Correlation of Nonionic Surfactant Structure and Solubility with Textile Wetting[1]

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Abstract

The effect of nonionic surfactant structure with respect to textile wetting efficiency has been studied. A correlation has been shown to exist between wetting speed and molecular diffusion rate, critical micelle concentration, area per molecule (as deduced from surface tension versus concentration measurements), extent of adsorption and temperature. The slope of the log wetting time versus log concentration curve is dependent upon temperature, cloud point, critical micelle concentration and area per molecule. Log concentration for ten-second wetting is shown to be inversely proportional to the diffusion constant which in turn is a function of the critical micelle concentration. Concentration coefficients of wetting indicate that the most efficient wetting is obtained at or very near to the critical micelle concentration.

Introduction

INDUSTRIAL PROCESSES which involve the wetting of textile fabrics are numerous and, to name just a few, include dyeing, desizing, mercerization, coating and detergency operations. Surfactants are normally incorporated into water-based systems to increase the rate of wetting or penetration of the solution into the fabric. In certain instances, surfactants might be chosen primarily for their adsorption characteristics, for example when one wishes to modify the rate of exhaustion of a dye onto a fiber, but we will not concern ourselves with this type of application in this discussion. Textile wetting, as opposed to solid surface wetting, involves solution penetration into myriad fiber capillaries with subsequent displacement of air. Washburn (1) derived the equation

$$dl/dt = (r\gamma \cos \Theta) / (4l\eta)$$

to express the rate or velocity of solution penetration into a capillary where r is the radius of the capillary, γ is the liquid surface tension, Θ the contact angle of the liquid with the capillary wall, l is the distance of penetration, and η is the viscosity. For a high rate of penetration it can be seen that the surface tension should be high but the contact angle small. Since one effect tends to cancel the other, a compromise between these two related properties is obviously required. Experience shows us, however, that this equation alone is not sufficient for predicting textile wetting efficiency. Caryl (2), in a study of the wetting activity of esters of sodium sulfosuccinic acid, found no definite relationship between wetting and reduction of surface tension. Lenher and Smith (3) likewise discovered no quantitative relationship between the surface tension of a surfactant solution and its ability to penetrate a bundle of textile fibers. Gruntfest (4), on the other hand, presented data which showed that the rate of surface tension lowering, in film-balance experiments, correlated quite well with wetting agent performance. Fisher and Gans

(5) developed a correlation between Draves wetting time, solution surface tension, and the contact angle of the wetting agent against paraffin wax. Durham and Camp (6), using a conductivity device, concluded that the diffusion of a surface active material to the air/water interface is a rate-governing process in the wetting of capillary systems such as cotton fabric by detergent solutions. Hansen and Purchase (7), using the vibrating jet technique for measuring dynamic surface tension, observed that the rate of wetting and surface tension lowering are dependent upon the adsorption of surfactant molecules at an interface and that the adsorption of a surfactant at the cloth/solution interface is diffusion controlled. Sinking times were found to be inversely proportional to the rates of surface tension depression over the first 10 msec of surface life and very nearly inversely proportional to the square of the detergent concentration. This correlation might be fortuitous, however, since in practice wetting times are on the order of a thousand or more times greater. Fowkes (8) claimed that the rate of wetting of cotton in the Draves test was dependent upon the contact angle of the solution on wax and upon the extent of adsorption, and that when adsorption is heavy, diffusion becomes a rate determining factor. Despite the wealth of literature on the subject, none of these authors indicate which surfactant structure will exhibit maximum wetting efficiency. In this paper we attempt to relate nonionic surfactant solubility, i.e. product cloud point and critical micelle concentration (cmc) to wetting performance. Data are included which permit cmc to be compared to surfactant composition.

Experiment and Discussion

Wetting and Temperature

Wetting agents were compared using the Draves test (9) by determining the wetting-out-time (WOT) of cotton skeins weighted with a 3-g hook as a function of the concentration (C) of the surface active agent. These data when plotted on log-log paper usually give a straight line relationship between 10 and 50 sec and often remains linear down to the point of instantaneous wetting. Such data obtained at several temperatures are plotted in Figure 1 for Igepal[2] CO-630, CO-710 and CO-730-nonylphenol ethoxylates containing 9.5, 10.5 and 15 moles (average) of ethylene oxide per molecule respectively. In general, these products show increased performance, i.e. a lower concentration required to give a 25-sec wetting out time, as the temperature approaches their cloud points. Igepal CO-630 and Igepal CO-710 go through a transition near their cloud points (56C and 72C, respectively) which is denoted by a reduction in the slope of the log WOT vs. log C curve. Above these transition temperatures these compounds become much less efficient when short wetting out times are considered; comparisions at longer wetting times (greater than 20 sec) often show

Composition	cmc at 25C (%)	Cloud point C	Concentration, % required for	
			50 sec	10 sec
1. iso C_8 alcohol + 4 EO	0.500	24	0.107	0.160
2. C_9 alcohol + 4 EO	0.345	29	0.065	0.097
3. oxo C_{10} alcohol + 10 EO	0.130	89	0.077	0.132
4. trimethylnonyl alcohol + 6 EO	0.084	29	0.029	0.053
5. oxo C_{10} alcohol + 4 EO	0.066	<0	0.032	0.051
6. n-C_{11} alcohol + 8 EO	0.023	66	0.022	0.064
7. n-C_{12} alcohol + 10 EO	0.0125	68	0.033	0.080
8. C_{13} alcohol + 10 EO	0.0094	59	0.028	0.068
9. C_9 phenol + 9.5 EO	0.0093	54	0.026	0.092
10. o,n-decylphenol + 11.2 EO	0.00215	63	0.022	0.100
11. p,n-decylphenol + 11.0 EO	0.0014	76	0.023	0.162
12. C_{16} alcohol + 14 EO	0.0013	>100	0.230	10.00

ionic wetting efficiency, and for maximum wetting speed a surfactant should have a cloud point just above the expected use temperature.

Wetting and Critical Micelle Concentration

Draves wetting data at 25C, cloud points, and cmc's were obtained for the simple ethoxylates of branched and linear alcohols and alkylphenols listed in Table I. Cloud points are defined as the temperature at which 1% solutions clarify upon cooling from a temperature above their cloud point. By convention, the point of intersection of the two straight lines on the standard equilibrium semilog plot of surface tension versus concentration is defined as the cmc.

The surfactants studied exhibit considerable variation in both cloud point and cmc. It is readily apparent that their cmc's decrease as the hydrophobic portion of the molecule is lengthened.

Selected data are shown plotted in Figure 2. It can be observed in this figure that the slope of the wetting curve varies with the cmc of the product under investigation. Because the wetting curves are linear over the range of practical interest (10–50 sec), any relationship between cmc and wetting performance can best be developed through a study of the two defining properties of a straight line, its slope and intercept.

The slopes of the wetting curves as normally plotted, Figure 2, are negatve. Since negative values introduce complications in subsequent development, we can make use of the simple equality

$$-\log\ C = +\ \log\ 1/C \qquad (1)$$

to write the equation for the wetting curve as follows:

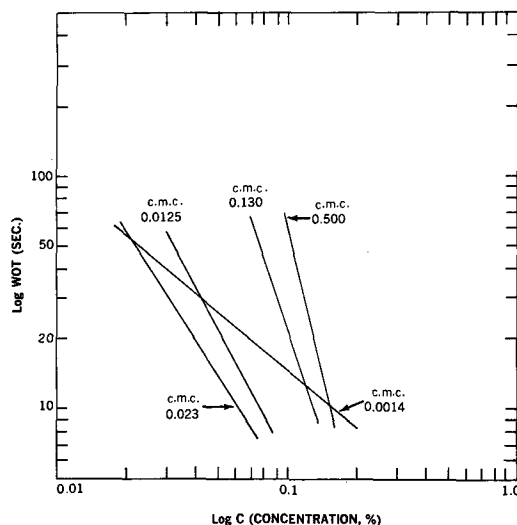$$\log\ WOT = m\ \log\ 1/C + b \qquad (2)$$

Fig. 1. Wetting vs. temperature.

wetting to improve with increasing temperature. Figure 1 also illustrates the transition effect by a plot of the slope of the log WOT vs. log C curve as a function of temperature. With Igepal CO-730, a product having a cloud point above 100C, the slope actually increases with increasing temperature and approaches the maximum slope observed for the other two members of the series. It is apparent, therefore, that temperature plays an important role in non-

Fig. 2. Wetting vs. concentration.
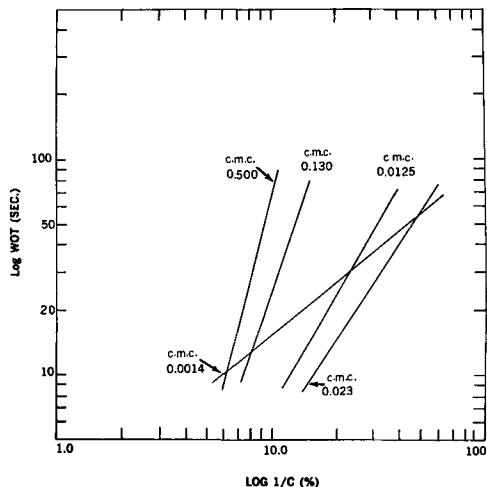
FIG. 3. Wetting vs. the reciprocal of the concentration.

FIG. 4. Log slope of wetting line vs. cmc.

where now m has positive values as shown in Figure 3.

The straight line constants were determined for the wetting data given in Table I for each compound giving the original equations presented in Table II.

Examination of the slopes and intercepts of these equations indicated that a correlation seemed to exist between cmc and both slope and intercept.

The log slope of the wetting line was plotted versus log cmc as in Figure 4 and regression analysis of these data gave

$$\log\ m = 0.3159\ \log\ \mathrm{cmc} + 0.7766 \qquad (3)$$

A correlation coefficient of 0.938 indicated that the correlation was significant at better than the 0.1% level. This regression line was drawn as the solid line in Figure 4 demonstrating excellent agreement with the data points.

From equation 3 it can be readily deduced that the slope, m, of the wetting curves is:

$$m = 5.978\ \mathrm{cmc}^{0.3159} \qquad (4)$$

The twelve wetting equations can then be rewritten:
$$\log\ \mathrm{WOT} = 5.978\ \mathrm{cmc}^{0.3159}\ \log\ 1/C\ -2.182 \qquad (5)$$
and so on
$$\log\ \mathrm{WOT} = 5.978\ \mathrm{cmc}^{0.3159}\ \log\ 1/C\ +1.4267 \qquad (6)$$

A plot of the intercepts, b, of the original equations versus log cmc indicated a straight line relationship between these functions. Regression analysis gave a correlation coefficient of −0.839 (significant at the 0.1% level). Better correlation was obtained by a recalculation of the intercepts using slopes calculated from the cmc function just developed. The intercepts were calculated using the experimentally determined concentration required for a WOT of 10 sec. Constants for the adjusted equations are also listed in Table II.

The intercepts of the adjusted equations were plotted versus log cmc in Figure 5. Regression analysis gave:

$$b = -1.605\ \log\ \mathrm{cmc}\ -3.773 \qquad (7)$$

and a correlation coefficient of 0.957. The regression equation was plotted in Figure 5, showing excellent agreement with the data.

From equation 7 it can be deduced that the intercept of the wetting line is:

$$b = \log\ (1.684 \times 10^{-4}\ \mathrm{cmc}^{-1.605}) \qquad (8)$$

and the straight line portion of the wetting curves for this entire series of surface active agents can be expressed in terms of concentration and cmc as follows:

$$\log\ \mathrm{WOT} = 5.978\ \mathrm{cmc}^{0.3159}\ \log\ 1/C\ +$$
$$\log\ (1.684 \times 10^{-4}\ \mathrm{cmc}^{-1.605}) \qquad (9)$$

Data points listed in Table III were calculated from equation 9 for 10 and 50 sec WOT's at various cmc's. These calculated points were plotted in Figure 6 giving the dotted curves.

Experimentally determined concentrations (log) required for both 10-sec and 50-sec WOT's were plotted (circled points) vs. log cmc giving the solid lines. The agreement between the experimental and calculated curves is quite reasonable. The shapes of the calculated and experimental curves are similar and it is important to note that all curves show a minimum which is displaced to lower values of the cmc as the WOT is increased.

More precise determination of experimental data via replication would undoubtedly improve the agreement between the experimental and calculated val-
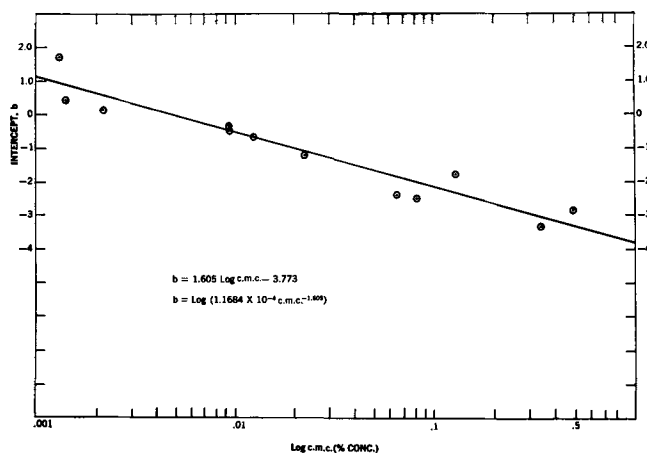
TABLE II
WOT Equations
log WOT = m log 1/C + b

cmc (%)	Original		Adjusted	
	m	b	m	b
0.500	3.999	−2.182	4.803	−2.822
0.345	4.093	−3.147	4.271	−3.3278
0.130	2.985	−1.625	3.138	−1.7596
0.084	2.670	−2.406	2.734	−2.4880
0.066	3.454	−3.464	2.592	−2.3501
0.023	1.508	−0.800	1.816	−1.1682
0.0125	1.814	−0.990	1.497	−0.6421
0.0094	1.815	−1.119	1.368	−0.5973
0.0093	1.274	−0.320	1.364	−0.4134
0.00215	1.063	−0.063	0.8590	+0.1410
0.0014	0.8245	−0.492	0.7496	+0.4074
0.0013	0.4267	+1.4267	0.7227	+1.7227

FIG. 5. Intercept of wetting curve vs. log cmc.

TABLE III

Calculated Wet Out Times for Various Critical Micelle Concentrations

cmc (%)	(%) Concentration required for	
	10 sec WOT	50 sec WOT
0.001	1.16	0.0675
0.002	0.286	0.0396
0.005	0.101	0.0231
0.01	0.0688	0.0210
0.02	0.0610	0.0235
0.05	0.0641	0.0314
0.10	0.0740	0.0417
0.20	0.0897	0.0565
0.50	0.120	0.0849

ues. It is important to emphasize that the wetting process is highly dependent upon the cmc of the surfactant and that WOT's can be expressed solely in terms of cmc, and the concentration used.

For a given rate of wetting, Figure 6, the required concentration of wetting agent decreases until this required concentration becomes equal to the cmc. After this minimum is reached the required concentration increases. There is, then, one surfactant which will give a desired WOT at a minimum concentration and that surface active agent will be the compound whose cmc is equal to the minimum concentration. It must be concluded, then, that an important transition in wetting mechanism takes place at this cmc. The ratio:concentration required for a given WOT/cmc, provides a value which we have termed the concentration coefficient. Compounds plotted to the left of the minimum in Figure 6 exhibit values >1 and with these products a wide range of WOT's are possible with solutions all exhibiting the same surface activity. Surfactants plotted to the right of the minimum have concentration coefficients <1 and provide wetting at concentrations less than their cmc. Significant depletion of such surfactants by adsorption would cause a large change in surface tension corresponding with a rapid loss of wetting performance. Although surface tension alone cannot be used to predict wetting, it is true that rapid wetting is only obtained with solutions having low surface tensions.

The most important difference that exists in solution when operating on the two branches of the log cmc vs. log C curve is that on the left hand branch, when one is operating with compounds of low cmc and the required concentration is higher than the cmc, micelles are present; while on the right hand branch, when operating with compounds of high cmc, micelles are not present.

It must be recognized that wetting is a dynamic process involving depletion of surface active agent by adsorption onto the substrate, diffusion of monomolecular surfactant units to the depleted wetting front, dissociation of micelles into monomolecular units, and diffusion of micelles through solution and capillaries to replenish adsorbed surfactant.
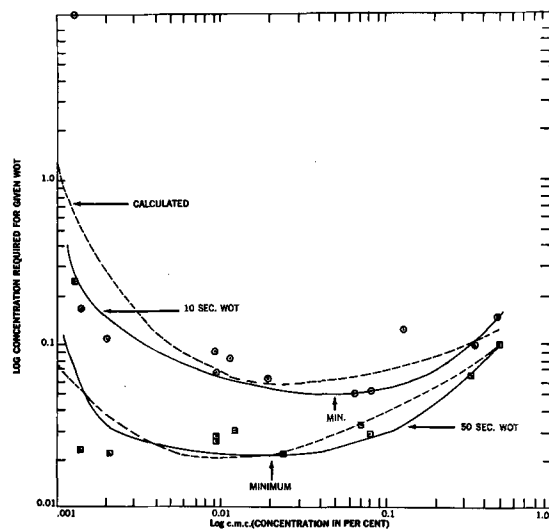

FIG. 6. Concentration required for wetting vs. equilibrium cmc.

Adsorption and diffusion of monomolecular species are involved in the wetting process whether operating above or below the cmc, and it is assumed that these are relatively fast processes. It is suggested, therefore, that with high cmc products, wetting is primarily a function of the surface tension attainable with the compound under investigation as shown previously by Fowkes. With low cmc products diffusion of micelles and dissociation of micelles into monomolecular units are the slow, rate-controlling processes.

Wetting and Area per Molecule

Since wetting is a rate governed process, textile wetting cannot be predicted from use of the Young equation which defines equilibrium conditions and where finite contact angles are observed. Fowkes, nevertheless, showed empirically that

$$\text{Cos } \Theta = 1.68 - 0.035 \, \gamma \quad \text{(on paraffin)} \qquad (10)$$

and that

$$\log \text{WOT} = A + B \, \gamma \qquad (11)$$

where A and B are test constants. Equation (11) is only valid, however, for situations where log WOT is linear with respect to surface tension and log C. Fowkes further combined (11) with

$$\gamma = C - \frac{2.303 \, \text{RT Z} \log C}{N\sigma} \qquad (12)$$

the integrated version of the Gibbs adsorption equation to give

$$\log \text{WOT} = A + BC - BD \log C \qquad (13)$$

where BD is the slope (m) of the straight line obtained from the log WOT vs. log C relation. Since BD is equal to $\dfrac{2.303 \text{BRTZ}}{N\sigma}$, then we may equate

TABLE IV

Data for Calculation of Diffusion Constants (10-sec WOT)

| Composition	Molecular weight	Area per molecule A$^{\circ 2}$	Area per gram of SAA m^2	C′ Conc. req. for surface tension 35.2 dynes/cm %	(C − C′) Calc. based on surface tension 35.2 dynes/cm %	Diffusion constant × 10^7 cm^2/sec
1. iso C$_8$ alcohol + 4 EO	306	53	1039	0.140	0.020	35.7
2. C$_9$ alcohol + 4 EO	320	55	1018	0.083	0.014	75.6
3. oxo C$_{10}$ alcohol + 10 EO	598	51	514	0.063	0.069	11.9
4. trimethylnonyl alcohol + 6 EO	408	64	941	0.020	0.0330	15.9
5. oxo C$_{10}$ alcohol + 4 EO	334	56	1009	0.0175	0.0335	13.5
6. n-C$_{11}$ alcohol + 8 EO	524	54	621	0.0088	0.0552	13.0
7. n-C$_{12}$ alcohol + 10 EO	626	61	586	0.00415	0.07585	7.81
8. C$_{13}$ alcohol + 10 EO	640	56	527	0.00325	0.06475	12.5
9. C$_9$ phenol + 9.5 EO	638	63	620	0.0049	0.0871	5.27
10. o,n-decylphenol + 11.2 EO	751	72	577	0.00125	0.09875	4.73
11. p,n-decylphenol + 11.0 EO	742	79	641	0.00086	0.16114	1.44
12. C$_{16}$ alcohol + 14 EO	858	41	288	....	....	......
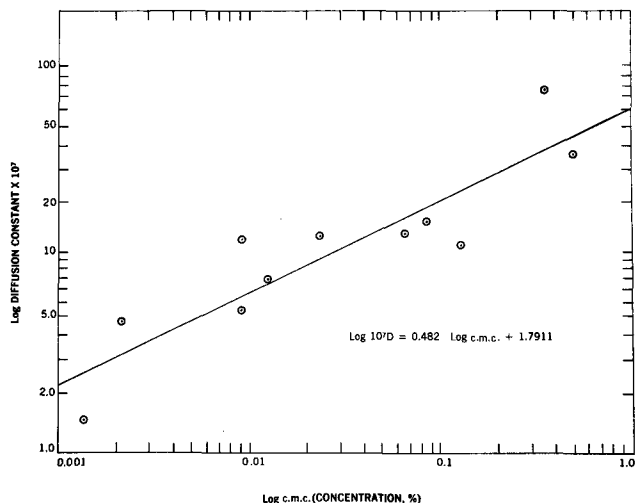
FIG. 7. Relationship between the diffusion constant and cmc (calculations based on 10 sec WOT).

this expression to equation (4), for compounds having concentration coefficients less than one, to yield

$$\frac{-2.303BRTZ}{N\sigma} = 5.978 \ cmc^{0.3159} \qquad (14)$$

where B is the slope of the surface tension vs. log WOT curve, R is the gas constant, Z is the number of particles per molecule in solution, T is the temperature, N is Avogadro's number and σ is the surface area per adsorbed molecule. We can thereby show mathematically with equation (14) that cmc is dependent upon the area per molecule (σ), and hence also that the slope of log WOT vs. log C is likewise proportional to the area per molecule.

Wetting and Diffusion

Fowkes explained the failure of Igepal type materials to fit the overall picture, when compared to anionic model compounds (Aerosol OT, MA and Tergitol 4), in terms of adsorption phenomena. Adsorption results in depletion of surfactant at the advancing solution front and thus the rate of wetting is actually controlled by a diffusion process. Thus if the advancing surfactant solution is to maintain a constant a value, then the transport of surfactant molecules from the bulk of the solution must be at least equivalent to the rate of adsorption. Hence, using the Fick diffusion equations, Fowkes derived the useful expression:

$$C - C' = \frac{1}{2} \cdot \frac{Sc}{Si} \cdot \left(\frac{\pi}{t_s}\right)^{\frac{1}{2}} \cdot \frac{1}{\sqrt{D} \ \frac{v}{s}} \qquad (15)$$

where: $C - C'$ = the concentration required to provide diffusion to maintain γ at the advancing solution front

Sc = surface area/gram of cotton

Si = area/gram of adsorbed surfactant

t_s = average skein sinking time

D = Fick's diffusion constant

$\frac{v}{s}$ = a test constant equal to the area of the water-air interface/gram of cotton

In his treatment of data Fowkes assumed that adsorption could be neglected for the anionic model
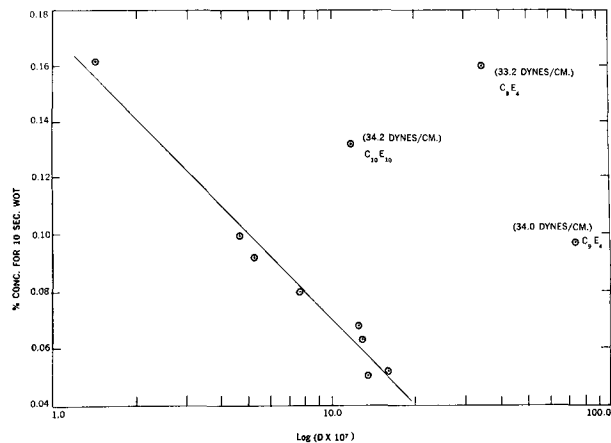

FIG. 8. Concentration required for 10 sec wetting vs. the diffusion constant.

compounds and thus t_s is ideally limited only by solution surface tension. We find, for Aerosol OT, that 10-sec WOT is attained with a solution having a surface tension of 35.2 dynes/cm and that 50-sec WOT with a surface tension of 39.2 dynes/cm.

With this background, diffusion constants for 10 sec WOT were calculated for virtually all the compounds shown in Table I and these data are plotted vs. cmc in Figure 7. It was assumed that 1) areas per molecule are the same at both the air/water and cotton/water interfaces, and 2) the surface area per skein was 0.3986 m²/g (cf. ref. 8).

It can be seen that the diffusion constant (D) appears to be proportional to cmc as determined by equilibrium measurements. Once again regression analysis was used to draw the line and the equation for the line becomes

$$\log 10^7 \ D = 0.482 \ \log \ cmc + 1.7911 \qquad (16)$$

The diffusion constant is also plotted vs. the concentration required for 10 sec WOT in Figure 8, resulting in a straight line for compounds having concentration coefficients >1. Compounds having concentration coefficients <1 deviated from this linear relationship indicating a change in wetting mechanism. Since these three compounds provided 10 sec WOT with solutions having surface tensions of 33.2–34.2 dynes/cm, surface tension alone appears to control their performance.

In summary, we have shown that textile wetting is primarily dependent upon cmc with interactions between diffusion, area per molecule, extent of adsorption and temperature. It is suggested that with low cmc products, diffusion of micelles and dissociation of micelles into monomolecular units are the slow rate-controlling processes.

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