Binary Systems Containing Hydrocarbons

Note III. Effect of Unsaturation, Cyclization and Isotopic Substitution on Critical Demixing Temperatures

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The demixing curves in binary systems of nitromethane with 11 1-alkenes, 6 cycloalkanes and 2 cycloalkenes, and of CD_3COCD_3 with 5 n.alkanes were measured. Critical demixing temperatures: a) are additively affected by unsaturation and cyclization in the first group of systems; b) are increased by a constant amount in the second group, in comparison to the corresponding systems containing CH_3COCH_3.

Liquid-liquid equilibria in more than fifty binary systems of methylacetate or nitromethane or acetone (component **1**) with $(C_5 - C_9)$-alkanes (component **2**) were recently studied by us [1], and rules were drawn which allowed to correlate the coordinates of the critical points to the number of carbon atoms, n_C, and to the number and quality of chain ramifications.

In the present work an attempt was made, on one hand, to extend such correlations to systems containing hydrocarbons whose molecules are unsaturated (owing to an ethylenic double bond), or cyclic, or both; on the other hand, to investigate the effect exerted on the critical temperature by an isotopic substitution in component **1**.

For what concerns the first point, the demixing curves have been determined for the systems of nitromethane (Fluka, $\geqq 99$ mole %) with the following Fluka hydrocarbons: 1-pentene (99.91), 3-methyl-1-butene (99.99), 2-methyl-1-pentene (99.99), 2,3-dimethyl-1-butene (99), 2-methyl-1-hexene ($\geqq 99$), 3-methyl-1-hexene ($\geqq 99$), 4-methyl-1-hexene ($\geqq 99$), 5-methyl-1-hexene ($\geqq 99$), 2,3-dimethyl-1-pentene ($\geqq 98$), 2-methyl-1-heptene ($\geqq 99$), 2,3-dimethyl-1-hexene ($\geqq 98$), cyclopentane (99.97), cyclohexane (99.99), methylcyclopentane (99.94), cycloheptane ($\geqq 99$), methylcyclohexane ($\geqq 99.5$), cyclooctane (purum), cyclopentene ($\geqq 99.9$), cyclohexene ($\geqq 99.5$).

As to the second point, the mixtures of CD_3COCD_3 (Fluka, $\geqq 99.5$) with Fluka n-pentane (99.91), n-hexane ($\geqq 99.96$), n-heptane (99.92), n-octane (99.81) and n-nonane (99.68) have been investigated.

Materials drying, samples preparation and experimental procedure were already described elsewhere [1].

[1] a) M. ROLLA, P. FRANZOSINI, R. RICCARDI, and L. BOTTELLI, Z. Naturforsch. **21 a**, 601 [1966]; b) **22 a**, 48 [1967]; c) P. FRANZOSINI, R. RICCARDI, and M. ROLLA, Ric. Sci. **38**, 123 [1968]; d) Ric. Sci. **38** [1968], in press.

Results and Discussion

1. Nitromethane + hydrocarbons systems. The critical demixing temperatures (T_{max} °K) taken on the mixtures of nitromethane with eleven 1-alkenes, six cycloalkanes and two cycloalkenes (Tables 1 – 3)

Alkene	$\overline{T}_{max}$ (°K)	T_{max}	ΔT
1-pentene	320.2	322.4	±2.2
3-methyl-1-butene	324.5		
2-methyl-1-pentene	335.5	334.7	±0.8
2,3-dimethyl-1-butene	333.9		
2-methyl-1-hexene	346.5	343.2	±3.5
3-methyl-1-hexene	345.6		
4-methyl-1-hexene	340.7		
5-methyl-1-hexene	339.7		
2,3-dimethyl-1-pentene	343.4		
2-methyl-1-heptene	356.4	357.2	±0.8
2,3-dimethyl-1-hexene	358.0		

Table 1. Critical demixing temperatures in nitromethane+1-alkenes mixtures.

Cycloalkane	T_{max} (°K)	$\overline{T}_{max}$	ΔT
Cyclopentane	353.2	353.2	–
Cyclohexane	365.8	364.2	±1.7
Methylcyclopentane	362.5		
Cycloheptane	374.6	372.5	±2.2
Methylcyclohexane	370.3		
Cyclooctane	382.7	382.7	–

Table 2. Critical demixing temperatures in nitromethane+cycloalkanes mixtures.

Cycloalkene	T_{max} (°K)
Cyclopentene	307.2
Cyclohexene	322.6

Table 3. Critical demixing temperatures in nitromethane + cycloalkenes mixtures.

are to be compared to those regarding the mixtures with n-pentane [2] and 27 other alkanes [1b, c].

From this comparison, the following remarks can be drawn: a) in addition to the number and quality of chain ramifications, such structural features as the double bond and cyclization do exert (as it might be expected) an influence on the critical temperature; b) the magnitude of this effect is a function of n_C; c) systems containing isomeric hydrocarbons of the same type always show critical temperatures ranging within rather close limits.

Let us consider, e. g., the (nitromethane + C_7-hydrocarbons) systems investigated by us. The critical temperatures are ranging: from 375.6 °K to 381.0 °K (mean value: $\bar{T}_{max} = 378.1 \pm 2.9$) for the C_7-alkanes [1c]; from 339.7 °K to 346.5 °K ($\bar{T}_{max} = 343.2 \pm 3.5$) for the C_7-1-alkenes (Table 1); from 370.3 °K to 374.6 °K ($\bar{T}_{max} = 372.5 \pm 2.2$) for the C_7-cycloalkanes (Table 2).

In other words, the critical demixing temperature of a C_7-alkane mixed with nitromethane is lowered, as an average, by 34.9° when a double bond is introduced into position 1, 2, and by 5.6° when passing from the C_7-alkane to a C_7-cycloalkane.

However, for C_r-hydrocarbons, with $r + 7$, the mentioned differences can increase, decrease, or even change their sign.

When the $\bar{T}_{max}$ values are plotted vs. n_C (Fig. 1), the points are rather satisfactorily fitted by the straight lines:

$$\bar{T}_{max} = 346.05 + 4.57\, n_C \quad \text{(alkanes)}, \qquad (1)$$

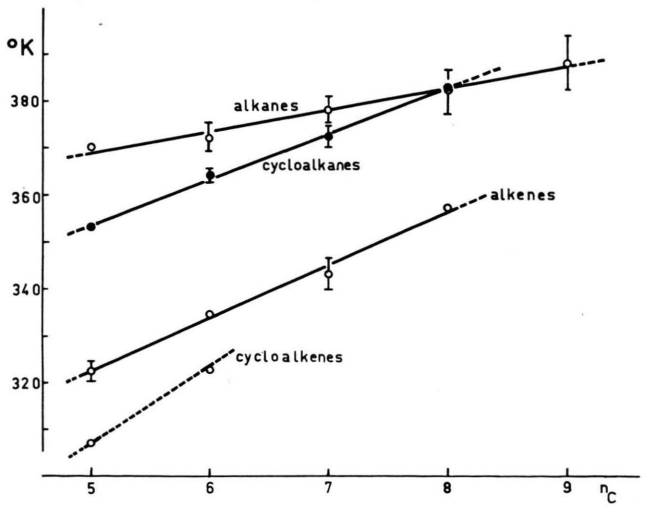

Fig. 1. Plot of $\bar{T}_{max}$ values vs. n_C for binary mixtures of nitromethane with hydrocarbons.

[2] Unpublished; $T_{max} = 370.7$ °K.

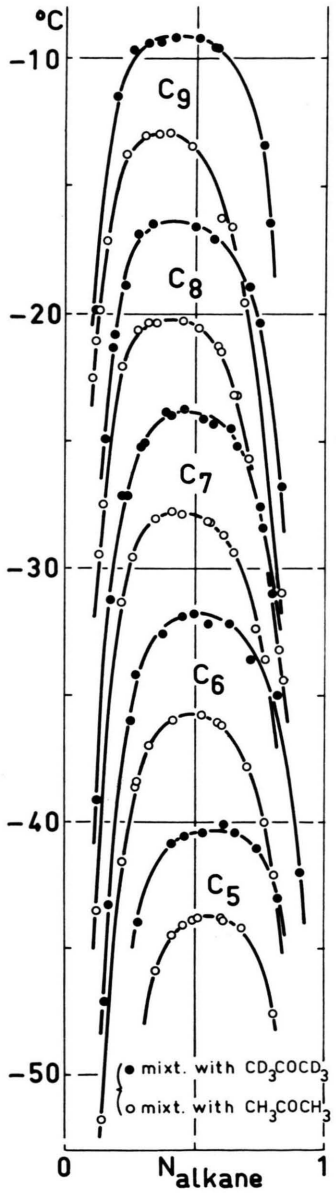

Fig. 2. Miscibility gaps in binary mixtures of acetone or hexadeuteroacetone with (C_5—C_9)-n-alkanes.

$$\bar{T}_{max} = 265.99 + 11.29\, n_C \quad \text{(alkenes)}, \qquad (2)$$

$$\bar{T}_{max} = 305.23 + 9.68\, n_C \quad \text{(cycloalkanes)}. \qquad (3)$$

Within the limits of the assumed approximations, the effects of the considered structural features seem to follow additivity rules. Thus, owing to Eqs. (1) to (3), a cyclic double-bonded hydrocarbon mixed with nitromethane ought to exhibit a T_{max} value close to the straight line (dashed in Fig. 1):

$$\bar{T}_{max} = 225.17 + 16.40\, n_C \quad \text{(cycloalkenes)}. \qquad (4)$$

Indeed, the critical demixing temperatures experimentally observed and calculated by Eq. (4) are 307.2 °K and 307.0 °K for cyclopentene, 322.6 °K and 323.6 °K for cyclohexene, respectively, with a very satisfactory agreement.

Alkanes	CH_3COCH_3		CD_3COCD_3	
	$N_{a,max}$	T_{max} (°K)	$N_{a,max}$	T_{max} (°K)
n-pentane	0.55	229.4	0.55	233.0
n-hexane	0.51	237.5	0.52	241.4
n-heptane	0.46	245.4	0.47	249.3
n-octane	0.42	253.0	0.43	257.0
n-nonane	0.38	260.3	0.41	264.1

Table 4. Critical points in acetone or hexadeuteroacetone + (C_5 – C_9)-n-alkanes.

2. CH_3COCH_3 or CD_3COCD_3 + (C_5 – C_9)-n-alkanes systems. The experimental demixing curves for the mixtures of hexadeuteroacetone with (C_5 – C_9)-n-alkanes are compared in Fig. 2 to those for the corresponding systems containing acetone [1d]. The coordinates of the critical points for both series are reported in Table 4.

The results show that, in each couple of corresponding systems, acetone deuteration essentially causes an increase of the critical temperature, which is approximatively constant and equal to $3.8 \pm 0.2°$.

Moreover, the miscibility gap widens, and the abscissa of the critical point shows a definite, though little, trend towards higher alkane molecular fractions.

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