Occurrence of Holes in Ternary Fluid Multiphase Systems of Near-Critical Carbon Dioxide and Certain Solutes

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Contents

I. Introduction

For practical applications of near-critical fluids, e.g., separations, reactions, materials processing, etc., in all cases a thorough knowledge of the phase behavior of such systems is a prerequisite. Although carbon dioxide is an abundant, inexpensive, nontoxic, and nonflammable solvent, in supercritical fluid applications it has the major disadvantage of having a poor solvency with respect to many low-volatile components, and cosolvents like, for instance, alkanols have to be used to enhance the solubility of the solutes in supercritical carbon dioxide, see for example Fulton et al.[1]

Another characteristic feature of carbon dioxide in supercritical fluid applications is that in many cases the fluid mixture is composed of, on one hand, a highly volatile near-critical solvent (carbon dioxide) and, on the other hand, one or more low-volatile solutes, i.e., in practice we are dealing with mixtures composed of physically and/or chemically very dissimilar molecules. From many investigations it is known,[2−4] to mention only a few, that in these kind of mixtures the presence of a second liquid phase is most likely to occur. The latter phenomenon also makes carbon dioxide a less attractive near-critical solvent.

Besides the occurrence of a second liquid phase, from extensive and systematic experimental research,[2,3] it became apparent that in binary mixtures of near-critical carbon dioxide with certain low-volatile solutes, belonging to a homologous series of substances, the nature of this multiphase behavior may undergo major changes. For instance, the nature of the fluid multiphase behavior in the binary mixture of near-critical carbon dioxide with dodecane is completely different compared to that with tetradecane. Although in both cases a three-phase equilibrium liquid−liquid−vapor (l_1l_2g) is present, their critical endpoints differ in nature. In the carbon dioxide system with dodecane the critical endpoint of the three-phase equilibrium l_1l_2g is characterized by criticality of the two liquid phases l_1 and l_2 ($l_1 = l_2 + g$), while in the critical endpoint of the three-phase equilibrium l_1l_2g of the carbon dioxide system with tetradecane the liquid-phase l_1 is critical with the gaseous phase g ($l_2 + l_1 = g$). The fluid multiphase behavior of the system near-critical carbon dioxide with tridecane is characterized by the presence of even three critical endpoints: two of them being of the nature $l_1 = l_2 + g$ and the other one showing the phenomenon $l_1 = g + l_2$.[2,5,6] In all, this demonstrates that minor changes in the size and/or shape of the solute molecules sometimes may cause major changes in its phase behavior. A closer look at the various phase diagrams of these binary mixtures will show that in each of the three systems mentioned above the connectivity of the critical loci is different, i.e., each system belongs to a different class of fluid phase behavior.[2,5] From detailed experimental studies[2−10] on the fluid multiphase behavior of these so-called asymmetric systems, it became apparent that the phenomena described above are not an exception but apply in general.

Another phenomenon of interest for supercritical fluid technology is the occurrence of cosolvency effects in ternary mixtures of a near-critical solvent and two different solutes. For instance, addition of a small amount of a 1-alkanol to a binary mixture carbon dioxide + *n*-alkane may cause a significant effect on the critical behavior of the system with as a consequence unexpected phase behavior like miscibility windows[11,12] and two-phase holes in three-phase surfaces.[13−15] In general, miscibility windows occur at higher pressures than holes.[11−15] Although it is expected that both phenomena may have a consider-

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Cor J. Peters was born in Gorinchem, The Netherlands, where he took his Masters at The Technical University of Delft in 1976. Along with a position at The Delft University of Technology, he prepared a Ph.D. thesis entitled: "Phase behavior of binary mixtures of ethane + *n*-eicosane and statistical mechanical treatment of fluid phases". He obtained his Ph.D. degree in 1986. In 1988 he became an Associate Professor in the group of Applied Thermodynamics and Phase Equilibria, also at the Technical University of Delft. His main field of interest is high-pressure phase equilibria with currently an emphasis on supercritical fluids, hydrates, interfacial phenomena, and thermodynamic modeling. He is co-author of more than 120 scientific papers and an IUPAC volume on equations of state (in press).

Kerstin Gauter was born in Berlin, Germany, where she graduated from the Technical University of Berlin in 1994 as "Diplom-Ingenieurin" in Energy Engineering. For her Masters she worked on two different topics: "Dimensional analysis and its application to non-pure technical systems" and "Experimental investigations on the applicability of the principle of congruence for certain fluid phase equilibria". The latter topic was carried out within the Erasmus exchange program between the Technical University of Berlin and Delft University of Technology. After her graduation, she joined the group of "Applied Thermodynamics and Phase Equilibria" of Delft University of Technology to prepare a Ph.D. thesis, entitled: "Fluid multiphase behavior in ternary systems of near-critical CO_2—Measurements, modeling, computation". The defense will take place in January 1999. Six months of her Ph.D. were spent with Professor Heidemann at The University of Calgary, Canada. She has agreed to a postdoctoral position with Professor Heidemann for 1999.

able influence on supercritical fluid applications, this review exclusively will focus on the holes in three-phase surfaces. It will be shown that the complex fluid multiphase behavior in ternary systems can be explained in terms of transformations between types of fluid phase behavior.

II. The Classification of Van Konynenburg and Scott

Van Konynenburg and Scott[16−18] introduced a classification of six types of binary fluid phase behavior encountered experimentally. With an exception of the closed loop immiscibility (type VI fluid phase behavior) all types could be generated from the simple van der Waals equation of state.

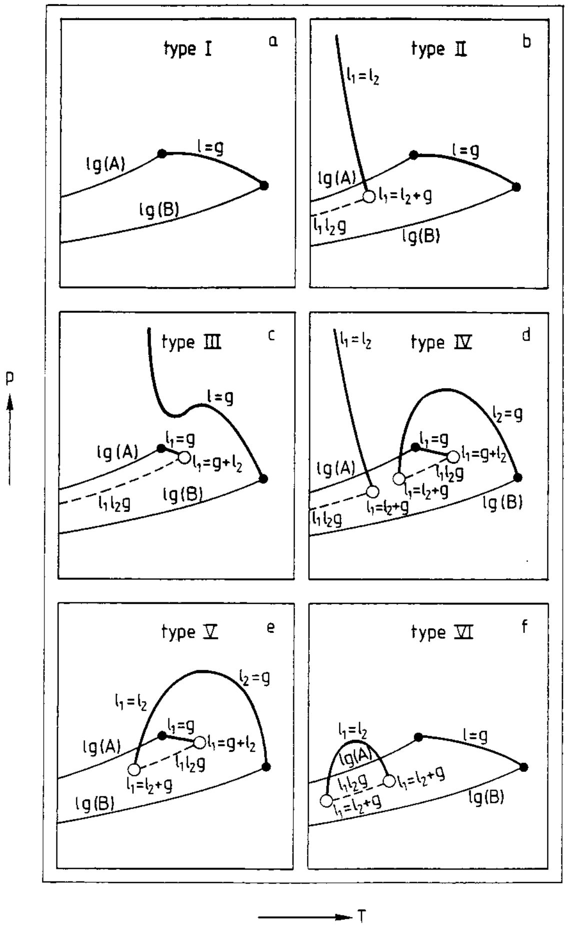

Figure 1. Classification of Van Konynenburg and Scott.

As pointed out in the previous section, in this study it will be discussed how various types of fluid phase behavior may transform into each other. Therefore, knowledge of the details of the basic types of fluid phase behavior is a prerequisite. With special attention to the nature of critical endpoints these types will be recalled briefly in this section.

Figure 1 shows the six types of fluid phase behavior as originally introduced by Van Konynenburg and Scott.[18] Type I (Figure 1a) has a continuous critical locus between both critical points of the pure components.

Figure 1b represents type II fluid behavior. This type is characterized by the presence of a three-phase equilibrium l_1l_2g (dashed line) ending at higher temperature in a critical endpoint of the nature $l_1 = l_2 + g$, i.e., the two liquid phases are critical in the presence of a gaseous phase.

Type III fluid phase behavior, shown in Figure 1c, also has a three-phase equilibrium l_1l_2g (dashed line). However, its critical endpoint has the nature $l_1 = g + l_2$, i.e., the liquid-phase l_1 and the gaseous phase g are critical in the presence of the liquid-phase l_2. Figure 1c also shows that one branch of the critical locus ($l_1 = g$) connects the critical point of pure component A to the critical endpoint of the three-phase equilibrium l_1l_2g. A second branch of the critical locus ($l_1 = g$) originates in the critical point of pure component B and extends to higher pressures with gradually changing its nature from $l = g$ into $l_1 = l_2$. This latter critical locus in type III systems can have a maximum and minimum in pressure, as shown in Figure 1c. At least three other alternative shapes of this critical locus are known (see for example Rowlinson and Swinton[19]).

The type of fluid phase behavior shown in Figure 1d (type IV) has two separate three-phase regions l_1l_2g (dashed lines). The critical endpoint of the low-temperature three-phase region has the nature $l_1 = l_2 + g$. The critical endpoint at the lowest temperature of the high-temperature three-phase equilibrium l_1l_2g also has the nature $l_1 = l_2 + g$, whereas the critical endpoint of this three-phase equilibrium at higher temperature has the nature $l_1 = g + l_2$. Figure 1d also shows the connectivity of the three critical loci to the critical points of the pure components and to the three critical endpoints.

If in Figure 1d (type IV fluid phase behavior) the low-temperature three-phase region and the related critical locus $l_1 = l_2$ are removed, type V fluid phase behavior results (Figure 1e). Both critical endpoints of type V have the same nature as those of the high-temperature three-phase equilibrium as shown in Figure 1d. Also, the critical loci have schematically the same connectivity to the various characteristic points in this figure.

Finally, Figure 1f represents type VI fluid phase behavior. It is the so-called closed-loop immiscibility. This type of fluid phase behavior is characterized by a three-phase region bounded by two critical endpoints of the same nature ($l_1 = l_2 + g$). Between both critical endpoints a continuous critical locus $l_1 = l_2$ is present. However, from experiments it became apparent that in most cases this critical locus is not continuous but consists of two branches with a tubelike shape and a narrowing at somewhat higher pressures. The critical points of both pure components are connected by a continuous $l_1 = g$ critical locus. For further details on the classification of fluid phase behavior one is referred to elsewhere.[19-22]

III. Tricritical Points and Double Critical Endpoints

A tricritical point (TCP) occurs when two critical endpoints of different nature ($l_1 = l_2 + g$ and $l_1 = g + l_2$) coincide. This leads to the phenomenon $l_1 = l_2 = g$, i.e., the three fluid phases l_1, l_2, and g of the three-phase equilibrium l_1l_2g are critical simultaneously. For instance, in a binary system belonging to type IV or type V (see parts d and e of Figure 1, respectively), in principle, such a phenomenon is possible to occur. However, an analysis of the phase rule[23,24] shows that in a binary system tricriticality is unlikely to occur. The phase rule is written as follows:

$$f = n - r + 2 - \phi \tag{1}$$

In this equation f is the number of degrees of freedom, n the number of components, r the number of phases, and ϕ the number of extra conditions. For a normal critical point, i.e., two fluid phases are becoming identical, the extra conditions ϕ in terms of derivatives of the molar Gibbs energy to composition are:

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{p,T} = 0$$

and

$$\left(\frac{\partial^3 G}{\partial x^3}\right)_{p,T} = 0 \tag{2}$$

However, for a tricritical point the number of extra conditions ϕ are

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{p,T} = 0$$

$$\left(\frac{\partial^3 G}{\partial x^3}\right)_{p,T} = 0$$

$$\left(\frac{\partial^4 G}{\partial x^4}\right)_{p,T} = 0$$

and

$$\left(\frac{\partial^5 G}{\partial x^5}\right)_{p,T} = 0 \tag{3}$$

Counting a critical phase as being one single phase, this means that according to eqs 1 and 3 for tricriticality to occur the minimum number of components has to be three. For instance, in binary mixtures of ethane or propane and n-alkanes, a tricritical point will not occur at integer values of the carbon number of the n-alkane.[25,26]

A double critical endpoint (DCEP) occurs when two critical endpoints of the nature $l_1 = l_2 + g$ coincide. From Figure 1, parts d and f, it can be concluded that in binary mixtures showing type IV and type VI fluid phase behavior a DCEP, in principle, may occur. A similar analysis for a DCEP, as mentioned above for a TCP, leads to the same number of degrees of freedom, i.e., also the presence of a DCEP in a binary mixture is unlikely to occur.

IV. Transformations between Types of Fluid Phase Behavior

A. Binary Mixtures

The phase behavior of binary mixtures of carbon dioxide with compounds belonging to certain homologous series have already been studied by Schneider and co-workers.[27-29] However, for the purpose of this study experimental results on the three-phase behavior l_1l_2g in binary systems of near-critical carbon dioxide and components belonging to the homologous series of n-alkanes and of 1-alkanols were adopted from studies of Luks and co-workers.[2,3] Considering diagrams with the temperatures of the critical endpoints of the three-phase equilibria l_1l_2g as a function

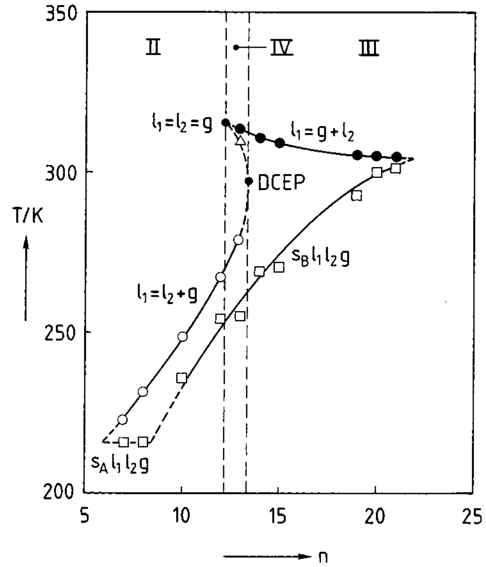

Figure 2. Transformation between types of fluid phase behavior in binary carbon dioxide + *n*-alkane systems.[2]

of carbon number, it became apparent that with increasing carbon number of the solute always the following transformation sequence in fluid phase behavior occurred:

$$\text{type II} \rightarrow \text{type IV} \rightarrow \text{type III}$$

For example, in binary mixtures of carbon dioxide with *n*-alkanes (Figure 2), it was established that the systems with a carbon number up to 12 (dodecane) have type II fluid phase behavior, the system with carbon number 13 (tridecane) has type IV and the systems with carbon number higher than 13 show type III fluid phase behavior. Figure 2 clearly demonstrates that within a range of only three carbon numbers the phase behavior of the binary mixtures changes significantly. Note that for the *n*-alkanes with high carbon numbers the three-phase equilibria l_1l_2g become partially or even completely hidden by the occurrence of a solid *n*-alkane phase ($s_Bl_1l_2g$), while for the *n*-alkanes with low carbon number the three-phase behavior may be hidden by the occurrence of a solid carbon dioxide phase ($s_Al_1l_2g$). For details on the multiphase behavior of binary carbon dioxide + *n*-alkane systems, one is referred to elsewhere.[2,4,30]

Until recently it was accepted that binary mixtures of carbon dioxide with 1-alkanols show type II fluid phase behavior up to pentanol, while binary systems with hexanol and higher as the solute, have type III fluid phase behavior.[3] From an additional quasi-binary study, however, it became apparent that the binary system CO_2 + 1-pentanol belongs to type IV fluid phase behavior.[31] Figure 3 shows graphically the critical endpoint temperatures as a function of the carbon number of the 1-alkanol in a series of binary mixtures of carbon dioxide + 1-alkanols. Similar to the carbon dioxide systems with *n*-alkanes, the three-phase behavior of the systems with low or high carbon numbers of the 1-alkanol may be partially or completely hidden by the precipitation of solid carbon dioxide ($s_Al_1l_2g$) or of solid 1-alkanol ($s_Bl_1l_2g$), respectively.

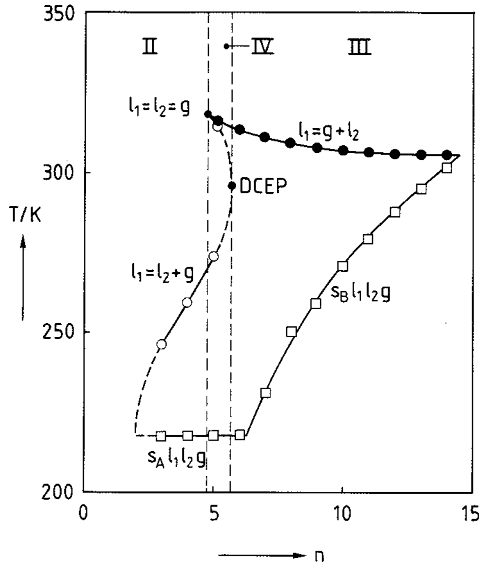

Figure 3. Transformation between types of fluid phase behavior in binary carbon dioxide + 1-alkanol systems.[3,31]

B. Ternary Mixtures

From Figures 2 and 3 it can easily be established that binary systems of carbon dioxide with tetradecane or decanol both have type III fluid phase behavior. Patton et al.[13] conducted phase equilibrium experiments in ternary mixtures of carbon dioxide + tetradecane + decanol. Much attention was given to determine critical endpoints of the three-phase equilibrium l_1l_2g in mixtures with about 95 mol % carbon dioxide and various ratios of both solutes with total concentration of the two solutes of about 5 mol %. As was to be expected, critical endpoints of the nature $l_1 = g + l_2$ of the three-phase equilibrium l_1l_2g could be measured in a straightforward manner. However, quite surprisingly it turned out that within a certain composition ratio of both solutes also critical endpoints of the nature $l_1 = l_2 + g$ could be established at somewhat lower temperatures and pressures. The experimental results of Patton et al.[13] along with those obtained by Peters et al.[14,15] for the system carbon dioxide + tetradecane + decanol are shown in Figure 4. In this figure the temperatures of the experimentally obtained critical endpoints are represented as a function of the mole fraction x^*, the tetradecane mole fraction on a carbon dioxide free basis. In Figure 4 the continuous critical endpoint locus of the nature $l_1 = g + l_2$ separates the three-phase surface l_1l_2g (lower temperature part of the diagram) from a two-phase region lg (higher temperature part of the diagram). In addition, Figure 4 shows a two-phase "hole" lg in the three-phase surface l_1l_2g. This hole is completely bounded by a closed-loop critical endpoint locus of the nature $l_1 = l_2 + g$. It should be noted that in Figure 4 the data point on the left-hand axis ($x^* = 0$) represents the critical endpoint $l_1 = g + l_2$ of the binary system carbon dioxide + decanol and the data point on the right-hand side of the diagram ($x^* = 1$) is the critical endpoint of the binary system carbon dioxide + tetradecane.

Patton et al.[13] explained the occurrence of a two-phase hole in the three-phase surface by assuming

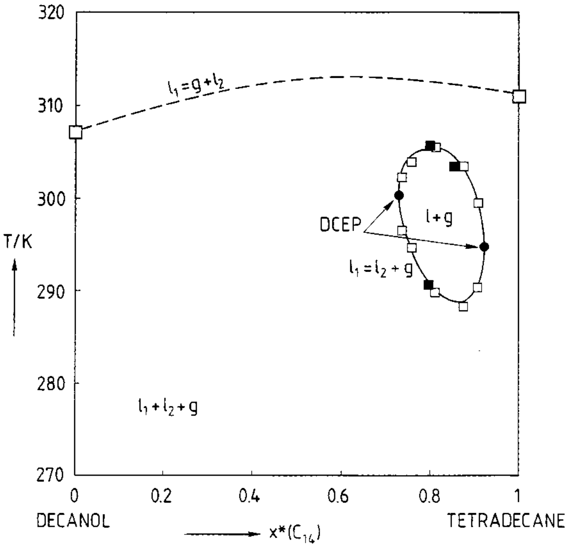

Figure 4. Occurrence of a two-phase hole in the three-phase surface of the ternary system carbon dioxide + tetradecane + decanol (open squares, from ref 13; filled squares, from refs 14 and 15).

the formation of aggregates of decanol molecules due to hydrogen bonding. If, for instance, in a binary mixture (95 mol % carbon dioxide and 5 mol % tetradecane) a minute amount of tetradecane is replaced by decanol, the formation of decanol aggregates will be almost negligible since the decanol concentration is very low. As long as hydrogen bonding between the decanol molecules can be neglected, a continuation of replacing tetradecane by decanol in the mixture will result in a decrease of the average carbon number of the solute mixture tetradecane + decanol. As a result, Patton et al.[13] argue that the mixture will more and more tend to change its nature from that of the binary system carbon dioxide + tetradecane into that of the binary system carbon dioxide + tridecane. Consequently, the ternary mixture also will tend to change its fluid phase behavior from that of the binary system carbon dioxide + tetradecane (type III) into that of the binary system carbon dioxide + tridecane (type IV), see Figure 2.[2,5,6] However, if we continue the process of replacing tetradecane by decanol, another phenomenon starts to play a significant role: the aggregation of the decanol molecules due to its increasing concentration. From spectroscopic studies of Fulton et al.,[1] it is known that alkanol aggregates of four molecules at the conditions of interest in this study are quite common. As a consequence, the average carbon number of the solute mixture tetradecane + decanol will increase with increasing decanol concentration, i.e., the phase behavior of that of the higher carbon dioxide + *n*-alkane systems (type III fluid phase behavior, see Figure 2) will return.

In a recent study by Scheidgen,[32] this behavior was ascribed to be a consequence of a cosolvency effect. Cosolvency is defined as the effect whereby a mixture of two solutes A and B is better solvable in a solvent than any of the solutes A and B individually. With the occurrence of cosolvency in a ternary mixture the liquid one-phase region is extended, i.e., compared to both critical loci of the individual binary systems, the ternary critical locus $l_1 = l_2$ is shifted to lower temperatures and pressures. Figure 5 illustrates schematically this cosolvency effect by means of a quasi-binary approach. Of course, the three-component systems presented in this review cannot be considered as quasi-binary systems, but are true ternary systems. Starting, for instance, with the binary system carbon dioxide + tetradecane one obtains the fluid phase behavior shown in Figure 5a (type III fluid phase behavior). Due to cosolvency, a gradual replacement of tetradecane by decanol, keeping the mole fraction of carbon dioxide constant, lowers the pressure minimum of the critical locus $l_1 = l_2$. At a certain solute ratio the minimum of this critical locus will become tangent to the three-phase equilibrium l_1l_2g (Figure 5b). This point is a double critical endpoint (DCEP) and, according to its earlier introduced definition, it marks the change of fluid phase behavior from type III into type IV. In Figure 4, this DCEP is located on the righ-hand side of the closed loop. A continuation of replacing tetradecane by decanol may bring the minimum of the critical locus even further down toward lower pressures with, as a consequence, a split of the three-phase equilibrium into two parts, a lower temperature and a higher temperature part (Figure 5c). This behavior can be found in Figure 4 for the solute ratios for which the two-phase hole lg in the three-phase surface l_1l_2g occurs. It is typically type IV fluid phase behavior (see also Figure 1d). Since by continuing the process of replacing tetradecane by decanol type III fluid phase behavior has to return, the minimum of the critical locus has to raise again to higher pressure. In Figure 5d, for a certain solute ratio, this

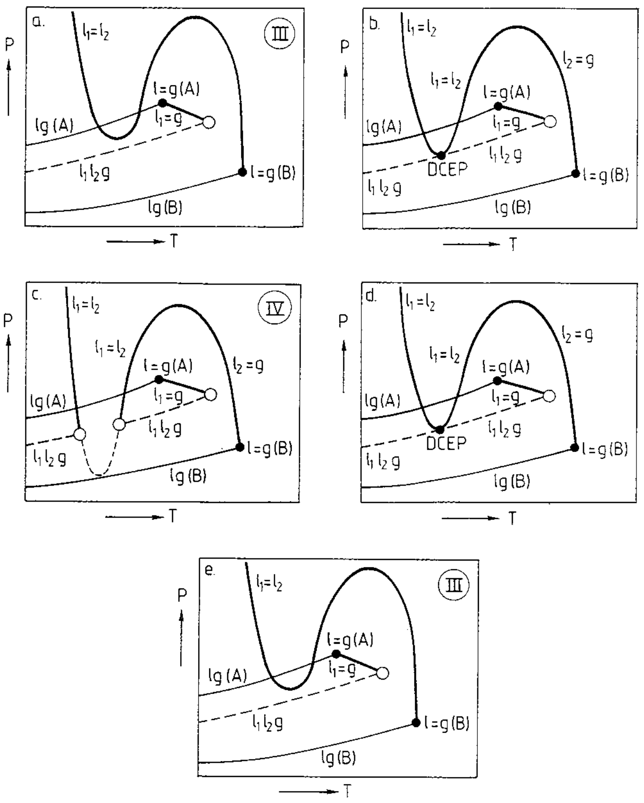

Figure 5. Schematical illustration of cosolvency by means of a quasi-binary approach, leading to the occurrence of a two-phase hole lg in a three-phase surface l_1l_2g.

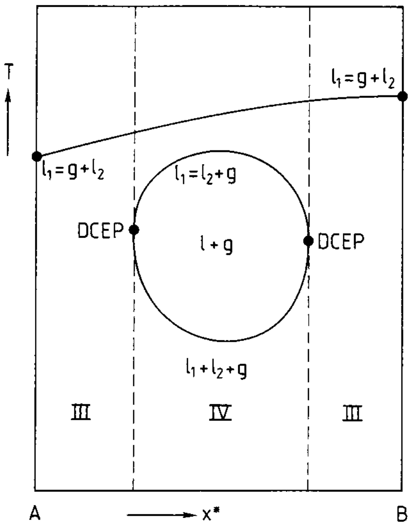

Figure 6. Transformation scheme of types of fluid phase behavior for the system carbon dioxide + tetradecane + decanol.

critical locus is again tangent to the three-phase equilibrium l_1l_2g leading to the occurrence of a second DCEP (see also the left-hand side DCEP in Figure 4), and the gap between both branches of this three-phase equilibrium is about to close again. Finally, in Figure 5e, type III fluid phase behavior has returned again, which is also the type of fluid phase behavior of the binary system carbon dioxide + decanol (see also Figure 3). Figure 6 shows schematically the description of this phenomenon in a T,x^* diagram. In this figure the components A and B represent tetradecane and decanol, respectively. Figure 6 clearly shows how, by changing the nature of the solute from that of decanol ($x^* = 0$) into that of tetradecane ($x^* = 1$), the following changes in type of fluid phase behavior occur:

$$\text{type III} \rightarrow \text{type IV} \rightarrow \text{type III}$$

In terms of a three-dimensional p,T,x^* representation it is easy to understand that the occurrence of a two-phase “hole” lg in the three-phase surface l_1l_2g simply is a consequence of the intersection of the minimum of the critical surface $l_1 = l_2$ with this three-phase surface l_1l_2g. Figure 6 simply is the T,x^* projection of this three-dimensional p,T,x^* representation.

At this point it is worthwhile to recall that with the occurrence of cosolvency in a particular ternary mixture carbon dioxide + solute A + solute B the phenomenon of miscibility windows can be observed. For instance, at a fixed pressure the critical surface may give rise to closed-loop one-phase regions in a two-phase region. Although miscibility windows and holes can be found in the same ternary system, miscibility windows mostly occur at higher pressures than the two-phase lg holes in three-phase surfaces l_1l_2g. For details on miscibility windows one is referred to elsewhere.[11,12,32]

V. Experimental Results

In this section the experimental results on the phenomenon “holes” in three-phase surfaces l_1l_2g of various ternary mixtures will be presented. For experimental details and techniques one is referred to elsewhere.[14,15,31,33,34] In all ternary mixtures investigated the concentration of carbon dioxide was always close to 95 mol % and, consequently, that of the two solutes sums up to 5 mol %.

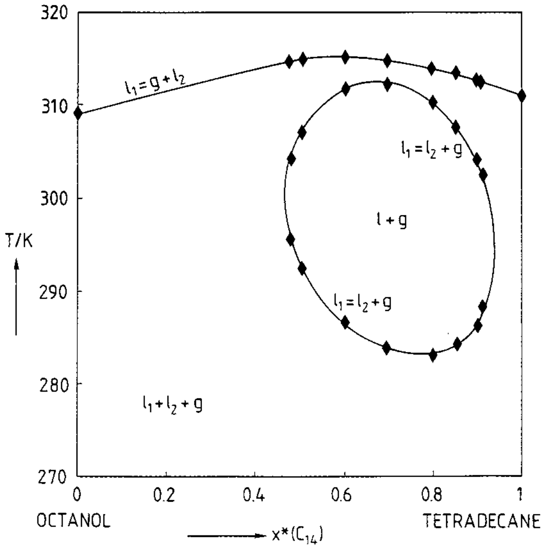

Figure 7. Fluid multiphase behavior in the system carbon dioxide + tetradecane + octanol:[14,15] filled diamonds, experimental data; full curves, best fit.

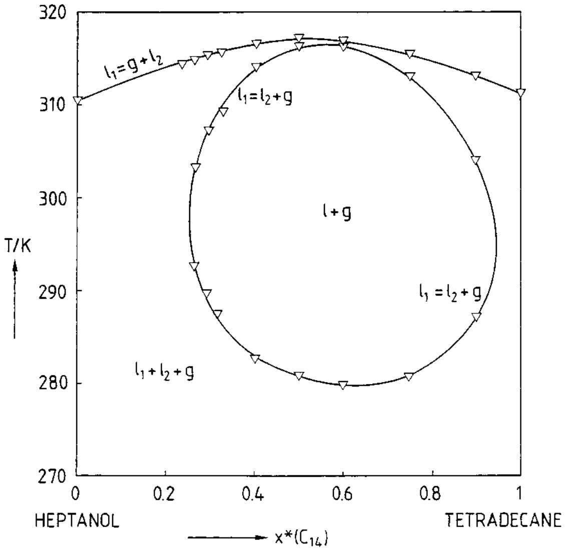

Figure 8. Fluid multiphase behavior in the system carbon dioxide + tetradecane + heptanol:[14,15] open triangles, experimental data; full curves, best fit.

A. Ternary Mixtures of Carbon Dioxide + Tetradecane + 1-Alkanols

In additional investigations, decanol was successively replaced by octanol and heptanol. The results are shown in Figures 7 and 8, respectively. Both figures show a quite similar behavior as already discussed for the ternary mixture carbon dioxide + tetradecane + decanol, be it that a lower carbon number of the 1-alkanol leads to a larger closed loop two-phase region lg. Figure 8 also shows that the two-phase region lg, bounded by the critical endpoint locus $l_1 = l_2 + g$, is about to intersect the critical

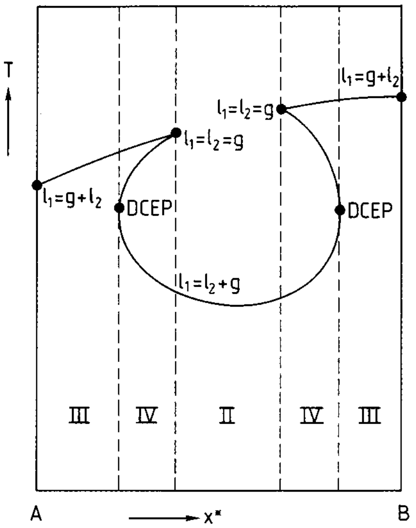

Figure 9. Transformation scheme of types of fluid phase behavior for the system carbon dioxide + tetradecane + hexanol.

endpoint locus $l_1 = g + l_2$. As pointed out already, coincidence of critical endpoints of different nature or intersection of critical endpoint loci of different nature results in the occurrence of tricriticality. This fluid phase behavior, to be expected for the ternary system carbon dioxide + tetradecane + hexanol, is shown schematically in Figure 9. From this figure it can be seen that two tricritical points are present, that the critical endpoint locus $l_1 = g + l_2$ is interrupted, and that the critical endpoint locus $l_1 = l_2 + g$ no longer forms a closed loop. In addition, this figure also shows that the following sequence of types of fluid phase behavior occurs by gradually changing the nature of the solute from that of hexanol ($x^* = 0$) into that of tetradecane ($x^* = 1$):

type III → type IV → type II → type IV → type III

To verify the expectation that the ternary system carbon dioxide + tetradecane + hexanol will show the fluid phase behavior presented in Figure 9, the relevant phase behavior of this ternary mixture was determined experimentally and the results are shown graphically in Figure 10. Considering Figure 3 again, it can be concluded that to lower carbon numbers of the 1-alkanols the binary system carbon dioxide + hexanol is the last binary mixture showing type III fluid phase behavior and that the binary mixture carbon dioxide + pentanol has type IV fluid phase behavior. Consequently, the ternary system carbon dioxide + pentanol + tetradecane cannot have a similar fluid phase behavior as shown in Figure 10 for the ternary system carbon dioxide + tetradecane + hexanol. The phase behavior to be expected is shown schematically in Figure 11. As can be seen from this figure, again two tricritical points will occur. The following sequence of types of fluid phase behavior will occur when gradually changing the nature of the solute from that of pentanol ($x^* = 0$) into that of tetradecane ($x^* = 1$):

type IV → type II → type IV → type III

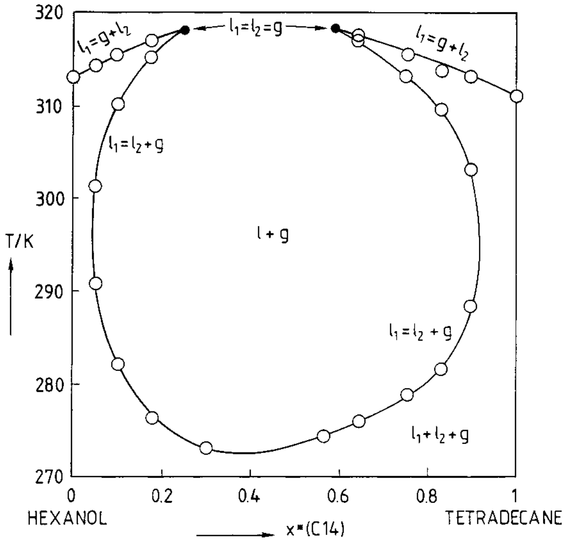

Figure 10. Fluid multiphase behavior in the system carbon dioxide + tetradecane + hexanol:[14,15] open dots, experimental data; full curves, best fit.

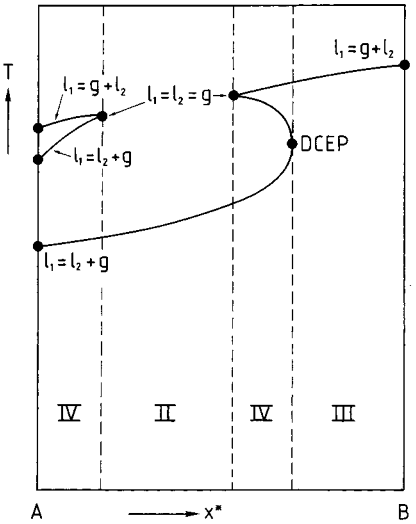

Figure 11. Transformation scheme of types of fluid phase behavior for the system carbon dioxide + tetradecane + pentanol.

Figure 12 shows the experimentally obtained results of the fluid phase behavior of the ternary system carbon dioxide + tetradecane + pentanol. Note that the lower temperature part of the $l_1 = l_2 + g$ critical endpoint locus is hidden by the occurrence of solid tetradecane (dashed part of the full curve).

B. Ternary Mixtures of Carbon Dioxide + Tridecane + 1-Alkanols

From Fall et al.[5] it is known that the binary system carbon dioxide + tridecane has type IV fluid phase behavior (see also Figure 2). This means that replacing tetradecane as one of the solutes by tridecane allows the transformations between various types of fluid phase behavior and type IV as one of the boundary systems to be studied. As the second solute again 1-alkanols (octanol, hexanol and pentanol) were tested.

Figures 13 and 14 show the results for the systems carbon dioxide + tridecane + octanol and carbon

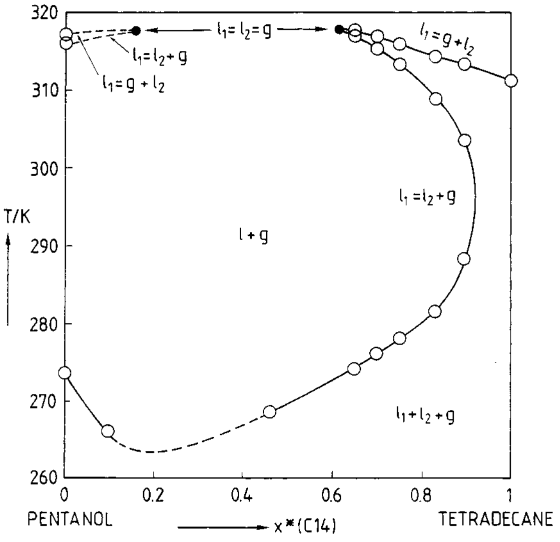

Figure 12. Fluid multiphase behavior in the system carbon dioxide + tetradecane + pentanol:[14,15] open dots, experimental data; full curves, best fit.

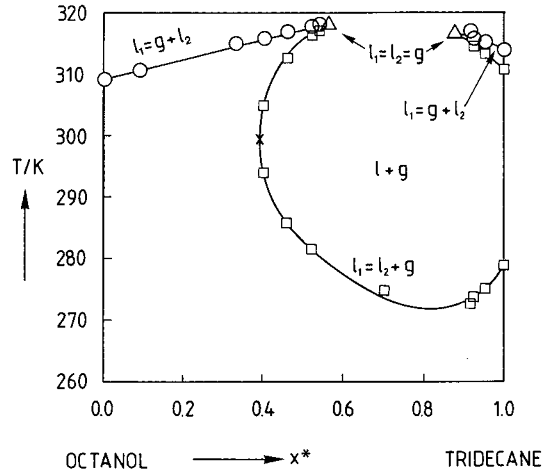

Figure 13. Fluid multiphase behavior in the system carbon dioxide + tridecane + octanol:[34] open dots, squares, and diamonds, experimental data; open triangles, tricritical points; cross, double critical endpoint; full curves, best fit.

dioxide + tridecane + hexanol, respectively. From both figures it can be seen that in both systems two tricritical points are present. The following sequence of types of fluid phase behavior occurs in these ternary systems:

type III → type IV → type II → type IV

Figure 15 represents the experimental results of the ternary system carbon dioxide + tridecane + pentanol. Since the binary system carbon dioxide + pentanol also has type IV fluid phase behavior,[31] also two tricritical points are present in the ternary system carbon dioxide + tridecane + pentanol. The following sequence of types of fluid phase behavior occur in this system:

type IV → type II → type IV

C. Ternary Mixtures of Carbon Dioxide + *o*-Nitrophenol + 1-Alkanols

In this section we will focus on transformations between on the one hand a binary system showing type V fluid phase behavior and on the other hand systems showing type III or type IV fluid phase behavior. To the best of our knowledge, in the literature only one binary carbon dioxide system is known showing type V fluid phase behavior, namely the system carbon dioxide + *o*-nitrophenol.[35] As the second solute 1-alkanols were chosen again. From a phase theoretical point of view a difficulty in the T,x^* diagrams arises for a transformation from type III or type IV into type V fluid phase behavior. Figure 16, parts a and b, shows schematically two possible options to make a transformation from type III (solvent + solute A) into type V fluid phase behavior (solvent + solute B). At the type V side of the diagrams, in principle, only two critical endpoints (see Figure 1e) can be present. Thus, in both parts a and b of Figure 16 the two dots highest in temperature on the right-hand axis (B axis), representing the critical endpoints of the binary mixture solvent + solute B, have with increasing temperature the nature $l_1 = l_2 + g$ and $l_1 = g + l_2$, respectively. On the left-hand axis (A axis) of the diagrams, representing the binary system solvent + solute A, type

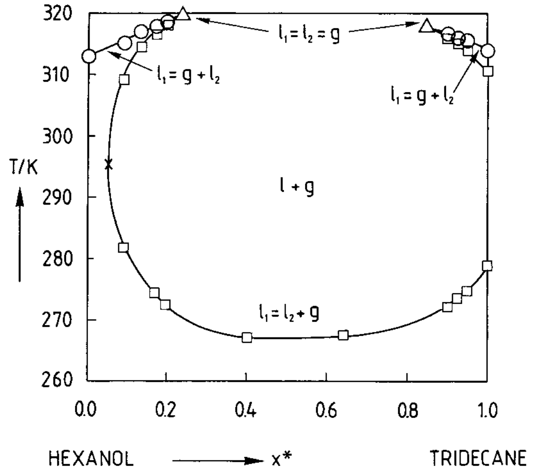

Figure 14. Fluid multiphase behavior in the system carbon dioxide + tridecane + hexanol:[34] open dots, squares, and diamonds, experimental data; open triangles, tricritical points; cross, double critical endpoint; full curves, best fit.

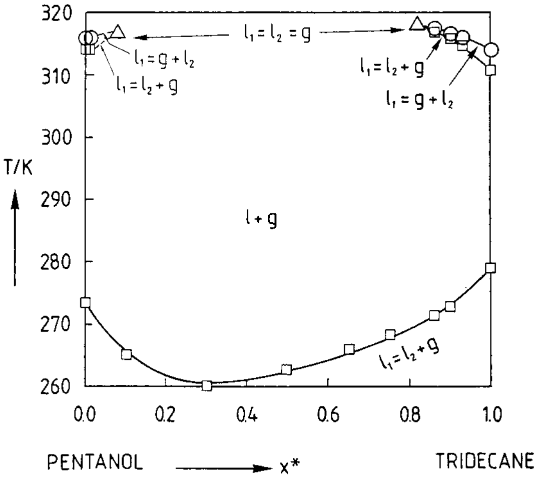

Figure 15. Fluid multiphase behavior in the system carbon dioxide + tridecane + pentanol:[34] open dots, squares, and diamonds, experimental data; open triangle, tricritical points; cross, double critical endpoint; full curves, best fit.

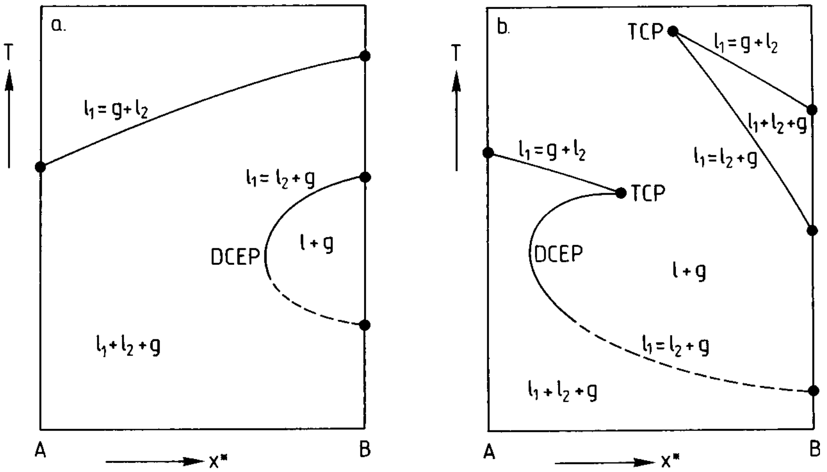

Figure 16. Possible transformation schemes from a type III system into a type V fluid phase behavior system: (a) transformation via a DCEP and (b) transformation via two TCPs and a DCEP.

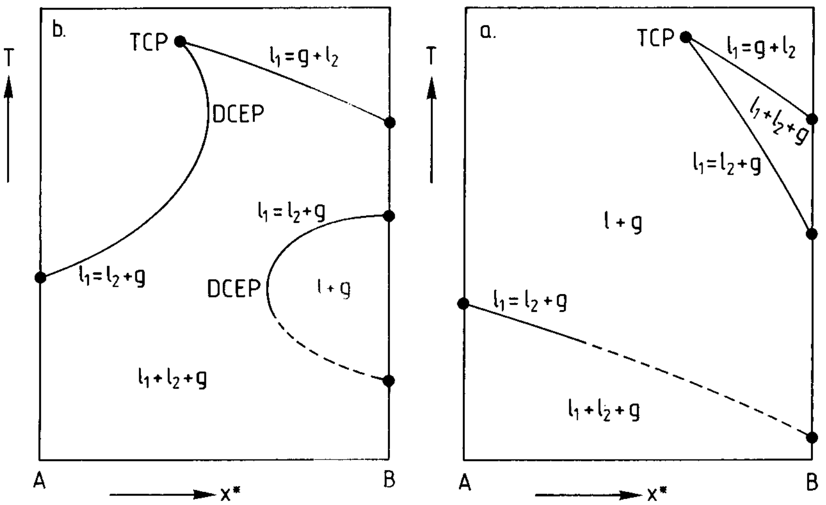

Figure 17. Possible transformation schemes from a type II system into a type V fluid phase behavior system: (a) transformation via a TCP and (b) transformation via two DCEPs and one TCP.

III fluid phase behavior is shown, with only one critical endpoint of the nature $l_1 = g + l_2$. Excluding the occurrence of more complicated phase behavior and a continuation of the lower temperature line of critical endpoints toward absolute zero temperature as well, it is impossible to connect these binary critical endpoints by means of ternary critical endpoint loci. This problem can be solved by assuming that an additional binary critical endpoint of the nature $l_1 = l_2 + g$ will be present at lower temperature on the B axis, which, of course, changes the binary fluid phase behavior on the B axis from type V into type IV. Now the proper connectivity between the binary critical endpoints by means of ternary critical endpoint loci is feasible. Theoretically, the inconsistency in the diagrams shown in both parts a and b of Figure 16, can also be resolved by assuming an additional binary critical endpoint of nature $l_1 = l_2 + g$ on the A axis. In our view, however, this is not very likely since it would have the consequence that the type III system in reality has to be a type V system, of which no examples are known in the literature. On the other hand, a number of cases are known[18,36,37] of which the accepted type V fluid phase behavior turned out to be a type IV system. Therefore, the option that the type V system should be a type IV system seems to be the most realistic one.

In case the type III binary system, for instance, is replaced by a type II system, a similar problem as pointed out above will arise. This is shown in Figure 17, parts a and b. Consistency in the T,x^* diagrams only can be attained again when an additional binary critical endpoint of the nature $l_1 = l_2 + g$ is present on the B axis, whereby the type V fluid phase behavior of this binary system is changed into type IV fluid phase behavior.

The following 1-alkanols were utilized as solutes for this part of the investigation: octanol, heptanol, hexanol, and pentanol. In the Figures 18 and 19 the phase behavior of the systems carbon dioxide + *o*-nitrophenol + octanol and carbon dioxide + *o*-nitrophenol + heptanol is shown, respectively. From these diagrams it becomes apparent that the critical endpoint locus $l_1 = l_2 + g$ tends to turn back to the axis of the type V system. Unfortunately, the critical endpoint loci $l_1 = l_2 + g$ could not be followed to lower temperatures due to precipitation of solid *o*-nitrophenol. However, the experimental results obtained in both cases suggest that most likely a (metastable) low-temperature critical endpoint in the binary sys-

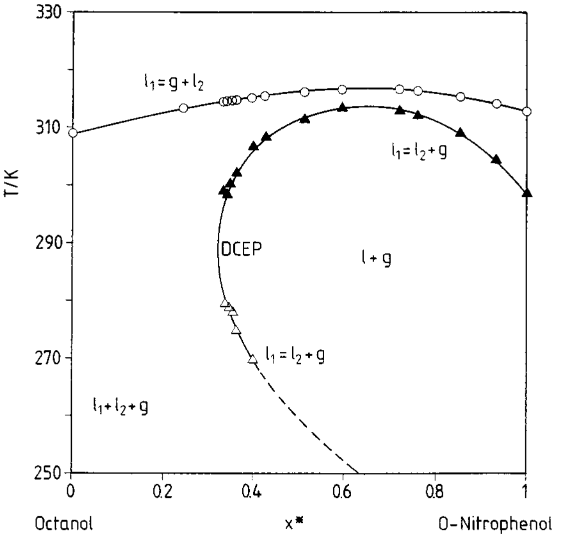

Figure 18. Fluid multiphase behavior in the system carbon dioxide + *o*-nitrophenol + octanol:[33] open dots and open and filled triangles, experimental data; full curves, best fit.

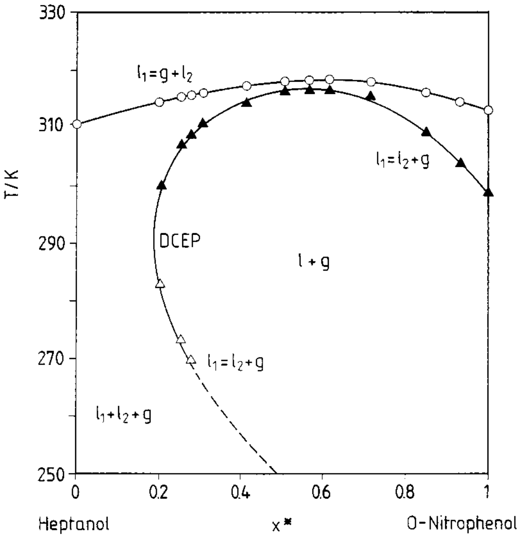

Figure 19. Fluid multiphase behavior in the system carbon dioxide + *o*-nitrophenol + heptanol:[33] open dots and open and filled triangles, experimental data; full curves, best fit.

tem carbon dioxide + *o*-nitrophenol should be present, although hidden by the solid *o*-nitrophenol phase.

According to this argumentation, the following sequence of types of fluid phase behavior holds for both ternary systems:

type III → type IV

Figure 20 shows the experimental results for the ternary system carbon dioxide + *o*-nitrophenol + hexanol. It can be observed that also in this system an additional critical endpoint in the binary system carbon dioxide can solve the inconsistency in the phase diagram. The sequence of types of fluid phase behavior is as follows for this ternary system:

type III → type IV → type II → type IV

Finally, Figure 21 shows the results for the ternary system carbon dioxide + *o*-nitrophenol + pentanol.

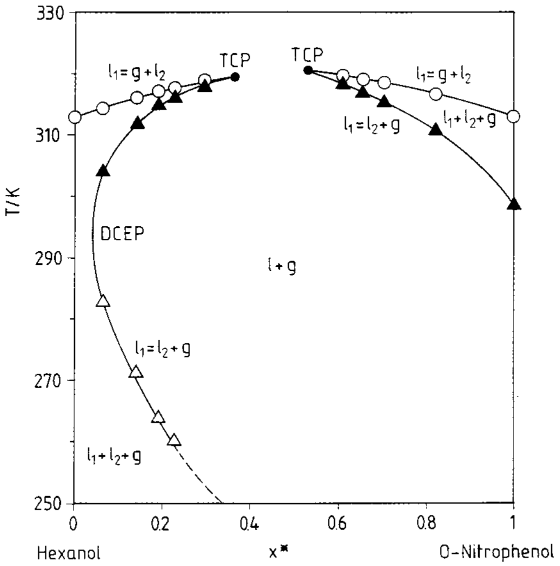

Figure 20. Fluid multiphase behavior in the system carbon dioxide + *o*-nitrophenol + hexanol:[33] open dots and open and filled triangles, experimental data; full curves, best fit.

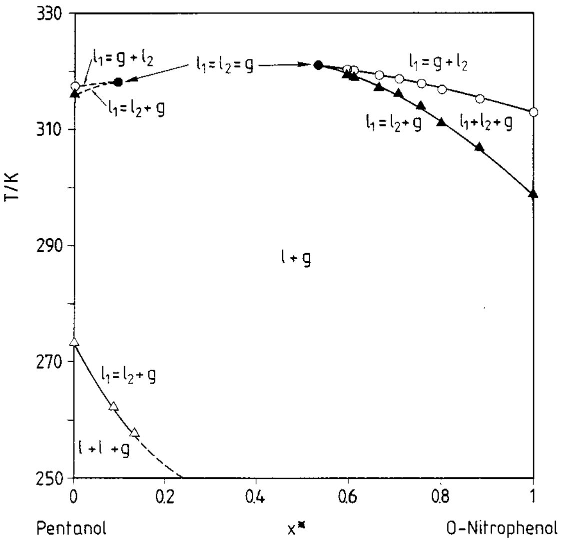

Figure 21. Fluid multiphase behavior in the system carbon dioxide + *o*-nitrophenol + pentanol:[33] open dots and open and filled triangles, experimental data; full curves, best fit.

On the basis of the results discussed above, the results are in agreement with what could be expected. The sequence of types of fluid behavior in this system is as follows:

type IV → type II → type IV

VI. Discussion and Conclusions

In this paper we reviewed the occurrence of holes as one of the complexities in fluid multiphase behavior that may occur in ternary mixtures of near-critical carbon dioxide and two low-volatile solutes (certain combinations of *n*-alkanes, 1-alkanols, and *o*-nitrophenol). It is believed that the selected systems are representative for systems to be met in supercritical fluid applications. From this study it became apparent that in the region of interest for supercritical fluid applications in very narrow concentration windows the nature of the fluid phase behavior sometimes may change several times or, in other words, the number of coexisting phases may change several times from two into three and vice versa. For obvious reasons this makes the design of processes with near-critical carbon dioxide extra complicated since it may be expected that the phenomena discussed in this review are very general and not only limited to the solutes investigated in this study.

From this study it also could be concluded that in the transformation schemes with a type V fluid phase behavior involved a phase theoretical problem may arise. The schematic Figures 16a,b and 17a,b show two possibilities of a transition from type III into type V and from type II into type V fluid phase behavior. In these figures, an extension of the lower-temperature line of critical endpoints to absolute zero temperature and the occurrence of more complicated phase behavior are excluded and, thus, an additional low-temperature critical endpoint of the nature $l_1 = l_2 + g$ has to be present in the original binary type V system, i.e., the phase behavior of this binary system is changed into type IV.

An example for this argumentation has been found in the binary system carbon dioxide + *o*-nitrophenol, formerly reported as a type V system.[35] From the experimental results obtained for the ternary systems with *o*-nitrophenol as one of the two solutes, it can be seen that the ternary critical endpoint locus $l_1 = l_2 + g$ tends to bend back to the axis of the binary carbon dioxide + *o*-nitrophenol system, although complete observation of this behavior is prevented by the precipitation of solid *o*-nitrophenol. Therefore, the binary system carbon dioxide + *o*-nitrophenol is believed to belong to type IV fluid phase behavior, with a lower temperature critical endpoint of the nature $l_1 = l_2 + g$ hidden by the occurrence of a solid *o*-nitrophenol phase.

For obvious reasons, a similar problem in the ternary transformation schemes may arise in case one of the composing binary systems has type I instead of type V fluid phase behavior. In this case the difficulty in the transformation schemes can be removed by replacing the type I system by a type II system. This means that some systems now classified as type I or as type V fluid phase behavior, may have a critical endpoint of the nature $l_1 = l_2 + g$ at low temperature, which can, however, be hidden by the crystallization surface of the less volatile component. Their behavior, thus, may be classified as type II or type IV fluid phase behavior, respectively.

The past few years quite a few new types of fluid phase behavior have been found.[20,21,38-42] In all cases these types were extracted from computational results with equations of state. Experimental evidence only exists for the six systems collected in the classification of Van Konynenburg and Scott[16-18] and so far not for any of the recently proposed types. In terms of the transformation schemes discussed in this review, it easily can be seen how these types may occur. In Figure 22 the transformation sequence from a type II system into a type IV system is shown, and Figure 23 shows the various types of fluid phase behavior that occur in this transformation. In Figure 24 the same transformation is shown schematically. However, the only difference is that both DCEPs have changed location with respect to the concentration axis. In Figure 25 the four types of fluid phase behavior that are involved in this transformation are shown. In this transformation scheme the so-called type VII fluid phase behavior is present, which has even three different three-phase regions l_1l_2g.

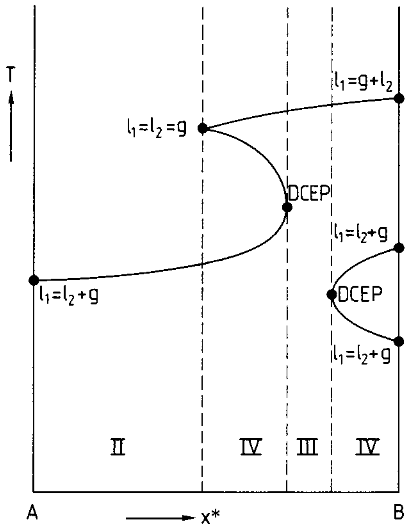

Figure 22. Possible transformation scheme from a type II system into a type IV fluid phase behavior system.

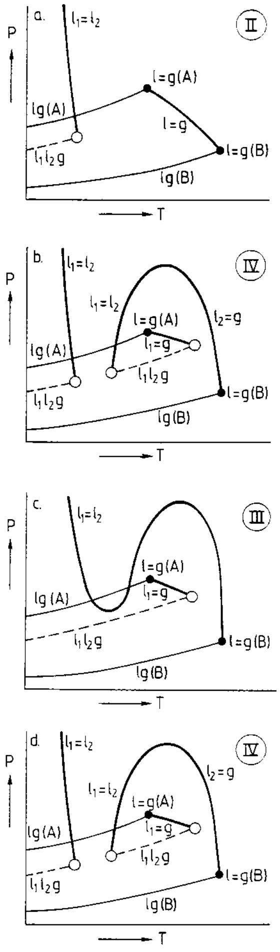

Figure 23. Types of fluid phase behavior occurring during the transformation shown in Figure 22.

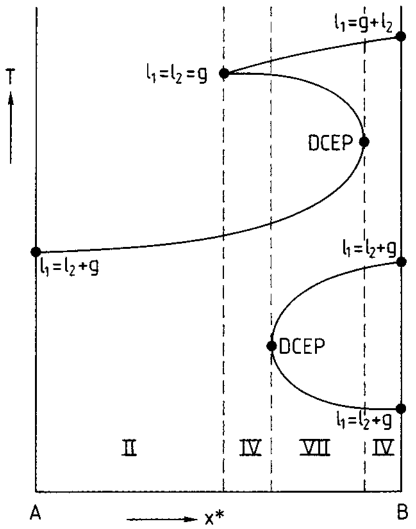

Figure 24. Possible transformation scheme from a type II system into a type IV fluid phase behavior system.

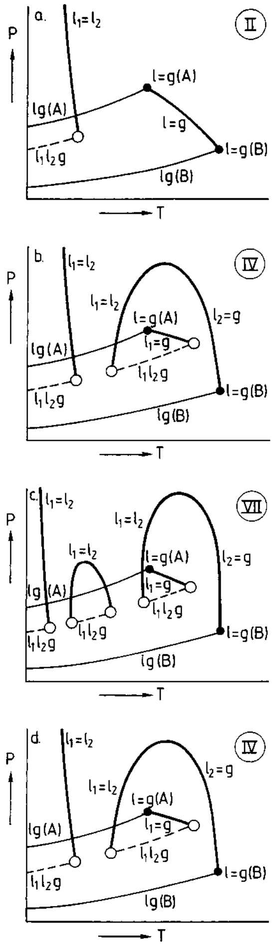

Figure 25. Types of fluid phase behavior occurring during the transformation shown in Figure 24. This figure shows that a type VII fluid phase behavior system may occur.

In summary, the following major conclusions can be drawn from this review:

- Two-phase holes lg in three-phase surfaces l_1l_2g, as observed experimentally in ternary carbon dioxide systems with certain solutes, are a consequence of cosolvency effects.
- The occurrence of holes is a general phenomenon.
- In narrow concentration windows of the two solutes the nature of the phase behavior sometimes may change even more than three times.
- The phenomenon of holes certainly will have consequences for supercritical fluid applications.
- In the transformation schemes with type I or type V fluid phase behavior as one of the two composing binary systems inconsistencies can occur, which can be circumvented by, for instance, replacing a type I by a type II system and a type V by a type IV system in the schemes. To make a general statement about the status of type I and type V fluid phase behavior, further investigations have to be carried out.
- Support for such a statement has been found in the binary system carbon dioxide + *o*-nitrophenol, which is believed to show type IV instead of type V fluid phase behavior.

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