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## Estimation of the effective number of $-CH_2-$ groups in long-chain surface active agents\*)

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With 4 figures and 3 tables

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### Introduction

The chainlength of surface active agents is an important parameter governing processes such as flotation, flocculation, foam separation and activated comminution and related interfacial phenomena such as adsorption and hemimicellization. The solution properties such as surface tension and micellization are also governed largely by the length of the chain of the surfactants. In the case of most commercial surface active agents, however, the effective chainlength is different from the actual length. The difference arises from the fact that commercial surfactants often contain one or more side chains and aromatic groups and in some cases even perfluoro groups in the chain increasing their hydrophobic character, or unsaturated bonds and substituted polar groups increasing their hydrophilic character. It is important to have a knowledge of the effective chainlength of the surface active agents and the characteristics that determine it since it is the effective chainlength that is of more practical relevance than the actual chainlength. In this paper, major structural modifications that affect the effective chainlength are considered and several methods for determining it are presented.

### Methods

The methods are based upon the identification of the relationships between various surface active properties of homologous series of  $n$ -alkyl surfactants and the actual number of methyl and

methylene groups in the chain and upon the subsequent evaluation of the effective chainlength of any similar surfactant with the help of the relationships. Surface active properties that are considered here are micellization, hemimicelle formation at solid/liquid interface, surface tension lowering and adsorption at solution/gas interface.

#### A. Micellization

Micelles of surfactants are formed in bulk aqueous solution above a given concentration for each surfactant and this concentration known as the critical micelle concentration (CMC) is related to the number of  $-CH_2-$  groups in a straight chain homologous series by the relation (1, 2).

$$CMC = A^* \exp\left(\frac{W_e - n\Phi_m}{kT}\right) \quad [1]$$

Where  $A$  is a constant,  $W_e$  is the electrostatic free energy of micellization per molecule,  $n$  is the total number of methyl end group and methylene chain groups,  $\Phi_m$  is the *van der Waals* cohesive energy of interaction per  $-CH_2-$  group,  $k$  is the *Boltzmann's* constant and  $T$  is the absolute temperature. Eq. [1] for simple  $n$ -alkyl amphiphiles can be rewritten in the form

$$\log CMC = a - bn. \quad [2]$$

Where  $a$  is

$$\log A + \frac{W_e}{2.303 kT}$$

$$\text{and } b \text{ is } \frac{\Phi_m}{2.303 kT}$$

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If  $W_c$  is independent of the chainlength, the relationship between  $\log \text{CMC}$  and  $n$  will be linear and it is in fact reported to be so (3). *Lin* and *Metzer* (4) determined the values of  $a$  and  $b$  for the homologous series of straight-chain alkylamine hydrochlorides using the data of *Ralston* and *Hoerr* (5). The values obtained for  $a$  and  $b$  are 1.252 and  $-0.265$  respectively. Eq. [2] for alkyl amine hydrochlorides is therefore

$$\log \text{CMC} = 1.252 - 0.265 n \quad [3]$$

Effective chainlength of any other surfactant system could now be obtained by determining its CMC and substituting it in eq. [3]. For example, from the data of *Lin* and *Metzer* for CMC's of ethane-saturated and propane-saturated dodecylammonium chloride solutions values of 12.35 and 12.80 were respectively obtained for the effective number of  $-\text{CH}_2-$  groups. The equivalent increase in the number of  $-\text{CH}_2-$  groups due to the dissolution of ethane is therefore 0.35 units and that due to the dissolution of propane is 0.8.

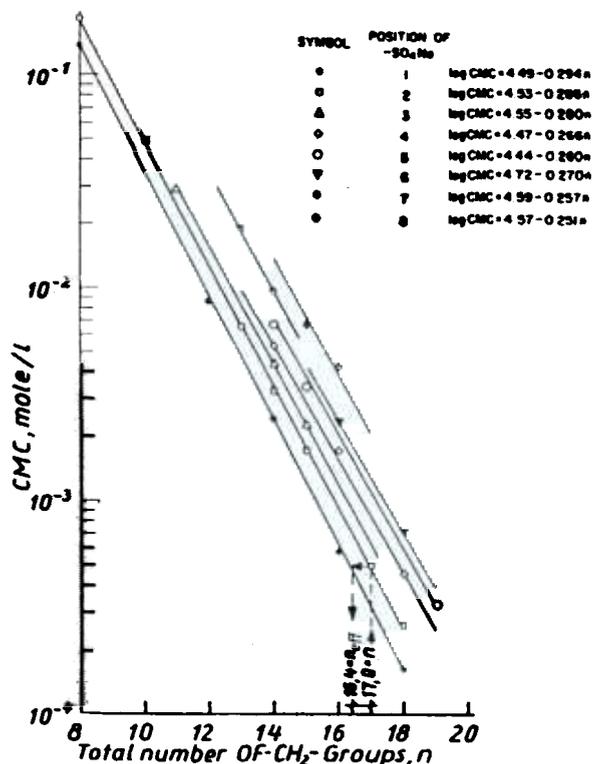


Fig. 1. Plot of critical micelle concentration as a function of the total number of  $-\text{CH}_2-$  groups in various sodium alkyl sulfates

An interesting application of this method is in the estimation of the effect of the position of the polar group in the hydrocarbon chain. Values for CMC's of sodium alkylsulfates containing a total of 8 to 18  $\text{CH}_2$  and  $\text{CH}_3$  groups but with the sulfate groups attached at various positions are given in table 1. The CMC data for alkyl sulfates with sulfate group attached to the terminal  $-\text{CH}_2-$  group (position 1), can now be used to evaluate the effective chain lengths of other sulfates. Towards this purpose the CMC value of alkyl (1) sulfates is first plotted as a function of chainlength as in fig. 1. The chainlength corresponding to the CMC of other sulfates is then read as the effective chainlength. For example, as illustrated in fig. 1, using a CMC value of  $4.9 \times 10^{-4}$ , an effective length of 16.4 is obtained for heptadecyl (2) sulfate. The effective chainlength of other sulfates evaluated in this manner is presented in table 1. It can be

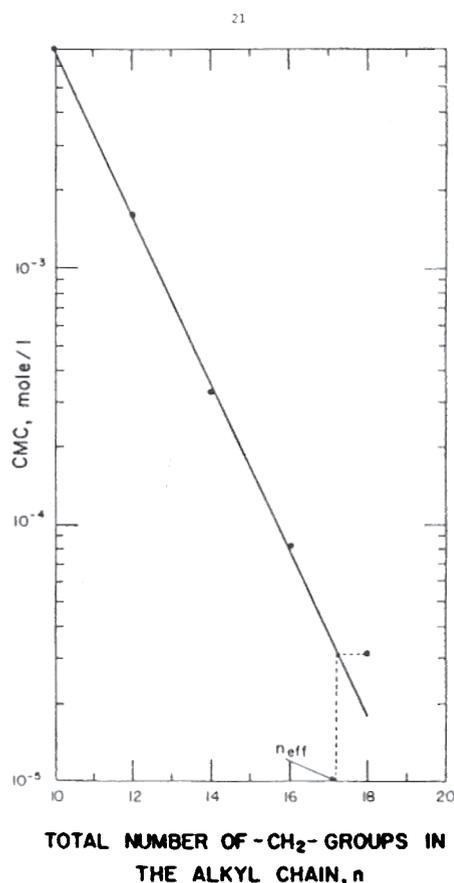


Fig. 2. Plot of critical micelle concentration of alkyl-trimethylammonium bromides as a function of the total number of  $-\text{CH}_2-$  groups in the alkyl chain

seen that the shifting of the sulfate group away from the terminal  $-\text{CH}_2$ -group does affect the effective chainlength significantly. For example, despite the fact that sodium diheptylsulfonate contains a total of 14  $-\text{CH}_2$ -groups its surface activity is apparently equal to only that of a straight chain sulfate containing about eleven  $-\text{CH}_2$ -groups.

It can also be seen that the relationship between CMC and the number of  $-\text{CH}_2$ -groups in the chain is linear for alkyl sulfates with the  $-\text{SO}_4\text{Na}$  group in positions other than 1. This makes it possible to evaluate the chainlength of any alkyl sulfate with any member of the homologous series as a basis.

Another interesting application of this technique is in the evaluation of the effect of coiling of long chained surfactant in water. Surfactants molecules which contain more than about 16  $-\text{CH}_2$ -groups are stated to coil around themselves (7). While in aqueous solution such coiling should produce an effective decrease in the chainlength. CMC data for alkyl trimethylammonium bromides (8) are plotted in fig. 2 as a function of chainlength. Non-linearity of the relationship between CMC and chainlength for longer chains is possibly due to the coiling. Using the straightline portion of the relationship as a basis, the effective chainlength of octadecyltrimethylammonium bromide is found to be 17.2. Thus the coiling has resulted in the removal of about 0.8  $\text{CH}_2$  group on the average from the aqueous solution. It must be noted that any increase in the tendency of the long-chained surfactants to form dimers, trimers etc. will also result in an effective decrease in the chainlength from the point of view of its micellization behavior. It might be noted that even though the above conclusions are on the basis of the micellization behavior of the surfactants, in general it is applicable for other surface active properties also.

### B. Hemimicellization

This method is based upon the observation that surfactant ions adsorbed at the solid-liquid interface associate to form two-dimensional aggregates called hemi-micelles at a given bulk concentration of the surfactant (9, 10). This concentration, like the critical micelle concentration, is determined largely by the chainlength of the surfactant. The following expression relating the concentration, HMC, at which the hemi-

micelles form to the number  $n$ , of  $-\text{CH}_2$ -groups in the chain has been developed earlier (11).

$$\log \text{HMC} = a' - b'n \quad [4]$$

where

$$a' = \log A' + \frac{W'_e}{2.303 kT}$$

and

$$b' = \frac{\Phi_{hm}}{2.303 kT}$$

$A'$  is a constant,  $W'_e$  is the electrostatic adsorption energy, and  $\Phi_{hm}$  is the *van der Waals* cohesive energy for the transfer of a  $-\text{CH}_2$ -group from bulk water into a hemi-micelle. If hemi-micelle concentrations of long-chain salts in a homologous series are known, the values of  $a'$  and  $b'$  for that series can be calculated. Effective chainlength of any other surfactant can then be easily evaluated if hemi-micelle concentration of it adsorbed on the same solid under the same condition of pH, ionic strength etc. is known. Dick, Fuerstenau and Healy (12) recently used this method to determine the effective chain length of various alkybenzene sulfonates. First they obtained a plot for hemi-micelle concentration of alkyl sulfonates as a function of the chainlength using the data of Wakamatsu and Fuerstenau (13) for the adsorption of sodium dodecylsulfonate, sodium tetradecylsulfonate, and sodium hexadecylsulfonate on alumina at pH 7.2 and a concentration of  $2 \times 10^{-3}$  mole/l  $\text{KNO}_3$ . The values obtained for hemi-micelle concentration of five dodecylbenzene sulfonate isomers were then placed along the plot obtained for straight-chain alkyl sulfonates and the effective chainlengths of the isomers were read from the plot. They observed the effective chainlength to vary from a value of 15.2 to 13.5 as the position of the benzene ring containing the sulfonate group was shifted from one end of the dodecyl chain to the center of it. This variation clearly showed the effect of branching of a surfactant chain on its interfacial activity. The results also showed that the addition of a benzene ring to the chain is equivalent to the addition of 3.2  $\text{CH}_2$  groups to the chain. This is in excellent agreement with the effectiveness of the benzene ring estimated by other techniques and thus proves the validity of the method of obtaining effective chainlength using hemi-

micelle concentration values. The method has been further utilized successfully for determining the effective length for the butane- and methane-saturated dodecylsulfonate solution/alumina/air system (14).

### C. Surface tension lowering

Reduction in the surface tension of water owing to the addition of organic compounds belonging to a homologous series is known to show certain regularities as expressed, for example, by *Traubes* rule. Interpretation of this phenomenon in terms of work gained on transfer of the surfactant species from the bulk to the surface yields a convenient way to evaluate the effective chainlength of surfactants. If  $W_n$  and  $W_{n-1}$  are the work involved in the transfer of 1 mole of a straight chain surfactant containing  $n$  and  $n-1$   $-\text{CH}_2$ -groups respectively

$$\begin{aligned} W_n - W_{n-1} &= RT \ln \frac{C_n^s C_{n-1}}{C_n C_{n-1}^s} \\ &= RT \ln \left[ \frac{\Gamma_n \tau_{n-1} C_{n-1}}{\tau_n C_n \Gamma_{n-1}} \right] \end{aligned} \quad [5]$$

where  $C^s$  and  $C$  are the surface and bulk concentration of the surfactants,  $\Gamma$  is the adsorption density, and  $\tau$  is the thickness of the surface region.  $W_n - W_{n-1}$  has been found experimentally to be about  $1.08 RT$  (7, 15). Assuming  $\tau$  to be constant, eq. [5] can be rewritten as

$$\ln \frac{\Gamma_n C_{n-1}}{C_n \Gamma_{n-1}} = 1.08. \quad [6]$$

The corresponding equation for the case of a surfactant with an effective chainlength  $m$  will be

$$\ln \frac{\Gamma_n C_m}{C_n \Gamma_m} = 1.08 (m - n). \quad [7]$$

The effective chainlength of a surfactant can be determined with the help of eq. [7] if the surface excesses  $\Gamma_m$  and  $\Gamma_n$  at bulk concentrations  $C_m$  and  $C_n$  are known. Surface excess quantities can of course be calculated from surface tension data using the *Gibbs* adsorption equation.

*Lin* and *Metzer* (4) used this method to calculate the effective number of  $-\text{CH}_2$ -groups in ethane and propane dissolved in dodecylammonium chloride solutions. Results obtained from surface tension data for dodecylammonium

chloride solutions saturated with air ( $d-a$ ), ethane ( $d-e$ ), and propane ( $d-p$ ) for the terms

$$\frac{\Gamma_{d-e} C_{d-a}}{\Gamma_{d-a} C_{d-e}} \text{ and } \frac{\Gamma_{d-p} C_{d-a}}{\Gamma_{d-a} C_{d-p}} \text{ at}$$

three different values of surface tension are given in table 2. Using this result, values of 0.46 and 0.72 were obtained for the effective number of  $-\text{CH}_2$ -groups in ethane and propane respectively. Dissolution of ethane and propane in dodecylammonium chloride solution is therefore of the same consequence as lengthening of the dodecyl chain by 0.46 and 0.72  $\text{CH}_2$ -group respectively.

### D. Adsorption at the liquid/gas interface

The previous method based on the *Gibbs* adsorption equation is simple and convenient but inadequate for describing the adsorption of long chain ions rigorously since it does not take into consideration the electrical energy involved in the formation of an electrical double layer at the interface when the long-chain ions are adsorbed there. *Davies* and *Rideal* (16) have derived a more rigorous isotherm for the case of adsorption of long-chain ionic surfactants. According to this the surface excess for the case of a symmetrical electrolyte is given by

$$\Gamma = \frac{(B_1/B_2) C \exp [(W_d - Ze\psi_0)/kT]}{1 + \left(\frac{B_1}{B_2}\right) A_0 C \exp \left(\frac{W_d - Ze\psi_0}{kT}\right)}. \quad [8]$$

Where

$$\frac{W_d}{kT} = \frac{521 n}{RT} + \frac{1200 n}{kT A^{1/2}} \quad [9]$$

and

$$\psi_0 = \frac{2kT}{e} \sinh^{-1} \left[ \frac{\sigma}{C_i^{1/2}} \left(\frac{500\pi}{DRT}\right)^{1/2} \right] \quad [10]$$

$B_1$  and  $B_2$  are constants characteristic of the adsorption and desorption rates respectively,  $W_d$  is the desorption energy of a hydrocarbon chain per molecule,  $Z$  is the valency of the polar head,  $e$  is the electronic charge,  $D$  is the dielectric constant of the medium,  $A$  is the area per molecule at the interface,  $A_0$  is the area per molecule for the case of a complete monolayer,  $\psi_0$  is the surface potential,  $n$  is the effective number of  $-\text{CH}_2$ -groups in the chain and  $\sigma_i$  is the surface charge density. For normally

encountered small values of  $C$  and  $\Gamma$ , eq. [8] can be rewritten as

$$\frac{C}{\Gamma} = \frac{B_2}{B_1} \exp\left(\frac{Ze\psi_0 - W_d}{kT}\right) + \frac{C}{\Gamma_{\max}} \quad [11]$$

Substitution of eq. [9] into the logarithmic form of [11] yields

$$\log\left(\frac{C}{\Gamma} - \frac{C}{\Gamma_{\max}}\right) - \frac{Ze\psi_0}{2.3kT} = \log\left(\frac{B_2}{B_1}\right) - \frac{521n}{2.3RT} - \frac{1200n}{2.3kTA^{1/2}} \quad [12]$$

Since  $A = 1/6.02 \times 10^7 \Gamma$

$$\log\left(\frac{C}{\Gamma} - \frac{C}{\Gamma_{\max}}\right) - \frac{Ze\psi_0}{2.3kT} = \log\left(\frac{B_2}{B_1}\right) - \frac{521n}{2.3RT} \left[ \frac{1200}{2.3kT} \left(6.02 \times 10^7\right)^{1/2} n \right] \Gamma^{1/2} \quad [13]$$

$\psi_0$  can be evaluated using eq. [10]. The left hand side of eq. [13] can then be calculated from experimental data and plotted as a function of  $\Gamma^{1/2}$  to obtain  $n$  and  $\log B_1/B_2$  from the slope and the intercept respectively. If the surface active molecule is not linear or if it contains hydrophilic groups or double and triple bonds in the chain,  $n$  will be actually the effective number of  $-\text{CH}_2$ -groups in the surfactant ion. This method has been used here for determining the effective number of  $-\text{CH}_2$ -groups in a dodecylammonium chain using data for its adsorption density at the liquid/air interface. The plot obtained for

$$\left(\frac{C}{\Gamma} - \frac{C}{\Gamma_{\max}}\right) - \frac{Ze\psi_0}{2.3kT}$$

as a function of  $\Gamma^{1/2}$  is given in fig. 3. A value close to 12 obtained for  $n$  is in agreement with the actual number of  $-\text{CH}_2$ -groups in the chain. *Jorne* and *Rubin* (17) have similarly determined the effective number of  $-\text{CH}_2$ -groups in a lauryl sulfate chain. They obtained a value of 11.6 for  $n$ . If the polar head of an adsorbed surfactant is assumed to be fully immersed in the bulk liquid, all the carbon atoms in the chain cannot be considered to be completely out of the aqueous environment. A value slightly smaller than the actual number of carbon atoms in the chain can hence be expected for  $n$  if it is evaluated using data for the adsorption at the solution/air interface. The

method has been further utilized successfully for determining the effective chain length for the ethane- and propane- saturated dodecylammonium chloride solution/quartz/paraffinic gas system (18).

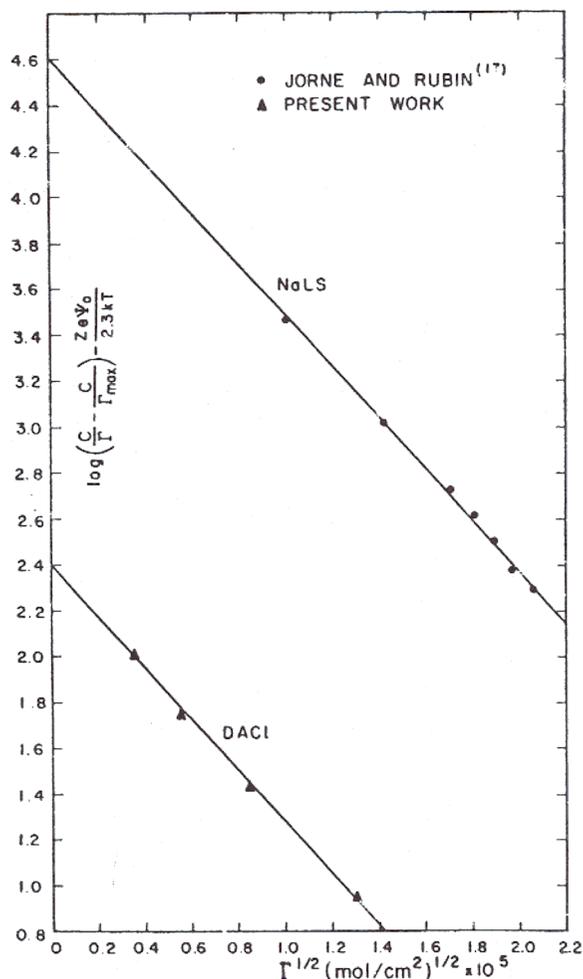


Fig. 3. Plot of  $\log$

$$\left(\frac{C}{\Gamma} - \frac{C}{\Gamma_{\max}}\right) - \frac{Ze\psi_0}{2.3kT}$$

as a function of  $\Gamma^{1/2}$  for dodecylammonium chloride and sodium lauryl sulfate

#### Discussion

Four methods based on various interfacial and colloidal properties of surfactants have been described for determining the effective number of  $-\text{CH}_2$ -groups in them. Ideally all the four methods should yield the same number.

However, depending on the difference in efficiencies with which a surfactant utilizes its various hydrophobic parts in different interfacial phenomena different values could be obtained for the effective number of  $-\text{CH}_2-$  groups.

The value obtained for the effective number is of course dependent upon the number of hydrophilic groups and the number of lipophilic groups present in the surfactant molecule or ion and the relative strengths of the groups. Surfactants have been classified in emulsion technology according to the balance between the above two opposite kinds of groups referred to as hydrophile-lipophile balance (HLB). This classification is on the basis of the total number of various groups present in the chain and do not take into account the effect of their structural position in it. Thus, a straight chain surfactant and a branched chain isomer of it would have the same HLB value even though the branched chain isomer would be less surface active than its straight-chain counterpart. Hence there is a need for a classification that is based upon the surface activity of a compound. A new classification that is based on the effective number  $-\text{CH}_2-$  groups is proposed here. It is useful for comparing the surface activity of two different surfactants as well as for defining changes in surface activities brought about by the presence of certain groups. For this classification we define a hydrophobicity index (HI), which is equal to the ratio of the effective number of  $-\text{CH}_2-$  groups in a chain to the actual number in it. A value greater than 1 due to the addition of a group thus means an increase in the hydrophobic character of the surfactant due to this addition and a value lesser than 1 means a decrease in it. For example, substitution of a single bond in the molecule with a double bond or a triple bond will yield a HI values less than 1 since the latter are less non-polar than the former. Addition of a benzene radical will however yield a value greater than 1 because of its relatively high hydrophobic nature. Addition of  $-\text{CF}_2-$  groups will also yield a value greater than 1 since perfluoro alkyl surfactants are much more surface active than the corresponding alkyl surfactants (19). *Shinoda, Hato and Hayashi* (20) have recently shown that the critical micelle concentration of a fluorinated surfactant is the same as that of a hydrocarbon surfactant whose chainlength

is about 1.5 times that of the fluorocarbon chain. An HI value of about 1.5 is therefore obtained for a perfluoro surfactant. Simple lengthening of a straight chain by the addition of  $-\text{CH}_2-$  groups can normally be expected to yield an HI value of 1. When the number of carbon atoms in the chain is greater than about 16, the value will however be less than 1 due to the coiling phenomenon discussed earlier. Addition of  $-\text{CH}_2-$  groups as side-chains would also yield lower HI value since these  $-\text{CH}_2-$  groups

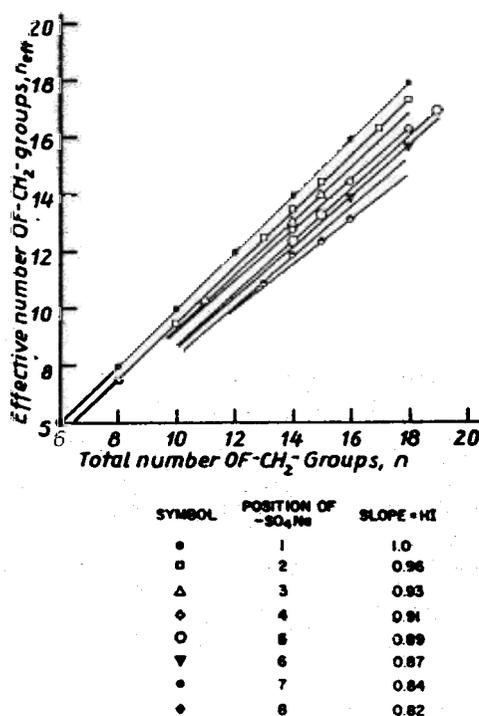


Fig. 4. Plot of effective number of  $-\text{CH}_2-$  groups in the various alkylsulfate chains as a function of the actual total number of  $-\text{CH}_2-$  groups in them

are not as effective in contributing to the surface activity as one added to elongate the straight chain portion of a surfactant (21). HI values of various sodium alkylsulfates listed in table 1 have been calculated by dividing the effective number by the actual number and are given in table 3. It can be seen from the table that a higher HI value is obtained by adding the  $-\text{CH}_2-$  groups to the longer branch of the surfactant rather than to the shorter one. A plot of the effective number as a function of the actual number is given in fig. 4. The slope of the plot obtained for each homologous series is a measure of the HI for that series. The difference

Table 1. Effect of the position of polar head group in the hydrocarbon chain of sodium alkyl sulfates on the CMC (6) and the effective number of  $-\text{CH}_2$ -groups,  $n_{\text{eff}}$ , at 40 °C

Position of $-\text{SO}_4\text{Na}$ Group	$n$	CMC, mole/l	$n_{\text{eff}}$
	8	0.136	8
1	12	0.0086	12
1	14	0.0024	14
1	16	0.00058	16
	18	0.00016	18
2	8	0.180	7.5
2	10	0.0495	9.5
2	13	0.0065	12.5
2	14	0.0033	13.5
2	15	0.0017	14.5
2	17	0.00049	16.4
2	18	0.00026	17.4
3	11	0.029	10.3
3	14	0.0043	13.1
3	15	0.0022	14.1
4	14	0.00515	12.8
4	16	0.00172	14.5
4	18	0.00045	16.4
5	14	0.00675	12.4
5	15	0.00340	13.3
5	19	0.00033	17.0
6	16	0.0023	14.0
6	18	0.0007	15.8
7	13	0.0193	10.9
7	14	0.0097	11.9
8	15	0.0066	12.4
8	16	0.0042	13.2

in values obtained for slope for various series clearly shows the effect of the position of the  $-\text{SO}_4\text{Na}$  group on the hydrophobicity of the surfactant ion. An examination of the plots in Figure 4 also shows that there is no measurable change in slope as the chainlength is increased

Table 3. Hydrophobicity Index of various sodium alkyl sulfates

Position of $-\text{SO}_4\text{Na}$ Group	Total number of $-\text{CH}_2$ -Groups, $n$	Hydrophobicity Index, HI
	8	1
	12	1
	14	1
	16	1
	18	1
2	8	0.937
	10	0.950
	13	0.961
	14	0.964
	15	0.966
	17	0.97
	18	0.97
3	11	0.936
	14	0.936
	15	0.940
4	14	0.914
	16	0.906
	18	0.911
5	14	0.885
	15	0.886
	19	0.894
6	16	0.875
	18	0.877
7	13	0.838
	14	0.850
8	15	0.826
	16	0.825

in any one given series. Thus there is no coiling exhibited even by octadecyl (1) sulfate chain. Considering the fact that the octadecyltrimethylammonium bromide showed a coiling effect, this observation indicates an additional effect of the  $-\text{SO}_4\text{Na}$  group.

A classification based on the effect of various groups and their position along with a know-

Table 2. Data for  $\Gamma_{d-e} C_{d-a} / \Gamma_{d-a} C_{d-e}$  and  $\Gamma_{d-p} C_{d-a} / \Gamma_{d-a} C_{d-p}$  at three different values of surface tension of dodecylammonium chloride solution saturated with air ( $d-a$ ), or ethane ( $d-e$ ) or propane ( $d-p$ )

Surface tension, dynes/cm	Adsorption density, mole/cm <sup>2</sup>			Solution concentration, mole/l			$\frac{\Gamma_{d-e} C_{d-a}}{\Gamma_{d-a} C_{d-e}}$	$\frac{\Gamma_{d-p} C_{d-a}}{\Gamma_{d-a} C_{d-p}}$
	Air, $\Gamma_{d-a}$	Ethane, $\Gamma_{d-e}$	Propane, $\Gamma_{d-p}$	Air, $C_{d-a}$	Ethane, $C_{d-e}$	Propane, $C_{d-p}$		
45				$9.5 \times 10^{-4}$	$5.5 \times 10^{-4}$	$3.8 \times 10^{-4}$	1.47	1.86
50	$4.7 \times 10^{-10}$	$4.0 \times 10^{-10}$	$3.5 \times 10^{-10}$	$6.2 \times 10^{-4}$	$3.3 \times 10^{-4}$	$2.2 \times 10^{-4}$	1.61	2.13
55				$2.0 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.3 \times 10^{-4}$	1.70	2.29
							1.59	2.09

ledge of the effective chainlength of various commonly-used surfactants should be helpful in making selection of surface active agents and in modifying reagents and designing new ones for various interfacial processes such as flotation, flocculation, emulsification and solubilization.

#### Summary

The effective length of long chain surfactants is a more important parameter than the actual chainlength in governing various interfacial and colloid phenomena such as adsorption and micellization and interfacial processes such as flotation, flocculation, emulsification and activated comminution. Various methods for determining the effective length (or effective number of  $-\text{CH}_2$ -groups) of ionic and non-ionic surfactants are presented here. These methods are based on treatment of experimental data for critical micelle concentrations, hemimicelle concentrations, surface tension lowerings and adsorption densities at liquid/gas interface. A new classification based on the ratio of the effective number of  $-\text{CH}_2$ -groups to the actual number, called the hydrophobic index, is proposed. The effects of various structural modifications and substitutions in the surfactant molecule or ion are discussed.

#### Zusammenfassung

Die wirksame Länge langkettiger Oberflächenwirkstoffe stellt einen wichtigeren Parameter dar als die eigentliche Kettenlänge, soweit es die Beherrschung der verschiedenen Grenzflächen- und Kolloidalerscheinungen – wie Adsorption und Mizellisierung – und Grenzflächenvorgänge – wie Flotation, Flockung, Emulsifizierung und geladene Zerkleinerung – anbelangt.

In der vorliegenden Arbeit werden eine Reihe von Methoden zur Bestimmung der wirksamen Länge (bzw. der wirksamen Anzahl  $-\text{CH}_2$ -Gruppen) ionischer und nichtionischer Oberflächenwirkstoffe dargestellt. Diese Methoden beruhen auf der Verarbeitung von Versuchsergebnissen und -daten für kritische Mizellenkonzentrationen, Halbmizellenkonzentrationen, Oberflächenspannungsverringerungen und Adsorptionsdichten an der Flüssigkeit/Gas-Grenzfläche. Es wird der Vorschlag einer neuen Klassifizierung, aufgebaut auf dem Verhältnis zwischen der wirksamen Anzahl von  $-\text{CH}_2$ -Gruppen und deren eigentlicher (nomineller) Anzahl, auch Hydrophobieindex oder Wasserscheuigkeitszahl oder Abnetzungsanzahl genannt, gemacht. Die Auswirkungen verschiedener Abänderungen und Einsetzungen im Molekül des Oberflächenwirkstoffs oder dessen Ion werden besprochen.

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