

Enhancement of Wetting Properties of Water-Insoluble Surfactants via Solubilization

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Water-insoluble surfactants generally show poor wetting behavior in the Draves skein wetting test. This does not appear to be due to high equilibrium or dynamic surface tension values, but to the presence of insoluble surfactant in the system. The replacement of a small percentage of the insoluble surfactant by a water-soluble one capable of solubilizing the former can produce a dramatic improvement in wetting behavior, even when the equilibrium or dynamic surface tension of the system is not significantly changed. Increase in the strength of the attractive interaction between the two surfactants generally improves the clarity of the system and decreases its wetting time.

KEY WORDS: Dynamic surface tension, equilibrium surface tension, skein wetting, solubilization, water-insoluble surfactants, wetting.

Previous work in this laboratory (1) has shown that the wetting time (WOT) in the Draves cotton skein wetting test (2), a commonly used technique for evaluating the textile wetting behavior of surfactants, is related to the dynamic surface tension of the surfactant solution rather than to its equilibrium tension. Log WOT was shown to have a linear relationship to the surface tension at 1 s surface age, γ_{1s} , for many surfactants, as determined by the maximum bubble pressure method.

Many surfactants show a log-log relationship between WOT and aqueous-phase initial surfactant concentration in the range 0.25–2.0 g/L, above which it decreases more slowly and below which it increases sharply. Because γ_{1s} shows a linear relationship to the log of the aqueous-phase surfactant concentration at concentrations below a value called its 1-s critical concentration C_{1s}^* (1), this presumably accounts for the log-log relationship over a limited concentration range between WOT and aqueous-phase surfactant concentration. The slow decrease in WOT at higher aqueous-phase surfactant concentrations presumably parallels the small decrease in γ_{1s} above its C_{1s}^* value, whereas the sharp increase in WOT often found at concentrations below 0.25 g/L might be due to sorption of the surfactant by the textile skein, resulting in a significant decrease in the aqueous-phase surfactant concentration. When this concentration is below the 1-s critical concentration (C_{1s}^*), such a decrease would produce a larger increase in γ_{1s} than expected from the initial concentration and a concomitant larger increase in the WOT value.

Surfactants whose solubility in water is less than 0.25 g/L generally show poor Draves skein wetting times at concentrations above their solubility limits, even when their equilibrium surface tension values are low. Some data are shown in Table 1. We have shown in our previous study (1) that the more hydrophobic and more surface-active the surfactant (*i.e.*, the larger its pC20 or the smaller its critical micelle concentration value), the greater the

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TABLE 1

Equilibrium (γ_{eq}) and 1-s (γ_{1s}) Surface Tensions and Wetting Time (WOT) Values of Some H₂O-Insoluble Surfactants at 1 g/L (25°C)

Surfactant	γ_{eq} (dyne/cm)	γ_{1s} (dyne/cm)	WOT (s) ^a
C ₁₂ EO ₃	27 ^b	45.0	129
C ₁₂ P	26.4 ^b	68.6	130
Neodol 23-3	26.0	51.9	82
Igepal CO-430	<29	70.1	114

^a~30°C; average of first three trials.

^bAt maximum solubility in water.

difference between dynamic and equilibrium values. Therefore, surfactants with low solubility in water would be expected to show γ_{1s} values that are high relative to their equilibrium surface tension, γ_{eq} values and, consequently, WOT values that are higher than expected from those values.

Another factor that could account for the poor wetting of these water-insoluble surfactants is deposition of insoluble surfactant onto the skein surface, thus mechanically delaying wetting. In an effort to investigate this phenomenon and to overcome the negative results of low water solubility, a study was undertaken on the effect on WOT values of solubilization for surfactants of low water solubility by micelles of water-soluble surfactants.

EXPERIMENTAL PROCEDURES

Dynamic surface tension values at 25°C were measured by the maximum bubble pressure method with an apparatus constructed in this laboratory (3). Equilibrium surface tension at 25°C was determined by the Wilhelmy plate method with quartz-condensed water (1). The pH of all solutions was about 5.8. An estimate for the extent of solubilization of the water-insoluble surfactant by the water-soluble one was obtained by measuring the absorbance of the aqueous solution or dispersion of the mixture at 600 nm after standing for 3 d. Solutions having an absorbance (1 cm pathlength) of 0.008 appear clear to the naked eye with only a trace of translucence, those of 0.020 have a slight translucence, and those of 0.100 or more are cloudy.

Materials. C₁₂H₂₅(OC₂H₄)₃OH (C₁₂EO₃) and C₁₂H₂₅(OC₂H₄)₈OH (C₁₂EO₈) were purchased from Nikko Chemical Co. (Tokyo, Japan) as compounds of >98% purity as indicated by gas chromatography. C₁₂H₂₅SO₃Na (C₁₂SO₃Na) and C₁₄H₂₉SO₃Na (C₁₄SO₃Na) of >98% purity were purchased from Research Plus (Bayonne, NJ). Disodium 1,3-*bis* decyl-3¹,5-disulfonatodiphenyl ether (DADS) was a research sample of >99.2% purity, courtesy of Dr. Charles E. Coburn of the Dow Chemical Co. (Midland, MI). C₁₄H₂₉N⁺(CH₃)(CH₂C₆H₅)CH₂COO⁻ (C₁₄BMG) (>99% purity) was synthesized in this laboratory (4). N-Dodecylpyrrolidinone (C₁₂P) (99% purity) was obtained from ISP Corporation (Wayne, NJ). C₁₂H₂₅N(CH₃)₃Br (C₁₂NBr) was prepared in our laboratory by reaction of

1-bromododecane with trimethylamine, followed by five crystallizations from methyl ethyl ketone. Purity was 99.6%, by titration with sodium dodecanesulfonate by means of the two-phase dye transfer technique (5). The following commercial surfactants were used as received: C550 sodium linear dodecylbenzenesulfonate (LAS) from Vista Chemical Co. (Houston, TX); Igepal CO-430, a 4-mol ethoxylate of nonylphenol, from Rhone-Poulenc (Cranbury, NJ); Neodol 23-3, a 3-mol ethoxylate of a $C_{12,13}$ alcohol mixture, from Shell Chemical (Houston, TX).

RESULTS AND DISCUSSION

Absorbance values of the individual surfactants and their mixtures at a total surfactant concentration of 1 g/L, together with equilibrium (γ_{eq}) and 1-s dynamic (γ_{1s})

surface tension values and WOT, are listed in Table 2. WOT in the absence of surfactant is >600 s.

$C_{12}EO_3$ - $C_{12}EO_8$ mixtures. The replacement of 20% by weight of the water-insoluble surfactant, $C_{12}EO_3$, by the water-soluble surfactant, $C_{12}EO_8$, converts the two-phase coarse dispersion of $C_{12}EO_3$ in water into a fine dispersion in which at least a portion of the $C_{12}EO_3$ is solubilized, presumably through the formation of mixed $C_{12}EO_3$ - $C_{12}EO_8$ micelles. The WOT value shows a marked decrease from 129 to 24.6 s. On the other hand, the value of γ_{1s} shows only a small decrease, implying that the large WOT value of the $C_{12}EO_3$ by itself may not be due to its γ_{1s} value but to insoluble surfactant in the system coating the skein surface and mechanically slowing the wetting. With an increase in the $C_{12}EO_8$ content of the mixture, solubilization of the insoluble surfactant

TABLE 2

Dynamic and Equilibrium Properties of 1 g/L Mixtures of H_2O -Insoluble with H_2O -Soluble Surfactants at 25°C^a

Property	Surfactant ratio (w/w) ^b				
	1:0	0.8/0.2	0.7/0.3	0.5/0.5	0:1
$C_{12}EO_3$ - $C_{12}EO_8$ mixtures					
Absorbance (600 nm)	cloudy	0.082	—	0.045	clear
γ_{eq} (dyne/cm)	27.1	27.7	—	28.1	34.8
γ_{1s} (dyne/cm)	45.9	43.9	—	35.9	37.3
WOT (s)	129	24.6	—	14.2	9
$C_{12}EO_3$ - $C_{12}SO_3Na$ mixtures					
Absorbance (600 nm)	cloudy	0.047	—	0.047	clear
γ_{eq} (dyne/cm)	27.1	27.0	—	26.9	54.5
γ_{1s} (dyne/cm)	45.0	37.9	—	37.7	56.5
WOT (s)	129	19.3	—	16.8	28.0
$C_{12}EO_3$ - $C_{10}DADS$ mixtures					
Absorbance (600 nm)	cloudy	0.031	0.008	0.005	clear
γ_{eq} (dyne/cm)	27.1	27.0	26.9	28.5	44.3
γ_{1s} (dyne/cm)	45.0	35.0	35.0	39.1	66.8
WOT (s)	129	14.5	14.7	17.5	431
Igepal CO-430-LAS mixtures					
Absorbance (600 nm)	cloudy	0.032	—	0.055	clear
WOT (s)	114	14.7	—	10.6	8.0
Igepal CO-430- $C_{10}DADS$ mixtures					
Absorbance (600 nm)	cloudy	0.024	0.018	0.006	clear
WOT (s)	114	11.0	10.9	10.0	430
$C_{14}BMG$ - $C_{12}SO_3Na$ mixtures					
Absorbance (600 nm)	0.740	0.006	—	0.004 ^c	clear
γ_{eq} (dyne/cm)	30.9	30.4	—	30.2 ^c	54.5
γ_{1s} (dyne/cm)	35.2	39.3	—	40.0 ^c	56.4
WOT (s)	22.2	10.5	—	11.7 ^c	28
$C_{12}P$ - $C_{10}DADS$ mixtures					
Absorbance (600 nm)	0.465	0.007	—	0.006	clear
γ_{eq} (dyne/cm)	26.6	26.8	—	29.7	44.3
γ_{1s} (dyne/cm)	68.6	33.1	—	39.0	66.8
WOT (s)	130	8.6	—	13.2	431
$C_{14}SO_3Na$ - $C_{12}NBr$ mixtures					
Absorbance (600 nm)	solid ppt.	0.005	0.002	—	clear
γ_{eq} (dyne/cm)	47.2	25.8	24.9	—	57.6
γ_{1s} (dyne/cm)	—	51.3	43.9	—	63.5
WOT (s)	>420	17.1	13.7	24.2 ^d	>600

^a Abbreviations as in Table 1. DADS, disodium 1,3-bisdecyl-3¹,5-disulfonatodiphenyl ether; LAS, sodium inear dodecylbenzene sulfonate.

^b First listed surfactant/second listed surfactant.

^c 0.58/0.42 Ratio.

^d 6/4 Ratio.

increases and the absorbance, γ_{1s} and WOT values all decrease.

WOT values obtained upon repeating the wetting test with fresh skeins, but with the same surfactant solution containing excess single insoluble surfactant (Table 3), also suggest that the large WOT values are at least partly due to the presence of insoluble surfactant in the system. The successive WOT values at 1 g/L, using a fresh skein each time, for both $C_{12}EO_3$ and $C_{14}BMG$, show a decrease in the wetting time, presumably because sorption of insoluble surfactant by each fresh skein reduces its delaying effect on wetting. When the amount of insoluble surfactant is increased (by bringing the surfactant concentration for $C_{14}BMG$ to 1.5 g/L), this decrease in wetting time is not observed for at least four trials; when the amount of insoluble surfactant is decreased (by reducing the concentration for $C_{12}EO_3$ to 0.5 g/L), the WOT is reduced more sharply by the next trial. In the absence of insoluble surfactant, WOT values in the first few trials on surfactant solutions in the 0.5–1.5 g/L concentration range generally do not vary by more than about 2 s.

Because $C_{12}EO_3$ and $C_{12}EO_8$ show little interaction with each other at the aqueous solution/air interface (6), it is to be expected that the WOT values at the different $C_{12}EO_3/C_{12}EO_8$ ratios will fall between those of the individual materials by themselves, *i.e.*, that they will not exhibit a synergistic interaction.

$C_{12}EO_3-C_{12}SO_3Na$ mixtures. Here, the replacement of 20% of more of the $C_{12}EO_3$ by an anionic surfactant results in more pronounced solubilization (as indicated by the absorbance value) and lower γ_{1s} and WOT values. This is consistent with observations by a number of investigators (6–10) that polyoxyethylenated nonionics interact more strongly with anionics than with other polyoxyethylenated surfactants. In this case, the system exhibits synergism in both dynamic surface tension lowering and in wetting rate, *i.e.*, the γ_{1s} and WOT values of the mixtures are significantly smaller than those of the individual surfactants by themselves.

$C_{12}EO_3-C_{10}DADS$ mixtures. The replacement of 20% or more of the $C_{12}EO_3$, in this case by a disulfonate anionic, produces an even larger decrease in absorbance, γ_{1s} and WOT values, which may be due to the fact that disulfonated anionics, compared to the corresponding monosulfonated anionics, interact more strongly with nonionic surfactants (Rosen, M.J., and Z.H. Zhu, unpublished results). This system shows marked synergism in dynamic

surface tension reduction and, consistent with that, reaches a lower WOT value than attained with the monosulfonated anionic.

Igepal CO-430-LAS and Igepal CO-430- $C_{10}DADS$ mixtures. These mixtures show behavior similar to the $C_{12}EO_3$ mixtures described above, in that the replacement of 20% of the water-insoluble surfactant by a water-soluble one markedly decreases the absorbance and the wetting time, with the disulfonate ($C_{10}DADS$) producing a larger effect in each case than the monosulfonate (LAS).

$C_{14}BMG-C_{12}SO_3Na$ mixtures. Anionic surfactants are known to show moderate to strong attractive interactions with zwitterionic surfactants of this type, which are capable of accepting a proton to become cationic (11). The presence of the anionic surfactant increases the basicity of the zwitterionic. The resulting cationic-anionic interaction produces increased solubilization of $C_{14}BMG$. The strength of the interaction is evidenced by the almost complete solubilization of the $C_{14}BMG$ by the replacement of only 20% by weight of it by $C_{12}SO_3Na$ and by the resulting low WOT value. On the other hand, the γ_{1s} value is unexpectedly high. This might be due to the anionic-cationic salt formed as a result of this interaction being more hydrophobic than the $C_{14}BMG$, with a resulting increase in the difference between γ_{1s} and γ_{eq} values (see above).

$C_{12}PC_{10}DADS$ mixtures. N-alkylpyrrolidinones interact with anionic surfactants in a manner similar to betaines, by accepting a proton to form an anionic-cationic salt (12). Although the interaction of N-alkylpyrrolidinones with monosulfonates is somewhat weaker than that of betaines, the presence of a disulfonated anionic in the mixtures may increase the strength of the interaction, as evidenced by the low absorbance at the 8:2 ratio and the very low WOT values of the mixtures relative to those of the individual surfactants by themselves.

$C_{14}SO_3Na-C_{12}NBr$ mixtures. Mixtures of anionic and cationic surfactants show the strongest attractive interactions (13). The low absorbance and γ_{eq} values are consistent with this. The high γ_{1s} relative to γ_{eq} values, noted above for the $C_{14}BMG-C_{12}SO_3Na$ mixtures, may again be the result of the more surface-active and the more hydrophobic character of the anionic-cationic salt produced by mutual neutralization of the charges of the two ionic surfactants. It is noteworthy that, in spite of the marked changes in wetting behavior produced upon the addition of the water-soluble to the insoluble surfactant, the value of the equilibrium surface tension remained almost unchanged in all the systems studied, except for the anionic-cationic mixture.

The results obtained allow the following conclusions to be drawn: (i) The poor wetting behavior (as measured by the Draves skein wetting test) of the water-insoluble surfactants investigated is not due to high equilibrium or dynamic surface tension values but to the presence of insoluble surfactant in the system. (ii) The solubilization of most, or all, of the insoluble surfactant by replacement of a small fraction of it by water-soluble surfactant can produce a dramatic improvement in wetting behavior. (iii) This improvement is not necessarily accompanied by a decrease in the equilibrium or dynamic surface tension of the system. (iv) When a small percentage of a given water-insoluble surfactant is replaced by a water-soluble surfactant, clarity increases and wetting time decreases

TABLE 3

Wetting Times^a in Successive Trials on Same Surfactant Solution at 23°C

Trial no.	$C_{12}EO_3$		$C_{14}BMG$	
	1 g/L	0.5 g/L	1 g/L	1.5 g/L
1	309	472	22	21
2	213	69	27	19
3	59		17	19
4	52		18	21
5	49		15	
6	39		14	
7			12	

^aIn seconds.

with an increase in the strength of the interaction between the two surfactants.

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