Binary Systems Containing Hydrocarbons

Note I. Miscibility Gaps in the Methylacetate + Alkanes Systems

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The miscibility gaps below 0 °C in the binary liquid systems of methylacetate with 14 alkanes having a number of carbon atoms n_C between 5 and 9 have been measured. It has been shown how the coordinates of the critical solution points on the (T_d, N_{alkane}) plane are parabolic functions of n_C for the n-alkanes. Moreover, according to MALESINSKA, a generalized demixing curve has been drawn on the (T_d/T_{max}, z) plane.

The literature reports about 6,000 cases of binary systems in which two liquid phases in equilibrium coexist within certain ranges of temperature and composition. The entity of this volume of data, however, is more seeming than real, as most experiences are only qualitative: often the demixing curve is not drawn, but a single datum is given, as in the case of the so called "aniline points".

As regards the systems containing hydrocarbons, careful measurements of miscibility gaps (MG) are comparatively few, above all when the MG's lie below 0 °C. In particular, practically no information is available for the methylacetate (MeOAc) + alkanes mixtures: in his up to date tables FRANCIS [1], for the critical solution points (CSP) of this family of systems, reports only the folowing data:

MeOAc + n-heptane	$t_{max} < 15$ °C,
+ 2,2,4-trimethylpentane	< 15 °C,
+ n-octadecane	< 20 °C.

Therefore, it was thought of interest to carry on a deeper research in this field. In the present paper we refer about the MG's in the binary liquid mixtures of MeOAc with: n-pentane (I) (99.98 mole %), isopentane (II) (99.99+), n-hexane (III) (99.96), 2-methylpentane (IV) (99.95), 3-methylpentane (V) (99.80), 2,2-dimethylbutane (VI) (99.99+), 2,3-dimethylbutane (VII) (99.87), n-heptane (VIII) (99.87), 2,4-dimethylpentane (IX) (99.72), n-octane (X) (99.81), 2,2,4-trimethylpentane (XI) (99.99), 2,3,4-trimethylpentane (XII) (99.50), n-nonane (XIII) (99.68) and 2,2,5-trimethylhexane (XIV) (99.78).

The alkanes (Fluka *puriss.*) have been dried by contact with metal Na and then by flowing the vapours through a tube filled with P_2O_5; MeOAc (C. Erba RP) has been treated and dried as described elsewhere [2].

A visual method has been employed: as for apparatus, procedure, and some general remarks, we refer to previous papers [2, 3].

Results

For each system the measurements have been taken in the widest concentration range, according to the possibility of observing in a clear and reproducible way the occurring of the opalescence that shows the beginning of the demixtion. The observation range was very narrow for the systems with (I) and (II), for which taking the demixing temperatures was also rather difficult: this is the reason why in Fig. 2 the data regarding these two systems are not shown.

In Table 1 the compositions of the samples as N_{alkane}, together with the corresponding demixing temperatures t_d °C, taken by slowly cooling (<0.1 °/min) and shaking, are summarized.

In Table 2 the CSP coordinates $(N_{alkane})_{max}$ and T_{max} °K of the various systems are tabulated. As for n-alkanes, from the latter table it can be inferred that the T_{max} value increases progressively as the number of carbon atoms n_C increases. This occurs, as shown in Fig. 1 A, according to a parabolic law expressed by the equation

$$T_{max} = 178.23 + 9.35\, n_C - 0.175\, n_C^2. \quad (1)$$

[1] A. W. FRANCIS, Critical Solution Temperatures, Advan. Chem. Ser. No. 31, Am. Chem. Soc. 1961.

[2] P. FRANZOSINI, R. RICCARDI, and M. SANESI, Ric. Sci. **35** (II-A), 700 [1965].

[3] P. FRANZOSINI, Z. Naturforschg. **18 a**, 224 [1963].

Alkane	N_{alkane}	$-t_d$ °C
(I)	0.320	54.0
	0.334	53.7
	0.454	52.5
	0.477	52.6
	0.527	52.7
(II)	0.274	59.3
	0.382	56.5
	0.423	56.3
	0.545	56.2
	0.565	56.3
	0.576	56.4
	0.587	56.6
(III)	0.206	49.4
	0.215	48.7
	0.360	45.3
	0.408	45.2
	0.467	45.2
	0.532	45.3
	0.532	45.4
	0.669	47.0
	0.747	50.9
(IV)	0.201	53.4
	0.228	51.7
	0.238	51.2
	0.282	49.8
	0.389	48.7
	0.460	48.7
	0.562	49.0
	0.583	49.3
	0.716	53.0
	0.739	54.3
(V)	0.175	57.4
	0.256	52.0
	0.264	52.0
	0.384	50.2
	0.415	50.2
	0.535	50.3
	0.587	50.7
	0.674	52.3
	0.681	52.9
	0.713	53.7
	0.839	62.9
(VI)	0.201	61.0
	0.202	60.7
	0.233	58.9
	0.233	59.0
	0.371	56.2
	0.395	56.1
	0.486	56.2
	0.576	56.5
	0.715	59.9
	0.725	60.4
	0.817	66.1
(VII)	0.185	60.4
	0.189	60.5
	0.263	56.0
	0.345	54.7
	0.509	54.4
	0.557	54.9
	0.709	57.5
	0.791	62.6
	0.824	64.7
(VIII)	0.088	53.9
	0.132	46.1
	0.138	45.4
	0.160	43.3
	0.284	38.5
	0.376	38.1
	0.424	38.1
	0.514	38.5
	0.556	39.2
	0.628	40.9
	0.736	46.0
	0.770	48.7
(IX)	0.083	63.8
	0.115	56.7
	0.152	52.1
	0.242	46.9
	0.245	46.7
	0.368	45.6
	0.413	45.6
	0.532	46.1
	0.580	46.7
	0.594	47.2
	0.670	49.7
	0.789	56.6
	0.870	66.6
(X)	0.053	55.4
	0.086	44.6
	0.104	41.0
	0.151	35.4
	0.221	32.4
	0.233	32.0
	0.311	31.4
	0.366	31.4
	0.422	31.4
	0.505	32.3
	0.643	36.4
	0.699	39.4
	0.857	56.0
(XI)	0.060	68.5
	0.110	55.1
	0.141	51.6
	0.207	47.5
	0.255	46.3
	0.365	45.9
	0.415	45.9
	0.507	46.6
	0.561	47.5
	0.654	50.5
	0.685	52.2
	0.812	62.4
(XII)	0.076	62.8
	0.105	55.5
	0.157	49.1
	0.218	45.9
	0.255	45.0
	0.311	44.5
	0.425	44.5
	0.428	44.5
	0.586	46.4
	0.604	46.9
	0.616	47.4
	0.745	54.1
	0.843	64.2
(XIII)	0.066	40.4
	0.093	34.0
	0.152	27.7
	0.216	25.6
	0.249	25.2
	0.338	25.0
	0.341	25.0
	0.370	25.1
	0.448	25.6
	0.519	26.9
	0.629	30.9
	0.756	40.1
(XIV)	0.089	48.2
	0.112	44.5
	0.120	43.6
	0.208	38.6
	0.270	37.8
	0.362	37.8
	0.480	38.6
	0.523	39.4
	0.658	44.7
	0.748	51.2
	0.803	56.8

Table 1. Systems of methyl acetate with alkanes.

Alkane	$(N_{alkane})_{max}$	T_{max}(°K)
(I)	about 0.5	$220._6$
(II)	about 0.5	$217._2$
(III)	$0.45_0 \pm 0.005$	228.0
(IV)	$0.45_0 \pm 0.005$	224.6
(V)	$0.45_0 \pm 0.005$	223.0
(VI)	$0.45_0 \pm 0.005$	217.1
(VII)	$0.45_0 \pm 0.005$	218.9
(VIII)	$0.40_5 \pm 0.005$	235.1
(IX)	$0.40_5 \pm 0.005$	227.6
(X)	$0.36_5 \pm 0.005$	241.9
(XI)	$0.36_5 \pm 0.005$	227.3
(XII)	$0.36_5 \pm 0.005$	228.8
(XIII)	$0.33_0 \pm 0.005$	248.2
(XIV)	$0.33_0 \pm 0.005$	235.5

Table 2. CSP's in the systems of methyl acetate with alkanes.

Moreover, the groups of alkanes having the same n_C show almost equal $(N_{alkane})_{max}$ values. As n_C increases, $(N_{alkane})_{max}$ diminishes, following once more a parabolic law according to

$$(N_{alkane})_{max} = 0.825 - 0.077_5\, n_C + 0.002_5\, n_C^2 \quad (2)$$

as shown in Fig. 1 B.

Eqs. (1) and (2) are obviously valid only when $5 \leqq n_C \leqq 9$.

Noteworthy is also what follows. On the (t_d, N_{alkane}) plane the demixing curves look rather asymmetrical. A procedure allowing to draw a symmetrical curve, common to the whole family of the systems studied, was proposed by MALESINSKA [4]. According to this procedure, the compositions of the mixtures have been calculated as fractions z:

[4] B. MALESINSKA, Bull. Acad. Polon. Sci., Sér. Sci. Chim. **8**, 53 [1960].

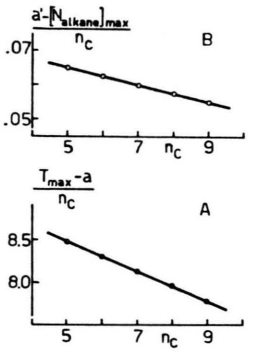

Fig. 1.
Plots of the ratios $(T_{max}-a)/n_C$ and $[a'-(N_{alkane})_{max}]/n_C$ vs. the number of carbon atoms n_C in the alkanes ($a=178.23$; $a'=0.825$). Fig. 1 A refers to n-alkanes only.

$$z_1' = N_1' q_1/(N_1' q_1 + N_2' q_2), \quad z_2' = 1 - z_1',$$

$$z_1'' = N_1'' q_1/(N_1'' q_1 + N_2'' q_2), z_2'' = 1 - z_1''$$

where 1 and 2 refer to MeOAc and to the alkane, while $'$ and $''$ to the solutions of 1 into 2 and to those of 2 into 1, respectively. The asymmetry factors q_2/q_1 (considering that, for all systems, the ratios $N_1' N_1''/N_2' N_2''$, evaluated from the interpolated curves, show unsignificant fluctuations when changing the temperature) have been taken as independent from T. Moreover, for each mixture a reduced demixing temperature T_d/T_{max} (with T_d and T_{max} in °K) has been calculated.

By plotting the experimental data on the $(T_d/T_{max}, z)$ plane, it has been seen that the MG's concerning the 12 systems with the $C_6 - C_9$ alkanes can be represented by a single generalized demixing curve, which is symmetrical with respect to $z = 0.5$ (see Fig. 2).

Acknowledgments

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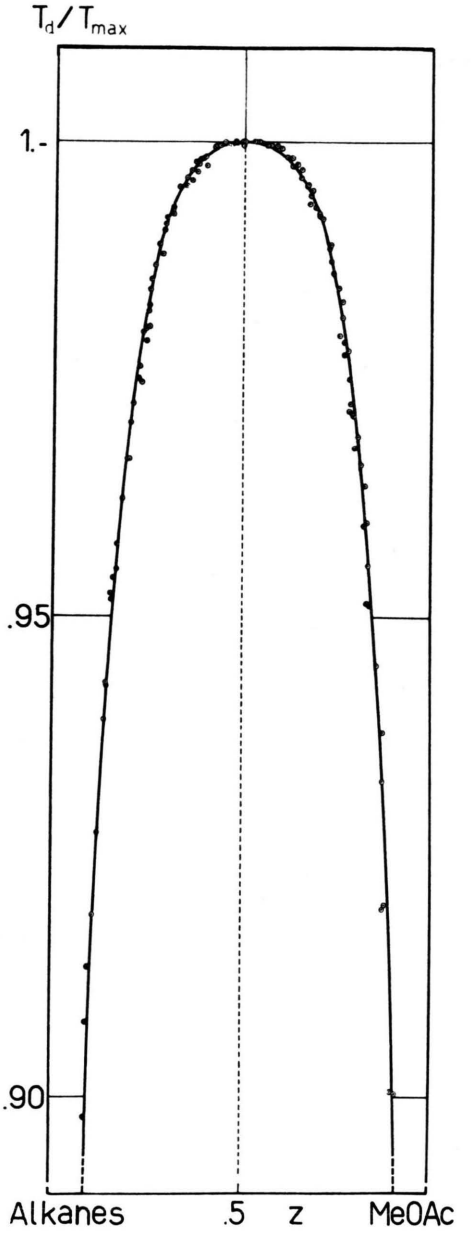

Fig. 2. Plot of reduced temperatures T_d/T_{max} vs. fraction z for 12 systems formed by MeOAc with C_6-C_9 alkanes.