Nonionic Surfactant Amides As Soil Wetting Agents

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Isomeric hydroxyethyl tertiary amides, $RCONR'CH_2CH_2OH$, where R and R′ are 7–8 carbon linear or branched aliphatic groups, were oxyethylated to form polydisperse adducts containing 5–20 moles of ethylene oxide. The adducts $RCONR'(E.O.)_xH$ were free of unreacted amide and contained minimum ester contaminant where R and R′ were branched. Ester content of the adducts does not change with time, but the monomer does revert to amide on standing. All series of adducts showed good wetting at intermediate chain lengths but instantaneous wetting only at short chain lengths where both R and R′ were branched. Good water solubility occurred at the intermediate chain length while maximum surface activity was found for short chain lengths corresponding to a hydrophile-lipophile balance of ~9. All adduct series were excellent wetting agents for cotton skeins and a burned over sandy loam. For this soil the adducts effectively promote wetting at 0.01% level.

Hydrophobic soils found in citrus orchards (1) and burned over brushland (2) result from the presence of water insoluble organic residues which in the former are due to normal plant growth and in the latter to a process of condensation on the cool soil surface. Both phenomena appear to be associated only with the top few inches of soil surface.

The key to sustained plant growth and revegetation of such soils depends on water infiltration through this nonwetting barrier. Improved water infiltration in such soils has been achieved by mechanical disking, incorporation of bentonite clays, emulsified asphalt, hydrophilic agents such as polyelectrolytes, and surfactant wetting agents (2). Nonionic surfactants are used as soil conditioners or greening agents on golf courses and in commercial nurseries, but even this use is on a limited scale. The attractive properties of nonionic wetting agents appear to stem from the fact that they are physically adsorbed by soils presumably prolonging their activity as wetting agents and maintaining their presence in the upper soil levels; they are not insolubilized by Ca^{++} and Mg^{++}; they exhibit low phytotoxicity when used as soil amendments; their water solubility and wetting properties are readily controlled by changing the ethylene oxide (E.O.) chain

length.

Attempts to relate wetting properties, water solubility and surface activity to the ethylene oxide chain length of nonionic surfactants and the organic substrate were begun at this laboratory. Early work (4) with essentially homogeneous oxyethylated alcohols and acids showed that the best wetting properties were achieved with alcohols and acids containing 8–10 carbon atoms and surfactants with ~2–3 E.O. groups. The low water solubility of these wetting agents suggested high activity at low concentration. Wetting properties were determined on samples of Glendora soil (burned over brushland soil) and peat moss. Other work (5) based on polydisperse adducts from various benzenesulfonamides, $ArSO_2NR'(E.O.)_xH$, showed that the best combination of wetting properties, water solubility and surface activity existed in the range $x = 5$ to 11. The drop penetration test on ground peat moss generally confirmed the results from the Draves wetting profiles. A search for better wetting agents continued with a recent study showing that the low pressure oxyethylation of secondary aliphatic amides resulted in only partial conversion to the desired adducts (6). Attempts to increase the activity of the amide by substituting aromatic (R) groups for aliphatic groups did indeed reduce unreacted amide concentration. However, the adducts now contained an aminoester contaminant showing titratable base in excess of what could be attributed to the catalyst. In spite of the high levels of unreacted amide and ester contaminant, some Draves wetting profiles for oxyethylated adducts $RCONR'(E.O.)_xH$ where R and R′ contained 8 to 10 carbon atoms showed quite attractive wetting properties.

For this reason, the present program was undertaken to synthesize and evaluate oxyethylated amides free of unreacted amide and ester contaminant. The earlier study (6) indicated that adducts derived from N-octyloctanamide and N-octyl-p-t-butylbenzamide showed the most attractive Draves wetting profiles of the various series examined. However, the former series contained unreacted amide while the latter series contained both unreacted amide and the ester contaminant. This study was therefore directed to determining the chemical structure based on aliphatic groups which would eliminate both of these undesirable features. The most attractive approach appeared to be a tertiary amide based solely on aliphatic groups. The ready availability of intermediates based on eight carbon atom chains and the last effort (6) led to the selection of this unit length. The following synthetic approach was employed: A primary amine was treated in a low pressure addition with E.O. to form N-alkylethanolamine (Equation 1). This intermediate was reacted with an acid chloride to form N-hydroxyethyl-N-alkylalkanamide (Equation 2), which was oxyethylated to a polydisperse adduct as shown using solid KOH catalyst (Equation 3).

$$R'NH_2 + C_2H_4O \rightarrow R'NHCH_2CH_2OH \quad [1]$$

$$R'NHCH_2CH_2OH + RCOCl \xrightarrow{C_2H_4Cl_2} RCONR'CH_2CH_2OH \quad [2]$$

$$RCONR'CH_2CH_2OH + C_2H_4O \xrightarrow{KOH} RCONR'(CH_2CH_2O)_xH \quad [3]$$

EXPERIMENTAL

Materials and apparatus. Ethylene oxide (E.O.) was purchased in 3-lb cylinders from the Matheson Company, East Rutherford, New Jersey. Amines and acid chlorides were obtained from Aldrich Chemical Co., Metuchen, New Jersey, or the Eastman Kodak Co., Rochester, New York. The reaction solvent 1,2-dichloroethane was Eastman white label. All reagents and solvents were used as received. Trycol 5951 is 100% alkylpolyethylene glycol (equivalent to soil penetrant 3586) from Emery Industries, Mauldin, South Carolina. Aqua-Gro is a 47% polyoxyethylene ester of cyclic acid, 47% polyoxyethylene ether of alkylated phenol and 6% silicone antifoam agent from Aquatrols Corporation of America, Pennsauken, New Jersey. N-alkylethanolamines and some N-hydroxyethyl-N-alkylalkanamides were purified by distillation through a 24″ spinning band column @ <0.2 mm. Infrared spectra were obtained with a Perkin Elmer 1310 microprocessor controlled infrared spectrophotometer. Oxyethylations were carried out in heavy walled glass half-liter round-bottomed flasks equipped with a thermometer well and an aerosol pressure coupling (#110-585) from Lab-Crest Scientific Division, Fischer Porter Company, Warminster, Pennsylvania. The aerosol coupling was connected to a pressure gauge (0–60 psi) and a release valve. A teflon coated bar magnet served as a stirrer. Glass pressure tubes, capacity ~90 ml, were used in oxyethylations with less than 50 ml of reactants.

N-Alkylethanolamine synthesis. To a half-liter pressure flask was added 1.5 M of alkylamine and 0.75 M of liquified ethylene oxide. The colorless solution was stirred at ~70 C until a pressure drop occurred. The temperature was raised to 90–100 C and maintained until the pressure decreased to zero. At 70 C the reaction required 3–6 hr with flask pressures less than 50 psi. Excess alkylamine was removed by distillation at 5 mm. The remaining residue was distilled through a 24″ spinning band column at ~0.2 mm to yield the N-alkylethanolamine and an oily residue, probably N-alkyldiethanolamine, which was always present in these syntheses.

N-Alkylethanolamine
$RNHCH_2CH_2OH$

R	bp °C	Press mm	% yield
octyl	75–8	0.15	57
2-ethylhexyl	66–70	0.15	64

N-Octyl-2-Ethylhexanamide synthesis. This intermediate was synthesized by a previously described method (6).

N-Hydroxyethyl-N-Alkylalkanamide synthesis. These amides were prepared by adding 0.25 mol of acid chloride to 0.50 mol of N-alkylethanolamine in 150 ml of 1,2-dichloroethane at room temperature over 30 min. The slightly basic mixture was stirred 3 hr, treated with 50 ml of 3N HCl and then extracted with 80-ml portions of water until the wash liquid was neutral and gave a negative chloride ion test. The organic layer was filtered and all solvent removed @ 50 C/0.2 mm. The crude amide was used as isolated or where possible distilled at 0.2 mm through a 24″ spinning band column. The amides are essentially colorless liquids whose elemental analysis agreed within ±0.3% of theory.

N-Hydroxyethyl-N-Alkylalkanamide
$RCONR'CH_2CH_2OH$

R	R′	bp °C	Press mm	% yield
heptyl	octyl	used as isolated		—
heptyl	2-ethylhexyl	used as isolated		—
3-heptyl	octyl	138–40	0.15	72
3-heptyl	2-ethylhexyl	135–40	0.10	80

Oxyethylation of tertiary amides. In a half-liter glass pressure flask was weighed 0.1 mol of N-hydroxyethyl-N-alkylalkanamide, 0.4 mol of liquified ethylene oxide and 0.1 mol percent of solid powdered potassium hydroxide. The aerosol coupling was hand tightened to the flask. The colorless reaction mixture was heated in an oil bath with vigorous stirring and adequate shielding to a pressure of 50 psi. The temperature was maintained at 60–70 C until a pressure drop occurred (6–24 hr), then the mixture was heated to 110 C until the pressure decreased to zero. The flask was reweighed to determine any E.O. loss. A sample of 5 molar adduct was removed, sufficient E.O. and a trace of catalyst were added and the procedure repeated to form adducts with 10, 15 and 20 mol of E.O.

Evaluation. A sample of burned brushland soil obtained from N. Valoras of the University of California at Riverside was used in this study. It was a Sandy Loam obtained from the San Jacinto mountain region near Idylwild, California. The soil was sieved to pass a #10 mesh screen and stored in a sealed container to maintain the initial moisture content.

Wetting properties were determined with a modified version of the Draves test (7) and the drop penetration test developed as a screening procedure for surfactants by Savage et al. (8). The Draves test measures the time in seconds for a standard 5-g cotton skein to sink in a 0.1% solution of surfactant at room temperature. With the drop penetration test, approximately one-half g of Idylwild soil was placed in a cylindrical polyethylene cup (dia. 1.5 cm × height 1.0 cm). The soil sample was leveled with a glass stirring rod and given a slight concave surface. 0.05 ml of surfactant solution or distilled water was applied to the surface and the time required for disappearance of free liquid was measured. Rewet time was determined by applying 0.05 ml of distilled water to the same soil surface. Two procedures were followed: wetted soil samples were dried overnight under ambient conditions and then rewet, or they were dried immediately for 30 min on the steam bath, equilibrated for 1 hr at room temperature and then rewetted.

Soil pellets from Idylwild soil were prepared with a KBr pellet press at 10,000 psi using sufficient soil to form pellets ~4 mm thick.

Cloud point was determined on 1% aqueous solutions of E.O. adduct. The temperature of the sample solution was decreased until it was clear. The solution was then slowly warmed to the onset of turbidity. This temperature was recorded as the cloud point. The procedure was repeated as a check on the first determination.

Surface tension was measured with a du Noüy tensiometer on 0.1% aqueous solutions with the values corrected to 25 C. Solutions used in determining critical micelle concentration were prepared as follows: A 0.01 molar solution was prepared and equilibrated overnight. The solution was diluted to the desired concentrations, which were equilibrated 2 hr and then used to determine surface tension. Each value was obtained as the average of five determinations.

Base content of hydroxyethyl tertiary amides and adducts derived from them were determined by potentiometric titration in isopropanol-ethylene glycol using a Beckman-Zeromatic pH meter and titrating with 0.1N HCl in the same solvent mixture.

RESULTS AND DISCUSSION

Synthesis. N-alkylethanolamines were prepared (~60%) by the low pressure, <50 psi, addition of one mol of E.O. to two mol of primary amine. Equimolar ratios of reactants gave poor yields <30%, of product, while ratios >2 did not lead to significantly better yields. N-alkylethanolamine reaction mixtures were not heated above 70 C in order to control the pressure and temperature.

Isomeric N-hydroxyethyl-N-octyloctanamides (Equation 2) were prepared where the alkyl groups were both linear, both branched or mixtures thereof. When R is a linear aliphatic group, these tertiary amides upon distillation at reduced pressure gave poor yields of distillate and large amounts of nondistillable residue. Infrared examination of both fractions showed these compounds were thermally labile yielding materials with intense ester absorptions at ~1730 cm^{-1}. This behavior was explained previously (6) by a well known rearrangement of certain hydroxyalkylamides to isomeric aminoesters. It was observed in this study, Figure 1, when R is heptyl and R′ is 2-ethylhexyl, that heating the tertiary amide under nitrogen generated base as shown. At room temperature, the base content slowly decreased with time. However, we never observed complete disappearance of base upon standing at ambient conditions. Base concentration beyond that shown was never exceeded because prolonged heating led to darkening and decomposition of the sam-

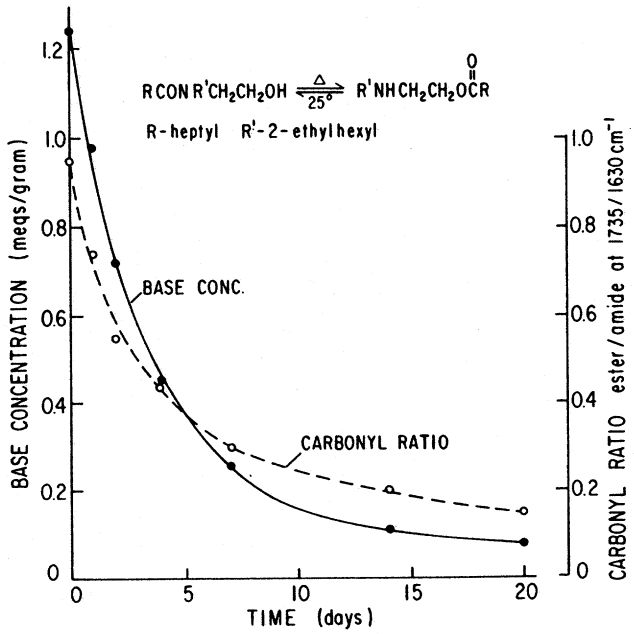

FIG. 1. Reversion of aminoester to isomeric amide.

ple. The ester carbonyl band decreased relative to the amide carbonyl as base concentration diminished with time. This time dependence was not observed with the oxyethylated adducts. The reason is readily apparent, because the active species of the acyl migration is

$$R'NHCH_2CH_2O\overset{O}{\overset{\|}{C}}R,$$

which is readily oxyethylated at the amino group, thereby precluding any reversion to the original tertiary amide.

The addition of E.O. to the hydroxyethyl tertiary amides occurred much more readily with the distilled amides than those used as isolated, suggesting the presence of inhibitors in the crude products. As noted previously (5), once the initial adduct was formed further oxyethylation occurred more readily. Other investigators (9) suggested that this increased reactivity is due to a catalytic effect. The adducts showed OH bands at ~3450 cm^{-1}, amide carbonyl 1630 cm^{-1}, ester carbonyl 1730 cm^{-1} with free amide and polyoxyethylene stretching at ~3300 and ~1100 cm^{-1} respectively.

Properties of oxyethylated amides. Figure 2 shows Draves wetting profiles for adducts from hydroxyethyl tertiary amides as the solid line plots and compares these with the same adducts from secondary amides as previously described (6). Values for x = 1 were excluded because they were greater than 100 seconds. Contact angle measurements were not used because this method does not distinguish between various members in a series of adducts. Aliphatic R groups each with eight carbon atoms were varied from linear to branched as shown. The solid line profiles are a distinct improvement over the adducts from the secondary amides. In each solid line plot the 10 and 15 molar adducts are comparable, regardless of branching in one or both R groups. Variations in wetting properties occur only at the 5 or 20 molar E.O. levels. The best overall wetting properties occurred when R is heptyl and R′ is 2-ethylhexyl, but instantaneous wetting was observed for the first time with a completely branched polydisperse adduct indicating that excellent wetting is possible with mixtures. The marked differences between the two sets of Draves profiles delineate the effects of incomplete reaction of the secondary amide and subsequent higher degree of oxyethylation of the adducts formed (6). The theoretical wetting curve would be U-shaped as from a composite of the linear and branched solid line plots. The general shape of the dashed line plots corresponds to the right side of the theoretical curve where the E.O. chain length has passed optimum wetting ability.

An infrared study of the adducts from the tertiary amides showed that each series contained some ester contaminant. The data in Table 1 correlate ester/amide carbonyl absorbance ratios in order of increasing branching from left to right with x values ranging from 1 to 20. Some ester was present in all the hydroxyethyl tertiary amides. The highest level occurred when both R groups were linear. A measurable decrease followed when R′ was branched and a further decrease when R was branched. Minimum ester concentrations occurred when both R groups were branched; this is the series showing instantaneous wetting properties. Steric hindrance apparently plays some role in decreasing ester formation as the R groups are branched. Based on the earlier study (6) none of these adduct series should contain any ester contaminant. The apparent explanation for this anomaly appears to be related to specie concentration and reaction velocity. In the oxyethylation of secondary amides the initial intermediate $RCONR'CH_2CH_2OH$, is present in very low concentration and adds additional E.O. groups more readily than the rearrangement (via acyl migration) can occur. Therefore, no ester contaminant was found. In the oxyethylation of hydroxyethyl tertiary amide, the large initial concentration of this species offers sufficient time for ester formation to occur concurrent with the main reaction.

In order to define the wetting properties more completely for the most effective adduct series found to date, Draves wetting time vs. concentration is shown in Figure 3 and compared with Trycol 5951 and AquaGro,

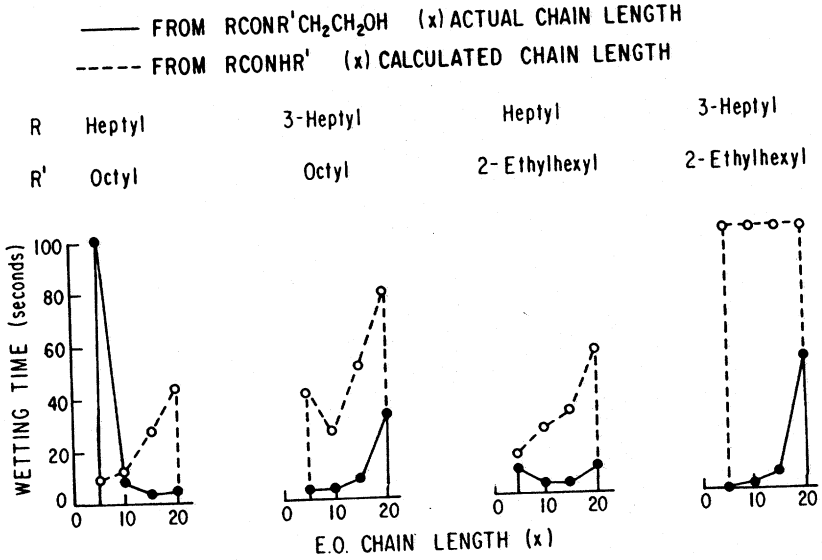

FIG. 2. Draves wetting profiles for $RCONR'(CH_2CH_2O)_xH$ adducts.

TABLE 1

Carbonyl Ratios[a] of Adducts From Hydroxyethyl Tertiary Amides $RCONR'(CH_2CH_2O)_xH$

R R′	Heptyl octyl	Heptyl 2-ethylhexyl	3-Heptyl octyl	3-Heptyl 2-ethylhexyl
x	Carbonyl ratio			
1	.18	.02	.11	.02
5	.56	.16	.08	.05
10	.29	.15	.11	.05
15	.25	.10	.06	.05
20	.25	.15	.07	.04

[a]Ester/amide carbonyl ratios measured @ ~1730/1630 cm^{-1}.

two commercial wetting agents finding some use in the turf and nursery industry. At concentrations less than the minimum shown for each curve, wetting times surpassed the 100 sec. limit set for this evaluation. At 0.025% the 5 molar adduct is essentially equal to Trycol 5951 at 0.05%. At 0.05% this adduct is twice as effective as Trycol 5951 and at 0.1% it gives instantaneous wetting. The 10 molar adduct wetted instantaneously at 0.15%, while the 15 molar adduct never reached this wetting power even at 0.2%.

Water solubility of the isomeric adducts is shown in Figure 4 where cloud point is plotted against E.O. chain length (x). Only partial water solubility was found for all adducts at X = 5. As would be expected, the linear adducts were the least water soluble at any value of x. A branched 2-ethylhexyl group at R′ and a linear group at R led to a perceptible increase in water solubility. However, maximum water solubility was found when both R and R′ were branched or when only R was a branched 3-heptyl group. The results shown here agree with previous findings (5) where complete water solubility at room temperature occurred in the region x = 10, in sharp contrast to the excessive solubility found for oxyethylated secondary amides at short chain lengths.

Table 2 correlates surface tension values corrected to 25 C with hydrophile-lipophile balance (HLB) values for the various series of oxyethylated isomeric tertiary amides. A HLB value of 9 corresponds to the minimum surface tension for all series where the adducts show only partial water solubility but would be considered to have excellent lipophilic character. Normally plots of surface tension versus E.O. chain length show minima corresponding to optimum surface activity. Here the minima apparently occur somewhere between an E.O. chain length of 1 and 5. A relationship between these values and Draves wetting profiles at short or intermediate E.O. chain lengths is not readily apparent.

Because the solution properties of surfactants change abruptly with the onset of micelle formation and most efficient wetting occurs at or above the CMC (10), we sought to determine the actual values for the most attractive series of adducts. Critical micelle concentrations were determined with the series $RCONR'(E.O.)_xH$ where R is 3-heptyl and R′ is 2-ethylhexyl. The determinations, Figure 5, show surface tension as a function of the log of the concentration. For these branched adducts, CMC equals $\sim 10^{-3}$ molar and increases with increasing E.O. chain length.

Generally CMC increases as the hydrophobic nature of the surfactant decreases. Nonionics ordinarily exhibit CMC's in the region 10^{-4} molar. However, when the hydrophilic group is moved from the terminal position of a carbon chain, the CMC increases. The results suggest that determinations at 0.1% concentration were essentially above the CMC for these adducts. It is presumed that the remaining series of isomeric adducts tending to greater linearity of the R groups would have comparable if somewhat lower CMC's.

The drop penetration test used previously on powdered peat moss and soils generally confirmed Draves wetting

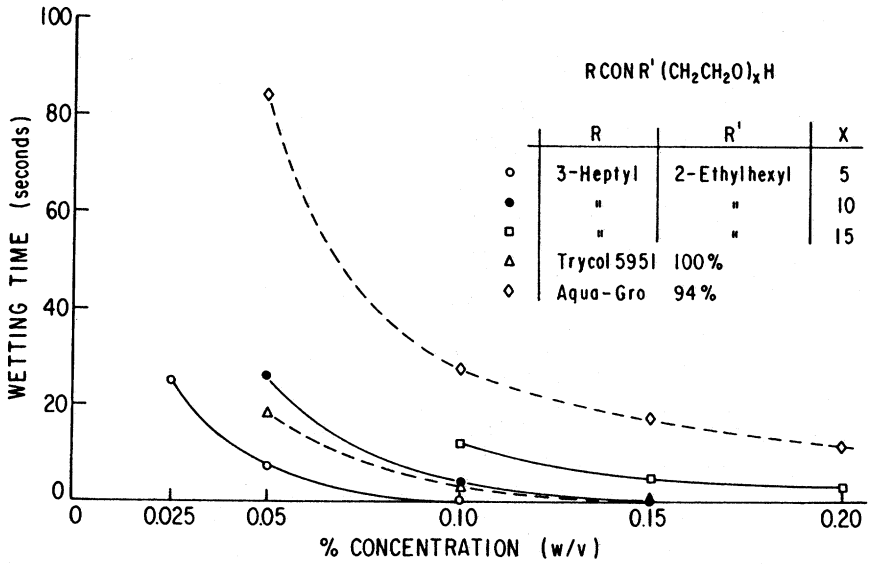

FIG. 3. Dependence of wetting ability on concentration of adducts derived from N-hydroxyethyl-N-2-ethylhexyl-2-ethylhexanamide.

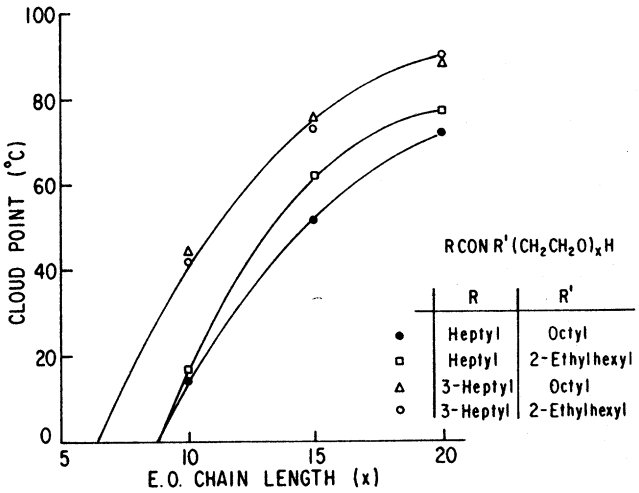

FIG. 4. Water solubility of oxyethylated adducts.

TABLE 2

Surface Tension and HLB For Isomeric Oxyethylated Adducts $RCONR'(CH_2CH_2O)_xH$

R R′	Heptyl octyl	Heptyl 2-ethylhexyl	3-Heptyl octyl	3-Heptyl 2-ethylhexyl	
X	Surface tension dynes/cm 25 C				HLB[a]
1	—	—	—	—*	3
5	26.1	27.3	27.7	28.2	9
10	26.8	27.8	28.6	28.3	13
15	27.8	28.8	30.7	29.3	14
20	29.6	30.3	32.6	32.3	15

[a]Hydrophile-lipophile balance calculated by Griffin's formula HLB = weight percent oxyethylene content/5; at x = 1 the adducts are still essentially water insoluble @ 0.1% w/v.

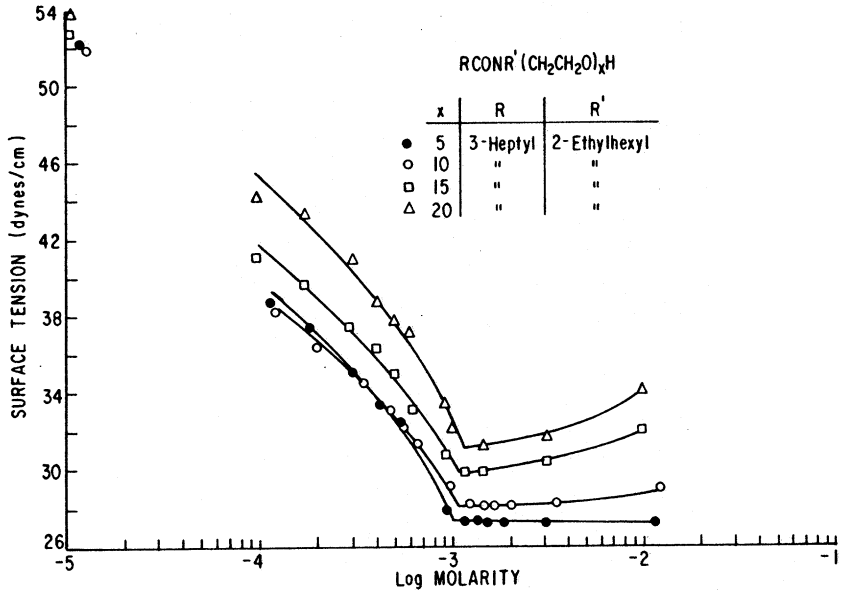

FIG. 5. Relation between surface tension at 25 C and concentration of oxyethylated adducts.

results (4,5). An evaluation of peat moss pellets was made because of the difficulty in determining the disappearance of free liquid when using a powdered substrate (6). Preliminary results here with pelletized Idylwild soil samples indicated (A) no dependence of wetting time on the pressure of pellet formation over the range 5–20,000 psi; (B) soil pelletization levels the wet and rewet times of sample solutions and water controls so as to minimize differences readily visible with powdered soil samples; (C) soil pellets formed at high pressures disintegrated more readily upon wetting than pellets formed at low pressure, and (D) pellets readily formed hairline cracks upon wetting with solutions or water, and these subsequently acted as sinkholes upon rewetting with water. The leveling of wetting times probably is related to fracturing soil particles and thereby generating fresh wettable surfaces.

The drop penetration test was employed on sieved Idylwild soil to determine the wetting behavior of the isomeric adducts as shown in Table 3. R and R′ range from both linear to both being branched. E.O. chain length x varies from 5 to 20. Wetting time in seconds was determined at three concentrations, 0.1, 0.01 and 0.001%. Water controls were run with each series. The rewet values shown were obtained by equilibrating the samples overnight at ambient conditions. Rapid rewet values obtained by drying soil samples on the steam bath and equilibrating for one hour were comparable with the values shown. The data indicate: (i) the adducts are effective at 0.1 and 0.01% and appear to have a positive effect at 0.001%; (ii) rewet times are generally shorter than the wetting times at all concentrations. However,

Drop Penetration Wetting of Idylwild Soil By Oxyethylated Adducts $RCONR'(CH_2CH_2O)_xH$

R R′	Heptyl octyl		Heptyl 2-ethylhexyl		3-Heptyl octyl		3-Heptyl 2-ethylhexyl		Water control	
	Time seconds @ 0.1%									
x	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet
5	19	20	2	5	2	3	2	2	540	95
10	7	3	2	3	1	1	3	1	540	95
15	4	4	4	2	3	1	2	1	540	95
20	8	3	5	1	4	1	3	1	540	95
					@ 0.01%					
5	175	30	150	26	103	20	200	12	565	170
10	170	15	140	11	115	21	150	15	565	170
15	130	13	155	17	165	52	250	17	565	170
20	180	15	165	29	125	13	210	19	565	170
					@ 0.001%					
5	290	45	180	240	190	46	270	40	650	155
10	320	52	210	95	340	50	410	300	650	155
15	540	230	150	280	350	40	410	180	650	155
20	380	71	220	250	345	81	190	420	650	155

this occurs even with the water controls; (iii) the adducts generally produce shorter rewet times relative to the controls, and (iv) there is no obvious distinction in wetting behavior with changing E.O. chain length or between various adduct series at the same concentration.

Accordingly, for adducts RCONR′ (E.O.)$_x$H where x is 5 to 20 and R,R′ are 7–8 carbon aliphatic groups: (a) addition of E.O. to a hydroxyethyl tertiary amide eliminates the low reactivity encountered with a secondary amide; (b) ester formation is minimized by branching R and R′; (c) instantaneous wetting ability was observed when R and R′ were branched and x was about five, and (d) these adducts were found to be effective wetting agents for Idylwild Soil at 0.01%.

ACKNOWLEDGMENT

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