pVT Measurements and Related Studies on the Binary System $nC_{16}H_{34}$ - $nC_{17}H_{36}$ and on $nC_{18}H_{38}$ at High Pressures

Albert Würflinger, Denise Mondieig[a], Fazil Rajabalee[a], and Miquel Angel Cuevas-Diarte[b]

Institute of Physical Chemistry II, Ruhr University, D-44780 Bochum, Germany
[a] Centre de Physique Moléculaire Optique et Hertzienne, UMR 5798 au CNRS, Université Bordeaux I, 351 Cours de la Libération, F-33405 Talence Cedex, France
[b] Departament de Cristallografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, c/Marti i Franquès, E-08028 Barcelona, Spain

Reprint requests to Prof. Dr. A. W.; Fax: +49-234-32-14183;
E-mail: Albert.Wuerflinger@ruhr-uni-bochum.de

Z. Naturforsch. **56 a,** 626–634 (2001); received July 18, 2001

The phase diagram of the binary system $nC_{16}H_{34}$ - $nC_{17}H_{36}$ has been established at ambient pressure using DSC and crystallographic measurements. At low temperatures below the rotator phase RI there exist two crystal forms Op (about $x(C_{17}) = 0.25$) and Mdci (about $x(C_{17}) = 0.67$) which are different from the crystal structures of the pure compounds (Tp for C_{16} and Oi for C_{17}). Furthermore two compositions: (a) $C_{16}/C_{17} = 3{:}1$ and (b) = 1:2, which correspond to the coexistence range of Op and Mdci, were chosen for high pressure DTA and *pVT* measurements, yielding the following findings: The specific volume of the rotator phase of C_{17} is distinctly lower than those of the binary systems at the same state point. Assuming the existence of a metastable rotator phase for C_{16}, an excess volume of $\Delta V^E/V \approx 0.01$ can be estimated. Due to the very enlarged coexistence range of RI, the mixtures reach their lower transition point at considerably lower temperatures (in isobaric measurements) or higher pressures (in isothermal measurements), where the specific volume is lower than that of C_{17} at its transition point. Furthermore, the volume and enthalpy changes of the Φ_{ord} – RI transition is distinctly smaller for the binary systems than for pure C_{17}. Thus the specific volumes of the phases Op and Mdci are appreciably larger than v(spec.) of C_{17}. Op and Mdci have practically the same specific volume in accordance with the crystallographic results. Enthalpy values are obtained with the aid of the Clausius-Clapeyron equation which agree well with enthalpies derived from the DSC measurements.

Furthermore, *pVT* data have been established for the liquid and solid phases of $nC_{18}H_{38}$ in the neighbourhood of the melting curve, allowing to determine volume and enthalpy changes of melting as a function of pressure.

Key words: Hexadecane, Heptadecane, Octadecane, *pVT*, Excess Volume, Phase Transition, High Pressure, X-ray.