discussions. They wish to thank Mr. K. Momoki for taking some of the powder and single crystal photographs. We are grateful to the Research Corporation for funds with which we obtained the precession camera used in this research.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, THE PROCTER & GAMBLE COMPANY, MIAMI VALLEY LABORATORIES]

Acetin Fats. III. The Binary Systems ASA–SAA and APA–PAA, Mixed Symmetrical and Unsymmetrical Stearoyl Diacetins and Palmitoyl Diacetins

BY E. S. LUTTON

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ASA (2-stearoyldiacetin) and APA (2-palmitoyldiacetin) occur in metastable subalpha and alpha forms and stable beta prime-like forms (alpha being questionable for the palmitic compound). Mixtures of the symmetrical and unsymmetrical isomers in the binary systems ASA–SAA and APA–PAA show greatly increased alpha stability over that of the pure compounds. Melting points of mixtures in the alpha form lie in a straight line joining those of the components. In the composition range 30–90% of unsymmetrical isomer, the alpha phase shows no transformation in 2 months, hence a high degree of stability is implied for this phase of a binary mix of saturated diacetins prepared via random interesterification (2/3 unsymmetrical.)

Waxy forms of acetylated monoglycerides, specifically of 1-stearoyldiacetin (SAA) and 1-palmitoyldiacetin (PAA) have been of interest for the high degree of stability of these metastable forms.[1–6] In practical methods of preparation, mixtures of symmetrical and unsymmetrical compounds may occur and some comparison of mixtures with individual isomers has been made.[5] Pure ASA and APA previously have not been available, however.

Experimental

ASA and APA were made by acetylation, respectively, of 2-monostearin and 2-monopalmitin, prepared as previously reported.[7] SAA and PAA were prepared by familiar methods.[3]

Approximately 0.2 g. mixes (20, 40, 50, 60 and 80% symmetrical) of the symmetrical and unsymmetrical isomers were weighed up and carefully stirred in both solid and liquid states. Capillary samples were prepared and m.p.'s determined as previously described[8] after melting, chilling and appropriately storing. The so-called rapid complete m.p., normally referring to alpha, was determined on fresh samples. The regular complete m.p. was performed on samples stored 2 months below the minimum alpha m.p. of the binary system, *i.e.*, at 28° for ASA–SAA and 15° for APA–PAA. The results appear in Fig. 1.

X-Ray diffraction data were obtained on metastable (subalpha and alpha, if observable) and stable forms of ASA and APA and on the apparently stable subalpha and alpha forms of 50% mixes of ASA and SAA and of APA and PAA. Flat-film diffraction patterns were obtained with a General Electric XRD-1 unit employing nickel-filtered Cu K$_\alpha$ radiation and a 0.025 in. pinhole system. Sample-to-film distance was either 5 or 10 cm. Low-temperature phases were kept in a small cold-block during exposure, subalpha at 0° except for APA at −20°; alpha at 15° for palmitoyl compositions and 25° for stearoyl compositions.

Thermal and X-ray diffraction data are listed in the following order:

Composition.—Polymorphic state: m.p. °C.; long spacing, L.S. (in Å.); short spacing, S.S. (in Å.). Relative intensities of diffraction lines are indicated by (VS) = very strong, (S) = strong, (M) = medium and (W) = weak.

ASA. Subalpha: no m.p.; L.S. 36.7; S.S. 4.20(S), 3.86(M). Alpha: 29.0°; L.S. 36.0; S.S. 4.16(S); stable: 37.0°; L.S. 30.0; S.S. 4.71(M), 4.21(S), 4.06(S), 3.86(M).

APA. Subalpha: no m.p. (?); L.S. 34.0; S.S. 4.20(S), 3.82(M). Alpha: 15.7° (presumably alpha); L.S. —; S.S.—; stable: 37.0°; L.S. 27.5; S.S. 4.68(M−), 4.42(M−), 4.20(S), 4.04(S+), 3.85(M).

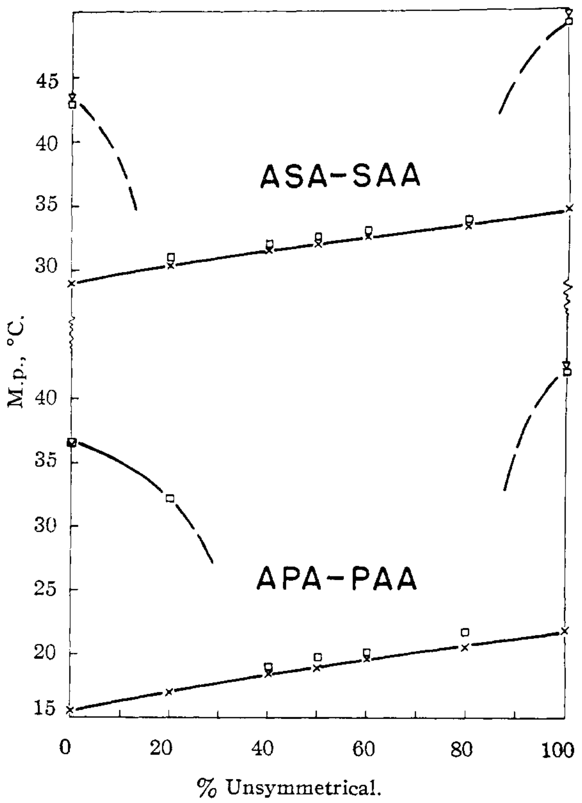

Fig. 1.—M.p.'s of binary mixtures of ASA–SAA and APA–PAA: ×, rapid complete m.p.; □, regular complete m.p. (ASA–SAA stored 2 mon., 28°; APA–PAA stored 2 mon., 15°); ∇, solvent crystals, m.p.

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(1) F. L. Jackson (to The Procter & Gamble Co.), U. S. Patent 2,615,159 (1952).

(2) F. J. Baur (to The Procter & Gamble Co.), U. S. Patent 2,615,160 (1952).

(3) F. L. Jackson and E. S. Lutton, THIS JOURNAL, **74**, 4827 (1952).

(4) R. O. Feuge, E. J. Vicknair and N. V. Lovegren, *J. Am. Oil Chem. Soc.*, **30**, 283 (1953).

(5) F. J. Baur, *ibid.*, **31**, 196 (1954).

(6) R. O. Feuge, E. J. Vicknair and K. S. Markley (to the Secretary of Agriculture), U. S. Patent 2,745,749 (1956).

(7) J. B. Martin, THIS JOURNAL, **75**, 5482 (1953).

(8) E. S. Lutton, F. L. Jackson and O. T. Quimby, *ibid.*, **70**, 2441 (1948).

50-50 ASA–SAA. Subalpha: no m.p.; L.S. 37.1; S.S.. 4.21(S), 3.79(M). Alpha: 31.9°; L.S. 36.8; S,S. 4.15(S).

50-50 APA–PAA. Subalpha: no m.p.; L.S. 34.2; S.S. 4.19(S), 3.90(M). Alpha: 18.9°; L.S. 33.7; S.S. 4.13(S).

Results and Discussion

The alpha m.p.'s (rapid complete m.p.) of mixtures lie on straight lines connecting the m.p.'s of the components. By storage, the components were transformed to the stable form as was the 20% unsymmetrical mix of APA–PAA. In all other mixtures, storage for 2 months effected no transformation. There is a possibility that the alpha form is actually thermodynamically stable in some range of composition. Such true alpha stability would occur if the (unrealized) equilibrium curves, dropping from the stable-form m.p.'s of the components, fall sufficiently steeply on addition of second component to intersect the nearly linear alpha m.p. curve before they intersect each other.

In any case, in the region of $^2/_3$ unsymmetrical isomer, which is the proportion to be expected from the interesterification method of preparing saturated diacetins,[2] it is expected that the waxy alpha form would remain indefinitely stable.

It is a matter of interest that the m.p.'s of symmetrical are lower than those of unsymmetrical isomers as is the case with monoglycerides but not with di- and more familiar triglycerides.

The diffraction data for subalpha and alpha forms of the 50/50 mixes, both short and long spacings, are close to and for the most part intermediate between those of the components. It is of interest to note again slightly shorter long spacings for alpha than subalpha. The fact that the short spacings of the subalpha form of the palmitoyl mixture are nearer together at 0° than those of the stearoyl mixture suggests a closer approach to the alpha configuration as is reasonable to expect for the lower melting palmitoyl mixture.

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CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Ultraviolet Absorption Spectra of Aromatic Compounds Adsorbed on Silicic Acid

BY MELVIN ROBIN[1] AND KENNETH N. TRUEBLOOD

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Ultraviolet absorption spectra of mono- and di-substituted benzene derivatives adsorbed on activated silicic acid have been measured by suspending the silicic acid in an inert liquid of the same refractive index and recording the transmission spectrum of a 0.3-cm. layer of the slurry. The spectra are interpreted in terms of the effect of the interactions between the adsorbent and the adsorbate on the electronic states of the adsorbate.

The light absorbing properties of many compounds frequently change markedly when the compounds pass from the unadsorbed to the adsorbed state. Thus, for example, when a pale yellow compound such as N,N-diethyl-4-nitroaniline is adsorbed onto silicic acid from a non-polar solvent it often acquires a golden yellow color, and a compound which is normally yellow-orange may appear orange-red when adsorbed. These color changes result from perturbations of the electronic states of the molecule upon adsorption. Measurements of absorption spectra of molecules in the adsorbed state thus can provide information which in favorable circumstances may permit estimation of the extent of the electronic perturbation on adsorption and determination of the nature of the electronic states involved in the transition, and may also provide clues about the orientation of the molecule on the surface and the nature of the adsorption forces.

A simple and practical method for studying the spectra of compounds adsorbed on silicic acid was first suggested by an observation made by Trappe,[2] who reported that a column of silicic acid became transparent when it was wet with chloroform and no pressure was applied. The close similarity in the refractive indices of chloroform (1.446) and silicic acid (*ca.* 1.420) resulted in a minimum of light scattering and refraction arising from optical inhomogeneities in the slurry. Slurries made from silicic acid and cyclohexane, which has a refractive index (1.426) closer to that of silicic acid than does chloroform, are sufficiently transparent in 0.3 cm. layers for spectrophotometric measurements at wave lengths above about 235 mμ. The lower limit on the wave length region available for investigation in the cyclohexane–silicic acid system is set by the divergence of the refractive indices for these two compounds in this region. Their refractive dispersions are sufficiently different that the transparency of the slurries decreases sharply at wave lengths below 260 mμ.[3]

The unhindered acidic proton of the silanol group of silicic acid appears to be ideal for hydrogen bonding and, in fact, the compounds most strongly adsorbed are those which are capable of acting as proton acceptors in hydrogen bonds.[4] In all of the adsorbent–adsorbate complexes studied here, except those formed by silicic acid with neutral compounds such as benzene and triphenylamine, it is believed that the silicic acid is acting as a proton donor in a hydrogen bond to some center of high electron density in the adsorbed molecule.

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(1) Department of Chemistry, University of Washington, Seattle, Washington.

(2) W. Trappe, *Biochem. Z.*, **305**, 150 (1940).

(3) This is essentially the well-known Christiansen-filter effect; see, *e.g.*, W. C. Price and K. S. Tetlow, *J. Chem. Phys.*, **16**, 1157 (1948).

(4) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955, p. 59.