Phase equilibrium data needs for the design of supercritical fluid extraction columns*

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Abstract: Fluid phase equilibrium data is essential for the design of supercritical fluid extraction columns. Examples are given of a feasibility study and an application to the design of a separation column involving the measurement of phase diagrams for ternary mixtures.

INTRODUCTION

Supercritical fluids have found applications as solvents in separation processes, especially in the extraction of valuable substances from natural products. CO_2, in particular, may provide clean alternatives to the environmentally unacceptable solvents currently used for many industrial scale processes. Most of the industrial uses of supercritical fluids have so far involved the manipulation of large quantities of solid material under pressure, as in the supercritical carbon dioxide coffee decaffeination process.

The promise of future applications lies however, in continuous separation processes from liquid matrices. In fact, it can lead to much lower operating costs than extraction from solids, as it is basically a continuous process that can be totally automated [1].

Those separations will typically be of one or several components from a complex mixture. This can be a fermentation broth, a reactive mixture of reactants, products and surfactants, an edible oil or a hydro-alcoholic extract from plants, for instance.

Industrial scale countercurrent fractionation columns will be needed. Methods for their design and scale-up from laboratory are known [1]. However, the physical property values that are essential in order to apply these methods are not well known yet for many systems of interest in possible applications. Supercritical fluid conditions involve high pressure and a high sensitivity of the density to pressure, temperature or composition. These combined make the measurement of physical properties much more complex than for conventional liquid solvents and solutions.

THE DESIGN OF COUNTERCURRENT LIQUID–SUPERCRITICAL FLUID EXTRACTION COLUMNS

The methods used to design this type of column are not essentially different from those for a standard liquid–liquid extraction unit. The concept of theoretical or equilibrium stage is well known [2]. The number of theoretical stages necessary to perform a certain separation can be calculated from phase equilibrium data alone. Although mass transfer and capacity of the column are also to be considered in order to obtain the actual size of a separation device, knowledge of relevant phase equilibrium ratios is a prerequisite in a design calculation.

In Fig. 1, two head-space chromatograms are represented. They were taken from a wine must (the fermentation broth that leads from grape juice to wine) and the corresponding extract obtained with

supercritical carbon dioxide, at 40 °C and 18 MPa [3]. The head space technique samples only the vapour phase in contact with the liquid, and it is not directly representative of the composition of the must and the extract. Some features are however, apparent:

1 The mixtures involved are extremely complex.

2 The proportions of the components in the feed mixture and in the extract are markedly different

Due to the complex nature of the mixtures, it is usually difficult to obtain meaningful phase equilibrium results with the real mixtures. Consequently, the definition of the problem usually starts with the choice of model mixtures of a few substances, each one representative of a class of compounds. For instance, in the example above, ethanol is the dominant component in both the feed and the extract. Two other substances were chosen to represent the 'lighter' and the 'heavier' fraction of the aroma, respectively: 3-methylbutanol (isoamylic alcohol) and 2-phenylethanol.
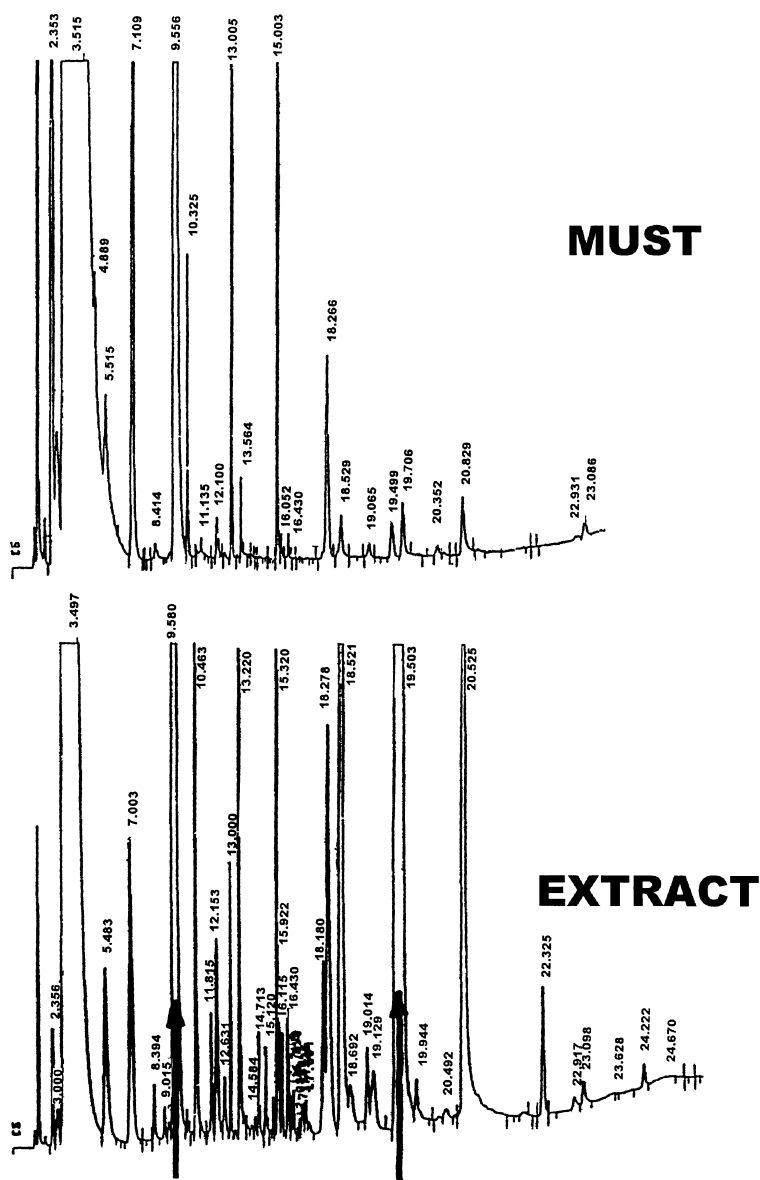

Fig. 1 Head-space chromatograms taken from a wine must and the corresponding extract obtained by supercritical CO_2. The large peak on the left is due to ethanol. The arrows indicate isoamylic alcohol (left) and 2-phenylethanol (right).

Exploring the phase diagram in terms of the critical lines that separate one, two and multiple-phase regions is the subsequent step. Finally, the two-phase region must be extensively studied, and compositions of the 'liquid' and 'gaseous' phases in equilibrium obtained, for wide ranges of pressure and total composition.

PHASE BOUNDARIES AND THE FEASIBILITY OF SEPARATION

The enhancement of the concentration of 2-phenylethanol in the extract, as seen in Fig. 1, suggested the possibility of fractionating wine must aroma with supercritical carbon dioxide. Extensive phase equilibrium measurements were performed on the binary mixtures $CO_2 +$ isoamylic alcohol and $CO_2 +$ 2-phenylethanol. In the first system, total miscibility between carbon dioxide and the alcohol is obtained above relatively low critical pressures (8.4 MPa at 40 °C). For $CO_2 +$ 2-phenylethanol, however, liquid-fluid phase separation is obtained up to the highest pressures in our work (27 MPa). Although these results seemed to contradict the conclusions that could be drawn from Fig. 1, studies with the ternary system $CO_2 +$ isoamylic alcohol + 2-phenylethanol confirmed high selectivity in the carbon dioxide-rich phase towards phenylethanol at pressures around 15 MPa and above. At lower pressures, the selectivity inverted, and below 10 MPa, isoamylic alcohol predominates in the gas.

In Fig. 2, equilibrium concentrations for the ternary system are plotted at two different pressures: 7 MPa and 10 MPa. At the lower pressure, only the liquid phase compositions are shown, as the gas phase line is too close to the pure CO_2 vertex to be distinguishable from it. The two phase area spans across the whole diagram, from one binary mixture to the other. At this pressure, however, no fractionation with supercritical carbon dioxide is feasible, because the solute concentration in the gas phase is too low. At 10 MPa, the pressure exceeds the critical pressure for the $CO_2 +$ isoamylic alcohol system. This is of course apparent in the ternary diagram, and the two phase region is limited by a critical concentration.
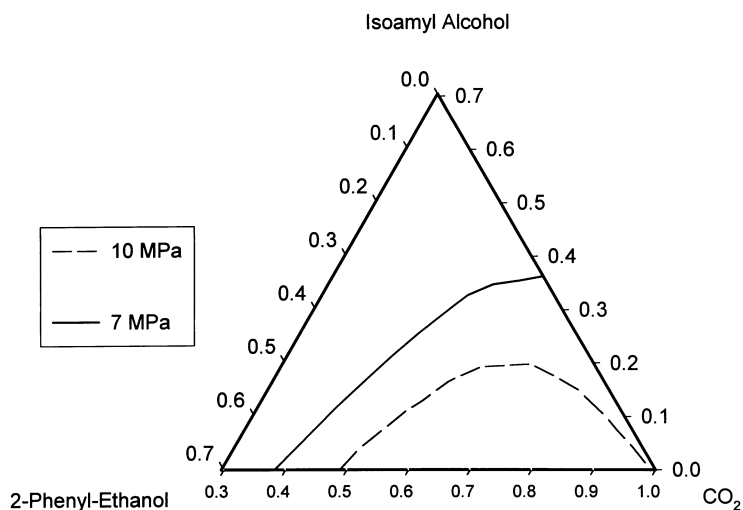

Fig. 2 Vapour–liquid equilibrium for the system isoamylic alcohol + 2-phenylethanol + carbon dioxide at 40 °C and two different pressures, 7 MPa (—) and 10 MPa (– – –).

As explained in [1] this situation implies that it is not possible to completely separate isoamylic alcohol from phenyl ethanol as bottom and top products in a fractionation column.

As stated above, the selectivity towards phenylethanol in the gas phase increases with pressure. At higher pressures (15 MPa, for instance) the two phase area in the diagram would be even smaller, and the critical concentration richer in phenylethanol. Consequently, more of this substance would be leaving the column, mixed with isoamylic alcohol, as raffinate (or bottom product).

GRAPHICAL METHODS FOR THE CALCULATION OF THEORETICAL STAGES—AN APPLICATION EXAMPLE

The simplest way to calculate the number of theoretical plates needed to achieve a separation is to model a mixture as a pseudo-ternary. One of the components will be the supercritical solvent and the other two representative components of the fractions at the bottom (raffinate) and at the top (extract) of the column. A graphical method can then be used.

In a recent publication [4], results on supercritical carbon dioxide de-acidification of olive oil were presented. In this case, free fatty acids are removed from a liquid matrix consisting mainly of triglycerides. The most abundant free fatty acid in olive oil is octadec-9-enoic acid (oleic acid) and the most abundant triglyceride is glyceroltrioleate (triolein). The separation can therefore be expressed on the basis of the ternary mixture carbon dioxide + triolein + oleic acid.

Figure 3 presents some results of a simulation of the de-acidification process carried out by Simões & Brunner [5]. The graphic plots the concentration profile of free fatty acids and triglycerides in the carbon dioxide-rich phase along a hypothetical column comprising eight theoretical stages. It can be seen that the free fatty acid content in the gas phase changes markedly along the extraction column. In fact, eight theoretical stages seem to be sufficient to completely de-acidify the olive oil (i.e. to obtain a free fatty acid content in the raffinate of less than 0.3 wt%). In order to design a column, information on the height equivalent to a theoretical stage is necessary. This can be obtained by combining phase equilibrium data with results of a separation actually carried out in a given column.
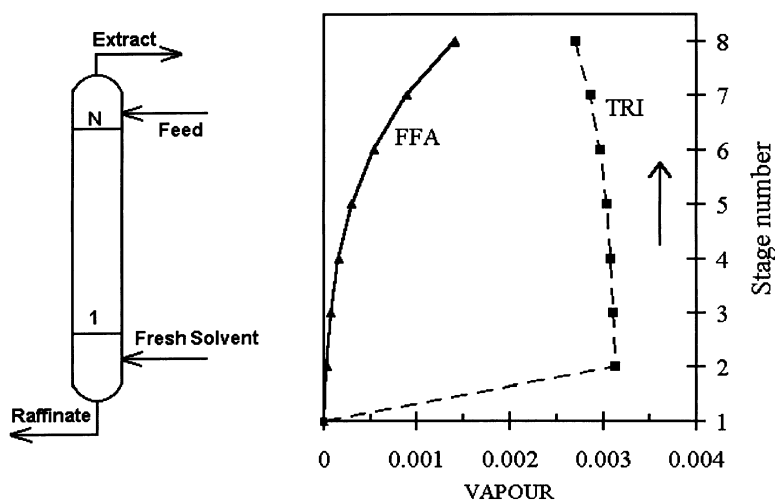

Fig. 3 Concentration profile of free fatty acids (FFA) and triglycerides (TRI) in the carbon dioxide-rich phase along a simulated column with eight equilibrium stages.

Phase equilibrium data for the binaries CO_2 + oleic acid and CO_2 + triolein and for the ternary carbon dioxide + triolein + oleic acid are available in the literature, from several authors [5–12]. There are, however, large discrepancies between the different sets of data. The most evident are the differences between the solubilities in carbon dioxide measured for each substance. The mass ratios of carbon dioxide over triolein at 40 °C and 18 MPa, for instance, vary from 155 to 476, while under the same conditions the ratios for oleic acid vary from 66 to 198.

The results available for ternary mixtures are scarcer. In our laboratory, we used a previously described extraction apparatus [4,13] to provide new data. The mass flow ratio of supercritical carbon dioxide to the liquid feed was adjusted to a low enough value, so that the conditions in the column would be as close to equilibrium as possible. This was done by measuring the extract composition at several diminishing solvent-to-feed flow ratios, and checking when a further reduction in the CO_2 flow would not change it significantly. The liquid feed to the column was olive oil with added oleic acid in different amounts, in order to obtain initial mixtures of varying composition. These are not truly ternary mixtures, because

olive oil is a complex ternary system. As explained above, the results were expressed in terms of triolein and oleic acid.

In Fig. 4, some of the results of this procedure are plotted, and compared with the results of Simões & Brunner [5]. These last values were obtained in a static equilibrium cell, with the same type of olive oil.
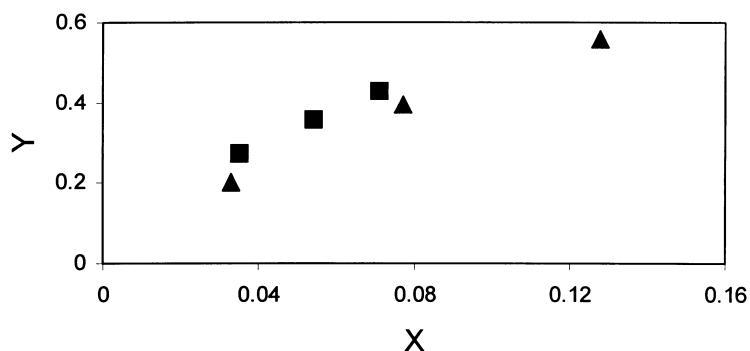

Fig. 4 Phase equilibrium data obtained by Carmelo *et al*. (■) and Simões *et al*. (▲). X and Y represent the mass fraction of Oleic acid on a solvent free basis in the liquid and vapour phase, respectively.

The differences shown in Fig. 4 can be partially attributed to the analytical method used in each case. In our work, the oleic acid was measured by titration, the acidity transformed into equivalent oleic acid content and the triolein amount in the sample calculated as the excess. In [5], the samples were analysed by gas chromatography. Components other than triglycerides and free fatty acids were detected and in particular squalene, which was present in considerable amounts in the gas phase (3–7 wt%, when in olive oil the average content is around 0.7 wt%). Another effect to be considered is that in a flow method, like the one we used, equilibrium conditions between the raffinate and the extract are never reached completely. Differences between our results and those of [5] were therefore to be expected.

These data were used to calculate the number of theoretical stages when the above mentioned extraction column [4,5] was used to de-acidify an olive oil of 7 wt% initial content in free oleic acid, with supercritical carbon dioxide, at 180 MPa and 40 °C.

As the compositions of each of the two phases in contact change markedly along the column, as shown in Fig. 3, the method to be used must take into account the amount of solvent present in each phase. A graphical method described by Brunner [1] was used. It is called the Ponchon–Savarit method and it involves the construction of a phase diagram for an equivalent ternary mixture called a Jänecke diagram. This is a graphic where the solvent ratio (mass of solvent divided by the mass of solutes) is plotted as a function of the mass fraction on a solvent free basis of one of the solutes. In this type of diagram, small differences in the solute concentration may appear much larger. This is especially true in supercritical fluid extraction, where the solute concentration in the gas phase is often of the order of 10^{-4}–10^{-2}. Data that differ by 0.001 mass fraction will appear in the ordinate of a Jänecke diagram at a distance of several hundred units.

Figure 4 shows that our results are in reasonable agreement with the data of Simões & Brunner [5]. When they are separately used in the Ponchon–Savarit method, they yield a height equivalent to a theoretical stage (HETS) for the column used in the deacidification process that differ by 60%.

If this is the case when essentially the same samples were used to obtain phase equilibrium data with different methods, much larger discrepancies would be obtained if data from other authors were included in the calculations. For instance, when all the results available in the literature [5–12] were used in the Jänecke diagram, the HETS obtained differ by 88%.

These examples are evidence that, even in relatively well studied cases, the peculiar conditions used in supercritical fluid extraction lead to large uncertainties in the design of separation devices. One of main factors to reduce these uncertainties will be the measurement (and eventually correlation or prediction) of accurate phase equilibrium ratios.

CONCLUSIONS

In the two examples discussed above, it was apparent that the existence of high pressure phase equilibrium results is the first necessary requisite in the analysis of any prospective supercritical fluid fractionation process. Due to the complexity of the mixtures involved and the difficulties inherent to the measurements themselves, there is a scarcity of reliable data that opens up new possibilities for experimental thermodynamicists.

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