Short Communication

THE MISCIBILITY GAPS IN MONOCARBOXYLIC–DICARBOXYLIC ALIPHATIC ACID MIXTURES

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The characteristics of the eutectic points and of the miscibility gaps are submitted for binary systems composed of margaric, palmitic or pentadecanoic acid as one component and succinic, glutaric or adipic acid as the other.

In a previous paper [1] the existence of liquid–liquid equilibrium regions in some binary stearic acid–dicarboxylic acid-systems was pointed out. This phenomenon was attributed to the more dipolar character of the molecules of the dicarboxylic acids. In this paper we analyze the influence of the chain length on the demixing phenomenon.

Experimental

The experimental method was described previously [1, 2]. The melts temperature was taken with a chromel–alumel thermocouple checked by comparison with an NBS-certified Pt-resistance thermometer and connected with a Leeds & Northrup K-5 potentiometer. The melts were cooled at a rate of $0.2-0.3$ K/min and the visual method was used to take the temperature of the first crystallization or of the first turbidity. The chemicals, Merck margaric, palmitic, pentadecanoic, succinic, glutaric and adipic acids were recrystallized from C_2H_5OH and dried under dynamic vacuum.

Results and discussion

The experimental results are shown in Fig. 1, while Table 1 contains the coordinates of the singular points of the liquid–liquid and liquid–solid equilibrium curves. The phase diagrams generally show an S-shaped curve in the region richer in dicarboxylic acid, probably owing to the equilibrium of the monocarboxylic acid:

$$\text{monomer} \rightleftharpoons \text{dimer}$$
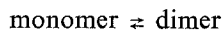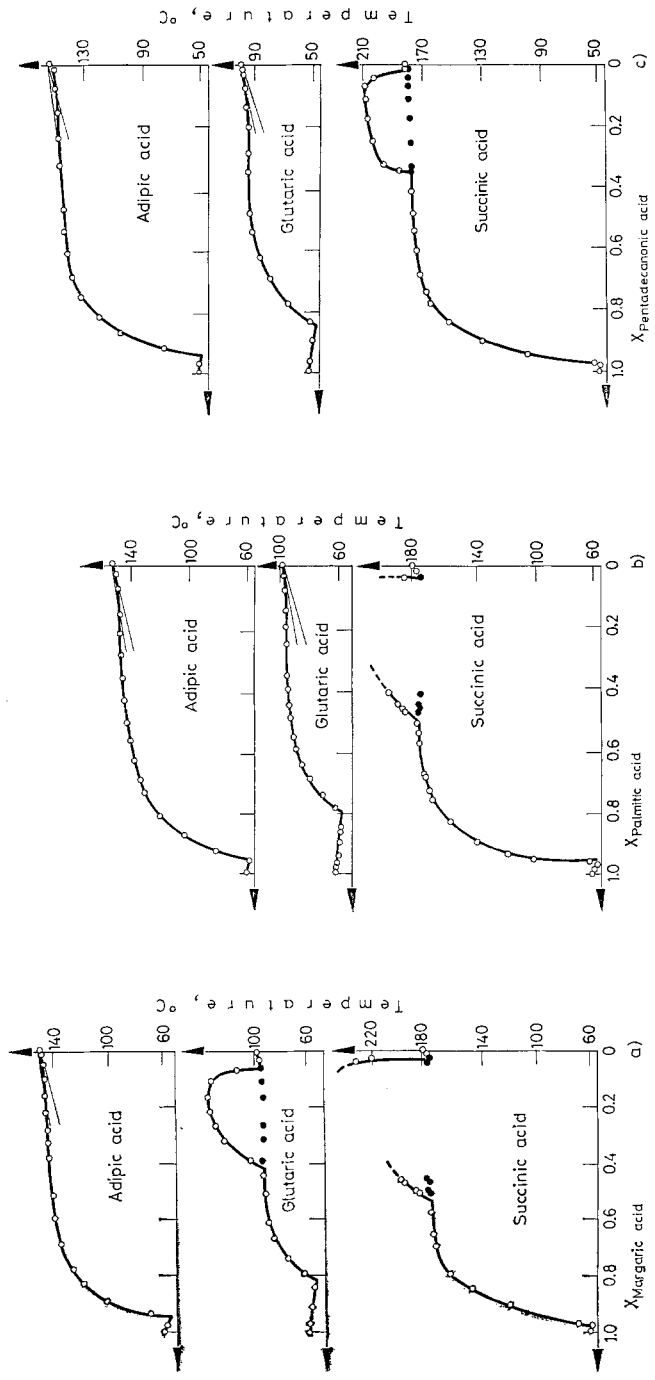
as in the case of stearic acid [1].

Fig. 1. Liquid—solid and liquid—liquid equilibrium curves of some binary monocarboxylic acid—dicarboxylic acid systems

In fact at low concentrations of the monocarboxylic acid (A) the experimental curve and the theoretical one [3], calculated considering the A molecule as monomeric, agree; however, with increasing concentration of A the experimental curve tends to the theoretical one calculated considering the A molecule as dimeric

Table 1

Component acid 1	Component acid 2	Eutectic		Miscibility gaps			
		$.X_2$	$.T$, °C	$.X_2^l$	$.X_2^r$	$.T_m$, °C	$.T_c$, °C
Margaric	succinic	0.9820	58.9	0.5230	0.0250	179.5	—
Margaric	glutaric	0.8110	56.2	0.4075	0.0550	95.0	133.8
Margaric	adipic	0.9420	55.0	—	—	—	—
Palmitic	succinic	0.9610	57.9	0.5130	0.0380	178.5	—
Palmitic	glutaric	0.8010	57.5	—	—	—	—
Palmitic	adipic	0.9560	59.2	—	—	—	—
Pentadecanoic	succinic	0.9730	50.3	0.3500	0.0230	179.1	209.3
Pentadecanoic	glutaric	0.8500	48.0	—	—	—	—
Pentadecanoic	adipic	0.9480	49.4	—	—	—	—

X_2^l, X_2^r = molar fraction of component 2 to the left and right of the miscibility gap
T_m, T_c = monotectic and consolute temperatures

The miscibility gaps are evident only in the following systems:

margaric acid + succinic or glutaric acids;
palmitic acid + succinic acid;
pentadecanoic acid + succinic acid.

The gaps disappear for the lower members of the monocarboxylic acids. From this trend it is possible to relate the demixing phenomenon to the polar character of the molecule. If the rapport R = (number of COOH groups)/(number of carbon atoms) is chosen as the index of the polar character of the molecules, it is note_
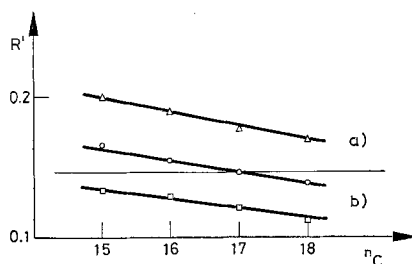

Fig. 2. Solubility (a) and demixing (b) regions in the binary monocarboxylic acid—dicarboxylic acid systems. R', $vs.$ n_C (number of carbon atoms in the monocarboxylic acids): △ adipic acid; ○ glutaric acid; □ succinic acid

worthy that in this family of binary systems the demixing phenomenon is evident if the index $R' = R_{monocarboxylic}/R_{dicarboxylic}$ does not exceed the value of 0.14_7, as shown in Fig. 2.

The demixing phenomenon is probably present for the higher members of A.

As in the case of stearic acid [1], the region of the liquid–liquid equilibrium arises above the crystallization curve of the dicarboxylic acid and begins from $X_{dicarboxylic\ acid} > 0.96$. This fact is probably to be attributed to a different structure of the liquids of these components: ultrasonic studies in the lower members of the monocarboxylic acids [4] indicate that the acid is dimeric in closed and open forms, but the equilibrium is displaced towards the closed form. Cryometric analysis of the higher members [1, 5] suggests that the dimer is the structural entity of these melts, while in addition the covolume obtained from viscometric measurements [6] is related to the volume of the rotating closed dimer, supporting the idea that the monocarboxylic acid molecules rotate in the fused state. In contrast the probable structure of the dicarboxylic acids is planar, with hydrogen bonds extending in two dimensions. The subsequent difference in rigidity may favour an effect of demixing, that disappears at low concentration of the dicarboxylic acid owing to the dissociation of these compounds and the consequent loss of rigidity.

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