

Some Remarks on methylformate + n. alkanes Binary Systems *

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We referred previously¹, among other things, on liquid-liquid equilibria occurring in methylacetate + (C₅—C₉)-n. alkanes binary mixtures: the investigation is now extended to analogous systems containing methylformate (indicated as component 1 in the following).

Fluka HCOOCH₃ (purum, > 98%), n. pentane (puriss., ~ 99.98), n. hexane (puriss., ~ 99.96), n. heptane (puriss., ~ 99.87), n. octane (puriss., ~ 99.81) and n. nonane (puriss., ~ 99.68) were employed. Before use, hydrocarbons were dried as previously described¹, while HCOOCH₃, after having been kept in contact overnight with K₂CO₃, decanted and distilled, was let to rest a fortnight over P₂O₅, then distilled twice more, and finally let to flow (as a vapour) through a tube filled with P₂O₅ into the storage flask of the sample preparing device.

Our usual procedure² was followed to prepare the samples and take the demixing temperatures. In each system the composition range explored was the widest in which the demixing temperatures could be taken in a satisfactorily reproducible way.

As already observed for the CH₃COOCH₃ containing mixtures, the co-ordinates of the critical solution points, T_m (°K) and $N_{2,m}$, are regularly varying with the n. alkane (component 2) chain length. The dependence

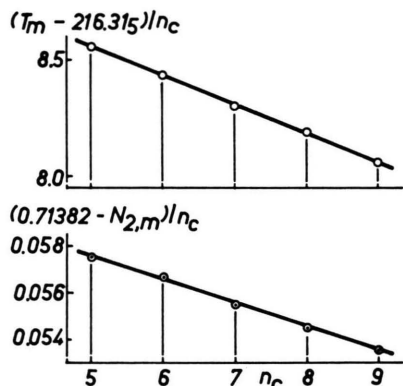


Fig. 1. Plots of the ratios $(T_m - 216.315)/n_c$ and $(0.71382 - N_{2,m})/n_c$ vs. n_c (explanation in text).

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is now expressed (see Fig. 1) by the equations

$$(T_m - 216.315)/n_c = 9.18 - 0.125 n_c \quad (1)$$

and

$$(0.71382 - N_{2,m})/n_c = 0.06706 - 0.00200 n_c \quad (2)$$

where $n_c = 5, 6, \dots, 9$ for n. pentane, n. hexane, ..., n. nonane, respectively.

alkane	T_m (°K)		$N_{2,m}$		q_2/q_1
	observed	calculated	observed	calculated	
n. pentane	259.1	259.1	0.42 ₉	0.4285	1.33
n. hexane	266.9	266.9	0.38 ₂	0.3835	1.61
n. heptane	274.4	274.4 ₅	0.34 ₃	0.3424	1.92
n. octane	281.8	281.8	0.30 ₆	0.3063	2.26
n. nonane	288.8	288.8	0.27 ₂	0.2723	2.67

Table 1. Main features of the HCOOCH₃+n. alkanes binary systems.

T_m and $N_{2,m}$ values singled out by applying the Cailletet-Mathias's rule are compared in Table 1 with those calculated by means of Eqs. (1) and (2). It may be noted that in the systems considered, taking HCOOCH₃ instead of CH₃COOCH₃ as the component 1 causes T_m to increase by 39.5 ± 1 °K, and $N_{2,m}$ to lower by 0.065 ± 0.007 molar fraction units.

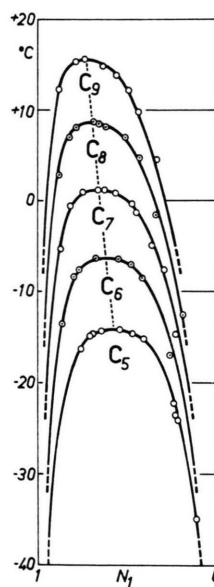


Fig. 2. Comparison between the calculated demixing curves and the experimental data.

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¹ M. ROLLA, P. FRANZOSINI, R. RICCARDI, and L. BOTTELLI, Z. Naturforsch. 21 a, 601 [1966].

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



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On the "generalized" demixing curve¹, common to the five systems, there is correspondence among the following reduced temperatures and z fractions:

T_{demixing}/T_m	: 1.0000	0.9990	0.9975	0.9950	0.9900
z	: 0.500	0.428	0.377	0.330	0.279
		0.572	0.623	0.670	0.721

T_{demixing}/T_m	: 0.9800	0.9700	0.9600	0.9400	0.9200
z	: 0.228	0.192	0.164	0.121	0.090
	0.772	0.808	0.836	0.879	0.910

The above values, together with the asymmetry factors $q_2/q_1 = N_{1,m}/N_{2,m}$ reported in Table 1, allowed us to calculate the liquid-liquid equilibrium curves shown in Fig. 2.

BERICHTIGUNGEN

Zu S. FRANCO and J. HEBERLE, Transmission of a Lorentzian Spectral Line Through a Layer of Lorentzian Absorbers. II, Z. Naturforsch. **25 a**, 134 [1970].

Die Gl. (10.5) soll lauten:

$$g_{j+1, m+1} = \frac{1}{m} \left[2(3j\gamma + m + j) g_{jm} + (m - j - 1) g_{j+1, m-2} \gamma(\gamma + 1) \frac{d}{d\gamma} g_{jm} \right].$$

Die Gl. (10.9) soll lauten:

$$\alpha(i, j, m) = \frac{j-i+1}{j} \binom{2j}{i-1} \binom{m+j-1}{m-1} = \frac{m}{j} \binom{2j}{i-1} \binom{m+j-i}{m}.$$

In Gl. (11.7) bedeutet E_r^1 $E_r^1 = \frac{1}{2}(s^r/r!) Q_r^1(\gamma, x)$.

Auf S. 138, rechte Spalte, lautet die 2. Gleichung: $2/(1+w_0^2) = 1$.

Die erste Zeile von Gl. (13.5a) lautet:

$$\frac{\partial^2 \lambda}{\partial w^2} = \frac{1}{2\gamma} \sum_{m=1}^{\infty} \frac{(-T)^{m-1}}{m!} \frac{d}{dw} \left[-\frac{2w}{1+w^2} q_m^1(w) \right].$$

Auf S. 139, rechte Spalte, lautet die erste Gleichung in der 12. Zeile $p_0 = -1$ statt $p = -1$.

Gleichung (13.9) lautet richtig:

$$\begin{aligned} & \left\{ \frac{d^5 w}{dT^5} \frac{\partial}{\partial w} + 5 \left[\frac{dw}{dT} \frac{d^4 w}{dT^4} + 2 \frac{d^2 w}{dT^2} \frac{d^3 w}{dT^3} \right] \frac{\partial^2}{\partial w^2} + 5 \frac{d^4 w}{dT^4} \frac{\partial^2}{\partial w \partial T} + 5 \frac{dw}{dT} \left[2 \frac{dw}{dT} \frac{d^3 w}{dT^3} + 3 \left(\frac{d^2 w}{dT^2} \right)^2 \right] \frac{\partial^3}{\partial w^3} \right. \\ & + 10 \frac{d^3 w}{dT^3} \frac{\partial^3}{\partial w \partial T^2} + 5 \left[3 \left(\frac{d^2 w}{dT^2} \right)^2 + 4 \frac{dw}{dT} \frac{d^3 w}{dT^3} \right] \frac{\partial^3}{\partial w^2 \partial T} + 10 \left(\frac{dw}{dT} \right)^3 \frac{d^2 w}{dT^2} \frac{\partial^4}{\partial w^4} + 30 \frac{dw}{dT} \frac{d^2 w}{dT^2} \left[\frac{dw}{dT} \frac{\partial^4}{\partial w^3 \partial T} + \frac{\partial^4}{\partial w^2 \partial T^2} \right] \\ & + 10 \frac{d^2 w}{dT^2} \frac{\partial^4}{\partial w \partial T^3} + \left(\frac{dw}{dT} \right)^5 \frac{\partial^5}{\partial w^5} + 5 \left(\frac{dw}{dT} \right)^2 \left[\left(\frac{dw}{dT} \right)^2 \frac{\partial^5}{\partial w^4 \partial T} + 2 \frac{dw}{dT} \frac{\partial^5}{\partial w^3 \partial T^2} + 2 \frac{\partial^5}{\partial w^2 \partial T^3} \right] \\ & \left. + 5 \frac{dw}{dT} \frac{\partial^5}{\partial w \partial T^4} + \frac{\partial^5}{\partial T^5} \right\} \lambda(w, T) = 0. \end{aligned}$$

Auf S. 140, rechte Spalte, lautet die erste Gleichung:

$$\varepsilon(\gamma, s, w_x) - \frac{1}{2} \varepsilon(\gamma, s; 0) = 0.$$

Zu H. KLINGENBERG, F. SARDEI, and W. ZIMMERMANN, Quantitative Experimental and Theoretical Investigations on the Interaction of Shock Waves with Magnetic Fields. Z. Naturforsch. **24 a**, 1449 [1969].

Auf S. 1452 lautet Gl. (11) vollständig:

$$\varepsilon_r = C Z^2 N_e^2 T^{-1/2} \quad \text{with} \quad \nu < \nu_g. \quad (11)$$

Auf S. 1452 a muß Fig. 3 c um 180° gedreht werden.