CHAPTER 5.1

Solubility of Solids and Liquids in Supercritical Fluids

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1. INTRODUCTION

The phase behavior of thermodynamic systems formed by solids and/or low-volatile liquids with supercritical fluids (SCF), i.e. fluids at temperatures and pressures exceeding the coordinates of the vapor-liquid critical point, has been receiving renewed and ever increasing interest since the mid-1970. Around that time it has been recognized that supercritical fluids can be useful as solvents in many practical applications, particularly in SCF extraction. At present, the processes involving SCF solvents are used in chemical, food, pharmaceutical, coal, and petroleum industries.

A more specific account of applications could be very long; only a very delimited list of examples may involve the recovery of polar compounds from aqueous solutions (e.g. from biochemical synthesis products), decaffeination of coffee, extraction of hops, spices and tobacco, extraction of flavors and fragrances from natural raw materials, drug separation, fractionation and purification of high boiling mixtures and polymers, extraction of relatively volatile components (e.g. aromas) from coal, oil recovery, upgrading, deasphalting of heavy petroleum fractions, fractionation of petroleum pitch, removal of adsorbed materials from activated carbon, removal of residual oil from spent bleaching clays, impregnation of coal by precursor of catalyst for coal liquefaction, decomposition of metallic salts and alkoxides to form submicron homogeneous oxide powders (ceramic precursors), water oxidation for the destruction of organic carbon-

containing wastes, cavity-free recrystallization of explosives, drying gels and biological specimens, and extraction of mineral deposits.

These and many other applications have been reviewed by Williams (1981), Paulaitis et al. (1983), McHugh (1986), McHugh and Krukonis (1986), Fages et al (1998) Perrut (2000), Chordia et al. (2000), Sarbu et al (2000) and Debenedetti (2000); they have also been subjects of a series of symposia which resulted in collections of papers to which we refer here as [C1] to [C12] collections, see the "References" section.

All applications are based on utilizing the unique properties of fluids at supercritical conditions (intermediate to those of liquids and gases), whose first observations date back to more than a century ago. The most remarkable among them is the solvent power, which is directly related to the SCF solvent density. The other favorable properties of the SCF solvents include the excellent mass transfer characteristics, related to high diffusion coefficients and low (nearly gas-like) viscosities. The variations of density with small changes in temperature and/or pressure can be readily seen from the supercritical region (delimited, say, by reduced pressures, $P_r = P/P_c$, from the range 1.0 to 1.5 and by reduced temperatures, $T_r = T/T_c$, from the range 1.0 to 1.2) of the pure fluid pressure vs. density phase diagram. It is then easily inferred that the SCF density and density-related properties (such as the solvent power) can be varied continuously from the typical liquid-like densities (where the fluid may be a very good solvent) to low gas-like densities (where it is a poor solvent) only by slight changes in temperature and/or pressure. Hence, the extent to which solids and liquids can dissolve in dense gases varies enormously. On one hand, the solubility enhancement of a solid or a liquid in dense gas can represent several orders of magnitude compared to the solubility predicted by the ideal gas law; on the other hand, the solubility may be so small that it is barely detectable.

To be more precise, in the mixture systems encountered in applications it is the critical region close either to the lower critical end-point or to the upper critical end-point in the mixture phase diagram where the above mentioned pressure and/or temperature control of the SCF solvent power applies. In fact, the advantages of modifying the solvent capacities through changes in system temperature and/or pressure may be utilized just in the systems where the mentioned critical phenomena occur. The highly asymmetric binary mixtures where the triple point temperature of the low-volatile (normally solid) component is significantly greater than the vapor-liquid critical point of the more volatile component (solvent) and in which the three-phase solid-liquid-vapor line (in pressure vs. temperature projection) interferes with the binary vapor-liquid critical locus represent such a type of system. In this case the three-phase line is shifted to higher

pressures and interrupts the vapor-liquid critical curve by intersecting it twice at two critical end-points. Similarly, the binary fluid systems, in which the liquid-liquid-vapor three-phase line interferes with the vapor-liquid critical locus giving rise to the occurrence of a critical end-point, are relevant for SCF solvent-based processes. For phenomenological analysis and well conceived phase diagrams of the binary and multicomponent systems of interest to applications involving SCF solvents we have to refer the reader e.g. to the reviews by Koningsveld et al. (1984), McHugh (1986), McHugh and Krukonis (1986), and Schneider (1991,1992).

The common requirements, which an SCF solvent is expected to fulfill, include high purity, chemical stability, inertness with respect to the extracted solute(s), low boiling point ensuring ease of separation of the extractant from the product(s) and solvent regeneration, non toxicity, and low price. From this viewpoint, carbon dioxide is almost an ideal SCF solvent since it is environmentally fully acceptable and nonflammable. In addition it also has a conveniently low critical temperature, thus enabling the treatment of heat-sensitive species at near ambient conditions, with a minimum danger of thermal degradation. This is why the overwhelming majority of applications and systems studied so far deals with carbon dioxide as the SCF solvent.

In a broader sense, however, fluids at supercritical conditions are also involved in high pressure systems which occur during the storage and transportation of fluids, in chemical processes conducted at high pressures, in enhanced oil recovery, geothermal processes and many other applications.

All the processes involving SCF solvents require understanding and detailed knowledge of the high-pressure phase behavior of the mixtures of interest, in particular of the solubilities of the low-volatile liquid and solid components in the dense SCF. At the same time, a high degree of data accuracy is required to optimize the processes where, among others, often the conditions have to be tuned so as to find a reasonable compromise between the yield and the selectivity of the process. However, the high-pressure fluid phase data are very difficult to predict since the practical systems are often highly complex in the sense that numerous constituents are present which differ significantly in molecular size, shape, structure, and polarity, giving rise to a great variety of phase behavior combined with critical phenomena.

These facts suggest the global need for accurate high-pressure fluid phase equilibria and solubility data to be measured. A more detailed discussion on relevant aspects and motivations is given in the introductory paragraph of the section on "Experimental determinations".

The experimental methods and the sources of data reported in this chapter will be centered on solubilities of solids and liquids in supercritical fluids. A more complete treatment of the phase behavior of binary and multicomponent fluid mixtures at high pressures is beyond the scope of this chapter and can be found in several books (e.g. Rowlinson and Swinton, 1982; Kreglewski, 1984; Prausnitz et al., 1998; Sadus, 1992). Nevertheless, even the recent literature dealing just with the investigations of the SCF solvent-containing systems, particularly those useful for SCF extraction, is really vast. To save some space, we therefore list in the "References" section several collections of papers and then refer to the single papers contained therein by the numbers of collections, namely [C1] to [C12].

2. BASIC EQUATIONS AND NOMENCLATURE

A very brief review of the basic equations defining the solubility in dense gases is given here, with the main objective to introduce the nomenclature hereafter adopted. The section is divided in two parts, according to the type of phase equilibrium system. Throughout the discussion, subscript 1 stands for the lighter component, i.e. the supercritical fluid (SCF) solvent, and subscript 2 stands for the heavier component, i.e. the solute (a solid or a low-volatile liquid).

2.1. Solubility of solids in supercritical fluids

For component 2, the isofugacity criterion (Prausnitz et al., 1998) for the equilibrium calculation has the following form:

$$f_2^S = f_2^V \tag{1}$$

where superscript S stands for the solid phase. Because the solid phase is considered a pure phase, the fugacity of component 2 may be written as:

$$f_2^S = P_2^S \varphi_2^S \exp\left(\int_{P_2^S}^{P} \frac{v_2^S}{RT} dP\right) \tag{2}$$

where P_2^S is the saturation vapor pressure of the pure solid, ϕ_2^S is the fugacity coefficient at saturation pressure and v_2^S is the solid molar volume, all at the system temperature T. Recalling the definition of fugacity coefficient ($\phi = f/yP$) and fugacity of the vapor phase, we obtain:

$$y_2 = \frac{P_2^S}{P}\left[\frac{\varphi_2^S \exp\left(\int_{P_2^S}^{P} \frac{v_2^S dP}{RT}\right)}{\varphi_2}\right]$$
(3)

The quantity in square brackets, defined as the "enhancement factor" is always greater than unity and represents the correction factor which must be applied to the ideal gas expression (valid only at very low pressure), to obtain the true value of the solubility in a real system. A detailed description of the enhancement factor as a function of pressure and temperature is given elsewhere (Prausnitz et al., 1998). Suffice to mention here that the most important term in eq. 3 is the ϕ_2 which can be very far from one and thus responsible for the enhancement factor values as high as 10^3 or even higher. Equation 3 defines the solubility of a solid phase in a supercritical fluid, and may be used for correlating, extrapolating and predicting the solubilities. The way to proceed is to select an equation of state and calculate all the quantities that appear in eq. 3. To do that one needs binary interaction parameters for calculating the mixture fugacity coefficient. Usually, these must be obtained by fitting to the experimental solubility data.

2.2. Solubility of liquids in supercritical fluids

The problem of the solubility of a liquid in a supercritical fluid is somewhat more complicated than the previous case because the gases are soluble in liquids, whereas the solubility of gases in solids is usually negligible. For the sake of simplicity, in this discussion we consider only the case of the solubility of the less-volatile (heavy) liquid component in the gas phase which contains the light component in excess. For the heavy component one can write the equilibrium equation:

$$f_2^L = f_2^V = \varphi_2 y_2 P$$
(4)

where subscripts L and V stand for the liquid and fluid phase, respectively. If the gas is only sparingly soluble, the liquid phase fugacity of component 2 can be calculated assuming a pressure corrected form of the Henry's law:

$$f_1^L = H_{1,2} x_1 \exp\left(\int_{P_2^S}^{P} \frac{v_1^\infty dP}{RT}\right)$$
(5)

In the above equation $H_{1,2}$ is the Henry's constant, v_i^∞ is the partial molar volume of component 1 in the liquid phase at infinite dilution and P_2^s is the saturation pressure of pure liquid component 2, all at system temperature T. Then, from the Gibbs-Duhem

equation, one can calculate the fugacity of the component 2 in the liquid and substitute it in eq. 4 so that, solving for the solubility we obtain:

$$y_2 = \frac{(1-x_1)P_2^S \varphi_2^S \exp\left(\int_{P_2^S}^{P} \frac{v_2^L dP}{RT}\right)}{\varphi_2 P} \tag{6}$$

Since x_1 φ_1 and φ_2 are functions of the vapor composition, an iterative method must be used to reach the solution. As pointed out in the previous paragraph, if an accurate description of the fugacity coefficient as a function of composition and state variables is available, the calculation of the solubility is straightforward. For more details on the calculation of solubilities by means of equations of state see e.g. the monographs by Prausnitz et al. (1998), McHugh and Krukonis (1986), and Sadus (1992).

3. EXPERIMENTAL DETERMINATION OF SOLUBILITIES IN DENSE GASES

3.1. Some general aspects and motivations

The definitions and equations given in the preceding section represent the exact classical-thermodynamic relationships relating the solubilities of solids and liquids in an SCF solvent phase to thermodynamic intensive and extensive properties in terms of fugacity coefficients. These equations form the basis for the methods of regression and prediction of solubility data and for the description of the temperature and pressure effects on the solubility. As a matter of fact, the understanding and the possibility of at least rough prediction of the temperature and pressure effects is of crucial importance even for the experimentalists.
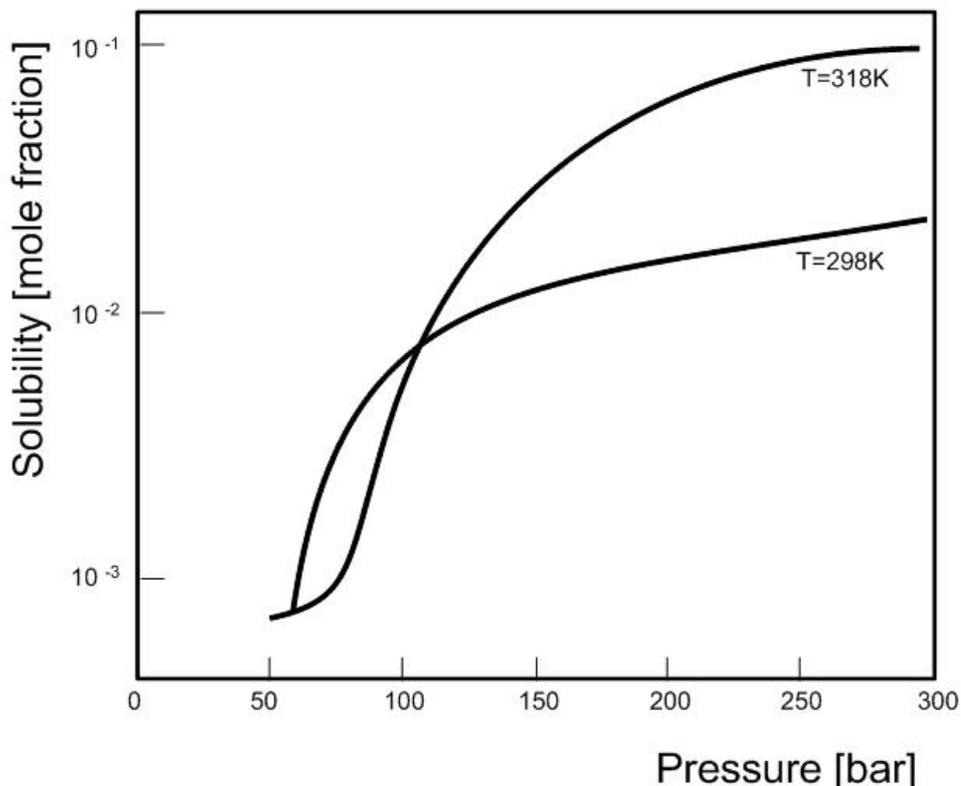
Figure 1. Solubility of naphthalene in dense ethylene as a function of pressure at two different temperatures: the solubility enhancement in the vicinity of the critical point as well as the cross-over effect is evident.

Figure 1 shows a typical trend of the solubility as a function of pressure along an isotherm: a very strong variation of the solubility with pressure is detected in the vicinity of the mixture critical end-point, whereas the variation with pressure is much smaller at higher pressures. A comparison of the behavior of two isotherms gives an idea of the state of the system examined kind of problems that one is facing: it can be seen that at relatively low pressure the solubility falls off by an order of magnitude for rising temperature, whereas at higher pressures it increases with increasing temperature. Already this simplest example of a binary system illustrates the sensitivity of the solubility to small changes in temperature and pressure as well as the additional complexity, manifested by the crossover of curves, which is a result of mutual competition of the solvent density and solute vapor pressure effects in combination. In order to obtain a representative sample of the mixture under investigation, this particular behavior must be accounted for, whenever relevant, in the experimental methods in which the pressure and/or temperature variations may occur during equilibration or during sampling. Particular care has to be exercised in the close vicinity

of the critical points, where even the small perturbations due to fluctuations (caused e.g. by pumping or pressure control) may lead to dramatic changes in the state of the system examined.

There are some related additional pitfalls encountered during the solubility studies of low-volatile solutes, common to several types of methods, in which the equilibrium high-pressure SCF solvent-rich phase saturated with solute(s) is expanded from the experimental pressure to ambient pressure, as required to facilitate the chemical or gravimetric analysis downstream of an equilibrium cell or saturator. In the retrograde region there is a solubility minimum at intermediate pressures for a given temperature. Since the isothermal expansion performed across a metering valve usually results in decreasing the equilibrium solubility, the solute(s) may precipitate. Therefore, it is necessary to heat the expansion valve and the downstream low-pressure tubing to a temperature for which the solubility minimum is greater than the measured solubility in the equilibrium cell. At the same time it is necessary to assure that, during the isobaric temperature increase between the equilibrium cell and the expansion valve, the solubility of the solute in the solvent increases monotonically. Otherwise, solute re-deposition at some intermediate location can falsify the experimental results because the measured solubility will be assigned erroneously to the temperature of that intermediate location.

These two problems encountered in the retrograde region dictate upper limits for the experimentally accessible ranges of temperature and pressure for a given system. For the simplest case, occurring already in binary systems, they document the usefulness of some a priori knowledge on a studied system for the experimenter on one hand, and the necessity to exercise care and carry out independent testing of various parts of an experimental assembly on the other hand. The possibility of formation of additional phases in various parts of an experimental set-up should be borne in mind, especially when treating multicomponent systems. Of course, there is no a posteriori consistency test available for the fluid phase equilibrium data at high pressures.

Moreover, the binary data are clearly of primary importance, but hardly sufficient for practical purposes, where at least three components are always present: in the separation of mixtures, there is a (at least) binary mixture to be separated plus the SCF solvent; in the extraction of substances from any natural matrix or reaction mixture, the number of species is usually much higher. Hence, besides the fundamental binary data, there are several types of (at least) ternary systems of great interest, namely (i) systems, in which the effect of a mixed SCF solvent on the extraction of a low-volatile solute is studied, (ii) systems, where an increase of the solubility of a low-volatile solute in an SCF

solvent is studied in dependence on the addition of an entrainer (co-solvent, modifier), and (iii) systems, where the extractive effect of an SCF solvent on the separation of two low-volatile components is studied.

Apart from carbon dioxide, the frequently used and investigated SCF solvents are nitrous oxide, ethane, ethylene, propane, butane, mono-chloro-difluoro-methane, dichloro-difluoro-methane, and water. The common co- solvents, employed mainly for systems with solutes of a certain degree of polarity, include methanol, ethanol, cyclic ethers, dichloro- and trichloro-methane, water, dimethyl sulfoxide, formic acid, and other substances.

The fact that many solute partial molar quantities diverge at the critical point of the pure solvent and that, even relatively far from the critical point (or from the critical end-point), the properties of the system are very sensitive to changes in pressure and temperature imply serious difficulties in the description, and particularly in the prediction, of thermodynamic properties in such regions of phase diagrams, even for binary systems.

As already mentioned, the calculation of solubilities in supercritical fluids is not a problem of classical thermodynamics. The above given relations expressing the solubility in terms of macroscopic properties are exact and may be solved by simple implementation in computer programs. The difficulty lies in the inability to accurately predict the configurational properties of pure fluids and their mixtures, i.e. in the prevailing absence of accurate mathematical models (equations of state) expressing the fugacity coefficients over the ranges of interest as a function of temperature, pressure (or density) and composition on the basis of available molecular parameters. This inability is a consequence of still insufficient molecular thermodynamic theory and also of insufficient knowledge of the intermolecular forces.

Thus at present only in a limited number of cases is it possible to reduce the required amount of experimental work on SCF solvent - low-volatile solute(s) systems by modeling the resultant phase behavior. The contemporary equations of state models allow rather interpolation between data, whereas reasonable extrapolation is restricted only to narrow ranges of conditions. Also, the phase behavior of multicomponent systems can hardly be computed on the basis of binary data only.

The outlined problems lead to the conclusion that there are two basic items of motivation to measure the solubilities of solids and liquids in SCF solvents. The first is to measure the data of direct use for systems of such degree of complexity that any prediction is difficult or impossible; this is usually the case of systems of interest for practical applications, especially when ill defined mixtures of natural origin or reaction

mixtures are involved. The second is that there is a great need for accurate experimental data on equilibrium properties of well defined (i.e. model) dense fluid mixtures involving different types of molecular interactions, since these data are prerequisite to developing and verifying the new theoretically based, accurate, and possibly predictive thermodynamic models.

3.2. Previous reviews

As it follows from the definition of the solubility of low-volatile substances in dense gases given in the preceding section, the measurement of the solubility of solids and nonvolatile liquids in supercritical fluids corresponds to the problem of determining the composition of a dense fluid phase saturated or equilibrated with a solid or with another fluid (liquid) phase at a given (high) pressure and temperature. The latter problem can be considered as a special case of determining the high-pressure fluid phase (or vapor-liquid) equilibrium in systems with components of very different volatility. (However, this does not necessarily mean that the densities of the coexisting phases differ very much. In fact, even the phenomenon of the inversion of densities may be observed in systems with dense SCF-containing phases.) Hence most of the techniques used for high pressure vapor-liquid equilibrium measurements are applicable for determining the solubility of liquids (and sometimes of solids) in supercritical fluids as well. That is why some of the more general reviews dealing with the experimental determinations of fluid phase equilibria are considered here.

Notably, in the monograph summarizing in comprehensive manner that-time knowledge on vapor-liquid equilibrium measurement and computation (Hala et al., 1967), a very little space has been devoted to equilibria at high pressures and focus was largely on methods suited to the normal pressure range. Aim and Hala (1990) updated such review of experimental techniques for determining the vapor-liquid equilibria at normal and slightly elevated pressures.

Regarding the high-pressure equilibria, i.e. studies at pressures approaching reaching or exceeding the critical pressure of at least one of the system components, Schneider (1975) and Young (1978) presented quite exhaustive accounts of experimental techniques with emphasis given to various constructions of static cells, including optical cells as well. Eubank et al. (1980) continued the effort, with special attention being paid to the developments at the Texas A&M University.

Deiters and Schneider (1986) also surveyed the experimental devices designed for high-pressure phase equilibrium studies, with particular emphasis on the static cells developed and employed at the Bochum University.

In the monograph by McHugh and Krukonis (1986), a chapter was devoted to experimental techniques used in high-pressure studies, including the methods for measuring the solubilities in supercritical fluids. The chapter is, however, of a very limited extent, concentrating practically just on the work done by the authors.

Fornari et al. (1990) listed the high-pressure fluid phase equilibrium investigations found in the literature over the years 1978-1987, along with a brief classification and description of the principles of the experimental methods employed.

Alessi and Cortesi (1990) reviewed the measurements of solubilities in dense gases, describing in more (or less) detail some of the experimental techniques.

Rainwater (1991) listed 129 critically selected sets of experimentally determined high pressure binary vapor-liquid equilibrium data searched in the literature through 1989.

Finally, Dohrn and Brunner (1995) report a survey of methods and systems investigated form 1988 up to 1993. Richon (1995 and 1996) published two review papers containing new experimental development of old methods specifically concerning fluids at supercritical conditions.

We mention that in most of the above cited surveys various attempts were made to classify the experimental methods. Often the main dividing line was drawn between the so called analytic and synthetic methods (see the section "Static methods" below). On one hand this categorization is rather limited (to static methods), on the other hand nowadays the devices making it possible to use both these options are not exceptions. Therefore we do not stick to this pattern, but rather adopt another classification (as specified in the next section), distinguishing also between some of the dynamic methods.

As a matter of fact, to our knowledge a commensurate review devoted explicitly and systematically to the experimental methods for determining the solubility of solids and liquids in supercritical fluids, involving a reasonable classification of the methods has not yet been presented.

3.3. Types of methods and scope

For the purpose of the present review we recognize the following categories of experimental techniques:

❒ static methods,

❒ dynamic methods, namely

    ☐ recirculation methods,

    ☐ flow methods,

    ☐ saturation (or transpiration) methods,

❒ dew and bubble point methods,

❏ SCF chromatographic methods.

The dynamic methods are all characterized by the fact that at least one of the phases occurring in the system is subject to a translatory flow with respect to the other(s). Clearly, the above listed three distinct classes of the dynamic methods can be recognized, based on the mode in which the contact between the equilibrated phases is established.

Nevertheless, this classification is still largely arbitrary and the distinctions between some of the recognized types are necessarily blurred at the edges; e.g. the recirculation and also the dew and bubble point cells can be viewed as extensions of the static cells and the like. In each section describing a type of experimental method, an attempt to try first to justify the adopted nomenclature (whenever needed) and then to explain briefly the underlying principles is made. Then an account of the general characteristics of the method is presented, including its main features, range of applicability, advantages, limitations, and pitfalls. Finally (in the "Examples" sections) focus is made on surveying selected papers (representing work that in some way contributed to the development of the methodology of experimental measurements) and describing the main innovations and particular features of some of the respective equipments developed.

The volume of work done in the field and reported in the literature is immense and within the allocated space it is not possible to present an exhaustive account of experiments. This is why for details on the experimental methods, treated here necessarily to a very limited extent, the reader is referred to the original documents. Further, in the reference section on a given method, a selection of some recent studies employing the method in question is presented: in the listed papers further details maybe looked up.

The reader should bear in mind, however, that in fact hardly ever is the description of an experimental set-up and procedure presented in a form making it possible to reproduce the measurements without any problem. Often a long-term painstaking effort maybe hidden behind a very simple statement describing a single step in an experimental procedure, or some important details maybe omitted, be it on purpose or not. Generally the experimental work on high pressure fluid phase equilibria is not a simple task; some skill, experience, and even a good deal of sophistication are needed. Particular modifications of experimental equipment, required in dependence on a type of system to be studied are by no means exceptions.

From what has been stated above it appears that this chapter does not provide a "cook book" on the determinations of the solubilities in SCF's. Neither is dealing explicitly with the instrumentation for the temperature and pressure measurement and control and

with the many analytical methods employed to determine the composition of the resulting single phases of dense fluids, saturated with nonvolatile liquid or solid solutes. The choice of a particular analytical method is strongly system-dependent and as such it is outside the scope of the present contribution. The main focus here is basically the methods making it possible to prepare, identify and isolate such dense-fluid equilibrium phases and, if need be, to transport them in a reproducible and dependable way, just to make them ready for analysis (usually by gas chromatography upon de pressurization) or for another direct (like spectrophotometry, continuous densitometry, refractometry, UV monitoring) or indirect (like isolating, collecting and weighing) methods of determining their composition.

Some general requirements on experimental methods can certainly be formulated. These may include: minimum consumption of investigated species, minimum equilibration time as well as minimum overall time needed for experiments, direct temperature and pressure determination, visual observation of the system, readiness of analysis, convenience, low-cost equipment etc. Clearly, none of the methods considered further in the text meets them all, but each represents a sort of compromise.

4. STATIC METHODS

4.1. Principles and characteristics

The principle of the static method is conceptually very simple (see Figure 2). The mixture to be investigated is loaded into an evacuated cell which is placed in a constant temperature environment, such as a liquid or air bath or a metal block thermostat. The contents of the cell, i.e. the segregated phases of different density, are brought to equilibrium by agitation, shaking or stirring and the equilibrium pressure is measured. (The cells where equilibration is facilitated by circulating streams of one or two phases in external loops are considered separately in the next section.).
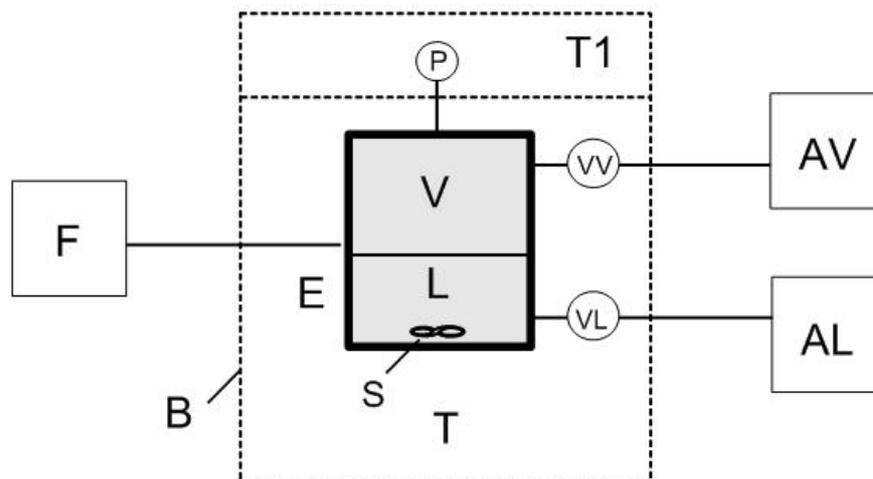
Figure 2. Schematic diagram of a typical static method for the determination of fluid phase equilibria (illustrated for vapor-liquid equilibrium): AL, batch analysis of the liquid phase; AV, batch analysis of the vapor phase, B, boundary of thermostated compartments; E, equilibrium cell; F, batch feed of degassed components (or a mixture); L, liquid phase; P, pressure meter; S, stirring facility; T, temperature of the cell; T1, temperature of the pressure sensor (greater than or equal to T); V, vapor phase; VL, VV, sampling valves.

The main characteristic, distinguishing the methods of this class from the dynamic methods, is that once loaded, the charge remains enclosed in the cell and no phase (or a part of the system) undergoes a mechanically driven translatory flow with respect to the others.

In the static technique, the determination of composition of the equilibrium phases can generally be accomplished in one of the following two ways:

(A) In the so called "synthetic" methods, known amounts of pure substances are charged into the cell, so that the overall composition of the mixture contained in the cell is known from the start of the measurements. The compositions of the coexistent equilibrium phases may then be recalculated by an iterative procedure from the known overall composition and equilibrium temperature and pressure data, provided that at the system state conditions the pressure-volume-temperature behavior as a function of composition is known to a sufficient accuracy (in the form of a mathematical model) for all the phases present in the system.

This condition is in most cases satisfied at low and normal pressures, where the amounts of constituents present in the light (gaseous or vapor) phase are so small that the appropriate corrections can be evaluated by using the rough state behavior (as a function of composition) predictions yielded by the virial or any other simple equation of state reasonably describing the low- density vapor phase; at the same time the

pressure effects on the behavior of the liquid phase may be simply approximated or even neglected. These (along with the difficulties connected with taking representative samples of the light phase without disturbing the equilibrium state) are the reasons why the so called total pressure static method is a useful and widely used tool for studying the vapor/gas - liquid equilibria at pressures not remote from the normal state conditions.

When dealing with systems at high pressures, however, the condition of having an accurate P-V-T-composition prediction method at hand is satisfied only scarcely, in practice just for the simplest (from the molecular point of view) systems. This means that some additional experimentally determined information is required. A possibility here is to locate a phase transition state, i.e. to determine the bubble or dew point in the vapor-liquid systems and their analogs in the solid-fluid systems (either optically or by studying the pressure-volume relations) using a cell of variable volume. In this approach a pressure value is found at which the composition of one of the present phases identifies with the known total composition at a given temperature. For determining the composition of only one of the coexistent phases (such as the solubility of a low volatile solute in a SCF) in binary systems this method is completely sufficient and no analysis is needed. Another possibility is to determine also the volumes of the coexistent phases in a visual, volume-calibrated cell and to calculate the equilibrium phase composition(s) by employing the mass balance.

(B) For some of the reasons outlined above, the so called "analytic" methods, in which the samples of one or both (or more) equilibrium phases formed in the system may be withdrawn and analyzed, are employed in the high pressure investigations much more frequently. In this case the initial overall composition of the mixture charged into the cell needs to be known only to the extent corresponding to the requirement of pre-determining the location of the measured equilibrium data point in the phase diagram. The approach is facilitated by the fact that, at the densities of phases encountered at high pressures, sufficiently representative samples of one or more phases may usually be taken without excessive risk of disturbing the equilibrium state. If for a given system the sampling can be achieved in a tractable and reproducible way, this method represents a well suited and relatively inexpensive means to acquire very accurate phase equilibrium and solubility data.

From what has been stated above, it is obvious that in the apparatus of "synthetic" type the main difficulty arises from the preparation of a mixture of known composition in the cell. At the same time, the way in which this step is accomplished represents one of the

characteristic features that may be used to distinguish between different equipments of the "synthetic" type.

On the other hand, the major difficulty of the "analytic" method still resides with the withdrawal of the samples of equilibrium phase(s) from the cell without disturbing the system equilibrium and with their transport to analytical devices (usually accompanied by de pressurization) while avoiding any changes in their homogeneity and composition. Particularly, in the case of direct sampling at elevated pressures, the preferential sampling of the more volatile constituents of the mixture has to be avoided. The sampling of phases that are near criticality is also difficult because large disturbances to equilibrium can occur during the sample withdrawal. Hence in this case it is the technique of sampling in which different experimentalist exhibit their inventive potentials in various ways.

It should be noted that in the static method one is always dealing with the closed system. This brings the requirement that prior to charging the apparatus with the examined mixture the cell and tubing must be carefully evacuated and the materials themselves must be thoroughly degassed to avoid errors in the readings of equilibrium pressure. Also during any transport the degassed substances have to be protected from being contaminated by hardly condensable gases (air). Even though at lower pressures the degassing is a crucial problem, in the high pressure studies the results are not extremely sensitive to the presence of traces of gases and thus the requirement is not so strict as to give rise to serious difficulties.

The static methods employ equilibrium cells of constant or variable volume; in the latter case the pressure may be continuously adjusted and controlled (at a fixed composition and temperature) by a movable piston, adding flexibility to the operation at the cost of a more complicated construction. As already mentioned, this facility may be used to detect the bubble and/or dew point pressures and also to locate the critical points. If the cell internal volume and its changes due to piston displacements are known, in addition the densities of phases can be determined as well.

Even if the static methods can in principle be applied to systems consisting of (dense) gases with liquids and solids, the difficulties connected with handling the systems containing a solid phase (particularly the longer equilibration times) restrict their practical applicability rather to systems consisting of fluid phases. Concerning the equilibration times in fluid systems, it should be pointed out that, unless an extremely viscous phase is involved, the period of time required to produce phases of equilibrium compositions need not be very long provided that the system under study has been properly degassed and that an adequate phase contacting and stirring is in effect. As a

matter of fact, the time period required bringing the cell to the desired uniform temperature as well as the time needed for disengagement and settling of phases (especially if they do not differ in density very much) is often comparable or even longer than the equilibration itself.

An obvious advantage of view cells is that any possible phase transitions and phase inversions may be immediately detected visually and hence the important solid-liquid-vapor and liquid-liquid-vapor phase boarder curves as well as critical loci may be determined. If more than two phases are present in a system under investigation, the visibility of the cell content is a must; in the analytical method, also the number and geometry of the sampling ports have to be appropriately arranged.

Regarding the complexity of systems, the number of components in the mixture under investigation is clearly limited by the capabilities of the analytical methods employed. In the synthetic approach, the facilities for detecting the phase transitions and phase volumes have to be modified according to the number of thermodynamic degrees of freedom of a given system. If it is possible to determine the volumes of all the equilibrium phases present in the cell, the general version of the stoichiometric method provides the means for determining the compositions of all the phases from repeated measurements at a given temperature, pressure and overall composition. (More details are given in the next paragraph.).

A general advantage of the static methods is that small amounts of substances are needed for the measurements.

4.2. Examples

A simple static apparatus adapted for determining the solubility of solids in SCF solvents has been developed by Diepen and Scheffer (1953). The assembly consists of two cells, an equilibrium cell and a sampling cell. The solid solute (naphthalene) is placed in a thermostated equilibrium autoclave, which is then pressurized by the SCF solvent (ethylene) to a desired pressure. During the dissolving of the solute, additional solvent is fed to the cell to maintain the pressure level (to compensate for the pressure loss due to dissolving). After the saturation of the fluid phase is completed (the pressure does not change), the connecting line and the sampling cell are slowly flushed and filled with the equilibrium fluid phase, being pushed (at constant temperature and pressure) out of the equilibrium cell by fresh ethylene. A representative sample of the saturated SCF phase is then available in the sampling cell for further analysis; in the system examined, the components were easily separated which facilitated the use of gravimetry.

An experimental assembly working on the same principle has been described by Dandge et al. (1985). The equilibrium cell is a vertically oriented sapphire tube containing a Teflon-covered magnetic stirring bar. After evacuation and purging with the solvent, the cell is loaded with a solute sample and compressed SCF solvent. The system is brought to equilibrium and a known amount of the saturated SCF solution is transferred to an assay chamber. The transfer of the SCF-rich phase is accomplished by its displacement with fresh pure solvent. The assay chamber consists of a test tube of 100-mesh glass beads enclosed in a separate pressure chamber of special design. On de pressurizing the chamber, the solvent leaves and the nonvolatile solute precipitated onto the beads in the test tube is weighed.

The same method, using a large (2.5 L in volume) equilibrium autoclave has been used by Raghuram Rao et al. (1992) for studying the co solvent effects in the SCF carbon dioxide extraction of fragrances from jasmine flowers.

Even simpler equipment has been employed for investigating the solubilities of nonvolatile solutes in SCF solvents by Chrastil (1982). A small amount of a solid or liquid is placed on the bottom of vertical tubing and pressurized by the solvent. The SCF-rich phase is stirred magnetically for about 3 hr to reach the saturation state. A high-pressure pipette is connected to the upper part of the tubing. After the state of saturation is achieved, a portion of the dense fluid phase is trapped in the pipette. The pipette is then disconnected and the sample analyzed.

Similar in concept is also the static apparatus designed by Yonker and Smith (1985) to study the solubility of caffeine and theophylline in SCF ammonia. A cylindrical cell is loaded with solute and pressurized with the SCF, with conditions determined by the bath temperature and pressure of the syringe pump. The system is equilibrated for 30 min., during which time the sample is stirred by rotating the cell and allowing two ball bearings to travel from one end of the equilibrium cell to the other end. After the saturation is completed, a system of valves is adjusted so that for a short period (roughly 10 s) the SCF solution is allowed to flow through a sample loop. This is sufficient for flushing and filling the sample loop with a representative sample of the saturated SCF.

As already stated in the preceding section, the static cells are most often used for systems where all phases in the system at experimental conditions are fluids, so that the heavier phase can be stirred; the stirring and hence the equilibration is most efficient when the phase interface is disturbed during the stirring. A particular case from this standpoint represents the variable- volume cells, in which the entire amount of solute (which may be also a solid) is dissolved at some stage of the experiment. A few examples of this kind follow.

McHugh et al. (1984) studied the solubility of solids in SCF in a static view cell with the pressure of the system being isothermally adjusted at a fixed overall composition by varying the mixture volume. A movable piston is driven by a syringe-type pressure generator using silicone oil as a hydraulic liquid. The mixture contained in the cylindrical (horizontally placed) cell is viewed through a quartz window that is secured by the cell end cap with a view slit. The solute is alternately solubilized by slow compression and precipitated by slow decompression and the pressure values corresponding to the solid phase disappearance and appearance, respectively, are recorded. This is repeated a number of times to decrease the transition pressure interval to the accuracy of approximately ± 1 per cent of the absolute pressure. The solubility is known from the measured amounts of SCF and solid loaded into the cell. The procedure is repeated for another temperature etc. A series of pressure - temperature points at a constant overall composition (an isopleth), equal in this case to the composition of the solute-saturated SCF phase, is thus obtained in the synthetic mode.

A very similar cell (applicable to 700 bar and 535 K) and analogous procedure have been used by Occhiogrosso et al. (1986) and by Suppes and McHugh (1989) to study the vapor-liquid equilibria in systems of carbon dioxide with aromatic solutes. Again by alternately changing the pressure and detecting the appearance/disappearance of the fog (or of the first newly formed bubble), the dew point pressure (or the bubble pressure) is determined at a given temperature and total composition. An advantage of this procedure is that, also the mixtures at conditions close to the mixture critical point as well as the mixture critical point itself can be investigated.

Basically the same experimental method was employed by Warzinski et al. (1992) to determine the solubility of molybdenum hexacarbonyl in SCF carbon dioxide. The internal piston permits the volume of the equilibrium cell to be varied from 10 to 40 ml. In the stage of the experiment in which all the solute is dissolved in the SCF, the repeated movement of the piston is applied to promote the mixing of the bulk cell contents also with the material contained in the space extending to the diaphragm seal of the pressure transducer.

In the following, a brief account of static cells primarily designed for studying the fluid phase equilibria is presented.

Dingrani and Thodos (1978) described a robust cell fabricated from a stainless steel bar, drilled and machined to incorporate within it the equilibrium chamber and mercury driven pressurizing piston assembly. The liquid level in the cell is visible through a vertical slit in a hold-down bar, holding fixed a flat Herculite glass, oval in shape. The cell operates at pressures to 7.6 MPa. Two valves provided with non-rotating stems are

used for trapping (and then releasing) the micro samples (about 0.05 ml) of the vapor and liquid phases. Gomez-Nieto and Thodos (1978a, 1978b) adapted the cell to work at higher compression ratios. Due to large cell mass, about 8 hr are needed to attain thermal equilibrium.

The static cell by Ng and Robinson (1978, 1979) is a stainless steel vertical tube of 150 ml in volume, equipped with a bulls-eye window to observe the interface between phases. The cell operates at temperatures to 600 deg F and pressures to 2500 psia. Two specially designed valves mounted directly into the cell body serve to sample the equilibrium vapor and liquid phases, the liquid sample being trapped in a cavity of a non rotating piston rod.

Li et al. (1981) described a variable-volume view cell (with a 1 in. thick quartz window backed by a metal plug except for a viewing slit) of maximum volume of 600 ml, mounted in a rocking air bath to facilitate the equilibration. The equilibrium vapor and liquid samples were taken in sampling valves.

Wichterle and coworkers developed a simple and efficient capillary sampling technique. The view cell by Lhotak and Wichterle (1981) is a ring made of tempered Kovar glass, whose parallel ground and polished faces are held between two stainless steel flanges connected by 6 bolts. The cell is tested to 20 MPa. Samples are taken by copper capillaries (approx. 0.1 mm id.), a pair of which extends to the liquid phase and another pair to the vapor phase. A stainless steel cell of similar shape equipped with two windows and the same sampling technique was used by Wagner and Wichterle (1987) in their study of systems of carbon dioxide with C6 hydrocarbons at pressures to 9 MPa. For such systems the samples of both equilibrium phases de pressurized through the capillaries segregate each into a vapor-liquid system again; therefore a sample homogenizer (a stirred vessel kept at a sufficiently high temperature) has to be inserted into the sampling line.

Dohrn and Brunner (1986) employed a similar sampling technique, wherein the samples could be withdrawn through fixed thermostated capillaries at three different heights in the cell, allowing the treatment of three-phase vapor- liquid-liquid systems.

King et al. (1983) described a large-size cell (500 ml in volume) equipped with two ports for sampling both the lighter and the heavier phase, in which the examined system is enclosed between the top of the cell and a meniscus of a mercury column extending into the base of the cell. The mercury injection is used to keep the system pressure constant during the process of sample withdrawal.

A series of static assemblies has been developed by Renon and co-workers for investigating fluid phase equilibria at various ranges of operating conditions; some of them were overviewed by Richon and Renon (1983).

Legret et al. (1980) designed a simple cell with the possibility to sample only the lighter (vapor) phase; usually the space occupied by the vapor is kept small and the composition of the liquid phase is evaluated from the a priori known total composition by making the appropriate correction for the vapor phase estimated by using an equation of state.

Figuiere et al (1980) developed a cell for two-phase systems at pressures to 40 MPa and temperatures to 400°C. Two sampling valves, with their small aperture openings at suitably different levels are machined directly in the cell body. The sampling is based on micro expansion obtained through very rapid opening (and closing) of the valve. The samples flow (for a few hundredths of a second) along the valve stems and encounter the chromatographic carrier gas at a point close to the equilibrium compartment, still in the cell body. In this case the system temperature has to be higher than the bubble temperature of the heaviest component at the carrier gas pressure to ensure fast total vaporization of liquid samples.

Legret et al. (1981) described a stainless steel horizontal cylinder cell (volume 100 ml) that may be used to study two-phase systems at 5 - 100 MPa and 233 - 433 K. An original sampling method is employed, in which the vapor and liquid samples are trapped in detachable micro cells (volume 15 micro liter) that fit specially designed heated injection ports of the chromatograph. The method allows the treatment of systems containing heavy hydrocarbons which need to be heated above the system temperature for complete vaporization.

Meskel-Lesavre et al. (1981) designed a light and small enough variable-volume cell so that it can be directly weighed with an accurate balance and thermostated with any temperature gradient. The cell is used to determine the bubble pressures and saturated liquid molar volumes from the break points on the isothermal pressure vs. volume dependence recorded for a given overall composition. Interesting is the design of the cell, whose top part is a stationary piston while the cell body is surrounded by the pressurizing liquid.

A modification of the preceding method, extending the operational range to 60 MPa at 573 K, has been presented by Rousseaux et al. (1983). The piston system is replaced by bellows; the main part of the static cell volume is inside the bellows and the volume of the cell is controlled by straining the bellows by pressurizing liquid from the outside.

Guillevic et al. (1983) developed another version of an equilibrium cell (50 ml in volume), enabling measurements up to 558 K and 7 MPa. Their cell, all made of a magnetic stainless steel, is a cylinder with a vertical axis, welded of two parts that had been initially machined separately. Directly mounted in the bottom part are the pressure transducer (sensitive to 10 Pa), a feeding valve, and two sampling micro valves of special design, with the chromatographic carrier gas flow inlets and outlets located directly in the valve seats, thus zeroing the dead volumes.

Fontalba et al. (1982, 1984) described a variable volume blind cell (a vertical cylinder, applicable to 45 MPa and 433 K) in which the equilibrium compositions and saturated densities of the two coexistent fluid phases in (binary systems) are determined simultaneously in the synthetic mode of operation. The data are calculated from known overall compositions and volumes of both phases obtained in two experiments (for two loadings of the cell differing in overall compositions and hence in the ratio of volumes of the individual phases) conveyed at the same temperature and pressure. The current total volume of the system is derived from the position of the piston (driven by pressurizing liquid), which extends into the base of the cell. The location of the phase interface level is determined by using a thermistor probe (detecting the difference in thermal conductivity) which extends into the cell from the top and whose position can also be read. (A more general synthetic method of this type was presented by DiAndreth at al., 1987, see below.)

The cell by Huang et al. (1985), designed to study the two- and three- phase regions in the CH_4 - CO_2 - H_2S - H_2O system, consists of a transparent sapphire cylinder mounted between two stainless steel headers; the top one contains all the necessary lead lines while the bottom header accommodates a movable manually driven piston. The cell is mounted in a controlled temperature air bath and the equilibration is achieved by rocking the entire bath assembly. After reading the equilibrium pressure and temperature, the bulk volumes of the phases are sequentially removed through the same port and sampled for chromatographic analysis. The dew and bubble points can also be visually detected.

For studying the methane - carbon dioxide - hydrogen sulfide mixture Ng et al. (1985) developed a vertical sapphire cylinder cell (tested to 19.3 MPa), enabling complete visibility of the system ranging from the appearance of the first crystals or droplets of the heavier phase (which is facilitated by a V-notched stainless steel insert at the bottom) up to the disappearance of the last bubble, i.e. to the bubble point. Stirring of the cell contents is achieved by vertical motion of a magnetically driven Teflon-coated steel body shaped so that even the smallest amount of liquid in the insert notch wets the

stirrer at its bottom position. Samples for analysis of any desired phase can be withdrawn through a hypodermic needle probe passing through a gland in the top cover plate of the cell and down the central axis of the sapphire tube through an opening in the stirrer.

Japas and Franck (1985) investigated the water - nitrogen system at pressures to 250 MPa in a stainless steel horizontal cylinder cell with windows on both ends, operated both in the synthetic and analytic mode. In the former, the pressure-temperature-liquid composition (and also molar volume) data are obtained by determining the break points on the pressure versus temperature isochore for a known overall composition and cell volume. In the analytic mode (used in the range of small gas concentrations), the liquid phase sample is extracted with a thin stainless steel capillary through a micrometric needle valve.

In their static cell designed primarily for studying high-pressure liquid- liquid equilibria, Nakayama et al. (1987) used two types of sampling devices, namely (i) the sliding rod sampler with a sampling cavity of volume 0.1 ml, which can be moved back and forth horizontally between the cell and sampling line, and (ii) a simple capillary tube sampler, where the sample is trapped in a capillary section between two valves. The pressure loss in the cell due to sampling is compensated by a pressurizing diaphragm.

Melpolder (1986) presented a simple 150-ml cell for operation up to 225°C and 1000 psia, connected directly to a 6-port sampling valve with two micro tubing lines (one for vapor and one for liquid) to provide alternate analysis of the condensed vapor and liquid phases. The entire set-up is built from commercially available parts.

DiAndreth et al. (1987) developed an entirely general form of the synthetic technique, applicable to studying multiphase fluid systems. The horizontal cylinder cell (tested to 28 MPa and 70°C) is equipped with sapphire windows on both faces; one permits illumination of the cell content and the other serves to view the coexistent phases and read the heights of the interfacial boundary menisci with a cathetometer. A movable piston is positioned perpendicular to the sample chamber axis and allows the cell volume to be varied from 10 to 29 ml. The piston position is monitored by visual observation of the position of a thin indicator wire attached to the piston and extended through the top of the cell into a high pressure glass tube. After vigorous shaking of the cell to equilibrate the system, the cell is leveled and the phases allowed disengaging and settling for 4 to 6 hr. From the meniscus height(s), piston position, and previous calibrations, the individual phase volumes are determined with uncertainty less than 1 per cent for the phase in excess. The calculation of compositions and densities of the individual phases is based on the fact (given by the phase rule) that in an n-component

n-phase system at a fixed temperature and pressure the compositions and densities of the coexistent phases are independent of the overall composition. Thus it can be easily shown that for an n-component n- phasic system the volumetric data for individual phases obtained at n different overall compositions (but at the same temperature and pressure) provide the sufficient input; the results are more accurate if the volumes of different phases dominate in different experiments. Even though in the case of a three-component three-phase system only three experiments would suffice, DiAndreth et al. (1987) preferred a procedure yielding more accurate results, namely to perform more experiments and to compute the compositions and densities of the coexisting phases by regression.

Lentz and Weber (1991) described a horizontal-tube variable-volume cell with two sapphire windows (volume 110 ml, max. pressure 200 MPa). The authors optionally use either the analytic or (for the critical region) synthetic mode of operation. The samples of both the lighter and heavier phase are withdrawn into two sample vessels, detachable from the cell. The volumes of the vessels are accurately known, thus also enabling the determination of the densities of both phases.

Zerda et al. (1986) described a static cell of special design, in which the solubility of anthracene in SCF carbon dioxide at pressures to 120 MPa is determined in situ from the infrared absorption. The layer of the phase of SCF saturated with anthracene is situated directly in the optical path of the FTIR spectrometer. The thickness of the layer, i.e. the distance of two sapphire windows enclosing the equilibrium compartment, can be varied from 0.2 to 16 mm.

Similarly, Fernandez and Fernandez-Prini (1992) determined the solubility of solid iodine in sub- and supercritical xenon by using an optical static cell able to withstand pressures up to 100 MPa. The cell is placed in the optical path of an UV-spectrophotometer and the iodine solubility is determined from the light absorption of the vapor phase in equilibrium with the excess of solute (upon taking appropriate corrections) and from previous calibration on samples of known compositions.

An interesting static assembly operated in the synthetic mode, consisting of a system of two interconnected variable-volume cells, has been described by Stenby et al. (1992). Besides the dew point and volumetric properties, the apparatus allows also the measurements of viscosity and spectroscopic investigations.

Recently, Tuma and Schneider (1999) presented a high pressure cell for the determination of the solubility of solid dyestuffs in near and supercritical fluids using UV spectroscopy

Many more applications of the static methods making use of the above mentioned principles and cell designs (only with minor modifications) can be found in the literature; the papers by Vera and Orbey (1984), Jangkamolchulkal and Luks (1989), Roop and Akgerman (1990), Subra and Tufeu (1990), Adisasmito et al. (1991), Armellini and Tester (1991), Jay et al. (1991), Laintz et al. (1991), Staby and Mollerup (1991), Tian et al. (1991), Gregg et al. (1992), Zabaloy et al. (1992), Crampons et al (1999), Mishima (1999), Knez and Stainer (1992), Shermann (2000), Guigard et al (1998), Hourriaet al (1998), Škerget et al (2000), Weider et al. (2000).

5. RECIRCULATION METHODS

5.1. Principles and characteristics

In a way, the recirculation methods can be viewed as an extension of the static methods, from which they evolved. The main part of the recirculation apparatus is a thermostated equilibrium cell similar to the cells used in static experiments. The difference and the principal characteristic of the recirculation apparatus (see Figure 3) is that the equilibrium cell has the facility for mechanically driven circulation through external loop(s) of either the lighter (i.e. the top) phase or the heavier (the bottom) phase or, as the case may be, of both these phases. The circulation is usually achieved by magnetically operated high-pressure pumps.

There are two main items of motivation behind introducing the external circulation of phases. The first is to make the stirring and contacting of the phases to be equilibrated more efficiently and thereby to improve the process of equilibration and reduce the period required. The second reason is that the sampling of the equilibrium phase(s) can be substantially facilitated. After the equilibration has been completed, the phase circulated through an external loop in a steady state regime represents already a separated equilibrium phase. A portion of such phase may be trapped in a compartment (or sampling cell) and taken for analysis or the phase may be temporarily circulated through an in-line sampling loop of an injection valve and then analyzed off- line. Or, if a suitable detection method is available (depending upon system and conditions), to a great advantage an on-line analysis may be performed (by using continuous refractometry, densitometry, UV/Vis monitoring, etc.) without disturbing the phase stream in the circulation loop at all.

Nevertheless, in many experimental set-ups the external circulation serves only as a means of intensive mixing while the sampling is accomplished through some static sampling ports, i.e. in the same manner as in the static methods.

A typical experimental procedure is usually such that after purging and evacuating the equipment, the cell is loaded by a mixture of roughly known composition and pressurized by pumping in the solvent to a desired pressure value. The operation of magnetically driven pump(s) is started and one or two phases are recirculated so that the lighter phase exits the cell at the top and is returned at the bottom, bubbling through the heavier phase, whereas the heavier phase leaves at the bottom and returns to the top of the cell, being sprayed into the lighter phase. The process of approaching the equilibrium state is followed by examining the stability of pressure and sometimes of density and/or composition. The equilibrium state is typically reached within 10 to 15 min. On allowing for some time at equilibrium, the phases are sampled and analyzed. Depending on system and mode of sampling, the recirculation is either stopped (and the phases let to settle and disengage) or continued without interruption.

It should be noted that the system examined in a recirculation apparatus is still a closed thermodynamic system and so the limitations and precautions related to this feature and mentioned in the "Static methods" section (particularly the necessity of degassing the system) have to be observed.
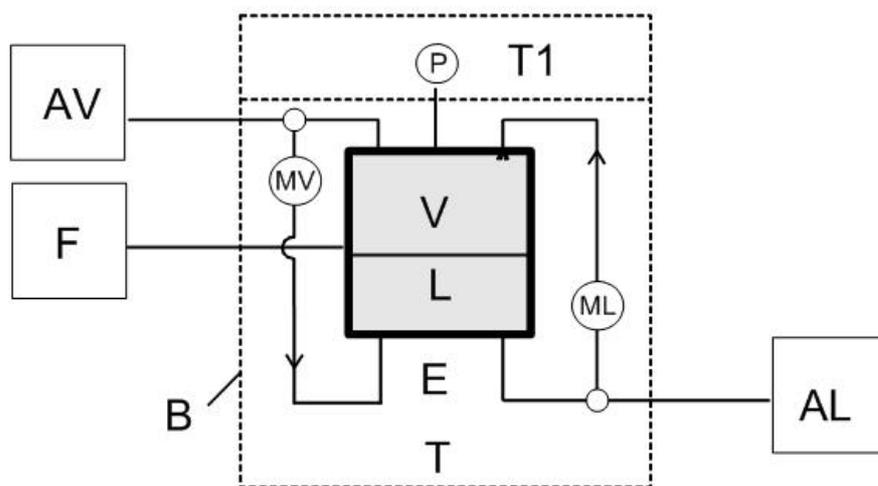

Figure 3. Schematic diagram of a typical dynamic recirculation method (illustrated for vapor-liquid equilibrium, with sampling from the circulation loops): AL, batch analysis of the liquid phase; AV, batch analysis of the vapor phase, B, boundary of thermostated compartments; E, equilibrium cell; F, batch feed of degassed components (or a mixture); L, liquid phase; ML, pump for liquid circulation; MV, pump for vapor circulation; P, pressure meter; T, temperature of the cell; T1, temperature of the pressure sensor (greater than or equal to T); V, vapor phase;

It should also be noted that the high-pressure recirculation methods described here differ in principle from the recirculation instruments widely used for studying the vapor-liquid equilibria at low and normal pressures. (In the latter devices the mixture is boiled and both phases, still blended with one another, travel via the so called Cottrell pump to an equilibrium chamber where they are flash-separated; the system is open, connected with a pressure control system.) However, both kinds of equipment have a common pitfall associated with sample withdrawal, namely the danger of entrainment of droplets (or bubbles) of the second phase with the circulated stream of the phase to be sampled for analysis. A caution has to be always exercised to avoid this phenomenon which could be a potential source of serious errors in determining the composition of the equilibrium phases. It is obvious that it is the more difficult to prevent the mutual entrainment of phases the closer are their equilibrium densities; such a unfavorable situation occurs e.g. near the critical point of the mixture. That is why the recirculation methods are not effective very near the critical points.

Understandably, also in the recirculation apparatus it may turn out necessary to prevent selective flashing and adsorption on the switching valve for the lighter phase sampling loop. This problem is easily solved by slight overheating of the valve compared to the system temperature.

The above mentioned predominant advantages of the recirculation cells (i.e. the rapid equilibration and availability of streams of single equilibrium phases) are, of course, gained at the expense of somewhat higher constructional complexity compared to simpler static cells; hence one has to be aware of the possible occurrence of additional dead volumes, increased risk of leaks etc.

A general capability of the recent experimental setups in this category is a visual equilibrium cell. The necessity to observe the phase behavior is getting more important as the complexity of the behavior of the investigated systems is increasing. In some cases a video camera with videotape is also connected to the cell in order to enlarge and record the view of the experiment.

5.2. Examples

Besserer and Robinson (1971) described an interesting cell consisting of three vertical cylindrical parts bolted together, namely two cylinder-piston end sections and a smaller diameter central window section. The window allows the visual observation of the cell contents and the determination of the refractive index of the phase extending to the central part. Mixing and equilibration are attained by running the pistons up and down. On the upstroke, the bottom phase is pumped via an external circulation line to be sprayed into the vapor phase in the upper cylinder, while on the down stroke the fluids

pass through the central part of the cell. Five to ten cycles usually suffice to reach equilibrium. Both the vapor and liquid samples are taken by sampling valves mounted in the body of the cell. The cell operates at pressures to 3000 psia and its volume can be changed from 10 to 175 ml. Kalra et al. (1978) further modified the cell by including the liquid sampling valve into the external circulation loop.

Tsang and Streett (1981) designed a vapor recirculation apparatus for temperatures to 250°C and pressures to 200 MPa, wherein the entire vapor phase passes through the liquid in about 1 min. The samples of both phases are withdrawn by capillary sampling lines: the liquid directly from the cell and the vapor from the space close to the pump in the circulation loop. Several modifications of this apparatus with the recirculation of the least dense phase, applicable for measuring the vapor-liquid, liquid-liquid, vapor-liquid-liquid, and SCF-liquid equilibria at different ranges of temperature and pressure, were reported by Pozo and Streett (1984), Cheng et al. (1989a), and Shah et al. (1990, 1991). In these equipments the samples for analysis are usually withdrawn directly from the equilibrium cell into a sampling chamber thermostated to a temperature higher than that of the cell in order to prevent partial condensation during throttling.

King et al. (1983) described two pieces of recirculation equipment using relatively large cells. (i) In the one designed for two-phase fluid systems, the cell applicable to 500°C and 500 bar has 300 ml in volume and is equipped with a solenoid-operated internal stirrer. The vapor is recirculated via the vapor sampling bomb and the liquid via the liquid sampling bomb in an alternating mode by using the same pump. After reaching the equilibrium state, the system pressure is recorded and the two sample bombs are sealed off. (ii) The second assembly is developed for studying the solubilities of solid or low-volatile liquid solutes in a 500-mL cell. The solid solute is placed between layers of knit mesh in a stainless steel gauze basket; if the solute is a liquid, a glass vapor-liquid contactor (saturator) is inserted into the cell. The state of saturation is reached after 20 min. of recirculating the fluid phase; the sample bomb is then disconnected from the circuit and its content is analyzed. This apparatus can also be used for extraction experiments, in which case it is operated in the one-pass mode, in fact as a saturation method.

Also the recirculation apparatus by Tan and Weng (1987), used to study the solubility of naphtol isomers in SCF carbon dioxide, has clearly evolved as an improvement of the saturation method. The solid solute is packed as a stationary phase in a saturator (extractor) of conventional design. Another cylindrical vessel of known volume, a separator, is inserted between the saturator and a three-way expansion valve. With the valve closed, the assembly is filled with the compressed solvent. Within a closed system

the solvent is circulated via the saturator and separator for a period of time required to reach the state of saturation. A portion of the SCF-rich phase is trapped and the separator is disconnected from the loop. A representative sample is thereby obtained, which can be conveniently analyzed. In this arrangement, the state of full saturation is ensured and the amount of solvent required is substantially less than in the one-pass saturation method. The most important advantage of this apparatus is that the variation of the solubility with time can be observed, thus avoiding the uncertainty of not reaching the equilibrium.

Maxwell et al. (1992) also adapted the recirculation technique for studying the solubility of solid sodium salts of polycyclic antibiotics in SCF of either pure carbon dioxide or its mixtures with modifiers. The "powder" of the solid is mixed with glass beads, forming a stationary phase in the equilibrium cell whereas the SCF phase is recirculated. (The technique can also be viewed as an improved saturation method.)

Radosz (1984, 1986) developed an apparatus with the recirculation of both the top and bottom (fluid) phases in a counter-current fashion. A variable-volume cylinder is included into the top phase recirculating loop in order to avoid the pressure drop while sampling. Pressure is maintained constant with this cylinder by pressurizing the piston with one of the feed components. The visual cell enables studying vapor-liquid-liquid equilibria by sampling all the three phases after disengagement. The equilibration times reported range from 15 min. for vapor-liquid to several hours for liquid-liquid equilibria.

Panagiotopoulos and Reid (1987) described another high pressure optical cell (Jerguson gage) applicable to studying three-phase systems. Connections at the bottom, top, and side of the cell permit withdrawal of the lower, upper and middle phases, any two of which can be recirculated externally with a dual high-pressure pump. An on-line vibrating density meter is used to measure the density of one of the recirculated phases; it can be switched to sample any of the recirculated streams. Sampling is performed directly from the recirculating loops with two high pressure switching valves; the samples are directly de pressurized into a GC carrier gas stream. The process of approaching the equilibrium (taking typically 15 min.) is monitored by the stability of pressure, density, and composition measurements.

The dual recirculation apparatus by Adams et al. (1988) using an optical sapphire equilibrium cell (applicable to 400 K and 40 MPa) is equipped with one sampling injection valve; the recirculating stream of the phase to be sampled is switched to circulate through the sample loop of this sampling valve. Switching the valve then injects the high pressure vapor (or liquid) sample into the dilution volume of the carrier

gas loop thermostated to elevated temperature ensuring complete vaporization of the samples. Cheng et al. (1989b) extended the apparatus by adding a micro dual-sampling system.

In the recirculation assembly reported by D'Souza and Teja (1988) both the equilibrium fluid phases are recirculated via 10-port switching valves which enable continuous recirculation of each phase after the sample had been trapped in the sample loop of the valve.

The apparatus by Kneisl et al. (1988) features a moveable probe which permits withdrawal of a sample from any phase within the high-pressure cell and hence it allows studying the multiphase multicomponent systems. A mercury piston enables easy pressure adjustment upon sample withdrawal. A special pump is employed with two heads, of which one is used for the circulation of vapor and the other for the circulation of liquid. Each head operates by a reciprocating plunger movement. Both plungers are driven by the same motor and operate 180 degrees out of phase, so that the cell volume and pressure remain constant during the pumping of recirculated phases. A typical data point for a binary system can be measured in approximately 1.5 hr.

Inomata et al. (1989) studied the solubility of fatty acid methyl esters in SCF carbon dioxide in a 500-mL windowed cell. Only the SCF-rich phase is circulated just to promote stirring of the system; a magnetic stirrer is also employed. When the system pressure remains constant, the recycling is stopped and the samples are taken directly from the cell. A piston cylinder connected to the recirculation loop serves to compensate for the decrease in pressure during sampling.

On the contrary, Kaminishi et al. (1989) inserted a sampling cell of known volume into the SCF phase recirculation loop; upon equilibration the sampling cell with a trapped sample is taken out of the circuit and its content is analyzed.

In the apparatus by Weber (1989) the main purpose for the recirculation of both phases is their convenient sampling. The liquid phase stream is withdrawn from and returned to the very bottom of the cell.

Shibata and Sandler (1989) presented a detailed description of apparatus and procedure, in which both the lighter and the heavier phase are circulated also through the density meter probes. The stability of densities (measured with the recirculation pumps off) serves as a criterion of reaching the equilibrium state. After a settling period, ensuring a complete separation of the phases in the cell, small separate samples of the equilibrated gas and liquid phases are drawn from the recirculation loops via sampling valves (located close to the cell) into evacuated and preheated gas bombs.

An effective method for measuring solubilities lower than those normally obtained gravimetrically has been proposed by Cygnarowicz et al. (1990). In their apparatus the recirculation loop of the SCF carbon dioxide stream leaving the equilibrium cell (where it is saturated with β-carotene) flows through a high pressure cell of a variable wavelength UV monitor. (Of course, the in-line UV detection method requires calibration and is not universal, but restricted to substances containing chromophoric groups.)

Zheng et al. (1990) designed an experimental assembly in which one external loop with a pump is used to circulate in an alternating regime both the lighter and the heavier phase. A high-pressure six-way ball valve is used to switch the recirculation mode from liquid to vapor and vice versa. The phase being circulated is sampled from the loop.

In the vapor-recirculation apparatus by Chou et al. (1990), the equilibrium cell is connected to two sampling ports. The samples of both the vapor and liquid equilibrium phases are collected in detachable micro cells.

Yanagiuchi et al. (1991) designed a large-size dual-windowed cell (1 L in volume, applicable to 200°C and 20 MPa) equipped with a very efficient helical ribbon impeller. The vapor phase sample is trapped in a sampler inserted in the vapor recirculation loop while the liquid is sampled directly from the bottom of the cell.

In the set-up reported by Zou et al. (1990) and Yu et al. (1992) a magnetic pump is used in an alternating regime to externally circulate both the SCF and liquid phase streams. Both phases are sampled from the circulated streams into sampling loops of known volume.

A recirculation equipment has been described by Noles and Zollweg (1992). The dual recirculation apparatus with a sapphire tube pressure cell can operate at temperatures to 520 K and pressures to 40 MPa. Two methods are available for obtaining equilibrium samples: in one method, samples are taken without disturbing the equilibrium, using a three-valve trap situated at the beginning of each circulation loop; in the second method, capillary tubing is used to draw small samples directly from the equilibrium cell into collecting cylinders.

To measure small solubilities (of glucose in a SCF phase), Dohrn et al. (1992) also designed an apparatus with a large cell (500 ml in volume), operating at pressures to 30 MPa. The cell is equipped with two capillaries extending to different heights for sampling the liquid phase(s). The vapor phase is recirculated by an air driven piston pump via a vapor sample bomb (300 ml in volume) which can be disconnected from the circuit. At the bottom of the equilibrium cell a porous sintered metal filter (20μm)

provides an even gas distribution and at the top a stainless steel mesh is inserted to prevent liquid from being entrained by the vapor phase.

Bouchot and Richon (1998) proposed a method for on-line analysis (by means of a vibrating tube densimeter) applicable to pressure up to 40 MPa and temperature up to 423 K. This method allows the simultaneous determination of volumetric properties in the compressed and saturated states and the phase equilibria, with generation of a considerable amount of data in a very short time.

Many other researchers employed the recirculation technique, either with the recirculation of only the vapor phase, such as Dorau et al. (1983) and Wang et al. (1991), or with the counter-current recirculation of two phases, such as e.g. Kuk and Montagna (1983), Kim et al. (1986, 1989), Jennings and Teja (1989), Daneshvar and Gulari (1989, 1992), Suzuki et al. (1990), Park et al. (1991), Reilly et al. (1992), Bouchot and Richon (1998), Huang et al. (2000).

6. FLOW METHODS

6.1. Principles and characteristics

By flow methods we mean in our nomenclature the class of experimental techniques, in which a pre-heated mixture of constant (yet only approximately known) overall composition continuously flows to the equilibrium cell, wherein it separates into two phases differing in density. The separated single phases then continuously flow out of the cell by different outlets (the lighter phase from the top and the heavier phase from the bottom) and are sampled for analysis. Sometimes the methods of this type are designated as the continuous flow methods. On the other hand, some researchers use the term flow method for the technique which we describe under the name of saturation (or transpiration) methods.

The flow methods have been developed primarily for systems containing thermally unstable compounds and for reacting systems. The impetus for the design of the flow technique was the intention to reduce (i) the time required to attain the required state conditions (in contrast to the time required to attain the steady state corresponding to equilibrium in a recirculation apparatus and in contrast to the time required to equilibrate the system in a static apparatus) and at the same time (ii) to reduce the residence time of the studied mixture in the high temperature compartment of the apparatus. The reduction of both these periods of time is necessary to minimize the changes in composition due to possibly proceeding reactions, particularly to minimize

the extent of thermal decomposition or initiated polymerization of thermally labile constituents in the studied system.

In this type of apparatus, see Figure 4, high pressure pumps are used to deliver in a continuous manner the components in a fluid state to form a steady mixture stream of constant composition at a desired system pressure, which may be either 'liquid' or 'gas' or a blend of both. The stream passes through a pre-heater, where it approaches the desired system temperature, then usually through a kind of static or mechanically driven mixer (or a series of mixers), and finally it is fed into an equilibrium chamber (often called also an equilibrium cell or column). At the inlet of the chamber, the mixture stream is already assumed to have been equilibrated at the system temperature and pressure.
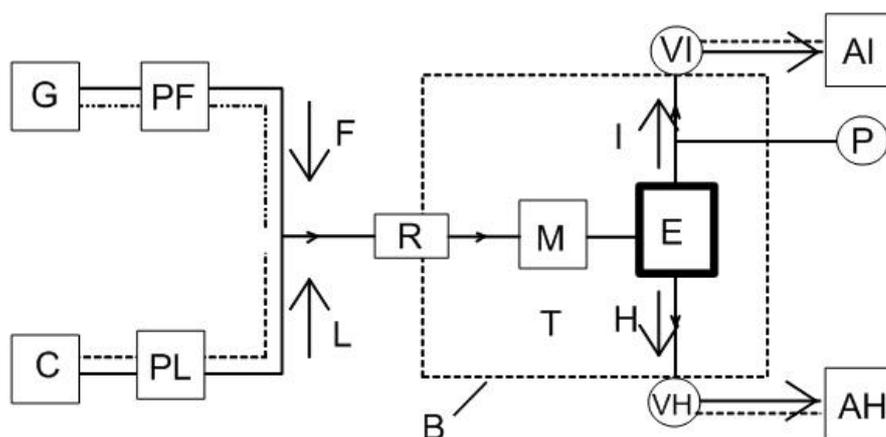

Figure 4. Schematic diagram of a typical dynamic (continuous) flow method: AH, analysis of the heavier phase; AI, analysis of the lighter phase; B, boundary of the thermostated compartment; C, liquid (solute) container; E, equilibrium cell (high-pressure phase separator); F, steady flow of pure SCF; G, liquefied gas (solvent) tank; H, steady stream of the heavier phase; I, steady stream of the lighter phase; L, steady flow of pure liquid solute; M, mixer; P, pressure meter; PF, (cooled) pump for the solvent fluid; PL (heated) pump for the solute liquid; R, pre-heater; T, temperature of the equilibrium cell; VH, metering valve (cell liquid level control); VI, metering valve (pressure control); -.-.- , cooled parts; - - - , heated parts.

The primary function of the equilibrium chamber is to immediately (or at least as quickly as possible) separate the two coexistent fluid phases differing in density. The lighter phase exits at the top of the cell while the heavier phase leaves the cell at the bottom. Typically the period of time during which the constituents are exposed to the (high) measured equilibrium temperature is of the order of seconds and certainly not exceeding a few minutes. The steady state effluent phases are then usually expanded to lower or normal pressure when passing through metering valves. The valves and the low pressure section still may require some heating to elevated temperature to avoid any

partial condensation on the way of the stream and so to preserve the representative equilibrium compositions of the phases all the way along the tubing up to the separators or analyzers, i.e. the precautions regarding the de pressurization and transportation of the sampled stream of the lighter phase (and sometimes of the heavier phase as well), discussed in the subsection on "Some general aspects ..." have to be taken into account.

For a given feed, the samples of equilibrium phases to be analyzed can thus be collected in sufficiently large amounts and quite rapidly, even though the initial period of approaching the ultimate steady state in the flow system (when the sample collecting period is started) may be of the order of tens of minutes, depending upon the system. The trait of getting samples of large enough size (given by the duration of the sample collecting period) maybe particularly valuable for investigations of dilute regions.

The flow technique is applicable to systems where the equilibrium phases as well as the pure components are fluids at all conditions encountered in the flow system of the experimental set-up. This is not a severe limitation, however. For a solvent like supercritical carbon dioxide this may only require cooling the solvent pumping section up to the point of mixing with the other component(s). On the other hand, an initially solid solute may be melted and/or dissolved in a portion of the solvent so that it enters the flow system already in a liquid form. The technique is in fact also applicable to typical liquid-liquid equilibrium systems provided that the difference in densities of the equilibrium phases is sufficiently large.

As a rule, the metering valve on exit of the lighter phase is used to control the system pressure while the metering valve on exit of the heavier phase is used to control the liquid level in the cell.

A viewing facility of the equilibrium chamber is virtually necessary in the flow method, to enable visual confirmation that the conditions are in the two- phase region and also to allow the liquid level in the cell to be controlled so that pressure fluctuations can be minimized.

Entrainment of one phase with another, particularly of the liquid phase droplets with the stream of the lighter phase has to be prevented. This is usually achieved by the geometry of the feed inlet port and of the cell itself and by a suitable porous insert (filter) in the top part of the cell.

Analysis of the separated equilibrium phase(s) of interest cannot be avoided in the flow method. The samples may be withdrawn directly from the high pressure streams exiting the cell, however, a still more usual and convenient way is to treat the samples upon expansion to atmospheric pressure. Very often (for SCF-containing systems) both the vapor and liquid de pressurized streams segregate into two phases again so that in many

cases the determination of compositions of the effluent phases may be carried out gravimetrically, simply by collecting and weighing the single less volatile component(s) frozen out of the de pressurized streams in cold traps. (Even a selective separation of constituents in a serial system of cold traps kept at different temperatures may be achieved). Eventually, the total amounts of the expanded gaseous solvent of both equilibrium phase streams can be determined in dry test or wet test gas meters (totalizers).

In the gravimetric and gas-metering determination of compositions, two kinds of corrections may be required: (i) the correction for the amount of low-volatile component(s) vapors carried away from the cold trap by the solvent gas stream, which can be estimated from the solute vapor pressure, and (ii) the correction for the amount of solvent dissolved in the trapped condensate, which can be estimated by using the Henry's law.

An obvious disadvantage of the flow method, namely a relatively large consumption of the studied substances, may be substantially weakened by a rational design of the experimental assembly, allowing at least partial recycling of the materials. In the SCF-containing systems this is facilitated by the ease, with which the gaseous solvent can be separated from the nonvolatile solute upon expansion.

A certain disadvantage of the method is the fact that the pressure fluctuations can hardly be suppressed completely, which makes a precise pressure control somewhat more difficult as compared to the other methods. Typically, the pressure can be kept constant to 0.3 - 0.5 percent of the measured value, which affects the attainable accuracy. Clearly, the flow experiments cannot be performed under the conditions very close to the system critical point.

6.2. Examples

As a representative of this type of experimental equipment the apparatus described in detail by Simnick et al. (1977) may be considered, which was originally designed for studying the system hydrogen + tetralin. The gaseous component stream coming directly from the gas cylinder (or, as the case may be for higher pressures, via a compressor) and the pure liquid stream coming from a liquid pump are mixed and pass though several meters of long tubing, in which the mixing of the flowing fluids is promoted by a notched twisted ribbon insertion. To reduce the pressure fluctuations, pressure vessels are installed in the pure component feed lines. Electrical heating tapes wound on the outside surface of the tubing ensure gradual heating of the mixed stream which finally attains a temperature within 1 K of the equilibrium cell temperature. The cell is a stainless steel vertical-cylinder pressure vessel, 90 ml in volume. Two nozzles

are welded on opposite sides at mid section of the cell, one of which provides the opening for the feed inlet and the other for electrical connection to a liquid level detector (capacitor). To avoid entrainment of gas in the liquid sample, the liquid level is controlled and a pool of liquid is continuously maintained. A demister pad in the upper part of the cell prevents liquid droplets from escaping overhead. There are two sampling and analysis systems for the apparatus. In one of them the effluent streams still at a high pressure and at a high temperature are diverted by means of a manifold valve. The diverted streams are then sampled and analyzed in a gas chromatograph. In the other system, the cell effluent streams are sampled after they are reduced in pressure and temperature; in this case the composition is determined by weighing (of cold-trapped low volatile liquid) and by volumetry (of the gas passed). With minor modifications the apparatus has been used for studying the systems of carbon dioxide with C9+ hydrocarbons by Sebastian et al. (1980) and by Kim et al. (1985).

A flow apparatus embodying all the typical features discussed in the preceding section has also been designed by Thies and Paulaitis (1984). The operating conditions of the view cell (60 ml in volume) are limited by the window seals to a maximum pressure of 5000 psia at 450°C. The equilibrium cell of Lin et al. (1985) is a horizontal cylinder of approximately 10 mL in volume. Transparent sapphire windows enclose the open space at both ends to allow visual observation of the liquid level. The copper- gold gaskets were used to seal the windows, which proved satisfactory for pressures to 250 bar at temperatures to 710 K. Normal flow rates adopted were 500 - 1000 mL/hr, corresponding to a plug flow residence time of 18 - 36 s. A similar equilibrium chamber has been employed in the flow method assembly by Niesen et al. (1986).

Radosz (1985, 1987) and Radosz et al. (1987) developed and used a flow apparatus for studying the phase behavior in systems of SCF with heavy hydrocarbons (such as oils and heavy petroleum residua). A high pressure windowed Jerguson gage (60 mL in volume) equipped with a de-entrainer is used as the equilibrium chamber. All the parts in contact with the high melting components are electrically heated. Two low-pressure separators are used, one for each effluent phase, which separate the de pressurized streams into gas and liquid; the amounts of liquids are determined gravimetrically and the volumes of the gas passed are determined by wet test meters. When three phases occur in the system, the apparatus is used to determine only the temperature and pressure of the phase transitions (but not the phase compositions).

In the apparatus by Gilbert and Paulaitis (1986), a crimped tubing mixer is used upstream of the cell. The heavier phase flowing out of the bottom of the view cell is flashed to atmospheric pressure directly across the back pressure regulator.

Inomata et al. (1986a, 1986b) described in detail a flow technique assembly, in which the mixed stream passes through two-stage preheating and enters the vertical cylindrical cell by an inclined nozzle to minimize the entrainment of liquid droplets with the lighter phase. For the same reason, a demister pad is inserted in the top of the cell. The liquid level in the cell is kept at a fixed position by means of an overflow-type self-control system equipped with a back pressure regulator. The liquid level is also detected by a capacitor sensor, which is useful for monitoring and keeping the steady state operation.

Briones et al. (1987) described a view cell, built for studying the vapor- liquid as well as liquid-liquid equilibria up to cca 350 bar. In their study of the acetic acid - water - SCF carbon dioxide system, two high-pressure pumps are used to deliver the aqueous acetic acid and SCF feeds at respective flow rates of 29-290 and 46-460 mL/hr. The two streams enter a mixing/equilibrium section and after reaching the system conditions, equilibrium phases are separated in the cell. Both the light and heavy phases are expanded through heated micro metering needle valves and enter the sampling system. After approximately 30 min. of reaching and stabilizing the equilibrium conditions, the streams are directed to the system of cold traps to start the sampling period. The traps for the light-phase stream are packed with stainless steel mesh and immersed in dry ice - acetone baths, while the traps for the heavy-phase stream are immersed in room temperature water baths. Only for the heavy phase the corrections for the gas absorbed in the liquid sample and for the residual vapor carried over with the gas are needed.

Thies et al. (1988) used the pre-heater mixer consisting of three sections of stainless steel tubing and a special modification of the liquid level Jerguson gauge adapted for use at high pressures and temperatures up to 670 K. The collected effluent phases were analyzed by gas chromatography. The apparatus has been applied by Hutchenson et al. (1990, 1991) for pressures as high as 350 bar and for systems with components which are solids at room temperature (such as the petroleum pitch). Towards this end the apparatus was supplemented by a high-pressure cylinder from which the molten pitch stream was pumped indirectly, by a floating piston displaced by the regulated flow of a working fluid.

Another distinct modification of the flow method has been reported by Lahiere and Fair (1987, 1989). In their experimental system, designed to study the distribution of alcohol solutes between the water phase and a near- or supercritical carbon dioxide phase, the principal component is a multistage countercurrent contactor (in fact a vertical extraction column, about 120 cm high, 1 inch in ID) furnished with five sieve trays and 12 pairs of borosilicate windows. The operation requires keeping the ratio of carbon dioxide solvent feed to the aqueous solution feed below an experimentally determined

maximum value. Under this condition, the aqueous phase feed stream entering the top of the column and the solvent-rich stream exiting the contactor reach equilibrium in about 30 min. A typical run required 45 - 60 min. to achieve the steady state; after reaching the steady state, a run was continued at the preset conditions for 20 - 30 min. before the conditions were changed.

A typical continuous flow assembly has been used by Jennings et al. (1991) for systems of carbon dioxide with alkanols at pressures of 4.6 to 11.8 MPa. The mixture is pumped through a section of tubing coils and two static mixers placed in a constant temperature air bath. The phases are separated in a high- pressure view cell (Jerguson liquid level gauge). The liquid level is set by adjusting the flow rate of the liquid phase. The period of collecting the samples for analysis is started after maintaining the steady state conditions for 20 to 30 min. at a desired pressure. The pressure fluctuations recorded were ± 0.24 bar and the accuracy reported was 0.24 bar.

Christensen and Paulaitis (1992) stressed the necessity of the visual capability of the flow equilibrium cell, allowing the observation of three-phase equilibria and critical opalescence as well as the phenomena caused by pressure fluctuations. A detailed description of the mechanism for sealing the polished sapphire windows of the equilibrium cell for operation at 175 atm and 400 deg C is presented. The authors report unavoidable system pressure fluctuations of ± 0.2 atm for vapor-liquid and of ± 0.7 atm for liquid- liquid equilibria (where the larger range is due to the low compressibility of both phases).

Other applications of the typical flow technique experiments have been reported by Lee and Chao (1988), Inomata et al (1989), Huang and Radosz (1990), Weng and Lee (1992), Watanasiri et al. (1986), Yu et al. (1989), Ghonasgi et al. (1991a, 1991b), Gupta et al. (1991), Beard et al. (1992), Bolanos et al. (1992), Gude and Teja (1992), and Walther et al. (1992).

7. SATURATION (TRANSPIRATION) METHODS

7.1. Principles and characteristics

Experimental equipment belonging to this category is perhaps the one most frequently applied for determining the solubility of solids and highly viscous heavy liquids in supercritical solvents. The principle of this class of methods is again quite simple, see Figure 5. The saturation technique differs from the flow method described in the previous section by the fact that the nonvolatile heavy phase (either liquid or solid, consisting of one or more species) is loaded batch wise in a saturator, or in a battery of

two or even more saturators connected in series, and stays there as a stationary phase during the entire experiment. (In the literature, the saturators are often denoted also as equilibrium cells or chambers, extraction columns, or phase contacting tubes). In most cases the saturator has the form of a packed column.

Under a measured constant pressure, controlled usually with a back-pressure regulator, a steady stream of SCF passes through a pre-heater, where it reaches the desired system temperature, and is then continuously fed to the saturator at its bottom, strips the solute(s) of the stationary heavy phase residing in the column and, saturated by the solute(s), leaves the saturator at its top.

The solubility of the heavy phase in SCF may be determined either by a direct sampling and analysis of the effluent stream or, which still prevails as a more common way in this case, from the total volume of gas (i.e. of SCF after expansion) passed through the saturator and from the known mass of solute(s) extracted during a sample-collecting period. To this end, the effluent stream is expanded from the experimental pressure to atmospheric pressure across a metering valve, then passes through a cold trap where the extract is quantitatively precipitated or condensed, and finally proceeds to a dry test or a wet test gas meter (totalizer), where the total amount of the passed gas is measured. The amount of extracted solute(s) is usually determined by weighing the sample collected in the cold trap but it can also be inferred from the difference in mass of the heavy phase placed in the saturator at the beginning and at the end of the measurement period. For the case when a multicomponent system is studied with the heavy phase consisting of more than one component, the multicomponent extract sample collected in a trap must further be analyzed.

As the case may be in the gravimetric determinations, similar corrections may apply as already mentioned in the "Flow methods" section. Namely, the correction for the solute(s) vaporized at the sample-collecting temperature into the stream of deliberated gas may be calculated from the solute vapor pressure, whereas the correction for the amount of SCF solvent dissolved in the condensate may be estimated by using the Henry's law.

The saturation method is often used to study the co solvent effects. In such a case a stream of solvent and co solvent mixture of known composition is fed to the saturator, so that the ratio of the concentrations of the volatile components is known a priori.
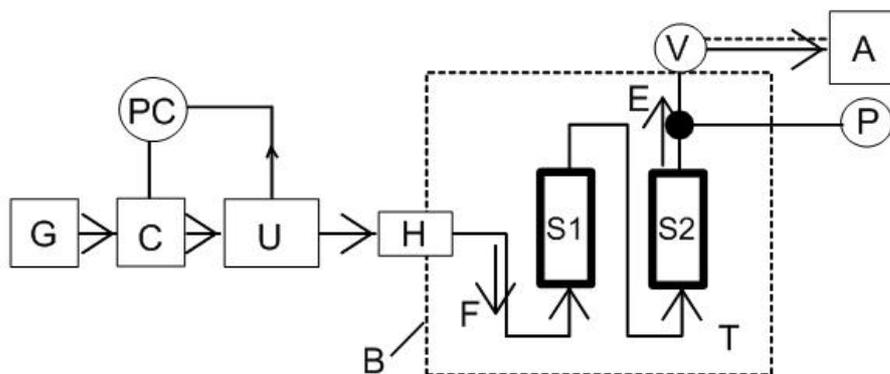
Figure 5. Schematic diagram of a typical dynamic saturation (transpiration) method: A, analysis (of the depressurized fluid phase stream); B, boundary of the thermostated compartment; C, compressor; E, steady stream of SCF saturated with solute; F, steady flow of pure SCF solvent; G, gas cylinder; H, pre-heater; P, pressure meter; PC, pressure control; S1, S2, saturators (equilibrium columns); T system temperature; U, surge tank (pressure buffer); V, metering (expansion) valve; - - - , heated parts.

The simplicity and straightforward sampling procedure are the main advantages of the method. Systems with extremely low-volatile solutes can be studied, since collecting a representative sample of reasonable size is only a question of time. Also, the technique may be employed not only for the equilibrium solubility studies but also for accumulating the data on stripping, extracting, and fractionating of the components of ill defined heavy phases, namely of natural or reaction mixture specimens. Such data are not easily obtained by using any of the other techniques considered. Moreover, only with minor modifications, the equipment maybe used as a laboratory- or even pilot-plant scale process batch unit.

On the other hand, the method is applicable only to two-phase systems and does not allow the location of phase transitions (i.e. of phase boundaries in phase diagrams). Since only the SCF-rich effluent phase is sampled, the composition of the equilibrium heavy phase cannot be determined.

Furthermore, there are several pitfalls in this technique, which the experimentalist has to be aware of. These are as follows:

(i) In connection with the mentioned impossibility to detect phase transitions, there is a danger that unnoticed phase changes occur in the saturators, distorting the results. Hence it is quite important in studies by this method to have some a priori knowledge on the types of phase behavior, particularly on the location of the operational region in relation to the possible location of the solid-liquid-vapor or liquid-liquid-vapor curves in the phase diagram.

(ii) It is necessary to avoid any entrainment of the particles or drops of the stationary heavy phase with the stream of the SCF-rich phase. A common precaution is to enclose the stationary phase between layers of glass wool supported by sieves made of some inert material such as stainless steel. Another or additional possibility is to modify the shape and geometry of the upper part of the saturator. The danger of entrainment of the stationary phase is the greater the closer are the densities of the two phases involved. It is obvious that in the limiting cases of approaching the critical point or of the occurrence of the inversion of densities of the phases, the method ceases to work.

(iii) It is essential that the SCF-rich phase stream be saturated with the solute(s), i.e. that the phase exiting at the top of the saturator be the phase in equilibrium with the stationary phase during the entire period of sampling or sample collecting. To ensure the attainment of equilibrium, the saturator has to be properly designed and often two saturators connected in series are used. Moreover, the area of contact of the two phases is usually maximized by depositing the heavy phase on the surface of a packing (such as glass beads) or, if it is a solid, by grinding the material to a suitable mesh. The ground solid may also be mixed with some packing or, alternatively, a solid layer can be deposited on the packing surface from a solution in a suitable solvent upon solvent evaporation. (Any of the two treatments is also desirable in order to prevent channeling or caking of the stationary phase bed.) Finally, the flow rate of the SCF stream has to be adjusted so that the residence time of the mobile phase is long enough to reach the state of full saturation on exit from the column. Typical equilibrium-type flow rates range from 50 to 500 ml/min. as determined at standard conditions.

(iv) It is necessary to avoid the precipitation or condensation and subsequent deposition of the extracted solute(s) from the effluent stream (or even possible dry ice formation when the SCF is carbon dioxide) during the expansion in the metering valve and also in the section of tubing before the stream reaches the collecting trap. Neglecting this phenomenon may not only result in erroneous data, but even in eventual clogging of the valve or tubing. That is why it is necessary to heat the relevant part including the metering valve to a safe, sufficiently high temperature. Also in this case the reasoning and necessary precautions mentioned in the subsection on "Some general aspects ..." fully apply. Direct sampling from the high pressure stream represents a way to bypass these problems: in some cases an analytical device (such as an UV-spectrometry or a gas chromatograph) may be directly connected to the outlet of the extraction tube.

7.2. Examples

As already stated in the preceding section, the saturation method is by far the most often used technique for determining the solubility of low volatile solutes in SCF solvents if

no additional item of information other than solubility is required and if there are no problems related to the location of the system conditions in the phase diagram (or, in other words, if there is no danger of undetected phase changes occurring in the system investigated).

Also, in the overwhelming majority of experimental studies, the experimental set-ups follow practically the same, already a standard pattern outlined in the preceding section. As a matter of fact, one can say that compared to the other experimental techniques there is a relatively small space for improvement and innovations in this method, except for the analytical methods. Nevertheless, some of the modifications can be clearly distinguished and worth mentioning and we briefly discuss them in the following.

The method has been originally used by Prausnitz and Benson (1959), D'Avila et al. (1976), and Kaul and Prausnitz (1978) for measuring the solubility of heavy liquid hydrocarbons in compressed gases. Usually two saturators in series were used, in which the dense gas stream was finely dispersed from a fritted gas sparger located at the saturator bottom.

The often cited - perhaps classical - early investigations on the systems of solids with SCF solvents involve the papers by Van Leer and Paulaitis (1980), Johnston and Eckert (1981), Kurnik et al. (1981), and Kurnik and Reid (1982). In the last two studies an on-line surge tank was inserted upstream of the saturators to dampen the pressure fluctuations in the SCF flow. The usual way of determining the composition was (and very often nowadays still is) applied: upon de pressurizing (flashing) the solute-saturated SCF stream across a metering valve, the solute is collected in a cold trap and weighed while the total volume of the expanded solvent is measured with a gas meter.

In the apparatus by Masuoka and Yorizane (1982), the de pressurized stream of ethylene and naphthalene enters directly the sampling loop of a gas chromatograph sampling valve. The entire section including the valve is heated to a temperature sufficiently high to prevent any condensation.

McHugh and Paulaitis (1980) and Paulaitis et al. (1983) introduced a high-pressure switching valve immediately on exit of the second saturator column (i.e. prior to the metering/expansion valve), in which a content of sample loop (about 0.2 mL in volume) can be isolated for analysis. The volume of carbon dioxide in the sample loop is determined by slowly expanding the carbon dioxide across a valve and displacing water. The sample loop is then flushed with a suitable solvent to recover the precipitated solid component. An internal standard is added to this solution and the amount of the heavy solute present is determined by using standard gas chromatographic techniques.

In the apparatus by Chang and Morrell (1985), the pressure is controlled by a back pressure regulator which allows excess solvent to recirculate back to the pump suction side. The pressure fluctuations due to pumping are thus less that 1 per cent of the operating pressure. The authors also installed a high-pressure glass gauge packed with the heavy solute in parallel with their saturators (packed columns). By this expedient it was possible to observe any phase changes that might occur during the experiment.

Gopal et al. (1985) and Kosal and Holder (1987) studied the solubility of solute mixtures in SCF carbon dioxide. Large amounts of substrate were used so that the overall composition of the condensed phase could be taken as constant. (The results for mixtures of naphthalene with phenanthrene, phenol and biphenyl indicate that the ratio of solute solubilities is constant at pressures above 10 MPa.) The effluent phase was de pressurized and the solute trapped in liquid toluene; also the metering valve and transfer lines were washed with toluene to recover and collect all the precipitated solute (which is a very frequently used operation in this type of experiment). The collected toluene solutions were mixed and analyzed by gas chromatography.

For determining the solubilities of complex liquid mixtures in dense gases, Monge and Prausnitz (1983a, 1983b) and Dimitrelis and Prausnitz (1989) developed the total vaporization method. In this method, a weighed amount of a heavy liquid fraction is totally vaporized by a measured amount of gas. The known amount of heavy narrow-boiling fraction is introduced into the saturator (equilibrium cell); the high-pressure SCF stream flows slowly through the cell and gets saturated with the heavy components, in the same way as in the conventional modifications of the method. The temperature of the saturated SCF leaving the packed bed is raised to a value sufficiently higher than that of the equilibrium system (i.e. of the bath) temperature to avoid precipitation of the heavy hydrocarbons. After expansion to ambient pressure, the gas flows to a wet test meter which measures the accumulated amount of gas passed through the equilibrium cell. Shortly downstream from the expansion valve a small gas sample is periodically withdrawn and flushed with helium into gas-liquid chromatograph. The chromatograph is used just to detect the presence of the heavy component(s) in the stream. At the moment when no heavy component is detected for the first time, the total volume of the gas in the gas meter is recorded as the amount of gas needed to vaporize totally the a priori known amount of the heavy liquid. As in the case of any other mixed solute, the stripping effects occur and their influence on the accuracy of results has to be assessed.

A distinct improvement over the single-pass methods considered here represent the modifications in which the SCF-rich phase is allowed to circulate for sometime through

the saturator(s) in a closed batch system. Several experimental devices of this kind were already briefly discussed within the "Recirculation methods" section, see the references given therein: King et al. (1983), Tan end Weng (1987), and Maxwell et al. (1992).

To expedite data acquisition, Schmitt and Reid (1985, 1986a, 1986b) use in their assembly two saturators (extractor columns) in parallel. These could be operated at different temperatures, but the pressures are identical since both saturators are fed from a common compressor and surge tank.

In a study on the solubility of a mixture of nonvolatile solutes in SCF carbon dioxide, Ikushima et al. (1988) equipped their assembly with a separator chamber, connected to the line between the extractor/saturator and the back pressure regulator, used for selective removal of the dissolved material from the loaded SCF phase.

To improve the saturation process, Foster et al. (1991) used a battery of five saturators connected in series packed with glass beads and loaded with the solute (oleic acid), of which the last was a sight gauge enabling visual assurance that entrainment of the liquid solute into the downstream cold trap did not occur.

To improve the attainment of thermal equilibrium of the SCF solvent stream and to dampen the pressure fluctuations, Ko et al. (1991) inserted before the saturator/extractor an additional high pressure vessel filled with glass beads.

Dobbs et al. (1986) and Dobbs and Johnston (1987) studied the co-solvent effects in multicomponent systems. In their apparatus, the effluent phase saturated with solute(s) was analyzed by capillary gas chromatography with a micro sampling apparatus, wherein 0.1 mL of the flowing equilibrated solution is isobarically and isothermally isolated in a sampling loop of a six-port sampling valve. The sample is expanded through a liquid solvent and the loop is rinsed with 1 - 2 ml of additional solvent to recover all the solute. The micro sampling technique offers several advantages, namely that multicomponent solvent and solute systems can be analyzed directly, the run time can be significantly reduced because of the smaller sample size, and the analysis itself is faster than in the conventional methods.

Dobbs et al. (1987) introduced into their experimental set-up the vibrating tube densitometer, with its probe placed immediately in front of the first saturator. This arrangement allowed the in-line monitoring of the density of the mixed solvent, i.e. of the SCF solvent plus co-solvent(s), mixture.

Lemert and Johnston (1990) further modified the previous equipments by relocating the densitometer downstream of the saturator and of the sampling valve and by adding a by-pass line around the saturator. These modifications allow the measurement of the true solvent density as well as periodical removal of solid deposits from the sampling valve

and densitometer. The micro sampling technique is used with an additional advantage that the actual density of the solution in the sample loop is measured (instead of being estimated). Moreover, by measuring the density of the effluent stream the authors were even able to detect the liquid phase formation in the solid -solvent - co-solvent system. This is based on the observation that the density of the saturated solution dropped well below the density of the solvent mixture (when liquid formation occurred) due to partitioning of the co-solvent into the liquid. When liquid formation did not occur, the mass density of the saturated solution was always greater than that of the solvent mixture.

Barber et al. (1991) made use of the quadrupole mass spectrometer directly coupled to the apparatus to analyze the effluent stream of the SCF carbon tetrafluoride - solid carbon tetrachloride system, providing a method of on-line analysis.

The gas stripping method developed for pressures up to 20 MPa by Legret et al.(1983) can also be considered as a particular variant of the saturation method. The technique enables rapid accumulation of data on partitioning of solvents at infinite dilution in systems of the type nonvolatile solute -volatile solvent. For the purpose, an efficient saturator for liquid solutes was described.

Other relevant references for the saturation method are the following: Czubryt (1970), Hemmaplardh and King (1972), Kwiatkowski et al. (1984), McHugh et al. (1984), Krukonis and Kurnik (1985), Moradinia and Teja (1986) and Pennisi and Chimowitz (1986).

The subsequent list of recent references dealing with experimental investigations by the saturation method well documents the explosion of the activity in the field over the last few years: Cygnarowicz-Provost et al. (1992), Hammam, H., (1992), Kramer and Thodos (1988), Iwai et al. (1990-1991), Jennings et al.(1992), Li et al.(1991), Li and Hartland (1992), M'Hamdi et al. (1992), Rijkers et al. (1992a-1992b), Sakaki (1992), Schaeffer et al. (1988), Smith and Wormald (1990), Suzuki et al. (1991), Tan et al. (1991), Wells et al. (1990), Yau and Tsai (1992), Yokoyama et al. (1992) and Yonemoto et al. (1990), Gurdial and Foster (1991), Cross at al. (1996), Subra et al (1997), Sauceau et al (2000), Rodrigues et al. (2000).

8. DEW- AND BUBBLE-POINT METHODS

8.1. Principles and characteristics

The dew- point and bubble- point method is an interesting application of the synthetic method for measuring fluid phase equilibria. (In the static method section we have

stressed the difference between the "synthetic" and "analytic" methods.) The principle on which it is based is different from the dynamic methods described in the preceding paragraphs. In the dynamic methods the phases are brought to equilibrium at given temperature and pressure and then the composition is, in one way or another, determined. In the dew- and bubble-point method a mixture of known composition is isothermally expanded (or isobarically heated) until a phase change is detected (see Figure 6). As it has been pointed out in the section dealing with the static techniques, the equipment used in this case is very similar to the static cells (variable volume static cells are in most cases dew- and bubble- point cells), even though the principle is different. The dew- and bubble- point method is a synthetic method making use of the visual location of a phase transition state: a pressure value is found at which the composition of one of the preset phases is equal to the known total composition at a given temperature. The main advantage of the method is that no sampling and analysis are required.

The main difficulty in running apparatus of this group lies in the preparation of a mixture of known composition in the cell, and it is this step that differentiates the apparatus developed by different experimentalists.

This method, developed in the fifties for the low pressure region, is almost exclusively used at high pressure, since it offers hardly any advantage over static methods at low pressure. At high pressure it may be preferred, because the complete degassing is less critical, not very high volume differences are involved in the phase change detection, and the volumetric properties as a function of pressure are by-products of interest. See also the static method part of the review.
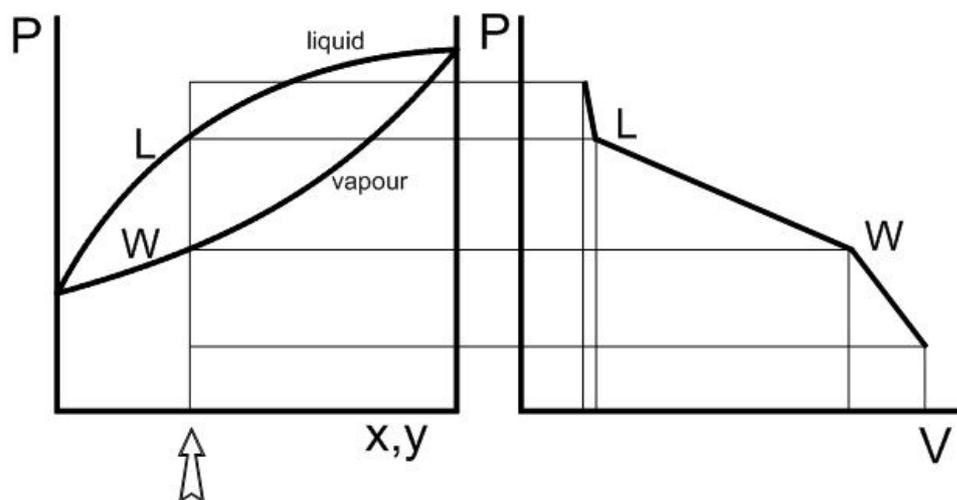
Figure 6. Principle of the phase-boundary methods (illustrated on the determination of dew- and bubble-points): The P-x,y diagram (on the left) may be constructed of the pairs of dew- and bubble- points (designated for the arrow-pointed overall composition by W and L, respectively), which are identified with the corresponding breaks on the P-V diagram for that overall composition (on the right). P, pressure; V, volume; x, liquid phase mole fraction; y, vapor phase mole fraction.

Apparatus belonging to this category are normally developed for the complete measurement of the phase behavior, nevertheless important examples of application of the method are also found in the literature for the direct determination of the solubility in dense gases as a function of pressure and temperature.

The typical results of synthetic experiments are a set of isopleths (phase boundaries at constant composition) from which the P-x or T-x diagrams must be obtained by cross plotting. The synthetic method does not require complicated analytical devices and procedures and is therefore relatively inexpensive, but the most important advantage is that it does not disturb the equilibrium condition. On the other hand the phase boundary is not detected directly, but as a consequence of the formation of a new phase. This formation, in order to be detectable, may occur at a temperature and pressure condition which actually corresponds to a point in the two phase region and not on the boundary. This fact will not result in a great uncertainty as long as the slope of the phase boundary lines vs. composition are small (as for example in the critical region), but will be more important remote from the critical region. A further disadvantage of the method is that it cannot be applied with success to systems whose coexisting phases have similar refractive indices and in the cases in which the liquid phase does not condense as a mist, but as a thin layer on the walls of the equilibrium cell. From the above reasoning it is clear that the method is applicable with success in the vicinity of the critical point, whereas most of the other methods considered suffer from serious disadvantages.

When dealing with multicomponent systems, it is important to point out that the facilities for detecting the phase transition and phase volumes have to be modified according to the number of degrees of freedom of the given system.

This method described in this section should be preferred for determining the solubility in dense gases in all the cases in which the phase behavior of the system is not qualitatively known. In other words, if there is any danger of phase changes occurring in the system investigated, simpler techniques, such as saturation methods, gives unreliable experimental results.

The usual way of determining dew and bubble points (saturation properties) at high pressure is the following: the sample volume/pressure is varied by injection or removal of mercury and the saturation point is visually observed as a phase formation or

disappearance. Bubble points can sometimes be detected as a break point in a pressure versus volume curve. The relative large sample volumes that are used in such cells make the re-establishment of equilibrium time consuming after a temperature or pressure change and the visual detection technique is in itself operator dependent and difficult to automate.

8.2. Examples

As mentioned in the pervious chapter, this method is widely used for determining T, P, x equilibrium data of binary and multicomponent mixtures in the critical region and for determining upper and lower critical end points. The solubility in dense fluid is rarely the only data measured with this group of apparatus, for this reason an extensive description of the cells is outside the scope of this review. The reader should refer, for example, to the papers published by the group working in Delft (Peters (1986), de Loos et al. (1983), Peters et al. (1987), De Leeuw et al. (1989)) for a complete description of the apparatus and methods, even if they rarely have applied their techniques to the measurement of the solubility of solutes in supercritical fluids.

An example of measurement of solubilities by this method is reported by Hong and Lucks (1992): they have used the apparatus previously developed by Fall and Luks (1984) and by Jangkamolkulchai and Luks (1989). They obtained solid-liquid-gas equilibrium data in which the solid phase is infinitesimal. This is accomplished by cooling down the solid-liquid system until crystals appear, and then slowly heating the stirred three-phase system until only a trace of crystals remains.

McHugh et al. (1988) have described an interesting apparatus for the determination of solubility of solids in dense gases. It is based on a variable volume view cell. The content of the cell can be projected onto a video monitor using a video camera linked to the boroscope which is part of the cell. Different phase transitions can be observed depending on the overall composition. The phase transition interesting for the determination of the solubility (i.e. the dew point) is detected by varying very slowly the pressure at constant temperature. The precision attained by the authors is comparable to those of other methods (error less than 2% in the solubility).

Micro sampling techniques (Fogh and Rasmussen, 1989) have been applied with great success to the saturation property measurements. The phase boundaries are determined from measurements of sample interaction with microwave energy. The sample is made part of microwave circuit that is sensible to changes in the dielectric properties of the sample. The microwave properties of the sample are in this way monitored while the pressure is reduced along an isotherm, beginning with a single phase sample. On a phase boundary the dielectric properties of the sample change because the sample is no

longer a homogeneous dielectric and the interfaces between the phases introduce reflections that were not present in the single phase sample. This is detected by the microwave circuit. The apparatus is computer controlled and completely automated. The technique has been used so far for investigating the phase behavior of petroleum fractions, but it can be used also for the determination of the solubility of a liquid in a dense gas (dew point).

Many cells and apparatus described in the static methods could have been included in this group. In fact the boundary between the dew- and bubble- point methods and the static methods (especially with the variable volume cell) is not well defined. McHugh et al. (1984) Occhiogrosso et al. (1986), Suppes and McHugh (1989) and Warzinski et al. (1992) are examples of apparatus, already described in the static methods section, which we could have classified in the dew- and bubble- point methods.

Recent applications and developments in this field are reported by Byun et al. (1996 and 2000).

9. SUPERCRITICAL FLUID CHROMATOGRAPHY

9.1. Principles and characteristics

An interesting alternative to the methods for measuring solubilities reported in the preceding sections comes from the use of a supercritical fluid chromatograph (SFC). This approach is very promising because chromatographic measurements are rapid, requires a small amount of solute, and inherently separates impurities from the solute. The chromatographic technique is extensively used in analysis and for the separation of a complex mixture in a wide range of pressure and temperature. For an overview of this technique see the monograph edited by Smith (1988). In analogy to the low pressure applications (GLC-LLC), it is possible to obtain thermodynamic properties, and hence solubilities in dense gases, from chromatographic data. The principle of operation of SFC is very simple: the supercritical fluid flows at high pressure through a column in which the stationary phase is loaded; the solute is injected before the column and it is distributed between the mobile and the stationary phases. The stationary phases normally used in the SFC are bonded phases.

The possibility of using the supercritical fluid chromatography for measuring solubilities derives from the basic relationships between retention and equilibrium properties. The retention properties are directly related to the equilibrium distribution of the solute between the phases through the dimensionless capacity factor.

$$k_i = \frac{t_i - t_o}{t_0} = \frac{x_i v^F V^S}{y_i v^S V^F} \tag{7}$$

where x and y are the mole fraction in the high and low density phases, respectively, v is the molar volumes of the mobile fluid (F) and the stationary (S) phase and V the total volume.

If the fugacity for the fluid phases is expressed as in eq. 4, eq. 7 becomes:

$$k_i = \frac{\varphi_i^F v^F V^S}{\varphi_i^S v^S V^F} \tag{8}$$

The main disadvantage in using this relation comes from the fact that in order to obtain the

φ_i^F, the value of φ_i^S (the fugacity coefficient of the solute i in the stationary phase at the system temperature and pressure) and the volumetric properties must be known. The calculation of φ_i^S is not straightforward in the case of bonded phases, for which the exact concentration of the stationary phase is not known. One possible approach is to assume Henry's law is valid in the stationary phase (the ∞ means that the solubility is normally so small that we can assume that the infinite dilution state is achieved):

$$\phi_i^{F\infty} = \frac{k_i H_i V^F v^S}{P v^F V^S} \tag{9}$$

The ratio $V^F v^S / V^S$ is a function of the column internal conditions and is of difficult a priori determination. This quantity can be determined by measuring capacity factors for a suitable reference solute (i.e. one for which φ_i^∞ is known). Once the fugacity coefficient is known, it is possible to calculate the enhancement factor and consequently the solubility of the solute in the compressed gas (see eq. 3).

Brown at al. (1987) and Bartle et al (1990) have shown that, by knowing the Henry's constant at the system temperature (and assuming very little variation of the Henry's constant with pressure, which is not always correct) and at least one known solubility at the same temperature, one can determine the variation of the solubility with pressure along that isotherm. Eckart and Eckert (1991) proposed to use two different mobile phases and calculate the ratio of the fugacity coefficients in the same stationary phase, thus canceling out the effects of retention mechanism other than bulk adsorption. This method allows direct determination of solubilities only if one of the two data is known and is based on the assumption that the stationary phase properties remain constant (i.e. they are not modified by the presence of a mixed mobile phase). This method is very

interesting for the determination of co solvent effects in the solubility of organics in supercritical fluids.

Another possibility (Kikic et al., 1991) is to determine the slope of the capacity factor versus density at constant temperature and calculate the partial molar volume of the solute at infinite dilution, thus again obtaining the variation of the solubility with pressure along an isotherm (the partial molar volume is directly proportional to the pressure partial derivative of the fugacity coefficient). The fugacity coefficient of the solute in the same stationary phase is obtained in a high pressure Gas Chromatograph (HPGLC), so that the absolute value of the solubility at the desired temperature and pressure is obtained.

All the authors cited above have obtained results consistent with those obtained with other "traditional" methods in their preliminary investigations.

If the object of the investigation is the determination of the variation of the solubility with pressure or the co solvent effect for the solubility in supercritical fluids then this method is very reliable, effective and recommended.

9.2. Examples

Several supercritical fluid chromatographs are available on the market and can be directly used for the solubility determination. The apparatus consists essentially of a pumping section, a column, a pressure reduction device and a detector. Substantial differences in the apparatus arise from the different capabilities of the part of which the measuring device is made up.

A schematic diagram of the apparatus is shown in Figure 7 (Brown et al., 1987). The system pressure is maintained using a back pressure regulator downstream of the UV detector. The pressure drop across the column strongly depends upon the fluid density and flow rate (for CO_2 and flow rate of 0.5 ml/min. is less than 2 bar). The measurement of the flow rates is another crucial problem and is currently made by a wet test meter downstream of the back pressure regulator. Column temperature stability is also important and should be as high as possible.

The column preparation can be done in different ways. The columns normally employed are packed columns. The use of capillary columns is at present restricted to analytical purposes and to determination of diffusion coefficients. The particular choice of column packing is based on the retention time obtained. In fact longer retention times are desirable because of the impact of experimental uncertainties in the retention time of the inert measurements is diminished. The injection of the solute in the column can be done either as a pure solute or as a solution with a solvent. In the latter case a pre column should be used to separate the solute and the solvent and to ensure that solubility

enhancement due to entrainer effects would not be a factor in measured residence times. The main characteristic of the solvents are the high volatility and the possibility to detect them with the UV detector (chloro-trifluoro-methane, carbon tetrafluoride). Particular care should be given to the calibration of the apparatus to account for the retention time of the solvent. Brown at al. (1987) suggested a test procedure for the selection of the solvent thus showing all the problems encountered by using this method. The precisions attained are ± 0.3 bar, ± 0.1K and about 2-3 % for the k values. This uncertainty strongly depends on the uncertainty of the net-retention-time.
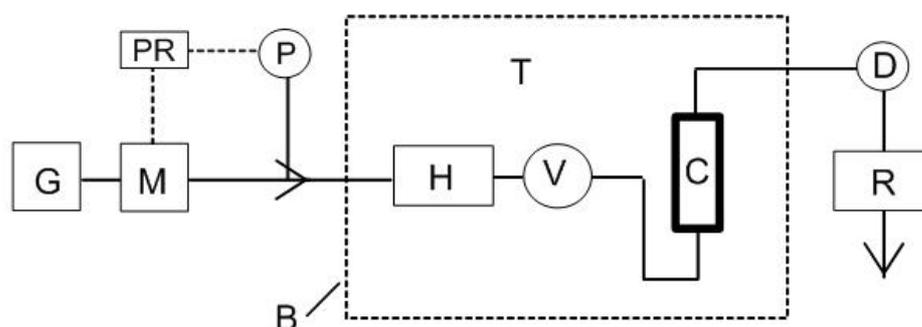

Figure 7. Schematic diagram of a supercritical fluid chromatography assembly: B, boundary of the thermostated compartment (oven); C, column; D, detector; H, pre-heater; M, pump; P, pressure transducer; PR, pressure programmer; R, restrictor; T, system temperature; V, injection valve.

Eckart and Eckert (1991) used a commercially available SFC with a UV detector and two capillary columns for measuring the co solvent effect in the solubility of solids in supercritical carbon dioxide. The mixtures of carbon dioxide + entrainer were prepared in advance in a bomb and then connected to syringe pump of the SFC. The solid solutes were injected in the SFC dissolved in n-pentane as solvent.

Most of the commercially available supercritical fluid chromatographs can be modified by including before the column an extractor (essentially an equilibrium cell), through which the supercritical fluid flows and is saturated by the substratum. Immediately after the extractor the flow is bypassed to the detector and analyzed. With this modification the apparatus becomes a saturation apparatus with the analysis performed by a UV or FI detector.

Direct measurement of the solubility is also possible with a supercritical fluid chromatograph if the solute is coated into the capillary column which is inserted between the injector and detector interface. The quantity of solute in the solvent (mobile phase) at a given temperature and pressure is determined by a mass spectrometer. This

method is the most costly and is limited to solute that may be coated (solids) into the column.

Other applications of SFC technique have been reported by Kragas et al. (1984), Yonker et al (1987), Kikic et al. (1991), Berger et al. (2000), Roth (2000).

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