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MISCIBILITY GAPS IN METHYL NONADECANOATE + DICARBOXYLIC ACID BINARY SYSTEMS

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The liquid-liquid and liquid-solid equilibria of the binary systems composed of methyl nonadecanoate and some aliphatic acids or stearic alcohol or diphenyl are presented; the enthalpy of fusion of the ester is given, and a discussion is carried out on the factors affecting the liquid-liquid equilibria studied to date.

Recently, we took interest in a possible graphical method of studying several binary systems exhibiting the demixing phenomenon, composed of one substance with a polar group and another substance with two polar groups.

In this note we give the liquid-liquid and liquid-solid equilibrium curves for the binary systems methyl nonadecanoate (component 1) + dicarboxylic acids, lauric and stearic acids, diphenyl, or stearic alcohol (components 2) and carry out a discussion in terms of the parameters a and b of the equation

$$\ln (x_1/x_1') = a - b(T - T_m)$$

previously proposed [1] for liquid-liquid equilibrium curves.

Experimental

The temperature of first crystallization or of demixing was measured visually by means of a Chromel Alumel thermocouple (checked with a Pt resistance thermometer) connected to a Leeds Northrup K-5 potentiometer. The fusion enthalpy is measured with a DSC–1B Perkin-Elmer calorimeter. The details of calibration are given in previous papers [2, 3]. When it was necessary to work below room temperature the cryostat was connected to a Lauda refrigerator.

The chemicals are: Fluka methyl nonadecanoate, glutaric, adipic, azelaic and lauric acids and stearic alcohol; Merck pimelic, succinic and suberic acids; Erba diphenyl. Methyl nonadecanoate (purity 98%) was employed without further purification; the other compounds were recrystallized from C_2H_5OH and dried under dynamic vacuum, at a temperature some degrees below the melting point.

Results and discussion

The thermodynamic fusion data are given in Table 1. The trend of the equilibrium curves is shown in Fig. 1, and in Table 2 the coordinates of the invariant points are given. As in the case of ethyl stearate, four gaps are found (also with pimelic acid). This fact was expected because ethyl stearate and methyl nonadecanoate are isomers and have identical polar characters.

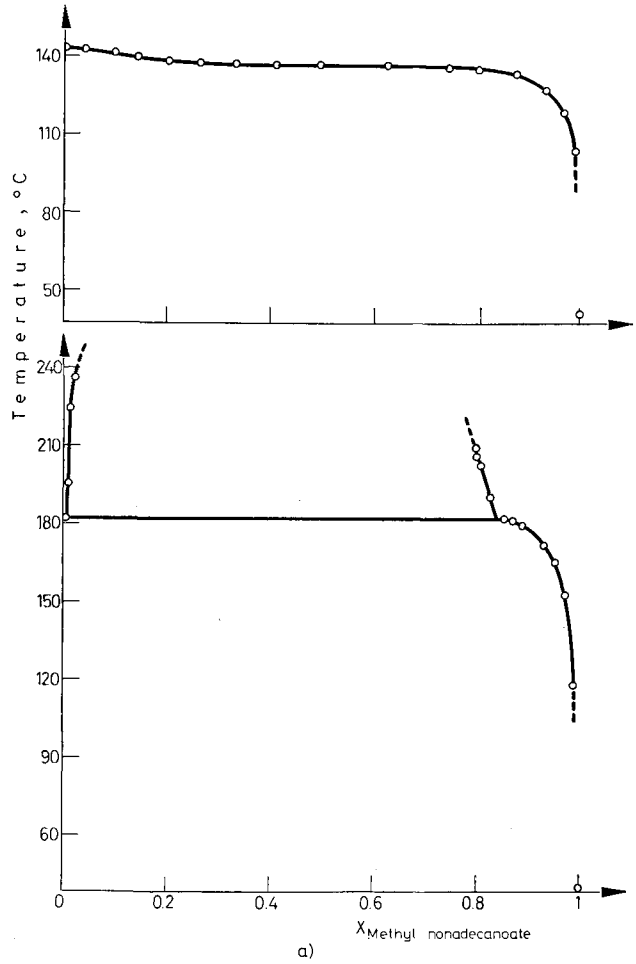


Fig. 1. Phase equilibrium curves concerning binary systems methyl nonadecanoate + a) from the top: suberic acid, succinic acid. b) from the top: lauric acid, pimelic acid. c) from the top: diphenyl, azelaic acid, glutaric acid. d) from the top: 1-octadecanol, stearic acid, adipic acid

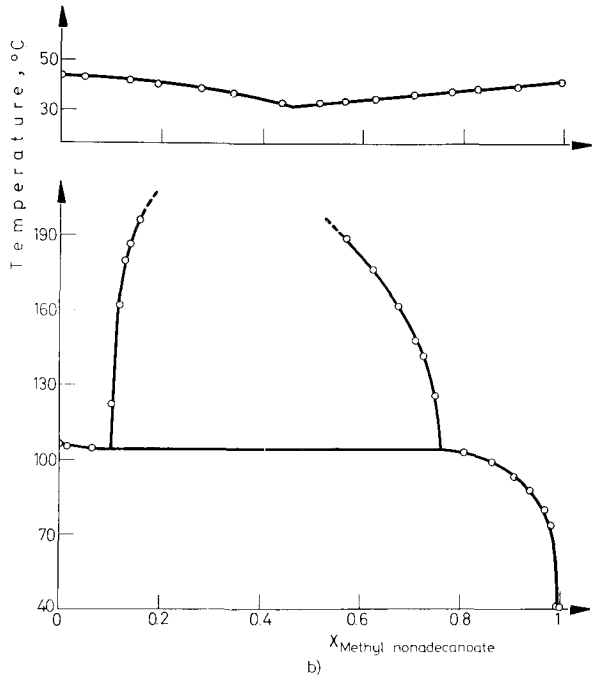


Table 1

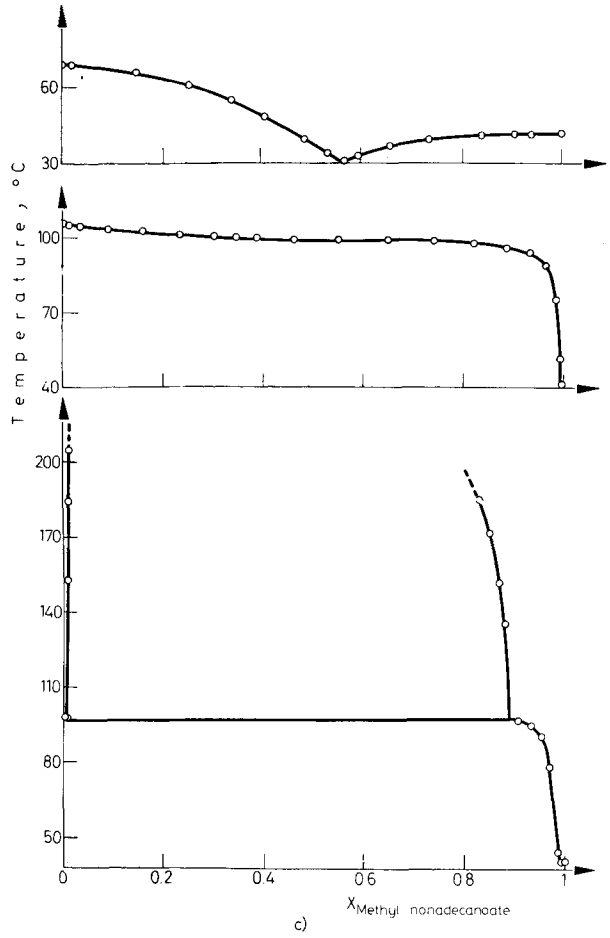
T_{fus}, K	ΔH_{fus}, kcal/mole	ΔS_{fus}, cal/K mole
313.7	9.93	31.7

Table 2

Added comp.	x_{eut}	T_{eut}K	x_m^l	x_m^r	T_mK
Succinic acid	—	—	0.010	0.840	454.7
Glutaric acid	0.990	313.2	0.010	0.896	370.2
Adipic acid	—	—	0.028	0.804	422.7
Pimelic acid	0.994	313.2	0.100	0.769	377.2
Azelaic acid	0.996	313.7	—	—	—
Suberic acid	—	—	—	—	—
Lauric acid	0.480	304.7	—	—	—
Stearic acid	0.908	313.7	—	—	—
1-Octadecanol	0.930	311.2	—	—	—
Diphenyl	0.564	302.7	—	—	—

x_{eut}, x_m^l, x_m^r molar fraction of methyl nonadecanoate in the eutectic mixture and in the mixtures in equilibrium at the monotectic temperature on the left (l) and right (r) hand of the gap, respectively;

T_{eut}; T_m eutectic and monotectic temperature, respectively.

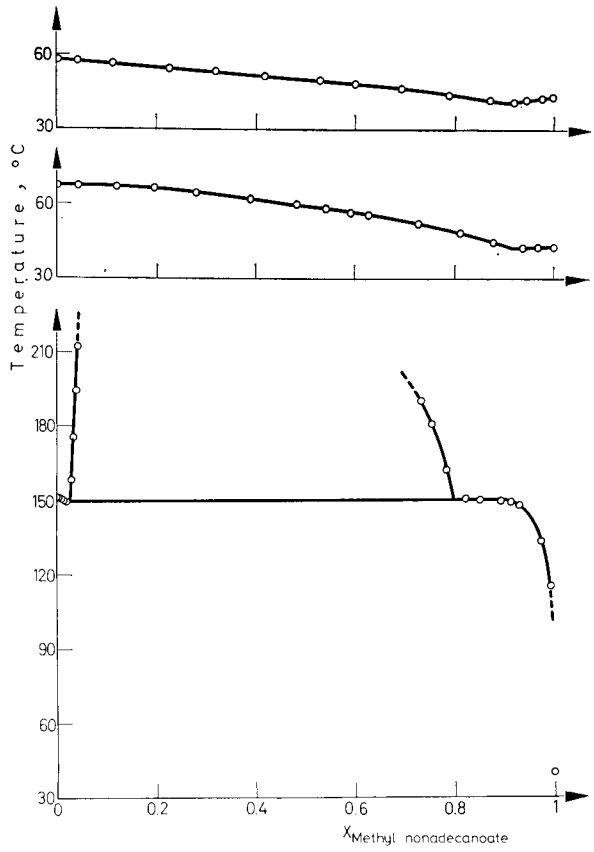


Also for these gaps, in the zone studied, the composition of the liquid-liquid equilibrium curves depends on the temperature, following a linear equation

$$\ln (x_1/x_1') = a - b(T - T_m)$$

whose parameters a and b are given in Table 3; this equation is a formally more correct modification of the equation previously proposed [1].

The b terms agree satisfactorily with other b terms studied earlier, as shown in Fig. 2. The a term of the equation seems to depend on the monotectic temperature and on the polar character of the components, as the value of $a/\gamma T_m$ (where $\gamma = R_2/R_1$), roughly constant around 0.0011 (standard deviation 0.0003), suggests.



d)

The meaning of R_i was given previously [1]. In the systems we have studied to date, the extension of the miscibility gap depends, therefore, on the respective polar characters of the two components and also on the temperature range where the gap lies. Other factors probably affect the miscibility gap extension, and a less rough dependence must be studied; this is the aim of a future study.

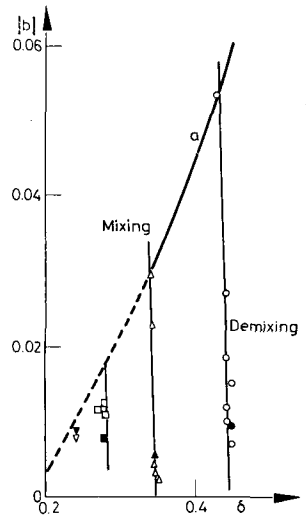


Fig. 2. / b / versus δ (the difference of polar character): ○ succinic, △ glutaric, □ adipic, ▽ pimelic. The points concerning the systems in methyl nonadecanoate are blackened

Table 3

System	a	b, K^{-1}	δ	γ	$a/\gamma T_m$	Ref.
Methyl stearate +						
Succinic acid	4.78	0.0150	0.447	9.5	0.0011	1
Glutaric acid	3.97	0.0032	0.347	7.6	0.0011	1
Adipic acid	2.98	0.0126	0.281	6.3	0.0011	1
Methyl palmitate +						
Succinic acid	4.22	0.0121	0.441	8.5	0.0011	4
Glutaric acid	3.56	0.0046	0.341	6.8	0.0014	4
Adipic acid	1.87	0.0117	0.275	5.7	0.0008	4
Ethyl stearate +						
Succinic acid	4.49	0.0069	0.450	10.0	0.0010	5
Glutaric acid	4.55	0.0028	0.350	8.0	0.0015	5
Adipic acid	3.42	0.0109	0.283	6.7	0.0012	5
Pimelic acid	1.91	0.0081	0.236	5.7	0.0009	5
Stearic acid +						
Glutaric acid	3.55	0.0230	0.344	7.2	0.0013	6
Margaric acid +						
Succinic acid	3.08	0.0100	0.441	8.5	0.0008	7
Glutaric acid	2.18	0.0295	0.341	6.8	0.0009	7
Palmitic acid +						
Succinic acid	2.66	0.0185	0.438	8.0	0.0007	7
Pentadecanoic acid +						
Succinic acid	3.13	0.0532	0.433	7.5	0.0009	7
1-Octadecanol +						
succinic acid	3.69	0.0269	0.444	9.0	0.0009	8

Table 3

System	a	b, K^{-1}	δ	γ	$a/\gamma T_m$	Ref.
Methyl nonadecanoate + Succinic acid	4.42	0.0094	0.450	10.0	0.0010	this note
Glutaric acid	4.76	0.0053	0.350	8.0	0.0016	this note
Adipic acid	3.36	0.0083	0.283	6.7	0.0012	this note
Pimelic acid	1.58	0.0078	0.236	5.7	0.0007	this note

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RÉSUMÉ — Les équilibres liquide-liquide et liquide-solide des systèmes binaires à base de nonadécanoate méthylique et de quelques acides aliphatiques ou alcool stéarique ou diphényle sont présentés. L'enthalpie de fusion des esters est donnée et les facteurs qui agissent sur les équilibres liquide-liquide étudiés jusqu'à présent sont discutés.

ZUSAMMENFASSUNG — Die flüssig-flüssig und flüssig-fest Gleichgewichte der aus Methylnonadekanat und einigen aliphatischen Säuren oder Stearinalkohol oder Diphenyl zusammengesetzten Binärsysteme werden angegeben. Die Schmelzenthalpien der Ester werden mitgeteilt und die, die bis zum heutigen Tage untersuchten flüssig-flüssig Gleichgewichte beeinflussenden Faktoren werden erörtert.

Резюме — Представлены равновесия типа жидкость-жидкость и жидкость-твердое состояние бинарных систем, состоящих из метилнонадеканоата и некоторых алифатических кислот или же стеаринового спирта или дифенила. Приведена энтальпия плавления эфира. Обсуждения проведены на основе изученных до настоящего времени факторов, затрагивающих равновесие жидкость-жидкость.