Binary Systems of Fatty Esters: Ethyl Stearate–Methyl Stearate

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THE HITHERTO unreported binary system ethyl stearate–methyl stearate involves components of rather different polymorphic behavior. The character of the polymorphism of fatty ethyl and methyl esters varies with chain length and is different for acyl chains containing odd and even numbers of carbons. Ethyl palmitate (EP) and ethyl stearate (ES) are very similar in behavior, however, as are methyl palmitate (MP) and methyl stearate (MS). The two ethyl esters have two forms—metastable α, translucent, fleeting and lower melting by 3° to 4° C.—and stable β, opaque (when in small crystals) and higher melting; only for β have diffraction data been reported, and these indicate tilted forms of single-chain length structure (*2, 5, 6*). The two methyl esters also have two forms—melting very closely together, about 1° C. apart—having very similar diffraction patterns, with long spacings and other data reported only for the higher-melting forms. From powder data, these appear to be of double-chain length structure (*2, 5, 6*) but upon detailed examination prove to be of quadruple-chain length (*1*). Ethyl and methyl margarate both exhibit single-chain length forms (*5*) probably both of vertical α type (although the methyl margarate phase has been said to have a tilt of 75°).

In the binary system EP-ES, mixture stabilizes the α states (*6*) and in MP-MS, it makes such states possible (*3*); from the course of the melting point curves, the alpha form appears to be thermodynamically stable at the melting point of certain mixtures.

In a re-examination of EP-ES and MP-MS, earlier thermal data were confirmed and hitherto unreported diffraction evidence supported the existence of stable α forms at the melting point of intermediate compositions.

Table I. Thermal Data for Components of Ester Systems

Compounds	Found M.p., ° C.[b]	Found S.p.,[a] C.	Previously Reported (2) M.p., ° C.	Previously Reported (2) S.p.,[a] ° C.
Ethyl palmitate	24.0	20.0	24.4	19.4
Ethyl stearate	34.0	31.1	33.9	31.0_5
Methyl palmitate	30.7	28.8	30.5_5	29.2
Methyl stearate	40.0	37.6	39.1	37.8_5

[a] Setting point = S.p.
[b] Solvent-crystallized.

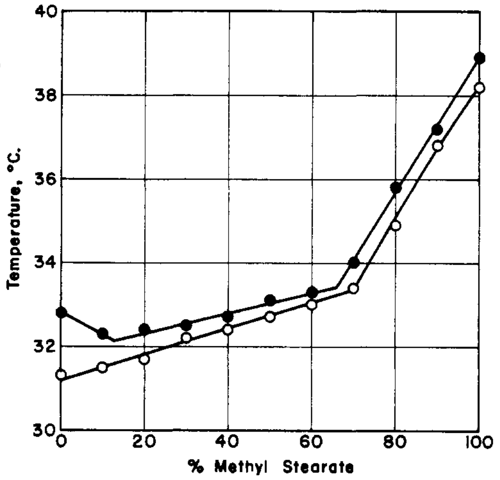

Figure 1. Melting points of binary system ethyl stearate–methyl stearate

● Chilled 1 day at 27° C., heated at 0.5° C. per minute
○ Rapid, complete melting point (*4*)

In a comparable examination of the previously unreported system ES-MS, similar existence of stable alpha forms at intermediate compositions was observed from both thermal and diffraction data.

The components used in these studies showed thermal properties comparable to the best previously reported samples as indicated in Table I.

Thermal studies were made at 0, 20, 50, 80, and 100% levels for the previously studied EP-ES and MP-MS systems and at each 10% level for the ES-MS system. Rapid complete melting points (*4*) were obtained and also ordinary complete melting points at a heating rate of 0.5° C. per minute, after melting, chilling, and storage under the following conditions: 1 day at 21° C. for EP-ES and for MP-MS and 1 day at 27° C. for ES-MS. The EP-ES and MP-MS data, which were in good agreement with earlier data, are shown in Table II. The data on the new system ES-MS appear in Figure 1.

Table II. Thermal Data on Previously Studied Ester Systems

System	Stearate, % 0	20	50	80	100
EP-ES, rapid complete m.p.	19.9	22.4	25.8	29.1	31.1
Regular, complete m.p.	24.0	22.6	26.2	31.1	34.0
MP-MS, rapid complete m.p.	29.4	24.5	28.0	31.4	38.5
Regular, complete m.p.	29.4	25.0	28.0	34.9	38.5

Table III. Diffraction Data on Various Ester Systems

(Long spacings in A.)

System	X-ray, at ° C.	Component 2, % 0	20	50 A.	80	100
EP-ES melt, chill 0° C.	0	23.0(23.0)[2]	24.8?	26.3(α?)	25.8	25.5(25.5)[2]
	15	23.4	23.8, 26.8α	27.4α	25.0	25.6
EP-ES melt, chill 0° C., 1 day 21° C.	21	23.0	26.5α	26.8α	25.0	25.5
MP-MS melt, chill 0° C.	0	43.2(43.2)[2]	44.6	45.8	46.7	47.5(47.8)[2]
MP-MS melt, chill 0° C., 1 day 21° C.	21	43.3	44.2	26.1α	46.8	47.6
MP-MS melt, chill 0° C.	25			26.1α		
ES-MS melt, chill 0° C.	0	25.5(25.5)[2]	25.2	24.4	24.1	47.5(47.8)[2]
ES-MS melt, chill 0° C., 1 day 21° C.	21	25.5	25.2	24.6	23.9	47.6
ES-MS melt, chill 0° C., 1 day 27° C.	27	25.1		27.7α		47

X-ray data were obtained on 0, 20, 50, 80, and 100% mixes of each system in 1-mm. borosilicate glass capillaries. An XRD unit (General Electric Co.) with nickel-filtered Cu$K\alpha$ radiation was used with 0.025-inch pinhole system and a sample-to-film-distance of 5 or 10 cm. After melting, cooling (and storage), patterns were taken at appropriate temperatures as indicated in Table III.

It is clear from thermal and diffraction data for all three systems, EP-ES, MP-MS, and ES-MS, that there is an intermediate composition region of stable α form at the melting point. At lower temperatures, the α form gives way to tilted forms. In the ES-MS case, as well as in the others, the stable α region is obviously a region of solid solution of ES and MS in the α form, although ES and MS are different in polymorphic behavior.

From the melting level, it may be inferred that the form from melt obtained for pure MS is the lower-melting polymorph. Presumably, there is a real phase difference not revealed by powder data, although indicated by more powerful technique (*1*).

The first order spacings are not easily observed for mixed methyl esters, but presumably they indicate double-chain length structures. There remains the problem of apparent solid solution in the non-alpha states in the ES-MS system when ES crystals are single-chain length and MS are double (or quadruple).

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Formation of Gaseous Detonation Waves

A Comparison of the Knallgas-Steam and Heavy Knallgas–Heavy Water Mixtures

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DETONATION in saturated knallgas ($2H_2 + O_2$)-steam mixtures has been investigated very completely. The effects of mode of ignition, reactor diameter, reactor length, and initial mixture density on the formation of detonation were previously considered and reported (*1, 6*). Since deuterium oxide (heavy water) is often used in atomic reactors, the heavy knallgas ($2D_2 + O_2$)-heavy water system has also been studied. The experimental procedure and the method of analysis and interpretation of these data were identical to those for the knallgas-steam mixtures (*6*). Presented are data for the formation of detonation in the heavy knallgas–heavy water system at 100° C. utilizing spark ignition (360 millijoules) in a 1-inch i.d. reactor of 13-foot length. Comparisons of these data to knallgas-steam data at identical conditions are presented.

RESULTS AND DISCUSSION

Figures 1 and 2 present the results of this study. From them comparisons may be drawn between the knallgas-steam and the heavy knallgas–heavy water media. In Figure 1 ideal detonation parameters of heavy knallgas-heavy water (*7*) from Table I are included for comparison with the measured reaction properties. The theoretical reflected detonation pressures for heavy knallgas–heavy water (Figure 1) were only approximately 10% lower than those for the knallgas-steam system while the measured reaction properties for the two systems differed markedly. In the predetonation region, reaction pressures for the heavy hydrogen system were significantly lower than those for the knallgas-steam system at comparable conditions and composition. Reaction characteristics of these mixtures indicates that the no reaction limit was 19 mole % heavy knallgas for the former mixture as compared to 6 mole % knallgas for the latter mixture. In a richer initial composition region (Figure 1), the transition from a combustion type mechanism of reaction to a shock-propagated reaction occurred at a much higher composition for the heavy hydrogen system. The induction composition [first intersection of measured and theoretical curves (*6*)] was 62 mole % heavy knallgas and 48 mole % knallgas, respectively.

In addition, knallgas-steam showed a much broader region of mixture compositions between the induction composition and the point the measured curve recrossed the theoretical detonation curve, signifying stable wave formation (*6*). Stable detonation waves occurred at 67 mole % knallgas and 72 mole % heavy knallgas.

In Figure 2, where percentage of combustible-reacted curve is plotted *vs.* the initial mixture composition, an abrupt rise in percentage of reacted curves occurred at approximately 53 mole % heavy knallgas and 45 mole % knallgas. These data substantiate the fact that shock-propagated reactions are more difficult to form in the heavy hydrogen system.

The marked differences which occurred in the explosive range might be explained by the fact that the kinetics of the deuterium-oxygen reaction is slower than the hydrogen-oxygen reaction (*3-5*). Experimental and theoretical properties of dry knallgas and heavy knallgas were compared recently (*2*). Even though the measured stable detonation pressures for heavy knallgas as reported by this investigation were subideal at low pressures (less than 2 to 3 atm.), in general the two dry hydrogen systems did not show the significant differences as reported for the two saturated systems. The heavy knallgas-heavy water system exhibits: a higher no-reaction limit, much lower pressure in the predetonation region, a higher induction