Oxyethylated Secondary Amides as Soil Wetting Agents

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ABSTRACT

Polydisperse adducts, $\mathrm{RCONR'(CH_2CH_2O)_xH}$, with attractive wetting properties were prepared by oxyethylating aliphatic and aromatic secondary amides to calculated x values of 5 to 20. Moderate wetting profiles were observed with adducts where R and R' contained 15 to 18 carbon atoms and had short ethylene oxide chains. These products, however, contained unreacted amide and/or ester contaminants. Consequently, the products showed high water solubility, fairly flat surface tension curves and average wetting ability. In the transition of adducts derived from aliphatic amides to those from aromatic amides, unreacted amide concentration decreased and ester contaminant increased.

INTRODUCTION

Hydrophobic soils are ubiquitous and generally associated with the deposition of organic residues from plant growth or forest fires (1). These soils are typical of, but not restricted to, aging citrus groves, chaparral regions and burned over brushland. This condition promotes water runoff, soil erosion and poor seed germination. Low water infiltration leads to deficient crop yields even with ample rainfall.

The use of chemical additives (1) as soil conditioners began about 30 years ago and depended on their ability to alter the physical properties of soils. Small amounts (<0.1% w/w) of additives improved water infiltration by changing the soil particle aggregation. This reduced evaporation and wind erosion. The ability to control moisture loss improved soil rewetting, stimulated seed germination and shortened the time to plant maturity. Typical chemical soil conditioners which showed promise ranged from high molecular weight hydrophilic polymers like polyacrylamide and polyvinyl acetate and polyelectrolytes such as carboxylated vinyl acetate-maleic acid copolymers (Krilium) to various surface active agents (1,2). Of this group, only nonionic surfactants still find some commercial use in the nursery industry. Nonionics are attractive by virtue of their low phytotoxicity in soil applications, insensitivity to hard water ions, adsorption by various soils and the ease of controlling their water solubility (1). Water solubility and adsorptivity on soils are directly related to the ethylene oxide (E.O.) chain length. Nonionics also afford stability to biodegradation. Valoras et al. indicated that increased adsorptivity of nonionics by soils decreased their rate of biodegradation (3). Furthermore, experience with ABS surfactants showed that branched alkylbenzene groups are very resistant to biodegradation.

Prior to the efforts from this laboratory, no studies appeared attempting to relate the wetting properties of nonionic surfactants to E.O. chain length and organic substrate structure. The initial study (4) described wetting characteristics of oxyethylated acids and alcohols obtained from purified polyethylene glycols. Optimum wetting ability was observed with materials containing 8-10 carbon atoms and 2-3 E.O. groups, but the compounds were incompletely water soluble at this ethylene oxide level. Wetting ability was determined on cotton skeins with a modified Draves test (5) and on various soils and peat moss with the drop penetration test (6). Another study (7) of polydisperse adducts based on aromatic sulfonamides $\mathrm{R\phi SO_2NR'(CH_2CH_2O)_xH}$ showed a range of wetting properties and water solubility. Adducts where x = 5-10 displayed optimum wetting ability, minimum surface tensions, cloud points ~25 C, and hydrophile-lipophile balance values of 10-12. Draves wetting profiles generally were confirmed by the drop penetration test on ground peat moss.

This program was undertaken to develop efficient moisture control agents for hydrophobic soils. An entire surfactant area has evolved around nonionics from primary fatty amides (8). To a lesser extent some literature exists dealing with the oxyethylation of unsaturated and polymeric amides (9). The effort reported in this paper was directed toward determining the structure of secondary amides required for the most effective wetting properties. Optimum wetting behavior usually is observed when a large hydrophilic group is centrally located on a long hydrocarbon chain (10). Secondary amides were treated with ethylene oxide using solid KOH catalyst to form polydisperse adducts, where R and R' are aliphatic or aromatic groups and x was calculated to contain 5-20 moles E.O. per mole of amide (Equation 1).

$$\mathrm{RCONHR'} + x\mathrm{C_2H_4O} \xrightarrow{\mathrm{KOH}} \underset{\mathrm{A}}{[\mathrm{RCONR'CH_2CH_2OH}]} \rightarrow \mathrm{RCONR'(CH_2CH_2O)_xH} \qquad [1]$$

EXPERIMENTAL

Material and Apparatus

Acid chlorides and amines were obtained from the Aldrich Chemical Company or the Eastman Kodak Company, and used as received. Crystallization solvents were reagent grade while 1,2-dichloroethane was Eastman white label. Ethylene oxide was purchased from Matheson Company. Infrared spectra were obtained with a Perkin Elmer 1310 microprocessor controlled infrared spectrophotometer. Oxyethylations were performed in heavy walled glass half liter round bottom flasks equipped with a thermometer well and an aerosol pressure coupling (#110-585) from Lab-Crest Scientific Division, Fischer Porter Company. The aerosol coupling was attached to a pressure gauge and a release valve. Stirring was accomplished with a teflon coated bar magent. For oxyethylations involving less than 50 ml of reactants, glass pressure tubes with a capacity of ~90 ml were used.

Synthesis Secondary Amide

All amides were prepared by adding 1 mole of acid chloride to 2 moles of amine, both as solutions in 1,2-dichloroethane. The addition was performed at ~25 C and the mixture refluxed for 1 hr. After the amine hydrochloride was extracted with water and the solvent evaporated, the crude amide was purified by vacuum distillation or crystallization to a constant melting solid. The amides are colorless liquids or crystalline solids melting below 100 C and obtained in 60-85% yields. Elemental analyses agreed within ±0.3% of theory.

Oxyethylation Secondary Amide

This synthesis was described previously (7).

Evaluation

Wetting properties were obtained using a modified Draves test (5) and the drop penetration test developed as a screening method by Savage et al. (6). The Draves test measures the time in seconds for a standard 5 g cotton skein to sink in 0.1% solution of compound at room temperature. In this study, the drop penetration method was applied to pressed

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peat moss pellets. Air dried Canadian sphagnum peat moss was ground in a Wiley mill to pass a #10 screen. Sufficient ground peat moss was placed in a KBr pellet press to form a pellet 3-4 mm thick using a compression of 6000 psi. One drop of 0.1% aqueous solution of E.O. adduct was applied to each pellet surface and the time required for disappearance of free liquid was measured. Five pellets per sample solution were used, and a wetting time was obtained with both sides of a pellet. Therefore, the resulting value was an average of 10 determinations. Reproducible rewet times were not obtained with these adducts.

Cloud point is the temperature at which a 1% aqueous solution of E.O. adducts becomes turbid.

Surface tension was measured with a duNoüy tensiometer on 0.1% aqueous solutions with the values corrected to 25 C.

Free Amide in E.O. Adducts

0.1 to 0.3 g of adduct was weighed into a 125 ml flask and dissolved in 100 ml of distilled water. The solution was stored 1-5 days at room temperature. The opalescent suspension was filtered by suction on a weighed filter paper and air dried to constant weight at ambient temperature. Based on the weight of adduct and the weight of dried solid plus filter paper, one determined the approximate crude amide in each sample of adduct. The free amide was identified by melting point and an infrared spectrum.

RESULTS AND DISCUSSION

Synthesis

Polydisperse oxyethylated amides were used as isolated. They generally contained some unreacted amide and an ester contaminant. Adducts obtained from aliphatic secondary amides contained unreacted amide and no ester contaminant. Adducts from aromatic secondary amides contained less unreacted amide but showed the presence of an ester contaminant at ~1720cm^{-1}. The initial product in the oxyethylation process is shown in Equation 1 as intermediate (A). If species (A) is more reactive than the original amide, oxyethylation will occur preferentially with intermediate (A) forming adducts containing unreacted amide. If the reverse is true, no free secondary amide will be found and the adducts will contain the calculated amount of ethylene oxide. Apparently, the amides in this study were less reactive with E.O. than intermediate (A).

The migration of acyl groups in substituted ethanolamines is a well known process (11). Amides of the type $ArCONR(CH_2)_nOH$ where R is hydrogen or ethyl, n = 2 to 4 and Ar is a benzene nucleus, undergo rearrangement in acidic media forming the isomeric aminoester $ArCO_2(CH_2)_nNHR$. It appears that the aromatic secondary amides of this study undergo an analogous transformation during oxyethylation to form aminoesters from the initial intermediate (A) as shown in equilibrium 2, where R or R' is a substituted benzene nucleus.

$$RCONR'CH_2CH_2OH \overset{\Delta}{\rightleftharpoons} R'NHCH_2CH_2OCOR \qquad [2]$$

In those adducts exhibiting an ester contaminant, excess base above and beyond that attributable to the added KOH was found. This can be explained only by the formation of an aminoester. Further studies of this presumed N → O acyl migration are in progress.

As noted earlier (7), the initial reaction between the amide and E.O. generally required the longest time (2-10 hr) with this period being much longer for highly branched amides. Subsequent oxyethylations required shorter reaction times (0.5-2 hr). The products generally showed broad OH bands at ~3400-3500 cm^{-1}, polyoxyethyl stretching at ~1110 cm^{-1}, and amide carbonyl at ~1640 cm^{-1}. Free amide NH and ester functionality appeared at ~3300 and ~1720 cm^{-1}, respectively.

Properties of Oxyethylated Amides

Figures 1 to 3 show Draves wetting profiles for various E.O. adducts derived from aliphatic and aromatic secondary amides. Wetting time in seconds is plotted as a function of the calculated E.O. chain length x over the interval 5-20. Figure 1 shows wetting profiles for adducts where R and R' are linear aliphatic groups containing 6-10 carbon atoms. Moderate wetting behavior was observed with adducts where the R groups contained 7-10 atoms. In these series, the most attractive wetting occurred where x = 5 with continuous deterioration of this property with increasing values of x. No wetting ability was observed with adducts from N-hexylhexanamide. Figure 2 summarizes the same type data for adducts from amides where R and R' each contain eight carbon atoms and where the groups are branched or aromatic. The profile for oxyethylated N-octyloctanamide from Figure 1 is included for comparison. The results suggest that branching on one R group has little effect on wetting, while branching in both R groups destroys wetting ability. The presence of a benzene nucleus in R or R' diminishes wetting ability. Wetting profiles for products derived from N-substituted p-t-butylbenzamides are shown in Figure 3. These plots are comparable to those from linear secondary amides when R' is an octyl or decyl group. Less attractive wetting ability was found when R' is hexyl, while a reversed pattern is seen with R' as a p-n-butylphenyl group.

The drop penetration test (7) on adducts in Figures 1 to 3 was not reproducible with powdered peat moss. The method was applied to pressed peat moss pellets. Determination of wetting times as a function of the pressure applied during pellet formation showed that reproducible wetting times were observed when pellets were formed at pressures > 5000 psi. Application of the test to several series of adducts showing the largest differences in wetting times for x = 5 to 20 revealed that the drop penetration test generally confirmed the Draves profiles but showed much lower sensitivity. Rewet determinations on these adducts were not reproducible.

Early in this program it became apparent that unreacted amide was present to some extent in nearly all the oxyethylated adducts described in Figures 1 to 3. An attempt to increase the activity of the amide proton was made by substituting an aromatic nucleus for one or both R groups. Figure 4 shows the approximate percent free amide present in the adducts as related to the calculated E.O. chain length. R and R' for the various series are listed in the order of decreasing amide concentration. Because the results are approximations, only three sets of data are shown to bracket the relative positions of the other series. The results show that free amide concentration was reduced but not eliminated. The actual E.O. chain length in these adducts is therefore somewhat higher than the calculated values, being about 2-4 moles E.O. per mole of amide higher based on the results in Figure 4. No unreacted amide was found in the adducts from N-(n-butylphenyl) p-t-butylbenzamide.

One might expect the higher degree of oxyethylation and the presence of unreacted amide to be reflected in the surface tension measurements and water solubility of the adducts. Variation between surface tension and calculated E.O. chain length is given in Figure 5 for a few series of data points to illustrate the general shape of the curves. In a polydisperse system, where calculated chain length equals actual chain length, a minimum should exist as vaguely seen here for the series where R is heptyl and R' is 2-ethylhexyl indicating the region of maximum surface activity. The

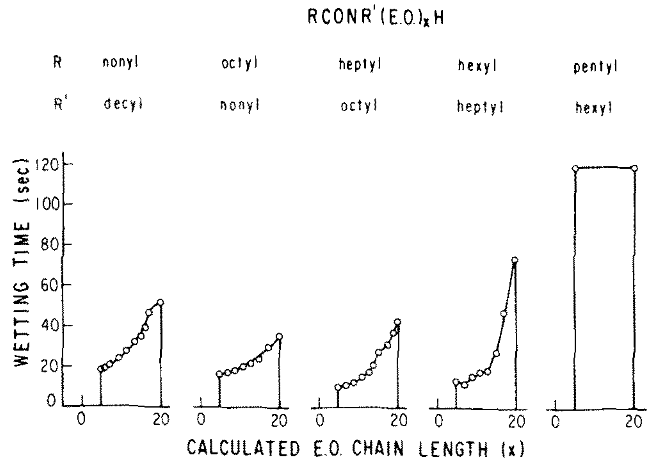

FIG. 1. Draves wetting profiles of oxyethylated linear aliphatic amides.

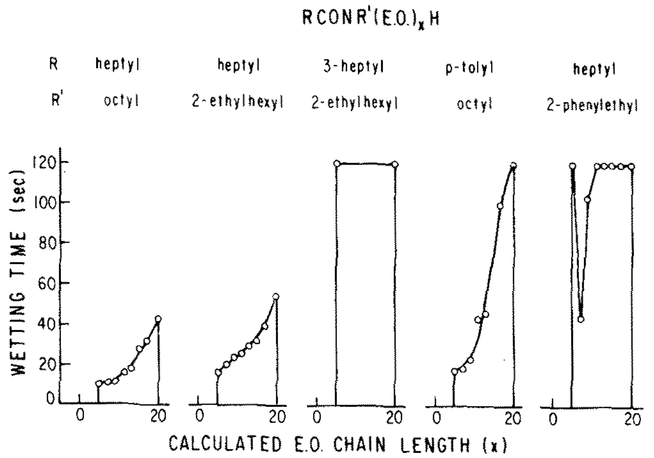

FIG. 2. Draves wetting profiles of oxyethylated branched amides.

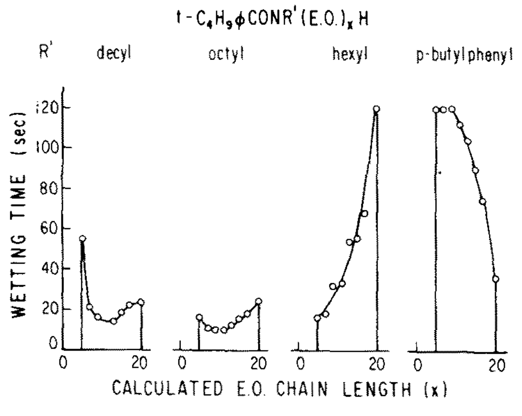

FIG. 3. Draves wetting profiles of oxyethylated aromatic amides.

scatter in the values is considerably greater than found in a previous study (7). However, some observations can be made. Oxyethylated N-hexylhexanamide is the least surface active series. The order of surface tension curves generally follows that of the Draves wetting profiles, the most surface active series being associated with aliphatic amides. In several series the most surface active adduct corresponds to the shortest E.O. chain length because of the actual high degree of oxyethylation.

The excessive oxyethylation should increase water solubility substantially. Figure 6 shows the relationship between

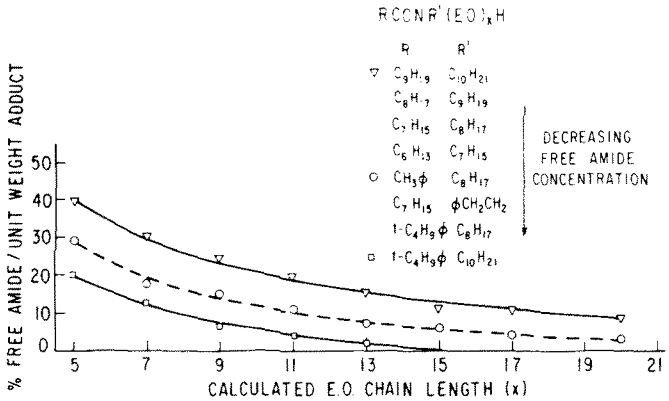

FIG. 4. Approximate free amide in oxyethylated adducts.

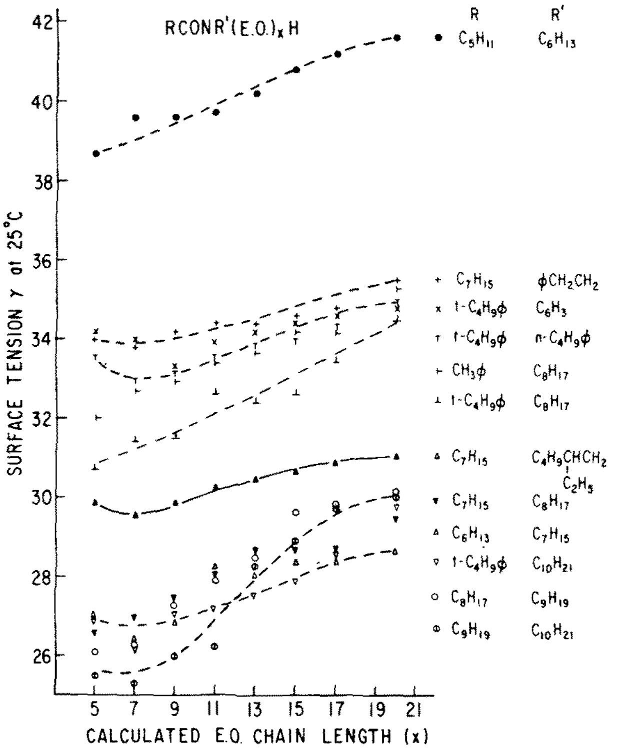

FIG. 5. Surface tension of oxyethylated amides.

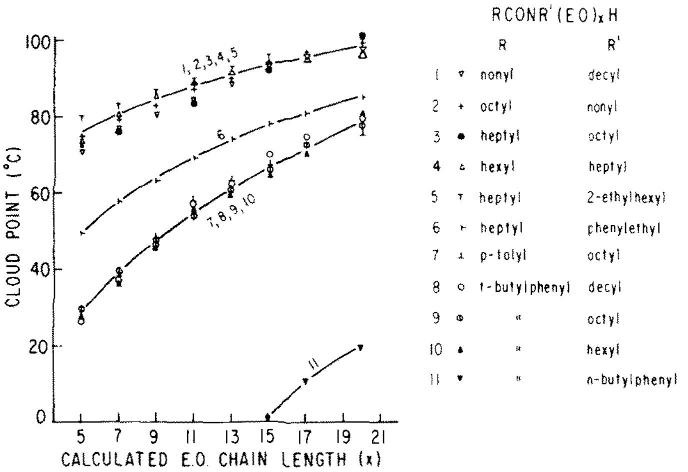

FIG. 6. Cloud point variation of amide adducts.

TABLE I

Amide/Ester Carbonyl Ratio in RCONR′(E.O.)$_x$H Adducts

Adduct		Carbonyl ratio[a]	
R	R′	x = 5	x = 15
Octyl	Nonyl	>100	>100
Heptyl	Phenethyl	40	14
p-Tolyl	Octyl	4	3
t-Butylphenyl	Decyl	3	3
t-Butylphenyl	n-Butylphenyl	0.7	0.7

[a] Arbitrary absorbance units @ 1630/1730 cm^{-1}.

cloud point and calculated E.O. chain length for most of the adduct series prepared in this program. All series with the exception of the aromatic amide #11 have excellent water solubility at room temperature for the shortest E.O. chain length. The order of decreasing solubility is linear aliphatic, branched aliphatic and aromatic compounds corresponding broadly to the order of decreasing free amide content.

The formation of ester presumably has a negative effect on the wetting properties of the adducts. Oxyethylation of aliphatic amides occurred without ester formation, whereas with aromatic amides large amounts of ester were formed. The results are summarized in Table I as amide/ester carbonyl ratios measured at the indicated frequencies. The transition from a purely aliphatic amide to an aromatic amide resulted in an amide/ester ratio ranging from >100 to <1. The insertion of a phenylethyl group in R′ immediately reduced the ratio to ~40 while p-tolyl or p-t-butylphenyl as an R group reduced it further to ~3. Hence, ester formation decreased in the following order for the oxyethylation of secondary amides where R is aliphatic and ϕ is aromatic:

$$\phi\text{CONH}\phi > \phi\text{CONHR} > \text{RCONHR}$$

Free amide and ester contaminants would appear to have noticeable effects on wetting, surface activity and water solubility. This seems evident for the unusual wetting profile in Figure 3 where R′ is a p-n-butylphenyl group. This adduct series showed relatively high surface tension values and poor water solubility.

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