Study of Binary Systems of Long Chain Alcohols and Acids

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ABSTRACT

Several binary phase diagrams of primary alcohol-secondary alcohol, secondary alcohol-secondary alcohol, odd-even fatty acids, and fatty acid-alcohol systems have been worked out. In many of these systems, freezing point curves give rise to eutectics. In some cases, molecular compound formation was detected; and in one system, dodecanoic acid-tridecanoic acid, the freezing points show solid solution type of curve with a minimum temperature. The solid state transition points of the pure compounds are found, invariably, to become lower when the second component is added. The freezing and transition point behaviors have been explained in terms of miscibility of the components in the solid state.

INTRODUCTION

A study of binary systems of long chain normal alcohol-secondary alcohol and secondary alcohol-secondary alcohol systems seemingly has not been undertaken. Although the binary systems of fatty acids have been studied (1) extensively, these studies are only limited to the freezing point (fp) behaviors; interactions among lower temperature crystal forms have not been investigated. It also is not known how the long chain alcohols interact with fatty acids. The present work was performed to achieve an understanding of these matters. This article includes information on binary freezing, as well as a discussion of the transition point behaviors of the systems studied.

EXPERIMENTAL PROCEDURES

Fluka purissimum grade hexadecanol was distilled under reduced pressure, and fraction boiling of 122-124 C under 0.8 mm pressure was used (fp 48.6 C; lit. fp 49.25 C [2]). Dihexyl carbinol, dinonyl carbinol, and ditridecyl carbinol were prepared from dihexyl ketone, dinonyl ketone, and myristone by Meerwein-Ponndorf-Verley reduction using aluminium isopropoxide (3,4). Dihexyl ketone and dinonyl ketone were Fluka purum grade, while myristone was Fluka practical grade. The fp of dihexyl carbinol, dinonyl carbinol, and ditridecyl carbinol were 40.6 C (lit. melting point [mp]: 40.0-40.5 C [5]), 62.8 C, and 80.7 C, respectively. Dodecanoic acid was Fluka purissimum grade once recrystallized from 40-60 petroleum ether, fp 43.4 C (lit. fp 43.9 C [6]). Tridecanoic acid was Koch-Light pure grade twice recrystallized from 40-60 petroleum ether, fp 41.3 C (lit. fp 41.5 C [7]). Pentadecanoic acid was Fluka purissimum grade twice recrystallized from 40-60 petroleum ether, fp 52.1 C (lit. fp 52.3 C [7]). Palmitic acid was Fluka purissimum grade once recrystallized from 40-60 petroleum ether, fp 61.4 C (lit. fp 62.6 C [8]).

The samples were made up by accurately weighing out one of the components into a test tube (7.5 cm long with internal diameter 0.85 cm) and then adding the weighed amount of the other component. The mixture, which occupied ca. 10-15% of the total volume of the test tube then was heated to melting, shaken, and subsequently brought to room temperature. The freezing and transition points were measured by slowly cooling (at the rate of ca. 0.3 C/min) the materials and recording the time-temperature curves. The temperature recordings were performed by a chromel-alumel thermocouple connected through a direct current amplifier to a potentiometric recorder. The thermocouple was protected by a glass sheath, and the junction of the thermocouple stood about in the middle of the sample during experiment (Fig. 1). The time-temperature curves showed flats at freezing and transition points. In general, any additional break in the cooling curve, other than fp, has been termed a transition point in this article. The reproducibility of the fp was better than the transition points. The latter were reproducible within 0.3 C.

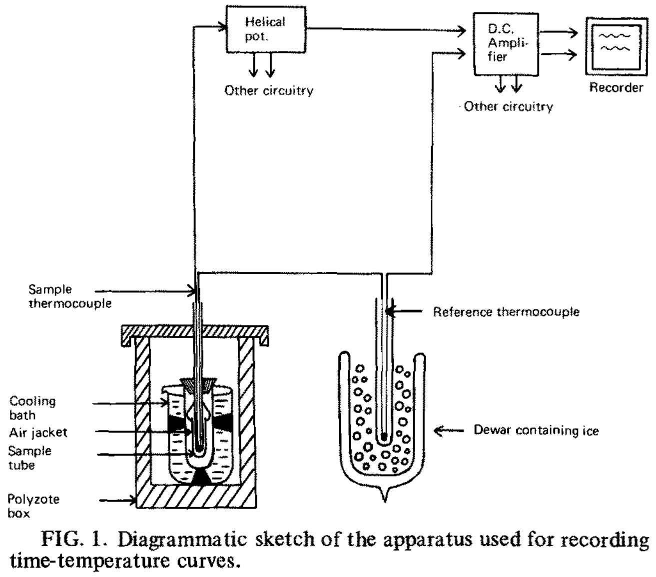

FIG. 1. Diagrammatic sketch of the apparatus used for recording time-temperature curves.

RESULTS

Primary Alcohol-Secondary Alcohol Systems

Hexadecanol-dinonyl carbinol: Figure 2 shows the phase diagram of hexadecanol-dinonyl carbinol. The fp curves form a eutectic at 24.63 mole percent dinonyl carbinol at 41.8 C. The transition point of hexadecanol is lowered by

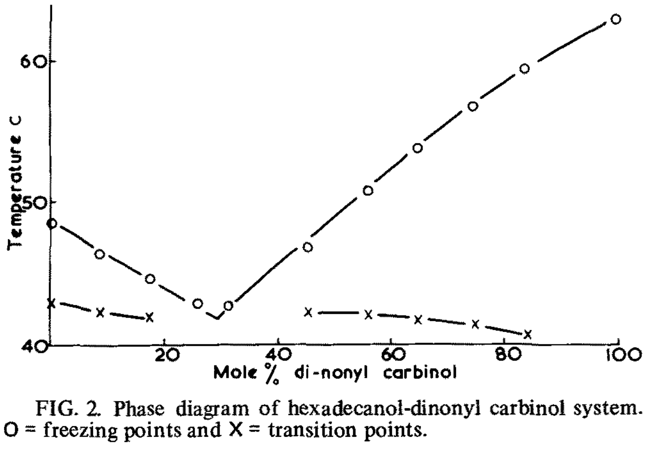

FIG. 2. Phase diagram of hexadecanol-dinonyl carbinol system. O = freezing points and X = transition points.

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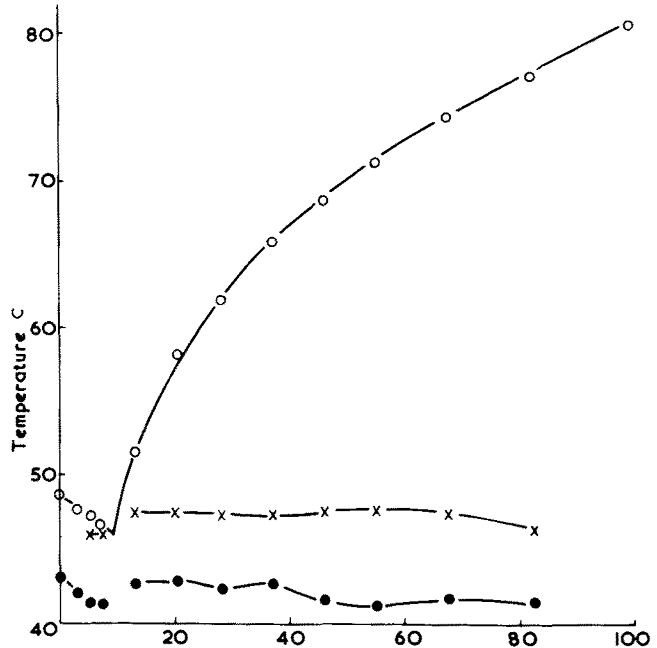

FIG. 3. Phase diagram of hexadecanol-ditridecyl carbinol system. O = freezing points and X and ● = transition points.

dinonyl carbinol by only 1.1°. On the other side of the eutectic, toward the dinonyl carbinol axis, some transitions occur below the fp. These transitions may be either the eutectic temperatures, since they are so close to the eutectic point, or they may be the temperatures at which some metastable crystals are transforming.

Hexadecanol-ditridecyl carbinol system: Figure 3 shows the phase diagram of hexadecanol-ditridecyl carbinol. The fp give rise to a simple eutectic system, the eutectic occurring at ca. 10% ditridecyl carbinol at 45.8 C. The transition point of hexadecanol is, at first, lowered rapidly by ditridecyl carbinol; but, after 5% of the latter, very little lowering of transition point occurs. On the hexadecanol side of the eutectic, before the transition point of hexadecanol is reached, an additional higher temperature break occurs in the cooling curve in the 5.35% and 7% ditridecyl carbinol samples. This behavior also is noticed on the other side of the eutectic where two solid state transition points run almost parallel until they disappear after 82.72% ditridecyl carbinol. Of these two transitions, the higher temperature ones, represented by crosses in the phase diagram, may be the eutectic temperatures because of their closeness to the eutectic point. However, the lower temperature transitions, represented by the solid circles toward the ditridecyl carbinol axis of the eutectic, are the temperatures at which some metastable crystals probably are transforming. Above these temperatures, the samples looked translucent; but below they turned opaque.

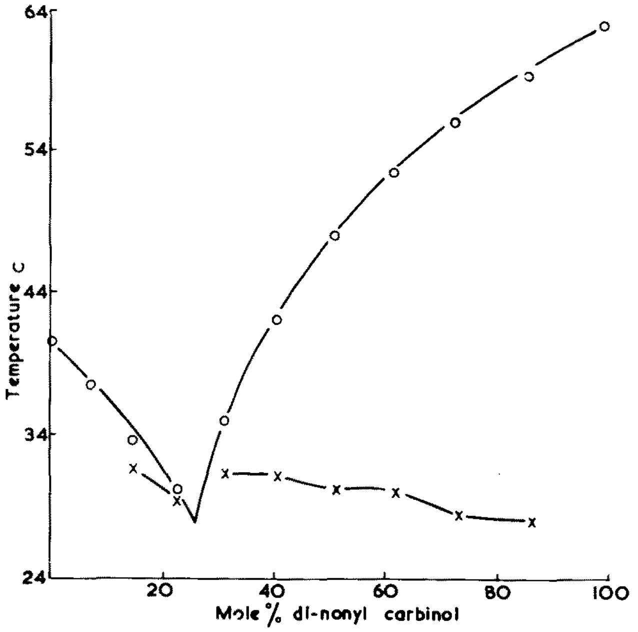

FIG. 4. Phase diagram of dihexyl carbinol-dinonyl carbinol system. O = freezing points and X = transition points.

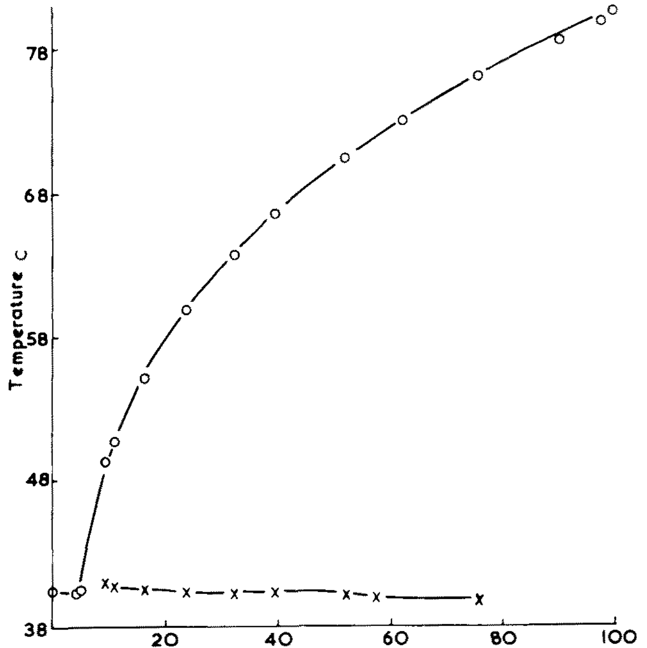

FIG. 5. Phase diagram of dihexyl carbinol-ditridecyl carbinol system. O = freezing points and X = transition points.

Secondary Alcohol-Secondary Alcohol Systems

Dihexyl carbinol-dinonyl carbinol system: The phase diagram of dihexyl carbinol-dinonyl carbinol is shown in Figure 4. The fp curves give rise to a simple eutectic at 26% dinonyl carbinol at 31.5 C. Before reaching eutectic from pure dihexyl carbinol, the cooling curves show breaks in the solid state in 14.63% and 22.60% dinonyl carbinol samples. Beyond the eutectic point, transitions are again found to occur in every sample, except that of pure dinonyl carbinol.

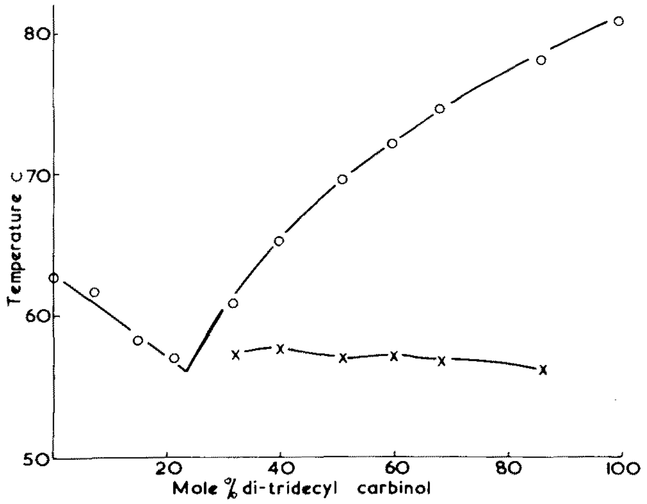

FIG. 6. Phase diagram of dinonyl carbinol-ditridecyl carbinol system. O = freezing points and X = transition points.

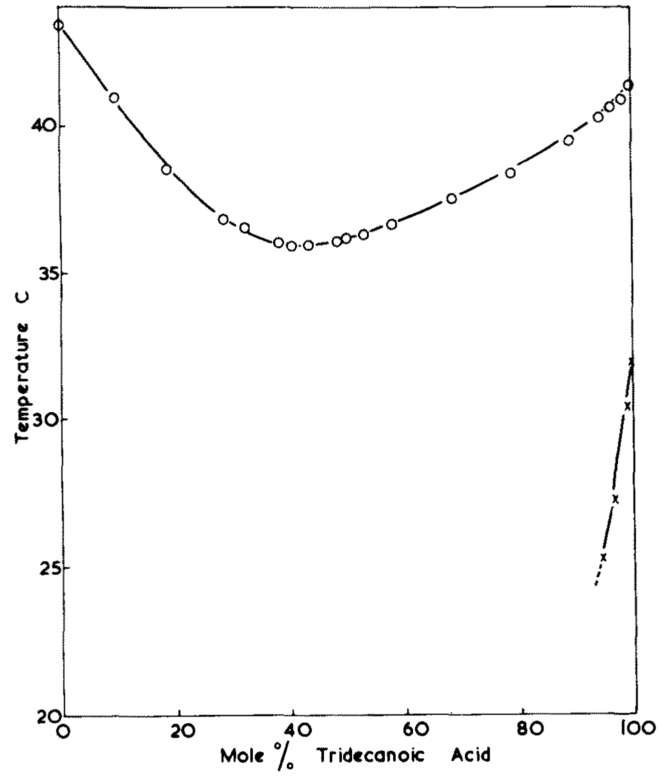

FIG. 7. Phase diagram of dodecanoic acid-tridecanoic acid system. O = freezing points and X = transition points.

These transition points are, probably, eutectic temperatures.

Dihexyl carbinol-ditridecyl carbinol system: Figure 5 gives the phase diagram of the dihexyl carbinol-ditridecyl carbinol system. FP curves form a very shallow eutectic close to the dihexyl carbinol axis at 40.2 C and at 4.73% ditridecyl carbinol. Similar to the binary systems described, cooling curves of samples from beyond the eutectic point up to 75.6% ditridecyl carbinol show, in addition to the fp breaks, breaks close to the eutectic point. These temperature breaks may correspond to eutectic temperatures.

Dinonyl carbinol-ditridecyl carbinol system: The phase diagram of dinonyl carbinol-ditridecyl carbinol is shown in Figure 6. The eutectic produced by the fp curves occurs at 23.5% ditridecyl carbinol and at 56.3 C. Similar to other systems described previously, the samples richer in ditridecyl carbinol over the eutectic composition show a second break in the cooling curve after the fp; and these temperatures, lying very close to the eutectic point, are shown by crosses in the phase diagram. Pure ditridecyl carbinol does not show any such breaks. These breaks may correspond to the eutectic temperatures.

Binary Systems of Long Chain Acids

Dodecanoic acid-tridecanoic acid system: The phase diagram of the binary dodecanoic acid-tridecanoic acid system is shown in Figure 7. As can be seen, the fp fall on a smooth curve convex toward the composition axis. The minimum of the curve occurs near 46% tridecanoic acid at 35.8 C. Like other even acids, dodecanoic acid does not show any solid state transition detectable in the cooling curves. Tridecanoic acid, similar to other odd acids, shows a transition at 31.8 C. From Stenhagen and von Sydow's (9) results on the study of the polymorphism of even and odd fatty acids by X-rays, it appears that this transition of tridecanoic acid corresponds to transformation from A′ (triclinic) to C′ (orthorhombic) form. Dodecanoic acid extensively lowers this transition point, and no transition could be detected in the sample containing 10.3% dodecanoic acid.

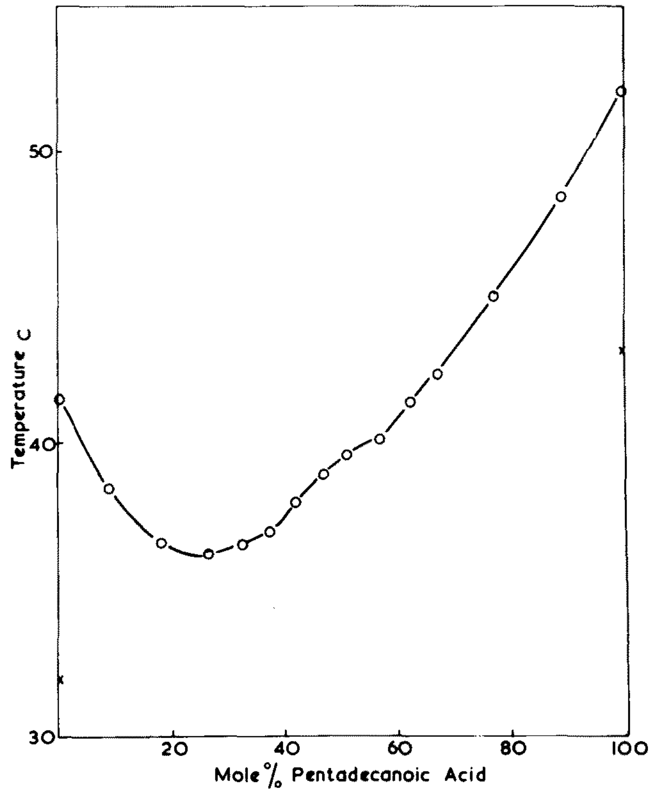

FIG. 8. Phase diagram of tridecanoic acid-pentadecanoic acid system. O = freezing points and X = transition points.

Tridecanoic acid-pentadecanoic acid system: Figure 8 shows the phase diagram of tridecanoic acid-pentadecanoic acid. Like tridecanoic acid, pentadecanoic acid also shows a transition in the solid state that can be obtained from the time-temperature curve. This transition occurs at 43.2 C and corresponds to either A′ (triclinic) to B′ (orthorhombic) or from B′ (orthorhombic) to C′ (orthorhombic but with different symmetry from B′) (9). The fp curve of the system shows a hump around 50% composition, suggesting the formation of 1 to 1 compound of the two acids congruently melting at 40.2 C. The two shallow eutectics can be identified at 38.2% and 56.9% pentadecanoic acid. Samples between 8.9% and 89.5% pentadecanoic acid did not show any solid state transitions.

Binary Systems of Long Chain Acids and Alcohols

Pentadecanoic acid-hexadecanol system: The phase diagram of the binary system of pentadecanoic acid-hexadecanol is given in Figure 9. The fp curves form two eutectics, one steep at 60.0% and the other shallow at 81.8% pentadecanoic acid. These two eutectics correspond to 37.1 C and 45.3 C respectively. The elevation between the eutectics occurring near 75% pentadecanoic acid suggests the formation of a molecular compound of 3 pentadecanoic acid to 1 hexadecanol congruently melting at 45.3 C. The transition point of hexadecanol is lowered extensively by pentadecanoic acid. In addition to the fp, a second arrest of temperature was observed in each of the samples containing pentadecanoic acid between 56.17%-79.17%. These are represented by crosses in the phase diagram. In the 60% pentadecanoic acid sample, the second arrest of temperature occurred at a higher temperature than the first, showing the metastable nature of the sample separating at first temperature arrest. Since these temperatures fall very close to the eutectic point, they may be the eutectic temperatures.

Palmitic Acid-Hexadecanol System

Figure 10 shows the binary phase diagram of palmitic

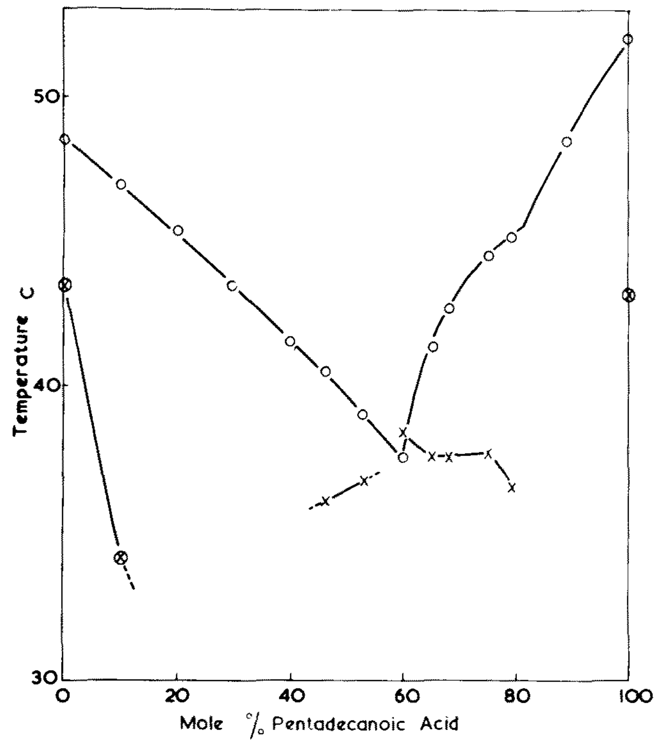

FIG. 9. Phase diagram of pentadecanoic acid-hexadecanol system. O = freezing points and X and ⊗ = transition points.

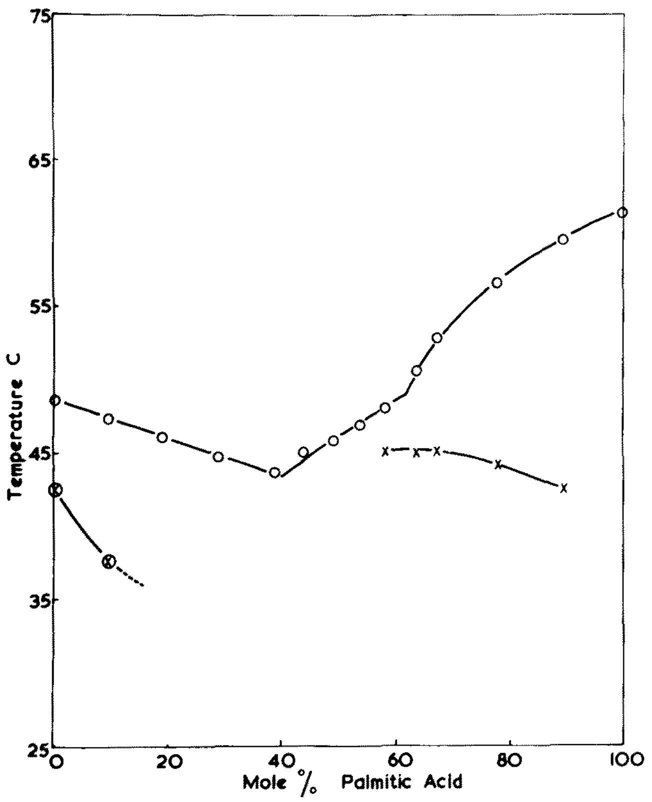

FIG. 10. Phase diagram of palmitic acid-hexadecanol system. O = freezing points and X and ⊗ = transition points.

acid-hexadecanol. The fp give rise to 2 eutectics, one at 39.2% palmitic acid and the other at 62.8% at 43.5 C and at 49.1 C, respectively. Between the two eutectics, there occurs a flat, the middle of which corresponds to ca. 50% palmitic acid. This flat between two eutectics is indicative of very weak compound formation and the composition suggests that a 1 to 1 compound is forming between hexadecanol and palmitic acid. The transition point of hexadecanol is lowered by the addition of palmitic acid, but the extent of lowering is less than that caused by pentadecanoic acid. In the samples from 19.6% palmitic acid onward, no hexadecanol transition could be detected. However, there occurred some second arrests of temperatures in the samples containing palmitic acid between 58.7-90.2%, which are represented by the crosses in the phase diagram. These points may be the eutectic temperatures.

DISCUSSION

In the hexadecanol-dinonyl carbinol and hexadecanol-ditridecyl carbinol systems, simple eutectic is produced at the fp. However, the eutectic of the hexadecanol-ditridecyl carbinol system contains more hexadecanol than does the hexadecanol-dinonyl carbinol system. The solid circles on the hexadecanol side of the eutectic are the transition points of pure hexadecanol and the mixtures. Ditridecyl carbinol seems to have more effect on the solid state transition point of hexadecanol than dinonyl carbinol; the former depresses the transition point more than the latter.

The shift of the eutectic composition toward the temperature axis of the lower melting component often is observed in binary systems where the components widely differ in mp. The extreme case is the formation of the monotectic in which the liquidus rises continuously up to the mp of the higher melting component without passing through an eutectic. An example is the monotectic system of tin and silicon (10).

In the binary system of primary alcohols, however, a solid solution type of curve is found to occur at the fp, if the chain length of the two components do not differ widely (11). But the higher temperature crystal modifications of long chain primary alcohols are fairly comparable with the melts, since, in those forms, the molecules are in a state of rotational disorder (12,13). Therefore, mixing between the components in the high temperature forms of primary alcohols can occur more easily than in primary alcohol-secondary alcohol and secondary alcohol-secondary alcohol systems. (The secondary alcohols do not exhibit similar polymorphism to primary alcohols.) The difference in the nature of fp curves may be due to that.

In the binary systems of secondary alcohols, as has already been stated, the eutectic is moved toward the low mol wt component axis, when the difference in carbon content between the components increases. On the other hand, the depth of the eutectic, with regard to temperature, increases as the difference in carbon content between the components diminishes.

The occurrence of the eutectics in the binary systems of secondary alcohols appears to be due to the lack of mixing between the components in the solid state. The structure of a secondary alcohol, ditridecyl carbinol, has been determined by Welsh (14) which shows that two hydrocarbon chains of equal length are parallel around the OH groups. Alcohols with such relatively more complex structure will show less mixing than the primary alcohols, which is reflected in the eutectic behaviors in the binary phase diagrams of secondary alcohols. As has been stated, in primary alcohols, the mixing between the homologues in the high temperature forms occurs because of the simplicity of their molecular structure and their rotational disorder in the high temperature form, a phenomenon conducive to greater mixing.

Binary fp behaviors of the fatty acids are well known (1), but the study of the even-odd and odd-odd fatty acid systems was undertaken to see the effect of the second component on the thermally realizable solid state transition point of the odd acids. Results show that such solid state transitions, unlike primary alcohol systems (11), disappear with the presence of ca. 10% second component. This might imply that the mixture has a different crystal form than that of the pure component. Definite information can be obtained from X-ray diffraction studies. A solid solution type fp curve of dodecanoic acid-tridecanoic acid system is quite different from the finding that heptadecanoic acid forms a molecular compound with octadecanoic acid (15). This suggests the need for the components to assume a certain length to form a molecular compound in such systems which ultimately refer to the steric effect determining the binding capacity of the two components in the solid state through polar groups. The fp behaviors of the pentadecanoic acid-tridecanoic acid system is fairly similar to that of even-even binary fatty acid systems of similar chain length. Thus, it seems that to increase the bonding affinity of the polar groups, sufficient length by the two components matters more than just their type.

Though there is evidence indicating that fatty acids form molecular compounds, alcohols do not form compounds the way acids do (11). Whether alcohols form compounds with acids was the question behind the studies of the binary systems of acids and alcohols, and the results suggest that they do form stoichiometric compounds. In this respect, the behavior of alcohol is quite similar to a carboxylic acid, though it is difficult to understand from pentadecanoic acid-hexadecanol system how three acid molecules associate with one alcohol molecule.

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