Wetting Properties of Nonionics From Branched Fatty Diamides

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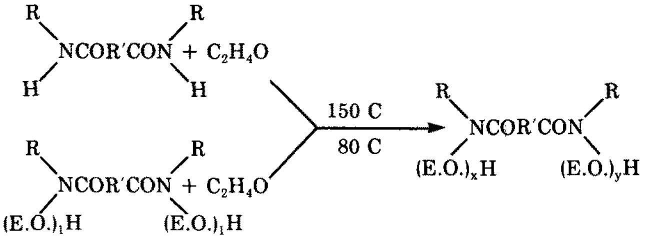
Low pressure oxyethylation of RNHCOR'CONHR or $RCONHCH_2CH_2NHCOR$ does not occur below 100 C where R represents branched aliphatic groups and R' is 0-4 methylene groups or -CH=CH-. These diamides add ethylene oxide at 140-170 C to give dark adducts highly contaminated with aminoester. The corresponding dihydroxyethyl derivatives undergo low pressure oxyethylation, yielding products with good room temperature solubility, low aminoester content and good wetting properties for cotton skeins and a hydrophobic soil. For these adduct series, most effective wetting was found with an ethylene oxide chain length of 8. For adducts based on fumaramide, excellent wetting properties were observed over a chain length range of 5-15 units. All adduct series effectively wet Idylwild hydrophobic soil at 0.01%, but no distinction was possible between series at the same concentration.

Hydrophobic soils, their genesis, characterization and occurrence have been described in a well documented review by L. F. Debano (1). Water repellency generally can be remedied by mechanical cultivation or the use of soil conditioners (2,3). Surfactants have found application as such because studies indicated they promote water infiltration (4,7) and moisture retention (5). Nonionics in particular are physically adsorbed by soils (6) and show an interesting decrease in biodegradation with increased adsorption (8). Being surfactants, they act at interfaces and therefore should function at very low concentrations; being neutral, they should be unaffected by multivalent ions.

Initial studies here (9) of homogeneous ethylene oxide (E.O.) adducts from alcohols and acids showed optimum wetting of Glendora hydrophobic soil with substrates containing 8-10 carbons and two to three E.O. groups. Subsequent efforts used polydisperse products as isolated. Branched aromatic sulfonamides, $R\phi SO_2NHR'$ oxyethylated readily (10) under low pressure conditions to adducts with attractive wetting and surface active properties at E.O. chain lengths of 5-11 units. Efforts to develop more efficient wetting agents from secondary aliphatic amides showed incomplete reaction with E.O., while aromatic secondary amides oxyethylated more readily but were found highly contaminated with an aminoester byproduct of low wetting potential (11). The former problem arose because of the large difference in relative reactivity between the secondary aliphatic amide and the initial hydroxyethyl intermediate, $RCONR'CH_2CH_2OH$, while the latter problem arose from a dynamic isomerization of aromatic hydroxyethyl tertiary amide to the isomeric aminoester, $RCONR'CH_2CH_2OH \rightleftharpoons R'NHCH_2CH_2OCOR$. A partial solution was achieved via the direct oxyethylation of aliphatic hydroxyethyl tertiary amides (12). This study showed that branched R groups result in a sharp decrease in aminoester concentration. For this adduct series with an E.O. chain length of 5, instantaneous wetting was observed for the first time with a polydisperse mixture. This series was superior to commercial soil wetting agents over the concentrations 0.024-0.1% and showed effective wetting for Idylwild hydrophobic soil at the 0.01% level. These results clearly indicated that homogeneous adducts are unnecessary and that excellent results can be achieved with polydisperse systems.

The basic wetting configuration locates a hydrophilic group at the center of a long carbon backbone. The positive results achieved by manipulating the amide structures (12) suggested that we might define optimum wetting structures more precisely by examining structural variations at the hydrophilic portion of the molecule. Thus arose the present program to develop property-structure relations of oxyethylated diamides as soil wetting agents. The object was to develop a structure which maintains its integrity while reacting completely under the conditions of low pressure oxyethylation. This study describes the effect of manipulating the diamide group by structural changes and varying the methylene chain length. Diamides and dihydroxyethyldiamides were treated with E.O. at atmospheric pressure and 50 psi using KOH catalyst to form adducts where x + y = 2 to 20.



R is a branched aliphatic group with 7-8 carbons and R' is 0-4 methylene groups or a -CH=CH- group. Diamides based on N,N'dihydroxyethylethylenediamine derivatives and 2-ethylhexanoyl chloride were also evaluated.

EXPERIMENTAL PROCEDURES

Materials and apparatus. Malonyl, succinyl, glutaryl, adipoyl and fumaryl chlorides, ethanolamine, diethyl oxalate, triethanolamine, 2-ethylhexylamine and triethylamine were obtained from the Aldrich Chemical Company, Metuchen, New Jersey. 1,2-Dichloroethane was from the Eastman Kodak Company, Rochester, New York, while ethylene oxide (E.O.) was supplied by Matheson Gas Products, Inc., East Rutherford, New Jersey, in 3-lb steel cylinders. Surface tension measurements were made with a duNoüy tensiometer at ambient temperatures. Infrared spectra were obtained with a Perkin Elmer 1310 microprocessor-controlled infrared spectrophotometer. Oxyethylations were performed in thick-walled glass half-liter pressure flasks equipped with a thermometer well, pressure gauge, 0-60 psi, pressure release valve and a Teflon stirring bar. Seals were made with aerosol pressure coupling 110-585 from Lab-Crest Scientific Glass Co., Warminster, Pennsylvania. Base content was measured potentiometrically with a Beckman Zeromatic pH meter. Purification by distillation was performed with a two-ft vacuum-jacketed spinning band column.

A sample of hydrophobic soil was obtained through the courtesy of J. Letey and coworkers at the University of California in Riverside. The soil sample is a sandy loam obtained from burned-over brushland in the San jacinto mountains near Idylwild, California. It was sieved to pass a #10 screen, air dried and stored in sealed containers to maintain a constant moisture level. This soil is similar to Glendora soil but is less water repellant.

Synthetic procedures: N-Alkylethanolamines. This procedure was described earlier (12) for the preparation of N-octyl and N-2-ethylhexylethanolamines.

Synthetic procedures: N,N'-Dialkylamides. These diamides of the type $RNHCOCH_2CH_2CONHR$ and $RCONHCH_2CH_2NHCOR$ were prepared by normal Schotten Baumann procedure using triethylamine in dichloroethane solvent.

Synthetic procedures: N,N'-Dialkyl-N,N'dihydroxyethyldiamide. The following procedure applied to fumaramides, succinamides, glutaramides and adipamides gave the cleanest products in reasonable yields. To a half-liter reaction flask was added 0.2 mol N-2-ethylhexylethanolamine and 0.25 mol triethanolamine in 100 ml of 1,2-dichloroethane. The solution was stirred, cooled to 10-15 C and 0.1 mol diacylchloride in 50 ml of solvent was added drop by drop over one to two hr while maintaining the temperature at $\sim$15 C. After adding the acid chloride, the mixture was stirred three to four hr at room temperature and filtered by suction. The amine hydrochloride was washed three times with 30 ml solvent and filtered. The wash liquids were combined with the original filtrate and extracted with 40-ml portions of distilled water until the aqueous phase was neutral and free of chloride ion. The organic phase was filtered by gravity and solvent evaporated under vacuum at 0.2 mm/40 C to constant weight. Liquid products were used as isolated while solids were recrystallized to constant melting point. Yields range from 31–81%. Elemental analyses were within ±0.3% of theory.

Synthetic procedures: N,N'Dihydroxyethylethylenediamine. This approach is based on a procedure of Petrov et al. (13). To 1.5 mol of ethanolamine at 130 C under a dry nitrogen atmosphere was added 0.5 mol of 1,2-dichloroethane at such a rate ($\sim$3 hr) that the temperature was kept at 150-155 C. After holding the mixture at this temperature for a total of five hr, it was cooled and treated with 150 ml ethanol and one mol sodium hydroxide. The mixture was stirred, precipitated sodium chloride was filtered and washed with ethanol. The combined filtrates were evaporated on the rotovac to remove solvent and free ethanolamine, leaving 104 g of a clear viscous oil. Repeated crystallizations of the crude product from absolute ethanol gave 23 g (30% yield) of crystalline solid m.p. 98 C with an elemental analysis within ±0.3% of theory.

Synthetic procedures: N,N'di-2-ethylhexyl-N,N'-dihydroxyethyloxamide. This method is a modification of the procedure of Rice et al. (14) for primary amines. Diethyloxalate (0.1 mol) was added to 0.2 mol N-2-ethylhexylethanolamine over 30 min. The reaction mixture was heated slowly to 150 C over a two-hr period with vigorous stirring. During this time 10 ml of ethanol was collected in a Barrett trap (theory 11.7 ml). When ethanol no longer evolved, the mixture was cooled to 100 C and all volatiles removed at 0.1 mm to constant weight. The crude oxamide, 38 g (theory 40 g), was obtained as a clear, almost colorless oil whose I.R. spectrum was consistent with the expected structure and whose C, H and N analysis agreed to within ±0.3% of theory. Ester/amide carbonyl ratio of 0.18 was observed. The aminoester content reverted to zero upon standing at room temperature (12).

Oxyethylation of free diamide. Atmospheric pressure reactions were performed in standard laboratory glassware using dry nitrogen as a carrier gas for ethylene oxide additions made at the rate of 2-4 g/hr. The reactions were catalyzed with potassium hydroxide and performed neat.

Oxyethylation of N,N'dihydroxyethyldiamide. The low pressure procedure was described previously (12).

Evaluation. The drop penetration test developed by Savage et al. (15) was used to evaluate the wetting candidates on hydrophobic Idylwild soil. A half gram of soil sample was leveled and given a slightly concave surface. Then, 0.05 ml of surfactant solution or distilled water was applied to the soil surface and the time required for disappearance of free liquid was measured. Rewet time was measured by applying 0.05 ml distilled water to the dried surfactant-treated sample and to the control. Two rewet procedures were employed as checks on one another. Wetted soil samples were dried for 30 min on the steambath, equilibrated at room temperature for one hr and rewetted. The soil samples were air dried overnight and then rewetted with distilled water.

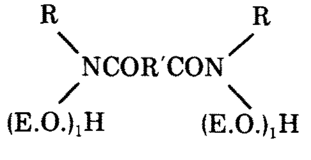
Differentiation of sample wetting ability was determined using a modified version of the Draves test (16). The test measures the time in seconds for a standard five-g cotton skein to sink in a 0.1% solution of surfactant at room temperature. The method permitted the construction of wetting profile diagrams for each series of adducts in contrast to contact angle measurements which distinguished only gross changes in wetting ability.

Surface tension was measured with a duNoüy tensiometer at 0.1% concentrations with values corrected to 25 C. Cloud point was determined using 1% aqueous solutions of wetting agent. The solution was cooled until it was clear and then slowly warmed until turbid. The temperature at which this occurred was the cloud point. The procedure was repeated one or more times as a check on the first determination.

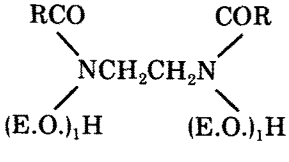
RESULTS AND DISCUSSION

Synthesis. Symmetrical diamides type A, $RNHCO(CH_2)_x$ CONHR and type B, $RCONHCH_2CH_2NHCOR$ where x = 0 or 2 and R is 3-heptyl, octyl or 2-ethylhexyl, were obtained as crystalline solids melting between 87 and 164 C. Treatment with E.O. at 80 C/50 psi in the presence of KOH catalyst for as long as four days gave no oxyethylation and recovery of essentially all the starting diamide. Even where solubilization of the low melting diamide occurred, no reaction was observed. The results suggest that inversion of the amide group, separation of the NH sites by as many as four carbons and the presence of linear or branched R Groups have no effect in promoting oxyethylation. These diamides do react with E.O. at atmospheric pressure from 140-170 C in the presence of catalyst to form adducts. Observed E.O. adsorption under the conditions employed was 25-50% of that added. The products were brown to black oils, highly contaminated with aminoester and showing no wetting properties or adequate water solubility even with a maximum E.O. content of 7.2 mol/mol diamide. The results were not totally unexpected considering the high reaction temperature and the presence of two amide groups per molecule. Here, apparently, the rate of acyl migration far exceeds the rate of chain extension (12). Between diamides A and B, the latter type appears more stable giving amber adducts with lower ester/amide carbonyl ratios (0.5).

A previous study (12) showed that the activity of secondary amides under low pressure oxyethylation was promoted by conversion to the hydroxyethyl derivative. Following the same strategy, we prepared a series of symmetrical dihydroxyethyl diamides of type A′ and B′ where:



(A′)



(B′)

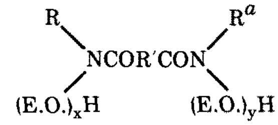
R is 3-heptyl or 2-ethylhexyl and R′ is 0-4 methylene groups or -CH=CH-. One example of the inverted structure type B′ derived from ethylenediamine was evaluated. Malonamide derivatives were not included because they could not be isolated in any reasonable purity. Aminoester formation and possible oligomerization reactions occurred readily regardless of reaction conditions. Direct aqueous extraction of the crude reaction mixtures to prepare type A′ diamides led to poor yields due to solubilization of the product by the amine hydrochloride. Triethanolamine was the most suitable acid scavenger in these preparations giving filterable hydrochlorides and colorless products. This was especially so for the fumaryl chloride preparations which gave unusable tars when triethylamine or pyridine were used as HCl scavengers. Likewise it was shown that diethyl oxalate can react with branched hydroxyethyl amines under vigorous conditions.

As might be expected N,N′ dihydroxyethyl diamides ($RCONR'CH_2CH_2OH \rightleftharpoons R'NHCH_2CH_2OCOR$) are more thermally labile than simple amides; however, reversion of the aminoester to the amide appeared slower. This appears evident from the initial carbonyl ratios in Table 1 where x + y = 2. Several values are comparable to those found for linear RCONR′ $(E.O.)_1H$ amides (12). The spectral properties of the amides and oxyethylated adducts were described earlier (11,12).

Properties of oxyethylated diamides. A relative measure of aminoester content is given in Table 1 by means of ester/amide carbonyl ratios. For the adducts shown where R′ is 0 to 4 methylene groups, an olefin group or an ethylenediamine based substrate, carbonyl ratios are given for the initial hydroxyethyl diamide where x + y = 2 and the average value over x + y = 5-20 which does not deviate more than .05. The data show that some aminoester is present in nearly all the initial substrates. Aminoester content increases with oxyethylation and with the number of methylene groups. An olefin group has a marked inhibiting effect on aminoester concentration, while no change was observed with adducts based on ethylenediamine. The formation of aminoester even with pure substrates suggests that its presence does not promote the acyl migration. With the exception of the adipamide series, these carbonyl ratios are considerably lower than found for simple diamides where the ratios ranged from 0.7 to >1.0. The aminoester level present when R′ is an olefin group is comparable to the best achieved with a branched hydroxyethyl tertiary amide (12) and indicates that these branched diamides can be stabilized by simple structural modifications.

TABLE 1

Ester/Amide Carbonyl Ratios For Diamide Adducts



Adduct	Carbonyl Ratio[b]	
R′	x + y = 2	x + y = 5 to 20
$(CH_2)_0$	0.18	0.25
$(CH_2)_2$	0.00	0.30
$(CH_2)_3$	0.20	0.40
$(CH_2)_4$	0.20	0.50
CH=CH	0.00	0.08
$N(CH_2)_2N$[c]	0.27	0.20

[a] R is a 2-ethylhexyl group.

[b] Carbonyl ratios measured at ∿ 1730/1630 cm^{-1}.

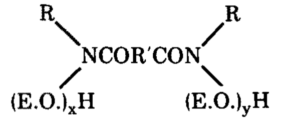
[c] Diamide derived from N,N′dihydroxyethylethylenediamine and 2-ethylhexanoyl chloride.

The effectiveness of these diamide adducts in wetting hydrophobic Idylwild soil was determined by the drop penetration test; the results are shown in Table 2. R is branched 7-8 carbon aliphatic groups, R′ varies as shown over an E.O. chain length of 2-20. Wetting time was determined at 0.1, 0.01 and 0.001% with water controls for each series. Rewet values were determined by the rapid method described earlier. Values obtained by overnight equilibration served to confirm these results. All adduct series were effective wetting and rewetting agents at 0.1 and 0.01% relative to the control samples. At 0.001% level their effectiveness was not readily apparent. At all concentration levels rewet times were shorter than the wetting times for these adduct series. The same effect was observed with the water controls but of a much lower magnitude. At any given concentration, there is no obvious difference between adducts in a given series or between series.

Figure 1 shows the water solubility of diamide adducts relative to E.O. chain length as established by cloud point determination. R′ is listed for the various

TABLE 2

Diamide Adducts[a] Drop Penetration Wetting of Idylwild Soil



$$\mathrm{(R)(E.O.)_xH\,NCOR'CON\,(R)(E.O.)_yH}$$

R	-(CH$_2$)$_0$-		-(CH$_2$)$_2$-		-(CH$_2$)$_3$-		-(CH$_2$)$_4$-		-CH=CH-		N-(CH$_2$)$_2$N[a]		Control	
x + y	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet	Wet	Rewet
Time in Seconds at 0.1%														
2	60	3	92	5	21	6	51	4	15	4	155	5	480	65
6	5	2	2	2	4	1	21	6	3	2	2	1	480	65
8	7	2	2	1	4	2	15	6	1	1	4	1	480	65
10	5	1	2	1	3	1	13	3	2	1	4	1	480	65
13	8	1	4	1	3	1	32	2	4	1	3	1	480	65
20	4	1	2	1	3	1	19	2	4	1	4	1	480	65
Time in seconds at 0.01%														
2	133	29	140	8	108	14	119	28	50	8	150	16	580	270
6	107	40	99	10	95	24	135	19	85	28	83	8	580	270
8	135	9	100	8	110	9	145	13	80	14	95	10	580	270
10	119	20	130	14	115	26	150	12	85	17	60	22	580	270
13	160	9	145	15	160	8	205	28	95	13	75	7	580	270
20	125	11	125	16	125	11	110	14	120	22	90	8	580	270
Time in seconds at 0.001%														
2	480	51	300	50	600	46	540	35	305	31	344	120	650	90
6	361	48	195	175	255	36	275	29	190	23	360	40	650	90
8	285	74	218	48	295	35	220	45	270	95	270	37	650	90
10	238	139	201	55	365	53	180	32	195	80	380	30	650	90
13	260	154	303	75	325	145	200	55	180	90	400	85	650	90
20	205	38	355	79	240	45	171	130	200	89	190	63	650	90

[a] R is a 2-ethylhexyl group; diamide derived from N,N′ dihydroxyethylethylenediamine and 2-ethylhexanoyl chloride.

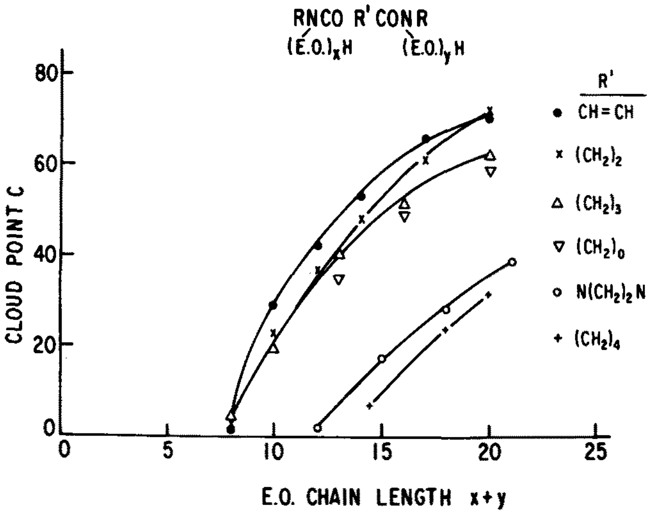


FIG. 1. Effect of E.O. chain length on cloud point at 1% diamide adduct concentrations.

diamide series in order of decreasing water solubility. It is evident that decreasing solubility does not follow a simple increase in the number of methylene groups as does the ester/amide carbonyl ratio. A broad correlation between the properties exists to the degree that the fumaramide series with minimal aminoester contaminant shows the best overall water solubility over the E.O. chain length studied, while the highly contaminated adipamide series shows the poorest solubility. The rather surprising poor solubility found with the ethylenediamine-based adducts suggests that structural differences may have more effect on solubility than aminoester contamination. The consequences of the structural changes are seen clearly from the values of E.O. chain length for complete solubility at 25 C which shifts from ∿9.5 when R′ is an olefin group to 18 when R′ is four methylene groups. Cloud points below the lowest values shown were less than one degree and could not be determined.

The relation between surface tension and E.O. chain length of the various E.O. adducts is summarized in Figure 2. The highest surface activity corresponds to

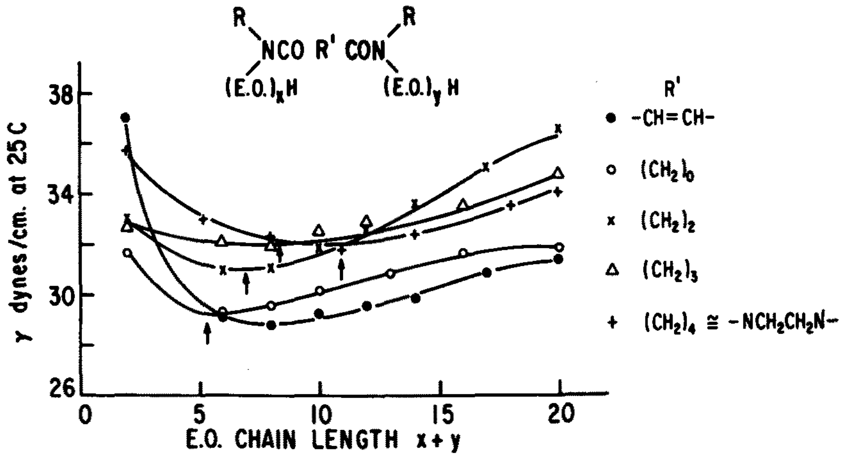


FIG. 2. Effect of E.O. chain length on surface tension at 0.1% diamide adduct concentrations.

the lowest surface tension values. Once again, the fumaramide series is generally the most surface active over the E.O. chain length studied. The remaining series all show minima at higher surface tension values. In contrast to water solubility behavior, surface activity generally tends to decrease as the number of methylene groups increases. The curve for the ethylenediamine based substrate (not shown) is essentially the same as for the adipamide series. As indicated by the arrows, it appears that as R′ increases from 0 to 4 methylene groups, minimum surface tension values shift to increasing E.O. chain length. The values here ranged from 5 to 11.

Draves wetting profiles for these series of adducts are shown in Figures 3 and 4, where wetting time was plotted against E.O. chain length and R is 2-ethylhexyl or 3-heptyl. The profiles generally follow the U-shaped Draves curve associated with increasing oxyethylation of an organic substrate. Figure 3 shows the best wetting properties were observed when R′ is two methylene groups. At zero or three methylenes the wetting profiles are comparable, while at four methylenes overall deterioration in wetting ability was observed. An E.O. chain length of eight units was required for optimum wetting for zero to three methylene groups. However, at four methylenes this value occurred at 14 E.O. units.

Because the best combination of properties was found initially for the succinamide adducts, we evaluated the wetting properties of adducts based on fumaramide and ethylenediamine, as shown in Figure 4. Marked changes in Draves wetting behavior occur with seemingly minor changes in configuration. For the first time, in the fumaramide series, a structure was found which conferred excellent wetting ability over a chain length of 5–15 E.O. units. The first and third profiles indicate localized and poor wetting ability, respectively. The results suggest the possibility of tailoring the organic substrate to the necessary wetting requirements. With the exception of the adipamides, an x + y of 8 is associated with optimum wetting. The excellent characteristics of the fumaramide series appear to be due to a combination of substrate configuration, good solubility, low surface tension and low aminoester concentra-

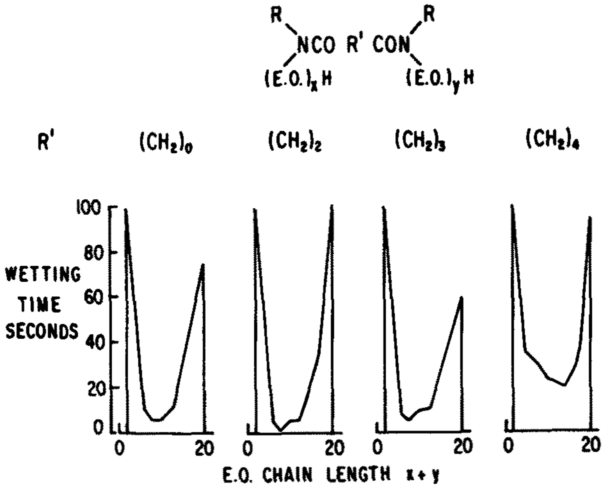


FIG. 3. Draves wetting profiles of diamide adducts.

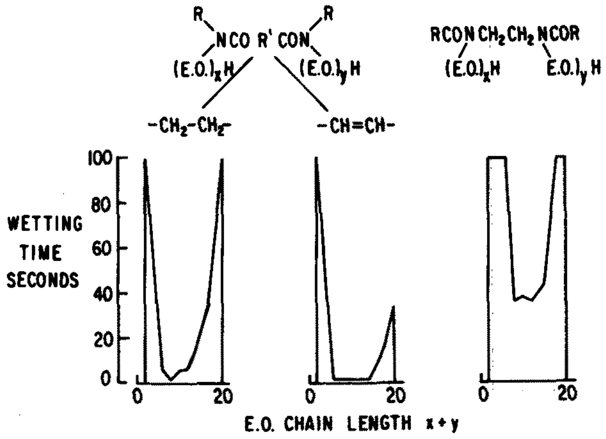


FIG. 4. Draves wetting profiles of similar diamide adducts.

tion. Aliphatic oxyethylated diamides where R was 2-ethylhexyl and R′ was a -CH=CH-group exhibited (i) superior wetting properties at $x + y \cong 5$ to 15; (ii) minimal surface tension and complete water solubility at $x + y \cong 7$ to 9.5, and (iii) excellent stability to aminoester formation over the entire E.O. chain length. When R′ was 0 to 4 methylenes or an ethylendiamine-based moiety these optimum properties were all diminished.

ACKNOWLEDGMENT

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