the sodium salt of taurine itself. The results of the investigation are given in Table 3.

The replacement of the methyl group in N-methyltaurine by hydrogen for a given hydrophobic end of the molecule has a favorable effect on the surface activity, as can be seen from Table 3. This may be explained by the high mobility of the hydrogen of the amide group and the formation of the enol form of the carbonyl, which increases the hydrophilic properties of the taurides.

SUMMARY

1. A series of anionic surface-active substances, namely N- ω -arylalkanoyl-N-methyltaurines, were prepared from aryl carboxylic acids.

2. The relation was shown of the surface activities of the substances to their chemical structures, mainly the structures of the hydrophobic parts of the molecules: the length of the alkyl chain $(C_9 - C_{13})$, the structure of the aryl group (phenyl, naphthyl), the effect of the presence of ether oxygen.

3. In hydrophobic character the hydrocarbon groups of 13-phenyltridecanoic and of 11-tolylundecanoic acids are equivalent to that of oleic acid and may replace it in the manufacture of surface-active substances.

LITERATURE CITED

- 1. A. N. Nesmeyanov and L. I. Zakharkin, Izv. AN SSSR. Otd. khim. n. 1955, 224.
- 2. R. Kh. Freidlina and E. I. Vasil'eva, Dokl. AN SSSR 100, 85 (1955).
- 3. A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, Uspekhi khimii 25, 6, 665 (1956).
- 4. G. B. Ovakimyan, M. A. Besprozvannyi and A. A. Beer, Khim. nauka i prom. 2, No. 1, 13 (1957).
- 5. Sh. A. Karapetyan, Priroda <u>11</u>, 9 (1958).
- 6. R. Kh. Freidlina and E. I. Vasil'eva, Izv. AN SSSR. Otd. khim. n. 1958, 35.
- 7. P. A. Rebinder Indtroduction to Collection "Physical Chemistry of Detergents" (All-Union Research Inst. for Fats) [in Russian] (Pishchepromizdat, 1935).
- 8. P. A. Rebinder, Khim. nauka i prom. 4, No. 5, 554 (1959).
- 9. A. B. Taubman, Khim. nauka i prom. 4, No. 5, 566 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.