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# THE SOLUBILITY OF *n*-ALKANES $C_{13}H_{28}$ TO $C_{36}H_{74}$ AND OF SOME BINARIES IN VARIOUS ORGANIC SOLVENTS

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## Abstract

The solubility of two *n*-alkanes in commercial organic liquids, such as diesel fuel and jet fuel represent a problem to industry, because they precipitate in an unpredictable fashion. First we calculated the metastable enthalpy and entropy of fusion of the low temperature forms of the *n*-alkanes. We analyzed the solubility of alkanes *n*-$C_{22}H_{46}$, *n*-$C_{23}H_{48}$, *n*-$C_{24}H_{50}$ and *n*-$C_{28}H_{58}$ in ethylbenzene, *m*-xylene, *n*-heptane and gas oil. All systems seem to be close ideal, possibly with a slight positive deviation. We analyzed the solubility at constant temperature of the ternary system solvent $C_{22}H_{46}$–$C_{24}H_{50}$, $C_{23}H_{48}$–$C_{24}H_{50}$, $C_{13}H_{28}$–$C_{16}H_{34}$, $C_{20}H_{42}$–$C_{22}H_{46}$, $C_{20}H_{42}$–$C_{24}H_{50}$ and $C_{20}H_{42}$–$C_{28}H_{58}$, and looked at cloud points in various ternary systems. When the difference in the number of carbon atoms in the two alkanes is small, four or less, a metastable solid solution precipitates from the solvent. If the difference in the number of carbon atoms is six or more, the 'equilibrium' phases, or at least phases with low solubility precipitate.

**Keywords:** enthalphy, entropy, metastable, *n*-alkane, phase diagram, solubility

## Introduction

The solubility of two *n*-alkanes in commercial organic liquids, such as diesel fuel and jet fuel represent a problem to industry. They precipitate as waxes and plug fuel lines. Reddy [1] applied a thermodynamic model to the systems, in which the properties of the two alkanes were 'combined' into one property. Our aim is to find the thermodynamic reason, why this unpredictable precipitation occurs.

First we will obtain the enthalpy and entropy of fusion of the low temperature form of the *n*-alkanes from the data of Barbillon *et al.* [2] and Schaerer *et al.* [3]. The entropy of fusion explains why the solubility of an *n*-alkane with an odd

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number of carbon atoms is the same as that of the *n*-alkane with one carbon atom less. Using the enthalpy of fusion of the low temperature form of the *n*-alkanes, we can calculate their solubility in various solvents, compare them with the experimental data of Ghogomu *et al.* [4], Provost and Dirand [5], Beiny and Mullin [6], Bronawell and Hollyday [7] and Holder and Winkler [8]. We will use the $C_p(L-s)$ model for metals and ceramics [9–11], because its results are not different when we use the values of $C_p(s)$ and $C_p(L)$ obtained for various alkanes [12].

## Results

We only evaluate other authors experimental data. The origin and purity of the various compounds are given by these authors. We divide all thermodynamic data by $R$, the gas constant, and the temperature is expressed in kK (kiloKelvin). The units of H, the enthalpy and other energy terms are in kK, and the entropy S and heat capacity $C_p$ are dimensionless.

### Binary systems

Table 1 shows the enthalpy of fusion and transition of the various alkanes from the data of Barbillon *et al.* [2], Schaerer *et al.* [3], Provost and Dirand [5] and Beiny and Mullin [6]. The metastable enthalpy and entropy of fusion of the low temperature form of the *n*-alkanes is obtained by $H^*_{\mathrm{fus}}=H_{\mathrm{fus}}+H_{\mathrm{trans}}$ and $S^*_{\mathrm{fus}}=S_{\mathrm{fus}}+S_{\mathrm{trans}}$.

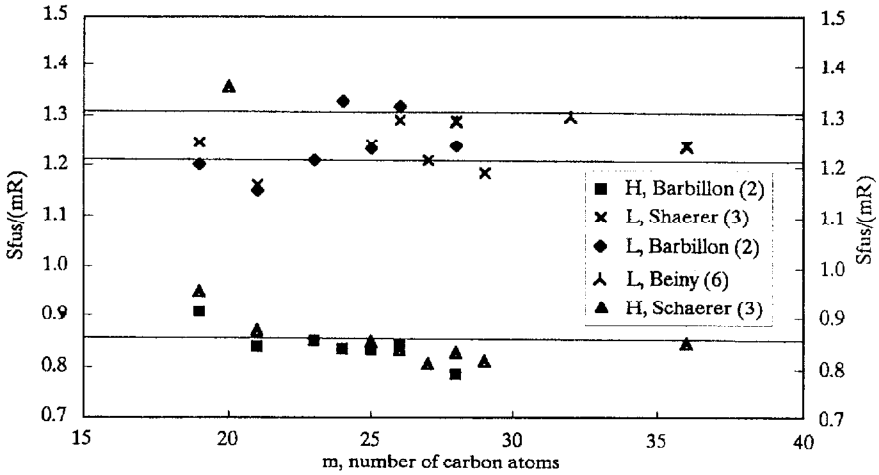
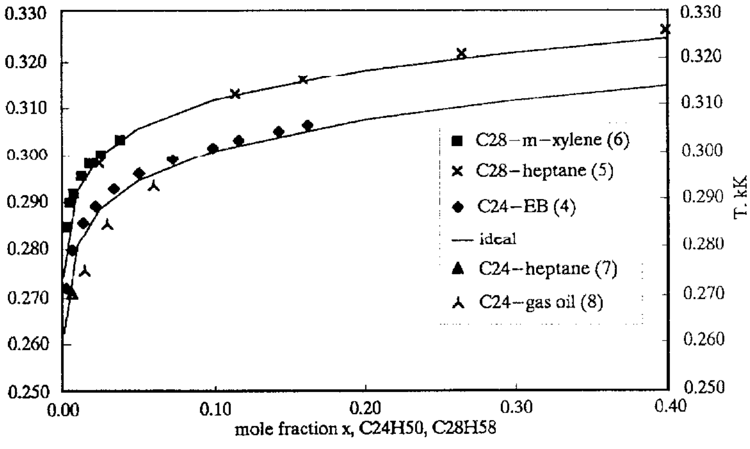


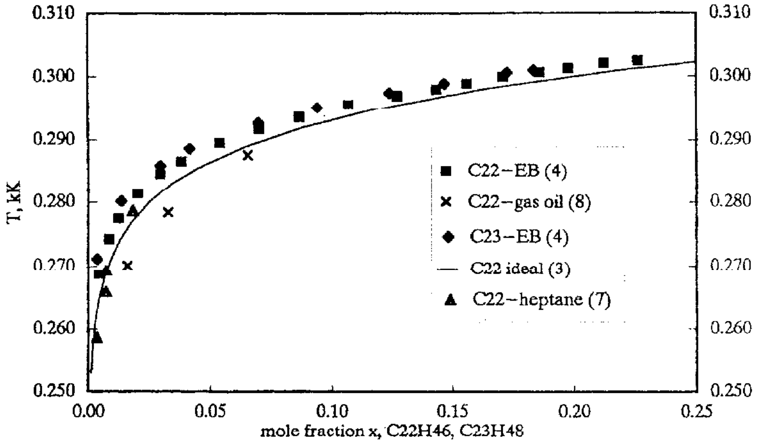
**Fig. 1** Entropy of fusion per carbon atom, $S_{\mathrm{fus}}/(mR)$ for *n*-alkanes, both high H and low L temperature forms. The data of Beiny ($H_{\mathrm{fus}}$ in their paper) gives the value for the low temperature form. $C_{20}H_{42}$ apparently has only one form, the L form. Value of the horizontal lines: $S_{\mathrm{fus}}/m$ 0.856±0.037, $S^*_{\mathrm{fus}}/m$ even 1.308±0.034, $S^*_{\mathrm{fus}}/m$ odd 1.211±0.035

$T^*_{fus}=H^*_{fus}/S^*_{fus}$ (the terms marked with * are the properties of the low temperature forms). We also calculated the entropies of fusion per carbon atom $S_{fus}/m$. These data are shown in Fig. 1. $S_{fus}/m$ for all $n$-alkanes lie on one horizontal line. The $S^*_{fus}/m$ data fall on two separate lines, one for the alkanes with an even number, the other for alkanes with odd number of carbon atoms. As the solubility curves are determined by $S^*_{fus}$ (the stability range of the low temperature form is



Gas oil: molecular weight of 250. EB is Ethylbenzene

**Fig. 2** Solubility of $n$-$C_{24}H_{50}$ and $n$-$C_{28}C_{58}$ in various solvents. All systems are close to ideal. 'ideal': there is no interaction between the alkane and the solvent. The solubility depends only on the properties of the alkane



Gas oil: Molecular weight 250. EB is ethylbenzene

**Fig. 3** Solubility of $n$-$C_{22}H_{46}$ and $n$ $C_{23}C_{48}$ in various solvents. All systems are close to ideal. 'ideal': there is no interaction between the alkane and the solvent. The solubility depends only on the properties of the alkane

**Table 1** Enthalpy and entropy of fusion of the high and low temperature forms of *n*-alkanes $C_{19}$ to $C_{36}$

| Reference | | $H_{fus}$/ kK | $T_{fus}$/ K | $S_{fus}/m$ | $H_{trans}$ kK | $T_{trans}$/ K | $H^*_{fus}$/ kK | $S^*_{fus}$/m | $T^*_{fus}$/ K | $S^*_{fus}/m$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Barbillon [2] | 18 | | 301.5 | | | | | | | |
| | 19 | 5.262 | 305.1 | 0.908 | 1.654 | 296.1 | 6.916 | 22.833 | 302.9 | 1.202 |
| | 20 | | 309.6 | | | | | | | |
| | 21 | 5.533 | 313.4 | 0.841 | 1.985 | 305.1 | 7.517 | 24.159 | 311.2 | 1.150 |
| | 22 | | 316.9 | | | | | | | |
| | 23 | 6.285 | 320.8 | 0.852 | 2.586 | 313.5 | 8.871 | 27.839 | 318.6 | 1.210 |
| | 24 | 6.495 | 323.5 | 0.837 | 3.789 | 321.1 | 10.284 | 31.877 | 322.6 | 1.328 |
| | 25 | 6.826 | 326.7 | 0.836 | 3.187 | 320.0 | 10.013 | 30.854 | 324.5 | 1.234 |
| | 26 | 7.217 | 329.2 | 0.843 | 4.029 | 325.6 | 11.246 | 34.297 | 327.9 | 1.319 |
| | 27 | | | | | | | | | |
| Provost [5] | 28 | 7.374 | 333.95 | 0.789 | 4.177 | 330.45 | 11.551 | 34.720 | 332.7 | 1.240 |
| | 29 | | | | | | | | | |
| Schaerer [3] | 18 | 7.383 | 301.4 | | | | | | | |
| | 19 | 5.511 | 305.2 | 0.950 | 1.661 | 296.0 | 7.172 | 23.671 | 303.0 | 1.246 |
| | 20 | 8.405 | 309.8 | 1.357 | | 309.4 | | | | |
| | 21 | 5.737 | 313.4 | 0.872 | 1.862 | 305.7 | 7.599 | 24.402 | 311.4 | 1.162 |

29.295

**Table 1** Continued

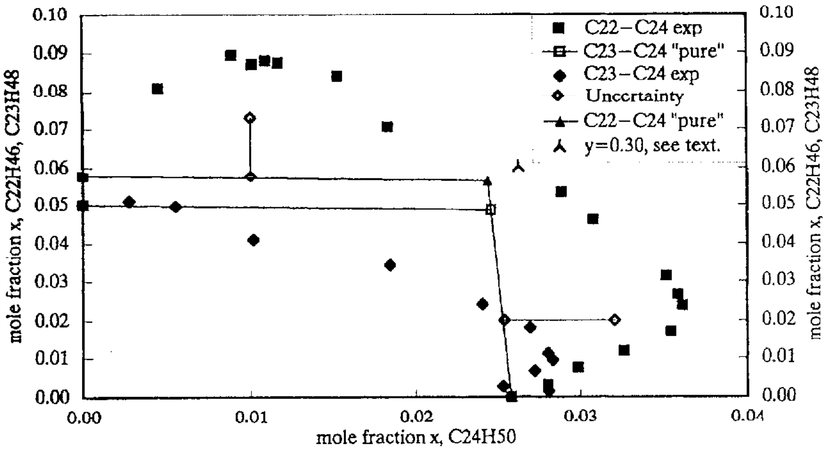
| Reference | | $H_{fus}$/ kK | $T_{fus}$/ K | $S_{fus}/m$ | $H_{trans}$/ kK | $T_{trans}$/ K | $H^*_{fus}$/ kK | $S^*_{fus}$/m | $T^*_{fus}$/ K | $S^*_{fus}/m$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | 22 | 5.888 | 317.2 | 0.844 | 3.392 | 316.2 | 9.280 | 29.295 | 316.8 | 1.332 |
| | 23 | 6.492 | 320.7 | 0.880 | 2.617 | 313.7 | 9.109 | 28.591 | 318.6 | 1.243 |
| | 24 | 6.603 | 323.8 | 0.850 | 3.764 | 321.3 | 10.367 | 32.113 | 322.8 | 1.338 |
| | 25 | 6.945 | 326.7 | 0.850 | 3.135 | 320.2 | 10.081 | 31.055 | 324.6 | 1.242 |
| | 26 | 7.157 | 329.5 | 0.835 | 3.875 | 326.5 | 11.032 | 33.593 | 328.4 | 1.292 |
| | 27 | 7.247 | 332.0 | 0.809 | 3.483 | 320.3 | 10.730 | 32.707 | 328.1 | 1.211 |
| | 28 | 7.776 | 334.4 | 0.831 | 4.263 | 331.2 | 12.038 | 36.128 | 333.2 | 1.290 |
| | 29 | 7.952 | 336.6 | 0.815 | 3.573 | 331.4 | 11.525 | 34.411 | 334.9 | 1.137 |
| | 30 | | 338.6 | | | 335.2 | | | | |
| | 36 | 10.684 | 349.1 | 0.850 | 4.867 | 345.3 | 15.551 | 44.706 | 347.9 | 1.242 |
| Beiny [6] | 28 | 12.028 | 333.3 | 1.289 | | | | | | |
| Hf | 32 | 14.193 | 341.0 | 1.301 | | | | | | |
| | 36 | 15.516 | 347.7 | 1.240 | | | | | | |
| Value of the horizontal lines in Fig. 1: | | | | | | | | | | |
| $S_{fus}/m$ | | 0.856 | ±0.037 | | | | | | | |
| $S^*_{fus}/m$ even | | 1.308 | ±0.034 | | | | | | | |
| $S^*_{fus}/m$ odd | | 1.211 | ±0.035 | | | | | | | |

All values divided by $R$, the gas constant. The properties marked with a * are those of the low temperature form much larger) this difference in $S^*_{fus}/m$ explains why the solubility of an alkane with odd number of carbon atom falls on the curve of the alkane with one less carbon atoms. The values of the horizontal lines shown in Fig. 1 are also given in Table 1.

Figure 2 shows the solubility of $n$-$C_{24}H_{50}$ and $n$-$C_{28}H_{58}$ in various solvents. The experimentally determined solubility curves fall on the calculated curves, calculated from the data of Barbillon *et al.* [3] and Provost and Dirand [5]. Similarly Fig. 3 shows the solubility of $n$-$C_{22}H_{46}$ and $n$-$C_{23}H_{48}$ in various solvents. The ideal curve was calculated from the data of Schaerer *et al.* [3] in Table 1, which as can be seen from Table 1 and Fig. 1 are somewhat different from the data of Barbillon *et al.* [2]. The data of Bronawell and Hollyday [7] and of Holder and Winkler [8] were read off small graphs. The systems are almost ideal, possibly with small positive deviation. 'ideal' means there is no interaction between the alkane and the solvent: The solubility is independent of the solvent used. The 'ideal' solubility was calculated using our model for metals and ceramics [9–11], as we showed that no difference is found if the heat capacity of the polymers is used [12].

## *Ternary systems*

Figure 4 shows the solubility of $C_{22}H_{46}$–$C_{24}H_{50}$ and $C_{23}H_{48}$–$C_{24}H_{50}$ in ethylbenzene at 290 K, calculated from the data of Ghogomu *et al.* [4] in their Table 2.



**EB is ethylbenzene.**
**y = 0.30: in the C22–C24 PhD a "metastable miscibility gap" closes.**

**Fig. 4** Solubility of $n$-alkane mixtures $C_{22}$–$C_{24}$ and $C_{23}$–$C_{24}$ in EB at 290 K. Data of Ghogomu *et al.* [4].The binary liquid systems are close to ideal. 'ideal': there is no interaction between the alkane and the solvent. The solubility depends only on the properties of the alkane

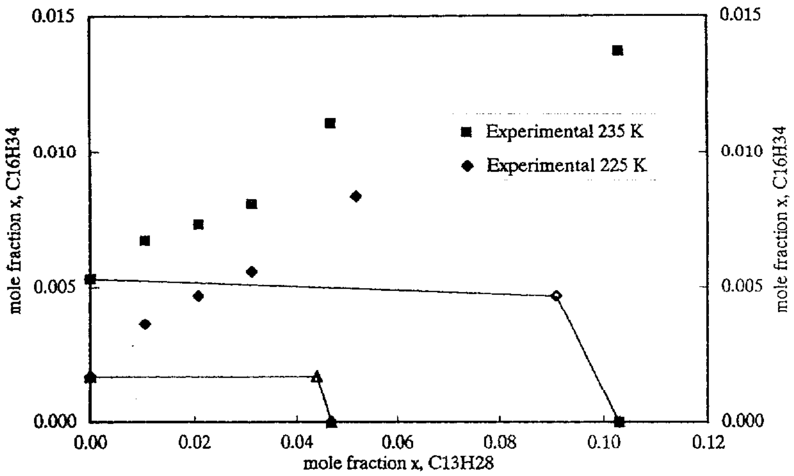
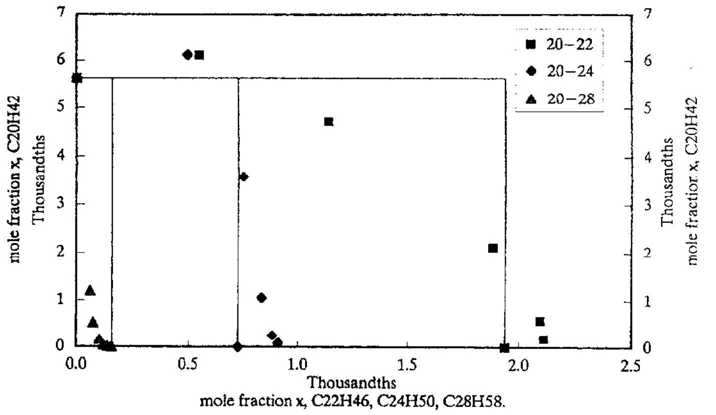


**Fig. 5** Solubility of $C_{13}H_{28}$–$C_{16}H_{34}$ *n*-alkane mixtures in Isopar-M at 225 and 235 K. Data of Affens *et al.* [13]. 'pure': pure C2x precipitates. C2x does not interact with the other alkane and the solvent



first vertical line C28, second C24, third C22.
Mol–wt of gas oil 250. Vertical and horizontal lines "pure".

**Fig. 6** Solubility of $C_{20}H_{42}$–$C_{22}H_{46}$, $C_{20}H_{42}$–$C_{24}$ $H_{50}$, $C_{20}H_{42}$–$C_{28}H_{58}$ in gas oil at 290 K. Data of Holder and Winkler [8]. 'pure': pure C2x precipitates. C2x does not interact with the other alkane and the solvent

The 'pure' curves assume that each compound precipitates independently of the other, forming pure solid components: alkane-1 does not interact with alkane-2 or the solvent. The solubility depends only on the properties of alkane-1 resp. alkane-2. The lines deviate somewhat from the horizontal resp. vertical, because when the second component is added, the molfraction of the first component decreases. Where the experimental points exceed the 'pure' line, metastable solid phases are precipitating.

In the $C_{22}H_{46}$–$C_{24}H_{50}$ system the specially marked point is close to the intersection of the 'pure' curves. The composition of the solid dissolved in the ethylbenzene is $y$=0.30 ($y$ being the molfraction of $C_{24}H_{50}$ in the $C_{22}H_{46}$–$C_{24}H_{50}$ binary). This is the composition where in an earlier paper [12] we discussed the possibility of a metastable miscibility gap between $\beta_1'$ and $\beta_2'$ at 305 K in the $C_{22}H_{46}$–$C_{24}H_{50}$ binary system.

The $C_{23}H_{48}$–$C_{24}H_{50}$ phase diagram does not show such a pronounced stability of the intermediate phases as the $C_{22}H_{46}$–$C_{24}H_{50}$ phase diagram, and no metastable miscibility gap can be drawn. This system precipitates below the pure values, and only close to $C_{24}H_{50}$ is there possibly a metastable precipitation.

Figure 5 shows the solubility of $C_{13}H_{28}$–$C_{16}H_{34}$ in Isopar-M at 225 and 235 K. The data were calculated from Table 4 of Affens *et al.* [13]. We see the same effects as in Fig. 6.

Figure 6 shows the solubility of $C_{20}H_{42}$–$C_{22}H_{48}$, $C_{20}H_{42}$–$C_{24}H_{50}$, and $C_{20}H_{42}$–$C_{28}H_{58}$ in a gas oil at 290 K. The data were calculated from all the points in the small Figs 1, 2 and 3 of Holder and Winkler [8]. The results for $C_{20}H_{42}$–$C_{22}H_{48}$ and $C_{20}H_{42}$–$C_{24}H_{50}$ are similar to those in Figs 4 and 5. For the $C_{20}H_{42}$–$C_{28}H_{58}$ binary the solubility curve drops very rapidly, indicating that no metastable phase or phases are precipitating.

The metastability is probably caused by the fact, that the compounds are stabilized by a large positive entropy, the enthalpy of formation being also positive. The precipitation mechanism and crystal growth process must be further investigated.

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