effect of alkoxide catalysis. Catalyzed, dimethylamine reacted in less than 15 min. at 30°C. to give a 95% yield of amide; uncatalyzed, no measurable reaction occurred in 24 hr. at this temperature. Catalyzed, piperidine and morpholine reacted within 2 hr. at 30°C. to produce yields of amide over 90%; uncatalyzed, little or no reaction occurred in 24 hr. even at 100°C.

REFERENCES

1. Grunwald, F.A. (Mead Johnson & Co.), U.S. 2,764,613 (1956).
2. Katzman, M.B., and Epstein, A.K. (Emulsol Corporation), U.S. 2,173,448 (1939).
3. Meade, E.M. (Lankro Chemicals Ltd.), U.S. 2,464,094 (1949).
4. Naudet, M., Sambuc, E., Desnuelle, P., and Reutenauer, G., Bull. Soc. Chim., France, 476–480 (1952).
5. Ricciardi, L.G., and DiGeronimo, J.P. (Colgate-Palmolive Co.), U.S. 2,843,612 (1958).
6. Russell, P.B., J. Am. Chem. Soc., *72*, 1853–1854 (1950).
7. Shapiro, S.L., Rose, I.M., and Freedman, L., J. Am. Chem. Soc., *80*, 6065–6071 (1958).
8. Tesoro, G.C. (Onyx Oil and Chemical Co.), U.S. 2,844,609 (1958).
9. Baltzly, R., Berger, I.M., and Rothstein, A.A., J. Am. Chem. Soc., *72*, 4149–4152 (1950).
10. Betts, R.L., and Hammett, L.P., J. Am. Chem. Soc., *59*. 1568–1572 (1937).
11. Bunnett, J.F. and Davis, G.T., J. Am. Chem. Soc., *82*, 665–674 (1960).
12. Watanabe, W.H., and De Fonso, L.R., J. Am. Chem. Soc., *78*, 4542–4549 (1956).
13. Baldy, J., Naudet, M., and Desnuelle, P., Bull. Soc. Chim., France, 1172–1176 (1954).
14. Gorvin, J.H., J. Chem. Soc., 732–735 (1945).
15. Kleinberg, J., and Audrieth, L.F., Organic Syntheses, Collective Vol. 3, 516–518 (1955).
16. Naudet, M., Baldy, J., and Desnuelle, P., Bull. Soc. Chim., France, 1167–1172 (1954).
17. Paden, J.H., and Adkins, H., J. Am. Chem. Soc., *58*, 2487–2499 (1936).
18. Roe, E.T., Scanlan, J.T., and Swern, D., J. Am. Chem. Soc., *71*, 2215–2218 (1949).
19. Roe, E.T., Stutzman, J.M., Scanlan, J.T., and Swern, D., J. Am. Oil Chemists' Soc., *29*, 18–22 (1952).
20. Wojcik, B., and Adkins, H., J. Am. Chem. Soc., *56*, 2419–2424 (1934).
21. Washburne, R.N., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *80*, 5963–5965 (1958) and preceding papers.
22. Arnett, E. McC., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *72*, 5635–5638 (1950).
23. Morrell, G.F., J. Chem. Soc., 2698–2707 (1914).
24. French, H.E., and Wrightsman, G.G., J. Am. Chem. Soc., *60*, 50–51 (1938).
25. Gordon, M., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *70*, 1946–1953 (1948).
26. Swern, D., and Jordan, E.F. Jr., J. Am. Chem. Soc., *70*, 2334–2339 (1948).
27. Gordon, M., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *71*, 1245–1250 (1949).
28. Arnett, E. McC., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *73*, 5393–5395 (1951).
29. Jung, S.L., Miller, J.G., and Day, A.R., J. Am. Chem. Soc., *75*, 4664–4665 (1953).
30. Ratchford, W.P., and Fisher, C.H., J. Am. Chem. Soc., *69*, 1911–1914 (1947).
31. Ratchford, W.P., Lengel, J.H., and Fisher, C.H., J. Am. Chem. Soc., *71*, 647–651 (1949).
32. Ratchford, W.P., and Fisher, C.H., J. Org. Chem., *15*, 317–325 (1950).
33. Magne, F.C., Dupuy, H.P., and Goldblatt, L.A., J. Am. Oil Chemists' Soc., *36*, 635–637 (1959) and preceding papers.
34. Walpole, A.L., Roberts, D.C., Rose, F.L., Hendry, J.A., and Homer, R.F., Brit. J. Pharmacal, *9*, 306 (1954).
35. Bunnett, J.F., Robison, M.M., and Pennington, F.C., J. Am. Chem. Soc., *72*, 2378–2381 (1950).
36. Magnani, A., and McElvain, S.M., J. Am. Chem. Soc., *60*, 813–820 (1938).
37. Adickes, F., v. Müddenhein, S., and Simson, W., Ber. *66*, 1904–1909 (1933).

[Received May 12, 1961]

Correlation Between Critical Micelle Concentration, Fatty Soil Removal, and Solubilization

M.E. GINN and J.C. HARRIS, Monsanto Chemical Company, Research and Engineering Division, Dayton, Ohio

Using two model soil-detergent systems (hard substrate/triglyceride; cotton/fat, mineral oil, graphite) it was shown that soil removal begins at, or near, critical micelle concentration (cmc), confirming the work of other investigators with different systems. Maximum detergency occurs at concentrations considerably in excess of cmc, varying some 6 to 10 times cmc for different surfactants. An equation for soil removal showed excellent fit of experimental values for both detergency systems.

Direct correlation between cmc, solubilization (of several materials), and soil removal was demonstrated. Marked differences between surfactant type and solubilization of triglycerides were found. The nonionic surfactants were excellent solubilizers for triolein correlating with their effective soil removal. Neither sodium oleate nor sodium tripolyphosphate effectively solubilized the triglyceride but both are effective soil removers, suggesting that their soil removal mechanism differs from the nonionics, possibly as an emulsification or displacement mechanism. Solubilization of triglyceride occurs most effectively considerably in excess of cmc.

EARLY INVESTIGATORS noted the dependence of optimum detergency upon detergent concentration, but Preston's (10) work is the most frequently quoted to show that detergency and critical micelle concentration are related. However, he stated that washing power had attained its maximum at critical micelle concentration (cmc), and that solubilization appeared to begin at cmc. Goette (5), in reviewing cmc and detergent power, noted that the peak break in the detergency curve did not necessarily coincide with cmc, and believed that further data were necessary to clarify this correlation. Removal of radioactive soils was found by Chandler and Shelberg (2) to begin with micelle formation and to increase rapidly when micelle concentration was 2- or 3-fold that of cmc. Demchenko (3) verified the practical significance of cmc, but claimed that soil removal started only when detergent concentration was in excess of cmc. The importance of cmc to soil removal therefore is well recognized and recent work suggests that the optimum in removal occurs at concentrations in excess of cmc, but systematic investigation on a sufficiently broad scale to fortify these opinions has not been available.

To help clarify the cmc-detergency correlation, it is proposed to use the data obtained for model systems using radiotagged triglycerides as soil, and substrates such as glass and metals. Detergent-concentration curves had been obtained (7, 8) for these systems, but no effort had heretofore been made to relate these curves to cmc. Additionally, data obtained for removal of graphite (by reflectance measurement) and fatty and mineral oil from cotton are included. Correlation of cmc and soil removal with solubilization data, from another paper (4), using essentially the same radiotagged fats in such systems was reserved for the present discussion.

TABLE I

Sample Calculation of Detergency Equation

Decanol + 15 EO, 75°C (cmc = 0.12% conc.)
Tristearin, Frosted Glass, Radiotracer Data

C_t (Total % conc.)	(x) C_m (C_t–cmc)	SR_t (% soil removal)	SR_n ($SR_t - SR_{H_2O}$*)	(y) C_m/SR_n	(xy) $(C_m/SR_n)C_m$	(x^2) C_m^2
0.50	0.38	50.8	45.5	0.0083516	0.0031736	0.1444
0.40	0.28	48.6	43.3	0.0064665	0.0018106	0.0784
0.30	0.18	41.8	36.5	0.0049315	0.0008877	0.0324
0.25	0.13	34.9	29.6	0.0043919	0.0005709	0.0169
0.20	0.08	23.0	17.7	0.0045198	0.0003616	0.0064
	$\Sigma x = 1.05$ $(\Sigma x)^2 = 1.102$			$\Sigma y = 0.02866$ $\Sigma x \cdot \Sigma y = 0.003009$	$\Sigma(xy) = 0.0068054$	$\Sigma(x^2) = 0.2785$

Model Equation: $SR_n = \dfrac{C_m}{a + b\,C_m}$; $\dfrac{C_m}{SR_n} = a + b\,C_m$

$$a = \frac{\Sigma y - b\Sigma x}{n} = \frac{0.02866 - (0.01359)(1.05)}{5} = 0.00288$$

$$C_{m90} = 9aSR_{n(max.)} = 9 \times 0.00288 \times 73.6 = 1.91$$

$$b = \frac{n\Sigma(xy) - \Sigma x\Sigma y}{n\Sigma(x^2) - (\Sigma x)^2} = \frac{5(0.0068054) - 0.03009}{5(0.2785) - 1.102} = 0.01359$$

$$SR_{n(max.)} = \frac{1}{b} = 73.6$$

$$SR_{t(max.)} = 73.6 + 5.3 = 78.9$$

and $SR_n = C_m/(0.00288 + 0.01359\,C_m)$

*Water value = 5.3 ± 1.7 for tristearin, 6.0 ± 1.7 for triolein.

Discussion

Equation Relating Detergency to Micellar Concentration.—It was apparent from previously reported soil removal-concentration curves (7) that some correlation between these and cmc existed, the curves varying somewhat, but generally showing a sharp increase in soil removal *above* cmc as exemplified in Figure 1. Important here is the fact that soil removal has only begun with attainment of cmc.

The data for cmc and soil removal for anionic surfactants shown in Figure 2 are more variable, sodium oleate, sodium dodecylbenzene sulfonate (NaDDBS) and sodium lauryl sulfate showing cmc values that approach the maximum for soil removal, but two other alkylbenzene sulfonates showing cmc at the point where detergency begins, as for the nonionic surfactants. These data frequently show that soil removal *begins* in the region of cmc, but near maximum detergency occurs at concentrations considerably in excess of cmc. Reference to Table IV shows that even for 90% of maximum soil removal nonionic, anionic, and the cationic surfactant required at least twice cmc values and more generally 6 to 10 times cmc for best results. These data support those of Chandler and Shelberg (2) for two soaps, and hard surfaces contaminated with yttrium trichloride, and further tend to verify Demchenko's (3) statement that detergency starts when cmc is exceeded.

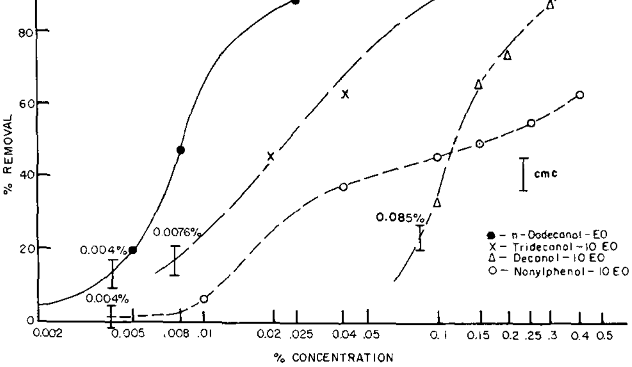

FIG. 1. Soil removal by nonionics and cmc. Radiotagged tristearin soil-frosted glass substrate: 75°C.—20 minute wash.

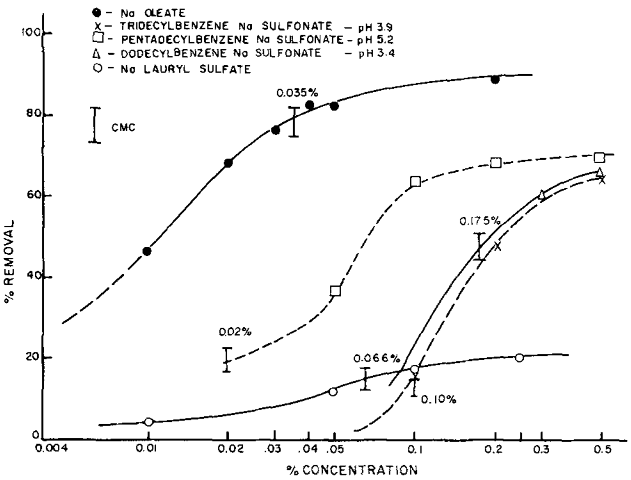

FIG. 2. Various anionic surfactants. Radiotagged tristearin—frosted glass: 75°C.—20 minute wash.

For systems where correlation was apparent between cmc and detergency commencement, data were fitted to the equation:

$$SR_n = \frac{C_m}{a + b\ C_m} \qquad (1)$$

or

$$\frac{C_m}{SR_n} = a + b\ C_m \text{ (the linear form)} \qquad (2)$$

where SR_n = % soil removal minus water blank,

C_m = micellar weight % concentration (total % conc.-cmc), a and b are constants, and 1/b estimates maximum detergency ($SR_{n\ max.}$).

Constants a and b were derived statistically by linear regression (1) from equation 2 above. Shown in Table I is an example of the calculation and data used for a single surfactant. Figures 1 and 2 show that a high level of soil removal frequently occurred just past the shoulder of the sigma-shaped curve, but that in many instances the slope of the curve continued upward slightly over a considerable range. The maximum detergency, $SR_{n\ max.}$, takes into account the continued slight increase in removal, hence may give impractically high concentration values. To circumvent this and to provide a more practical approach, an arbitrary 90% $SR_{n\ max.}$ level was chosen:

$$C_{m90} = 9a(SR_{n\ max.}) \qquad (3)$$

to give 90% of maximum detergency as shown in Table I.

Using data developed with the radiotracer method for measuring triglyceride removal from glass (8), and the more conventional reflectance method for measuring removal of graphite, fatty and petroleum oil from cotton (6), the fit of the detergency equation to both systems was estimated. Eighteen systems were calculated covering the variables of triolein vs. tristearin, temperature, EO ratio for a given hydrophobe, and various hydrophobes, pertinent calculations being shown in Table II. The excellent fit of the equation for several rigid substrates is apparent. Utilizing the same procedure, but for oily carbon removal from cotton, the data of Table III show the good fit for the several types of surfactants tested.

TABLE II

Fit of Detergency Equations for Fatty Soil Removal from Rigid Substrates

% Conc.	% Soil removal data* (SR_t)			
	Calc'd	Observed		
		Av.	95% CL	Spread
Decanol + 10 EO, 75°C (cmc = 0.085%) Tristearin, Frosted Glass: $SR_n = C_m/(0.000446 + 0.01019\ C_m)$				
0.50	94.1	94.5	0.7	2.3
0.30	86.8	86.8	1.2	4.3
0.20	76.4	73.0	1.9	9.7
0.15	64.0	63.3	2.2	7.7
0.10	30.3	33.7	1.7	8.7
n-Dodecanol + 10 EO, 75°C (cmc = 0.004%) Tristearin, Steel: $SR_n = C_m/(0.000095 + 0.009736\ C_m)$				
0.10	98.5	97.8	2.6	4.1
0.025	75.5	83.1	4.2	8.3
0.01	44.5	52.1	2.4	1.8
0.005	14.9	12.8	3.1	6.0
n-Dodecanol + 10 EO, 75°C (cmc = 0.004%) Tristearin, Frosted Glass: $SR_n = C_m/(0.000048 + 0.01044\ C_m)$				
0.250	99.3	99.2	0.3	0.2
0.050	92.4	94.6	0.6	1.2
0.025	84.0	89.3	1.2	2.4
0.008	49.7	47.0	3.5	4.8
0.005	22.5	17.8	3.3	3.3
Decanol + 10 EO, 35°C (cmc = 0.10%) Triolein, Frosted Glass: $SR_n = C_m/(0.00209 + 0.01693\ C_m)$				
1.00	57.9	57.7	4.0	7.8
0.50	51.1	53.4	1.9	3.8
0.25	38.4	37.3	1.6	2.2
Decanol + 15 EO, 75°C (cmc = 0.12%) Tristearin, Frosted Glass: $SR_n = C_m/(0.00288 + 0.01359\ C_m)$				
0.50	52.6	50.8	3.1	7.7
0.40	47.3	48.6	2.4	6.1
0.30	39.1	41.8	2.2	6.8
0.25	33.3	34.9	1.4	4.8
0.20	25.5	23.0	1.6	3.9
Dodecylphenol + 10 EO, 75°C (cmc = 0.0005%) Tristearin, Frosted Porcelain: $SR_n = C_m/(0.000014 + 0.01216\ C_m)$				
0.10	86.6	87.2	2.5	3.5
0.05	85.6	83.2	1.2	1.5
0.01	78.7	81.4	3.2	4.5
0.001	26.4	33.9	1.9	1.3
Tridecanol + 10 EO, 75°C (cmc = 0.0076%) Tristearin, Frosted Glass: $SR_n = C_m/(0.00161 + 0.01160\ C_m)$				
0.250	86.8	87.6	0.8	2.8
0.150	83.8	83.9	2.0	7.0
0.100	80.2	81.4	1.4	4.7
0.065	74.3	72.1	2.3	5.8
0.040	65.8	64.3	2.3	5.7
0.015	35.3	45.0	6.0	20.9
0.010	22.3	28.5	6.4	1.0

* Average replication 5×, 2–12 replicates used throughout.

TABLE III

Detergency Equations for Oily Carbon Soil Removal from Cotton at 25°C

% Conc.	% Soil removal data*		
	Calc'd	Observed	
		Av.	95% CL
Dodecylphenol + 10 EO (cmc = 0.0024%): $SR_n = C_m/(0.00060 + 0.0247\ C_m)$			
0.20	53.8	54.1	1.5
0.10	53.3	52.0	1.6
0.04	51.6	52.1	2.0
0.01	44.4	46.1	2.2
0.005	34.8	39.2	1.8
Cetyltrimethylammonium Bromide (cmc = 0.033%): $SR_n = C_m/(0.00068 + 0.0371\ C_m)$			
1.00	34.7	32.5	3.3
0.50	32.2	33.2	2.4
0.20	30.9	31.2	1.9
0.15	29.7	30.4	3.8
0.10	26.8	27.6	1.4
0.075	23.9	23.0	2.6
0.05	17.6	14.8	2.2
Na Lauryl Sulfate (cmc = 0.072%): $SR_n = C_m/(0.00150 + 0.0357\ C_m)$			
1.00	34.6	34.6	1.4
0.50	33.3	33.2	2.0
0.30	31.5	31.2	0.8
0.20	28.9	29.4	0.6
0.15	26.0	24.5	1.3
0.10	19.0	20.6	0.6
Tridecanol + 10 EO (cmc = 0.0092%): $SR_n = C_m/(0.000164 + 0.0274\ C_m)$			
0.20	49.2	49.6	2.6
0.10	48.2	46.6	2.0
0.08	47.5	46.8	4.3
0.06	46.6	46.8	2.9
0.042	44.7	44.4	2.0
0.017	34.4	36.1	2.2
0.013	28.2	29.2	1.8
Sodium Oleate (cmc = 0.029%): $SR_n = C_m/(0.000764 + 0.0256\ C_m)$			
0.40	50.0	49.6	2.6
0.30	49.0	49.4	2.0
0.20	47.1	48.1	4.8
0.10	42.3	41.4	3.0
0.075	37.5	36.6	3.0
0.044	26.9	28.1	2.5
Sodium Dodecylbenzene Sulfonate (cmc = 0.117%): $SR_n = C_m/(0.00048 + 0.045\ C_m)$			
1.00	37.0	36.7	1.7
0.50	36.7	36.5	0.8
0.40	36.5	37.7	0.6
0.30	36.1	35.9	1.2
0.20	34.8	33.6	1.9
0.17	33.6	32.9	3.2
0.13	26.9	27.6	1.1

* % Soil removal data (SR_t), 4–8 determinations.

Earlier it was pointed out that the present data show soil removal commencing at near cmc, as in Figures 1 and 2. On the basis of 90% of maximum soil removal level, the removal at cmc for the several types of surfactants for a cotton substrate were only a small fraction of the maximum possible, Table IV showing for this substrate and soil system as for hard substrates, that soil removal only commences at near cmc.

It might be generalized that low values of cmc might prove a method for characterizing surfactants: Nonionic surfactants had lower cmc values than anionics tested, and also provided higher soil removal values. But this correlation fails in some instances, for example with tridecanol-5 EO, which is a very poor detergent, but also has a very low cmc. However, with possible exceptions in mind, surfactants with low cmc values frequently can be used at lower active in-

TABLE IV

Correlation of cmc with Launder-Ometer Detergency Data at 25°C (Oily, Carbon Soil, Reflectance Data)

Sample	cmc	% Soil removal for water	Maximum % soil removal		SR_n at cmc	% of 90% SR_n at cmc	Required conc. for 90% of max. SR_n		Multiples of cmc for 90% max. SR_n
			(SR_t) Total	Minus water value (SR_n)			C_m	C_t	
Dodecylphenol + 10 EO	0.0024	13.8 ± 1.5*	54.1 ± 1.5*	40.3	12.0	33	0.022	0.024	10
Tridecanol (TDA) + 10 EO	0.0092	13.8 ± 1.5	49.6 ± 2.6	35.8	9.3	29	0.054	0.063	7
Sodium oleate	0.029	13.8 ± 1.5	49.6 ± 2.6	35.8	8.4	26	0.27	0.30	10
Cetyltrimethyl-ammonium bromide	0.033	6.3 ± 1.8	33.2 ± 2.4	26.9	4.4	16	0.17	0.20	7
Na lauryl sulfate	0.072	7.8 ± 0.9	34.6 ± 1.4	26.8	10.0	37	0.39	0.46	6
Na dodecylbenzene-sulfonate (NaDDBS)	0.117	15.1 ± 2.7	37.7 ± 0.6	22.4	6.0	27	0.096	0.21	2

* 95% Confidence Limits.

TABLE V

Concentration—Solubilization—Soil removal. Tristearin soil—Temperature 75°C. Frosted glass substrate in soil removal test.

Detergent	cmc (% Conc.) at 75°C.	Multiples of cmc at 0.25%	Solubilization — % × 10^3 at detergent concentrations		% Soil removal at detergent concentrations	
			0.25%	0.05%	0.25%	0.05%
Water	....	....	0.07	....	5	
Sodium tripolyphosphate	....	....	0.12	....	82	
Tridecanol–10 EO	0.0076	33	30	2	88	70
Decanol–10 EO	0.085	3	15	0.6	80	10
Nonylphenol–10 EO	0.004	62	12	2	55	38
n-Dodecanol–10 EO	0.004	62	27	2	100	95
Sodium oleate	0.035	7	0.5		88	
Sodium lauryl sulfate	0.066	4	0.4		20	
Sodium dodecylbenzene sulfonate	0.175	1.4	0.2		pH 7.5: 8 pH 3.4: 58	5

gredient concentrations or combined with larger percentages of other constituents than those with higher cmc values.

The sigmoid shape of the soil removal curve suggests that the attractive forces holding the soil to the substrate are "neutralized" or over-ridden when sufficient surfactant is used. The soil in effect then either acquires a repulsive charge or is removed by dissolution, as by incorporation into the micelle (8).

Relationship Between Soil Removal, cmc, and Solubilization. It was pointed out (4) that fatty soil is an important constituent of many natural soils, and acts as a binder and modifier of particulate soils. In the two model systems already discussed, the amount of fatty soil present was as follows:

1. The labelled soil on the solid substrate was present in relatively minute amounts, e.g., about 10 or more monolayers of at least 46 μg/substrate disk. At this low level if solubilized in the detergent solution, this would amount to about 0.00001% triglyceride concentration. These systems produced clear solutions except where ineffective surfactants were used.
2. The cotton fabric soiled with a mixture of 51.1% Wesson Oil, 26.1% Nujol, 10.2% Oildag (graphite in mineral oil), and 11.5% Dixon's graphite, when solvent extracted showed about 1% by weight of the oily constituents based on the soiled cloth. In the washing system the ratio of fabric to detergent solution was 1:29, such that about 0.03% concentration of oily materials would result if completely removed. A previous paper (4) showed that for a single effective nonionic surfactant (tridecanol-10 EO at 0.25%) the amount of triolein solubilized increased linearly with the level added, up to a saturation point of 0.044% for equilibrium conditions at 60°C. Higher temperatures (up to the cloud point) and higher surfactant concentrations can increase the fatty soil solubilized beyond the value given. The tridecanol compound is effective, but lies at an intermediate level of soil removal, so that other nonionics can solubilize larger amounts of triolein.

The foregoing discussion shows that the levels of oily soil present lie well within the solubilization capability of the surfactants tested.

Evidence for correlation of solubilization and soil removal is shown by Figure 3. Here solubilization of a water-insoluble dye (1-o-tolylazo-2-naphthol) is compared to fatty soil removal by two nonionic detergents. It is notable that solubilization and soil removal began in the same concentration region and increased progressively with surfactant concentration.

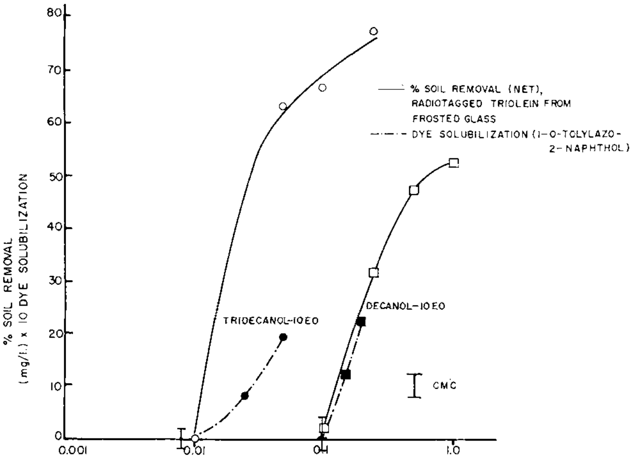

FIG. 3. CMC, solublization, detergency: nonionics at 35°C.

The importance of solubilization is best assessed by comparing data for the same solubilizate involved in the soil removal systems. Such data are given in Table V for tristearin solubilization and removal from the frosted glass substrate. With the exceptions of sodium tripolyphosphate and sodium oleate, nonionic surfactants were most effective solubilizers and yielded highest soil removal. Effective soil removal and solubilization occurred at concentrations considerably in excess of cmc. (Note results for Decanol-10 EO). The two synthetic anionic surfactants tested were ineffective as solubilizers and as detergents, suggesting that neither had the optimum hydrophobe balance required for this system. Both sodium oleate and sodium tripolyphosphate were effective detergents but displayed essentially no solubilization. This suggests that these agents operate by an entirely different removal mechanism compared to the nonionics tested. Displacement and emulsification are probable routes for the ionic agents. It is also suggested that different mechanisms of soil removal can arise depending on the surfactant type employed.

Conclusions

These data demonstrate for two quite dissimilar systems and evaluation methods, that soil removal for surfactants frequently begins at or near cmc. These findings supplement those of Chandler and Shelberg (2) and the claims of Demchenko (3), and prove that Preston's (10) correlation of cmc and maximum washing power is not the general rule. Maximum soil removal effectiveness occurs when cmc has been exceeded many-fold, the multiple depending upon the surfactant in question.

Because of the correlation between cmc and soil removal, an equation for soil removal could be developed:

$$SR_n = \frac{C_m}{a + b\,C_m},$$

where SR_n = % soil removal minus water blank,

C_m = micellar weight % concentration (total % conc.-cmc), a and b are constants, and 1/b estimates maximum detergency ($SR_{n\,max.}$).

Excellent fit of experimental values to the derived equation for both model systems was found.

Correlation between soil removal and solubilization was shown. Solubilization may be an important mechanism in soil removal for systems comprising fatty and oily soils.

Different types of surfactants vary in their ability to solubilize triolein: Nonionics tested show relatively high capability, anionics and sodium tripolyphosphate solubilize little if any triolein. This shows that since these surfactants are effective soil removers, they operate through different mechanisms: The nonionic by displacement and solubilization, the anionics essentially by displacement: Both can function by emulsifying cohesively bound soil.

Acknowledgment

Thanks are extended to co-workers F. B. Kinney, E. L. Brown, R. L. Evers, and J. J. Satanek for preparation of data used in this paper.

REFERENCES

1. Bennett, C. A., and Franklin, N. L., "Statistical Analysis in Chemistry and the Chemical Industry," pp. 222–224, John Wiley and Sons, Inc., N. Y. (1954).
2. Chandler, R. C., and Shelberg, W. E., J. Colloid Sci. *10*, 393 (1955).
3. Demchenko, P. A., Masloboino-Zhirovaya Prom. *25*, 7 (1959).
4. Ginn, M. E., Brown, E. L., and Harris, J. C., To be published, J. Am. Oil Chemists' Soc.
5. Goette, E. K., J. Colloid Sci. *4*, 459 (1949).
6. Harris, J. C., "Detergency Evaluation and Testing," p. 94, Interscience Publishers, Inc., New York (1954).
7. Harris, J. C., Anderson, R. M., and Satanek, J., J. Am. Oil Chemists' Soc. *38*, No. 3, 123 (1961).
8. Harris, J. C., and Satanek, J., J. Am. Oil Chemists' Soc. *38*, No. 5, 244 (1961).
9. Kolthoff, I. M., and Stricks, W., J. Phys. & Colloid Chem. *53*, 424 (1949).
10. Preston, W. C., J. Phys. & Colloid Chem. *52*, 84 (1948).

[Received April 25, 1961]

Chromatostrip Analysis of Fatty Acid Derivatives[1]

T.H. APPLEWHITE, M.J. DIAMOND, and L.A. GOLDBLATT, Western Regional Research Laboratory,[2] Albany, California

Chromatostrips provide a rapid and convenient method of examination of samples by spot tests and by ascending or descending chromatography. Ascending chromatography for the examination of mixtures is carried out on 12 x 140-mm. glass strips coated with 5% starch-bonded silicic acid, while descending chromatography is done on 12 x 200-mm. strips. The 5% starch-bonded silicic acid coatings are resistant to normal handling, may be marked with a soft lead pencil, and may be stored indefinitely for reference. Three detection systems are employed: fluorescent minerals for conjugated unsaturates, fluorescein-bromine for unsaturates, and 2′,7′-dichlorofluorescein for all types of compounds. Positive tests result in characteristic spots when observed under normal or ultraviolet illumination. This permits the classification of components, after separation on the chromatostrips, into the groupings of conjugated unsaturated, unsaturated (or easily brominated), and saturated compounds.

In the past few years the technique of chromatography employing thin coatings of adsorbent bonded to glass surfaces has received considerable attention. A modified technique called "thin layer chromatography" (TLC) was reported by Stahl (1) in 1956. This method was further investigated by this author (2-4), and more recently by Mangold and coworkers (5-7) and others in the field of lipids (8-15), steroids (16, 17), amino acids (18), and other areas (19-24). After noting the success of Morris *et al.* (9) in applying this technique to the analysis of fatty acid derivatives, the conveniently available "chromatostrip" technique of Kirchner, Miller, and Keller (25) was investigated in this same area. The

---

[1] Presented before the American Oil Chemists' Society, May 2, 1961, St. Louis, Mo.

[2] Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.