Binary Systems Containing Hydrocarbons

IV. Miscibility Gaps in 18 Nitromethane + 1-, 2-, 3- and 4-alkenes *

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Liquid-liquid equilibria in binary systems of nitromethane with 1-(C_8-C_9)-, trans-2-(C_5-C_9)-, trans-3-(C_6-C_9)-, trans-4-(C_8-C_9)-, 3-methyl-1-(C_5)-, 2-methyl-2-(C_5-C_7)- and cis-2-(C_6)-alkenes were investigated. Some regularities obeyed by the critical temperatures and compositions, as well as the possibility of foreseeing (on empirical basis) the two liquids region boundaries are discussed.

1. Data on the miscibility gaps in a few binary systems formed with nitromethane (referred to in the following as component **1**) and 1-alkenes were already reported in the third paper of the present series[1], and compared to those concerning binaries whose components were **1** and a number of alkanes, cycloalkanes and cycloalkenes.

Since it seemed worthwhile to have more detailed information about the effect exerted by the presence of a double bond in component **2** on the critical solution temperature (CST), demixing measurements (to which the present paper is devoted) were performed on mixtures of **1** with eighteen more alkenes which recently became available to us.

2. Fluka nitromethane ($\geqq$ 99.7 mole %) and the following Fluka hydrocarbons: trans-2-pentene ($\sim$ 99 mole%), cis-2-hexene ($\geqq$ 99.5), trans-2-hexene ($\sim$ 99), trans-3-hexene ($\sim$ 99), trans-2-heptene ($\sim$ 99), trans-3-heptene ($\sim$ 99), 1-octene (99.73), trans-2-octene ($\geqq$ 99), trans-3-octene ($\geqq$99), trans-4-octene ($\geqq$ 99), 1-nonene ($>$ 97), trans-2-nonene ($\geqq$ 99), trans-3-nonene ($\geqq$ 99), trans-4-nonene ($\geqq$ 99), 3-methyl-1-pentene ($\geqq$ 99), 2-methyl-2-pentene ($\geqq$ 99), 2-methyl-2-hexene ($\geqq$ 99), and 2-methyl-2-heptene ($\geqq$ 99) were employed.

The sample containers were tightly flame-sealed Pyrex tubes, and, for each system, at least two sets of air and moisture free samples were prepared differing in that the nitromethane and hydrocarbon used came from different purification and drying cycles.

As for octenes, nonenes and 2-methyl-2-alkenes liquid-liquid equilibria were investigated over a quite large composition range (see Tab. 1 and 2, where mole fractions, N_{alkene}, and demixing temperatures, t_d °C, are summarized), whereas only less extensive measurements could be taken on the systems with the remaining mentioned alkenes, owing to the limited hydrocarbon amounts at disposal and/or experimental difficulties. Concerning the latter, it may be said, e.g., that studying the (**1** + 1-hexene)-mixtures was prevented by the fact that in each sample the demarcation line between the two liquid phases was nearly evanescent and in practice undetectable with a reasonable degree of

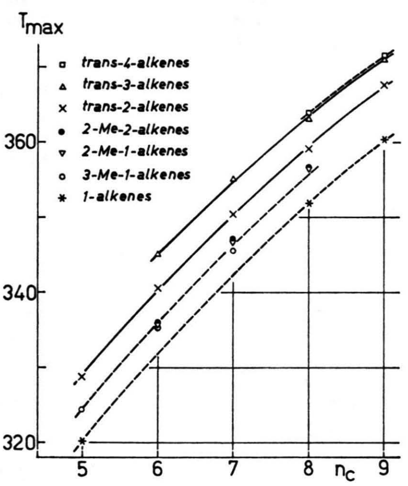

Fig. 1. CST dependence on n_C in seven series of (**1** + alkene)-mixtures.

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[1] R. RICCARDI, P. FRANZOSINI, and M. ROLLA, Z. Naturforsch. **23 a**, 1816 [1968].

Table 1. Systems of nitromethane with octenes and nonenes.

Alkene	N_{alkene}	t_d °C	Alkene	N_{alkene}	t_d °C
1-octene	0.050	44.7	1-nonene	0.067	67.8
	0.089	62.5		0.092	76.1
	0.185	76.6		0.124	81.9
	0.204	77.5		0.191	86.3
	0.222	78.1		0.204	86.8
	0.270	78.7		0.237	87.3
	0.286	78.6		0.385	86.7
	0.479	77.1		0.447	85.7
	0.488	76.8		0.480	84.8
	0.543	74.8		0.511	83.3
	0.698	63.5		0.626	75.8
	0.777	53.5		0.636	74.8
				0.767	59.3
trans-2-octene	0.061	57.6		0.823	48.4
	0.132	78.7			
	0.205	84.8	trans-2-nonene	0.029	41.4
	0.216	85.2		0.033	51.3
	0.268	85.3		0.102	85.3
	0.298	86.0		0.109	87.0
	0.435	85.2		0.192	94.1
	0.478	84.3		0.249	94.5
	0.636	76.6		0.345	94.4
	0.698	70.9		0.380	94.2
	0.848	46.2		0.514	89.7
				0.612	84.4
trans-3-octene	0.045	51.9		0.716	73.8
	0.071	65.9		0.875	38.2
	0.092	74.1			
	0.184	87.7	trans-3-nonene	0.025	44.9
	0.242	89.4		0.037	55.1
	0.250	89.7		0.073	79.7
	0.360	89.9		0.113	90.4
	0.450	88.9		0.163	95.6
	0.539	86.1		0.251	97.9
	0.660	78.2		0.390	97.5
	0.692	75.1		0.407	96.9
	0.862	45.7		0.521	93.0
				0.674	79.7
trans-4-octene	0.045	52.1		0.769	68.8
	0.121	82.1		0.810	60.9
	0.129	83.2		0.849	52.4
	0.137	84.5			
	0.146	85.6	trans-4-nonene	0.028	50.2
	0.193	89.2		0.040	62.8
	0.246	90.6		0.099	88.1
	0.247	90.6		0.148	95.0
	0.378	90.6		0.244	98.4
	0.389	90.6		0.246	98.5
	0.404	90.4		0.305	98.5
	0.632	81.5		0.328	98.5
	0.716	73.3		0.453	96.5
	0.847	50.2		0.613	88.4
				0.652	84.2
				0.754	71.2
				0.816	59.7

Table 2. Systems of nitromethane with 2-methyl-2-alkenes.

Alkene	N_{alkene}	t_d °C	Alkene	N_{alkene}	t_d °C
2-methyl-2-pentene	0.125	42.9		0.460	73.7
	0.154	49.9		0.535	72.9
	0.174	52.8		0.712	61.0
	0.186	54.6		0.753	56.5
	0.196	56.0		0.787	52.5
	0.254	60.4		0.788	52.1
	0.320	62.2			
	0.347	62.6	2-methyl-2-heptene	0.035	32.6
	0.390	62.7		0.095	67.6
	0.446	62.7		0.169	79.6
	0.490	62.3		0.170	80.6
	0.544	61.8		0.173	80.4
	0.552	61.5		0.200	82.3
	0.597	60.3		0.239	83.1
	0.654	58.0		0.251	83.1
	0.673	56.6		0.299	83.2
	0.737	52.0		0.358	83.5
	0.760	48.9		0.403	83.5
	0.816	40.6		0.418	83.3
				0.484	81.9
2-methyl-2-hexene	0.068	40.1		0.507	81.8
	0.077	43.6		0.530	80.6
	0.146	64.6		0.578	78.6
	0.171	68.1		0.589	77.8
	0.207	70.9		0.626	75.6
	0.319	73.9		0.719	66.4
	0.346	74.0		0.781	55.7
	0.359	74.1		0.886	33.4
	0.404	74.0			

accuracy, at least by the visual method we adopted (and described elsewhere[2]).

3. The CST's, $T_{\max}$ °K, of the eighteen systems considered are collected in Tab. 3, together with those of six other previously examined[1] pertinent binaries[3]: the same data are shown in Fig. 1.

It may be first observed that, in binaries where **1** is the fixed component, the replacement of a (C_5—C_9)-n-alkane[4] with an alkene characterized by the same number, n_C, of carbon atoms always depresses the CST (to this purpose, see also Ref. [1]): concerning the mixtures which the upper part of Tab. 3 refers to, the sharpest effects, caused by 1-alkenes, are progressively attenuated when 3-methyl-1-, 2-methyl-1-, 2-methyl-2-, trans-2-, trans-3-, and trans-4-alkenes are successively taken into account.

The seven groups of points corresponding to the mentioned alkenes may then be rather satisfactorily interpolated by a set of smooth curves (slightly diverging as n_C decreases), which are probably weakly bent parabolas. In fact, the two richest groups [(a) trans-2-alkenes, 5 points; (b) trans-3-

[2] P. Franzosini, Z. Naturforsch. **18 a**, 224 [1963].

[3] formed with **1** and 1-pentene, 3-methyl-1-butene, 3-methyl-1-hexene, 2-methyl-1-pentene, 2-methyl-1-hexene and 2-methyl-1-heptene.

[4] P. Franzosini, R. Riccardi, and M. Rolla, Ric. Sci. **38**, 123 [1968].

alkenes, 4 points;] were least square treated with the following results:

a) $T_{\max} = 257.32_7 + 16.93_7 n_C - 0.52_1 n_C^2$, (1)

b) $T_{\max} = 265.18_9 + 16.44_7 n_C - 0.52_1 n_C^2$. (2)

Noteworthy is finally the remarkable CST depression associated to the substitution of a trans-alkene with its cis-isomer, as observed in the case of the isomeric pair trans- and cis-2-hexene.

4. Two regularities, previously[4] pointed out in the (**1** + alkane)-mixtures, seem to be still obeyed, i.e.: a) the greater n_C is, the lower becomes $(N_{\text{alkene}})_{\max}$; b) binaries containing isomeric alkenes exhibit rather close $(N_{\text{alkene}})_{\max}$ values, which moreover lie not far from those found in the (**1** + alkane)-systems.

As an example, the mean $(\bar{N}_{\text{alkane}})_{\max}$ values concerning: a) eight (**1** + C_9-alkane)-, b) nine (**1** + C_8-alkane)-, c) four (**1** + C_7-alkane)-, d) five (**1** + C_6-alkane)-systems were 0.31 ± 0.01, 0.33 ± 0.01, $0.36_5 \pm 0.01$, and $0.41_5 \pm 0.01$, respectively, while, by applying the Cailletet-Mathias rule to the Tab. 1 and 2 measurements, the following figures can be drawn:

a) **1** + 1-nonene : $(N_{\text{alkene}})_{\max} = 0.29_5$
trans-2-nonene 0.29
trans-3-nonene 0.30
trans-4-nonene 0.29_5

b) **1** + 1-octene : $(N_{\text{alkene}})_{\max} = 0.32_5$
trans-2-octene 0.33
trans-3-octene 0.32_5
trans-4-octene 0.32_5
2-methyl-2-heptene 0.33

c) **1** + 2-methyl-2-hexene : $(N_{\text{alkene}})_{\max} = 0.37_5$

d) **1** + 2-methyl-2-pentene : $(N_{\text{alkene}})_{\max} = 0.41_5$

5. The four pairs of systems formed with **1** and: 1-octene, 1-nonene; trans-2-octene, trans-2-nonene; trans-3-octene, trans-3-nonene; trans-4-octene, trans-4-nonene, respectively, exhibit ,,generalized,, curves[5] hardly distinguishable from each other. Therefore (see Fig. 2) all of the Tab. 1 experimental points, plotted on the $(T_d/T_{\max}, z)$-plane, were interpolated by means of a unique curve[6].

Table 3. Critical solution temperatures ($T_{\max}$ °K) in the systems of nitromethane with a number of 1-, 2-, 3- and 4-alkenes and of (2 or 3)-monomethyl-(1 or 2)-alkenes.

	$n_C = 9$	8	7	6	5
1-alkenes	360.5	351.9	—	—	320.2 *
3-methyl-1-alkenes	—	—	345.6 *	335.4	324.5 *
2-methyl-1-alkenes	—	356.4 *	346.5 *	335.5 *	—
2-methyl-2-alkenes	—	356.7	347.2	335.9	—
trans-2-alkenes	367.8	359.1	350.4	340.6	328.8
trans-3-alkenes	371.1	363.1	355.1	345.0	
trans-4-alkenes	371.7	363.9			
cis-2-alkenes	—	—	—	332.6	—

* see Ref. [1]

[5] B. MALESINSKA, Bull. Acad. Pol. Sci., Sér. Sci. Chim. 8, 53 [1960].

[6] The asymmetry factors (as a first approximation supposed to be T-independent):

$$Q_{\text{nonenes}} = \frac{1 - (\bar{N}_{\text{nonenes}})_{\max}}{(\bar{N}_{\text{nonenes}})_{\max}} = \frac{0.70_5}{0.29_5} = 2.39\,,$$

$$Q_{\text{octenes}} = \frac{1 - (\bar{N}_{\text{octenes}})_{\max}}{(\bar{N}_{\text{octenes}})_{\max}} = \frac{0.67_5}{0.32_5} = 2.08\,,$$

were employed, while the z fractions in Fig. 2 are to be intended as

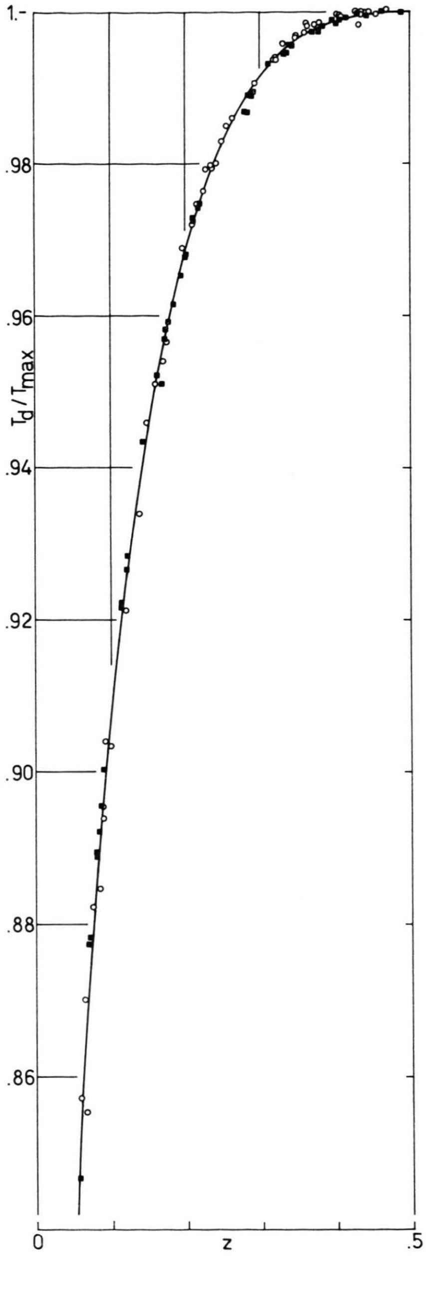
$z'_1 = N'_1/(N'_1 + QN'_{\text{alkene}})$ when $N_{\text{alkene}} > (N_{\text{alkene}})_{\max}$

and as

$$z''_{\text{alkene}} = QN''_{\text{alkene}}/(N''_1 + N''_{\text{alkene}})$$

when $N_{\text{alkene}} < (N_{\text{alkene}})_{\max}$

(′ and ″ then obviously refer to solutions of **1** into the alkene and of the alkene into **1**, respectively).



The latter might then be used to draw the boundaries of the whole demixing regions proper to systems formed with **1** and any alkene which can be considered a sufficiently next relative of those mentioned in Table 1 provided that the critical solution point co-ordinates are either known or foreseeable [as for T_{max}, a trustworthy forecast might in fact be made, e.g., on the basis of equations such as Eqs. (1) and (2), while $(N_{\text{alkene}})_{\text{max}}$ might be argued from suitable literature data].

Taking into account the following $T_{\text{d}}/T_{\text{max}}$ and z values:

$T_{\text{d}}/T_{\text{max}}$	0.998	0.994	0.990	0.980	0.970	0.960
z	0.381	0.325	0.292	0.238	0.203	0.178

(drawn from the curve in Fig. 2), and the asymmetry factor $Q_{\text{hexenes}} = 0.58_5/0.41_5 = 1.41$, the boundaries of the demixing regions in the (**1** + trans-2-hexene)- and (**1** + trans-3-hexene)-mixtures were thus reckoned: it is interesting to point out that still acceptable results may also be achieved in the case of the 2-hexene cis-isomer.

A comparison between the calculated curves and the experimental data is made in Fig. 3.

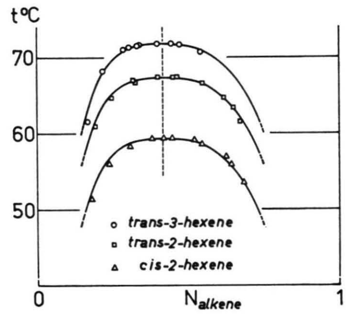


Fig. 3. Calculated demixing curves and experimental data in three (**1** + hexene)-systems.

Fig. 2. "Generalized" demixing curve common to the eight ← Table 1 systems (black squares: z_1'; open circles: z_{alkene}'').