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The interfacial tension of aqueous solutions of surfactants were determined against three model fluids: o-dichlorobenzene, methyl salicylate and malathion. The effect of surfactant structure and model fluid on the adsorption process were catalogued with the aid of the Szyszkowski equation and the Girifalco-Good parameters for the specific solution-fluid pairs.

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CONTENTS

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HARD SURFACE DETERGENCY PART I: INTERFACIAL TENSIONS OF CANDIDATE SURFACE DECONTAMINATING AGENTS IN CONTACT WITH MODEL FLUIDS

I. Introduction

The contamination of a given material by another unwanted material may be conveniently classified in several groups. Such a classification which depends upon the characteristics of the contaminants and the given material together with their interactions is described in Table 1. Materials may range from non-porous non-swelling materials to porous swelling materials (with respect to the given material-contaminant pair). That is, contaminants may be virtually insoluble in the material (no observable swelling) or soluble (high degree of material swelling observed). In the case of non-swelling materials, the liquid contaminant interaction may range from non-wetting (180° contact angle) to complete wetting (0° contact angle). Contaminants may range from volatile liquids to non-volatile ones. They may further range from low viscosity liquids to high viscosity liquids or even solids. The least complex system to treat from the viewpoint of detergency is the interaction of an essentially insoluble liquid contaminant with the surface of a non-swelling material. Many practical surfaces fall into this category luckily. In this case, the overall detergency process may be conveniently observed optically with a contact angle goniometer. That is, the work of adhesion of such liquid contaminants to various surfaces may be studied through relationships involving the interfacial tension and the contact angle, i.e.

$$W_A = \tau_{o/w} (1 + \mathrm{Cos}\ \Theta) \qquad (1)$$

where $\tau_{o/w}$ is the interfacial tension, Θ is the contact angle and W_A is the work of adhesion. The wettability of the surface by the liquid is, as mentioned earlier, indexed by the contact angle, Θ, of the liquid on the surface.

Manuscript submitted February 23, 1982.

Table 1 — Contaminant-material combinations

	Contaminant Properties		
Material Property/Interaction	Swelling Tendency	Volatility	Voscosity
Non-swelling	None	Volatile	Low
Non-swelling but has internal surface	↓	↓	↓
Swells			
Swells and has internal surface	High	Non-volatile	High

A liquid contaminant drop on a smooth non-swollen surface may be displaced by a surfactant in two ways (a) by progressive displacement of adsorbed contaminant molecules by more strongly adsorbed surfactant molecules and (b) by significantly lowering the interfacial tension (1). In most cases, both processes take place concurrently. It is certain that lowering the interfacial tension between a contaminant and a surrounding aqueous solution greatly improves the probability of its removal with minimal mechanical energy being required to dislodge the increasingly spherical drop of liquid contaminant from a solid surface (2). Moreover, a low interfacial tension promotes facile emulsification of fluids, again with minimal mechanical energy requirements (3).

The lowering of interfacial tension as a function of surfactant concentration also provides a method by which the critical micelle concentration (CMC) may be estimated. This is the point at which surfactant molecules form aggregates with their non-polar moieties clustered together in a central portion and the polar groups forming the outer sheath in contact with the aqueous medium. The presence of micelles is an important factor in the phenomenon of solubilization which is considered sometimes to be a factor in the detergency process. Recent work has also suggested that the CMC may be an important variable in the rating of surfactants for oil dispersion effectiveness (4) and has been correlated with the Standard EPA Dispersant Effectiveness Test Procedure (5). The dispersion of oil spill fluids by surfactants has much in common with the removal and dispersion of contaminants deposited on surfaces. This report is concerned with the development of interfacial tension and critical micelle concentration information in the first phase of a practical surface decontamination study involving selection of candidate surfactants. The practical detergency process considered as the model towards which this information will be collected is that of a hard sur [illegible] over which flowing surfactant solution to applied. Re [illegible] ion of the contaminant on the surface will not be consi [illegible] n the model. Displaced or eroded contaminants will be carried away from the surface to be cleaned by the flowing surfactant solution thereby negating redeposition once displacement or removal of the contaminant has occurred. As mentioned earlier, contaminant may be removed by displacement through preferential adsorption of surfactant, thus significantly lowering the interfacial tension. It should also be noted that the reduction of the interfacial tension to low values by the surfactant when combined with the kinetic energy of the flow process assists in significant erosion of the contaminant even if classical displacement (roll-up mechanism) does not occur (1). This report is concerned with the selection of surfactants - based on their effects on the oily contaminant-water interface preliminary to studies on contaminant removal from hard surfaces (to be concluded in a second paper).

II. Experimental

Materials. The surfactants used were of two types - pure surfactants synthesized by American Cyanamid Laboratories, and commercial surfactants supplied by American Cyanamid, 3M and Witco Chemical Companies. These are as shown in Table 2. Contaminant fluids used were methyl salicylate, malathion and ortho-dichlorobenzene. The interfacial tension properties of the fluids used are shown in Table 3. The surface tension of the distilled water used was 71.5 dynes/cm.

Methods. The interfacial tension measurements were made at 25.0 ± 0:3°C employing the drop volume method. Volumes of at least 10 drops were used for each determination. The drops of oil were produced by an Agla micrometer syringe with a needle radius of .0457 cm. The micrometer was driven by a motor which pushed the oil out of the syringe at a rate of approximately .012 cc/sec. Drops smaller than .4 cc were formed entirely by the action of the motor. For larger drops, the drops were formed by turning the micrometer quickly by hand but completing the last .2 cc slowly by the motor drive. In most cases, 2 or 3 runs of 10 drops each were averaged to find the drop volume.

Table 2 — List of surfactants studied

Compound	Manufacturer	Lot Number	Molecular Weight
Pure Surfactants			
Dialkyl sulfosuccinates			
di-n-butyl sodium	Am. Cyanamid	-	332.3
di-n-nonyl	"	-	472
di-n-decyl	"	-	500
di-n-lauryl	"	-	556
di-n-cetyl	"	-	668
di(2-ethyl-hexyl)	"	-	444.5
di(1-methyl-butyl)	"	-	360
di(1-methyl-propyl)	"	-	332
Commercial Surfactants			
A. Aerosol OS	"	13397	272.3
Aerosol OT	"		444.5
Aersol OT-S	"	13461	444.5
Aerosol-AY-B	"	SPS# 12421	360
Aerosol A-103	"	SPS# 13183	Unknown
Aerosol 22 Special	"	13290	"
Aerosol 501	"	13398	"
B. Encol CC38-10M	Witco	4478-49	"
Emphos CS-136	"	D9-G-6584	"
CS-141	"	L-1386	"
PS-121	"	4891-40	"

Table 2 (Cont'd) — List of surfactants studied

Compound	Manufacturer	Lot Number	Molecular Weight
Emphos PS-220	Witco	K5-107	Unknown
PS-236	"	PE-3900	"
PS-400	"	M-0632	"
PS-1361	"	H-1296	"
Witcomul H-50A	"	D6-7584	"
Witconate P10-59	"	J-3070	"
Witcamide 511	"	C-1310	"
Witconal H-31A	"	H-1467	"
14	"	D5-1555	"
Light Water Concentrate 3% Type	3M Corp.	-	"

Table 3 — Interfacial tensions of model fluids

Fluid	Interfacial Tensions		
	Air (dynes/cm)	Distilled Water (dynes/cm)	Density
Methyl Salicylate	38.37	21.65	1.184
Malathion (pure grade, 99.5%)	36.59	16.64	1.230
(technical grade, 91%)	36.37	11.81	1.230
Orthodichlorobenzene	37.35	33.84	1.300

The interfacial tension was calculated according to the following formula:

$$\gamma = \frac{V(\Delta\rho)gF}{r}$$

where V is the average drop volume

$\Delta\rho$ is the water/oil density difference

g is the acceleration due to gravity

F is a correction factor which is a function of tip radius and drop volume (7)

r is the capillary radius

The outer radius of the syringe needle was generally used for the calculations. However, for some high concentrations of surfactants, the oil did not wet the tip of the syringe and the inner radius was substituted in the computations.

III. Results and Discussion

Interfacial Tensions and Surfactant CMC's in Methyl Salicylate/Water Systems

The displacement or erosion of contaminant deposited on hard surfaces is, as previously cited, greatly assisted by low values of interfacial tension between the contaminant and the aqueous cleaning solution (1). If the detergency process system is not an enclosed system, then the problem of redeposition of removed contaminant need not be considered and therefore emulsion stability involving the removed contaminant will not be a requirement.

Recent work by Rewick, et al. (4) has suggested that oil spill dispersants may be evaluated through measurements of interfacial tension between the model oil and the aqueous medium. Such oil dispersants operate by reduction of the interfacial tension between the crude oil and seawater. Lowering the interfacial tension to minimal values reduces the energy requirements for the creation of additional oil-water surface, that is, the production of small droplets. Coalescence of the droplets to reform larger droplets is prevented if a resilient interfacial layer is also formed at the oil-water interface during the creation of new additional interfacial area. However, in the detergency model considered here the flowing aqueous surfactant will effect transport of the contaminant away from the surface upon completion of the displacement or erosion processes. Rewick and his coworkers have proposed that the Standard EPA Dispersant Effectiveness Test (5) may be correlated with the critical micelle concentration of commercial oil dispersants. Such a relationship may be fortuitous since the ability of surfactants to promote emulsification (or dispersion) is a function of many variables. The production of very stable emulsions is dependent on still additional factors not the least of which lies in the structural nature of the interface itself (6,7). However, a relationship nonetheless seems to exist between EPA test maximum percent oil dispersed and the dispersant CMC. Nonetheless, it is also noted that the interfacial tension also ranks the dispersants in order when taken at the highest concentrations (200 ppm) measured by these workers although not in a linear relationship as with the CMC.

It would appear that the low values of the interfacial tension are necessary to aid removal whether it be through displacement or erosion processes. Fielding and Fryar (3) have proposed removal of contaminant from hard surfaces through a combination of low interfacial tension and flow energy. The lower the interfacial tension, the less the flow energy required to displace or erode the contaminant. In their experiments, test tubes containing 0.02 ml of dyed o-dichlorobenzene and 10 ml of surfactant solution were rocked plus and minus eight degrees from the horizontal on a four second cycle. They found when looking at a surfactant concentration range of .002 to 1.0 percent that good emulsification began at the 0.1% di-isopropyl naphthalene sulfonate level where an interfacial tension of 0.7 dynes/cm was observed. At the 0.05% level, corresponding to an interfacial tension level of 4.0 dynes/cm, emulsification was marginally successful under the extremely gentle condition of the experiment. The authors refer to this method as "low energy emulsification."

With respect to the oil dispersion (emulsification) process under the simulated conditions of use, there is merit in the views of Rewick, et al. and Fielding and Fryar. In the former work (5), the interfacial tensions rank with decreasing values of the surfactant CMC. In the latter work (3), gentle flow agitation results in emulsification when interfacial tensions drop somewhere below 4 dynes/cm. For economy of use and application, it is important that the surfactant have a low CMC since beyond this point micelles will be formed and little or no further lowering of interfacial tension will occur - i.e., the interface will be packed with a monomolecular layer of surfactant molecules. The lower the CMC the sooner, concentration-wise, this saturation of the interface by surfactant will occur. The selection of surfactants for our detergency model will therefore be based on low CMC and low values of the interfacial tension at the CMC.

The interfacial tension-concentration (γ-c) plots for a series of sulfosuccinate salts are shown in Figure 1 at the methyl salicylate/distilled water interface. The commercial surfactants are reported in Figures 2 to 4, also for the methyl salicylate/distilled water interface. Table 4 summarizes the relevant data extracted from the figures and reports the results in terms of the CMC (determined by an abrupt change in slope of the γ-c plots) and the interfacial tension between phases corresponding to the surfactant concentration equal to the CMC. Aerosol OT, sodium di-2-ethylhexyl sulfosuccinate, sodium dinonyl sulfosuccinate, Emcol CC 3810-M and Witconate P10-59 appear to be good candidates for future work in the study of detergent processes on hard surfaces and subsequent oil dispersion effects (low energy emulsification). The choice of best surfactants from Table 4 was made by selecting those materials which gave interfacial tensions lower than 4 dynes/cm at a concentration no greater than 0.2 percent.

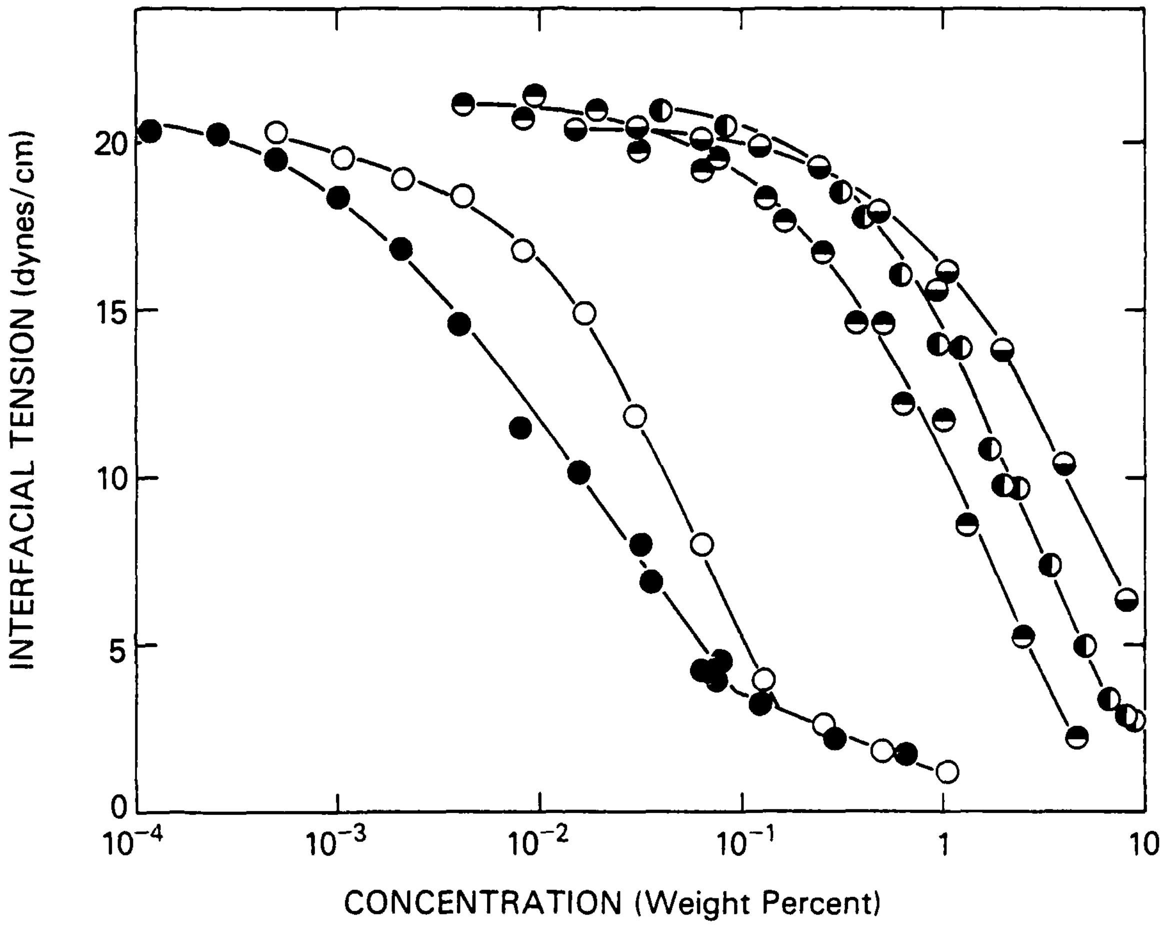

Fig. 1 - Interfacial tension against methyl salicylate for selected aqueous solutions of sulfosuccinate salts;
● di-nonyl, ○ di-ethylhexyl, ◒ di-methybutyl,
◐ di-butyl, ◓ di-l-methybutyl

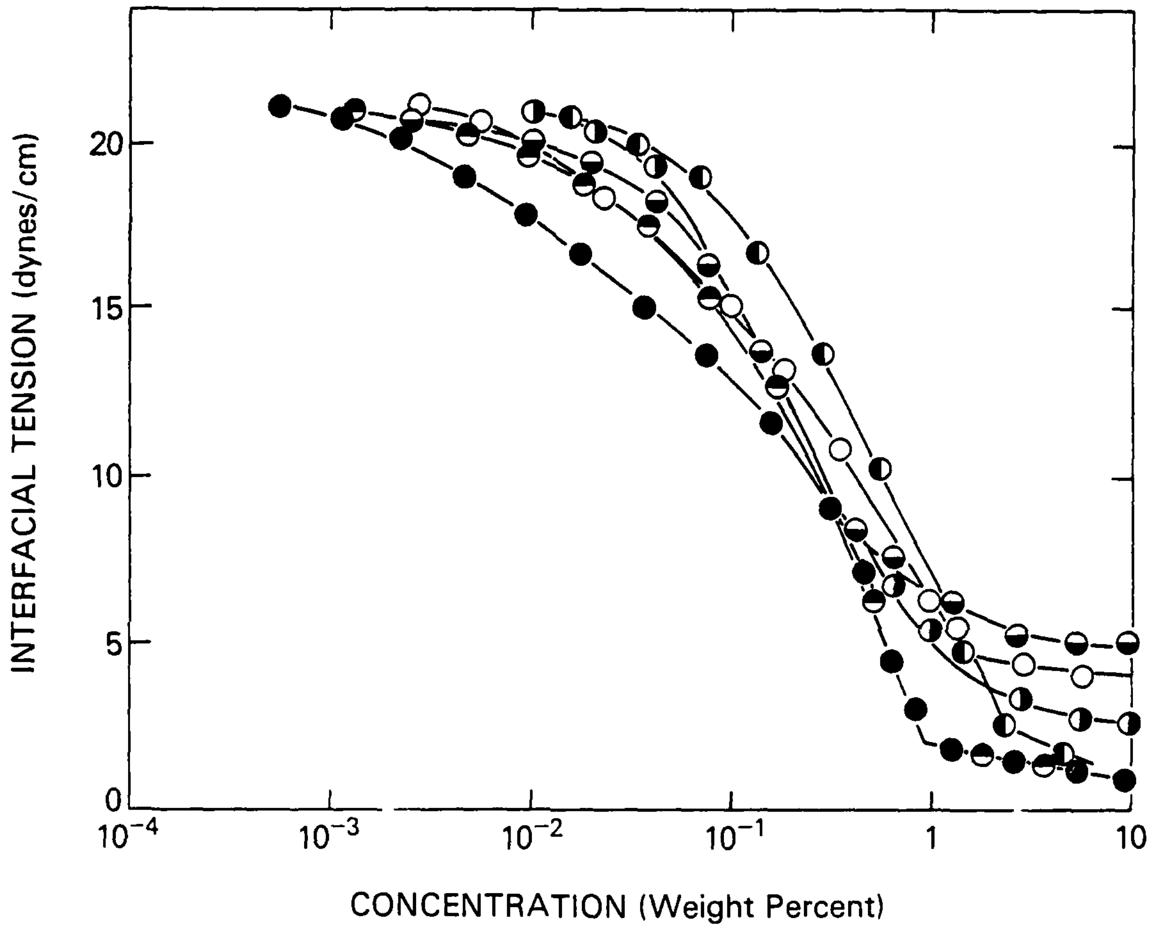

Fig. 2 - Interfacial tension against methyl salicylate for aqueous Commercial Surfactants, American Cyanamid Co. and 3M;
● Aerosol A-103, ◓ Aerosol OS, ○ Aerosol 501 (3M Co.),
◒ Aerosol 22-Special, ◑ Light Water Concentrate,
◐ Aerosol AY-B (amyl)

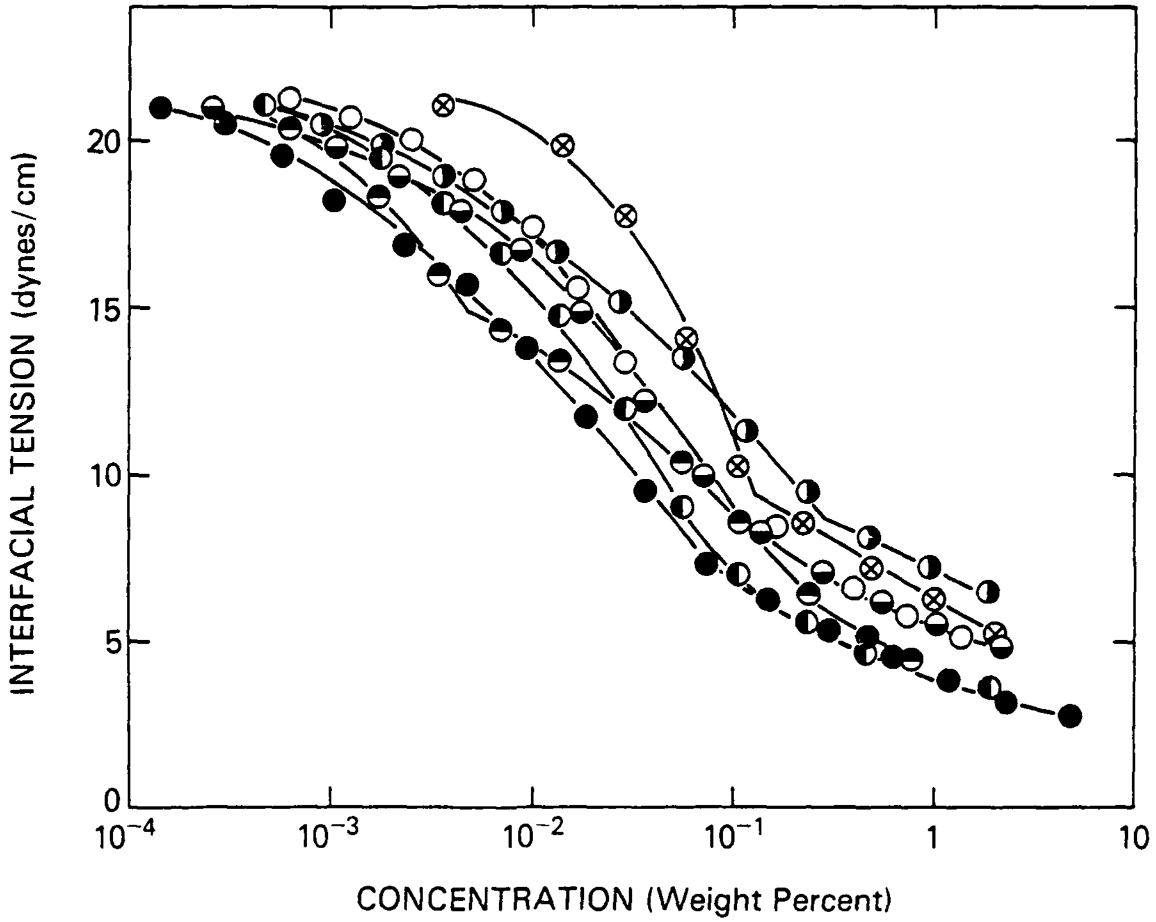

Fig. 3 - Interfacial tension against methyl salicylate for aqueous Commercial Surfactants, Witco Chemical Co.;
● Emphos CS-141, ◓ Emphos PS-1361, ◒ Emphos CS-136,
◐ Emphos PS-121, ◑ Emphos PS-236, ○ Emphos PS-220,
⊗ Emphos PS-400

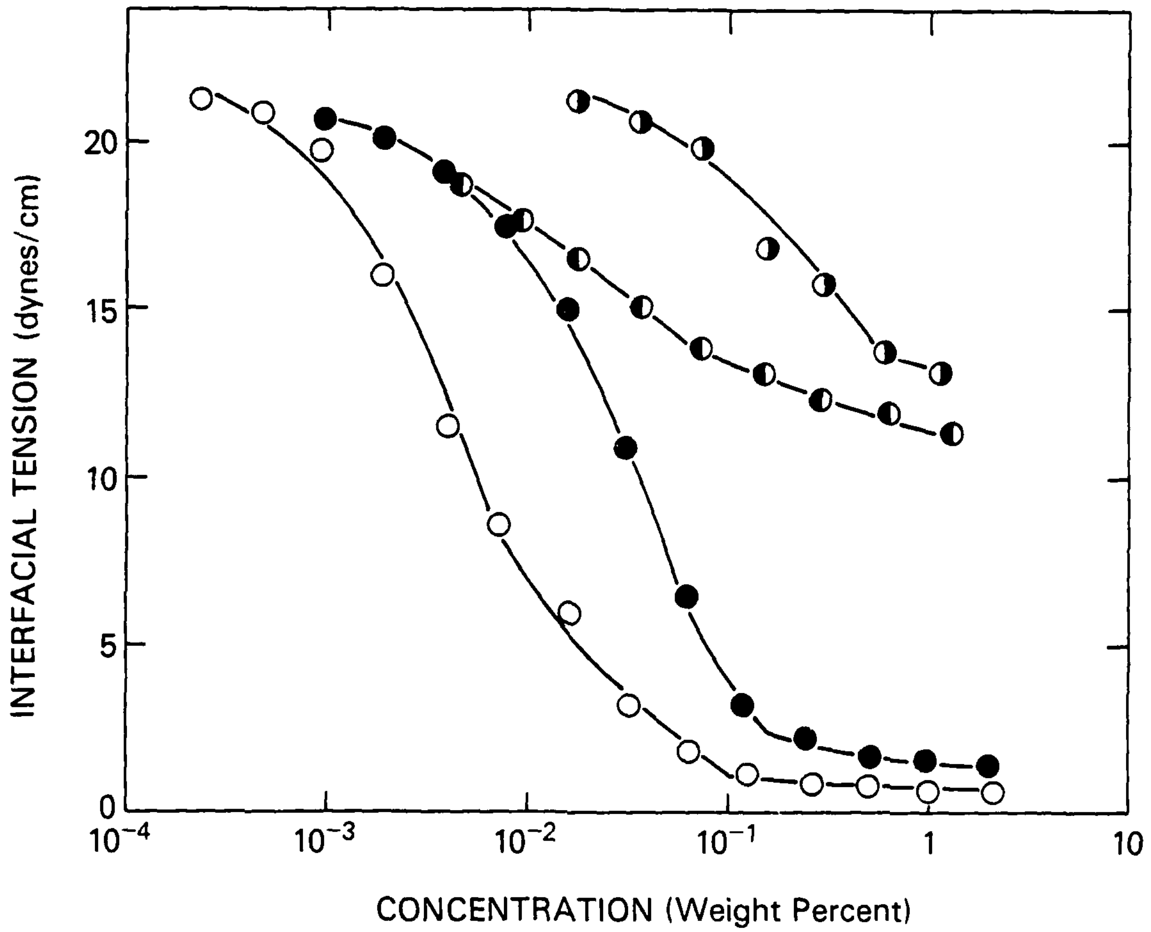

Fig. 4 - Interfacial tension against methyl salicylate for aqueous Commercial Surfactants, Witco Chemical Co., ○ Emcol CC-3810N, ● Witconate P10-59, ◐ Witcomul H50-A, ◑ Witconal 14

Table 4 — Interfacial tensions against methyl salicylate at CMC of surfactant

	Concentration (%)	IFT (dynes/cm)
Na di-n-decyl sulfosuccinate	.00325	12.0
Emcol CC3810-M	.045	2.1
Aerosol OT	.09	3.5
Witcomul H50-A	.09	13.4
Emphos CS-141	.10	6.8
Na di-n-lauryl sulfosuccinate	.11	16.2
Witconate P10-59	.11	3.3
Emphos PS-121	.12	6.6
Emphos PS-220	.12	9.2
Emphos PS-400	.14	9.2
Na 2-ethyl-hexyl sulfosuccinate	.15	3.2
Na di-n-nonyl sulfosuccinate	.15	2.8
Na di-n-cetyl sulfosuccinate	.15	14.2
Emphos CS-136	.18	7.8
Aerosol OT-S	.20	3.7
Emphos PS-236	.32	5.8
Emphos PS-1361	.33	8.4
Aerosol 22-Special	.39	8.5
Witconal 14	.45	14.2
Aerosol A-103	.78	6.2
Light Water Concentrate	.80	5.5
Aerosol OS	1.1	2.0
Aerosol 501	1.95	4.9
Aerosol AY-B	2.4	2.3
Na 1-methyl-butyl sulfosuccinate	$\geq$4.5	$\leq$2.2
Na di-n-butyl sulfosuccinate	7.0	3.0
Na 1-methyl propyl sulfosuccinate	$\geq$8.5	$\leq$6.4

Effect of Surfactant Structure

In order to gain information on the interfacial adsorption process, it was useful to summarize the experimental data on the homologous series of sulfosuccinate compounds. The data obtained were similar to those reported by Dixon, et al. (8) for surface tensions of sulfosuccinate salts against air. The CMC's determined from the interfacial tension-concentration plots were plotted against the number of carbons in the hydrocarbon radical and are shown in Figure 5. The solid line is that reported by Dixon, et al. Such relationships for surfactants were first proposed by Corrin (9) and also derived by Hobbs (10). That is, log CMC = 0.290N + 1.63, where N is the number of carbons in the alkyl chains. The decyl, amyl and butyl sulfosuccinates (normal di-alkyl salts) lie on the curve. The branched salts lie above the line as was reported by Dixon, et al. Solubility problems were experienced with the di-lauryl and di-cetyl salts. The di-nonyl salt was considerably higher in CMC than would be required by the linear relationship of Figure 5.

In order to deduce more about the interfacial adsorption process, it was decided to employ the Szyszkowski equation (11) as has been done by Rosen (12) for a variety of both ionic and nonionic surfactants. The equation constants allow an estimate of the free energy of adsorption and also the area per molecule at interfacial saturation. The equation is as follows:

$$\gamma_o - \gamma = \alpha \ln (C/\beta + 1)$$

where γ_o = the interfacial tension between pure liquids
γ = the interfacial tension of the surfactant solution
α = constant
ln = natural logarithm
C = concentration in moles/liter
β = constant

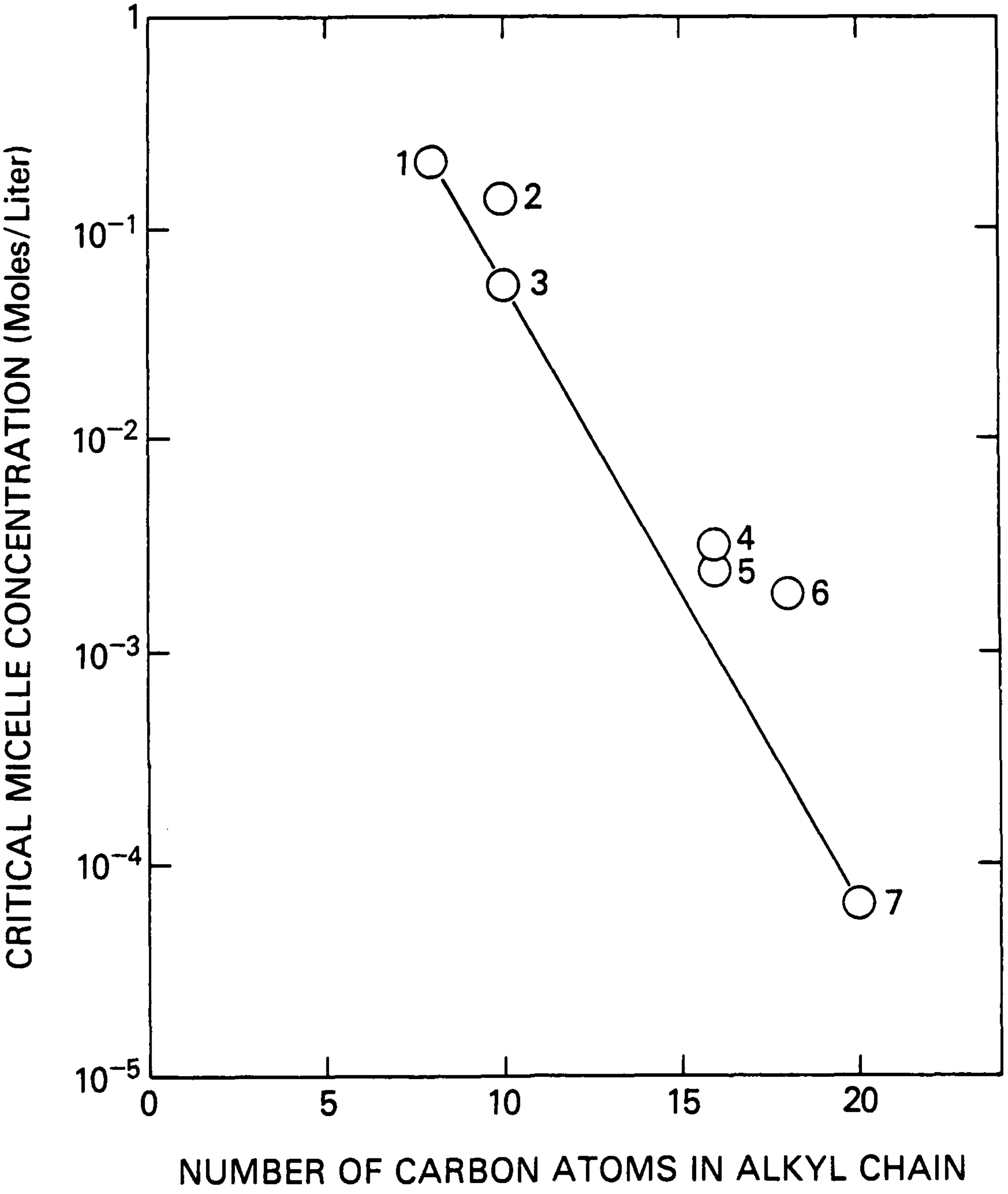

Fig. 5 - Effect of chain length on critical micelle concentration: (1) di-n-butyl (2) di-1-methylbutyl (3) Aerosol AY-B (4) di-ethylhexyl (5) Aerosol OT (6) di-n-nonyl (7) di-n-decyl

The relationship of the constants to the terms in the Langmuir and Gibbs adsorption isotherms (from which the Szyszkowski equation is derived) is as follows (13):

$$\alpha = RT\ \Gamma\infty$$

where R and T have their usual meaning and $\Gamma\infty$ is the surface excess at saturation and

$$\beta = W \exp\ (\Delta F_{ads.}/RT)$$

where W = the number of moles of water at temperature T and $\Delta F_{ads.}$ is the free energy of adsorption at the interface. The free energy of micellization, $\Delta F_{mic.}$, may be calculated by the expression

$$\Delta F_{mic.} = RT\ \ln\ (CMC/W)$$

as has been done by Corkill, et al. (14). It was hoped that the use of these equations would help to ascertain aggregation and interfacial adsorption changes as a function of surfactant structure and solvent effects.

Table 5 lists the results of this exercise with five sulfosuccinate salts. As was found by Rosen at the water-air interface, it appears that $\Delta F_{ads.}$ and $\Delta F_{mic.}$ are affected in similar ways as demonstrated by the unchanged difference between $\Delta F_{ads.}$ and $\Delta F_{mic.}$ as the number of carbon atoms are changed from the di-butyl to di-decyl salts. The effect of branching has a much greater effect on interfacial adsorption than on micellization. Upon addition of a methyl group to the butyl radical the absolute value of the free energy of adsorption is increased 0.52 kcals, whereas the free energy of micellization is increased less than half that amount, i.e., 0.24 kcals. The area per molecule increases with increase in the number of carbon atoms and also the methyl side group increases the area per molecule over that of an additional carbon atom in the normal chain (compare di-amyl and di-1-methylbutyl salts). These results are in agreement with the literature (12) but it is more useful to determine oil or solvent effects if surfactants are to be used for removal of a variety of contaminant oils.

Table 5 — Free energies of adsorption and micellization for normal and branched sulfosuccinates at the methyl salicylate-water interface

Alkyl Group	Area/molecule ($Å^2$)	$\Delta F_{ads.}$ (kcals/mole)	$\Delta F_{mic.}$ (kcals/mole)	$\Delta F_{ads.} - \Delta F_{mic.}$
Di-n-butyl	73.8	-5.20	-3.29	-1.9
Di-n-amyl	74.8	-6.06	-4.06	-2.0
Di-n-decyl	138	-9.94	-8.06	-1.9
Di-1-methyl butyl	78.9	-5.72	-3.70	-2.0
Di-2-ethyl hexyl	77.8	-8.03	-5.96	-2.0

Effect of Contaminant Oil

Figures 6 and 7 present data showing the effect of selected surfactants on the interfacial tensions of three water-oil systems. The contaminant oils used in the comparison were ortho-dichlorobenzene, methyl salicylate and malathion. The curves reverse their order (top to bottom) when one proceeds from very low surfactant concentrations to concentrations above the critical micelle concentration. At very low surfactant concentrations, the surfactant has only a minimal effect on the interfacial tension and the interfacial tension is a result of the hydrogen bonding contribution (and allied electrostatic effects) in the solvent pair. As the concentration increases to the CMC and somewhat above, the order of the curves is completely reversed. The surfactant apparently acts to reduce the hydrogen bonding contribution to the interfacial energy (15).

Table 6 reports data taken for selected surfactant-oil systems at approximately twice their CMC's. (The CMC's are listed in Table 7.) The interfacial tensions between the three oil contaminants and the indicated surfactant solutions are reported in the table. As has been done by Becher (15), the Girifalco-Good equation (16)

$$\gamma_{o/s} = \gamma_o + \gamma_s - 2\Phi(\gamma_o \gamma_s)^{1/2}$$

(where Φ = constant and the subscripts have their usual meaning) and the Fowkes' relations (17)

$$\gamma_{o/s} + \gamma_s + \gamma_o - 2 (\gamma_s^w \gamma_o^w)^{1/2}$$

$$\gamma = \gamma^w + \gamma^h$$

where w refers to the dispersion forces and h to the hydrogen bonding forces) have been used to estimate the dispersion forces and hydrogen bonding forces contributions to the interfacial tension. As can be seen from the table, the hydrogen bonding

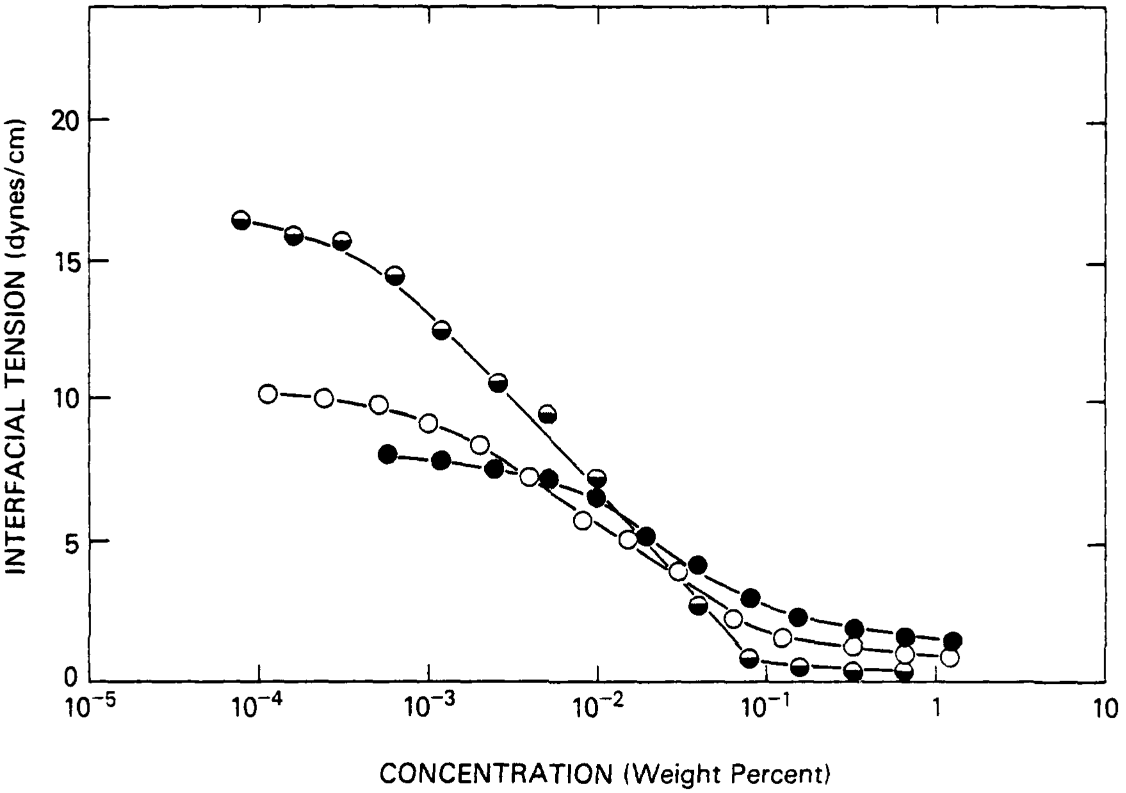

Fig. 6 - Interfacial tension of sodium d-n-nonyl sulfosuccinate solutions against ● malathion, ○ methyl salicylate and ◒ orthodichlorobenzene

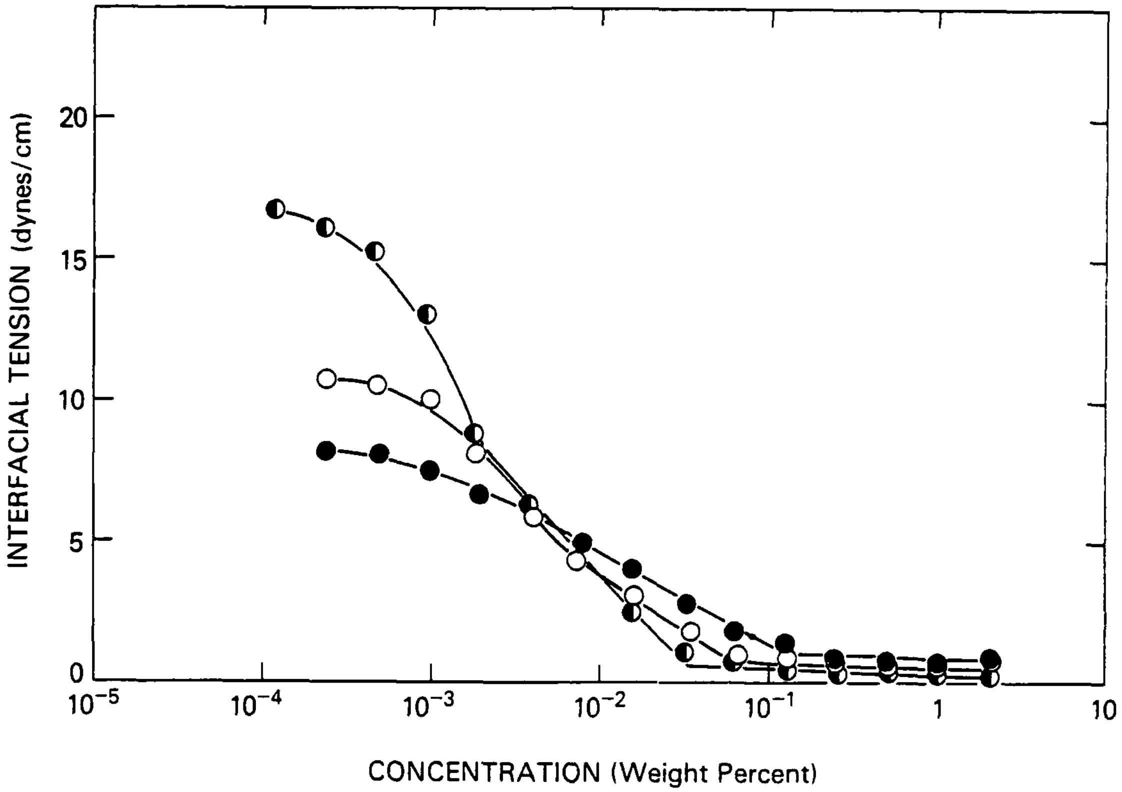

Fig. 7 - Interfacial tension of Emcol CC-3810M solution against ● malathion, ○ methyl salicylate and ◐ orthodichlorobenzene

Table 6 — Fowkes and Girifalco-Good parameters for sulfosuccinate salt solutions

Alkyl Group	Oil Phase	G-G Parameter Oil/Water $\Phi_{o/w}$	Surface Tension at ~ Twice CMC dynes/cm	Surface Tension Oil dynes/cm	Interfacial Tension dynes/cm	γ^d_s dynes/cm	γ^p_s dynes/cm	G-G Parameter Oil/Solution Φ_{os}
Di-n-octyl	Methyl Salicylate	0.342	27.3	38.7	2.0	26.5	0.8	0.985
Di-n-amyl	" "	"	28.0	38.7	2.5	26.6	1.4	0.975
Di-n-butyl	" "	"	36.0	38.7	5.0	31.4	4.6	0.934
Di-2-ethylhexyl	Carbon Tetrachloride	0.613	27.3	26.4	1.0	26.3	1.0	0.982
"	o-dichlorobenzene	0.726	27.3	37.4	0.8	27.3	0	1.00
"	Malathion	0.894	27.3	36.6	4.4	24.2	3.1	0.941
Di-methylbutyl	o-dichlorobenzene	0.726	32.5	37.4	1.4	31.4	1.1	0.982
	Methyl Salicylate	0.342	32.5	38.7	1.9	31.0	1.5	0.977
	Malathion	0.394	32.5	36.6	2.5	30.3	2.2	0.965

Table 7 — Effect of oil on critical micelle concentrations

	CMC in Weight Percent		
Surfactant	o-dichlorobenzene	Methyl Salicylate	Malathion
Di-1-methyl butyl Sulfosuccinate	4.0	3.8	3.1
Di-2-ethylhexyl Sulfosuccinate	0.16	0.13	0.18
Di-n-nonyl Sulfosuccinate	0.076	0.085	0.099
Aerosol A-103	0.51	0.78	0.60
Emcol CC3810M	0.035	0.045	0.070

contribution appears to be the major factor in the interfacial tension as one observes the surfactant-solvent pairs listed. As was found in Becher's studies (15), on nonionic surfactant solutions against 1 a variety of oils, decreasing values of the hydrogen bonding term correlate with increasing values of ϕ. This is a consequence of the relation

$$\gamma^{h} = \gamma_{s} (1 - \varphi^{2})$$

which is obtained when the three equations are algebraically combined.

Table 6 suggests that a systematic increase in the hydrocarbon chain length at a given oil water interface produces a decrease in the hydrogen bonding contribution to the interfacial tension. Thus in the series dibutyl, diamyl and dioctyl sulfosuccinates this contribution decreases from 4.61 to 0.81 dynes/cm. The increased interfacial tension for the shorter chain length sulfosuccinates may be due to a limited penetration of the surfactant polar group into the oil phase or, conversely, a limited penetration of the hydrocarbon radical into the aqueous phase. The higher molecular weight dioctyl sulfosuccinate presumably lies ideally in the oil-water interface with the polar group in the aqueous phase and the hydrocarbon radical in the organic phase. Table 6 also indicates that the reduction in interfacial tension as the oil phase is varied for a given sulfosuccinate appears to be in proportion to the initial hydrogen bonding component of the oil-water pair before surfactant is added. Thus, the lowest interfacial tensions are achieved against orthodichlorobenzne followed by methyl salicylate then malathion. This indicates that interfacial adsorption of surfactant must be greatest for oil-water pairs having low values of Φ.

Table 8 reports data obtained on the three contaminant oil-water systems through use of the Szyszkowski equation. When the data for the surface excess at saturation for a sulfosuccinate, Aerosol OT, is plotted versus the increment in Φ as a result of surfactant addition (at twice its CMC) a reasonably smooth increase in surface excess is experienced with increasing Φ.

Table 8 — Influence of oil on Szyszkowski equation parameters of sulfosuccinate salts

Alkyl Group	Oil Phase	Surface Excess Γ moles x 10^{10} cm^{-2}	Area/Molecule A^2	ΔF ads. kcals mole	F [illegible] kcals mole	F [illegible] - F [illegible] kcals mole
Di-1-methyl butyl	o-dichlorobenzene	2.52	65.8	-6.61	-3.66	[illegible]
	Methyl Salicylate	2.10	78.9	-5.72	-3.70	[illegible]
	Malathion	1.35	123	-5.09	-3.82	[illegible]
Di-2-ethyl hexyl	o-dichlorobenzene	2.71	61.3	-8.51	-3.68	[illegible]
	Methyl Salicylate	1.95	85.0	-8.03	-5.96	[illegible]
	Malathion	1.31	127	-7.39	-5.62	[illegible]
	Carbon Tetrachloride	3.09	54.0	-9.42		

Analysis of the Aerosol OT data leads to a relation of the form:

$$\Gamma_{\text{monolayer}} = \frac{\Delta\Phi\, B}{A + \Delta\Phi}$$

where $B = 4.01 \times 10^{-10}\ cm^2$

$A = 0.128$

and $\Delta\Phi = \Phi_{o/s} - \Phi_{o/w}$

The data of Rehfeld (17) for the adsorption of sodium dodecyl sulfate has also been examined with this relation and a reasonably good fit was also found with $B = 4.41 \times 10^{-10}\ cm^{-2}$ and $A = 0.105$. It would appear that reasonable estimates of Aerosol OT and sodium dodecyl sulfate saturation adsorption at the interface can be made when the Φ of the oil-water system and the Φ of the oil-surfactant solution (above its CMC) are determined. Decreasing values of ΔΦ suggest an oil-swollen surfactant monlayer. Penetration of the oil into the monolayer (low surface excesses of surfactant) may result in less favorable values of the interfacial tension. The value of B appears to represent a limiting highly compressed packing of surfactant molecules in terms of area per molecule. This would correspond, for example, to $41.5A^2$ for Aerosol OT. For sodium dodecyl sulfate, a value of $37.6A^2$ would be obtained, slightly lower than the value of $43.9A^2$ obtained at the air surfactant interface (16). If the surfactant does not adsorb at the interface there will be little or no change in interfacial tension and ΔΦ will be zero. The converse is also true, of course. The effect of oil on surfactant adsorption at the interface is summarized in Table 8. First of all, the area per surfactant molecule increases as Φ increases. The free energy of adsorption predictably decreases as the Girifalco-Good constant Φ increases. Interestingly, the free energy of micellization does not vary appreciably. It should be noted that when the hydrocarbon residue of the sulfosuccinate salt is increased from 10 to 16 carbons both the free energy of adsorption and the free energy of micellization are increased by approximately the same amounts, i.e., about 1.8 to 2.2 kcals in a given oil-water pair. Moreover, the difference between the free energy of adsorption and the free energy of micellization appears to become increasingly less as the Girifalco-Good parameter increases from 0.726 to 0.894. Plotting the available data points for the two salts in the three oils suggests that the difference in the free energy of adsorption and the free energy of micellization will be zero (i.e., they will be equal) in an oil-water pair whose Girifalco-Good constant is about 1.06.

IV. Conclusions

1. Economical use of surfactants in hard surface detergency problems will be defined by low values of CMC combined with low interfacial tension values at that CMC.

2. Within the homologous series of sulfosuccinate salts, increased hydrocarbon radical length promotes adsorption at the oil/water interface until defeated by greatly reduced solubility in the aqueous phase. This should also hold true for commercial surfactants.

3. Surfactants having low CMC's will probably be strongly adsorbed at the oil/water interface but the CMC of a specific surfactant - as measured from the interfacial tension data - will not necessarily index its adsorption at the oil/water interface as the nature of the oil is varied.

4. Surfactants will be most strongly adsorbed at the oil/water interface (as evidenced by low values of the interfacial tension) for those oil/water pairs whose Girifalco-Good parameters

are initially low (before addition of surfactant). If the Girifalco-Good parameter is increased to higher values (by varying the oil/water pair), then surfactant adsorption will tend to decrease. This may result in slightly higher values for the interfacial tension (at surfactant monolayer coverage).

5. As the Girifalco-Good parameter increases (as the oil/water pair is systematically varied) the free energy of adsorption and the surface excess (at monolayer coverage) will decrease in magnitude probably as a result of increased oil penetration into the interfacial surfactant film. The area per surfactant molecule will, of course, increase as a result of this penetration.

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