Short Communication

A CORRELATION BETWEEN THE EXTENSION OF THE MISCIBILITY GAPS AND THE NATURE OF THE COMPONENTS IN SOME BINARY SYSTEMS

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The liquid-liquid equilibrium regions in binary systems, one component of which is a dicarboxylic aliphatic acid, are examined by the linear equation $\ln (x_1/x'_1) = a + bT$. The b term is plotted *vs.* the difference of polar character and one graph is obtained for the different systems.

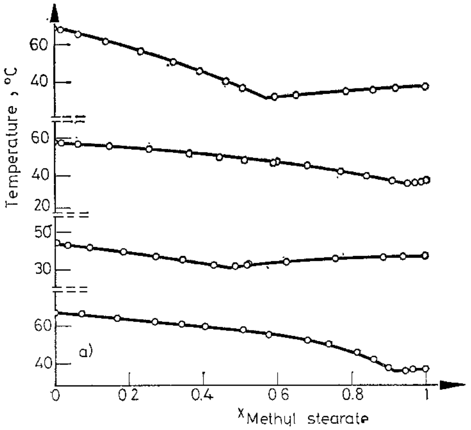
A large number of binary systems were recently studied [1–5] in order to obtain evidence on a possible correlation between the extension of the miscibility gaps and the nature of the components. For a strictly homogeneous family [2] of systems (aliphatic dicarboxylic acids + aliphatic monocarboxylic acids) a graphical procedure was proposed which allowed one to foresee whether a given system may or may not exhibit demixing. In order to prove the validity of such a procedure in the case of less homogeneous systems, more binary systems have been studied, containing stearic alcohol [4], ethyl stearate [5], and in the present paper methyl stearate.

Experimental

The temperatures were measured with a chromel alumel thermocouple checked against a Pt-resistance thermometer (NBS-certified) and connected with a Leeds and 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 the first turbidity. Each measurement was repeated, and an agreement of 0.1° was always obtained. The high-purity Fluka or Schuchardt chemicals were treated as previously described [1–5].

Results and discussion

The liquid-liquid and solid-liquid equilibrium curves and the co-ordinates of the invariants for a number of methyl stearate (component 1) + A(A = dicarboxylic acid, monocarboxylic acid, diphenyl or stearic alcohol) binaries are reported in Fig. 1 and Table 1, respectively.



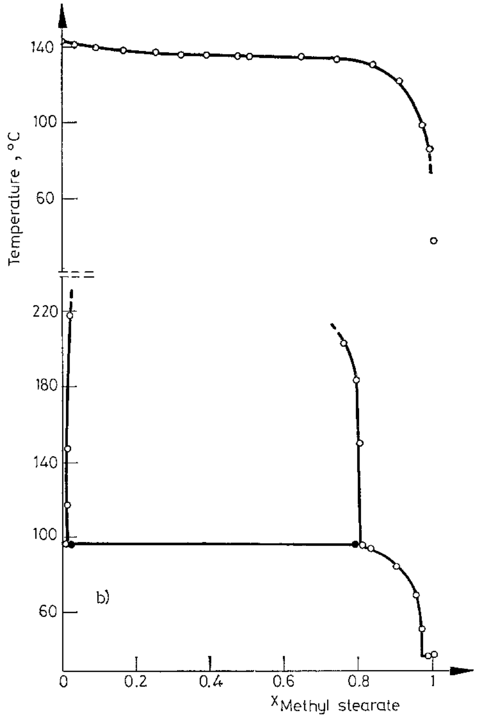
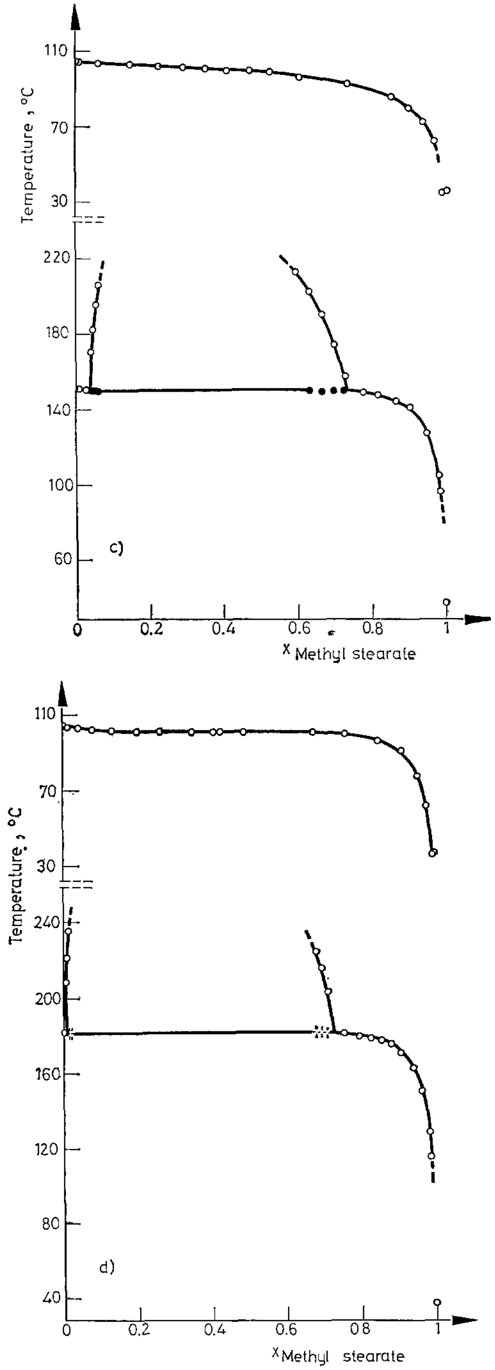


Fig. 1. Solid-liquid and liquid-liquid equilibrium curves of the binary systems: a) from the bottom: methyl stearate + stearic acid; methyl stearate + lauric acid; methyl stearate + + stearic alcohol; methyl stearate + diphenyl; b) from the bottom: methyl stearate + glutaric acid; methyl stearate + suberic acid.



c) from the bottom: methyl stearate + adipic acid; methyl stearate + azelaic acid; d) from the bottom: methyl stearate + succinic acid; methyl stearate + pimelic acid

Table 1

System	Eutectic		Monotectic		
methyl stearate +	T°	x_1	T°	$x_{1,r}$	$x_{1,l}$
Succinic acid	—	—	182.0	0.7270	0.0050
Glutaric acid	36.0	0.9710	96.0	0.8025	0.0150
Adipic acid	—	—	150.0	0.7400	0.0400
Pimelic acid	36.0	0.9900	—	—	—
Suberic acid	—	—	—	—	—
Azelaic acid	—	—	—	—	—
Lauric acid	31.0	0.4650	—	—	—
Stearic acid	36.0	0.9150	—	—	—
Diphenyl	31.5	0.5700	—	—	—
Stearic alcohol	35.5	0.9450	—	—	—

x_1 = mole fraction of methyl stearate

$x_{1,r}$, $x_{1,l}$ = mole fractions of methyl stearate at the monotectic temperature on the right and left hand sides of the miscibility gap

Liquid-liquid equilibria could be demonstrated only for the lower terms of the dicarboxylic acid series, whereas the other systems studied (i.e. those containing a monocarboxylic acid or stearic alcohol or diphenyl) do not demix. The liquid-liquid equilibrium regions were investigated up to a temperature beyond which the components became thermally unstable. A comparison with the available data on the analogous binary systems where component 1 was ethyl stearate showed that in the latter systems the miscibility gaps are larger and more frequent. In order to compare the different systems more easily, the liquid-liquid equilibria are expressed in the form:

$$\ln (x_1/x_1') = f(T) \tag{1}$$

where x_1 and x_1 are the mole fractions ($x_1 > x_1'$) of component 1 in the two liquid phases in equilibrium at the temperature T.

In the temperature range studied, the above relationship may be written as

$$\ln (x_1/x_1') = a + bT \tag{2}$$

In Table 2 the pertinent parametric values are given together with a δ value, defined as the difference in polar character of the components. The ratio

$$R = \frac{\text{number of polar groups}}{\text{total number of carbon atoms}} \tag{3}$$

was chosen as an index of the polar character:

$$\delta = R_{\text{dicarboxylic acid}} - R_{\text{other component}} \tag{4}$$

Table 2 and Fig. 2 show that δ and b are roughly interdependent; in fact, in a plane $|b|/\delta$, values $|b|$ belonging to the identical component 2 crowd around

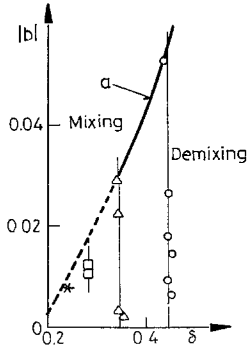


Fig. 2. Dependence of *b* on *δ*, for the following binary system: o: from the bottom: succinic acid + ethyl stearate; succinic acid + margaric acid; succinic acid + methyl stearate; succinic acid + palmitic acid; succinic acid + stearic alcohol; succinic acid + pentadecanoic acid; △: from the bottom: glutaric acid + ethyl stearate; glutaric acid + methyl stearate; glutaric acid + stearic acid; glutaric acid + margaric acid; □: from the bottom: adipic acid + ethyl stearate; adipic acid + methyl stearate; *: pimelic acid + ethyl stearate

straight lines with negative slope. $(x_{1,r} - x_{1,l})$ may be considered a measure of the gap width and in a family of systems it regularly decreases with decreasing δ, as can be seen from the following $(x_{1,r} - x_{1,l})$ values for the systems succinic acid + monocarboxylic acids or esters: 0.780 (ethyl stearate); 0.722 (methyl stearate); 0.498 (margaric acid); 0.475 (palmitic acid); 0.327 (pentadecanoic acid). That is, $|b|$ may also be considered to be related with the gap width: it roughly increases with decreasing gap extension. These straight lines do not have a physical meaning, for a family of systems, beyond the value $|b|$ of the system

Table 2

Components		*a*	$-b(\mathrm{K}^{-1})$	*δ*
1	2			
ethyl stearate	pimelic acid	4.95	0.0081	0.236
methyl stearate	adipic acid	8.31	0.0126	0.281
ethyl stearate	adipic acid	8.04	0.0109	0.283
stearic acid	glutaric acid	12.03	0.0230	0.344
margaric acid	glutaric acid	13.04	0.0295	0.341
methyl stearate	glutaric acid	5.15	0.0032	0.347
ethyl stearate	glutaric acid	5.59	0.0028	0.350
pentadecanoic acid	succinic acid	27.19	0.0532	0.433
stearic alcohol	succinic acid	15.92	0.0269	0.444
methyl stearate	succinic acid	11.61	0.0150	0.447
palmitic acid	succinic acid	11.02	0.0185	0.437
margaric acid	succinic acid	7.61	0.0100	0.441
ethyl stearate	succinic acid	7.62	0.0069	0.450

which (in that system family) represents the limit of demixing; for example, in the family of binary systems succinic acid + monocarboxylic acids, the extension of the miscibility gaps decreases in the sense margaric → palmitic → pentadecanoic; with lower members the presence of the demixing phenomenon is not evident. For this reason the $|b|$ value of the system succinic acid + pentadecanoic acid, that gives the smallest gap, denotes the boundary of demixing in the straight line $|b|/\delta$. The curve that connects the b limit-values of each b/δ straight line delimits a *zone of demixing* as in Fig. 2 for the monocarboxylic – dicarboxylic acid binary systems. This zone of demixing is probably still valid for the aliphatic alcohols.

For the moment, other miscibility gaps are expected below the a line, i.e. for lower dicarboxylic acids (malonic) or for higher monocarboxylic acids and alcohols. In fact, $|b|$ decreases with the increase of n_c.

Continuation of this research will enable us to decide if the esters have the same or a different line that delimits a *zone of demixing.*

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