

Phase equilibrium investigations of fluid systems at high pressures

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Abstract - In the present review some selected results on the thermodynamics of pure and mixed fluids under high pressure are presented that have been obtained in the author's group at the University of Bochum since about 1990. Thus the paper is a continuation and extension of a more comprehensive earlier review in this Journal (Pure & Appl. Chem. 63, 1313 (1991)) where the fundamentals as well as the thermodynamical and theoretical background are discussed in more detail.

The accent of the present review is on some applications e.g., in Supercritical Fluid Extraction (SFE) of low-volatile and/or thermolabile substances and recent high-pressure results are presented for some binary, ternary and quaternary systems (as solutions of fatty alcohols, fatty acids, alkanes etc in supercritical carbon dioxide) being of interest for the use of moderators in SFE. The phenomena are discussed with respect to cosolvency effects and the appearance of miscibility windows in the isobaric $T(w_1, w_2)$ and isothermal $p(w_1, w_2)$ phase prisms (w = mass fraction) as well as of closed miscibility gaps (so-called islands) in the triangular Gibbs phase diagrams at constant temperature and pressure. Some new applications of supercritical fluid solvents are shortly reviewed e.g., the dyeing of fibers. Analytical separations using Supercritical Fluid Chromatography (SFC) and the determination of some physico-chemical properties (such as capacity ratios, binary diffusion coefficients) from constant-density or density-programmed SFC runs (e.g., on liquid crystalline compounds) are also considered. Finally the effect of high pressures on the mesomorphic phase stability of pure as well as gas-saturated thermotropic liquid crystals is demonstrated using differential thermal analysis (dta).

1. INTRODUCTION

The present review considers some selected high-pressure phenomena of fluid mixtures especially concerning phase transitions from a homogeneous fluid to heterogeneous states e.g., to liquid-liquid or gas-gas equilibria as well as to the exhibition of solid and anisotropic liquid phases. By this it is a continuation and extension of a recent review of the author in this Journal (ref.1) including some (mostly unpublished) work that has been performed since then in the author's group at the University of Bochum. It has, however, to be emphasized that the effects described here are only treated in terms of some selected examples. For the fundamentals and for details the reader is referred to the paper mentioned above (ref.1) and several other reviews of the author (as in ref. 2,3,4) where many additional examples and references are given.

Fig.1 (see ref.1) gives an idea about the conditions of temperatures and pressures that are involved. The homogeneous isotropic liquid range might be limited to lower temperatures

- by the appearance of liquid-liquid equilibria (section 2) or
- by the exhibition of solid phases, e.g. s_2 and s_1 (where s_2 can be a so-called "plastic" phase) (section 2), or
- by the formation of anisotropic liquid states, e.g. nematic (n) or smectic (sm) phases (section 4),

and to higher temperatures the liquid range is bounded

- by high-pressure gas-liquid equilibria or
- by the so-called gas-gas equilibria that have been found experimentally for the first time by Russian workers (section 3).

2. LIQUID-LIQUID PHASE EQUILIBRIA IN SOME BINARY AND TERNARY SYSTEMS

The pressure dependence of liquid + liquid phase equilibria of binary mixtures including the exhibition of upper or lower critical solution temperatures (UCSTs, LCSTs) or pressures (UCSPs, LCSPs) respectively has been extensively studied in the author's group over a period of about thirty years and has been discussed in detail in numerous preceding review papers (see e.g., ref. 1,2,5).

The measurements have been performed in several high-pressure autoclaves for use between about 120 and 700 K and up to a maximum pressure of about 600 MPa according to the synthetic and/or analytical methods or to much higher pressures (up to 3 GPa) with the diamond anvil cell technique (DAC). For a review of the experimental techniques and set-ups see ref.6.

In Fig.2 and 3 some results on the system $\text{CHF}_3 + \text{Xe}$ are given that have recently been obtained by Dahmen (ref. 7,8). Fig.2 shows some characteristic $p(T)$ isopleths. The system exhibits upper solution temperatures that increase with rising pressure. The envelope of all $p(T)$ isopleths is the $p(T)$ projection of the critical curve; it coincides about with the isopleth for $x(\text{CHF}_3) = 0.339$. The discontinuities in the slopes of some of the $p(T)$ isopleths in Fig.2 correspond to the appearance of a solid phase (here Xe).

Some characteristic sections are represented in Fig.3a and 3b. They demonstrate that this system exhibits lower critical solution pressures (LCSPs) in the isothermal $p(x)$ sections (see Fig.3a) as well as upper critical solution temperatures (UCSTs) in the isobaric $T(x)$ sections (see Fig.3b) respectively. The isothermal $p(x)$ and the isobaric $T(x)$ diagrams in Fig.3a and 3b show a striking symmetry that is of fundamental phase-theoretical importance.

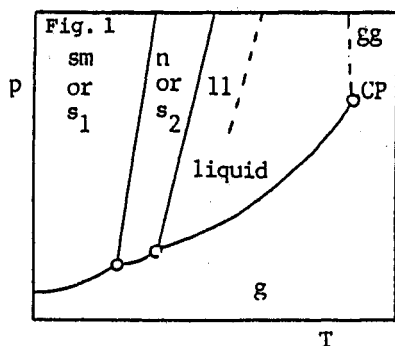


Fig. 1. $p(T)$ projection of the phase diagram of a pure component or a binary mixture (schematically, not complete, see text; for details with respect to binary mixtures see e.g., Fig.10 in ref.1) (reproduced from ref.1).

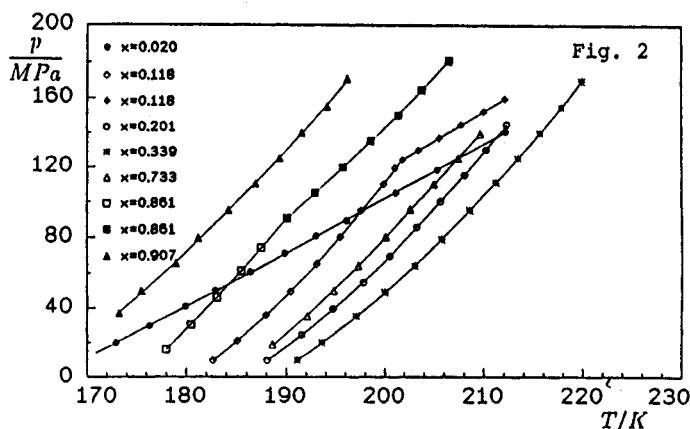


Fig. 2. Experimental $p(T)$ isopleths of the system $x\text{CHF}_3 + (1-x)\text{Xe}$ at constant mole fractions $x\text{CHF}_3$ (liquid-liquid: open symbols, solid-liquid: filled symbols) (Dahmen, ref. 7,8).

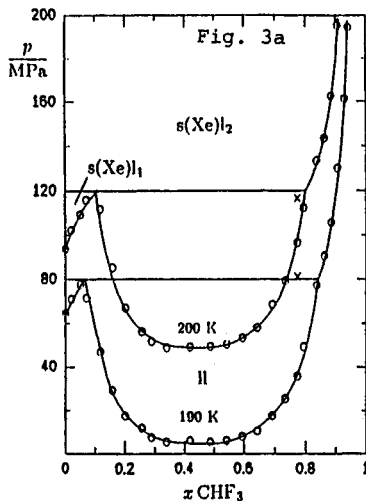
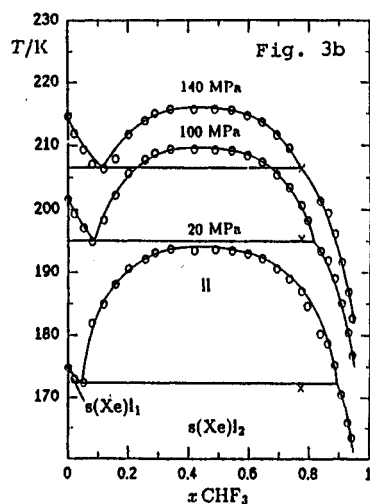


Fig. 3. Liquid-liquid and solid-liquid phase equilibria of $x\text{CHF}_3 + (1-x)\text{Xe}$. (Dahmen, ref. 7,8).

Fig. 3a. Isothermal $p(x)$ diagrams.

Fig. 3b. Isobaric $T(x)$ diagrams.



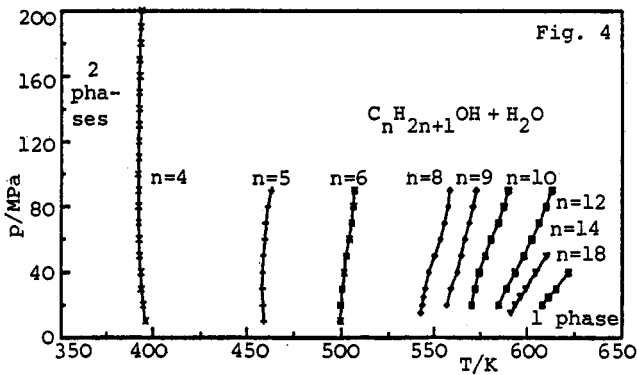


Fig. 4.

Experimental $p(T)$ isopleths of some 1-alkanol + water systems at $x(\text{alkanol}) = \text{const} \approx 0.3$ (Becker, ref.13; see text).

The mixture is also of theoretical interest since noble gas molecules with a perfectly spherically symmetrical potential are mixed with small molecules having a strong permanent dipole moment (for calculations from an equation of state (EOS) see ref.9).

An especially interesting pressure dependence has been found in binary butanol + water systems as well as in ternary mixtures of two butanols with water (see Fig.4 in ref.1) or in butanol + water mixtures with the addition of a third component e.g. a salt (see ref. 1,5,10,11,12). A very recent continuation of this work is shown in Fig.4 where $p(T)$ isopleths are given for some 1-alkanol + water mixtures from 1-butanol + H_2O to 1-octadecanol + H_2O (Becker, ref. 13,14); these $p(T)$ isopleths are expected to be characteristic for the critical $p(T)$ curves, too. The $p(T)$ isopleth for 1-butanol + H_2O in Fig.4 starts with a negative slope and runs through a slight temperature minimum with increasing pressure; besides the LCST region of this system is not shown here (see e.g., Fig.4 in ref.1 and ref. 10,11,12). This pressure dependence gives evidence for a change of the sign of the molar excess enthalpy H_m^E from minus to plus with increasing temperature and of the molar excess volume V_m^E also from minus to plus with increasing pressure (see ref.1). For 1-pentanol + H_2O a temperature minimum is within the limits of experimental error whereas for the other 1-alkanol + H_2O systems in Fig.4 the $p(T)$ isopleths start with a positive slope (dp/dT) becoming smaller with increasing alkyl chain length of the 1-alkanol; this gives evidence that V_m^E is positive and small and increases for the aqueous solutions of the longer chained 1-alkanols. These findings are of interest for the phase-theoretical and statistical understanding of alkanol + water mixtures as well as for applications e.g., in lubrication problems where fatty alcohols are increasingly used (e.g., for ecological reasons).

For a summary of extensive investigations on the kinetics of phase separation in liquid mixtures by pressure-jump relaxation techniques see for instance ref.1.

3. FLUID PHASE EQUILIBRIA IN BINARY, TERNARY AND QUATERNARY SYSTEMS INVOLVING A SUPERCRITICAL COMPONENT: ISLANDS, COSOLVENCY AND MISCIBILITY WINDOWS

3.1. Continuity hypothesis and "families"

Normally the three different types of two-phase equilibrium in fluid mixtures namely liquid-liquid (ll), liquid-gas (lg), and gas-gas (gg) equilibria are discussed separately. During the last twenty-five years systematic investigations first in the author's laboratory and later, additionally, in other groups have shown, however, that the limits between these three forms of heterogeneous phase equilibrium are not well defined and that continuous transitions occur. This hypothesis of a continuity of all phase equilibria in fluid mixtures has been demonstrated by systematic measurements on so-called "families" of binary systems where one component is maintained constant (e.g., CO_2) whereas the other is changed systematically in size (e.g., through the homologous series of the n-alkanes), shape and/or polarity. This continuity has also been confirmed more recently by computer calculations e.g. using equations of state (EOS) (see ref.20). The effects found have been discussed extensively in numerous review papers of the author where also examples and additional references are given; for a recent summary see ref.1.

3.2. Cosolvency and miscibility windows

In a preceding review (ref.1) some types of ternary and quaternary systems that are important for practical applications have been discussed. Here only data for one model system that has been studied very recently by Kordikowski (ref. 15,16) will be presented in

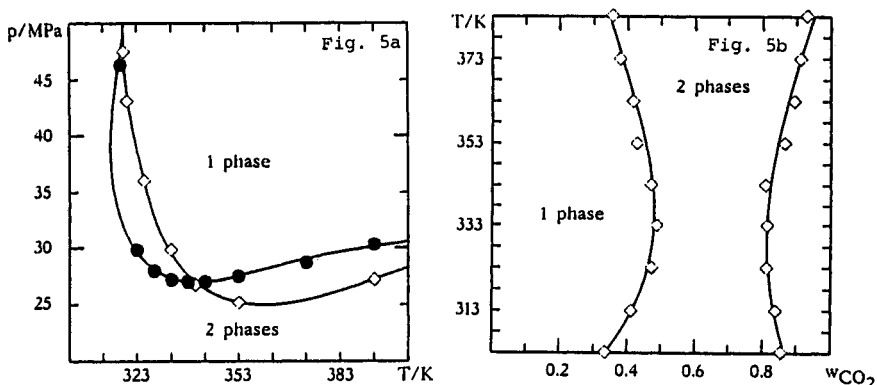


Fig. 5. Fluid-fluid phase equilibria of the binary systems carbon dioxide + 1-dodecanol and carbon dioxide + nonadecane (Kordikowski, ref. 15,16).

Fig. 5a. $p(T)$ projections of the binary critical curves
 (● = carbon dioxide + nonadecane, ◇ = carbon dioxide + 1-dodecanol).

Fig. 5b. Isobaric $T(w)$ diagram of the system carbon dioxide + nonadecane at 25 MPa.

somewhat more detail. The ternary system consists of carbon dioxide (as the supercritical solvent), nonadecane and 1-dodecanol (as low-volatile components to be dissolved and separated) whereas the quaternary system is made up of the ternary system mentioned above with the addition of a moderator (here quinoxaline or 1,8-octanediol; see also section 5).

In Fig.5a and 5b some data for the binary systems CO_2 + nonadecane and CO_2 + 1-dodecanol are given according to measurements of Spee (ref. 17,18)², Pöhler (ref.19), and Kordikowski (ref. 15,16). In Fig.5a the $p(T)$ projections of the critical curves are plotted and in Fig.5b the isobaric $T(w)$ diagram (w = mass fraction) of CO_2 + nonadecane at 25 MPa that is just below the pressure minimum of both binary critical $p(T)$ curves. Both systems show a very similar critical phase behaviour and have to be attributed to class III according to the classification of van Konynenburg and Scott.

In Fig.6a a characteristic isothermal ternary $p(w_1, w_2)$ phase prism for $T = \text{const} = 353.2$ K is given. It shows that the ternary critical curve runs through a distinct pressure minimum giving evidence for a so-called "cosolvency effect", i.e. a mixture of nonadecane + 1-dodecanol is better soluble in supercritical CO_2 than each of the two pure components alone.

This cosolvency effect is even better visible in the $p(w^{\text{red}})$ diagrams given in Fig.7a where ternary critical pressures are plotted against the CO_2 free mass fraction w^{red} of the alkane ($w^{\text{red}} = w_{\text{alk}} / (w_{\text{alk}} + w_{\text{ol}})$) at a constant temperature of 353.2 K. They demonstrate that cosolvency is found for CO_2 + n-alkane + 1-dodecanol where the n-alkane is hexadecane or nonadecane or eicosane. For CO_2 + tetracosane + 1-dodecanol no pressure minimum and consequently no cosolvency effect any longer exists; the same will hold for an alkane being sufficiently smaller than hexadecane.

The consequence of such a cosolvency effect is the appearance of a so-called (isobaric) "miscibility window" such as shown in Fig.6b and 8a, the one-phase region being inside the curve (and not outside as for a so-called closed miscibility gap e.g., in a binary liquid mixture). According to Fig.8a this miscibility window is larger for CO_2 + nonadecane + 1-dodecanol than that of CO_2 + eicosane + 1-dodecanol also studied by Kordikowski (ref. 15,16) whereas that of CO_2 + hexadecane + 1-dodecanol (Spee, ref. 17,18) is not closed on the alkane-rich side of the diagram. For CO_2 + tetracosane + 1-dodecanol no miscibility window exists.

The whole critical phase behaviour of this system can easily be deduced from the semiquantitative $pT w^{\text{red}}$ phase diagram in Fig.9. It can be seen that isobaric $T(w^{\text{red}})$ miscibility windows will be found for constant pressures being adequately chosen just below the pressure minima of both binary critical $p(T)$ curves (here e.g., at 25 MPa, see Fig. 6b and 8a).

Since the binary critical $p(T)$ curves run additionally through temperature minima, a similar cosolvency effect unknown up to now can also be found in isobaric $T(w^{\text{red}})$ diagrams resulting in isothermal $p(w^{\text{red}})$ miscibility windows at a constant temperature just below the temperature minima of both binary critical $p(T)$ curves (here e.g., at 308.2 K; see Fig. 6c and 8b).

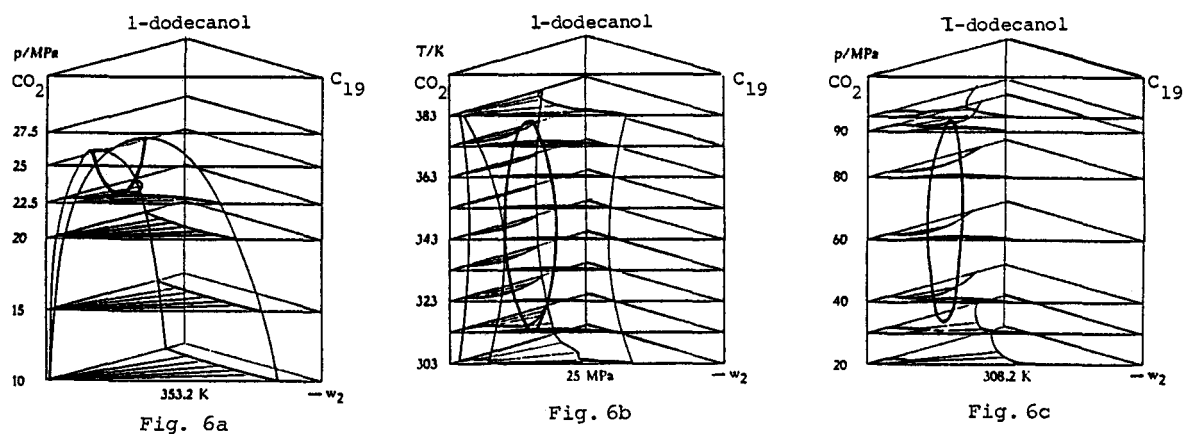


Fig. 6. Ternary phase prisms of the system carbon dioxide + nonadecane + 1-dodecanol (Kordikowski, ref. 15,16; see text) - Fig. 6a. Isothermal $p(w_1, w_2)$ phase prism at 353.2 K. Fig. 6b. Isobaric $T(w_1, w_2)$ phase prism at 25 MPa. Fig. 6c. Isothermal $p(w_1, w_2)$ phase prism at 308.2 K.

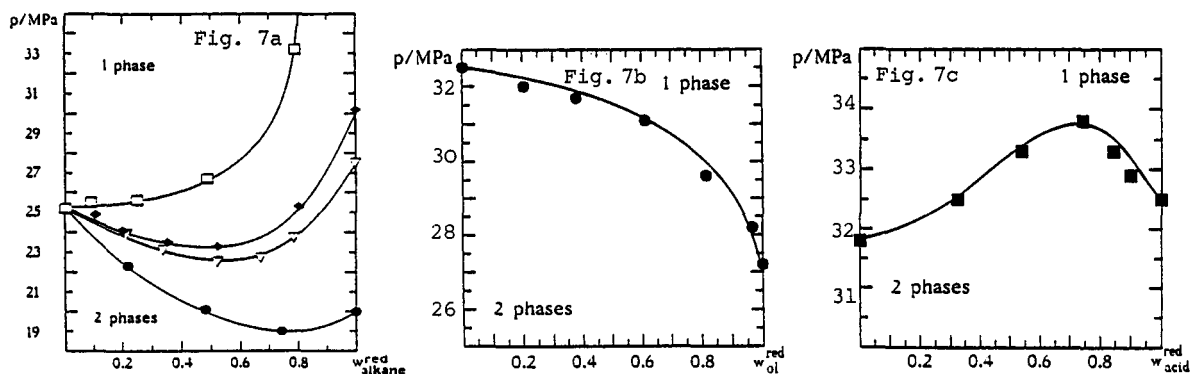


Fig. 7. Isothermal ternary critical $p(w^{\text{red}})$ curves (w^{red} = carbon dioxide free mass fraction) (Kordikowski, ref.15,16)

Fig. 7a. carbon dioxide + n-alkane + 1-dodecanol at 353.2 K (● = hexadecane, ▽ = nonadecane, ◇ = eicosane, □ = tetracosane). - Fig. 7b. carbon dioxide + 1-dodecanol + dodecanoic acid at 393.2 K. - Fig. 7c. carbon dioxide + dodecanoic acid + quinoxaline at 393.2 K.

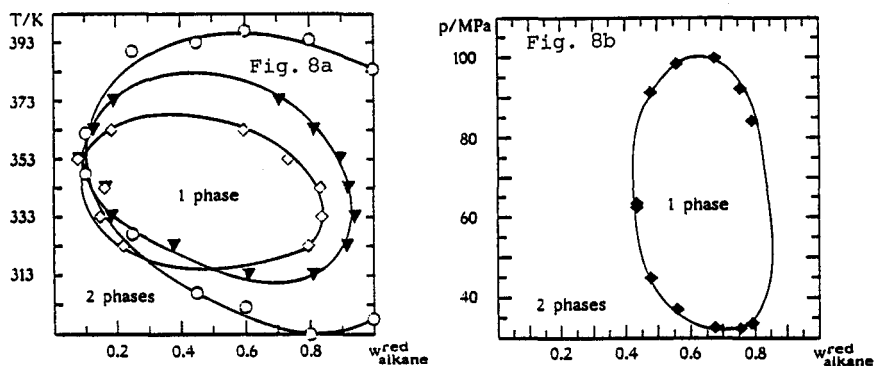


Fig. 8. Miscibility windows in carbon dioxide + n-alkane + 1-dodecanol systems (w^{red} = carbon dioxide free mass fraction) (Kordikowski, ref. 15,16).

Fig. 8a. Isobaric $T(w^{\text{red}})$ sections at $x(\text{CO}_2) = 0.63$ and 25 MPa (o = hexadecane (ref. 17), ▽ = nonadecane and ◇ = eicosane).

Fig. 8b. Isothermal $p(w^{\text{red}})$ projections of the critical curve of the system carbon dioxide + nonadecane + 1-dodecanol at 308.2 K.

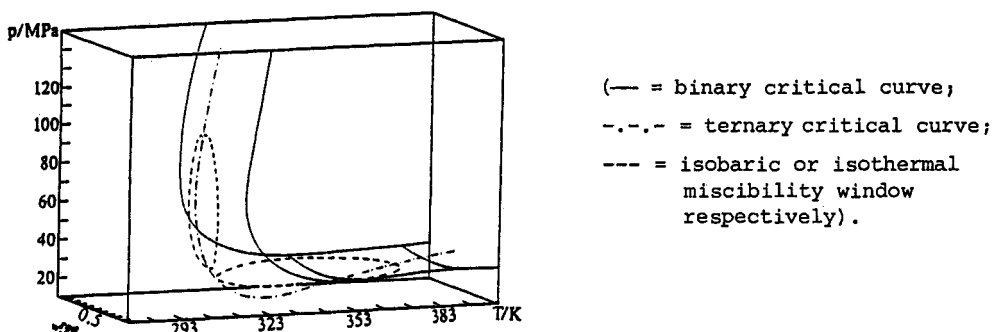


Fig. 9. The system carbon dioxide + nonadecane + 1-dodecanol in a p, T, w^{red} phase cube (w^{red} = carbon dioxide free mass fraction) (Kordikowski, ref. 15,16).

3.3. Island systems

Cosolvency effects and miscibility windows will be found quite often in mixtures of this type and they are quite common for the solubility of polymers in mixed solvents. Their existence, however, is not the rule and other interesting phenomena might be found e.g., the appearance of so-called "islands". Fig. 7 shows the critical $p(w^{\text{red}})$ curves at constant temperature for some ternary CO_2 -systems. Whereas in Fig. 7a the low-volatile substances are quite similar (here 1-dodecanol and an alkane) resulting in a positive curvature of the $p(w^{\text{red}})$ isotherms, the $p(w^{\text{red}})$ curve of CO_2 + 1-dodecanol + dodecanoic acid at 393.2 K exhibits a negative curvature (see Fig. 7b) and that of CO_2 + dodecanoic acid + quinoxaline (as a moderator) runs through a distinct pressure maximum (Fig. 7c) giving origin to a closed immiscibility region in an isothermal-isobaric Gibbs triangle, a so-called "island" (here at 393.2 K and at a pressure between the pressure maximum and the binary critical pressure of the system CO_2 + dodecanoic acid at the same temperature). Thus Fig. 7a-7c show that for very similar low-volatile components there is a tendency for the formation of miscibility windows whereas for more and more dissimilar ones the exhibition of islands is more and more favoured.

Fig. 6-9 demonstrate that very difficult and interesting phase equilibrium phenomena (especially in the transition ranges between different types of phase behaviour) exist that are still widely unknown and merit intensive research in the future.

4. PHASE TRANSITIONS IN LIQUID CRYSTALLINE SYSTEMS

The pressure dependence of the phase behaviour of liquid crystalline compounds was already investigated intensively in the past. Here a wide pattern of different phenomena can occur e.g., the exhibition of pressure-induced and pressure-limited phases, the appearance of triple or tricritical points etc; for a summary and many references see e.g., ref. 1.

As a characteristic example Fig. 10a shows the $p(T)$ diagram of the pure liquid crystal 4-n-decyloxy-4'-cyanobiphenyl (10OCB) determined recently from dta experiments by Krombach (ref. 21,22). At low pressures the sequence of phases in a heating run is solid \rightarrow smA \rightarrow liquid isotropic, both $p(T)$ transition curves s/smA and smA/l having a positive slope respectively. At a triple point s/smA/n at 369 K and 35 MPa a pressure-induced nematic phase n appears the stability range of which increases with further increasing pressure.

This pressure-induced nematic phase can still be observed when the liquid crystal is saturated with helium gas (Fig. 10b) as a pressurizing medium that acts directly on the substance in an open dta cell made from lead. The quadruple point smA/n/l/g (that corresponds to the triple point smA/n/l of the pure substance in Fig. 10a) is shifted to 383 K and 125 MPa.

With rising pressures of N_2 or Ar (Fig. 10c) a destabilization of the smectic and even a disappearance of the nematic ranges are found. Measurements with Ar/ CO_2 gas mixtures also demonstrate a strong influence on the s/smA and smA/l transition curves. When pressurized with an Ar/ CO_2 mixture in a molar ratio of 30:1 even an intersection point of the s/smA and smA/l transition curves at about 130 MPa and 332 K is found (Fig. 10d); at pressures above this intersection point the smectic phase can only be observed in cooling runs where undercooling of the solid phase occurs and the smectic phase becomes metastable with respect to the crystalline solid.

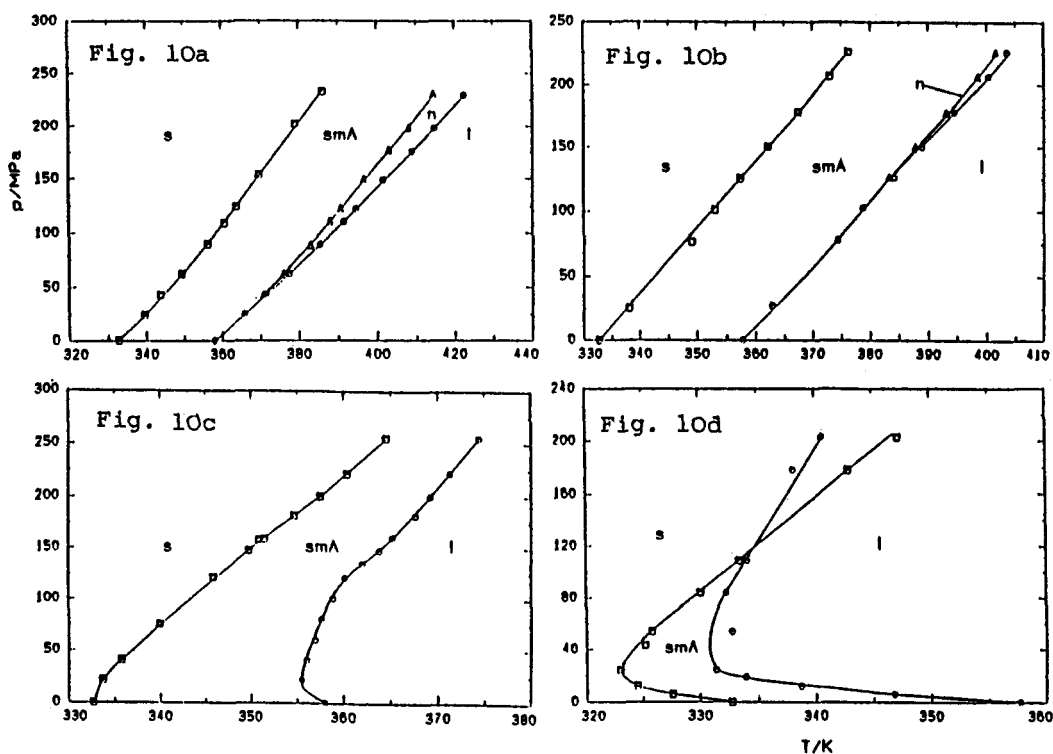


Fig. 10. $p(T)$ phase behaviour of 4-decyloxy-4'-cyanobiphenyl ($l\text{ØOCB}$) (Krombach, ref. 21,22).

Fig. 10a. Pure $l\text{ØOCB}$.

Fig. 10c. $l\text{ØOCB}$ saturated with argon.

Fig. 10b. $l\text{ØOCB}$ saturated with helium.

Fig. 10d. $l\text{ØOCB}$ saturated with an Ar/CO_2 mixture (molar ratio 30:1).

These phenomena can be qualitatively understood taking into account two competing pressure effects:

- The transition temperatures have the tendency to increase with rising pressure as it is already known for the pure substances (see e.g., the smA/l , smA/n and n/l transition lines in Fig.10a) (effect I).
- The solubility of the gas (and by this the concentration of an inert impurity) in the liquid and liquid crystalline phases increases with rising pressure resulting in a decrease of the transition temperatures (effect II).

For helium gas that is only slightly soluble in liquids effect I dominates and the $p(T)$ phase diagram (Fig.10b) resembles that of the pure substance (Fig.10a). In the sequence nitrogen, argon and even more carbon dioxide (here as a component of the binary gas mixtures) the gas solubility at a given pressure becomes gradually higher and consequently the decrease of the transition temperatures more and more important according to effect II. From the competition of effect I and II even temperature minima on the transition curves can appear (see Fig.10c and 10d). For a detailed discussion see ref. 21 and 22.

5. APPLICATIONS

Fluid mixtures with at least one supercritical component are of considerable interest for applications in many fields, especially for Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC). For a compilation of different applications and a list of references, symposia, books, review articles etc see ref.1; interesting new books are given in ref.23 (SFE) and ref.24 and 25 (SFC).

In the following some results very recently obtained in our laboratory are shortly presented:

Moderators in SFE - Much work has been done on fundamental research on moderators (for examples and references see e.g., ref.1). A very recent example is shown in Fig.11 (Kordikowski, ref. 15,16). Whereas the volatile moderator quinoxaline had no important effect on selecti-

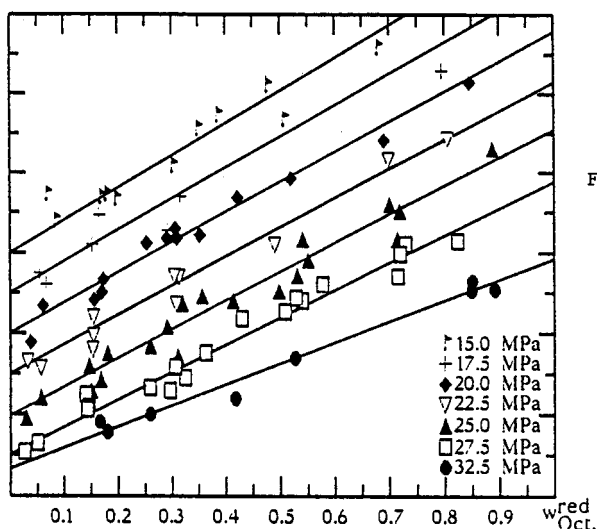


Fig. 11. Separation factors α_{12} of the system $\text{CO}_2 + 1\text{-dodecanol} + \text{dodecanoic acid} + 1,8\text{-octanediol}$ as a function of the carbon dioxide free mass fraction of the moderator 1,8-octanediol $w_{\text{Oct}}^{\text{red}}$ at 393.2 K and at pressures between 15.0 and 32.5 MPa (with $\alpha_{12} = K_{\text{Ol}}/K_{\text{acid}}$ where $K_i = w_i^g/w_i^l$ = distribution coefficient) (Kordikowski, ref. 15,16).

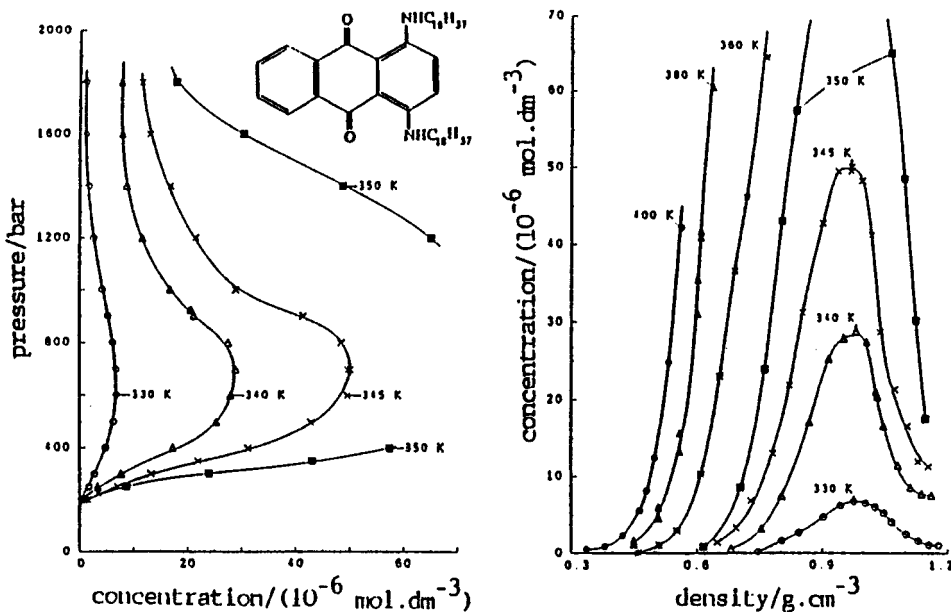


Fig. 12. Solubility of 1,4-bis-(octadecylamine)-9,10-anthraquinone in supercritical carbon dioxide at different temperatures as a function of pressure and density (Haarhaus, ref. 28,29).

vity in the system $\text{CO}_2 + 1\text{-dodecanol} + \text{dodecanoic acid}$, addition of the low-volatile moderator 1,8-octanediol (that had already been used very successfully earlier, see ref. 17,18) increased the separation factor $\alpha_{\text{Ol/acid}}$ ($= K_{\text{Ol}}/K_{\text{acid}}$ where $K_i = w_i^g/w_i^l$ = distribution coefficient) by a factor of about 2 when increasing the carbon dioxide free mass fraction of the moderator from zero to about 0.7. For details see Kordikowski, ref. 15,16.

Dyeing of fibers - Supercritical carbon dioxide has shown to be also a very powerful solvent for dyestuffs and for the dyeing of fibers (see e.g. ref. 26,27).

Some of our very recent results are presented in Fig. 12a and 12b where the concentrations of 1,4-bis-(octadecylamine)-9,10-anthraquinone (that is a good dyestuff for polypropylene) in supercritical carbon dioxide are plotted as a function of pressure and density according to measurements of Haarhaus (ref. 28,29). It is of considerable thermodynamical, theoretical and practical interest that the dyestuff concentrations are rather high and even run through distinct maximum values as a function of pressure and density. These measurements are continuing (Swidersky, ref.30).

SFC on liquid crystals - Supercritical Fluid Chromatography (SFC) has become a well-established method of analysis and in the meantime SFC chromatographs are already widely commercialized. For details and references see e.g., ref. 1,24,25.

An informative example for an SFC separation using supercritical carbon dioxide as a mobile phase is given in Fig.13 where the SFC separation of a homologous series of liquid crystalline substances (here 4-n-alkoxy-4'-cyanobiphenyls from 5OCB to 10OCB) is shown according to measurements by Dahlmann (ref. 31,32). From systematic SFC measurements capacity ratios k' (where $k'_i \equiv (c_i^{\text{stat}}/c_i^{\text{mob}}) (V^{\text{stat}}/V^{\text{mob}}) = (t_{ri} - t_0)/t_0$; see ref.1) were determined by Jacobs (ref. 33,32). In Fig.14a $\log k'$ is plotted against density ρ for constant temperature and in Fig.14b against the reciprocal absolute temperature $1/T$ for a constant density of $\rho = 0.70 \text{ g}\cdot\text{cm}^{-3}$; straight lines result from which thermodynamic information can be obtained. For a detailed discussion see ref. 1,4,31-33 etc. For the determination of binary diffusion coefficients D_{12} from SFC experiments see ref.1.

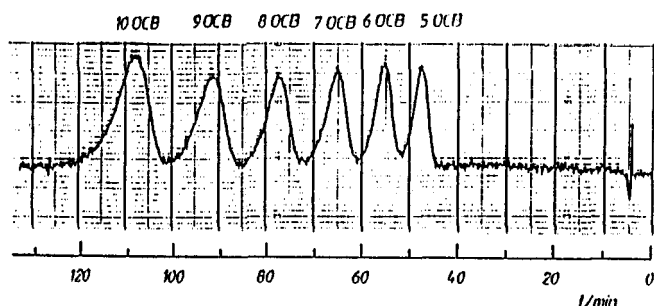


Fig. 13. SFC chromatogram of a mixture of the 4-n-alkoxy-4'-cyanobiphenyls from 5OCB to 10OCB on Spherisorb ODB-2 with carbon dioxide as mobile phase ($T = 312 \text{ K}$, $P = 9.9 \text{ MPa}$, $\rho = 0.65 \text{ g}\cdot\text{cm}^{-3}$, $\dot{V}(\text{NTP}) = 153 \text{ cm}^3 \cdot \text{min}^{-1}$) (Dahlmann, ref. 31,32).

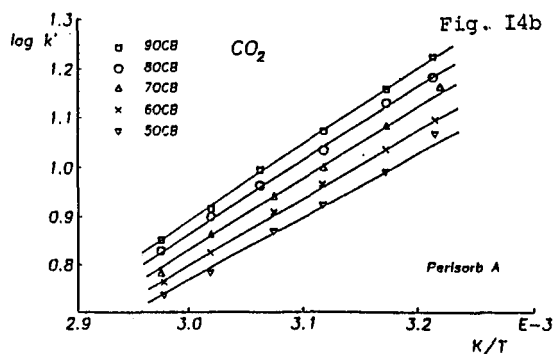
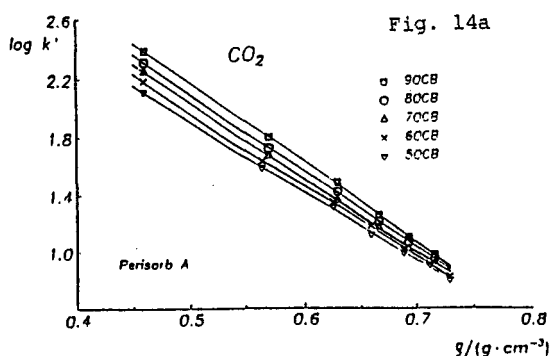


Fig. 14. Capacity ratios k' of the 4-n-alkoxy-4'-cyanobiphenyls from 5OCB to 9OCB on Perisorb A with carbon dioxide as mobile phase determined from SFC experiments (Jacobs, ref. 32,33). Fig. 14a. $\log k'(\rho)$ at 320.9 K ($\dot{V}(\text{NTP}) = 576 \text{ cm}^3 \cdot \text{min}^{-1}$). Fig. 14b. $\log k'(1/T)$ at $\rho = \text{const} = 0.70 \text{ g}\cdot\text{cm}^{-3}$.

6. OUTLOOK

As already accentuated in earlier reviews (e.g., ref.1) investigations on fluid systems at high pressure are still of increasing importance. New fields and new applications are being opened such as the dyeing of fibers or the use of chemical reactions in supercritical solvents (e.g., for the degradation of pollutants in supercritical steam). For some recent progress in these and other fields see ref.1 (as well as ref. 17,20,77-81 given there), the proceedings mentioned in ref.4 or the book cited in ref.23 etc. More and more conferences and symposia and even summer schools (as in ref.34) are concerned with related problems. For all these applications investigations on the properties of fluid systems as a function of temperature, pressure, composition and other parameters are and will remain to be a challenge to experiment, theory and application at least during this decade.

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