# High pressure dew points, bubble points and wax appearance temperatures in reservoir model fluids[1]

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**ABSTRACT**

High-pressure, high-temperature reservoirs are not only a challenge for drilling equipment and other technology. It is also questionable whether the conventionally used models to describe and predict the phase behavior are suited for these conditions and the fluids found in these reservoirs. These fluids are characterized by an asymmetric compositional distribution. This results in as well elevated dew- and/or bubble-point pressures as the potential for the precipitation of solid hydrocarbon phases. In this contribution experimental high pressure data on the phase behavior of four asymmetric binary model systems and a ternary system are reported. Additional computational results obtained by employing the Peng-Robinson equation of state are presented.

KEY WORDS: asymmetric methane + hydrocarbon systems,high pressure, solid-fluid equilibria, vapor-liquid equilibria

## 1. INTRODUCTION

High-pressure, high-temperature reservoirs as for example found in the North Sea and in the Caspian Sea can be expected to be exploited in the future. The fluids of these reservoirs are sometimes called 'hyperbaric reservoir fluids'. The presence of large methane fractions and also significant amounts of heavy hydrocarbons up to C40 account for elevated dew- and/or bubble-point pressures, and the potential for the precipitation of wax phases [1,2].

Due to the conditions described above, elevated reservoir temperatures and pressures and an 'asymmetric' composition of the reservoir fluid, the reliability of the conventionally applied models to describe the phase behavior of reservoir fluids is questionable for hyperbaric reservoir fluids. This in particular true for the employment of models for the precipitation of solid hydrocarbon phases (waxes) because this phenomenon is normally encountered and modeled for less asymmetric mixtures at moderate pressures, e.g., for stock tank oils.

To allow the evaluation of existing models and the possible development of new sound models to describe the phase behavior of 'asymmetric' hydrocarbon mixtures an adequate data base has to be available. Since accurate experimental data on the phenomena considered are scarce, we conducted a systematic study on the phase behavior of model fluids for hyperbaric reservoir fluids.

At first, the phase behavior of four binary systems was extensively studied. The systems all contained methane as a light component and either tetracosane, 1-phenyldodecane, phenanthrene, or cholestane as a heavy constituent. For these systems the solid-fluid and vapor-liquid equilibria were studied covering the composition range from pure heavy component to almost pure methane. Secondly, to study the possible formation of mixed crystals also the phase behavior of some ternary mixtures of methane, docosane, and tetracosane was studied.

The type of phase behavior found for the four binary systems is depicted in Fig. 1 as a pressure versus temperature projection. In the high temperature region, of interest in

this work the phase behavior is characterized through the presence of a three-phase curve of the type (solid heavy component + liquid + vapor) (slg). This curve starts at the triple point of the pure heavy component and ends at a so-called second critical endpoint. Here, the three-phase curve is intercepted by the vapor-liquid critical curve, and consequently a solid phase is in equilibrium with a critical fluid phase.

In this contribution also data on the phase behavior of the ternary system methane + docosane + tetracosane are reported. To interpret the results on the solidification behavior in this system at high pressures, it is worthwhile to discuss the phase behavior of the binary subsystem docosane + tetracosane. In Fig. 2 a schematic representation of the phase behavior of this system is given. At low pressures (part I) the liquid is in equilibrium with a so-called rotator phase that has a hexagonal structure α. This rotator phase extends over the whole composition range. At lower temperatures up to five different crystalline structures are reported in literature. The outer ones indicated β is of triclinic or monoclinic structure, while γ indicates an orthorhombic structure. With increasing pressure the presence of the hexagonal structure as the least dense one is less favorable (part I to IV). Above the triple point (solid α + solid β + liquid) of the pure components the hexagonal structure is only found in the intermediate composition range (part III). This means that the structure in which the mixed crystals solidify does change with pressure.

## 2. MEASUREMENTS

### 2.1. Specimens

The methane used for the measurements was of ultra high purity (99.995 wt%), supplied by Air Products. The docosane and tetracosane were supplied by Janssen Chemicals and had a stated purity of at least 99 wt%.1-Phenyldodecane was supplied by Merck-Scuchardt with a stated purity of better than 99 wt%, phenanthrene by Aldrich Chemicals with stated purity of at least 99.5 wt%. The 5-α-cholestane was supplied by Aldrich Chemicals and had a stated purity of at least 99 wt%. All chemicals were used without further purification.

2.2. Procedure

The experiments were carried out according to the synthetic method employing sapphire-windowed autoclaves [3]. This experimental setup allows to determine phase boundaries visually over a wide temperature range and for pressures up to 400 MPa. The experimental procedure itself involves the determination of the transition from a heterogeneous two-phase state to a homogeneous one-phase state upon gradual pressure changes at fixed temperature. A detailed description of the experimental procedure and the experimental accuracies can be found elsewhere [4].

**3. RESULTS AND DISCUSSION**

In Figures 3 to 6 some experimental data as isothermal sections are shown. Additional to the experimental data also computational results are included. For the modeling the Peng-Robinson equation of state [5] was used. The following quadratic mixing rules were used for the a and b parameter of the equation of state

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}$$

with

$$a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_{ii} a_{jj}}$$

and

$$b_{ij} = \left(1 - l_{ij}\right)\frac{b_{ii} + b_{jj}}{2}$$

The two interaction coefficients $k_{ij}$ and $l_{ij}$ for the quadratic mixing rules were fitted

simultaneously to describe the solid -liquid and vapor-liquid equilibria.

In Fig. 3 the vapor-liquid and solid-fluid equilibria found for mixtures of methane and phenanthrene at temperatures of 405 K and 400 K respectively are shown. The interaction coefficients determined are $k_{ij}=l_{ij}=-0.013$. Figure 4 depicts the phase boundaries studied in the system composed of methane and 1-phenyldodecane at T=280 K. Here, the optimal interaction coefficients are found to be $k_{ij}=0.018$ and $l_{ij}=0.002$. The bubble- and dew-point pressures determined for mixtures of methane and cholestane at a temperature of 340 K are graphically presented in Fig. 5. The critical pressure of cholestane is not experimentally determined. Therefore, along with the interaction coefficient $k_{ij}$ the critical pressure of cholestane was optimized. The interaction coefficient $l_{ij}$ was set equal to zereo. The optimal value found for the interaction coefficient is $k_{ij}=0.069$ and for the critical pressure of cholestane 1.29 MPa. The phase behavior found for the system methane and tetracosane is documented in Fig. 6. At a temperature of 325 K the optimal values of the interaction coefficients are $k_{ij}=0.028$ and $l_{ij}=0.015$. To document the variation of the isothermal solid-fluid phase equilibrium boundary curve also the wax appearance pressures at a temperature of 323 K are included in this figure. The sequence of figures documents on one hand the influence of the properties of the heavy component, size and aromaticity, on the phase behavior. With increasing aromaticity of the heavy component the dew- and bubble-point pressures increase dramatically - see the pressures found in the methane + phenanthrene system. The concentration of the heavy component in the critical fluid phase decreases with increasing size of the heavy component. A more detailed description of the phase behavior found for the four binary systems can be found elsewhere [4,6,7]. On the other hand one sees that the overall description of the experimental findings by the model is quite good.

The study of the phase behavior of the ternary system composed of methane, docosane, and tetracosane concentrated on the solidification behavior, namely the possible formation of mixed crystals. For this investigation the phase behavior of various

mixtures with the same methane content but variations in the ratio of the tetracosane to docosane content were studied. To illustrate the experimental results two isobaric sections at pressures of 120 and 150 MPa are shown in Fig. 7. The mole fraction of methane in the mixture was x(methane)=0.97. Beginning from either side of the diagram one finds that partial substitution of the less concentrated n-alkane for the dominantly present one, results in decreasing wax appearance temperatures. This effect is more pronounced for the substitution of tetracosane for docosane than for the reversed case. Taking into account that the distortion of a crystal matrix is stronger for the incorporation of a too large species than for the incorporation of a too small species, this is easily understood. In the intermediate range of the substitution level (15 to 50 mole % dococsane) a linear relation between the wax appearance temperatures and the substitution level is found. To interpret these patterns of wax appearance temperatures the phase behavior of the subsystem composed of docosane and tetracosane should be considered (see Fig. 2). Doing so, the conclusion that the intermediate level of substitution is related to a mixed crystal of orthorhombic structure is justified. The two other regions close to the axes propose that here a mixed crystal of triclinic or monoclinic structure exists. This interpretation is in agreement with interpretations of similar experimental data at atmospheric pressure.

## 4. CONCLUSIONS

The solid-fluid and vapor-liquid equilibria of four asymmetric binary hydrocarbon systems were studied extensively. It was found that increasing aromaticity of the heavy component leads to dramatically increased pressures at the second critical endpoint. The Peng-Robinson equation of state describes the experimental data - solid-fluid and vapour-liquid equilibria simultaneously - quite well if the optimization of two interaction coefficients is allowed. The high-pressure solidification behavior of ternary mixtures of methane, docosane, and tetracosane has been measured. The experimental results, showing two discontinuities in the curve of wax appearance temperatures, allow the

conclusion that a pair of homologous n-alkane solutes forms mixed crystals when precipitating from a supercritical fluid. The interpretation of the occurring solid phases can, taking the pressure influence on the phase behavior of the binary subsystem into account, be deducted from the behavior of similar systems with non-volatile solvents at atmospheric pressure.

## REFERENCES


1. P. Ungerer, B. Faissat, C. Leibovici, H. Zhou, E. Behar, G. Moracchini, and J.P. Courcy, *Fluid Phase Equilibria*, **111**: 287 (1995).
2. B. Lagrouette, J.L. Daridon, J.F. Gaubert, and H. Saint-Guirons, *J. Chem. Thermodyn.*: **27**: 259 (1995).
3. Th.W. de Loos, A.J.M. Wijen, and G.A.M. Diepen, *J. Chem. Thermodyn.*: **12** 193 (1980).
4. E. Flöter, Th.W. de Loos, and J. de Swaan Arons, *Fluid Phase Equil.*:**127**: 129 (1997).
5. D.B. Robinson and D.-Y. Peng, *GPA Research Report 28* (GPA, Tulsa, 1978).
6. E. Flöter, P. v.d. Pijl, Th.W. de Loos, and J. de Swaan Arons, *Fluid Phase Equilib.*: in press.
7. E. Flöter, C.Brumm, Th.W. de Loos, and J. de Swaan Arons, *J.Chem Eng. Data*: **42** 64 (1997).

**FIGURE CAPTIONS**

Figure 1. Schematic phase behavior of asymmetric binary hydrocarbon systems. ○ pure component critical point;□ quadruple point; Δ triple point; ▲ critical endpoint .

Figure 2. Schematic phase behavior of the system (C22 + C24). p(I)<p(II)<p(III)<p(IV).

Figure 3. Dew- and bubblepoints and WAP in the system (methane + phenanthrene) at 405 resp. 400 K, lines: PR-EoS with kij=lij=-.013.

Figure 4. Dew- and bubblepoints and WAP in the system (methane + phenyldodecane) at 280 K, lines: PR-EoS, kij=.018, lij=.002.

Figure 5. Dew- and bubblepoints in the system (methane + cholestane) at 340 K, lines: PR-EoS with kij=.069, $p_C$(C27)=1.29 Mpa.

Figure 6. Dew- and bubblepoints and WAP in the.system (methane + tetracosane) at 325 resp. 323 and 325 K, lines: PR-EoS with kij=.028, lij=0.015.

Figure 7. Wax appearance temperatures in the ternary system (C1+C22+C24) at p=120, 150 MPa. x(C1)=0.97.

Figure 1
Schematic phase behavior of asymmetric binary hydrocarbon systems.
○ pure component critical point;□ quadruple point; Δ triple point; ▲ critical endpoint

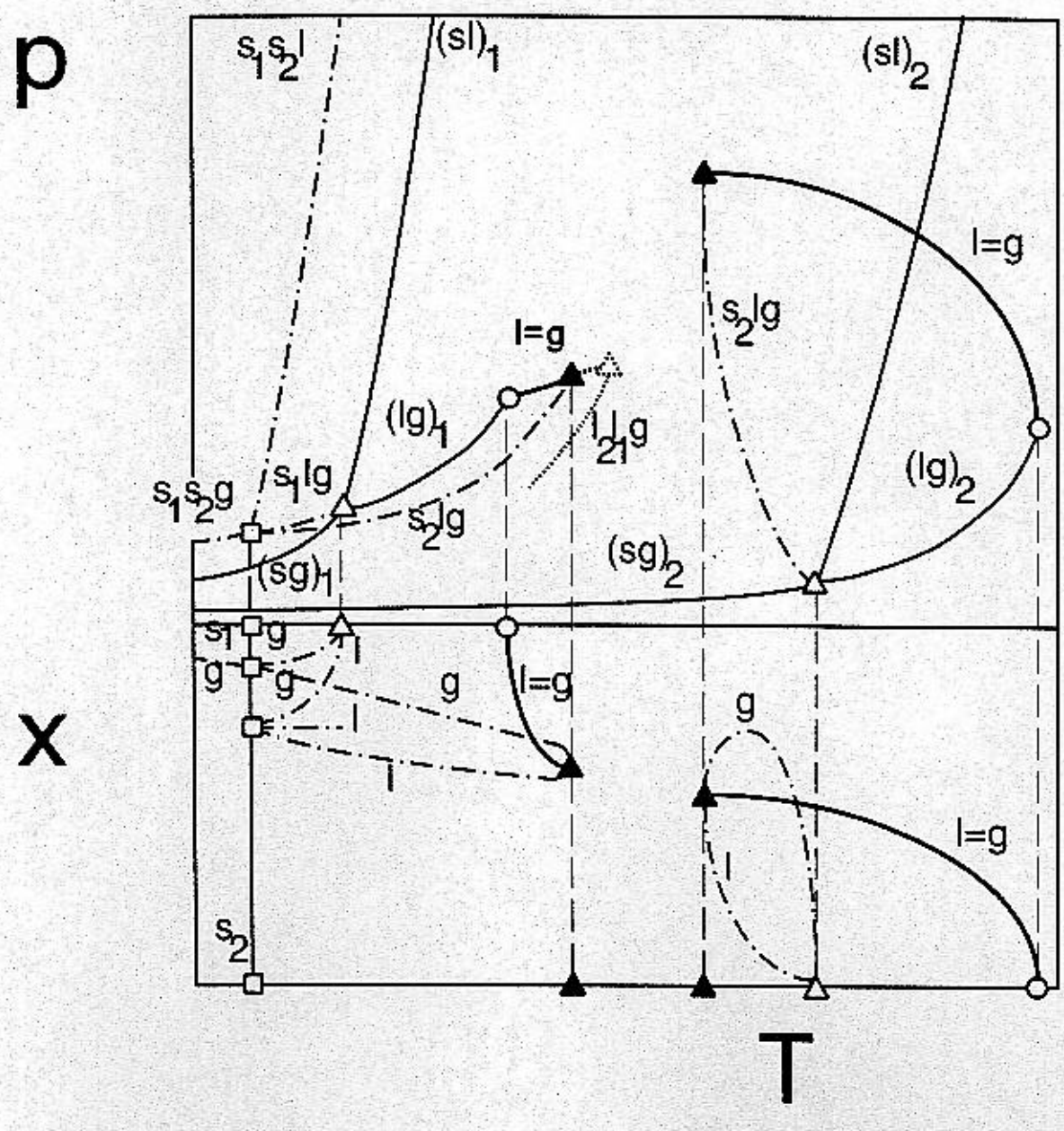

Figure 2
Schematic phase behavior of the system (C22 + C24). p(I)<p(II)<p(III)<p(IV)

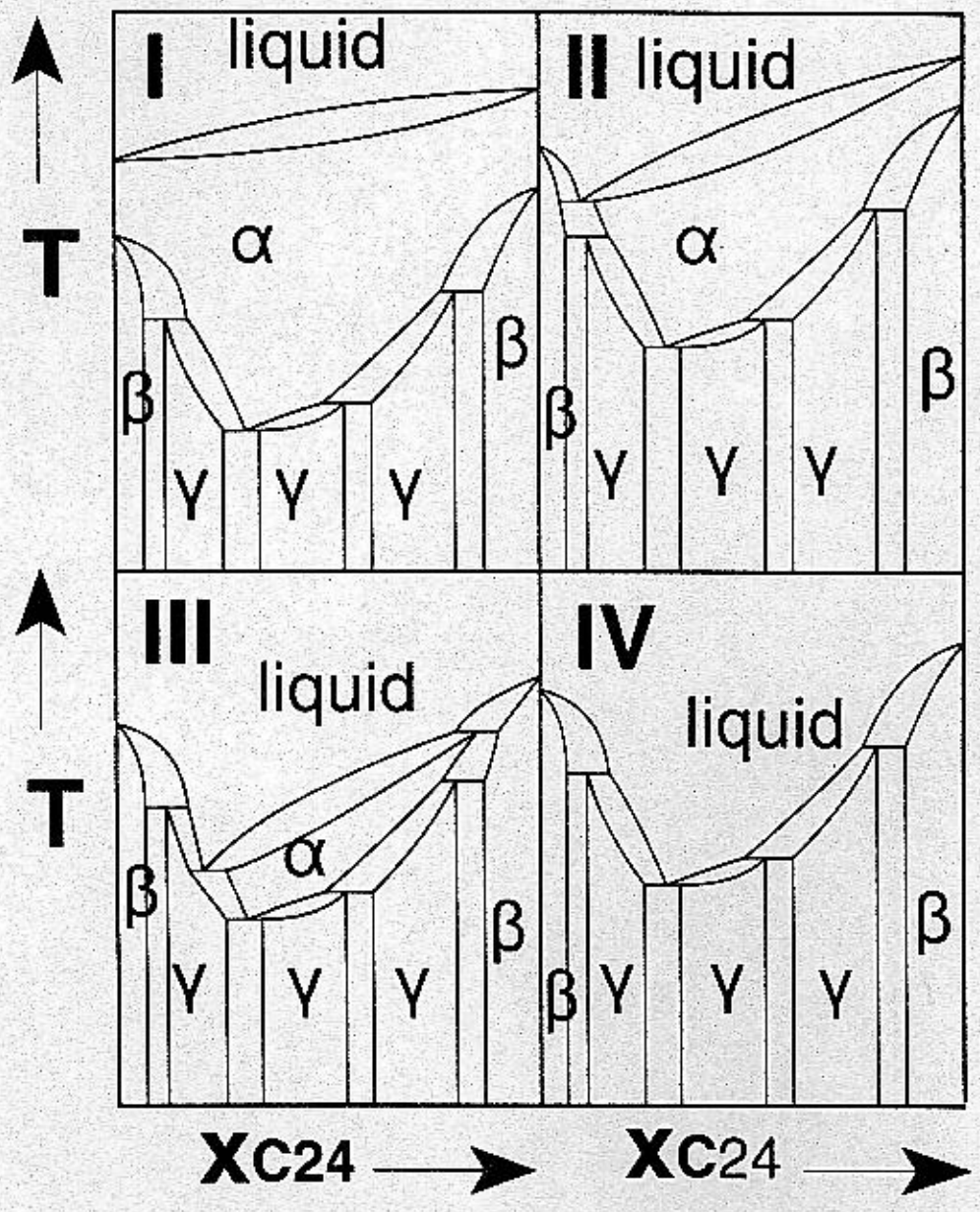

Figure 3
Dew- and bubblepoints and WAP in the system (methane + phenanthrene) at 405 resp. 400 K,
lines: PR-EoS with kij=lij=-.013

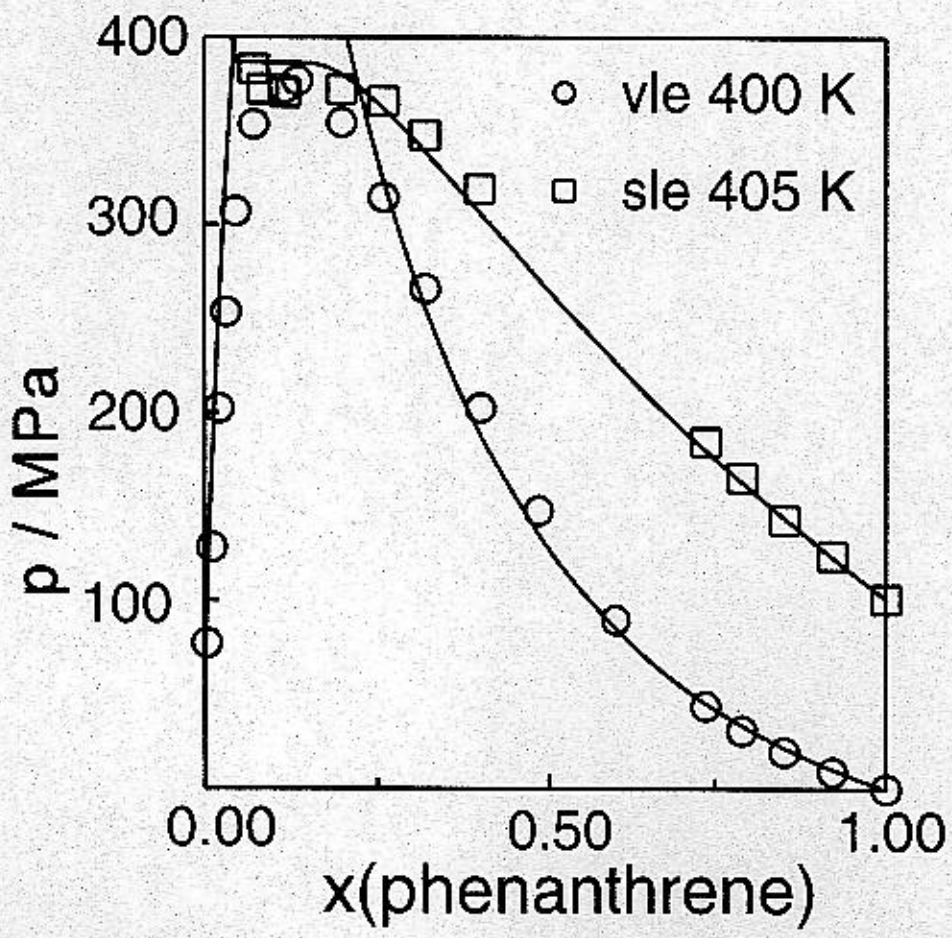

Figure 4
Dew- and bubblepoints and WAP in the system (methane + phenyldodecane) at 280 K, lines: PR-EoS, kij=.018, lij=.002

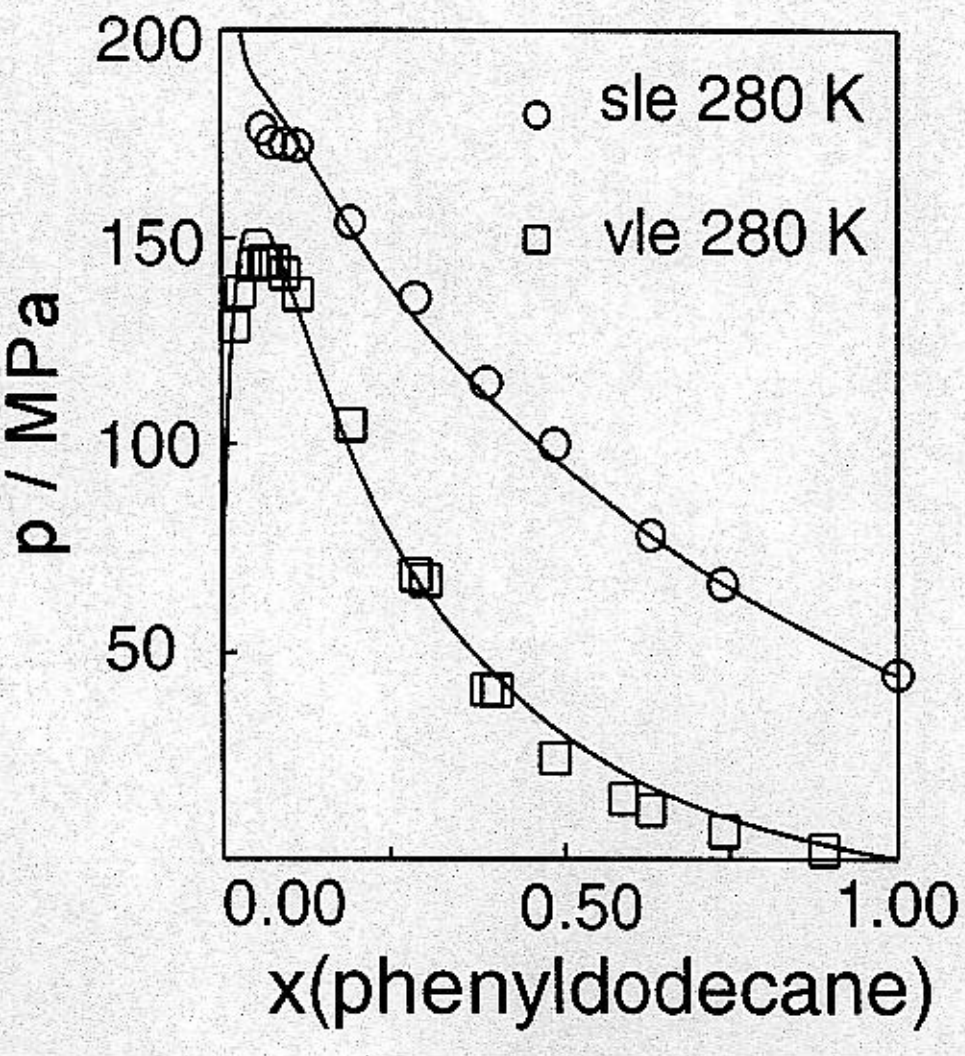

Figure 5
Dew- and bubblepoints in the system (methane + cholestane) at 340 K, lines: PR-EoS with kij=.069, $p_c$(C27)=1.29 MPa

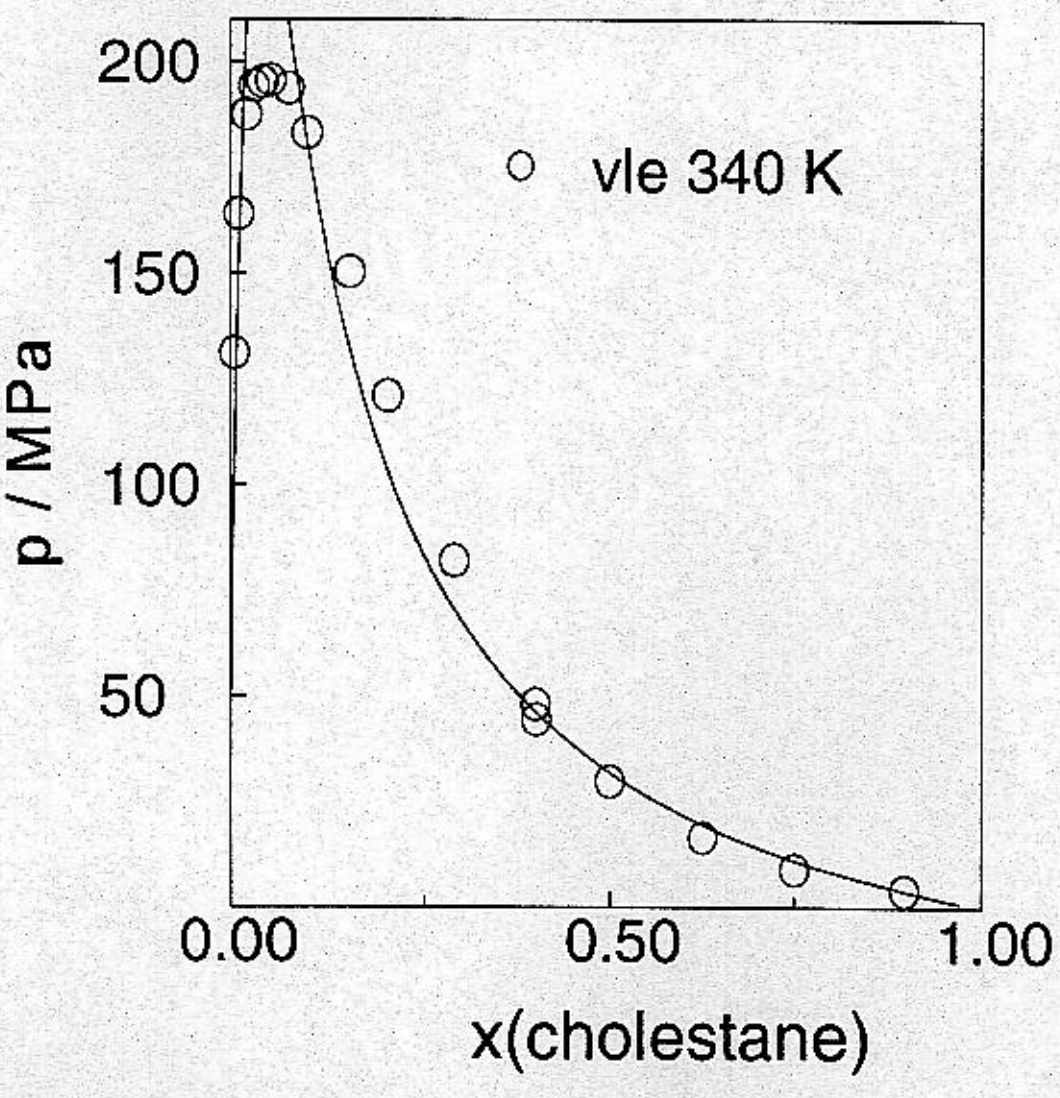

Figure 6
Dew- and bubblepoints and WAP in the system (methane + tetracosane) at 325 resp. 323 and 325 K,
lines: PR-EoS with kij=.028, lij=0.015

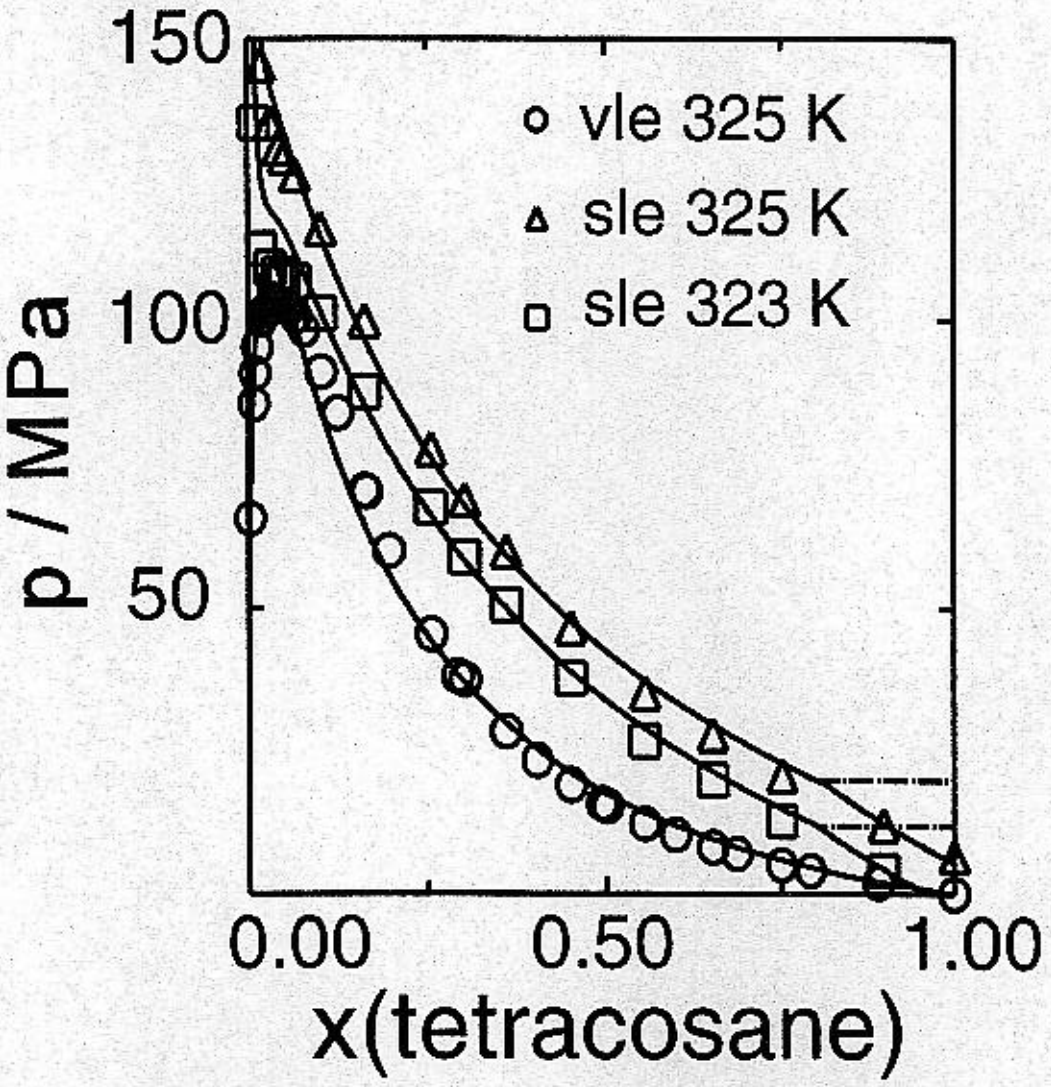

Figure 7
Wax appearance temperatures in the ternary system (C1+C22+C24) at p=120, 150 MPa. x(C1)=0.97.