

Molecular Weight Distribution of Nonionic Surfactants. III. Foam, Wetting, Detergency, Emulsification and Solubility Properties of Normal Distribution and Homogeneous p,t-Octylphenoxyethoxyethanols

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Abstract

The effect of mol wt distribution on the foaming, wetting, detergency, emulsification and solubility properties of p,t-octylphenoxyethoxyethanols (OPE's) has been studied by comparing normal distribution and homogeneous compounds. Ross-Miles foam studies indicate that, although homogeneous OPE₇₋₁₀ are higher in initial foam height than normal distribution OPE₇₋₁₀, their foam stability is poorer. Hard surface and textile wetting were studied by contact angle determinations and the Draves' skein test, respectively. An exact correlation exists between hard surface wetting by solutions of OPE's of a Teflon surface and surface tension lowering. Normal distribution OPE's are, in general, better hard surface wetting agents than the corresponding homogeneous compounds. In textile wetting, normal distribution OPE₅₋₁₀ are approximately equivalent in performance and by implication are probably equivalent in wetting performance to the corresponding homogeneous compounds. Hard surface detergency studies show that normal distribution OPE's are generally slightly superior in deterative power to homogeneous OPE's at corresponding ethylene oxide chain lengths. OPE₁₀ is the best hard surface detergent of the OPE series, there being no distinguishable difference in performance between homogeneous and normal distribution OPE₁₀. Emulsification studies on the system, water-isooctane, show that only normal distribution OPE₅ is capable of forming stable o/w emulsions. Both homogeneous and normal distribution OPE₃ and OPE₄ form stable w/o (invert) emulsions. Solubility studies in isooctane and Ultrasene show that homogeneous OPE₄ is soluble at lower temp than the corresponding normal distribution compound. Studies of aqueous OPE solutions at temp above their cloud points show that solubility of both homogeneous and normal distribution materials is of the same order of magnitude as their critical micelle concn and that homogeneous OPE₄ is more soluble than normal distribution OPE₄.

Introduction

IN CONSIDERING the application properties of nonionic surfactants, it is not apparent that a surfactant having a Poisson distribution of mol wt will have performance superior to materials of the same average mol wt but having a broader or narrower mol wt distribution. Indeed, Mayhew and Hyatt (1) for a number of molecularly distilled nonylphenoxyethoxyethanols have shown that: 1) by narrowing the mol wt distribution, improved textile wetting characteristics may be obtained; 2) certain fractions

from the distilled surfactant demonstrate slight increases in initial foam volume over the corresponding undistilled material of comparable mol wt but no noticeable change in foam stability; 3) although there exists an optimum ratio of ethylene oxide to hydrophobic base at which maximum cotton or wool detergency is obtained, detergency itself is relatively unaffected by mole ratio distribution; 4) emulsifying properties of nonyl phenol adducts of ethylene oxide are adversely affected by narrowing the mole ratio distribution.

The conclusions of Mayhew and Hyatt (1) are of considerable interest to an understanding of the effect of mol wt distribution on the properties of nonionic surfactants. A knowledge of the contributions of the individual ethylene oxide adducts of alkyl phenols to the over-all physical properties of nonionic surfactants having a Poisson distribution mol wt should elucidate this effect even further. Thus, a study of the application properties of homogeneous OPE's vs. their corresponding normal distribution analogs was conducted.

Experimental

Materials. Details of the preparation and characterization of the homogeneous and normal distribution OPE's used in this study are to be reported (2). Sodium metasilicate was an anhydrous material obtained from the Philadelphia Quartz Co. Sodium hydroxide was a J. T. Baker Chemical Co. reagent grade (97%) chemical. Sodium carbonate was technical grade. Tetrapotassium pyrophosphate was a product of the Virginia-Carolina Chemical Corp. furnished in liquid form (ca. 60% solids). The solid residue was analyzed to be 98% K₄P₂O₇. The soil used in the hard surface detergency studies was Sun 150 Brightstock Oil (Sun Oil Co.). All water that was used in these studies was distilled from alkaline permanganate solution to insure the absence of organic materials. The specific conductance of the water was ca. 1×10^{-6} ohm⁻¹ cm.⁻¹ which indicates a substantial lack of inorganic materials. The isooctane used was a "Spectro Grade" Eastman Organic Chemicals reagent. Ultrasene was a refined grade of kerosene supplied by the Atlantic Refining Co.

Procedure. Foam was evaluated using the Ross-Miles foam test (3). One-tenth percent solutions of surfactant were prepared and foam heights were recorded in 1-min increments for 5 min to determine foam stability. Measurements were also carried out as a function of temp.

Hard surface wetting was determined by measuring the contact angle of OPE solutions as a function of time at 25C on a Teflon substrate. After placing the Teflon substrate in a contact angle cell, drops of surfactant solution were placed on the surface with the aid of a microsyringe. The dimensions of the drops

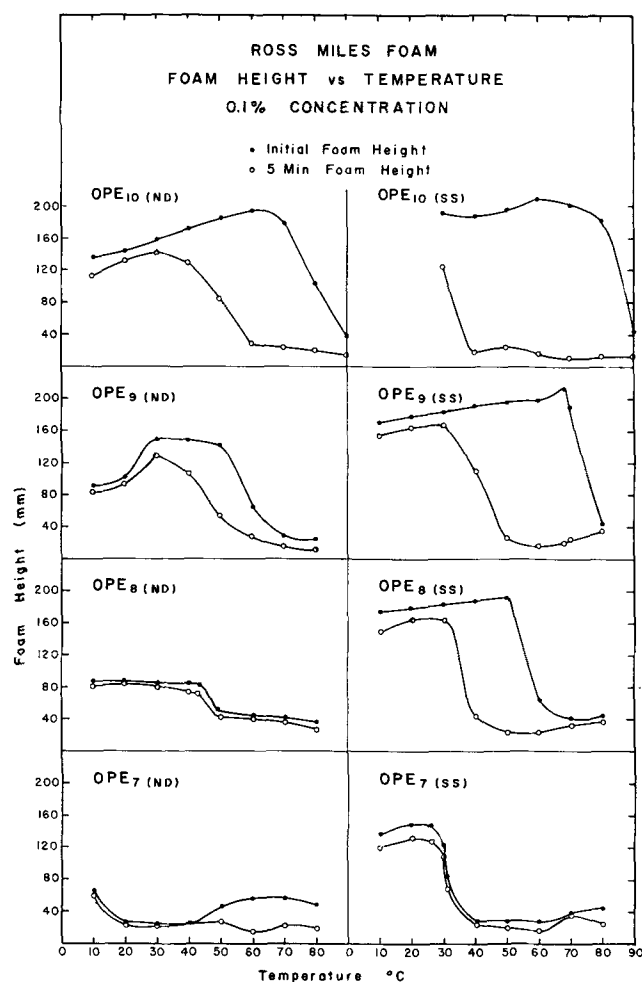


FIG. 1. Ross Miles foam vs. temp for single species and normal distribution OPE₇₋₁₀, C = 0.1%.

were determined as a function of time until an equilibrium value of the contact angle was obtained. The contact angle, θ , was calculated from the expression (4):

$$\tan(\theta/2) = 2(a/b) \quad [1]$$

where a is the height and b is the length of the drop. Four drops were examined simultaneously at a surfactant concentration of 0.1%. The viewing system consisted of a Graflex camera with a ground glass viewing plate mounted on an optical bench, an adjustable stage for raising and lowering the cell and a microscope lamp for illumination.

Textile wetting was determined by means of the Draves' cotton skein test (5) at 25°C. The time necessary for the cotton skein to be wet by the surfactant solution was recorded as a function of concn.

Hard surface detergency was evaluated by cleaning mild steel panels which had been previously soiled with Sun 150 mineral oil and subsequently determining the area free of oil. In preparation for the test, the panels were dipped in CCl₄, twice in methanol, rinsed in deionized water and finally rinsed in reagent grade acetone. The precleaned panels were stored overnight in a desiccator, dipped in Sun 150 mineral oil at 35°C and allowed to drain 1 hr (also at 35°C). The panels were then placed in a detergent bath and cleaned. The bath consisted of 0.03% surfactant and 5% builders (sodium hydroxide, sodium metasilicate and sodium carbonate on an equal wt basis) maintained at 82°C. (180°F). The panels were rotated slowly 5 min in the bath, removed and rinsed in a water bath. The panels were sprayed with water mist

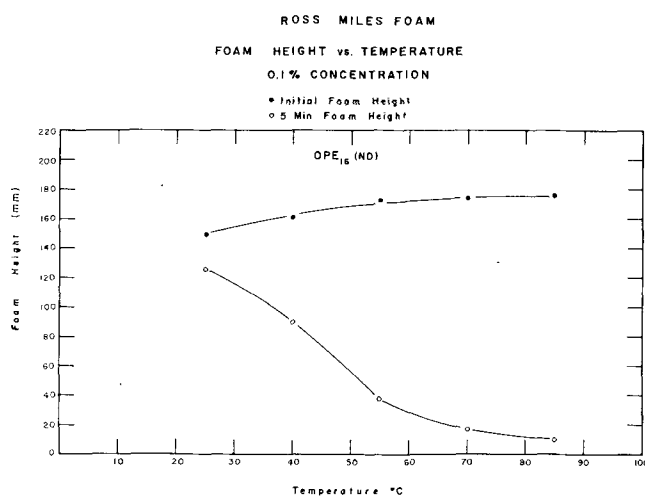


FIG. 2. Ross Miles foam vs. temp for normal distribution OPE₁₆, C = 0.1%.

and the area remaining covered with oil determined.

For comparison of the emulsification properties of normal distribution and single species OPE's, the system, water-isooctane (9:1 water:oil ratio), was selected using 2.5% surfactant in the oil phase. The surfactant was generally incorporated in the phase in which it had the greater solubility. The oil phase was added to the water phase in 4-oz jars, then shaken on an Atlab shaking device for 2 min. The emulsions thus formed were poured into glass tubes and evaluated as a function of time in an Atlab viewer maintained at 25°C.

For determination of the solubility of OPE's in oil, the turbidity temp was measured as a function of concn. Twenty-five ml surfactant solutions were cooled to temp below the turbidity point and the temp of the solutions were slowly increased until a clear solution resulted.

In water solubility studies, 5% solutions (or dispersions) of surfactant contained in sealed 50-ml glass stoppered, volumetric cylinders were equilibrated in a constant temp bath for 7-20 days until complete phase separation occurred. After the phase volumes had assumed constant proportions, samples were removed from the upper phase with a hypodermic syringe and subjected to UV analysis (6) to determine their concentration.

Results and Conclusions

Foam. In general, nonionic surfactants at elevated temp, both below and above their cloud points, have rather poor foam stability compared to anionic surfactants such as the alkyl aryl sulfonates or alkyl sulfates. It is, consequently, of interest to determine whether single species nonionics (OPE's) give higher foam stability than do the corresponding normal distribution compounds.

Foam heights are presented in Figures 1 and 2 for single species OPE₇₋₁₀ and normal distribution OPE_{7-10,16} as a function of time and temp. In general, the foam height decreases very rapidly in the vicinity of the cloud point. Both single species and normal distribution OPE₇ are characterized by a decrease in foam height at their cloud points followed by a subsequent increase in initial foam height at higher temp. This increased foam is paralleled by a decrease in turbidity of the surfactant solution which probably is indicative of increased solubilization of surfactant contra the normal dehydration of the ethylene oxide chain of the surfactant molecules. Comparing the

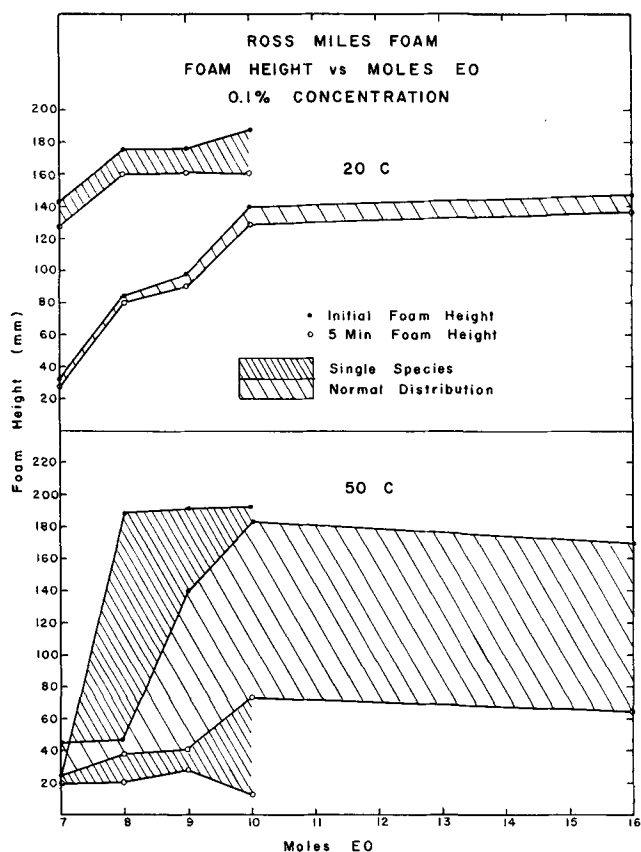


FIG. 3. Foam stability at 20 and 50C for single species and normal distribution OPE's.

initial and 5-min foam heights at 20 and 50C (Fig. 3) for single species and normal distribution OPE's, one notes that: 1) the initial foam height for single species OPE's is somewhat greater than for normal distribution compounds of corresponding ethylene oxide chain lengths, while 2) the foam stability at 50C is less than that of normal distribution OPE's.

In the case of the normal distribution OPE's, there are substantial quantities of shorter ethylene oxide chain length members which are inherently lower foamers (7) than longer chain length members. Since it is these shorter chain length, more surface active species (e.g. OPE₃₋₆) which preferentially adsorb at the air-water interface (8), it is not surprising that the foam obtained with normal distribution compounds is lower than that obtained with the corresponding single species compounds (note, too, that the initial foam height and foam stability of the single species OPE's of ethylene oxide chain length of 8, or greater, are practically constant, such that the presence of longer chain length members in the normal distribution compounds would not counterbalance the decreasing foam effect of the shorter chain length compounds).

Although no absolutely conclusive explanation can be advanced for the greater foam stability of the normal distribution OPE's vs. the corresponding single species compounds, this behavior is perhaps related to the more efficient healing (9) capability of the normal distribution materials in which a variety of molecules are available to alleviate strains in the film; whereas, with the single species materials, only one entity is available for orientation at the air-water interface.

By plotting the temp coefficient of foam height as a function of temp as suggested by Fineman et al. (7) for single species and normal distribution OPE₇₋₁₀

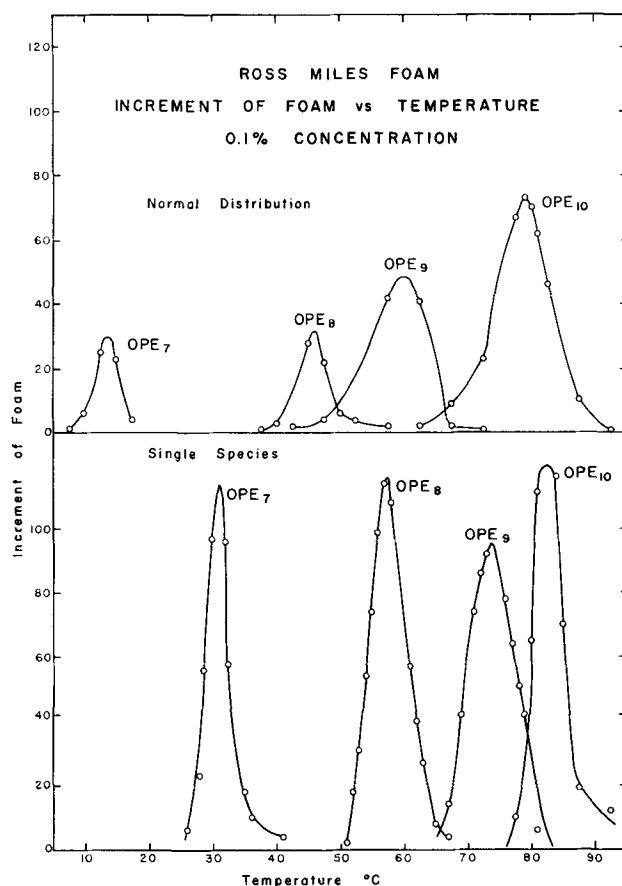


FIG. 4. Increment of foam vs. temp for normal distribution and single species OPE₇₋₁₀.

(Fig. 4), one notes that sharper peaks are obtained for single species OPE's than for the corresponding normal distribution compounds. Such behavior might be expected (7) because of the homogeneity of the micelles extant in the former system and their subsequent dehydration (10) in the vicinity of the cloud point. With normal distribution OPE's, a greater range of micellar sizes is probably present due to the polydispersity of the system. During dehydration prior to the cloud point, it is probable that micelles richer in shorter ethylene oxide chain length members would agglomerate at temp lower than the normally observed cloud point and remove substantial quantities of surfactant from the interface, thus decreasing the amount of surfactant available for foam formation. At temp greater than the nominal cloud point, micelles richer in longer ethylene oxide chain length molecules would dehydrate to form aggregates. Both processes would tend to lessen the sharpness of the temp coefficient vs. temp relationship.

Hard Surface Wetting. In hard surface wetting, a knowledge of the wetting behavior is obtainable from a calculation of the spreading coefficient, S , from surface tension (γ) and contact angle (θ) data (11). Assuming minimal adsorption of water on the solid substrate, the spreading coefficient may be approximated by the expression:

$$S = \gamma (\cos \theta - 1) \quad [2]$$

Where a finite contact angle is observed, S is negative. As $S \rightarrow 0$ wetting improves.

Spreading coefficient is presented in Figure 5 as a function of ethylene oxide chain length for single species and normal distribution OPE's at 0.1% concn and 25C. The same general behavior is noted for the spreading coefficient results (although S is a function of both γ and θ , comparison of θ with γ as

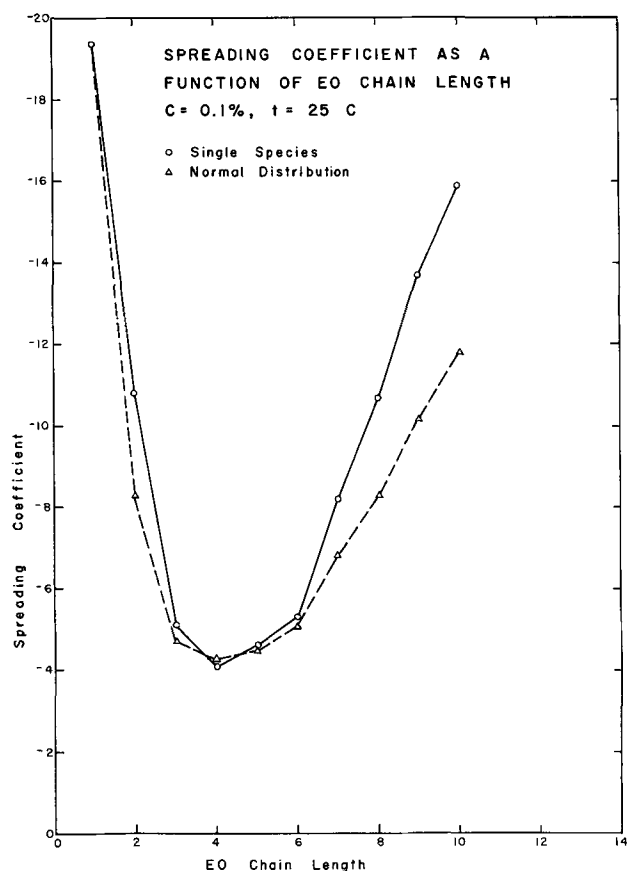


Fig. 5. Spreading coefficient as a function of EO chain length, $t = 25\text{C}$.

well as S with γ as a function of ethylene oxide chain length gives the same result) as was found previously for the surface tension dependence upon ethylene oxide chain length (8); i.e., OPE_4 is the best wetting agent of the OPE series, with species of shorter and longer ethylene oxide chain lengths giving poorer wetting. Burnett and Zisman (12) have shown that such behavior should be expected with surfaces that do not specifically interact with substituents of the surfactant molecule. As previously indicated by surface tension data (8), normal distribution OPE's generally exhibit wetting properties which are superior to those of the corresponding single species OPE's because of the preferential adsorption of the more surface active species (OPE_{3-6}) at the water-Teflon interface; whereas, in the case of single species OPE's, only a single entity is available to the interface. In summary, for hard surface wetting: 1) OPE_4 is the best wetting agent for substrates with which there are no specific interactions; 2) single species OPE_4 is not appreciably better as a hard surface wetter than normal distribution OPE_4 ; and 3) at ethylene oxide chain lengths greater or less than 4, normal distribution OPE's are superior to their single species analogs as hard surface wetting agents.

Textile Wetting. To investigate the rate of wetting of textiles by OPE's (only normal distribution compounds were studied because insufficient amounts of single species OPE's were available), the Draves' skein test was utilized. Times required for the wetting of a cotton skein as a function of concentration were determined for normal distribution $\text{OPE}_{4-10,16}$. Logarithmic values of the wetting time were plotted vs. logarithmic values of the concentration of surfactant. From these data the concn required for 10, 25 and 50-sec wetting were interpolated and are presented in

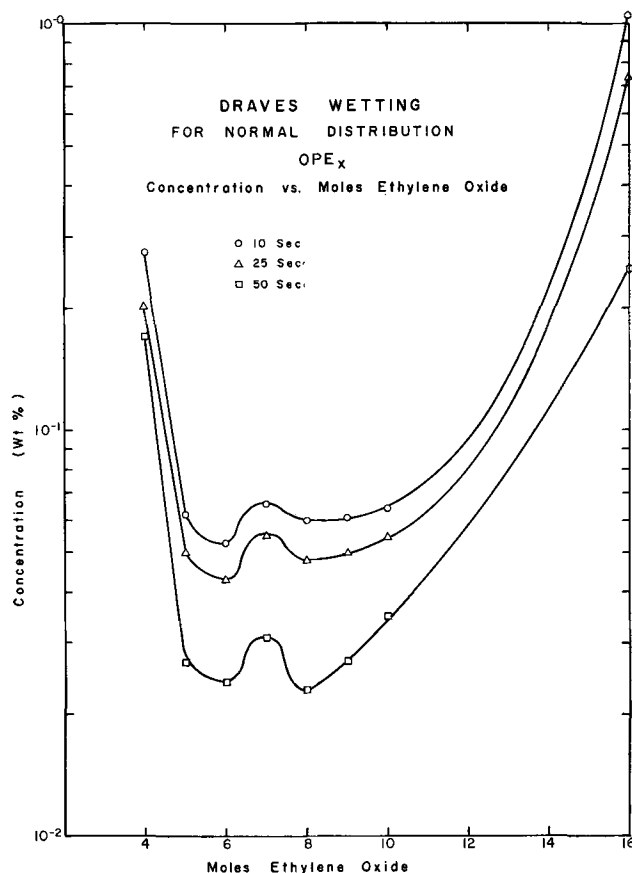


Fig. 6. Concn for 10, 15 and 50-sec Draves wetting vs. EO chain length, $t = 25\text{C}$.

Figure 6 as a function of ethylene oxide chain length. At EO chain lengths < 5 and > 10 , the concn required for 10, 25 and 50-sec wetting increase rapidly. There is little distinguishable difference among OPE_{5-10} within the experimental error of the measurements (the slight discontinuity which occurs at OPE_7 is paralleled by an increase in turbidity of the solution at the measurement temp, increased turbidity being related to an increase in aggregation of the micelles (10) which leads to less available surfactant in the continuous phase).

Hansen and Purchase (13) have shown that for alkyl aryl sulfonates, textile wetting speed is directly related to the rate at which the surfactant lowers the surface tension of water during the first 10 milliseconds after formation of a new surface. It is likely that such a correlation is also true for nonionic surfactants (confirmation awaits the measurement of dynamic surface tension of the presently investigated solutions).

In summary, 1) OPE_{5-10} are approximately equivalent in textile wetting performance; and 2) OPE_4 (and by implication OPE_{1-3}) and OPE_x (where $x > 10$) are poorer textile wetters than OPE_{5-10} . Although textile wetting measurements were not carried out with single species OPE's, it is likely that only small differences in performance would occur in contrast to the normal distribution materials since within the normal distribution series there is little to choose among OPE_{5-10} .

Hard Surface Detergency. For an evaluation of the deterative power of single species and normal distribution OPE's, cleaning of a hard surface was selected since the substrate surface could be better defined, the soil more easily characterized and the amount of surfactant required for the study mini-

mized compared to textile detergency determinations. Under conditions of constant temp, builder concn, soiling, agitation and surfactant concn, the relative effectiveness of various surfactants can be evaluated in terms of percentage of total substrate area cleaned.

The results of hard surface detergency studies on 0.03% solutions of normal distribution $OPE_{4,6,8,10,16}$ and single species $OPE_{4,6,8,10}$ are presented in Figure 7. The over-all behavior of both single species and normal distribution OPE 's is the same. The percentage of cleaning efficiency (area of panel cleaned) increases rapidly with increasing ethylene oxide chain length from OPE_4 through OPE_{10} and decreases gradually thereafter (only in the case of normal distribution OPE 's; no single species OPE 's of EO chain length greater than 10 were available). For comparable EO chain lengths, the normal distribution OPE 's are better hard surface detergents than the single species materials. This is attributable to the distribution of species present in the normal distribution compounds which contain substantial numbers of longer EO chain length molecules which contribute the major portion of detergency. It is clear, however, that in the OPE series maximum hard surface detergency is obtained at an EO chain length of ca. 10. The primary reason that the shorter EO chain length molecules; e.g. OPE_4 , are not effective hard surface detergents in this system is that most of the surfactant is insolubilized because of the high builder concn and temp. By the use of suitable hydrotropes, the full detergency capabilities of the shorter EO chain length members could be utilized.

Emulsification. Single species OPE 's might be expected to have different emulsification properties than the corresponding normal distribution compounds because of the specificity of some systems to surfactants of narrow hydrophile-lipophile balance (HLB) range (14). With homogeneous OPE 's all the molecules have the same HLB, while in the case of the corresponding normal distribution OPE 's there are molecules of varying ethylene oxide chain length, each having a different HLB. Such homogeneity of single species compounds could give excellent emulsification properties with some specific oil-water system but would probably lead to less general applicability for a number of oil-water systems in which the solubility parameter of the oil varies appreciably. The following results were obtained for emulsification of the system, isooctane-water (1:9), by single species and normal distribution OPE_{1-10} . For both single species and normal distribution OPE 's with ethylene oxide chain lengths <3 and >6 the emulsions formed are all of the o/w type and show instability within 5 min, there being no discernible difference between single species and normal distribution compounds. Normal distribution OPE_5 forms the only o/w emulsion which maintains substantial stability after 24 hr while single species and normal distribution OPE_3 and OPE_4 form w/o (invert) emulsions which also maintain substantial stability up to 24 hr after formation. In general, emulsion stability varies in the following order: $S-OPE_4 > P-OPE_4 > S-OPE_3 > P-OPE_3$ (the symbols S and P refer to single species and Poisson distribution OPE 's, respectively); i.e., single species OPE_4 is the best w/o (invert) emulsifier.

Two further studies were carried out with normal distribution and single species OPE_3 and OPE_4 : 1) decreasing the surfactant concentration in the isooctane phase while holding the phase volume ratio constant; and 2) varying the phase volume ratio while

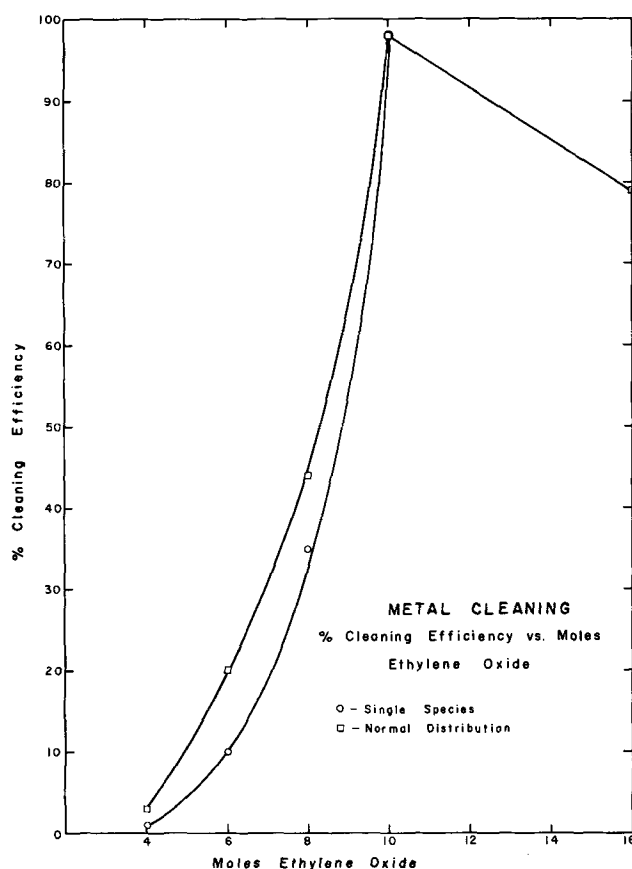


Fig. 7. Detergency vs. EO chain length for single species and normal distribution OPE 's.

holding the isooctane phase surfactant concentration constant. At constant phase volume ratio smaller quantities of single species OPE_3 and OPE_4 than the corresponding normal distribution compounds were required to maintain stable w/o (invert) emulsions. At constant surfactant concn (2.5% in the isooctane phase), the isooctane-water phase volume ratio could be varied from 1:9 to 1:1 and w/o (invert) emulsions were still formed (emulsion viscosity and consequently emulsion stability decreased as the isooctane:water phase volume ratio increased).

The results indicate that normal distribution OPE_4 can form w/o (invert) emulsions but at a concn of surfactant higher than that for single species OPE_4 . This is not surprising since in the normal distribution compound there are substantial numbers of molecules which are not as effective at lowering the interfacial tension of the system, isooctane-water, as is single species OPE_4 . It is likely in the case of normal distribution OPE_4 that at higher concn of surfactant there are sufficient numbers of OPE_4 molecules present to replace some of the less oil soluble, longer chain length OPE 's at the isooctane-water interface. This interpretation is derived from an analogy between surface tension and interfacial tension data. With normal distribution OPE 's at concn above the critical micelle concn (CMC) the surface tension increases (8) as the concn increases. This occurs because of a replacement at the air-water interface of the more surface active species (OPE_4) by less surface active molecules (e.g. OPE_{10}) since the shorter chain length OPE 's are thermodynamically more stable while solubilized within the micelles. In the case of the isooctane-water system there is a slight decrease of the interfacial tension at concentrations above the "apparent" CMC (8) of the compound. This behavior

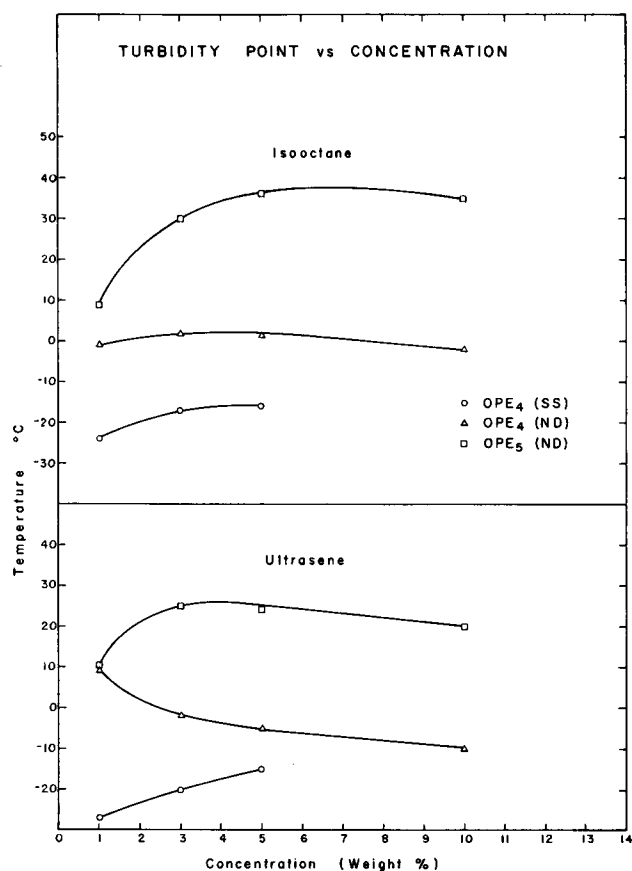


FIG. 8. Turbidity temp vs. concn for OPE's in isooctane and Ultrasene.

corresponds to a replacement at the isooctane-water interface of longer EO chain length molecules by shorter chain length (more surface active) molecules. The longer EO chain length molecules prefer the micellar state within the aqueous phase to the isooctane-water interface. Such an effect should increase as the nominal concn of surfactant is increased above the CMC and more of the shorter EO chain length molecules are available for orientation at the isooctane-water interface. This is what is observed (8) in the case of normal distribution OPE's.

Oil Solubility. Another property in which a difference between the behavior of single species and normal distribution OPE's might be expected is the solubility of the surfactants in various solvents. Temperatures of insolubility are presented in Figure 8 (below this temp turbidity occurs) of single species OPE₄ and normal distribution OPE₄ and OPE₅ as a function of concn for the oils, isooctane and Ultrasene. It is clear that single species OPE₄ maintains solubility in the oils studied at lower temp than do normal distribution OPE₄ and OPE₅ (the solubility behavior of the OPE's in isooctane and Ultrasene closely parallels the behavior of the distribution coefficient results for the system isooctane-water (8)). This insolubility of the normal distribution compounds at temp higher than for the corresponding single species compounds

TABLE I

Upper Phase Concentrations as a Function of Initial Concentration for Single Species OPE's and OPE₄, t = 50C

Compound	Initial concentration wt % (m/l)	Concentration, upper phase (m/l)	CMC (m/l) 25C	% Difference
OPE ₃	1.0 (2.96×10^{-4})	1.14×10^{-4}	9.7×10^{-5}	17.5
OPE ₃	5.0 (1.48×10^{-3})	1.22×10^{-4}	9.7×10^{-5}	25.8
OPE ₄	1.0 (2.62×10^{-2})	1.73×10^{-4}	1.25×10^{-4}	38.4
OPE ₄	5.0 (1.31×10^{-1})	1.55×10^{-4}	1.25×10^{-4}	24.0

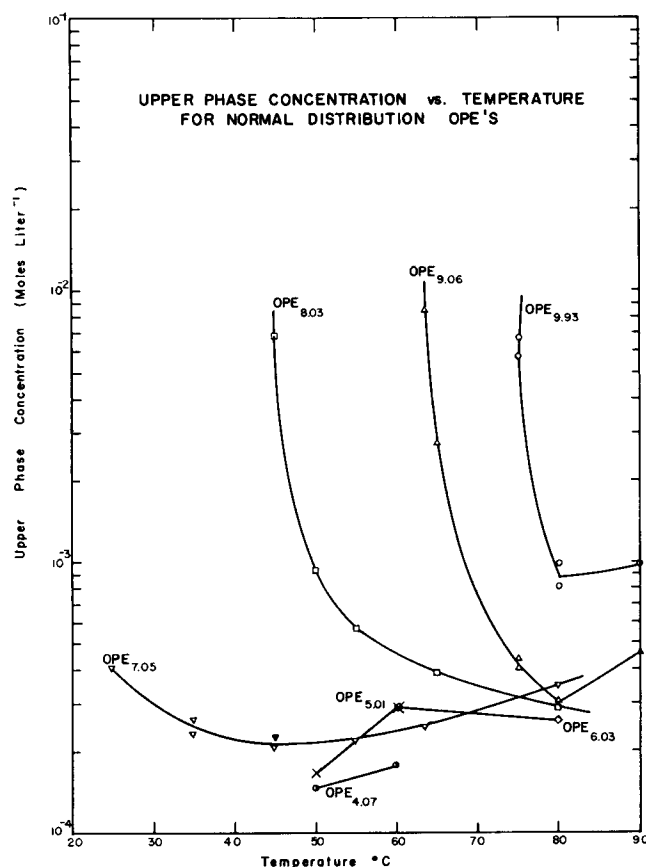


FIG. 9. Water solubility of normal distribution OPE₄₋₁₀ as a function of temp.

is brought about by the presence of substantial numbers of longer ethylene oxide chain length molecules which, due to their considerable hydrophilic content, are less oil soluble.

Water Solubility. The water solubility of nonionic surfactants at temp above their cloud points was investigated for 5% solutions of normal distribution OPE₄₋₁₀ and 1 and 5% solutions of single species OPE₃ and OPE₄ (further studies of single species compounds were not carried out because of insufficient quantities of materials). The results obtained for the upper phase concn (continuous phase) of the normal distribution OPE's are presented in Figure 9, and the data obtained for single species OPE₃ and OPE₄ are presented in Table I.

With the normal distribution materials, a rapid decrease in the continuous phase concn occurs in the vicinity of the cloud point with the resultant concn being of the same order as the critical micelle concn of the materials; i.e., very little surfactant remains in the continuous phase at 15C or higher above the cloud point of the materials. Although only OPE₄ was investigated for both normal distribution and single species OPE's at 50C, the single species material is somewhat more soluble than is the normal distribution compound. This is in agreement with the relative order of the CMC's of the two compounds (8) in which the single species material has a CMC higher than that of the corresponding normal distribution compound (1.25×10^{-4} m/l vs. 1.05×10^{-4} m/l, respectively). In general, the water solubility of the OPE's above their cloud points is a function of the length of the ethylene oxide chain; i.e., the hydrophilicity of the molecule.

It is not surprising that continuous phase concn of the order of the CMC of these materials should be ob-

tained since the disperse phase consists of the aggregated micelles (10) which are formed at the cloud point and above.

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The Preparation and Plasticizing Characteristics of Piperidides of Long Chain Fatty Acids and N-Fatty Acyl Derivatives of Other Cyclic Imines¹

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Abstract

Forty-six N-acyl derivatives of cyclic imines have been prepared, characterized, and screened as primary plasticizers for poly(vinyl chloride-vinyl acetate) copolymer. Among these were the piperidides of decanoic, palmitic, stearic, oleic, erucic, ricinoleic, epoxystearic, epoxyoleic, diepoxystearic, sebacic, pinic, cottonseed, hydrogenated cottonseed, rapeseed, *Limnanthes douglasii*, animal, 2-ethylhexanoic, naphthenic, and dimer acids, as well as the N-oleoyl derivatives of a number of substituted piperidines and other cyclic imines including pyrrolidine, piperazine, hexamethylenimine, tetrahydroquinoline, 3-azabicyclo[3.2.2]nonane, dipyridylamine, and carbazole.

In general these amides of the 5-, 6-, and 7-membered cyclic imines exhibited exceptionally high plasticizing efficiencies. The compatibilities observed were the best to date for fatty acid derivatives on the basis of both individual and ternary fatty acid composition-compatibility data. Several of these amides exhibited low-temp characteristics in the adipate plasticizer range without the adverse volatility characteristics of the adipates. There are indications that some of them have appreciable antifungal activity. It has been concluded that cyclic imines will, in general, produce fatty acid derivatives of better than average compatibility as vinyl plasticizers.

Introduction

IN PREVIOUS PUBLICATIONS from this laboratory it was shown that the morpholides (1) and N-bis(acyloxyethyl)amides (2) of long chain fatty acids were in many instances acceptable plasticizers for vinyl chloride resins. This publication deals with the preparation, characterization, and plasticizer evaluation of a number of N-fatty acyl derivatives of various cyclic imines, including a study of the ternary composition-compatibility relations for the system N-oleoylpiperidine (OP), N-linoleoylpiperidine (LP), and N-palmitoylpiperidine (PP) with polyvinyl chloride resin. As a class, these amides also proved to be highly efficient primary plasticizers. Their compatibilities seem to be superior to any amides that we have so far examined.

Experimental

The substituted piperidines were Reilly products; piperidine, 1,2,3,4-tetrahydroquinoline, 3-azabicyclo[3.2.2]nonane, pyrrolidine, and carbazole were Eastman Kodak chemicals; piperazine was obtained from Jefferson Chemical Co.; hexamethylenimine from Dupont Co. and N-methylpiperazine from Union Carbide Co. With the exception of oleic acid, which was Emery Industries Emersol 233 LL Elaine, and linoleic acid, which was a laboratory preparation of 95% purity, all acids were Eastman Kodak Co. products.

The densities were determined pycnometrically (3), the constant temp bath being controlled within 0.1C while the refractive indices were determined at $30.0 \pm 0.1C$ with a precision Bausch and Lomb refractometer using the D sodium line.

With the exception of N-ricinoleoylpiperidine, N-oleoylcarbazole, the N-epoxyacylpiperidines, and N-oleoyl-4-(3-acetoxypropyl)piperidine, all of the compounds were prepared by the general procedure previously described by Magne et al. (4) or by the interaction of equimolar quantities of acid chloride and imine in the presence of pyridine. The N-ricinoleoylpiperidine was prepared from methyl esters as described by Dupuy et al. (5). The N-oleoylcarbazole was prepared by refluxing carbazole with a slight excess of oleoyl chloride in xylene for 4 hr, then removing the free acid by percolation through an alumina column. The N-epoxystearoylpiperidine was prepared by epoxidation of the N-oleoylpiperidine. The N-epoxyoleoylpiperidine and N-diepoxy-stearoylpiperidine were prepared by epoxidation of the N-linoleoylpiperidine.

N-Oleoyl-4-(3-acetoxypropyl)piperidine was prepared by slowly adding 50 g (0.17 mole) methyl oleate to a vigorously stirred mixture of 24.2 g (0.17 mole) 4-propanolpiperidine and 0.61 g (0.026 mole) metallic sodium dissolved in absolute methanol maintained at 65–70C under 60 mm pressure. The reaction was judged complete upon cessation of the evolution of methanol. The product of this reaction was found to be N-oleoyl-4(3-oleoxypropyl)piperidine (I). The desired product, N-oleoyl-4-propanolpiperidine (II) was obtained by a 24-hr cold saponification of the ester linkage in I, using 2.0 equivalents of alcoholic KOH, followed by acidification with HCl, solution in hexane, washing with water, and drying over anhydrous sodium sulfate. Any residual free

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