In the first procedure the amount of acid required in titrating the sodium hydroxide solution of gossypol to pH 8.2 was subtracted from the amount used in titrating the same amount of alkali under the same conditions without the gossypol. The difference is a measure of the amount of sodium hydroxide reacting with the gossypol. Gossypol reacts as a dibasic acid. The value obtained for the molecular weight of gossypol (520) is in close agreement with the value (518.54) calculated from its molecular formula.

A similar procedure was used in determining the molecular weight of gossypol-acetic acid. Gossypol-acetic acid reacts as a tribasic acid. The molecular weight calculated from the titration data (578) is in close agreement with the theoretical value (578.5) calculated from the molecular formula for gossypol-acetic acid.

In the second procedure acetic acid was extracted from the gossypol-acetic acid by the procedure used for the determination of water-soluble acid. The acetic acid was titrated with sodium hydroxide solution to the phenolphthalein end-point. The molecular weight of gossypol-acetic acid calculated from these data is 577 and that of gossypol 517.

Standards of Purity

From these results the following standards of purity are suggested. Gossypol prepared by the improved procedure should consist of small, pale yellow, rod-like crystals free from extraneous material. Total volatile matter, including moisture, xylene, and other solvents, should not exceed 2% by weight. A 1-g. portion of the sample should dissolve in 20 ml. of ether, and no more than a trace of insoluble material should remain; when diluted to 100 ml., the solution should be pale yellow in color. The water-soluble acid extracted from the ether solution should be neutralized with one drop of N/10 sodium hydroxide solution. Total gossypol determined by alkalimetric titration may vary from 98 to 102% and by spectrophotometric measurement from 98.5 to 100.7%. The molecular weight of gossypol calculated from alkalimetric titration data should be approximately 518 and that of gossypol-acetic acid approximately 578.

Summary

Methods of dissociating the gossypol-acetic acid complex prepared from the butanone extract of defatted cottonseed flakes and methods of recrystallizing gossypol were studied. The study led to the development of an improved rapid procedure for the purification of gossypol.

In this procedure gossypol-acetic acid is dissociated with aqueous sodium hydroxide containing sodium hydrosulfite; the gossypol is precipitated with hydrochloric acid, extracted with ether, and recrystallized from a mixture of ether and xylene. Two crystallizations by this procedure gave gossypol free from acetic acid and of a high degree of purity. Gossypol-acetic acid of a high degree of purity was prepared by a modification of this procedure.

The degree of purity of the gossypol prepared by the improved procedure was determined by a number of tests, which are described. Spectral and titration curves for pure gossypol are presented, and standards of purity are suggested.

The molecular weight of gossypol and gossypol-acetic acid prepared by the procedures described is approximately 518 and 578, respectively.

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Structure and Aggregation in Dilute Solutions of Surface Active Agents[1]

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EXTENSIVE data have been published regarding the effect of structure of surface active agents on various properties such as detergency, bacteriostatic action, etc. These involve very dilute solutions, the concentrations of which are usually well below the critical micelle concentration (CMC). We shall be chiefly concerned in this report with solutions of somewhat higher concentrations and the manner in which structure of the surface active agents affects aggregation, i.e., micelle formation. In addition, these data are discussed in the light of recent concepts of micelle structure. Data presented below are taken in

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part from the literature and in part from our unpublished work. These unpublished CMC values have been obtained by the dye titration method (1, 12, 24), by refraction (25), and by conductivity measurements. Those data which have no definite literature reference have not been reported previously and have been determined in order to either check contradictory values found in the literature or to partially supplement the reported values when necessary.

The number of carbon atoms in normal straight chain colloidal electrolytes of one particular class is known to be a determining factor in the value of the CMC (1, 16, 21, 28). Recently it has been shown that the CMC decreases logarithmically with the increase in the number of carbon atoms in those fatty acid soaps having between eight and 14 carbon atoms (25). For various cationics and anionics the CMC data have been shown to be satisfied by an equation (25) which may be simplified and rewritten in the following manner:

$$\log \mathrm{CMC} = A - B\mathrm{N}$$

where N = number of carbon atoms in the chain,

B = an empirical constant (may be taken to be log 2 with sufficient accuracy),

and A = a constant for the particular temperature and homologous series, which may be determined from a known value of CMC for one member of the series.

For a number of different homologs the values of A (the intercept) in Table I are seen to vary considerably whereas B (the slope) is approximately equal to log 2 (0.301). The CMC values used to obtain A and B were the best values reported in the literature or were determined by refraction and/or dye titration.

The different values of A suggest that even though the CMC is dependent on the number of carbon atoms in the chain for any one homologous series, various types of colloidal electrolytes can not be compared in this manner. However if the length of the various paraffin-chain salts are compared, it is possible to obtain a relationship between the various surface active agents. Table II shows the CMC values, and chain lengths, computed using an extended zig-zag form for this comparison. Bond distances and bond angles collected by Pauling (34) are used in calculations of overall lengths of these colloidal electrolytes. Included are the straight chain fatty acid soaps, the straight chain alkyl sulfonates and alkyl sulfates, all anionic, and the cationic detergents, alkyl ammonium chlorides. The various colloidal electrolytes are matched as to chain length of their surface active group. The chain length is measured from the hydrogen of the ultimate carbon to the charged atom at the hydrophilic end of the paraffin chain. Thus a C_{13} fatty acid, a C_{12} sulfonate, a C_{11} sulfate, and a C_{12} ammonium chloride belong to the C_{12} family. When these straight chain soaps and detergents are grouped in this manner, it is seen that the CMC is essentially independent of the nature of the non-colloidal electrolyte ion and is a function primarily of the length of the surface active ion.

TABLE I

Values of A and B for Various Anionic and Cationic Surface Active Agents

	Temp. (°C.)	A	B	Method	Ref.
K fatty acids soaps......	25	1.92	0.290	dye[a], n[b]	1, 25
K fatty acids soaps......	45	2.03	0.292	n	25
Alkane sulfonates........	40	1.59	0.294	cond.[c], n	25, 49
Alkane sulfonates........	50	1.63	0.294	cond., n	25, 49
Alkyl sulfates..............	45	1.42	0.295	dye, n	This work
Alkyl ammonium chlorides..................	45	1.79	0.296	cond.	35
Alkyltrimethyl ammonium bromides....	60	1.77	0.292	cond.	44

CMC values determined by [a] dye titration; [b] refraction; [c] conductivity.

The effect of the length of the surface active ion on CMC at 35°C. is indicated in Fig. 1. Each group of compounds falls within a CMC region which is well within experimental error differences in methods of CMC determination. The equation of this curve can be represented by:

$$\log \mathrm{CMC} = 2.26 - 0.231\ \mathrm{L}$$

where L is the overall length of the surface active ion in Å.

The data in Tables II and III confirm the opinion of Hartley (15) that the CMC depends only on the length of the colloidal electrolyte chain and is not markedly dependent on the nature of the counter ion. This is, of course, only true in the case of uni-univalent systems as can be seen from a comparison of the CMC values of 0.00023-0.00044M for the uni-univalent octadecyltrimethyl ammonium salts and about 0.0001 for the oxalate salt. Lottermoser and Püschel (28)

TABLE II

The Change in Critical Micelle Concentration of Various Anionic and Cationic Soaps and Detergents With Length of the Lipophilic Portion of the Molecule

Type of detergent	Lipophilic group	Length (Å) of lipophilic group	CMC (moles per liter)	Method	Temp. °C.	Ref.
Fatty acid..	n–C_{11}O–	15.3	0.050	dye[a]	25	This work
Sulfonates..	n–C_{10}SO–	15.8	0.041	n[b]	25	25
Sulfates..	n–C_9OSO–	15.6	0.052	calc.[c]	25	
Amine HCl..	n–C_{10}NH+	15.1	0.048	n	25	25
Fatty acid..	n–C_{13}O–	17.8	0.012	dye	25	This work
Sulfonates..	n–C_{12}SO–	18.3	0.010	n	30	25
Sulfates..	n–C_{11}OSO–	18.1	0.013	calc.	30	
Amine HCl..	n–C_{12}NH+	17.6	0.014	n	30	25
Fatty acid..	n–C_{15}O–	20.4	0.0034	calc.	45	
Sulfonates..	n–C_{14}SO–	20.9	0.0030	n	45	25
Sulfates..	n–C_{13}OSO–	20.7	0.0033	calc.	45	
Amine HCl..	n–C_{14}NH+	20.2	0.0031	n	40	25
Fatty acid..	n–C_{17}O–	22.9	0.0009_5	calc.	55	
Sulfonates..	n–C_{16}SO–	23.4	0.0009_0	n	55	25
Sulfates..	n–C_{15}OSO–	23.3	0.0008_5	calc.	55	
Amine HCl..	n–C_{16}NH+	22.7	0.0008_5	n	55	This work

CMC values determined by [a] dye titration; [b] refraction; [c] calculation by use of an empirical equation (25) since no data on odd carbon atom alkyl sulfates are available.

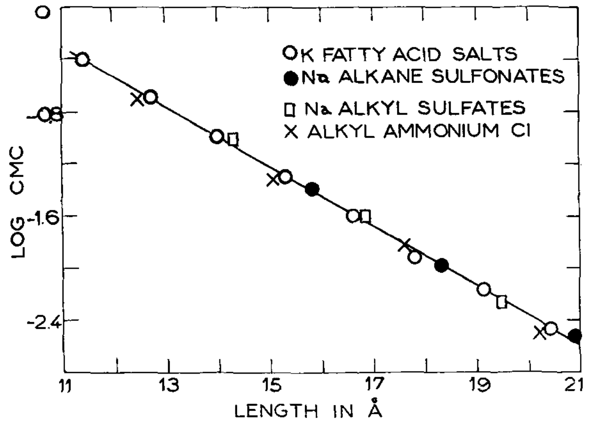

FIG. 1. Effect of chain length on critical micelle concentrations. All values are for 35°C.

have reported correspondingly smaller CMC values for the divalent Cu and Zn than for the univalent Na, K and H salts of the alkylsulfates. Within a particular chain length group it is to be expected that differences in the degree of average ionization of the molecules making up the micelle would affect the CMC value.

TABLE III

Effect of Counter Ion on Critical Micelle Concentration (Moles per Liter)

Detergent	CMC	Temp. (°C.)	Method	Ref.
Dodecanoates				
Sodium	0.026	25	dye[a]	This work
Potassium	0.0255	25	dye	This work
Cesium	0.025	25	dye	This work
Dodecylammonium				
Chloride	0.014	30	dye	This work
Bromide	0.012	30	dye	This work
Acetate	0.0151	25	cond.[b]	39
Nitrate	0.0115	25	cond.	35
Dodecylpyridinium				
Chloride	0.015	25	dye	This work
Bromide	0.016	25	dye	This work
Octadecylammonium				
Chloride	0.00055	60	cond.	35
Acetate	0.00040	60	cond.	35
Octadecyltrimethylammonium				
Chloride	0.00034	25	cond.	8
Oxalate	0.0001	25	cond.	8
Bromate	0.00031	25	cond.	8
Formate	0.00044	25	cond.	8
Nitrate	0.00023	25	cond.	8

CMC values determined by [a] dye titration; [b] conductivity.

According to the Debye-Hückel theory, one would expect the energy of repulsion to be proportional to the total charges squared. However it has been recently shown by Debye (3) that in these colloidal electrolyte systems, this energy is proportional to about the 3/2 power of the charge. Cushman, Brady, and McBain (2) have shown that when the counter ion becomes very large, the CMC decreases. Thus the CMC values of benzyltrimethylammonium and morpholine dodecanoate are about 0.010-0.015N as compared with a value of 0.025 for the potassium salt. These differences may be due to minor differences in the degree of ionization of the micelles for it has been observed that the presence of small amounts of unionized additives will markedly decrease the CMC whereas the use of an ionized additive of an equivalent chain length and same charge will result in little change (24).

Substitutions in the Hydrophilic Portion of the Molecule

The CMC data in Table IV show the effect of substitution of methyl or other groups for the hydrogens in the hydrophilic region (within one or at most two carbons from the charged atoms) of various cationic detergents. The data in Table I as well as other published data (see Table VI), ref. 25) indicate that for each decrease in chain length of the surface active ion by one carbon, the CMC would be doubled. Except for a small increase, substitution of a small group in the region of the hydrophilic portion of the molecule has no effect on the CMC. In these substituted detergents, as well as in the straight chain ones, the CMC seems to depend solely on the chain length of the hydrophobic group. The introduction of three methyls or one or more hydroxyethyls (37), or a pyridinium group (15) in place of the amine hydrogens, thus is seen to exert little or no influence on micelle formation. It is possible that the large degree of disorder in the micelles of these cationics [as is evidenced by their larger intermicellar spacing (9) and solubilizing power] as compared with the anionics may negate the influence of the branched chain. It is to be noted that the length of the group substituted in the region of the charged head of the paraffin chain salt and the relative lengths of the substitution and the paraffin chain are factors involved in micelle formation. Thus although the substitution of one or more hydroxyethyl groups in the dodecylammonium chloride results in a slight decrease in the CMC (37), the substitution with 2,3-dihydroxypropyl groups in the C_{12} compound is accompanied by a decided modification of the colloidal character as is indicated by the absence of a well defined critical micelle point (37). On the other hand, substitution with 2,3-dihydroxypropyl groups in the C_{16} compound has no effect on CMC nor on the conductivity characteristics of these detergents (37).

As the length of the side chain increases, it is to be expected that a change in the CMC will take place. From the surface tension — concentration curves of the very interesting positional isomers (with respect to position in the alkyl chain of the $-OSO_3^-$ group) prepared by Dreger, Keim, Miles, Shedlovsky, and Ross (4), the following can be qualitatively advanced:

1. If the two isomers (i.e. those compounds in which the sulfate group is in the 2 position) are compared, it is seen that the two-fold rule holds, for in those cases where the chain length is increased by two carbon atoms. the CMC is reduced to approximately one-fourth its previous value.
2. If the sulfate group is on the center carbon in the chain, an increase in length by addition of one carbon at each end will result, as expected, in more than a two-fold decrease in CMC but not as much as a four-fold decrease which would occur if both carbon atoms had been added at one end of the alkyl chain. The actual decrease appears to be approximately 2.5-fold.

TABLE IV

Change in Critical Micelle Concentration of Cationic Detergents With Substitution in the Region of the Hydrophilic Group

Detergent	CMC (moles per liter)	Method	Temp. (°C.)	Ref.
n–C_8–NH_3Cl	0.175; 0.20	n[a]; cond.[b]	25	This work; 38
n–C_8–$N(CH_3)_3Br$	0.137	cond.	25	44
n–C_{10}–NH_3Cl	0.048; 0.042	n; cond.	25	This work; 38
n–C_{10}–$N(CH_3)_3Cl$	0.065	dye[c]	25	This work
n–C_{10}–$N(CH_3)_3Br$	0.065	cond.	25	This work
n–C_{12}–NH_3Cl	0.014	n	30	This work
n–C_{12}–$N(CH_3)_3Cl$	0.016; 0.020	dye; cond.	30	This work; 36
n–C_{12}–$N(CH_3)_3Br$	0.016	cond.	25	44
n–C_{12}–Pyr–Cl[f]	0.015	n	30	This work
n–C_{14}–NH_3Cl	0.0031	n	40	This work
n–C_{14}–$N(CH_3)_3Cl$	0.0040; 0.0036	n; dye	40	This work
n–C_{14}–Pyr–Cl	0.0036	calc.[d]	40	
n–C_{16}–NH_3Cl	0.0008_5	n	55	25
n–C_{16}–$N(CH_3)_3Br$	0.0010	cond.	60	44
n–C_{16}–$N(CH_3)_3Cl$	0.0013; 0.0014	cond.	30	37; 36
n–C_{16}–$N(CH_3)_2(C_2H_4OH)Cl$	0.0012	cond.	30	37
n–C_{16}–$N(CH_3)(C_2H_4OH)_2Cl$	0.0010	cond.	30	37
n–C_{16}–$N(C_2H_4OH)_3Cl$	0.0010	cond.	30	37
n–C_{16}–Pyr–Cl	0.0009	cond.	30	15
n–C_{16}–Pyr–Br	0.0008	trans.[e]	30	13

CMC values determined by [a] refraction; [b] conductivity; [c] dye titration; [d] empirical rule; [e] transport number. [f] Pyr = pyridinium.

3. For one alkyl chain length, there is an increase in CMC as the sulfate group is moved from the terminal position.

Somewhat more quantitative data on the effect of position of charged group in the alkyl chain can be seen in the comparison of the data in Table V, part of which have been reported by Winsor (48). The comparison with the straight chain sulfates [heading marked CMC(2)] having the same length of alkyl chain as the longer portion of the branched sulfates indicates that a branching of more than one carbon atom in length at a position four atoms removed from the ionic charge is necessary before the CMC is affected.

TABLE V

Effect of Position of $-SO_4Na$ Group of *n*-Tetradecane Sodium Sulfates on Critical Micelle Concentrations (Moles per Liter × 10^3)

Position of $-SO_4Na$	Tetradecane sulfates	Straight chain sulfates		$\frac{CMC(2)}{CMC(1)}$
	CMC (1)	CMC (2)	No. C atoms	
–1	1.65	1.65	14	1.0
–2	3.26	3.30	13	1.01
–3	4.52	5.8	12	1.28
–4	5.76	12.0	11	2.09
–5	7.95	25.0	10	3.14
–6	12.3	52.0	9	4.23
–7	15.8	100.0	8	6.22

Similar effects have been observed in the branched dialkylsulfosuccinates. Three of these detergents, with a reported purity of 98-99 ± 1%, 1-2% is probably water, have been obtained from Dr. J. K. Dixon, American Cyanamid Co. The effect of position of the charged group in these detergents on CMC is seen from the data in Table VI to be similar to that of the *n*-tetradecane sodium sulfates. The CMC values have been obtained from refraction measurements at 35°C., using the procedure described previously (25). The length of these branched molecules is taken as the distance between the charged head and the atom farthest from it in the hydrophobic chain. These CMC values are compared with those of the straight chain surface active agents of the same class.

TABLE VI

Critical Micelle Concentrations of a Series of Dialkyldimethylammonium Chlorides and of Some Aerosols (Dialkyl Sodium Sulfosuccinates)

Dialkyl sodium sulfosuccinates			Straight chain sulfates		$\frac{CMC(2)}{CMC(1)}$
	CMC[a]	CMC(1)[b]	CMC(2)	No. C atoms	
bis-(4-methyl-2-amyl)	0.042	0.048	0.17	8	3.5
bis-(2-ethylhexyl)	0.0041	0.0051	0.041	10	8.1
bis-(*n*-octyl)	0.00065	0.0007	0.010	12	14.3

Dialkyldimethylammonium chlorides		Straight chain ammonium chlorides		$\frac{CMC(2)}{CMC(1)}$
	CMC(1)[c]	CMC(2)	No. C atoms	
$(C_8H_{17})_2(CH_3)_2NCl$	0.0266	0.137	8	5
$(C_{10}H_{21})_2(CH_3)_2NCl$	0.0020	0.065	10	33
$(C_8H_{17})(C_{12}H_{25})(CH_3)_2NCl$	0.0018	0.020	12	11
$(C_{12}H_{25})_2(CH_3)_2NCl$	0.00018	0.020	12	110

CMC values determined by [a] dye titration (courtesy of J. K. Dixon); [b] refraction (this work); [c] conductivity (36).

Substitution in the Hydrophobic Portion of the Molecule

There are two ways in which the character of the hydrophobic portion of the molecule may be changed. The first would involve interruption in the chain itself by replacing one or more C to C single bonds by a double bond, or by replacing a number of C atoms by aromatic groups of various sizes. The second class is the addition of a side group at some point in the alkyl chain. This substitution might involve a) polar groups, b) alkyl groups, and c) aryl groups.

a) *Effect of unsaturation on CMC.* Various CMC values have been reported in the literature for sodium and potassium oleate which ranged from 0.23M as determined by viscosity (19) to one of 0.0007 to 0.0012M (1). Ekwall (5) could find no definite value from conductivity studies, and Ralston *et al.* (37) noted that unsaturation causes little or no change in CMC when compared to saturated compounds of the same chain length. It is probable that the initial discrepancies in reported values are due to marked differences in the samples used as well as in the methods used for the determinations.

A sample of potassium oleate (cis $C_{18}^{=}$) was prepared in this laboratory by neutralization of an oleic acid which has been shown to be 97-98% oleic acid by unsaturation tests and spectroscopic measurements (40). No fatty acids of higher degree of unsaturation were present in this mixture, and the only impurity was some saturated fatty acids of approximately the same chain length. The CMC of this soap determined by refraction and by spectral changes of dye solutions is found to be 0.0008N and 0.0009-0.0010N, respectively, at 25°C. From reported studies of the CMC of soap mixtures (24) the value of CMC would not be changed by the presence of as little as 3% saturated fatty acid soap of shorter chain lengths and would be decreased about 5% in the presence of higher molecular weight soaps. Further potassium oleate and potassium elaidate (trans $C_{18}^{=}$), prepared from 97% oleic acid[3] and 93% elaidic acid (7% saturated), followed by recrystallization have CMC values of 0.0010 and 0.0015 at 50°C. The data for the unsaturated and the corresponding saturated compounds are collected in Table VII.

It is evident from these results that the presence of unsaturation causes a slight but definite increase in the CMC as compared with other soaps having the same number of C atoms. A similar small but definite difference in CMC has also been noted in the comparison of potassium abietate[4] with a value of 0.012M and potassium dehydroabietate[4] with one of 0.027M. Further, potassium dilinoleate, a dimer of linoleate prepared by the Eastern Regional Research Laboratories, is found to have a CMC of 0.0002_5M. It is worth noting that the marked differences in solubility between the saturated and unsaturated soaps does not carry over to their association properties, i.e., in the formation of micelles.

b) *Alkyl-aryl systems.* Although very large amounts of detergents of this type, the alkyl benzene sulfonates for example, have been produced commercially, no extensive data have been reported for these systems. Paquette, Lingafelter, and Tartar (33) have compared the CMC of *n*-octyl and *n*-dodecyl benzene sulfonate (values 0.15N and 0.0012N respectively at 60°C.) with the corresponding alkyl sulfonates and report that the presence of the benzene ring in the chain is equivalent to about 3.5 C atoms. It is apparent that the bulk of the benzene ring in the vicinity of the charged head of the detergent has only a minor effect on the value of the CMC. When the length of the benzene ring, about 2.65Å, is compared with that of 3.5 C atoms, about 4.35Å, there is apparent some enhancement of the effect of the benzene group in the chain. This effect is even more apparent when one considers the CMC value of 0.061N (determined by the spectral dye method, 50°C.) of a mixture of sodium triisopropylbenzene sulfonates (41). This value is considerably below one found for a corresponding straight chain alkyl sulfonate of the same chain length which would have a CMC of about 0.8N.

c) *Polar substitution in the chain.* The effect of substitution of polar groups for hydrogen in the paraffin chain results in marked increase in solubility of the colloidal electrolytes and for these systems much higher CMC values are found. Gregory and Tartar (7) report a CMC value of 0.0075N for potassium 9,10-dihydroxystearate (acid m. pt. = 131.6°C.) in 0.001N KOH as compared with one of about 0.0005N for potassium stearate as determined conductimetrically at 60°C. A preparation of 9,10-dihydroxystearate obtained by repeated recrystallization of the acid,[5] m. pt. 130.2-130.5°C., followed by neutralization and further recrystallization has a CMC of 0.0080N at a pH = 9.5. This value was determined by refraction and compares with a similarly obtained value of 0.0004_5N for potassium stearate. Another 9,10-dihydroxystearic acid,[5] m. pt. 94.2-94.4°C., has been neutralized as was its higher melting point isomer, and its CMC is found to be 0.011N. The various results obtained in these measurements are compared in Table VII with those found in the literature.

CMC data on a purified ricinoleate (12-hydroxy-9-octadecenoic acid) and its isomer, ricinelaidate, are included in Table VII. Methyl ricinoleate[6] and ricinelaidic acid[6] were purified as follows. The ester was fractionally distilled under vacuo in a micro Podbielniak column of about 50 theoretical plates. The center cut after two distillations was saponified with alcoholic KOH and the resulting compound was recrystallized a number of times and then dried in vacuo. The acid was recrystallized from alcohol, neutralized, recrystallized twice, and vacuum dried. The CMC values for the ricinoleate and its isomer, ricinelaidate, are seen to fall between the oleate and the dihydroxystearate values.

The more polar the compound becomes, the greater would be its solubility in polar solvents, and it is expected that the CMC value correspondingly would be higher. Thus it would be expected that the CMC values would be as follows: saturated compound < one with one C = C < one with one —OH < one with one C = C and one —OH and < one with two —OH groups. The somewhat meager data available at the present time support this concept, but it is very likely that the effect of position of these polar substitutions would play an equally marked role in micelle formation.

Recently a very interesting amino acid, N-dodecyl-β-alanine ($C_{12}H_{25}NHCH_2CH_2COOH$), has been made available.[7] In common with all amino acids it is possible to obtain both cationic and anionic derivatives of this compound. The acid was carefully recrystallized a number of times from various mixtures of alcohol, acetone, and dioxane until it crystallized as minute colorless crystals. These were then either neutralized with hydrochloric acid or potassium hydroxide. The anionic detergent prepared from this amino acid, potassium N-dodecyl-β-alaninate, is seen to have a CMC of 0.0026N and 0.0030N at 35° and 50°C., respectively. This is only slightly higher than the CMC of the fatty acid soap of the same chain length, the palmitate, which is 0.0022N at 50°C. The cationic amine hydrochloride, $C_{12}H_{25}N(HCl)HCH_2CH_2COOH$, is seen to have a CMC value of 0.010N, which is lower than that of 0.014N for the dodecyl ammonium chloride. The polar $—CH_2CH_2COOH$ group on the nitrogen decreases slightly the CMC of this detergent in the same direction that the $—CH_2CH_2OH$ group does as the data in Table IV indicate.

Shape and Size of Micelles

Various models have been proposed for micelle structures. McBain (29) has postulated two kinds of

---

[3] Supplied by Dr. Daniel Swern of the Eastern Regional Research Laboratories of the U.S.D.A.

[4] Prepared from corresponding acids supplied by Dr. R. S. George, Hercules Powder Co.

[5] Supplied by Dr. Daniel Swern of the Eastern Regional Research Laboratories of the U.S.D.A.

[6] Supplied by Dr. J. Nichols, Interchemical Corp., New York, N. Y.

[7] Supplied by the B. F. Goodrich Chemical Co., Cleveland, Ohio.

TABLE VII

Effect of Unsaturation and Polar Substitution on Critical Micelle Concentration

Potassium soap	CMC (moles per liter)	Temp. (°C.)	Method	Ref.
Stearate (satd. C_{18})	0.0004_5	55	n[a]	This work
Stearate (satd. C_{18})	0.0005	60	cond.[b]	7
Oleate (*cis*-$C_{18}^{=}$)	0.0008	25	n	This work
Oleate (*cis*-$C_{18}^{=}$)	0.0009-0.0010	25	dye[c]	This work
Oleate (*cis*-$C_{18}^{=}$)	0.0012	50	n	This work
Oleate (*cis*-$C_{18}^{=}$)	0.0012-0.0014	50	dye	This work
Elaidate (*trans*-$C_{18}^{=}$)	0.0015	50	n	This work
Abietate	0.012	25	dye	This work
Dehydroabietate	0.027	25	dye	This work
9,10-Dihydroxystearate (131.6°C. acid)	0.0075	60	cond.	7
9,10-Dihydroxystearate (130.2-130.5°C. acid)	0.0080	55	n	This work
9,10-Dihydroxystearate (94.2-94.4°C. acid)	0.011	55	n	This work
Ricinoleate (12-OH oleate)	0.0036	55	n	This work
Ricinelaidate (12-OH elaidate)	0.0055	55	n	This work
N-dodecyl-β-alaninate	0.0026	35	n	This work
N-dodecyl-β-alaninate	0.0030	50	n	This work
Palmitate (satd. C_{16})	0.0022	50	n	This work
N-dodecyl-β-alanine hydrochloride	0.010	30	n	This work
Dodecyl ammonium chloride	0.014	30	n	This work

CMC values determined by [a]refraction; [b]conductivity; [c]dye titration.

micelles, ionic spherical and neutral lamellar, and has had much support for the latter type of micelle from the x-ray work of Stauff (46), Hess (18), and more recently Harkins, Mattoon, and Corrin (9). Hartley has proposed only one type of micelle, a spherical one (14). An ellipsoid of rotation has been proposed by Hughes (23) as an interpretation of his x-ray data on solubilization and by Müeller (32) from work on association phenomena. Mattoon subsequently proposed a two-layer sandwich micelle as another possible model (31). Vetter (47) has supported the idea of the spherical micelle of Hartley based on conductivity and diffusion measurements with sodium di(2-ethylhexyl)sulfosuccinate. He mentioned two critical zones, one at about 0.025-0.030M, which is in the region of the CMC [0.050M as determined by refraction (27) and 0.055M determined by the dye method], and the other at about 0.13M. Harkins (10) recently has proposed a cylindrical model for a micelle which agrees with the x-ray data for the M-band (equivalent to twice the length of the soap molecule). He also mentions a second critical concentration, about 0.3N for potassium myristate, where, because of the concentration effects, the micelles lose some of their freedom of motion and the x-ray band which indicates distances between micelles begins to appear. Hartley, Collie, and Samis (13) previously advanced the same idea of partial loss of free motion in attempting to show that the use of the Debye-Hückel theory would introduce a very large uncertainty when applied to micelles, 40Å in diameter, carrying enormous charges of about 30, and with their mean distance apart, center to center, of only about 58Å as occurs in a 0.5N C_{16} soap solution. The quasi-ellipsoid (cross between a cylinder and an oblate spheroid) is the most recent model for the ionic micelle proposed by Harkins (11), which is postulated because of the improbability of an extensive hydrocarbon-water interface necessary in the previous models proposed by this author.

Recently Schulman and Riley (42) and Schulman and Friend (43), by means of x-ray and light scattering investigations of oil-water disperse systems, conclude that a hydrocarbon-swollen spherical micelle is a better structure for aggregated soap molecules than the lamellar or the cylindrical form. Further, McBain (30) has emphasized the presence of small spherical micelles present at low soap concentrations (as in the region of the CMC). If one accepts the idea of a spherical micelle swollen with solubilized hydrocarbon, removal of this hydrocarbon will result in some collapsing of the micelle. The micelle must be considered as a dynamic system with individual soap molecules probably a part of the aggregate and a free electrolyte at different times, and thus, in collapsing, the number of soap molecules per micelle will be less than in the swollen micelle. This is in accord with the calculations of Mattoon, Stearns, and Harkins (31), from x-ray measurements which indicate an increase in the number of soap molecules per micelle upon the addition of hydrocarbons. Recent light scattering measurements by Debye and Hagen (3) indicate that there are about 150 detergent molecules per micelle in the hydrocarbon swollen micelles of dodecyltrimethyl ammonium bromide-benzene with or without added potassium bromide. Ultracentrifugal studies, now in progress, will show whether these last mentioned results are correct. An analysis of their data leads these authors (3) to suggest a spherical model for the swollen micelles similar to one proposed previously (26). It is unlikely that a spherical model for the hydrocarbon-free micelle postulated by Hartley (14) and supported by Vetter (44) can be accepted, primarily because of the difficulty of trying to correlate micelle thicknesses (D_M) as determined by x-ray sudies with the packing of the hydrocarbon tails of the soap monomers in the micelle center necessary for the concept of a spherical model. The collapsed, hydrocarbon-free micelle may be assumed to have the general form of an oblate or a prolate spheroid, or a cylinder, or, what is more likely, some indeterminate, intermediate shape. This model will probably vary with type and chain length of detergent, with temperature, and with the presence of various additives such as electrolytes, polar and apolar compounds. It is not as yet known whether the possible degree of order within the micelle can be a further factor which will affect the micellar shape and size. Dodecyl ammonium chloride has a large degree of disorder as is evidenced by its large intramicellar spacing (D_M) and its large solubilizing power (moles oil dissolved per mole soap) (26) when compared with potassium dodecanoate and tetradecanoate which have much smaller values of D_M and solubilizing power for apolar compounds. The micelle of the C_{12} cationic is supposed to be an aggregate of some

50-60 molecules according to light scattering measurements (3) whereas free diffusion studies indicate some 30-35 (6) and diffusion in an electrical field, using a trace of Sudan IV as an indicator shows about 140-150 molecules of potassium dodecanoate per micelle, each micelle having an effective charge of about 20 (22).

It is not too difficult to picture or build a model of a soap micelle containing some 150 molecules, using a spheroid as a model, but this would be essentially impossible for an aggregate of 25-30 molecules. This latter number would allow only 12-15 (roughly 4 x 3 or 4 x 4) molecules per layer in the two-layer micelle, and in any form postulated there would have to be some order in the arrangement of the hydrocarbon tails to account for the short spacing pattern (about 5.0-5.5Å) found in x-ray studies on these systems.

In conjunction with swollen micelles the question of the possible penetration of apolar additives into the palisade layer may have an important bearing on the size of these micelles. Benzene is the only hydrocarbon which appears additively to swell the micelle, as x-ray studies indicate. The addition of small amounts of long chain methylalkylamides, nitriles, and hydrocarbons to alkylammonium chloride solutions results in slight decreases in CMC values coupled with marked lowering of the conductivity (38) and indicates a possible penetration of these additives into the palisade layer. This penetration is of such a magnitude that it results in a change of the effective charge on the micelle surface as is seen by the marked decrease in the conductivity in these solutions.

This problem of assigning a definite size and shape to micelles appears to be slightly premature at the present time. In addition to the fact that the structure of the soap monomer, the presence of various additives, and the temperature are factors which influence association and the type of aggregate which may be formed, it is also seen that the various methods of determination do not appear as yet to yield concordant results.

Summary

Critical micelle concentrations (CMC) are shown to depend on chain length. All straight chain saturated surface active agents of equal ion length have approximately *the same* CMC. Thus a C_{13} fatty acid soap, a C_{12} sulfonate, a C_{11} sulfate, and a C_{12} ammonium chloride have CMC values of 0.010-0.014M. Values of CMC are not changed to any extent by substitution near the hydrophilic head of one, two, or three groups, even as large as hydroxyethyl, in place of the amine hydrogens in the cationic detergents. However substitution with dihydroxypropyl groups has a marked effect on association in C_{12} but not in the C_{16} series, indicating that the relative lengths of the two chains must be considered as an important factor in association. This is well illustrated in the dialkylsulfosuccinate series, and in a tetradecane sulfate series in which the —SO_4Na group was progressively moved down the chain, particularly when the branched chain compounds are compared with the corresponding straight chain detergents of length equal to the maximum length from the charged head to the ultimate carbon atom. Introduction of double bonds causes a small but definite increase in CMC whereas polar substitution in the chain results in a marked increase in CMC. Possible micelle structures are discussed in the light of these association phenomena, and it is concluded that the assignment of a definite size and shape to micelles appears at the present time to be slightly premature. However if one includes the concept of relative order-disorder in the micelle as one of the factors, in addition to chain length, type of detergent, and environment, which are important in micelle structure, it is possible to explain partially the apparent marked differences which have been reported for micelles of different surface active agents.

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