Physical Properties of Fatty Acids

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SUMMARY

The chemical composition, molecular configuration, and crystal structure of fatty acid molecules contribute to the more than twenty distinct physical properties associated with this class of organic compounds. This discussion will be limited to only a few of these fatty acid properties and will include melting and solidification phenomena, vapor pressure-boiling point relationships and solubility behavior of fatty acids.

A graph of the melting points of fatty acids versus carbon chain length for both saturated and unsaturated, even- and odd-numbered fatty acids illustrates even-numbered acids melt proportionately higher than adjacent odd-numbered acids. Likewise, unsaturation has a pronounced lowering effect on melting points. In isomeric pairs, the *trans* form of the acid (Fig. 1) will show higher melting. Graphs of the binary system of palmitic-stearic acid mixtures clearly indicate eutectic formation at ca. 72 mol % of the palmitic component (Fig. 2), and this behavior is typical for pairs of saturated acids which differ by 2 carbons in chain length. Binary pairs of unsaturated fatty acids, particularly oleic-linoleic and oleic-linolenic acids yield similar eutectic formations, but the linoleic-linolenic system shows only a continuous series of solid solutions. The binary fatty acid systems oleic-palmitic and oleic-stearic (Fig. 3), and elaidic-stearic give simple eutectic curves. Methyl esters of fatty acids have melting behavior similar to the patterns exhibited by the fatty acids. The binary phase diagram for methyl palmitate-methyl oleate as defined by Differential Scanning Calorimetry indicates eutectic formation at 5% palmitate concentration.

Vapor pressure is an important physical property of fatty acids since the relationship between vapor pressure and boiling point is utilized in commercial distillation practice. Vapor pressure for fatty acids shows deviation from ideal behavior making it difficult to separate acids differing by only two carbons. However, caprylic, capric, lauric, myristic, palmitic and stearic acids have been prepared commercially by distillation with purities of 90%. Methyl esters of fatty acids behave almost ideally, and their boiling points average 30 degrees lower than their fatty acid homologs. Methyl esters give excellent separation of saturated fatty acid mixtures, but the separation of methyl oleate-methyl stearate and methyl oleate-methyl linoleate mixtures does not appear practical.

The solubility behavior of fatty acids in organic solvents is also of considerable industrial importance. Solubility ratios for binary mixtures show the mutual solubility effect of one acid on another and the difficulty of obtaining a pure component by crystallization. Temperature-solubility curves for binary fatty acid mixtures indicate the melting point to be the chief factor governing solubility. Solubility relationships are not appreciably changed in solvents of increasing polarity, i.e., benzene (nonpolar), chloroform, ethyl acetate and acetone (polar).

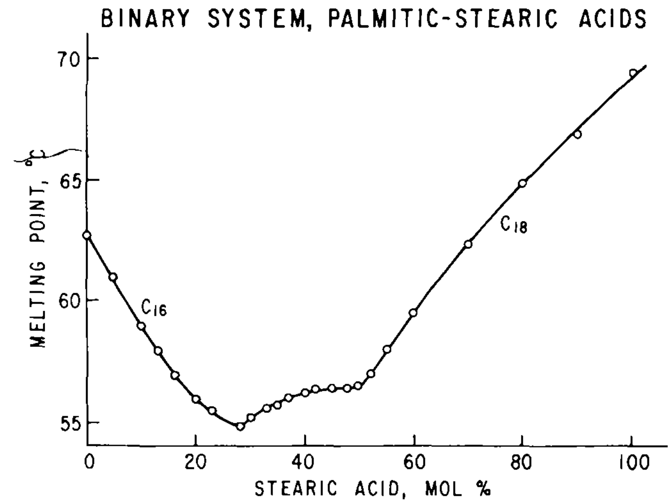

FIG. 2. Binary systems, palmitic-stearic acids.

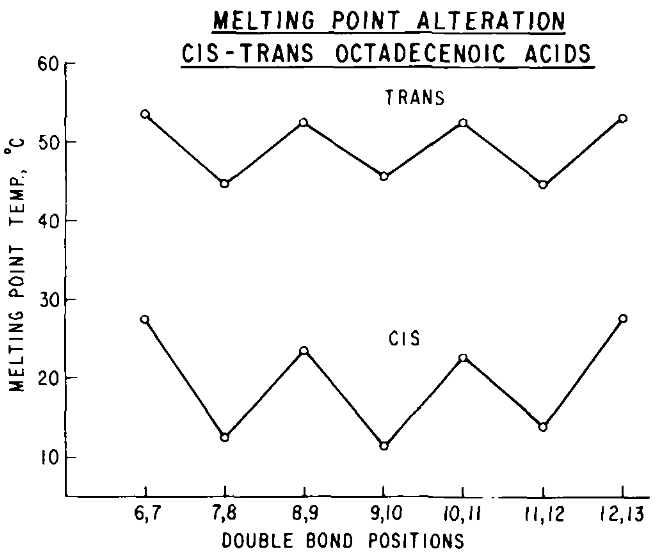

FIG. 1. Melting point alteration *cis-trans* octadecenoic acids.

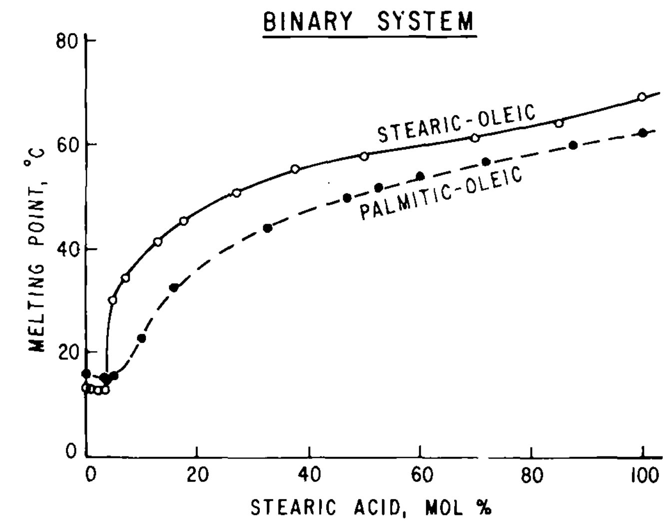

FIG. 3. Binary system.