

ABSTRACTS

R. A. REINERS, Editor. ABSTRACTORS: J. G. Endres, Kazuo Fukuzumi, J. Iavicoli, K. Kitsuta, F. A. Kummerow, C. C. Litchfield, Gladys Macy,

Louise R. Morrow, E. G. Perkins, and T. H. Smouse

• Fats and Oils

EPOXIDATION OF ANCHOVY OILS. J. Wisniak, A. Cancino, and J. C. Vega (Depart. of Chem. Eng., Universidad Catolica de Chile, Santiago, Chile), *Ind. Eng. Chem. Product Res. Dev.* **3**, 306-11 (1964). Anchovy oil has been epoxidized *in situ* to determine the effect of operating variables on the maximum oxirane oxygen attainable. Variables studied included temperature, catalyst nature and concentration, hydrogen peroxide strength and proportion, and acetic acid proportion. An epoxidized oil with 7.8% epoxy content and iodine value of 14.1 can be prepared when operating at 53°C to 73°C, using a 33 weight % hydrogen peroxide solution in a proportion of 1.4 moles per mole of ethylenic unsaturation, 15% concentration of styrene-sulfonic resin as catalyst, and acetic acid in the proportion of 0.5 mole per mole of ethylenic unsaturation.

SEPARATION OF VOLATILE CARBONYL COMPOUNDS BY GAS LIQUID CHROMATOGRAPHY. G. Mizuno, Evelyn McMeans, J. R. Chipault (The Hormel Institute, Univ. of Minnesota, Austin, Minn.). *Anal. Chem.* **37**, 151-52 (1965). Separation of a mixture of 7 carbonyl compounds with 2 to 4 carbon atoms is described using nitrobenzene or 2-nitrobiphenyl as stationary phases.

DEVELOPMENT AND FLAVOR PROPERTIES OF METHYL KETONES IN MILK FAT. J. E. Langer and E. A. Day (Dept. of Food Science and Technology, Oregon State University, Corvallis). *J. Dairy Sci.* **47**, 1291-96 (1964). Temperature during heat treatment, time of heat treatment, and presence of water in milk fat all influenced the quantity of methyl ketones produced. Maximum yield of ketones was obtained by heating a degassed fat sample for 3 hr at 140°C; heating an additional 15 hr had no further effect. Milk fat prepared by degassing at 2 to 5 μ Hg for 1 hr at 40°C still contained sufficient water for maximum ketone production. When milk fat was dried over calcium hydride for 18 hr prior to heat treatment, methyl ketone formation was inhibited. Hence, water appears essential for significant heat-induced ketone formation in milk fat. Heating the fat in the presence of air caused a slight increase in yield of ketones. The average flavor threshold (AFT) for each of the methyl ketones, produced by heating milk fat, was determined in homogenized milk. Based upon the AFT of individual ketones and the AFT of the ketone mixture, prepared in the ratios found in the fat, the following conclusions are warranted: 1) The ketone mixture exhibits a synergistic interaction whereby a perceptible flavor is evident when the concentrations of all components in the mixture are below their AFT; 2) There is sufficient methyl ketone precursor in milk fat to give rise to perceptible flavors in a beverage-type milk.

DETERMINATION OF BETA-OLEFINIC METHYL GROUPS IN ESTERS OF FATTY ACIDS BY NUCLEAR MAGNETIC RESONANCE. A. C. Glass and H. J. Dutton (Northern Research Laboratory, ARS, USDA, Peoria, Ill.). *Anal. Chem.* **36**, 2401-04 (1964). An analytical method for determining 15,16-unsaturation in fatty acids by nuclear magnetic resonance spectrometry is described. Utilized in the determination are the low field member of the beta-olefinic methyl proton triplet and the central peak of non-beta-olefinic methyl proton triplet. The areas of these signals are determined by the instrumental integral and by paper tracings, and precision of the two methods is compared. Application to the kinetics of hydrogenation is presented.

COMPARISON OF THEORETICAL LIMIT OF SEPARATING SPEED IN GAS AND LIQUID CHROMATOGRAPHY. J. C. Giddings (Depart. of Chemistry, Univ. of Utah, Salt Lake City, Utah). *Anal. Chem.* **37**, 60-63 (1965). An investigation was made of the principal factors affecting separating speed in gas and liquid chromatography. Following an earlier proposal by Knox, it is assumed that the maximum inlet pressure is one of the basic limitations on analysis speed. This assumption is fully justified by this work. It is further shown that the comparative speed of separation de-

pends, to a large extent, on the relative viscosity and diffusivity of liquids and gases. For moderately difficult separations gas chromatography is superior because of its small C term. For extremely difficult separations liquid chromatography is superior because of its low critical inlet pressure, the latter mainly resulting from the slow diffusivity of liquid systems. The approach to further increases in speed is discussed for both methods.

GAS CHROMATOGRAPHIC EXAMINATION OF THE FATTY ACIDS OF COFFEE OIL. A. Carisano and L. Gariboldi (Compagnia Italiana Liebig, S.p.A. Tortona, Italy). *J. Sci. Food Agr.* **15**, 619-22 (1964). The fatty acids of the oil extracted from coffee have been examined by gas chromatography. Composition of the oil did not vary with the geographical origin; roasting did not affect the composition of the oil. Samples of coffee contained from about 10-16% oil (on wet weight). The oil from roasted coffee contained 31-35% palmitic, 7-9% stearic, 7-10% oleic, 44-46% linoleic, 3-4% arachidic, 1.1-1.7% linolenic, 0.5% behenic, and traces of myristic, palmitoleic, margaric and gadoleic acids. The authors suggest that coffee oil with its high content of linoleic acid might be recommended for human nutrition.

FATTY MATERIALS STABILIZED WITH THIODIALKANOIC POLYESTERS. C. E. Tholstrup, A. Bell, and C. J. Kibler (Eastman Kodak Co.). *U.S. 3,157,517*. Described is a composition of matter which consists of a normally oxidizable fatty organic edible material stabilized with from 0.001% to 5% by weight of a thiodialkanoic polyester.

TREATMENT OF TALL OIL FATTY ACIDS. P. D. Patrick, Jr. (West Virginia Pulp & Paper Co.). *U.S. 3,157,629*. Described is a method for treating a tall oil fatty acid product containing less than 10% rosin acids and substantial quantities of both linoleic and oleic acids. The tall oil product is heated at a temperature between 450 and 550°F in the presence of iodine in an amount equal to between 0.01 and 2% by weight of the tall oil for a period of time (10 minutes to 6 hours) sufficient to reduce the iodine value of the tall oil to between 60 and 110.

• Fatty Acid Derivatives

POLYESTERS FROM EPOXY-CONTAINING OLEAGINOUS MATERIALS. T. W. Findley, J. L. Ohlson, and F. E. Kuester (Swift & Co.). *U.S. 3,155,696*. A method of polymerizing an epoxidized fatty material to form a linear polymer comprises: mixing an epoxidized fatty material containing an average of not more than 1 epoxy group per molecule with a dicarboxylic acid anhydride, the fatty material being epoxidized fatty glycerides, fatty acids or methyl epoxystearate and being free of terminal epoxy groups; heating the mixture to a temperature sufficient to initiate an exothermic reaction and to cause scission of the epoxy groups; and cooling the reaction product to obtain a fusible polyester polymer. The resulting polymer is soluble in organic solvents.

POLYMERIC FAT ACIDS. E. M. Fischer (General Mills, Inc.). *U.S. 3,157,681*. A process of polymerizing higher unsaturated fatty acids comprises heating the acids in the presence of an acid clay having a pH of about 5.7 and a Karl Fischer moisture content of 10-17% thereby providing a polymeric fat acid having a dimer to trimer ratio greater than 4.0, a Gardner color not greater than 8, an acid value not less than 185, and a saponification value not less than 196.5. The analyses of two suitable clays are given.

• Biology and Nutrition

STUDIES ON THE METABOLISM OF ADIPOSE TISSUE. XVII. IN VITRO EFFECTS OF INSULIN UPON THE METABOLISM OF THE CARBOHYDRATE AND TRIGLYCERIDE STORES OF ADIPOSE TISSUE FROM FASTED-REFED RATS. R. L. Jungas and E. G. Ball (Dept. of Biological Chemistry, Harvard Med. School, Boston, Mass.). *Biochem.* **3**, 1696-1702 (1964). Adipose tissue from fasted-refed rats exhibits a high rate of glycerol release and oxygen consumption when incubated *in vitro* in the absence of added substrate. The free fatty acid content of the tissue remains low throughout the incubation. The addition of insulin, 1000 m μ units 9 ml, inhibits glycerol production 85% and oxygen consumption 30% while free fatty acid values are unaffected. These results are interpreted to indicate a high rate of spontaneous hydrolysis of triglyceride to fatty acids and glycerol in this tissue and

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the inhibition of the process by insulin. The low fatty acid values indicate that rapid re-esterification of this product to triglyceride must occur with glycerophosphate furnished by the abundant glycogen stores found in this tissue. The decrease in oxygen consumption produced by insulin is to be accounted for by the diminished demand for high-energy phosphate needed for re-esterification purposes attendant upon the curtailed lipolytic process. Lactate production in this tissue is also high and this process is likewise inhibited by the presence of insulin.

IONIC PROPERTIES OF AQUEOUS DISPERSIONS OF PHOSPHATIDIC ACID. M. B. Abramson, R. Katzman, C. E. Wilson, and H. P. Gregor (Dept. of Neurology, Albert Einstein College of Med., N.Y. 61, N.Y.). *J. Biol. Chem.* 239, 4066-72 (1964). Stable aqueous dispersions of phosphatidic acid were prepared by ultrasonic treatment. When freed from Ca^{++} , these dispersions were at pH 3.05 to 3.29. The titration curves showed well defined inflection points with a pK_1 of 3.8 and a pK_2 of 8.6 in water and a pK_1 of 3.0 and a pK_2 of 8.0 in 0.8 N NaCl or KCl. The stoichiometry of the titrations indicate that all of the acid groups in these miscelles are obtained so as to be available to the aqueous medium. Sodium and potassium salts of phosphatidic acid were prepared, and dispersions of these gave pH values consistent with their cation content and titration curves. At pH 7.4, the micelles contain 1.2 μ eq of sodium or potassium per μ mole of phosphorus. The presence of Ca^{++} either in the phosphatidic acid preparation or in the medium reduced the number of groups that could be titrated, indicating both stronger binding of this cation than of Na^+ or K^+ and probable rearrangement of the micelle. Phosphatidic acid groups present in micellar dispersions of lecithin and phosphatidic acid were titrable, indicating that all of the phosphatidic acid groups were on the surface of the micelles.

METABOLISM OF THE RETINA. V. THE ROLE OF MICROSOMES IN VITAMIN A ESTERIFICATION IN THE VISUAL CYCLE. J. S. Andrews and S. Futterman (Howe Lab. of Ophthalmology, Harvard Med. School, Boston, Mass.). *J. Biol. Chem.* 239, 4073-76 (1964). In light adaptation in the retina, the vitamin A synthesized by the visual cell outer segments is subsequently converted to vitamin A ester by retinal microsomes. The visual cell outer segments play no role in vitamin A esterification. The esterification of vitamin A by retinal microsomes occurs without the addition of supplements or cofactors. The principal fatty acids present in vitamin A ester synthesized by retinal microsomes are palmitic, stearic, and oleic acids. The microsomal reaction product is similar in composition to the vitamin A ester synthesized by the intact retina.

INTERRELATIONSHIP OF STEROL AND FATTY ACID BIOSYNTHESIS IN RAT LIVER SLICES AS RELATED TO DIETARY LIPID. E. R. Diller and O. A. Harvey (Lilly Res. Lab., Indianapolis, Indiana). *Biochemistry* 3, 2004-7 (1964). *In vitro* studies on cholesterol and fatty acid biosynthesis were made using liver slices from rats maintained on four levels of dietary fat. With acetate-1- C^{14} as precursor, cholesterol biosynthesis was found to be directly related to the fat content of the diet, whereas an inverse relationship was found in lipogenesis. In a more detailed study on the sterol biosynthetic pathway with mevalonate-2- C^{14} , the incorporation of this precursor into isoprenol, squalene, and cholesterol was determined. Sterol biosynthesis from mevalonate was found to be related to the amount of dietary lipid. The incorporation of the precursors into sterol was found to be directly related to the hepatic sterol levels.

USE OF RADIOIODINATED FATTY ACID FOR PHOTOSCANS OF THE HEART. J. R. Evans, D. Phil, R. W. Gunton, R. G. Baker, D. S. Spears (Depts. of Med. and Medical Biophysics, Univ. of Toronto; Toronto, Canada). *Circulation Res.* 16, 1-10 (1965). Radioiodinated fatty acid bound to albumin (RIFA) was given by intravenous injection to dogs and moribund human subjects in order to label heart muscle. Photoscans of the thorax of dogs given RIFA revealed concentration of radioactivity in the ventricular region of the heart due to incorporation of the labeled fatty acids into myocardial triglyceride and phospholipid. At necropsy the concentration of radioactivity was much higher

in healthy myocardium than in infarcted muscle. The same distribution of radioactivity was observed in hearts from three human subjects with myocardial infarction given RIFA shortly before death. It is proposed that areas of myocardial infarction might be demonstrated during life by photoscans of the thorax following intravenous injection of RIFA.

THE COMPOSITION OF LIVER VITAMIN A ESTER AND THE SYNTHESIS OF VITAMIN A ESTER BY LIVER MICROSOMES. S. Futterman and J. S. Andrews (Howe Lab. of Ophthalmology, Harvard Med. School, Boston, Mass.). *J. Biol. Chem.* 239, 4077-80 (1964). The vitamin A ester isolated from calf, sheep, rabbit, human, rat, frog, trout, and cat liver is a complex mixture. In general, the major components are vitamin A palmitate, stearate, and oleate. The esterification of vitamin A occurs in the microsomes. The reaction does not require the addition of supplements or cofactors. The yield of vitamin A ester synthesized by liver microsomes can be increased by the addition of the supernatant fluid fraction of liver. The process by which vitamin A ester is synthesized in the liver appears to be the same as that found in the retina. There are two optimal pH values for the esterification of vitamin A by cat liver microsomes, one in the region of pH 4.5 and another in the vicinity of pH 8.2. Only at the higher pH is the fatty acid composition of the reaction product similar to that of the vitamin A ester which occurs naturally in the liver of the cat. Liver microsomes esterify vitamin A by a different reaction than the one that has been described for the esterification of cholesterol.

INCORPORATION OF FORMATE INTO LIPIDS OF ADIPOSE TISSUE. J. Gliemann and V. P. Dole (Rockefeller Institute, New York 21, N.Y.). *J. Biol. Chem.* 239, 4062-5 (1964). Formate- C^{14} was found to be incorporated into neutral lipids of adipose tissue *in vitro*. When insulin and glucose were lacking in the medium, most of the label was found in the glycerol moiety. With insulin or ribonucleic acid, plus glucose, a greater fraction of label appeared in the fatty acid constituents. Under the latter conditions label was distributed among fatty acids of even chain length in a pattern indistinguishable from that seen when fatty acids were synthesized from acetate-1- C^{14} . Serine-3- C^{14} , synthesized from formate, may serve as an intermediate in the conversion of formate to lipid.

THE PHOSPHOLIPIDS IN MEMBRANE GHOSTS FROM STREPTOCOCCUS FAECALIS PROTOPLASTS. F. A. Ibbott and A. Abrams (Dept. of Biochem., Univ. of Colorado Med. Sch., Denver, Colorado). *Biochemistry* 3, 2008-12 (1964). The total lipid of the membrane ghost fraction prepared from *Streptococcus faecalis* (ATCC 9790) in the stationary phase of growth was found to be 21% of the membrane dry weight. Silicic acid chromatography indicated that two main types of lipid were present, polar lipid (77%) and a lipid resembling glyceride (22%). The polar lipid was further fractionated on a silicic acid column into two components. The first component (faster moving on thin-layer chromatography) constituted 54% of the total lipid and the second component (slower moving on thin-layer chromatography) constituted 23% of the total lipid. Reagents sprayed onto thin-layer plates failed to detect the presence of choline or amino nitrogen in either polar lipid, but did indicate the presence of carbohydrate in the slow polar lipid. Chemical analysis of the fast polar lipid showed that it was 3.75% phosphorus and had an ester-phosphorus ratio of 4.9:2. The slow polar lipid had an ester-phosphorus ratio of 6.1:1. Paper chromatography of the deacylated fast polar lipid before and after HCl hydrolysis indicated that the water-soluble moiety was diglycerolphosphorylglycerol. The fast polar lipid thus appears to be a diphosphatidylglyceride.

METHIONINE DEFICIENCY AND FATTY LIVER IN MALE AND FEMALE RATS. R. L. Lyman, Shirley Thenen and C. R. Cook (Department of Nutritional Sciences, University of California, Berkeley). *Proc. Soc. Exp. Biol. Med.* 117, 696-99 (1964). Male and female rats were made deficient in methionine by force-feeding a methionine-free diet for 10 days. Female, but not male rats developed fatty liver, evidenced by an increase solely in triglycerides. There was no evidence of increased fatty acid synthesis by the deficient animals, as estimated by acetate-2- C^{14} incorporation studies, or by dilution of the triglyceride linoleic acid. Deficient female rats, however, had significantly lower serum cholesterol and phospholipid levels than did controls. The results suggest that methionine-deficient female rats developed fatty livers principally because of impaired transport of lipid from liver to the blood.

PROSTAGLANDINS AND RELATED FACTORS. 27. SYNTHESIS OF TRITIUM-LABELED PROSTAGLANDIN E_1 AND THE STUDIES ON ITS DISTRIBUTION AND EXCRETION IN THE RAT. B. Samuelsson (Dept.

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of Chem., Karolinska Institute, Stockholm, Sweden). *J. Biol. Chem.* 239, 4091-96 (1964). The synthesis of tritium-labeled prostaglandin E_1 is described. The excretion of isotope after administration of tritium-labeled prostaglandin E_1 to rats occurred both in urine and in feces. After 40 hours, about 50% of the administered dose was recovered in urine and about 10% in feces. Rats with cannulated bile ducts excreted comparative amounts of the isotope in urine and bile. Following administration of tritium-labeled prostaglandin E_1 to rats, the concentration of isotope in various tissues was determined. High concentrations of isotope were observed in the kidneys and the liver. Intermediate concentrations were found in the lungs, pituitary gland, adrenals, ovaries, uterus, and heart and low concentrations in the brain, muscle, adipose tissue, and thymus. The labeled products appearing in urine, plasma, liver, and kidney after administration of tritium-labeled prostaglandin E_1 were characterized by chromatography. Labeled 11 α , 15-dihydroxy-9-ketoprostanic acid and 11 α -hydroxy-9, 15-diketoprostanic acid were found in plasma.

PATHOLOGICAL CHANGES IN RATS ASSOCIATED WITH FEEDING FREE FATTY ACIDS AND FATTY ACID METHYL ESTERS. A. R. Spining III, W. P. Norman and O. H. M. Wilder (Divisions of Animal Feeds and Histology, American Meat Inst. Found., Chicago, Ill.). *Proc. Soc. Exp. Biol. Med.* 117, 774-77 (1964). Triglycerides, free fatty acids and methyl esters of fatty acids were compared for their effects on growth, feed conversion ratios, absorbability, serum polyunsaturated fatty acid and cholesterol levels, organ weights, carcass composition and liver and kidney histology when fed to young male rats. The livers from the animals fed fatty acid and methyl esters of fatty acids showed evidence of cellular degeneration. Animals fed free fatty acids also showed some fatty infiltration. Kidneys from the animals fed methyl esters of fatty acids had numerous calculi. Neither the free fatty acids nor the preparations containing methyl esters of fatty acids were absorbed as well as the intact triglycerides. Rats fed the free fatty acids or methyl esters of fatty acids required more feed per unit gain than did the animals fed the intact triglycerides. No differences were found in weight gains, organ weights, carcass composition or serum cholesterol levels. Serum polyunsaturated fatty acid levels were not changed by feeding fatty acids in the different forms. Corn oil did elevate the polyunsaturated acid levels in the serum above those observed in the lard-fed group of rats.

THE FATTY ACID COMPOSITION OF INTESTINAL-LYMPH LIPIDS IN SHEEP AND LAMBS. T. J. Heath, E. P. Adams and B. Morris (Australian National Univ.). *Biochem. J.* 92, 511-15 (1964). The intestinal-lymph lipids in sheep fed on lucerne chaff contain only small amounts of polyunsaturated fatty acids although these acids represent about 60% of the total fatty acids in lucerne chaff. When maize oil was given into the rumen of sheep, there was no increase in the content of polyunsaturated fatty acids in the intestinal lymph. When given into the abomasum or into young lambs, the content of polyunsaturated fatty increased. Both *cis* and *trans* isomers of monoenoic acids were produced in the rumen and absorbed into the intestinal lymph. Linolic acid was predominant in the lymph phospholipids. Several branched-chain fatty acids were present in low concentration in the intestinal lymph; these were presumed to be formed in the rumen.

BLOOD LIPIDS. 5. THE LIPIDS OF SHEEP PLASMA. G. A. Garton and W. R. H. Duncan (Rowett Res. Inst., Aberdeen). *Biochem. J.* 92, 472-5 (1964). Sheep plasma lipids were fractionated and the fatty acid composition of the fractions determined by gas-liquid chromatography; *trans*- and conjugated double bonds were also determined. Sheep plasma contained only about half the total amount of lipid in ox plasma (163 vs 291 mg/ml), due largely to a lower content of cholesterol esters in the former. These cholesterol esters contained more C_{15} monounsaturated acid and less C_{15} di- and triunsaturated acids than did the corresponding fraction of ox plasma lipids. The highest content of *trans*-unsaturated fatty acid was present in the triglycerides. Conjugated unsaturated acids appeared as a small proportion of the total acids of each class of plasma lipid; however, the highest content was in the triglycerides.

• Detergents

MOLECULAR ASSOCIATIONS IN PAIRS OF LONG-CHAIN COMPOUNDS. II. ALKYL ALCOHOLS AND SULFATES. H. C. Kunz and E. D. Goddard (Res. Center, Lever Bros., Edgewater, N.J.). *J. Phys. Chem.* 68, 3465 (1964). Previous work described the formation of 1:2 association complexes by a dry melt method. The present work involves studies on samples prepared from aqueous or aqueous-ethanol solutions of lauryl alcohol and sulfate and of myristyl alcohol and sulfate. It is shown that, over a range of concentration, mixing ratio, and solvent concentration, the specimens which settle out of solution have a composition corresponding to a 1:2 alcohol-sulfate ratio and that their differential thermal, infrared, and X-ray patterns correspond to those of the previously reported complexes. No evidence of free alcohol was obtained. Difficulty in preparing the "1:1" adducts was encountered.

THE EFFECT OF VARYING CENTRIFUGAL FIELD AND INTERFACIAL AREA ON THE ULTRACENTRIFUGAL STABILITY OF EMULSIONS. R. D. Vald and R. C. Groot (Dept. of Chem., Univ. So. Cal., Los Angeles, Calif.). *J. Phys. Chem.* 68, 3477 (1964). The steady-state rate at which oil separates from 50 vol. % emulsions of Nujol in water stabilized with 0.2 or 0.4% sodium dodecyl sulfate and the quantity separating rapidly near the beginning of ultracentrifugation were determined as a function of ultracentrifugal speed and of specific interfacial area. The rate of separation of oil is directly proportional to the strength of the applied centrifugal field and varies inversely with the specific interfacial area of the emulsion. The data obtained are consistent with the hypothesis that the observed rate of separation of oil is a measure of the rate of coalescence between the polyhedral "drops" in the flocculated emulsion layer and the bulk oil phase. The initial rapid separation of a considerable quantity of oil near the beginning of ultracentrifugation is attributed to initial distortion of the drops with temporary excessive increase in area as they transform from spherical to polyhedral shape.

THE CORRELATION BETWEEN PHASE INVERSION TEMPERATURE IN EMULSION AND CLOUD POINT IN SOLUTION OF NONIONIC EMULSIFIER. K. Shinoda and H. Arai (Dept. of Chem., Yokohama Univ., Yokohama, Japan). *J. Phys. Chem.* 68, 3485 (1964). A model has been advanced in which it is proposed to regard the

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cloud point in solution of nonionic agent as akin to the phase inversion temperature in emulsion. In the latter, the mixing is macroscopic, whereas in the former the mixing is microscopic or on the bimolecular leaflet scale, and the agent serves as an oil as well as an emulsifier. Phase inversion temperatures in hydrocarbon-water emulsions stabilized with polyoxyethylene alkyl phenyl ether have been determined for different hydrocarbons as a function of emulsifier concentration. It was found that the more soluble the hydrocarbon for a nonionic emulsifier, the lower is the phase inversion temperature, above which O/W type emulsions invert to W/O type. A similar rule, that the more soluble the nonionic emulsifier for a definite hydrocarbon, the lower the phase inversion temperature, also holds. The effects of polyoxyethylene chain length and hydrocarbon chain length of the emulsifier on the phase inversion temperature have been studied. It was found that the cloud points in solutions of nonionic emulsifiers saturated with various hydrocarbons and the phase inversion temperatures in emulsions were parallel, which supports the present model. The effect of temperature on the emulsion stability in connection with the phase inversion temperature is briefly discussed.

A THREE-COMPONENT LIGHT SCATTERING THEORY FOR SURFACTANT SOLUTIONS CONTAINING ADDED ELECTROLYTE. E. W. Anacker and A. E. Westwell (Dept. of Chem., Montana State College, Bozeman, Mont.). *J. Phys. Chem.* **68**, 3490 (1964). Although several light scattering procedures which lead in principle to "true" molecular weights of charged colloidal particles have recently appeared, the older Prins-Hermans-Mysels-Princen theory is still useful for estimating aggregation numbers of surfactant micelles. In the present paper, the theory is simplified and three working equations are developed. The new equations, equations from the Prins-Hermans-Mysels-Princen theory, and the equations originating from two other approaches (Scatchard-Bregman and Stigter) are applied to scattering data obtained from solutions of dodecyltrimethylammonium bromide in NaBr solution. The calculated aggregation numbers are in reasonable agreement.

NONIONIC SURFACE-ACTIVE COMPOUNDS. VIII. FILM DRAINAGE TRANSITION TEMPERATURES BY SURFACE VISCOSITY. P. Becher and A. J. Del Vecchio (Chem. Res. Dept., Atlas Chem Ind., Wilmington, Del.). *J. Phys. Chem.* **68**, 3511 (1964). Film drainage transition temperatures (FDTT) have been studied for polyoxyethylene (12) lauryl alcohol in the presence of added lauryl alcohol, and of polyoxyethylene (23) lauryl alcohol in the presence of added lauryl and cetyl alcohol. The FDTT were determined principally by measurements of surface viscosity (although direct observations were also made) in the temperature range 10 to 60C and at total concentrations of 0.0001 to 1.0 g./dl. The concentration of additive alcohol ranged up to 10%. In the absence of additive, fast-draining films are obtained in all cases; however, the addition of fatty alcohol gives rise to slow-draining films, with a transition to fast-draining, in complete analogy to the behavior of anionic materials. The FDTT for systems involving a particular alcohol appears to depend only on the mole ratio of nonionic agent and is independent of the nature of the agent. The analogy with melting point depression phenomena is indicated.

IDEAL TWO-DIMENSIONAL SOLUTION. IV. PENETRATION OF MONOLAYERS OF POLYMERS. F. M. Fowkes (Sprague Elec. Co., North Adams, Mass.). *J. Phys. Chem.* **68**, 3515 (1964). Monomolecular films of polymers or proteins on the surface of water (or at liquid-liquid or liquid-solid interfaces) are often subject to swelling by penetration into the film of water, organic solvents, or surface-active molecules. This effect results in an expanded pressure-area isotherm which can be explained as a two-dimensional solution in which the polymer molecules of the film reduce the free energy of the penetrants. This concept leads to equations which accurately predict the degree of swelling. The equations are for athermal swelling (zero heat of mixing) and use a statistically derived entropy of dilution which molecules of the penetrant and monomer units of the polymer occupy fixed sites. This expression allows for difference in size of the sites occupied by the penetrant and by the monomer units. The equations are useful for predicting penetration of polymer films by organic solvents or surface-active materials, or by water in the case of hydrophilic-expanded films of polymers. The results predicted by these equations check closely with experimental observation.

PROPERTIES OF MONOLAYERS OF ω -MONOHALOGENATED FATTY ACIDS AND ALCOHOLS ADSORBED ON WATER. Marianne K. Bern-

ett, N. L. Jarvis and W. A. Zisman (U.S. Naval Res. Lab., Wash., D.C.). *J. Phys. Chem.* **68**, 3520 (1964). Force-area, surface potential-area, and surface moment-area relations of ω -monohalogenated compounds spread as monolayers on aqueous substrates were studied at various pH values in the absence or presence of multi-valent ions. The compounds investigated were ω -monosubstituted bromo-, chloro-, and iodohexadecanoic acids, bromooctadecanoic acid, and fluoroctadecanol, along with their corresponding unsubstituted compounds. Mechanical properties of the substituted and unsubstituted alcohols were essentially the same and were not influenced by changes in pH or the presence of multivalent ions in the substrate. The halogenated hexadecanoic acids, however, gave unstable monolayers at all pH values on distilled and divalent ion-containing water at 20C; it was necessary to add tetravalent ions and lower the temperature to condense the monolayers to close-packed films. The change in surface potential of each substituted acid film was larger than that of any unsubstituted acid and showed the dipole orientation to be in the opposite direction. The vertical components of the apparent dipole moment were computed from the film potentials by use of the Helmholtz equation. Estimated values are given for the vertical components of the dipole contributed by the carbon-halogen bond. The results are discussed in terms of orientation and packing of the terminal polar groups and the resulting laterally induced polarization.

INFLUENCE OF WATER STRUCTURE ON THE SURFACE PRESSURE, SURFACE POTENTIAL AND AREA OF SOAP MONOLAYERS OF LITHIUM, SODIUM, POTASSIUM AND CALCIUM. D. F. Sears and J. H. Schulman (Tulane Univ., New Orleans, La.). *J. Phys. Chem.* **68**, 3529 (1964). Force-area and surface potential-area curves were obtained at 15C, 25C, and 37C for stearic acid on 0.1N HCl and 0.5N hydroxides of lithium, sodium, and potassium. Differences in areas per molecule at the same temperature and surface pressure on the different substrates indicated that the hydrated ion associated with carboxyl group of the stearate determined the expansion of the monolayer. Areas per molecule increased in the sequence $Li < Na < K$. Trace amounts of calcium, when added to the hydroxide substances, markedly decreased the

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expansion effected by the monovalent ions. On bicarbonate substrates of sodium and potassium, compression of the monolayer promoted removal of the respective cation. This removal allowed the area per molecule at high surface pressures to compress to the area of stearic acid on 0.1N HCl. Calculation of the surface compressional modulus indicated that the monolayers on the hydroxide substrates were liquid expanded. The effect of temperature was examined by determining the change in surface pressure with change in temperature at constant area per molecule ($\Delta \Delta \pi / \Delta T$). The values varied with temperature and with the compression of the monolayer. Stearic acid on the acid substrate gave $\Delta \Delta \pi / \Delta T$ values which increased with increasing areas per molecule, whereas on hydroxide substrates the monolayers gave decreasing values with increasing area. Within the same temperature range and for the same area per soap molecule, values for $\Delta \Delta \pi / \Delta T$ increased in the sequence $Li < Na < K$.

THE INFLUENCE OF DETERGENTS ON THE DEWETTING OF CALCIUM PALMITATE. F. van Voorst Vader and H. Dekker (Unilever Res. Lab., Vlaardingen, The Netherlands). *J. Phys. Chem.* **68**, 3556 (1964). The changes in surface composition of a solid because of replacement of one adjoining fluid by another can be derived from measurements of the contact angle between these two fluids and the solid interface and of the interfacial tension between the fluids. The changes in the solid surface are calculated from these data by means of formulas combining Young's equation with the Gibbs adsorption equations valid at the two solid-fluid interfaces considered. This method was applied to the system calcium palmitate-aqueous buffered detergent solution-air in the pH range 7.5-9.2. It was found that the calcium palmitate becomes nearly completely covered by a monolayer of acid soap on replacing the buffer solution by air in the absence of detergent. The presence of potassium N-lauroyl-N-methyltaurate, ethoxylated lauryl alcohol, or bis (methylsulfinyl) dodecane in the solution markedly reduces the increase in fatty acid adsorption during dewetting. It was found by direct titration that the presence of these detergents increased the fatty acid adsorption at the calcium palmitate-solution interface.

ULTRAFILTRATION OF NONIONIC DETERGENT SOLUTIONS. H. Schott (Res. Center, Lever Bros. Co., Edgewater, N.J.). *J. Phys. Chem.* **68**, 3612 (1964). The ultrafiltration of nonionic detergent solutions through cellophane was used as a method of purification. Since the hydrated micelles are about twice the average pore size, the ultrafiltrate consisted chiefly of water-soluble impurities and nonassociated detergent molecules. This permitted removal of carbonylated oxidation products, polyethylene glycol, and sodium chloride. Because of the low c.m.c., the loss of detergent was small. Some fractionation occurred; molecules of longer EO chains filtered through preferentially. Below the c.m.c., purified detergent passed the membrane unhindered. Above it, the detergent concentration in the ultrafiltrate increased linearly with the filtrand concentration. This line intersected the 45° line through the origin at the c.m.c., which can be determined in this manner. The increase in ultrafiltrate concentration was chiefly due to increasing monomer concentration of the filtrand although a few micelles also permeated the membrane, as was shown by the dye tagging technique. An approximately linear increase of monomer concentration with over-all detergent concentration was thus shown by ultrafiltration.

WORLD DETERGENT CONGRESS. R. W. Moncrieff. *Soap Chem. Specialties* **40** (10), 67-71, 135-8 (1964). The author outlines papers presented at the IVth International Congress on Surface Active Substances. Topics included biodegradability of anionics, detergent problem in U. S., U.K., and Germany, degradability of non-ionics, breakdown of alkyl sulfates, analytical evaluation, new non-ionic surfactants, safety of non-ionics and testing fabric whiteness.

FABRIC LAUNDRY COMPOSITIONS. R. C. Speak and P. H. McConnell (U.S. Borax & Chemical Corp.). U.S. *3,154,494*. Described is a dry, stable, multifunctional washing and bleaching laundry tablet for sequential introduction of effective amounts of fabric washing agents and laundry additives and then effective amounts of bleach into a laundry washing solution. The core of the tablet consists of oxygen or chlorine water soluble solid bleach; the coating consists of at least one water-soluble fabric washing agent selected from the class consisting of soaps, non-soap synthetic organic detergents, organic sequestering agents, and inorganic water softeners. The coating is present in an amount such that when the tablet is exposed to the laundry solution the coating requires a minimum period of time within the range of 1-5 minutes to substantially completely dissolve while the inner core remains intact until the outer coating has dissolved. The bleach is thus introduced into the washing solution with freedom from local heavy concentration for affording maximum effectiveness of the laundering agents and maximum safety for the articles to be laundered.

METHOD OF IMPROVING THE STORAGE PROPERTIES OF ALKALINE DETERGENT COMPOSITIONS. A. Mankowich (U.S.A., Sec'y. of Army). U.S. *3,154,497*. A method of preparing a non-caking, storage stable, alkaline detergent composition comprises mixing 2% of nonyl phenyl pentadecylene glycol ether in a blender with 35% of sodium metasilicate pentahydrate after which 52.5% of sodium tripolyphosphate is added and the product mixed again. Then 10.5% of sodium primary phosphate monohydrate is added and the product given a final mixing.

HEAVY DUTY LIQUID DETERGENT COMPOSITION. W. M. Bright (Lever Bros. Co.). U.S. *3,156,655*. A readily pourable, heavy duty liquid detergent composition consists of an aqueous emulsion of 1) 7-10% by weight of a synthetic organic nonionic, non-soap detergent mixture selected from the group consisting of a) 5-9% of an alkyl phenol-ethylene oxide condensate having an alkyl group containing from 9-12 carbon atoms and containing 9-15 oxyethylene units plus 1-3% of a polyoxyalkylene alkanol having the empirical formula $HO(C_2H_4O)_a(C_3H_5O)_b(C_2H_4O)_cH$ where b is an integer from 26-30 and a plus c is an integer such that the molecule contains from 0-20% of ethylene oxide and b) 5-7.5% of a tridecyloxypolyethoxyethanol having the formula $C_{13}H_{27}O(CH_2CH_2O)_9CH_2CH_2OH$ plus 1-3% of a material selected from the group consisting of a) a dodecylphenoxy polyethoxyethanol and b) a polyoxyalkylene alkanol having the empirical formula $HO(C_2H_4O)_a(C_3H_5O)_b(C_2H_4O)_cH$ where b is an integer from 26-30 and a plus c is an integer such that the molecule contains from 0-20% ethylene oxide, 2) 18-30% potassium pyrophosphate, 3) 1-3% of an alkali metal salt of an interpolymers of vinyl methyl ether and maleic anhydride, 4) 1-4% of an alkali metal soap selected from the group consisting of caprate, laurate and oleate, and 5) 2-6% of sodium xylene sulfonate. The alkali metal cations of components 3) and 4) may be either sodium or potassium.

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