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THE LIQUID-LIQUID AND LIQUID-SOLID EQUILIBRIA IN SOME BINARY SYSTEMS CONTAINING ALKALI METAL STEARATES

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The characteristics are submitted of the crystallization curves of binary systems composed of sodium or potassium stearate as one component and succinic, glutaric, adipic, pimelic, suberic or azelaic acid as the other.

The miscibility gaps in the binary systems $COOH(CH_2)_nCOOH + CH_3(CH_2)_n COOH$ were described previously [1]. The present note deals with the liquid–liquid equilibrium regions in the binary systems $COOH(CH_2)_nCOOH +$ $+ CH_3(CH_2)_nCOO(K, Na)$.

Experimental

The visual method adopted to take the temperatures of the melts is described in previous papers [2–4]. The chemicals employed, succinic, glutaric and adipic acids (C. Erba RP), pimelic and suberic acids (Schuckardt) and azelaic acid (K & K), were purified by crystallization from C_2H_5OH and dried under dynamic vacuum at increasing temperatures up to 10° below the melting point. The soaps were prepared by reaction of a warm and concentrated alcoholic solution of stearic acid with the stoichiometric quantities of the respective carbonate. The soap was next recrystallized from C_2H_5OH and dried. The equilibrium curves were determined only in the region of thermal stability and while good agitation was possible. In fact, the viscosity of the melt increases strongly with the concentration of the soap.

Results and discussion

Figure 1 shows the equilibrium curves, and Table 1 the coordinates of the individual points. As clear from Fig. 1, the crystallization curve of the dicarboxylic acid almost coincides with the theoretical one calculated considering the soap to be dissociated into two ions (continuous lower line).

The extension of the crystallization curve of the dicarboxylic acid increases with increasing length of the acid molecule and with decreasing radius of the cation of the soap.

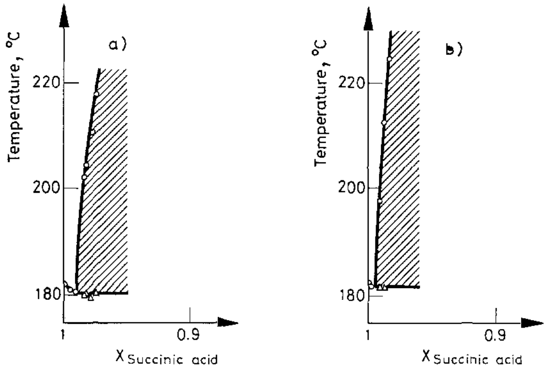


Fig. 1a Binary system: succinic acid + Na stearate
Fig. 1b Binary system: succinic acid + K stearate

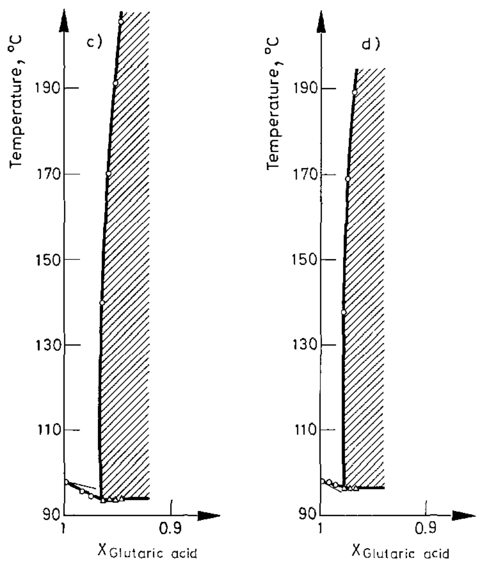


Fig. 1c Binary system: glutaric acid + Na stearate
Fig. 1d Binary system: glutaric acid + K stearate

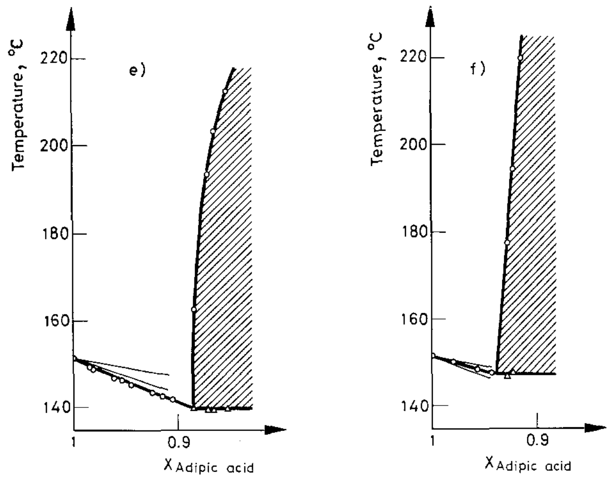


Fig. 1e Binary system: adipic acid + Na stearate
Fig. 1f Binary system: adipic acid + K stearate

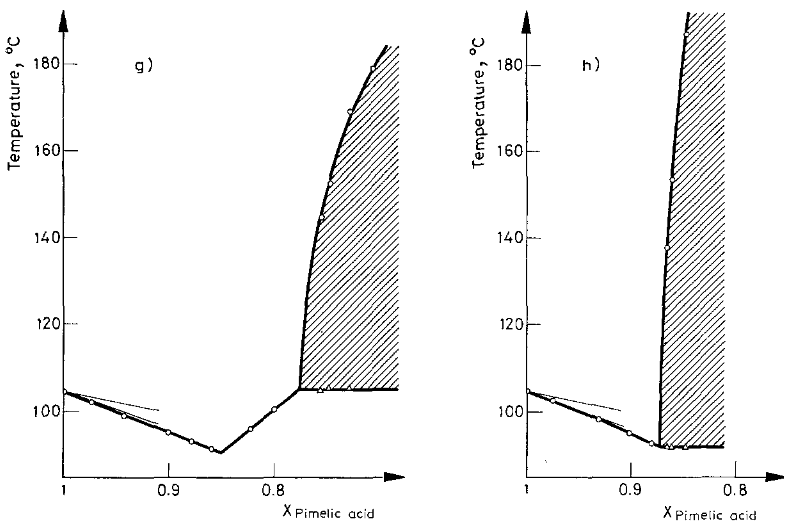
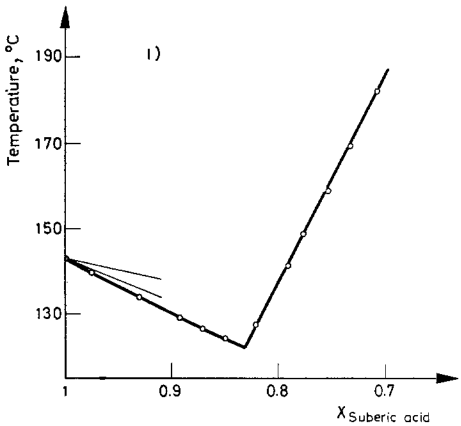


Fig. 1g Binary system: pimelic acid + Na stearate
Fig. 1h Binary system: pimelic acid + K stearate



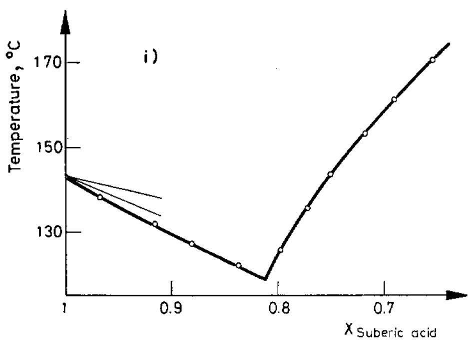


Fig. 1i Binary system: suberic acid + Na stearate
Fig. 1l Binary system: suberic acid + K stearate

Table 1

Singular points in the investigated region of the binary dicarboxylic acid + (K, Na) stearate systems. The molar fraction refers to the dicarboxylic acid

System	$x_{eut.}$	$T_{eut.}$, °C	$x_{mon.}$	$T_{mon.}$, °C
Azelaic acid + Na stearate	0.8710	92.0		
Azelaic acid + K stearate	0.8890	96.2		
Suberic acid + Na stearate	0.8120	118.8		
Suberic acid + K stearate	0.8315	122.2		
Pimelic acid + Na stearate	0.8500	90.6	0.7750	105.3
Pimelic acid + K stearate			0.8730	92.0
Adipic acid + Na stearate			0.8860	139.6
Adipic acid + K stearate			0.9380	147.2
Glutaric acid + Na stearate			0.9650	93.8
Glutaric acid + K stearate			0.9780	96.5
Succinic acid + Na stearate			0.9885	180.1
Succinic acid + K stearate			0.9940	181.5

The fact that the K stearates are less soluble in the acids than the Na soaps can be explained via a higher interaction between the Na^+ ion and the carboxylic group because of its higher electric density.

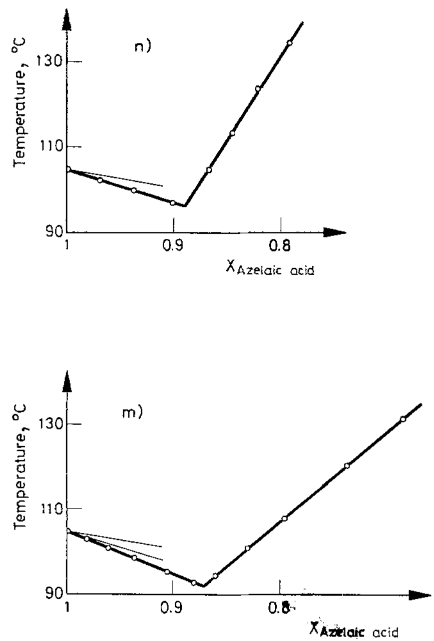


Fig. 1m Binary system: azelaic acid + Na stearate
Fig. 1n Binary system: azelaic acid + K stearate

Further, the stearates are more soluble in the higher acids investigated; this fact can be explained by supposing that the interaction between the ion chain and the acid chain is a very important factor in the solvation, and consequently in the stabilization of the stearate ion. This was pointed out in other systems [1, 2].

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References

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