Some Remarks on methylformate + n. alkanes
Binary Systems *

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We referred previously 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 described, 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 procedure 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, Tₘ (°K) and $N_{2,m}$, are regularly varying with the n. alkane (component 2) chain length. The dependence

$$\frac{(T_m - 216.315)}{n_C}$$

and

$$\frac{(0.71382 - N_{2,m})}{n_C}$$

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

$$\frac{(T_m - 216.315)}{n_C} = 9.18 - 0.12 n_C$$  \hspace{1cm} (1)

and

$$\frac{(0.71382 - N_{2,m})}{n_C} = 0.06706 - 0.00200 n_C$$  \hspace{1cm} (2)

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

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

<table>
<thead>
<tr>
<th>alkane</th>
<th>$T_m$ (°K)</th>
<th>$N_{2,m}$</th>
<th>$q_2/q_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>observed</td>
<td>calculated</td>
<td>observed</td>
<td>calculated</td>
</tr>
<tr>
<td>n. pentane</td>
<td>259.1</td>
<td>0.42</td>
<td>0.4285</td>
</tr>
<tr>
<td>n. hexane</td>
<td>266.9</td>
<td>0.38</td>
<td>0.3835</td>
</tr>
<tr>
<td>n. heptane</td>
<td>274.4</td>
<td>0.34</td>
<td>0.3424</td>
</tr>
<tr>
<td>n. octane</td>
<td>281.8</td>
<td>0.30</td>
<td>0.3063</td>
</tr>
<tr>
<td>n. nonane</td>
<td>288.8</td>
<td>0.27</td>
<td>0.2723</td>
</tr>
</tbody>
</table>

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 $39.5 \pm 1$ °K, and $N_{2,m}$ to lower by $0.06 \pm 0.00$ molar fraction units.

\[ T_m = 216.315 + 9.18 - 0.12 n_C \]

\[ (0.71382 - N_{2,m}) = 0.06706 - 0.00200 n_C \]

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).

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

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2 P. FRANZOSINI, Z. Naturforsch. 18 a, 224 [1963].
On the “generalized” demixing curve, common to the five systems, there is correspondence among the following reduced temperatures and $z$ fractions:

$$
\begin{array}{cccccc}
T_{\text{demixing}}/T_m & 1.0000 & 0.9990 & 0.9975 & 0.9950 & 0.9900 \\
& 0.228 & 0.192 & 0.164 & 0.121 & 0.090 \\
z & 0.500 & 0.428 & 0.377 & 0.330 & 0.279 \\
& 0.572 & 0.623 & 0.670 & 0.721
\end{array}
$$

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.

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**BERICHTIGUNGEN**


Die Gl. (10.5) soll lauten:

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

Die Gl. (10.9) soll lauten:

$$
z(i, j, m) = \frac{j - i + 1}{j - i - 1} \left( \begin{array}{c} 2 j + m + j \\ j - i - 1 \end{array} \right) = m \left( \begin{array}{c} 2 j + m - j - 1 \\ j - i - 1 \end{array} \right).
$$

In Gl. (11.7) bedeuten $E^1$ und $E^2 = \frac{1}{2} (s'/v') Q^1 (\gamma, x)$.

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

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

$$
\frac{\Delta z}{\Delta w^2} = \frac{1}{2 \gamma} \left( \frac{- (T)m-1}{m!} \right) \frac{d}{dw} \left[ - \frac{2 w}{1 + w^2} q_2(w) \right].
$$

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

Gleichung (13.9) lautet richtig:

$$
\begin{align*}
& \left| \frac{dx}{dT} \right|^2 \left[ \left( \frac{dw}{dT} \right)^2 + \frac{3}{4} \left( \frac{d\delta}{dT} \right)^2 \right] + 5 \left( \frac{d\delta}{dT} \right)^2 = 0, \\
& + 10 \left( \frac{d\delta}{dT} \right)^2 + 10 \left( \frac{d\delta}{dT} \right)^2 = 0.
\end{align*}
$$

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

$$
\epsilon(\gamma, s, w_x) = - \frac{1}{2} \left[ \epsilon(\gamma, s, v) \right] = 0.
$$


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

$$
\epsilon_x = C Z^2 N_{1,m} T^{-\nu_x} \quad \text{with} \quad \nu < \nu_x.
$$

(11)

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