Acknowledgment

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Summary

Extensive analyses have been made of American and Australian woolwaxes. Combined hydroxy acids have been shown to be the most characteristic and important components of these waxes. Both contained considerable amounts (about 91.5% in the case of the American wax and 31.7% in the Australian sample) of diestolidic esters of the alcohols of the unsaponifiable fraction. This conclusion is supported by calculations of composition, by observations of viscosity and emulsifying properties, and by determinations of mean molecular weight by the Prahl method.

REFERENCES

1. E. S. Lowers, Lanolin (woolwax) 1946.
A. W. Weitkamp, J. Am. Chem. Soc. *67*, 447 (1945).
Velluz and Lederer, Bull. Soc. chim. biol. *27*, 211 (1945).
2. Lifschütz, 1. Zeitschr. phys. Chem. *56*, 451 (1908).
2.. Zeitschr. phys. Chem. *110*, 19 (1920).
3. Drummond and Baker, J. Soc. Chem. Ind. *48*, 232 (1931).
4. Holde, Kohlenwasserstoffoele und Fette 7th ed., p. 986.
5. W. Prahl, Z. angew. Chem. *52*, 481 (1939).
6. A. Weissberger, Physic. Methods of Org. Chem. 1945.

Types and Mechanisms of Solubilization

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THE solubility of various compounds such as hydrocarbons, dyes, long chain alcohols, fatty acids, and insoluble soaps in water is increased by the addition of soluble soaps and other detergents. This phenomenon is usually designated as solubilization. A considerable number of investigators have studied the solubilization of compounds of varying polarity, size, charge, etc., with quite inconsistent results. An attempt is made here to show relationships between these various, seemingly conflicting, data and to add some new data from this laboratory which increases the validity of these correlations.

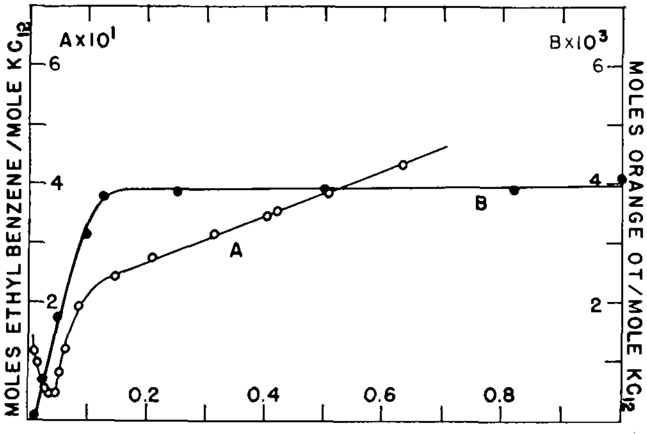

FIG. 1. Solubilization of ethyl benzene (A) and Orange OT (B) in potassium laurate solutions (25°C.).

Some typical solubilization data are shown in Fig. 1, where MR (moles of material solubilized per mole soap) is plotted as a function of soap concentration. Two main types of solubilization occur depending on the compound solubilized.

The first group is exemplified by hydrocarbons. For example, Curve A shows the solubilization of ethyl benzene in potassium laurate solutions (1) which is typical of systems in which MR increases at all soap concentrations, up to almost 1.0 M, above the critical micelle concentration (CMC). The initial decrease in solubility below the CMC is probably a salting out effect, and a minimum is reached at the CMC. Further examples of this type are the solubilization of benzene by cetyl pyridinium chloride as determined by Hartley (2), of propylene and other vapors by potassium oleate reported by McBain and O'Connor (3), and of liquid hydrocarbons such as n-decane and benzene solubilized by potassium laurate and by potassium myristate (4).

Curve B in Fig. 1 is taken from McBain and Green (5) and shows the solubilization of Orange OT (1-o-tolylazo-2-naphthol) in potassium laurate solutions. A constant MR at a concentration above 0.15 M potassium laurate is typical of compounds such as dyes, fatty acids, and long chain alcohols. Another example of this second type is shown by McBain, Merrill, and Vinograd for the solubilization of Yellow AB (phenyl-azo-p-naphthylamine) in aqueous sodium desoxycholate solutions and also in lauryl sulfonic acid solutions (6). A relatively unrecognized case of this type of solubilization is the increase in solubility of insoluble calcium dodecyl sulfonate and calcium dodecyl sulfate in solutions of their corresponding sodium salts (7). Soap mixtures such as potassium laurate and potassium palmitate, and sodium laurate and sodium palmitate (8) should be also included in this group for the palmitate should be considered to be solubilized by the laurate.

These two sets of data *indicate* that solubilization begins in the region of the CMC. Below this concentration, the soap acts like an electrolyte causing a decrease in solubility of the hydrocarbon or the polar compound, such as another soap, below that in water due to a salting out effect. This has been shown to occur in the case of ethylbenzene in the presence of potassium laurate (1) and in the decrease in solubility of calcium dodecyl sulfonate in solutions of sodium dodecyl sulfonate below the CMC of the latter soap (7). It might be supposed that solubilization begins below the CMC as observed in the appearance of color in insoluble dye-soap (below the CMC) mixtures (9). However, these amounts dissolved are so small, often only a few per cent more than is soluble in water, that the individual dye molecule must be considered to be bound, at first, either by electrostatic or van der Waals type of attractive forces, with an individual soap molecule.

The curves in Fig. 1 indicate that colloidal properties of potassium laurate start just above the CMC, 0.025 M, and that this soap in the presence of hydrocarbons reaches full colloidal form at about 0.15 M. It is probable that, in the region between the CMC and 0.15 M where the change in MR per unit soap concentration is greatest, both the size and number of solubilizing soap aggregates, probably micelles, increases. Above the concentration where the soap reaches its full colloidal form, there is probably no change in micelle size, considering only the soap molecules and not the solubilized materials, but only a change in number of micelles. Indirect evidence for this is obtained from the fact that the number of polymer particles formed in emulsion polymerization is directly a function of the amount of micellar soap used as emulsifier (10). The interpretation of this increase in solubilization of simple hydrocarbons, where MR increases with increasing soap concentration, is that there is more soap in micellar form at higher soap concentrations, and that the area and/or volume available per mole of a soap for solubilization of hydrocarbons is larger than that for polar compounds, as will be shown below. This follows the findings of Hartley (2) that the micelle concentration increases more rapidly than the total concentration, in which case some of the single long chain electrolyte ions present are incorporated into the micelles along with those added.

Hydrocarbons

The addition of hydrocarbons such as benzene and n-heptane to soap solutions is accompanied by an increase in the long spacing as determined by X-ray measurements (11-20). Kiessig and Philippoff have shown that the long spacing of a 9.12% solution of sodium oleate changes from 91 Å to 127 Å upon the addition of 0.791 gm. benzene per gm. oleate (14). Hughes, Sawyer, and Vinograd have reported that the increase in double layer thickness in potassium laurate solutions is a linear function of the molar volume of the liquid additive (18). The slope of this line is larger in the case of normal straight chain hydrocarbons than for substituted benzenes. Various authors assume a lamellar type of micelle with the increase in spacing due to the entrance of the hydrocarbon into the hydrophobic region of the micelle (12-16, 19). The equivalent change in spacing could be explained if the idea of the spherical micelle as advanced by Hartley (21) or of the double layer disc or oblate spheroid micelle is considered (22). These changes in spacing are shown in Fig. 2 for the case of 0.63 M potassium laurate saturated with ethyl benzene for two of the proposed structures (19). This increase in X-ray spacing has been reported only upon the addition of simple hydrocarbons such as benzene, n-heptane, etc. In this type of solubilization, the MR is always found to increase with increasing soap concentration above the CMC up to at least 1.0 M.

Polar Compounds

In the second type of solubilization where the MR is constant above the concentration where the soap reaches its full colloidal form, there should be no increase in the distance between adjacent layers upon the addition of a dye, a long chain fatty acid, a long chain alcohol, or another soap. The X-ray data of Mattoon have shown that the long spacings of mixtures of soap solutions are linear functions of the mole ratios of the two soaps (23). If this type of solubilization involved the closure of the material being solubilized in the hydrocarbon-like central region of the micelle, then one would expect an increase in spacing, in the case of the soap mixtures, which would at all times be larger than the reported linear variation of the long layer spacings. X-ray studies on mixed soap-fatty acid crystals show that the cell dimensions of the mixtures are equivelent to those of the pure soap (24). In addition, the critical concentration for the formation of micelles of soap mixtures lies between the CMC of the pure soaps (25). Preliminary reports of soap-fatty acid and soap-long chain alcohols indicate that there is no change in the long X-ray spacings of these mixtures (26, 27) as one would expect from the case of the soap-soap mixtures.

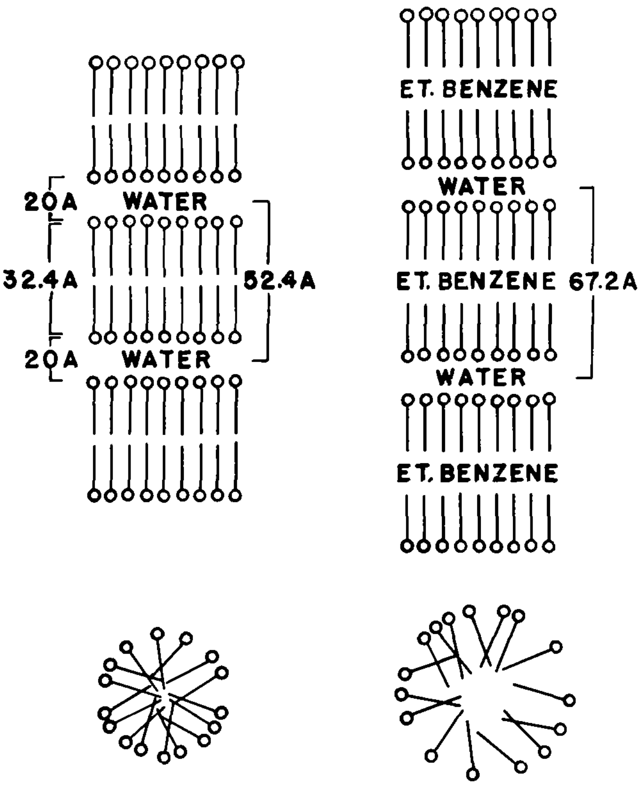

FIG. 2. Highly idealized schematic diagram of 0.63 N potassium laurate solutions showing effect of added ethyl benzene. Lamellar micelle of McBain and spherical micelle as pictured by Hartley are shown.

Thus, it appears that solubilization of this type involves the incorporation of the solubilized molecules with their long axes lying approximately parallel to those of the soap molecules. This can be exemplified further by considering the observed change in spacing in the case of soap mixtures (23). This change in long spacing is a linear function of the mole ratio of the mixtures. When two anionic detergents having the same anion but different cations as in the case where calcium and sodium dodecyl sulfate are mixed, no differences in spacing should be observed in solutions of each detergent alone and in solutions of their mixtures. Similarly, there should be no change in spacing for solutions of soap-fatty acid mixtures, and soap-long chain alcohol systems. According to this interpretation, mixed micelles are formed in which the solubilized material is interspersed in the plane of the long axes of the soap molecules lying approximately parallel to the closest neighboring soap molecules. It is not meant, of course, that the area occupied per OH group in the alcohol is the same as that of the hydrophylic head of the soap molecule. Rather, it must be pointed out that the large area, 30-50 A^2 or more per soap molecule is due to the long range repulsion of like charged heads and is to be compared with about 20-25 A^2 occupied per OH group in the solubilized alcohol.

The solubilization of a dye may be a sub-class of the type just described. The MR in dye solubilization is constant beyond that concentration where the soap attains its full colloidal form. In addition to the actual solubilization of a dye an increase in fluorescence has been noted in many soap-dye systems. When a soap is added to a dye solution such as dichlorofluorescein or pinacyanol chloride, a marked increase in fluorescence is observed as the critical concentration is passed, depending on the particular soap-dye system (28). An increase in fluorescence in a dye is probably associated with a deaggregation of the dye polymer. This same phenomenon occurs in solubilization of some dyes and should show no change in long spacing.

Initially, some dyes in suitable media will fluoresce. Thus, there is some fluorescence observed in solutions of a dye such as acridine, which is insoluble in hydrocarbons such as benzene and n-heptane, in alcohols. The addition of soap at concentrations below the CMC to a water solution of this dye, as well as others such as pinacyanol chloride, will cause a marked change in color. The monomer $\rightleftharpoons$ polymer ratio is changed due to the binding of some dye molecules, like an unionized salt, with the soap of opposite charge. Further increase of soap to bring the concentration to the CMC will result in a further color change and/or fluorescence which is indicative of micelle formation.

The question now to be considered is whether the soap-dye system forms a mixed micelle of the soap-soap and soap-alcohol type and whether, in this case, aggregation of soap-dye molecules would require fewer soap molecules (as is indicated in soap-soap and soap-alcohol mixtures by a decrease in CMC) or the same number of soap molecules as in soap alone to form a micelle. Unfortunately, no X-ray data have been reported for soap-dye systems, probably due to the complexity of the spectra which measure spacings of soap aggregates and dye aggregates and/or soap-dye aggregates of various proportions.

A 160-fold difference in dye concentration seems not to affect the value of the CMC as determined by dye titration. Thus, potassium myristate titrated with 5×10^{-6} M pinacyanol chloride has a CMC of 0.006 M, with 5×10^{-5} M dye a value of 0.0058 M, and with 8×10^{-4} M dye a value of 0.0063 M. Similarly, changes in concentration of other dyes such as anisidine, acridine, etc., show the same effects. Thus, it is indicated that the dye, bound to the soap by electrostatic forces, does not extend far enough into the hydrocarbon interior of the soap micelle to add any energy in the form of van der Waals type of attractive forces for micelle formation. A decrease in CMC would be expected if the soap-dye system were comparable to the soap-soap and soap-alcohol mixtures.

Fluorescence indicates that the dye must be in an environment having a dielectric constant, ϵ, of about 22 to 60, because acridine, for example, is reddish-orange (no fluorescence) in water ($\epsilon = 82$), is not soluble in benzene, n-heptane, or in ethyl ether ($\epsilon =$ 2 to 4), and fluoresces in alcohols and in soap solutions above the CMC. Qualitatively, in the presence of soap micelles, the intensity of fluorescence indicates that the dye must be in a medium having a dielectric constant of about 27 to 40. Quantitative values are now being obtained by actual measurements of fluorescence intensities of various alcohol-dye and soap-dye solutions and should make it possible to show more accurately the dielectric of the environment of the dye molecules in the presence of soap micelles.

Dye molecules have been thought to be solubilized by being incorporated in the micelle center ($\epsilon = 2$ to 4) and this may be true for the case of uncharged dyes, or bound by electrostatic forces to micelle surfaces ($\epsilon = 82$). However, the above qualitative approach seems to indicate that the charged dye, at least, is a part of the micelle, held near the region of the charged soap head, not, however, sticking out into the water layer. It is indicated that the hydrocarbon density in the soap micelle is inversely proportional to the distance, r, from the micelle center, squared (29). Similarly, it is probable that the dielectric constant is directly proportional to r^2. It should be noted that if one considers only that the density of the hydrocarbon decreases as r increases, the dielectric constant would also decrease. However, there must be some penetration of the water into the micelles which, with decrease in density as the water molecules are farther removed from the charged micellar surface, will extend some 3 to 5 Å. Thus, for $r = 20$ Å, the dye molecule, about 11 Å long, would extend about 7 Å into the micelle from the charged surface, and would be oriented to some extent, through van der Waals forces between dye and soap molecules, with respect to adjacent dye molecules.

Discussion

It is recognized that many factors play a part in solubilization. The tendency of a soap to form micelles is of prime importance. The solubility of ethylbenzene in 15% soap solutions changes from a mole ratio of 0.0031 for potassium caproate (KC_6), 0.080 for potassium caprylate (KC_8), 0.207 for potassium caprate (KC_{10}), 0.433 for potassium laurate (KC_{12}), to 0.870 for potassium myristate (KC_{14}) (1). In addition to the effect of chain length in a homologous series, the structure of the soap molecules plays an important part in solubilization. The molar volume, polarity, charge, and structure of the compound to be solubilized, also affect the degree of solubilization. Hughes, Sawyer, and Vinograd have shown that for equimolar hydrocarbon concentrations, the amount solubilized (increase in X-ray spacing per mole hydrocarbon per mole soap) is a linear function of the molar volume of the hydrocarbons (18). Thus, the amount of hydrocarbon solubilized is an inverse function of the molar volume for a homologous series.

The effect of polarity can be shown from the fact that 0.5 M potassium myristate solubilizes 85 gm. per liter of n-decanol but only 30 gm. per liter of n-decane. The non-polar compound principally occupies the space between and around the hydrophobic ends of the soap molecules in the micelle, and this is equivalent to an increase in the length of the hydrocarbon tail of the soap by 1-2 C atoms (22). The polar compound lies in the plane of the long axis of the soap molecules, oriented as the soap molecule with reference to the hydrophylic and hydrophobic ends, as is indicated from X-ray studies on soap-soap and soap-alcohol mixtures (26) as well as on fluorescence effects, and little is taken into the hydrophobic region of the soap micelle for there is essentially no increase in the long X-ray spacing.

It is evident that with increase in soap concentration the area available per molecule to be solubilized remains constant for the more polar compounds such as dyes, insoluble soaps, fatty acids, and long chain alcohols, whereas this value can increase for simple hydrocarbons. The differences observed in Fig. 1 can be explained in this manner.

McBain and McHan have postulated that dimethyl phthalate is solubilized in a 0.1 N potassium laurate solution by adsorption on the surface of the McBain spherical ionic micelle (27). This explanation is based on the fact that no increase in X-ray spacing was noted upon the addition of the phthalate. Even though the dimethyl ester is slightly less polar than the corresponding acid, it is to be expected that the ester will be solubilized in the same manner as the charged dyes discussed above. The previous discussion of the type of solubilization which involves no increase in long X-ray spacing can be advanced as a possible explanation of these experimental findings in the phthalate-laurate system.

Kolthoff and Harris have shown that changes in molecular weight distribution are possible through control of mercaptan availability by increment addition of mercaptan or by changes in mercaptan solubility by structural modification (30). These types of solubilization discussed above can be applied to explain the formation and properties of certain polymers prepared with identical formulae except that the modifier, usually a long chain mercaptan, in one case is added initially to the soap-water-persulfate mixture before the addition of monomers, and in the second polymerization is added dissolved in the monomers. Depending on the relative reactivity of the monomers used, quite different molecular weight distributions should be possible.

These results can only be explained on the basis of mercaptan availability, for in one case the mercaptan is a part of a mixed micelle, with the –SH group oriented toward the water-detergent interface, and in the other it is partially solubilized with the monomer occupying the center portion of the micelle around the hydrocarbon tails of the soap molecules. If the soap micelle is the initial locus of emulsion polymerization as has been indicated (10, 31), then the availability of mercaptan, in the first case, as part of a mixed soap-mercaptan micelle, and in the second, readily available in the solubilized monomer, will markedly affect the molecular weight distribution of the initially polymerized product.

Application to Biological Systems

The addition of paraffin-chain salts to protein cannot be considered as solubilization as discussed above, but, in a larger definition of this term, may fall into this classification. Many water soluble proteins react with soap molecules usually by attraction of oppositely charged ions. This is supported, in part, by the finding that any reaction of non-ionic detergents with proteins does not involve this type of electrostatic binding (32), for the interaction in this case, probably of a van der Waals type, is far less effective than in colloidal electrolyte-protein systems. It is not expected that individual micelles would react as a unit with a single protein molecule for this would mean that about 65-75 soap molecules (number composing a micelle of a C_{12} soap) would combine with any protein molecule.

Thus, sodium alkyl benzene sulfonate will react with three times its weight of native egg albumin at a pH alkaline to its isoelectric point (33). Putnam and Neurath have indicated that protein-detergent reaction will occur at pH on both sides of the isoelectric point (34). The reaction of serum albumin with sodium lauryl sulfate will occur at a pH below the isoelectric point (where protein and detergent are oppositely charged) with the appearance of a precipitate over the mole ratio range of protein to soap of about 0.01-0.02. This would indicate an increase in the hydrophobic nature of this complex due to the hydrocarbon tails of the detergent at the protein interface and would account for turbidity through flocculation. A first complex would be formed, for example at a pH 4.5, with the binding of 52 molecules of sodium lauryl sulfate per horse serum albumin (mol. wt. = 67,000) molecule and the second complex would be composed of about 100 detergent molecules per protein molecule (34). Similarly, egg albumin will react with 15 and 28 molecules of detergent per protein molecule at the isoelectric point (35). Addition of further detergent results in a loss of opacity through the formation of another complex (34). This, an example of solubilization in these systems, is due to the binding of the hydrocarbon tail of the added detergent with the hydrophobic portion of the soap molecule of the original complex, replacing each detergent hydrophobic tail of the original complex with a hydrophylic group.

Detergents will bring about a number of changes when added to protein systems, such as denaturation (36), stabilization as by inhibition of coagulation (36), complex formation and precipitation, inactivation of enzymatic properties, etc., all of which have been discussed in a recent review (37). Foster was able to make a physical chemical study of the water-insoluble protein, zein, in aqueous detergent solutions (38). These complexes of zein and detergent, in which the detergent must be considered to be bound by van der Waals forces through its hydrophobic tails with corresponding hydrophobic groups on the protein surface, are similar in properties to the soluble complex mentioned above. The original protein, zein, the material being solubilized, must correspond to the insoluble protein-detergent complex as well as to such other compounds as the insoluble dyes.

The author is indebted to Dr. Leo Shedlovsky for discussion of this paper and to Dr. Frank W. Putnam for the opportunity to see his manuscript on protein-detergent interaction prior to publication.

Summary

Two, or possibly three, types of solubilization are shown to occur which depend on the compound being solubilized. Those systems in which the mole ratio, MR (moles material being solubilized per mole solu-

bilizer) increases with increasing soap concentration are characterized by an increase in long X-ray spacings to the point at which the system becomes saturated with the compound being solubilized. Hydrocarbons such as benzene, ethyl benzene, and normal paraffins fall into this class. Another type is that in which the MR remains constant above the concentration where the soap assumes its full colloidal properties, and this is characterized by no change in long X-ray spacing. Examples of this type are soap-soap, soap-fatty acid, soap-alcohol, and possibly as a subtype, soap-dye systems. These systems are shown to be mixed micelles in which the solubilized compound is oriented with the long axis of the solubilized compound lying approximately parallel and in the plane of the long axis of the soap molecules, the hydrophylic group of both constituents being toward the water interface. Protein-detergent complexes are discussed from the point of view of solubilization.

REFERENCES

1. W. Heller and H. B. Klevens, J. Chem. Phys. *14*, 567 (1946).
2. G. S. Hartley, J. Chem. Soc. *1938*, 1968.
3. J. W. McBain and J. J. O'Connor, J. Am. Chem. Soc. *63*, 875 (1941).
4. H. B. Klevens, unpublished data.
5. J. W. McBain and A. A. Green, J. Am. Chem. Soc. *68*, 1731 (1946).
6. J. W. McBain, R. C. Merrill, Jr., and J. R. Vinograd, J. Am. Chem. Soc. *63*, 670 (1941).
7. H. V. Tartar and R. D. Cadle, J. Phys. Chem. *43*, 1173 (1939).
8. L. Shedlovsky, G. D. Miles, and G. V. Scott, J. Phys. Colloid Chem. *51*, 391 (1947).
9. I. M. Kolthoff and W. Stricks, J. Phys. Colloid Chem. *52*, 915 (1948).
10. W. Heller and H. B. Klevens, High Polymer Forum, Am. Chem. Soc. Meeting, Chicago, Illinois, Sept. 9-13, 1946.
11. P. A. Thiessen and R. Spychalski, Z. physik. Chem. *156A*, 435 (1931).
12. K. Hess and J. Gundermann, Ber. *70B*, 1800 (1937).
13. J. Stauff, Kolloid Z. *89*, 224 (1939); *96*, 244 (1941).
14. H. Kiessig and W. Philippoff, Naturwissenschaften *27*, 593 (1939).
15. H. Kiessig, Kolloid Z. *96*, 252 (1941); *98*, 213 (1942).
16. W. Philippoff, Kolloid Z. *96*, 255 (1941).
17. S. Ross, J. Phys. Chem. *46*, 414 (1942).
18. E. W. Hughes, W. M. Sawyer, and J. R. Vinograd, J. Chem. Phys. *13*, 131 (1945).
19. W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Colloid Sci. *1*, 108 (1946).
20. R. W. Mattoon, R. S. Stearns, and W. D. Harkins, J. Chem. Phys. *16*, 644 (1948).
21. G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936.
22. H. B. Klevens, Colloid Symposium, Am. Chem. Soc., Cambridge, Mass., June 23-25, 1948.
23. W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. *68*, 220 (1946).
24. M. J. Buerger, Am. Mineralogist *30*, 551 (1945).
25. H. B. Klevens, J. Chem. Phys. *14*, 742 (1946); J. Phys. Colloid Chem. *52*, 130 (1947).
26. W. D. Harkins, R. W. Mattoon, and R. Mittlemann, J. Chem. Phys. *15*, 763 (1947).
27. J. W. McBain and H. McHan, Colloid Division, Am. Chem. Soc., New York, Sept. 15-19, 1947.
28. H. B. Klevens, J. Phys. Colloid Chem. *51*, 1143 (1947); J. Colloid Sci. *2*, 365 (1947).
29. H. B. Klevens, "Effect of Structure on Critical Micelle Concentration, III," in preparation.
30. I. M. Kolthoff and W. E. Harris, J. Polymer Sci. *2*, 49 (1947); *2*, 72 (1947).
31. W. D. Harkins, J. Am. Chem. Soc. *69*, 1428 (1947).
32. E. I. Valko, Ann. N. Y. Acad. Sci. *45*, 451 (1946).
33. H. P. Lundgren, D. W. Elam, R. A. O'Connell, J. Biol. Chem. *149*, 183 (1943).
34. F. W. Putnam and H. Neurath, J. Am. Chem. Soc. *66*, 692 (1944); J. Biol. Chem. *159*, 195 (1945).
35. H. B. Bull, J. Am. Chem. Soc. *67*, 10 (1945).
36. M. L. Anson, J. Gen. Physiol. *23*, 233 (1939).
37. F. W. Putnam, Advances in Protein Chemistry *4*, 79 (1948).
38. J. F. Foster, Colloid Symposium, Am. Chem. Soc., Cambridge, Mass., June 23-25, 1948.

Factors Which Affect the Stability of Highly Unsaturated Fatty Acids.[1] II. The Autoxidation of Linoleic and Alkali Conjugated Acid in the Presence of Metallic Naphthenates[2]

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DRIERS have been in commercial use for some time, yet no concise mechanism has been advanced as to their role in olefin oxidation. Riemenschneider (1) suggested that they may function by increasing the efficiency of energy transfer from one molecule to another. Furthermore, Nicholson (2) has shown that it is the concentration of drier cation that determines the catalytic activity. The activity was not destroyed by adsorption (3) or by saturating coordination valence of the drier (4).

In addition to listing the relation of driers to polymerization and gelation, Elm (5) stated that the metal portion oscillated between two stages allowing it to activate the atmospheric oxygen and pass it on to a drying oil molecule. A "reducing inhibitor" destroying action (6) and an initial peroxide stabilizing role (5) have been suggested. Gardner and Waddell (7) believed that driers form a series of unstable complexes with several of the products and reactants produced during autoxidation, polymerization, and gelation. It is now generally believed that driers function as promoters, or as pseudo rather than true catalysts.

A plausible chemical mechanism for drier action during the autoxidation of tetralin has been postulated. Yamada (8) has shown that Mn, Co, and Pb compounds raise the decomposition reaction order of tetralin hydroperoxide one step, that is from the first to the second order. Ivanov *et al.* (9) and Medvedev (10) have demonstrated a similar role for the transition metals in hydrocarbon autoxidation.

Robertson and Waters (11) have classified metallic salts as "secondary catalysts" and have pointed out why it is of no particular advantage to increase the concentration of the promoters above a certain value.

In this laboratory we have been concerned with the factors affecting the stability of highly unsaturated fatty acids (12, 13). A study of the autoxidation of linoleic and alkali conjugated linoleic acid was presented in another paper (14). The modifica-

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[1] The subject matter of this paper has been undertaken in cooperation with the Office of Naval Research. The opinions or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Navy Department.

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