tion was demonstrated to be extremely valuable for detecting fatty acids present in trace amounts. This was accomplished by separating all of the fatty acids present in the original sample so that in most cases each peak on a gas chromatogram represented only one fatty acid. The long chain saturated and polyunsaturated fatty acids present in small amounts were readily detected by overloading the GLC column and temperature programming the instrument. Except for lanolin acids, it was impossible to detect *iso* and *anteiso* fatty acids without prior urea fractionation of these acids eluted together with more prevalent monounsaturated fatty acids having one less carbon atom.

Urea fractionation does not provide a quantitative means of separating individual fatty acids. However, formation of urea complexes proceeds in a predictable manner. A more detailed knowledge of the order in which it proceeds aids in assigning the proper identity to GLC peaks, and should also aid in establishing the identity of abnormal fatty acids present in heated or used fats.

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Phase Behavior of Aqueous Systems of Monoglycerides

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Abstract

Monoglyceride-H_2O systems in the range above about 5% H_2O exhibit a varied phase behavior with a number of mesomorphic states reminiscent of those found for soap-H_2O systems. There are fluid neat, stiff and "short" viscous isotropic, and plastic or stringy middle states.

In the case of saturated monoglycerides, neat states prevail at low molecular weight as with monolaurin, but viscous isotropic and finally middle states appear at higher chain length as with monoarchidin and monobehenin.

The phase diagrams for systems of unsaturated compounds resemble those for systems of saturated compounds, with corresponding phase regions occurring at lower temperatures. The monoelaidin-H_2O system closely resembles a shifted monostearin-H_2O system, neither system showing middle. Middle phase appears in a small island for monoolein and monolinolein near 90C and 20% water.

Water dissolves negligible amounts of monoglycerides so that phases which are nearly 100% H_2O exist for substantially all systems and conditions when H_2O content is 60% or more.

Introduction

THE FORMATION OF MESOMORPHIC states in anhydrous polar long-chain compounds is well recognized (1). Much more familiar is the formation of such states, specifically neat and middle, in aqueous systems of such compounds (2). While the phenomena are more common with ionic compounds, they have been recognized in nonionic materials (3). A lengthy study of gels in aqueous monoglyceride systems has been reported (4). Except for certain crystal dispersions they were said to be "amorphous by x-ray diffraction." No mention of mesomorphic states was made.

Lawrence (5) reports the formation of liquid crystalline phase in aqueous systems of 1-monolaurin but without presenting a phase diagram.

Because of the interest in monoglycerides as familiar components of foods, their membership in the family of nonionic polar long-chain compounds, and the intriguing nature of the gel states reported, a systematic study of monoglyceride-H_2O systems was launched. It was soon discovered that these systems exhibit a variety of mesomorphic states quite analogous to those of soap-H_2O systems, and show profound variations of phase behavior with composition.

There is increasing evidence of the widespread occurrence and fundamental significance of such mesomorphic states (6) and their importance technically and biologically is not to be underestimated.

Experimental

Several 1-monoglycerides were prepared by recognized methods and purified by solvent crystallization. The following compounds, all substantially free of 2-monoglyceride and diglyceride and of high constituent fatty acid purity except for monopalmitin (a saturated monoglyceride from cottonseed oil), were studied: name [complete mp, Lit. mp (7)] — monolinolein (18.0C, 12 3C) [alpha form (-15.5C, -22.8C)]; monoolein (35.1C, 35.0C) [alpha form 9.5C, 12.5C]; monoelaidin (59.3C, 58.5C); monolaurin (62.5C, 63.0C); monomyristin (68.8C, 70.5C); monopalmitin (74.5C, 77.0C); monostearin (81.3C, 81.5C); monoarachidin (84 4C, 83.5C); monobehenin (90.5C, —); monoerucin (49.5C, 50.0C).

A simple technique was used to prepare and examine the aqueous mixes. Samples containing approximately 3 g were prepared at 5% H_2O intervals from 0 to 45% H_2O and centrifuged back and forth in 20 cc sealed tubes made from 15 mm I.D. Pyrex tubing with a 2 mm O.D. constriction in the middle of the tube.

The tubes were then observed between crossed polaroids as they were heated in 10-degree steps from 25C to 140C. Note was taken of the sample consistency by tilting the tubes. There was normally no problem of phase identification. In a few cases, tubes were opened and phase identification was made microscopically (8). For microscopic phase examination above room temperature, a heating block was used and care was taken that observations were sufficiently rapid to avoid serious water loss. In the tubes, phase transformations were quite reversible although there was some "hysteresis," particularly in moving to lower temperatures.

The results of the observations are recorded in Figure 1. These graphs were obtained by drawing phase boundaries between adjacent points showing phase difference on a plot of temperature vs. H_2O content.

Discussion

The diagrams of Figure 1 immediately suggest the more familar phase diagrams of soap-H_2O systems. Similar neat and middle structures occur and they are readily identifiable by microscope. There are differences from the soap diagrams which are striking, however, and a most interesting sequence of phase behavior occurs with change in composition.

Water is unable to dissolve more than a small fraction of a percent of monoglyceride. However, above and near their melting points monoglycerides incorporate (in various mesomorphic phases) 20% and more, even up to 50% of H_2O.

Water lowers the melting point of crystalline monoglyceride, but not far before a neat phase is encountered. Neat is the only mesomorphic phase of monolaurin and it occupies a large proportion of the phase diagram. With monomyristin, a new state enters the picture. This is the gel state of Brokaw (4) and is probably related to the "cubic" state of Luzatti (9). To avoid commitment to structure type, it is here called simply "viscous isotropic." It seems to be a separate phase readily distinguishable from "aqueous isotropic" (> 99% H_2O) on one hand and "oily isotropic" on the other. Unlike these states, "viscous isotropic" appears to have a considerable amount of structure as evidenced by its stiff, rather "short" consistency and by strong low-angle diffraction lines. Changes of state from viscous to fluid isotropic appear quite sharp. No attempt has been made to represent in Figure 1 the two-phase region theoretically called for between fluid isotropic and viscous isotropic.

With monopalmitin the neat area has shrunk considerably and viscous isotropic has grown. The upper limit of neat still hovers around 110C; so also with monostearin where viscous isotropic covers nearly as great a region as neat.

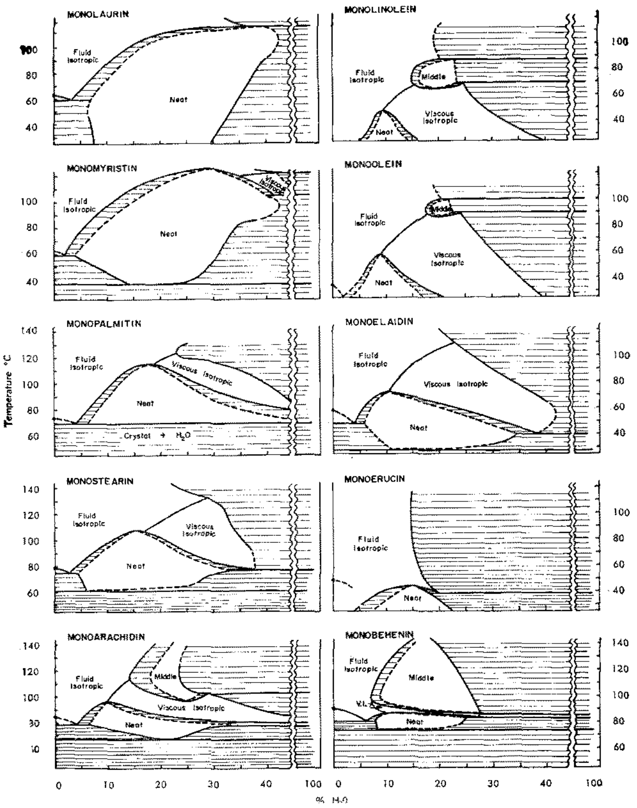

FIG. 1. Aqueous monoglyceride systems.

Then with monoarachidin there is the striking advent of middle which with monobehenin occupies far more of the phase diagram than neat or the small "tongue" of viscous isotropic.

Neat is recognized to be a lamellar structure. Luzatti (10) has proposed a structure comprising close-packed infinite cylinders for middle phase. X-ray diffraction, by showing long-spacings in the ratio $1:\sqrt{3}:\sqrt{4}$, supports this concept for middle phase of monoglyceride-H_2O systems. Although Luzatti (9) has proposed a "cubic" structure for isotropic states of potassium soap systems, it is premature to propose a structure type for viscous isotropic of monoglyceride systems, and whether its isotropy is due to small particle size or basically isotropic architecture is not known.

If middle has a cylindrical structure, it is interesting to wonder why monoarachidin can show it but monostearin cannot. The longer hydrocarbon tails of arachidin would seem to be involved. More nonpolar hydrocarbon-type matter with monostearin might then produce middle. This is indeed the case, for 10% of tristearin added to an 80% monostearin-20% H_2O mix yielded a middle phase at 100C.

With the unsaturated monoglycerides, the behavior is different and no less interesting. The diagram of the *trans*-unsaturated monoelaidin is much like that of monostearin but with the temperature scale shifted some 30C downward. Monoolein shows a further drop in the neat region and an outcropping of middle phase in an area near 100C. Monolinolein shows corresponding behavior at slightly lower temperatures and with expanded middle region. (Similar is the behavior of Myverol 18–85 of commerce.)

With the strong middle-forming tendency shown with great chain length and with unsaturation it would seem that monoerucin and H_2O should be particularly apt to form middle phase, but such is not the case. Neither middle nor viscous isotropic was observed. The salient features of the binary diagram are the 50C mp of monoerucin, a maximum neat temperature of 45C, and a liquid immiscibility line for melted monoerucin and H_2O running between 15 and 20% H_2O. The combination of high degree of immiscibility with H_2O due to chain length and chain mobility due to unsaturation perhaps militates against middle phase with monoerucin.

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High Voltage Electrical Discharge Reactions of Fats and Related Compounds

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Abstract

Studies are reported on the modification of fats and related compounds by electrical discharge reactions. Several types of fatty compounds were subjected to silent electrical discharge of the ozonizer type of 15,000 volts AC and analyzed by gas-liquid and thin-layer chromatography, infrared spectral and elemental analyses.

Evidence was obtained for a free radical reaction in accordance with the general theory of discharge reactions.

The major products of the reaction were polymers of varying degrees of complexity. Short-chain hydrocarbons were also detected. Hydrogenations via the formation of hydrogen radicals was demonstrated; branching via long-chain radical interreactions was also indicated. The incorporation of nitrogen and oxygen into polymeric products was demonstrated when the reaction was carried out in the presence of these gases.

Reaction mechanisms are proposed to explain the products formed under various conditions.

Introduction

DISCHARGE REACTIONS have been investigated extensively and comprehensive reviews of the subject have been published by Glockler and Lind (1), Thomas et al. (2) and Steacie (3). The most common large scale applications of discharge reactions are those of the ozone generator type (1,4) and the Cottrell precipitator (5). The latter has been used mainly for the precipitation and collection of harmful industrial smokes. Discharge reactions have been employed for the synthesis of various organic compounds (6–8), gasolenes, acetylene and lubricants (2).

In the present study the application of discharge reactions to hexadecane, methyl oleate and related compounds were investigated to define basic mechanisms and products of the reaction with fats.

Experimental

Electrical Discharge Apparatus

A schematic diagram of the apparatus for the discharge reactions is shown in Figure 1. The outer electrode of the apparatus is an aluminum sheet wrapped around the outer cylinder. The inner electrode is a copper wire, sealed in glass. This arrangement prevents contact of the sample with metal and gives a silent discharge. Alternating current (AC) high voltage was supplied from a 60 cycle, 30 ma transformer (Acme Electric Co., Chicago) with a voltage range up to 15 kv. The voltage was regulated by means of a "Variac" variable transformer connected into the primary circuit. However, unless specified differently 15 kv was employed.

The reaction tube may be loaded with sample in several ways. It may be passed into the electrical field in the form of an aerosol in helium or nitrogen, for example, or it may be applied directly on the electrode if it is a liquid or in solution if it is a solid. In the latter case the solvent evaporates and leaves the sample in the electric field as a more-less uniform layer.

Materials

Grade A Helium and "Dry-High Purity Nitrogen" purchased from the National Welding Supply, Albert Lea, Minnesota, were used as the medium for the discharge reactions.

Hexadecane (99%, olefin free) was obtained from Matheson Coleman and Bell Company, Cincinnati, Ohio. Methyl oleate, stearic acid, methyl linoleate, methyl palmitate, palmityl alcohol, methyl laurate, capryl alcohol, caprylic and methyl arachidonate were obtained from The Hormel Institute, Austin, Minnesota. All of these compounds were also greater than 99% purity except methyl arachidonate. This preparation was 95% pure; the impurities consisted of other polyunsaturated esters of lower unsaturation and a small amount of eicosapentaenoate.

Methods

Gas-liquid chromatography of methyl esters of molecular weights of the order of the compounds listed