Some Remarks on methylformate + n. alkanes Binary Systems *

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(Z. Naturforsch. **25 a**, 457—458 [1970]; received 20 February 1970)

We referred previously [1], among other things, on liquid-liquid equilibria occurring in methylacetate + ($C_5 - C_9$)-n. alkanes binary mixtures: the investigation is now extended to analogous systems containing methylformate (indicated as component 1 in the following).

Fluka $HCOOCH_3$ (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 described [1], while $HCOOCH_3$, after having been kept in contact overnight with K_2CO_3, decanted and distilled, was let to rest a fortnight over P_2O_5, then distilled twice more, and finally let to flow (as a vapour) through a tube filled with P_2O_5 into the storage flask of the sample preparing device.

Our usual procedure [2] 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 CH_3COOCH_3 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 is now expressed (see Fig. 1) by the equations

$$(T_m - 216.31_5)/n_C = 9.18 - 0.12_5\, n_C \quad (1)$$

and

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

where $n_C = 5, 6, \ldots, 9$ for n. pentane, n. hexane, ..., n. nonane, respectively.

alkane	T_m (°K) observed	T_m (°K) calculated	$N_{2,m}$ observed	$N_{2,m}$ calculated	q_2/q_1
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 $HCOOCH_3$+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 $HCOOCH_3$ instead of CH_3COOCH_3 as the component 1 causes T_m to increase by 39.5 ± 1 °K, and $N_{2,m}$ to lower by $0.06_5 \pm 0.00_7$ molar fraction units.

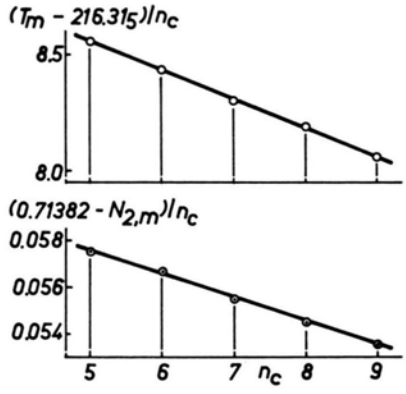

Fig. 1. Plots of the ratios $(T_m - 216.31_5)/n_C$ and $(0.71382 - N_{2,m})/n_C$ vs. n_C (explanation in text).

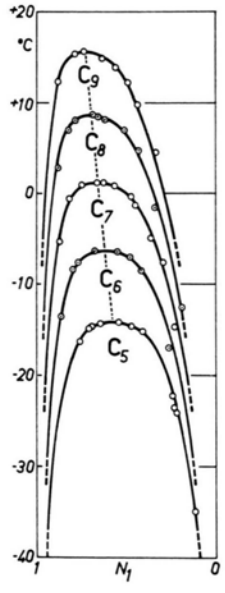

Fig. 2. Comparison between the calculated demixing curves and the experimental data.

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* Research supported by the Petroleum Research Fund, administered by the American Chemical Society. The apparatus was partially built with the financial aid of the Italian National Research Council (Rome).

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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].

On the "generalized" demixing curve [1], common to the five systems, there is correspondence among the following reduced temperatures and z fractions:

$T_{\text{demixing}}/T_{\text{m}}$	:	1.0000	0.9990	0.9975	0.9950	0.9900
z	:	0.500	0.428 0.572	0.377 0.623	0.330 0.670	0.279 0.721
$T_{\text{demixing}}/T_{\text{m}}$	:	0.9800	0.9700	0.9600	0.9400	0.9200
z	:	0.228 0.772	0.192 0.808	0.164 0.836	0.121 0.879	0.090 0.910

The above values, together with the asymmetry factors $q_2/q_1 = N_{1,\text{m}}/N_{2,\text{m}}$ 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:

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

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_ν $\qquad E_\nu = \tfrac{1}{2}(s^\nu/\nu!)\; Q_\nu^{\,1}(\gamma, x)$.

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

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

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

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

Gleichung (13.9) lautet richtig:

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

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

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

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:

$$\varepsilon_\nu = C\,Z^2\,N_e^{\,2}\,T^{-1/2} \quad \text{with} \quad \nu < \nu_g. \tag{11}$$

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

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg