Wetting Properties of Nonionic Surfactants of Homogeneous Structure $C_{12}H_{25}(OC_2H_4)_xOH$[1]

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ABSTRACT

The wetting of cotton skeins by aqueous solutions of individual surfactants of structure $C_{12}H_{25}(OC_2H_4)_xOH$, where x = 4-8, with homogeneous head groups, and of a Poisson distribution mixture containing an average of 5.5 oxyethylene groups, has been measured at various temperatures using the Draves technique. An individual compound with a homogeneous polyoxyethylene head group is a more effective wetting agent than a Poisson distribution mixture with the same average number of oxyethylene units. Log-log plots of wetting time vs surfactant concentration are linear in the concentration range of 0.25 to 1 g/L. The best wetting agents at any temperature have slopes in the -1.5 to -1.6 range and Y-intercepts from +0.6 to +0.7. Wetting in these systems appears to be diffusion-controlled. The wetting time at 1 g/L concentration is a measure of the wetting effectiveness of the surfactant, because it is roughly inversely proportional to the diffusion constant of the surfactant at that concentration. For materials 30 C or more below their cloud point, temperature increase causes an increase in wetting effectiveness. As the cloud point of the surfactant solution is approached, however, both the slope and the Y-intercept of the log-log plot of wetting time vs surfactant concentration change sharply. The absolute value of the negative slope decreases and the positive value of the Y-intercept increases, resulting in greatly reduced wetting effectiveness.

INTRODUCTION

The commercial availability of a series of nonionic surfactants, $C_{12}H_{25}(OC_2H_4)_xOH$, of high purity with homogeneous head groups, has stimulated a reexamination of the fundamental (1) and performance properties of these materials. This study is concerned with the wetting properties of these materials as measured by the Draves test (2). It includes a comparison between the wetting properties of these compounds with homogeneous head groups and a mixture of them, somewhat similar to what might be found in an industrial surfactant of this type.

EXPERIMENTAL

Materials

$C_{12}H_{25}(OC_2H_4)_2OH$ (EO2), $C_{12}H_{25}(OC_2H_4)_3OH$ (EO3), $C_{12}H_{25}(OC_2H_4)_4OH$ (EO4), $C_{12}H_{25}(OC_2H_4)_5OH$ (EO5), $C_{12}H_{25}(OC_2H_4)_6OH$ (EO6), $C_{12}H_{25}(OC_2H_4)_7OH$ (EO7), and $C_{12}H_{25}(OC_2H_4)_8OH$ (EO8), with homogeneous head groups of >98% purity as shown by gas chromatography, were purchased from Nikko Chemical Co., Tokyo, Japan, and used without further purification. A mixture of the compounds having an approximate Poisson distribution of hydrophilic head groups with an average number of oxyethylene units of 5.5 (EO5.5) was prepared by mixing EO3, EO4, EO5, EO6, EO7 and EO8 in a molar ratio of 0.1: 0.5:1.0:1.0:0.5:0.1, respectively.

Standard cotton skeins of gray, unboiled, 2-ply yarn, folded to form 18-in. loops, each skein weighing 5.00 g, were purchased from Testfabrics, Inc., Middlesex, NJ.

Wetting Measurements

Wetting of the cotton skeins by aqueous solutions of each of the individual surfactants and by the Poisson distribution mixture (EO5.5) was measured at 10, 25, 40 and 60 C by the Draves technique (2). Wetting times at concentrations of 1 g/L or higher were done at least in triplicate; those at lower concentrations were done in duplicate or triplicate. Deionized, distilled water was used in the preparation of all solutions. Temperature control was maintained within ±1 C by placing the 500-mL graduated cylinder, in which the tests were performed, in a large, thermostated water bath. Wetting-out times (WOT) were measured on the cotton skeins that were weighted with a 3-g stainless steel hook. Concentrations used were all above the critical micelle concentration (cmc) of the compound tested as determined by surface tension measurements (1).

Cloud Points

The cloud points of the individual compounds and of the mixture (EO5.5) were determined by preparing a 1% solution of each material and making dilutions of it down to the cmc. For materials with cloud points above room temperature, about 15 mL of each solution in a 30-mL test tube was placed in a water bath that was slowly heated while the solution was stirred with a thermometer. The temperature at the first visual sign of cloudiness or opalescence was recorded. The solution was then removed from the water bath and allowed to cool slowly while being stirred. The first visual sign of clearing was recorded. The 2 temperatures were generally within 0.5 C of each other. For materials with cloud points below room temperature, the test tube containing the solution was placed in an ice-water bath and the mixture stirred with a thermometer until it cleared. This temperature was recorded. The solution was then removed from the ice-water bath and allowed to warm slowly, with stirring. The temperature at the first sign of cloudiness was recorded. Agreement was again within 0.5 C. Figure 1 shows the cloud points of the materials tested as a function of the concentration of the solution.

RESULTS AND DISCUSSION

Log-log plots of wetting-out time (in sec) as a function of initial concentration (C) of surfactant (in g/L) at 10, 25, 40 and 60 C are linear in the concentration range 0.25-1.0 g/L. The slopes and Y-intercepts of those lines are given in Table I, together with the order of wetting effectiveness of each surfactant tested at a particular temperature. (An effectiveness rating of 1 indicates lowest wetting-out times for that surfactant over the range of concentrations investigated.)

Effectiveness of Wetting

At 10 C, EO6 is the most effective wetting agent, followed closely by EO5. EO5.5 is slightly poorer than either EO5 or

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[1] Presented at the AOCS meeting in New Orleans, May 1981.

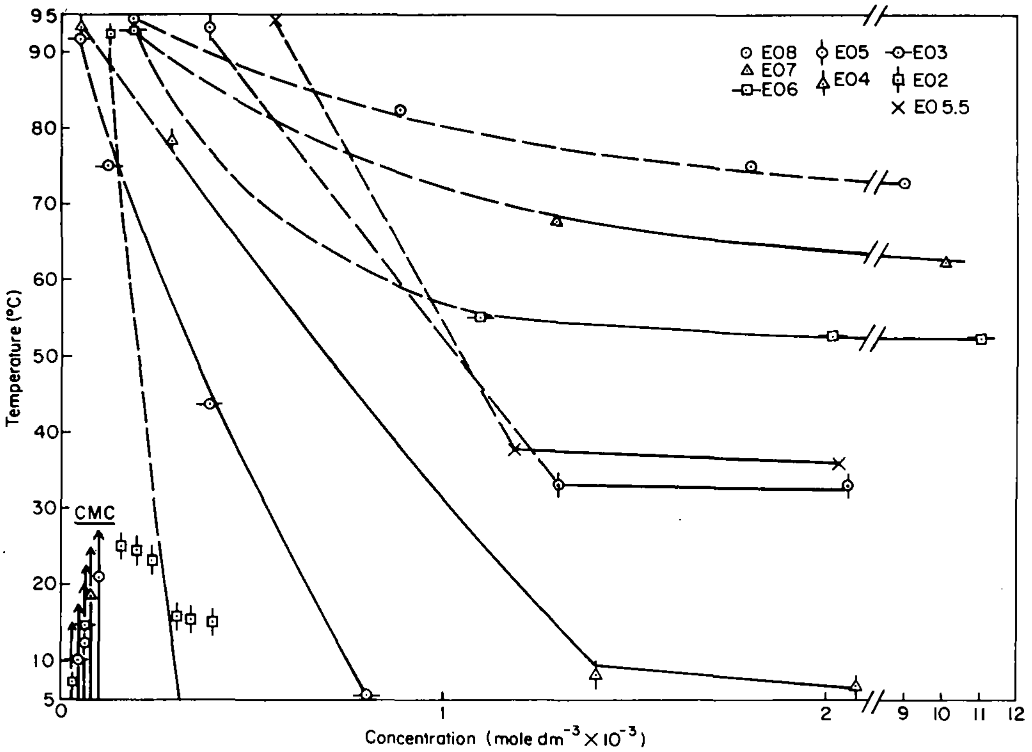

FIG. 1. Cloud points of $C_{12}H_{25}(OC_2H_4)_xOH$ as a function of concentration.

EO6. EO7 is considerably poorer than EO6, EO5 or EO5.5. EO8 is even poorer, and EO4, whose cloud point is slightly below the test temperature for most of the concentration range investigated, is the worst. At 25 C, EO6 is again the best, followed by EO5, with EO5.5 again slightly poorer. EO7 has now become a close fourth and EO8 has also moved closer to the leaders. EO4, which is now considerably above its cloud point, except for the lowest concentration used, is again the worst. At 40 C, EO7 is now equal to EO6 in wetting effectiveness, EO8 is now third and EO5 and EO5.5, both above their cloud points except at the lowest concentration used, have become the poorest wetters (EO4 was not investigated at temperatures above 25 C). Again, EO5.5 is poorer than EO5 and much poorer than EO6. At 60 C, EO8 is now equal to EO7 and they are the best wetters. EO6 is now above its cloud point except at the lowest concentration used and is much poorer than either EO8 or EO7. It is apparent, therefore, that an individual compound with a homogeneous polyoxyethylene head group is a more effective wetting agent than a Poisson distribution mixture with the same average number of oxyethylene units and that compounds above their cloud points are poor wetting agents.

Slopes and Y-Intercepts of the Linear Log-Log Plots

It is notable that the most effective wetting agents at each temperature have slopes in the -1.5 to -1.6 range and Y-intercepts in the +0.6 to +0.7 range. There is an excellent correlation between the value of the Y-intercept and the order of effectiveness of wetting; the smaller the value of the intercept, the better its wetting effectiveness. Because the Y-intercept equals log WOT when log C = 0 (i.e., when the surfactant concentration is 1 g/L), it appears that the wetting time at this surfactant concentration is a good measure of the wetting effectiveness of the material being tested.

The values of the slopes obtained may be explained by assuming that wetting for all these materials is diffusion-controlled. An equation for the wetting of these hydrophobic cotton skeins by nonionics under diffusion-controlled conditions has been developed by Fowkes (3):

$$(C - C') = \tfrac{1}{2} \times \frac{S_c}{S_i} \times \left(\frac{\pi}{D.\,WOT}\right)^{1/2} \times \left(\frac{v}{s}\right)^{-1}, \qquad [1]$$

where C = initial surfactant concentration (g/L); C′ = surfactant concentration (g/L) at the skein-solution interface required to produce a given WOT; Sc = skein-solution interfacial area/g of cotton (a test constant); D = diffusion constant of the surfactant; S_i = interfacial area/g of adsorbed surfactant at the hydrophobic skein-aqueous solution interface; ≈ surface area/g of adsorbed surfactant at the air-aqueous solution interface (= A/MW, where A is

TABLE I

Slopes and Y-Intercepts of Log WOT -Log C Plots

Temp. (C)	Compd.	Effectiveness	Slope	Intercept
10	EO6	1	-1.48	+0.72
10	EO5	2	-1.48	+0.76
10	EO5.5	3	-1.54	+0.76
10	EO7	4	-1.17	+1.02
10	EO8	5	-1.27	+1.24
10	EO4	6	-0.50	+1.50
25	EO6	1	-1.53	+0.59
25	EO5	2	-1.60	+0.68
25	EO5.5	3	-1.31	+0.74
25	EO7	4	-1.52	+0.77
25	EO8	5	-1.33	+0.92
25	EO4	6	-0.93	+1.28
40	EO7	1	-1.52	+0.58
40	EO6	2	-1.57	+0.60
40	EO8	3	-1.31	+0.80
40	EO5	4	-0.99	+1.14
40	EO5.5	5	-0.50	+1.35
60	EO7	1	-1.60	+0.58
60	EO8	2	-1.55	+0.61
60	EO6	3	-1.20	+1.00

the molar area of the surfactant at the air-aqueous solution interface and MW its molecular weight); $\frac{v}{s}$ = area of the aqueous solution-air interface/g of cotton skein (a test constant).

From Equation I, WOT is given by the equation:

$$\mathrm{WOT} = \left(\frac{SC \cdot s}{2v}\right)^2 \cdot \frac{\pi}{D} \cdot \frac{1}{(C - C')^2} \cdot \left(\frac{1}{S'}\right)^2, \qquad [II]$$

and

$$\log \mathrm{WOT} = 2 \log\left(\frac{Sc \cdot s \cdot \sqrt{\pi}}{2v}\right) - 2 \log (C - C') - \log D - 2 \log\left(\frac{A}{MW}\right) \qquad [III]$$

For a given surfactant, using similar cotton skeins, the first and last terms on the right hand side of Equation III are constants, therefore,

$$\log \mathrm{WOT} = K - 2 \log (C - C') - \log D, \qquad [IV]$$

where $K = 2 \log\left(\frac{Sc \cdot s \cdot \sqrt{\pi}}{2v}\right) - 2 \log\left(\frac{A}{MW}\right)$. At concentrations where $C >> C'$ which, for the materials investigated, is when C is >0.25 g/L (log C>-0.6), the slope of the log-log plot should be -2, if D, the diffusion constant, remains constant with change in C, the concentration of the surfactant. However, previous investigators have shown that the micellar size increases with concentration above the cmc (4) and that D decreases with concentration (3), presumably due to this increase in the micellar volume. This decrease in D will result in a smaller absolute value for the slope. The data available on D for solutions of nonionics considerably below their cloud points, but above their cmc (4), indicate that D decreases by a factor of about 2 in the concentration range where the log-log plot of WOT vs C is linear. Such a change in D will yield, by Equation IV, a slope of about -1.5, similar to the maximal slopes observed.

The Y-intercept of the linear portion of the log-log plot of WOT vs C, i.e., where log C = 0, or C = 1 g/L, is related to the diffusion constant, D, of the surfactant at that concentration. From Equation II, for 2 different surfactants, using similar cotton skeins, at the same temperature,

$$\frac{\mathrm{WOT}_1}{\mathrm{WOT}_2} = \frac{D_2}{D_1} \cdot \frac{(C_2 - C_2')^2}{(C_1 - C_1')^2} \cdot \left(\frac{MW_1}{A_1}\right)^2 \cdot \left(\frac{A_2}{MW_2}\right)^2 \qquad [V]$$

When C = 1 g/L and $C >> C'$,

$$\frac{\mathrm{WOT}_1^\circ}{\mathrm{WOT}_2^\circ} = \frac{D_2}{D_1}\left(\frac{MW_1}{A_1} \cdot \frac{A_2}{MW_2}\right)^2, \qquad [VI]$$

where the superscript ° indicates WOT when log C = 0. Table II lists diffusion constants calculated by Equation II, using the test constants for these cotton skeins obtained by Fowkes (3) and values of A from surface tension data (1). For comparison, diffusion constants calculated by Equation VI, using the Y-intercepts in Table I and the value of D for EO6 at that same temperature, as calculated from Equation II, are included in Table II. The close agreement confirms the validity of Equation VI for these systems.

Because the value of the quantity $\left(\frac{MW_1}{A_1} \cdot \frac{A_2}{MW_2}\right)$ for these compounds is close to unity,

$$\frac{\mathrm{WOT}_1^\circ}{\mathrm{WOT}_2^\circ} \approx \frac{D_2}{D_1}. \qquad [VII]$$

The wetting time at 1 g/L is, therefore, roughly inversely proportional to the diffusion constant of the surfactant at the same concentration. This accounts for the observation above that the Y-intercept is a good indicator of the wetting effectiveness of the surfactant.

Effect of Temperature

The slopes of the linear log-log plots in Table I are plotted in Figure 2 against the distance (in C) of the test temperature from the cloud point of the surfactant at each concentration of surfactant. The shaded region at slopes between -1.48 and -1.60 represents the slopes of the most effective wetting agents at each temperature. The slope increases to its maximal negative value in most cases when the test temperature is as much as 50 C below the cloud point of the solution, remains fairly constant to about 8-20 C below the cloud point, and then drops sharply to a much less negative value.

The values of the Y-intercepts of the log-log plots of WOT vs C are plotted against distance of the test temperature from the cloud point of the surfactant in Figure 3. Here, the intercept reaches its smallest positive value about

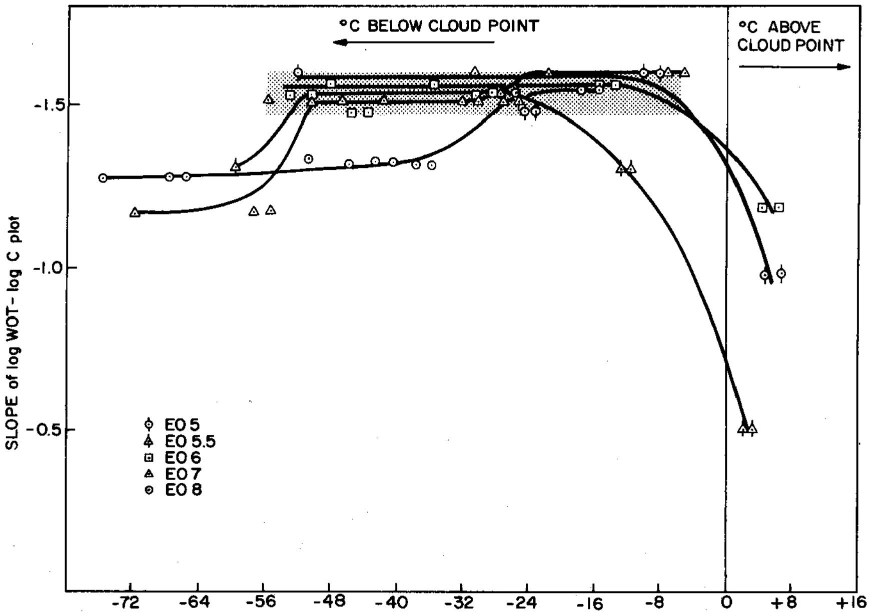

FIG. 2. Slope of linear portion of log WOT-log C plot vs distance (C) from cloud point.

TABLE II

Diffusion Constants of $C_{12}H_{25}(OC_2H_4)_XOH$

Compound	Temp. (C)	δ(Cl. pt.) (C)	D X 10^7 cm^2/sec Equation II	 Equation VI[a]
EO4	10	+3.5	1.0_3	1.0_8
EO4	25	+18.5	1.4_1	1.4_5
EO5	10	-22.5	5.3	5.4_5
EO5	25	-7.5	6.0	6.1
EO5	40	+7.5	2.1	2.1
EO5.5	10	-26.5	5.3	5.4
EO5.5	25	-11.5	5.2	5.3
EO5.5	40	+3.5	1.2_5	1.2_7
EO6	10	-42.5	6.2	–
EO6	25	-27.5	7.8	–
EO6	40	-12.5	7.2	–
EO7	10	-54	3.1	3.1
EO7	25	-39	5.4	5.4
EO7	40	-24	7.9	7.8
EO8	10	-64	1.8_1	1.7_8
EO8	25	-49	3.6	3.5
EO8	40	-34	4.5	4.4

[a] Using D for EO6 at same temperature, as calculated from Equation II.

30 C below the cloud point of the solution, remains constant, and becomes sharply more positive as the cloud point is approached.

The changes with temperature in Figures 2 and 3 are readily explained in terms of the changes in the micellar structure with temperature increase. When the temperature of the solution is far below the cloud point of the surfactant at that concentration, e.g., EO8 at 10 C at all concentrations investigated, temperature increase causes dehydration of some of the polyoxyethylene units of the hydrophilic head groups with a consequent decrease in the hydrodynamic radius of the micelle. This produces an increase in its diffusion constant, with a resulting decrease in the Y-intercept of the wetting curve. The slope of the curve may also become somewhat more negative, although this effect is not as pronounced as that on the Y-intercept. As the cloud point is approached, however, further dehydration of the polyoxyethylene units causes the aggregation number of the micelle to increase rapidly, which produces a sharp decrease in the diffusion constant. This, in turn, results in a sharp increase in the value of the Y-intercept (Fig. 3). There is also a sharp decrease in the value of the negative slope. From Equation IV, this appears to be due to a larger decrease in D as the concentration of surfactant increases, compared to that observed below the cloud point.

We can see, therefore, that for materials 30 C or more below their cloud point, temperature increase causes an increase in wetting effectiveness. As the cloud point of the surfactant solution is approached, however, both the

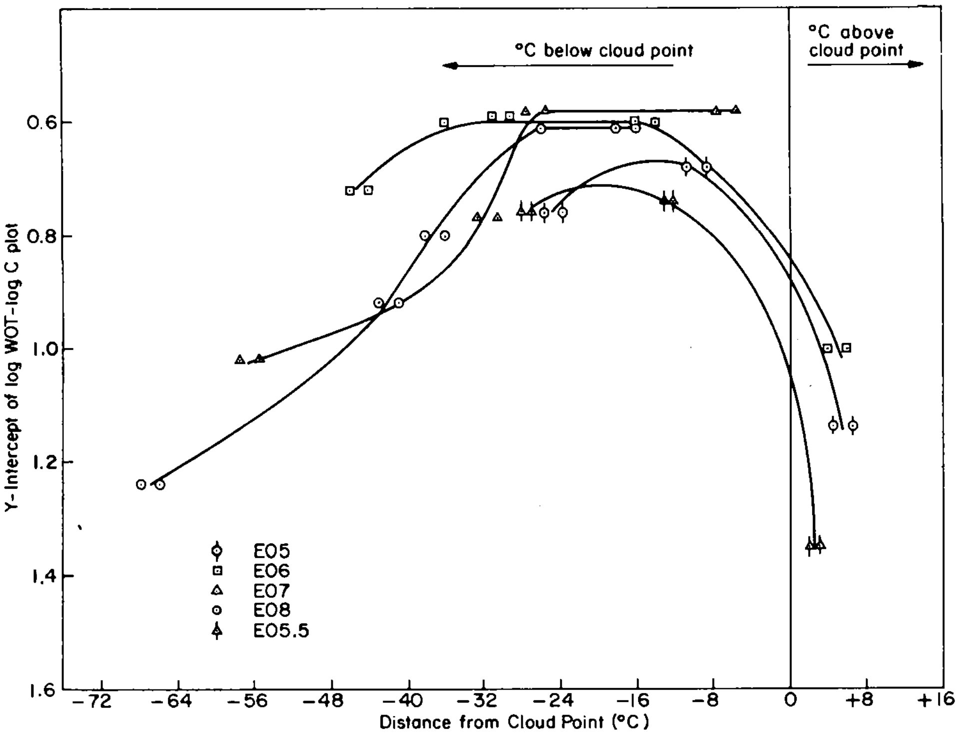

FIG. 3. Y-intercept of linear portion of log WOT-log C plot vs distance (C) from cloud point.

slope and the Y-intercept of the log-log plot of wetting time vs surfactant concentration change sharply. The absolute value of the negative slope decreases and the positive value of the Y-intercept increases, resulting in greatly reduced wetting effectiveness.

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