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High-Pressure Phase Equilibrium Methodologies Applied to Food Systems

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Abstract In addition to new methods to produce safe, healthy and shelf-stable products, food industries aim to recover valuable products or to separate undesirable compounds from natural food matrices. One possible alternative to achieve this goal is to apply high-pressure technologies such as supercritical fluid extraction (SFE), pressurized liquid extraction etc. Phase equilibrium and thermodynamic properties of food systems as well as transport properties, such as viscosity, thermal conductivity, or diffusivity, are important parameters for the food industry. In the design and operation of such high-pressure technological processes, a large amount of reliable data on the equilibrium properties of materials is necessary, for instance, in the case of SFE the separation step in entirely depended on the phase equilibria of the extract and the supercritical fluid. Experimental techniques for high-pressure phase equilibrium measurements of substances relevant to the food industry are summarized in this review in terms of the advantages, disadvantages and common applications of the methods.

Keywords Food systems, High pressure, Supercritical fluids, Phase equilibria apparatus, Phase equilibrium

1. Introduction

Foods, a mixture of volatile and nonvolatile components, are considered multiphase systems composed of liquid, solid, and gaseous phases. A practical example is the partition between phases of flavor compounds that can change the perceived flavor of food during consumption due to the affinity of each compound for different phases [1].

The use of high pressure as a technology for pasteurization of different types of foods, such as juices, ham, sauces and seafood, has been a growing trend in the food industry sector since the 1990s [2].

Cheeses manufactured from pressurized milk achieve higher production yields compared with cheeses prepared using thermally treated milk [3].

High-pressure processing helps to retain the antioxidant activity of individual fruit juices and the intensity of green characteristics due to cell disruption and the subsequent leakage of pigments [4].

In 2014, more than 252 pieces of high-pressure equipment produced over 500000 metric tons of high-pressure-treated foods, which were placed on the market worldwide [2].

The knowledge of the phase equilibrium behavior of the volatile and nonvolatile fractions of foods is of crucial importance for many applications in the food industry, such as the design of distillation processes in alcoholic beverage production [5], the extraction of limonene from citrus peel [6], the extraction of phenolic compounds from cashew shell [7] and the separation of triacylglycerols from sardines [8].

The growing interest in the high-pressure carbon dioxide treatment used for the pasteurization and sterilization of liquid foods emphasizes the importance of a better understanding of the physical behavior of systems composed of water-based liquid food and carbon dioxide [9].

High-pressure processing claims to retain the sensory and nutritious value of food, maintaining the original freshness, color, flavor and taste. However, the high pressure may cause changes in the crystal structure of the lipids, thus changing the characteristics of the raw material [10].

The products of a process using supercritical fluids are frequently formed at high temperatures and pressures. For the recovery of heat and of the hydrocarbon products, a recovery process must be designed using phase equilibria as the basis [11].

The importance of reliable and precise experimental phase equilibrium data is unanimously recognized by the scientific community, although the accuracy of published experimental data does not always correspond to the accuracy claimed by the authors for the apparatus used [12].

The choice of an adequate experimental method for the determination of reliable and precise experimental phase equilibrium data should match the best compromise from the viewpoint of speed, simplicity and precision of measurements [13].

The fluid phase behavior of mixtures is inherently complicated at high pressures. Deviations from ideal behavior are stronger at high pressures than under ambient or

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low-pressure conditions, and the phase behavior is often more complex and difficult to predict with thermodynamic models. In the majority of cases, attaining these data is difficult and involves elevated costs [14].

A variety of experimental equipment and techniques designed to perform phase equilibrium measurements are available. However, such equipment typically requires a large volume of chemical species to obtain measurements. Therefore, new techniques and equipment must be developed to measure phase equilibrium data for small volumes over reasonable temperature and pressure ranges [15].

An understanding of the different methods and of the respective error sources is crucial. Experience and practical knowledge are essential because experimental problems and mistakes are seldom published [16].

A large number of recent scientific investigations concerning phase equilibrium for food systems has been published. Table 1 shows the literature search results from the “Scopus” database using the keywords “phase equilibria”, “experiments” and “food”.

Table 1. Number and type of documents published in the Scopus database between 2010 and 2014

Year	**Publications**
2014	350
2013	435
2012	364
2011	347
2010	278
Document Type	
Article	1261
Review	337
Book chapter	72
Conference paper	35

Table 2 provides a summary of the available literature review on the high-pressure phase behavior experimental methods.

Table 2. Reviews of experimental methods for phase equilibrium measurements

Publication	**Period**	**Reference**
Chemical Thermodynamics	1970 – 1980	[17]
DECHEMA Chemical Data Series	1970 – 1980	[18]
Fluid Phase Equilibria	1978 – 1987	[19]
Fluid Phase Equilibria	1988 – 1993	[20]
Fluid Phase Equilibria	1994 – 1999	[21]
Fluid Phase Equilibria	2000 – 2004	[22]
Fluid Phase Equilibria	2005 – 2008	[23]

Other interesting reviews that describe the specificity of certain methodologies have been published [14, 24-29].

This review summarizes various techniques available for measuring phase equilibrium data of substances that are relevant to the food industry in terms of main characteristics, advantages, disadvantages and common applications of each method. Initially, the food systems are shown, followed by descriptions of the methods to measure phase equilibrium data for these substances.

2. Food Systems

Most foods are multiphase dispersions structured either by nature, e.g., plant or animal tissues, or by man. The man-made structured foods use assembly or texturing processes, such as emulsification processes (e.g., margarine, ice cream, sauces, mayonnaise) or foaming (e.g., whipped cream, extrusion, dough kneading, baking) [30].

Fewer information sources that contemplate complex matrices or real foods can be found due to the variety and complexity of the chemical functional groups that compose these systems, such as proteins, carbohydrates, lipids, volatile oils and oleoresins. The determination of the phase equilibrium of these systems would not be trivial.

For the separation of components, it is necessary to know the phase equilibrium of the extract in the solvent of interest and of the pure components from the extract in the solvent of interest, as well as the mass transfer aspects of the process [31].

Vapor-liquid equilibria (VLE) are important in oxygen absorption during aerobic fermentation, in de-aeration of liquid foods, and in absorption or stripping of carbon dioxide. Liquid-liquid equilibria (LLE) of two partially miscible phases can be represented in triangular diagrams (equilateral or right-angled). Each of the corners of the triangle represents a pure component, and the two-phase region is enveloped by an equilibrium line [32].

The knowledge of solid–liquid boundaries and of the behavior of simple fatty systems can be helpful to understand the physical properties of complex lipids and their mixtures [33].

For process design, phase equilibrium data for real systems are more appropriate. The sorption of oxygen on solid foods is related to the oxidation of lipids and other labile components. Vapor-solid equilibria (VSE) are important for the study of the behavior of these compounds. The equilibrium data can be fitted to semi-empirical relationships, such as the Freundlich, the Langmuir, and the Brunauer-Emmett-Teller (BET) equations [32].

2.1. Nonvolatile Fraction

2.1.1. Water

Water is an important and common solvent in chemistry and is the main component in most foods. Water in food systems acts as a solvent and as a plasticizer in low-water food solids and in freeze-concentrated solids in the unfrozen phase.

Equilibrium properties of water such as water activity are considered reference properties in food processing in freezing, dehydration, evaporation, and high-pressure processing [34]. However, the presence of water in certain systems can have undesired effects on their properties. Examples of susceptible systems include powdered foods, agricultural chemicals, explosives, nutraceuticals, and pharmaceuticals [35].

2.1.2. Carbohydrate Solutions

Carbohydrate solutions have many applications in the food and pharmaceutical industries. Solubility data for these solutions are needed for many process designs, such as separation and purification processes [36].

Carbohydrates can also lead to retention of flavor compounds in the matrix. This reduction in volatility is due to interactions that can occur between carbohydrates such as starches and flavor compounds [37].

Interactions between proteins and polysaccharides in aqueous systems influence the phase behavior of such ternary blended systems, impacting their structural and textural properties, hence affecting their stability [38].

Almost all empirical correlations developed to design, analyze, optimize or control industrial sugar processes are based on a ternary system characterization: sugar, sucrose, non-sugar and water. Despite extrapolation problems related to these correlations, the characterization using a ternary system cannot take into account phenomena such as degradation reactions or specific effects of some impurities on sucrose solubility [39].

2.1.3. Ethanol

Ethanol in foods can be present as a product of agri-food waste fermentation, a residue after baking, an additive in packed products and an ingredient in candies, confectionery products, sweets, etc. Liquid-vapor partition of ethanol in aqueous systems depends not only on environmental factors such as temperature and water activity but also on its concentration and on the nature and concentration of other compounds that can be present in the food matrix [40].

Several drinks with low ethanol content or without ethanol have been introduced to the market in recent years. Reduction of ethanol content in alcoholic drinks can be accomplished by restricting fermentation or by removing ethanol after the complete fermentation process [41].

The thermodynamic modeling of the CO_2-SFE de-alcoholization of drinks can be carried out representing the beverage as the ethanol + water binary mixture because other components in alcoholic beverages usually represent less than 1% [42].

In the assessment of volatiles in grape and wine, the matrix consists predominantly of the nonvolatile components including sugars, ethanol (in wine) and water (Figure 1). Organic acids, amino acids, phenolic compounds and inorganic ions in water are part of the volatile fraction [43].

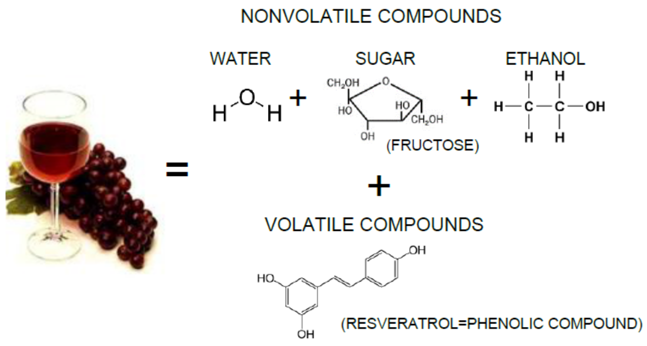

Figure 1. Multicomponent system existing in wine

2.1.4. Lipids

Fatty acids are the major components of oils and fats, and they have critical implications in the understanding of the biological behavior of various lipid systems. Fatty acids have recently been used in the production of coverings, plastics, and cleaning products, phase change materials for energy storage and biodiesel [10].

Vegetable oils consist mainly of triglycerides, with a low fraction of diglycerides, free fatty acids and a number of minor components (sterols, tocopherols, phospholipids, etc.) that have added value as pharmaceuticals and food additives [44].

Lipids are the food ingredients that have been shown to have the most effect on the partitioning of flavor compounds between product and vapor phase [37].

The raw material for the production of omega-3 oils is typically represented by fish oils. Most of the fatty acid chains in fish oil triglycerides have a number of carbon atoms ranging from 14 to 22. Fractionation processes are usually performed on fish oil ethyl esters (FOEEs) to obtain a considerable enrichment in a specific fatty acid, where using supercritical CO_2 is a potential alternative [45].

2.1.5. Proteins

The increasing commercial interest in the contents of protein have led to extensive studies to extract, and/or isolate the proteins [46].

Food proteins have little flavor of their own but are known to bind and trap aroma compounds. Depending on the nature and the strength of the binding, the release of aroma compounds in the vapor phase will be more or less decreased, and this decrease will have a significant impact on the overall aroma perception due to changes in the aromatic balance [47].

Purification of recombinant proteins makes high demands on downstream processes as the target proteins have to be separated from very similar protein variants to very high purities. Among different separation modes such as size exclusion, hydrophobic interaction or affinity chromatography, ion exchange chromatography (IEC) is commonly used; therefore, it is a major unit operation in the purification processes of therapeutic proteins [48].

2.2. Volatile Fraction

2.2.1. Pigments

At low and moderate temperatures high-pressure technologies have a limited effect on pigments (e.g., chlorophyll, carotenoids, anthocyanins, etc.) responsible for the color of fruits and vegetables. The high-pressure process increases the extraction yields of carotenes from the plant matrix and in many cases, increases the intensity of chlorophyll in green vegetables [49].

The volatile products of the degradation of carotenoids can be desirable, as in black tea and wine where they become part of the characteristic aroma. In some processed foods, however, degradation/cleavage of carotenoids is undesirable because it is responsible for the appearance of an off flavor, as in dehydrated carrots and in certain types of wine [50].

Processed mango pulp retained a maximum of 85, 92 and 90% of its original ascorbic acid, total phenolics and in-vitro antioxidant capacity, respectively using high pressure processing at 100 – 600MPa, 303K during 1-20 minutes [51].

2.2.2. Vitamins

Vitamins are usually present at low levels and are accompanied by other compounds. Extraction from foods requires specific conditions, depending on the stability of each vitamin with pH, temperature, light, and oxygen, and its bond to the food matrix [52].

In the chemical and pharmaceutical industries, vegetable oils and their distillates from oil refining are principal sources of valuable components such as squalene, vitamins, sterols and fatty acids [53].

Vitamin C is one of the most important vitamins; thus, reliable information about its content in foodstuffs is a concern to both consumers and quality control agencies [54].

Alpha-Tocopherol is a member of the vitamin E family representing the high biological activities. Most tocopherols are obtained by energetically intensive vacuum distillation of deodorizing step residues generated in the refining of vegetable oils, including several steps such as solvent recovery and purification associated with abundant amounts of organic solvents [55].

2.2.3. Volatile Oils

The volatile oils (or essential oils) are a multicomponent mixture of terpenoids (mono-, sesqui-, and diterpenes, various alcohols, ketones, and aldehydes of terpenoids). Considering the similarities and differences between both types of fluids (mineral oils and volatile oils), it is not surprising that the thermodynamic description and/or prediction of the phase behavior and other related thermodynamic properties of systems with volatile oils is much more problematic [56].

Citrus oils are mixtures of over a hundred compounds, including terpenes, oxygenated compounds, and nonvolatile compounds [57].

Orange volatile oil is widely used in the food industry as an additive, conferring taste to diverse products such as ice cream, candies, carbonated beverages and cakes [58].

The removal of monoterpenes from citrus oils, which is the so-called de-terpenation process, is a common industrial practice that obtains a product more stable and more soluble in water, while maintaining its characteristic flavor and fragrance [59] as shown briefly in Figure 2.

Figure 2. Terpene (limonene) obtained from citrus peel volatile oils

Understanding the physicochemical interactions that occur between aroma compounds and other food constituents is also of great importance when considering each step of the production process. For example, encapsulation may be required to control flavor losses that occur during heating and storage. Eating could also be considered to be a unit operation during which volatile compounds are released in the mouth [60].

The implementation of high-pressure technologies in food industry requires the knowledge of many properties in order to design efficient process that will permit to achieve the expected quality and the stability of the processed products.

3. Thermophysical Properties of Foods

Thermophysical properties can be defined as material properties that vary with temperature without altering the chemical identity of the material, such as density, enthalpy, entropy, viscosity, Joule-Thomson coefficient, thermal conductivity, thermal diffusivity, refractive index, and others.

Since many stages in the processing and preservation of foods involve heat transfer, it is important to understand the thermophysical properties of foods. An energy balance for heating or cooling process cannot be made and the temperature profile within the material cannot be determined without knowing the thermophysical properties of these materials [61].

An appropriate modeling implies a precise knowledge of the thermophysical properties of the involved materials. In the case of conductive heat transfer, thermophysical properties include density, thermal conductivity and specific heat. When the process to model involve a change of phase, the ice fraction, the enthalpy and the initial freezing point are important [62].

The variation of enthalpy can be used to estimate the energy that must be added or removed to effect a temperature change. Above the freezing point, enthalpy consists of sensible energy; below the freezing point, enthalpy consists of both sensible and latent energy. Enthalpy (expressed in

Joule, or J) may be obtained from the definition of constant-pressure specific heat:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1}$$

Where C_P (kJ/kg°C) is constant pressure specific heat, H is enthalpy, and T is temperature (°C). Mathematical models for enthalpy may be obtained by integrating expressions of specific heat with respect to temperature.

For a phase change process involving either melting or freezing, energy conservation can be expressed in terms of total volumetric enthalpy and temperature for constant thermophysical properties [63].

For cases where there are no experimental values of C_P, it is possible to estimate its value using group contribution methods, such as Joback [64] and Constantinou and Gani [65].

Thermal conductivity relates the conduction heat transfer rate to the temperature gradient and it is dependent of composition, structure, and temperature [62].

$$k = k_C \frac{1-\left\{\left[1-a\left(\frac{k_D}{k_C}\right)\right]b\right\}}{1+\left[(a-1)b\right]} \tag{2}$$

Where k (W/m°C) is the thermal conductivity of the mixture, k_C (W/m°C) is the thermal conductivity of continuous phase, k_D (W/m°C) is the thermal conductivity of the dispersed phase,

$$a = \frac{3k_C}{(2k_C + k_D)} \tag{3}$$

$$b = \frac{V_D}{(V_C + V_D)} \tag{4}$$

V_D (ml) is the volume of the dispersed phase and V_C (ml) is the volume of the continuous phase. For transient heat transfer, the important thermophysical property is thermal diffusivity, α, which appears in the Fourier equation:

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right] \tag{5}$$

Where x, y and z are Cartesian coordinates, T is the temperature and t is the time (s).

Thermal diffusivity (α), expressed as m^2/s, is used in the determination of heat transfer rates in solid food objects of any shape. Physically it relates the ability of a material to conduct heat to its ability to store heat [66].

This term is defined in the Equation 6:

$$\alpha = \frac{k}{\rho C_P} \tag{6}$$

Where is the density (kg/m^3).

Phase stability during freezing melting would help towards setting heat storage and high density is desirable to allow a smaller size of storage container. Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem [63].

In literature are available a multitude of food items. In Table 3 are summarized thermophysical properties correlations of the main food components.

4. Classification of Phase Equilibrium Methodologies

The methodologies used to obtain phase equilibrium data for food systems are based on the classification systems proposed by Dohrn et al. [22] depending on how the composition of the two coexisting phases is determined, the methods are divided into analytical and synthetic.

At high pressures, the classification of experimental methods is not always simple. In addition, the expression “elevated pressure’’ is relative [23].

Any method for determining reactive phase equilibrium will be analytical in that it has to rely on some analysis of the phase composition, most often accomplished via gas chromatography (GC). Moreover, because conversion is unavoidable, one is concerned with multicomponent mixtures [69].

In the synthetic approach, known amounts of pure substances are charged in a temperature- and pressure-controllable view cell. The overall composition of the mixture is known as well as the volume occupied by the compounds, and the temperature or the pressure is adjusted until a homogeneous phase is obtained [70].

Publications [13, 71-73] have classified these methods, according to the regime of the process, into static (subdivided into analytical and synthetic methods) and dynamic (subdivided into continuous flow and circulation methods) depending on the technique used for equilibration of the phases.

Static methods may be further divided into two categories (analytical and synthetic) according to the type of adopted vessel. In the dynamic methods, one phase is in contact with the other phase, and the adopted operative conditions are chosen so that the outlet streams can be assumed to be at equilibrium [13].

However, static and dynamic methods were considered a subdivision of analytical methods by Fornari et al. [19] who investigated the methods and systems in the period 1978-1987.

To inform the reader through a historical approach, Figure 3 shows a diagram for classification of experimental methods for phase equilibrium measurement divided by the periods of 1990 and 2010.

Table 3. Thermophysical properties for food components (-40 ≤ T ≤ 150ºC)

Food Component	Thermophysical property Model	Reference
Ash	$\rho = 2423.8\text{-}0.28063\text{T}$	[67]
	$\text{C}_\text{P} = 1.0926\text{+}1.8896\times10^{-3}\text{T-}3.6817\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 3.2962\times10^{-1}\text{+}1.4011\times10^{-3}\text{T-}2.9069\times10^{-6}\text{T}^2$	[67]
	$\alpha = 1.2461\times10^{-7}\text{+}3.7321\times10^{-10}\text{T-}1.2244\times10^{-12}\text{T}^2$	[68]
Carbohydrate	$\rho = 625.59\text{-}0.41757\text{T}$	[67]
	$\text{C}_\text{P} = 1.5488\text{+}1.9625\times10^{-3}\text{T-}5.9399\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 1.8071\times10^{-1}\text{-}2.7604\times10^{-4}\text{T-}1.7749\times10^{-7}\text{T}^2$	[67]
	$\alpha = 8.0842\times10^{-8} + 5.3052\times10^{-10}\text{T-}2.3218\times10^{-12}\text{T}^2$	[68]
Fiber	$\rho = 1311.5\text{-}0.36589\text{T}$	[67]
	$\text{C}_\text{P} = 1.8459\text{+}1.8306\times10^{-3}\text{T-}4.6509\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 1.8331\times10^{-1} + 1.2497\times10^{-3}\text{T-}3.1683\times10^{-6}\text{T}^2$	[67]
	$\alpha = 7.3976\times10^{-8} + 5.1902\times10^{-10}\text{T-}2.2202\times10^{-12}\text{T}^2$	[68]
Lipid	$\rho = 1599.1\text{-}0.31046\text{T}$	[67]
	$\text{C}_\text{P} = 1.9842\text{+}1.4733\times10^{-5}\text{T-}4.8008\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 2.0141\times10^{-1} + 1.3874\times10^{-3}\text{T-}2.7178\times10^{-6}\text{T}^2$	[67]
	$\alpha = 9.8777\times10^{-8} - 1.2569\times10^{-10}\text{T-}3.8286\times10^{-14}\text{T}^2$	[68]
Protein	$\rho = 1329.9\text{-}0.5184\text{T}$	[67]
	$\text{C}_\text{P} = 2.0082\text{+}1.2089\times10^{-3}\text{T-}1.3129\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 1.788\times10^{-1} + 1{,}1958\times10^{-3}\text{T-}2.7178\times10^{-6}\text{T}^2$	[67]
	$\alpha = 6.8714\times10^{-8} + 4.7578\times10^{-10}\text{T-}1.4646\times10^{-12}\text{T}^2$	[68]
Water	$\rho = 997.18\text{+}3.1439\times10^{-3}\text{T-}3.7574\times10^{-3}\text{T}^2$	[67]
	$\text{C}_\text{P} = 4.1762\text{-}9.0864\times10^{-5}\text{T-}5.473\times10^{-6}\text{T}^2$	[67]
	$\text{k} = 5.7109\times10^{-1} + 1.7625\times10^{-3}\text{T-}6.7036\times10^{-6}\text{T}^2$	[67]
	$\alpha = 1.3168\times10^{-7} + 6.2477\times10^{-10}\text{T-}2.4022\times10^{-12}\text{T}^2$	[68]

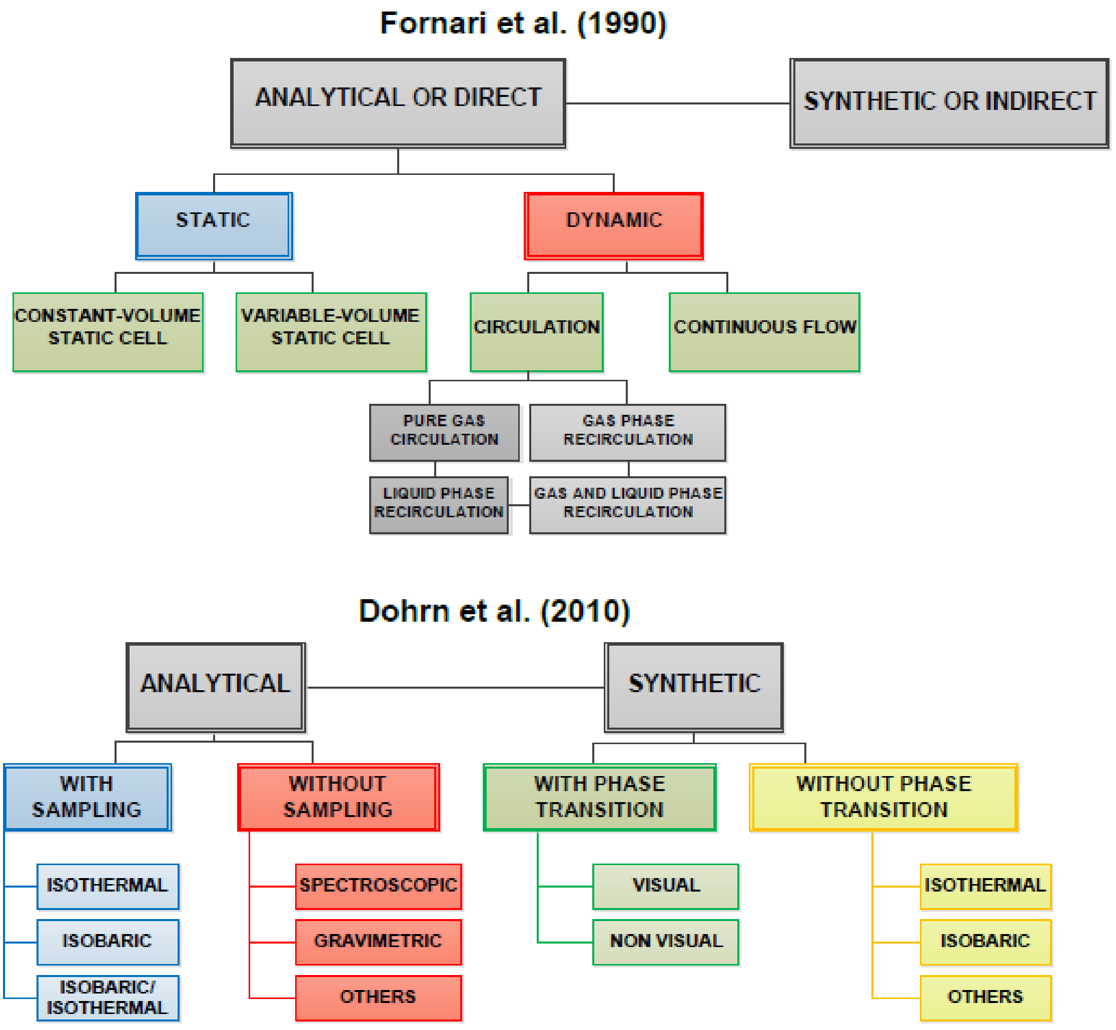

Figure 3. Classification of high-pressure phase equilibrium experimental methods

The variety of experimental methods is even more confusing to the reader because different authors use different names for the same method, and the expressions 'static' and 'dynamic' are used in connection with many different methods [22].

In addition to the confusion in nomenclature, mixing the terms in some papers further complicates the understanding. For example, "isothermal" vapor–liquid equilibrium (according to the phase transition) data using an apparatus based on the "static-analytic" (a method according to the process regime) equipped with a movable ROLSI^{TM} capillary [74].

A "dynamic-analytical" technique was used to measure the solubility of β-carotene in carbon dioxide (CO_2), triolein-modified CO_2 and in ethanol-modified CO_2 using a stirred equilibrium cell with sapphire windows for visual observations, syringe pump to reach the desired system pressure and after reaching equilibrium, the samples were analyzed by high performance liquid chromatography, HPLC [75]. The description of such a method suggests the classification as an analytical isobaric-isothermal method, which are often called dynamic methods.

5. Analytical Methods

The determination of the composition from the coexisting phase by sampling each of them is involved in analytical methods. The samples are analyzed inside (spectroscopy) or outside (refractometry, chromatography or pressure drop) the equilibrium cell.

The drawback of this method is that the withdrawal of the samples of equilibrium phases from the cell can easily modify the equilibrium of the system, and their transport to analytical devices might change their homogeneity [70].

Sampling at high pressures is a hard task, and it can cause disturbances in the equilibrium. The sample may not be representative of the desired phase [76].

According to the withdrawal of the samples from the equilibrium cell, analytical methods are subdivided into isothermal, isobaric and isobaric-isothermal. Analytical methods are dependent on the procedure used to achieve the equilibrium [22].

5.1. Analytical Methods with Sampling

5.1.1. Isothermal

The temperature of the system is maintained constant during the equilibrium. The other equilibrium properties like the pressure and the composition of the phases reach equilibrium values, depending on other variables like mole numbers and volume.

Before taking samples from the coexisting phases, the mixture is given sufficient time without stirring, rocking or recirculation for the separation of the phases. Otherwise the sample might not be homogeneous but contain material from another phase, e.g. droplets, bubbles or solid particles [22].

A two-phase mixture is enclosed in a pressure vessel with no phase recirculation. Equilibrium is attained via rapid agitation, usually through efficient stirring, and the vapor and liquid phases are carefully sampled and analyzed at equilibrium [77].

At the beginning of an experiment, an equilibrium cell is charged with the substances of interest. The pressure is adjusted above or below the desired equilibrium value, depending on whether the pressure will rise or fall during equilibration [21].

VLEs of β-caryophyllene+CO_2 were obtained by the recirculation method, with an apparatus consisting of two isothermal chambers (one loaded with solute and another empty) where CO_2 is fed to both chambers up to the desired pressure. Then, the gas phase is continuously recirculated (for approximately 6 h) between the two chambers to reach equilibrium in the cell. After the recirculation period, the two chambers are separated by closing valves to allow the whole content of the gas chamber to be sampled [78].

Isothermal recirculation methods appear aim at solving the problem of pressure drop inherent to the withdrawals of samples and are based on the circulation of one phase, for example, volatile substance as vapor are entered into the liquid, and the exit vapor is analysed [79].

5.1.2. Isobaric

Both the vapor and the liquid phase circulate continuously to provide intimate contact of the phases [80]. Tipically, isobaric experiments are performed in an ebulliometer [23]. A mixture of known composition is brought to a boil at a controlled pressure.

Isobaric vapor–liquid equilibrium data for the binary system of cinnamaldehyde and benzaldehyde (natural flavors from cinnamon oil) were measured in a circulation VLE-type still (a modified Othmer still), in which pressure was maintained constant by using a vacuum pump. Later, a given liquid solution was charged into the equilibrium still and heated, when condensed vapor was delivered to the mixing chamber through the vapor-phase sampling port and continuously circulated to provide intimate contact of the phases to reach equilibrium. Finally, samples of the equilibrium phases were taken out from a vapor and liquid sampling port, respectively [81].

Isobaric vapor–liquid equilibrium (VLE) data for the reactive quaternary system ethanol+water+ethyl lactate +lactic acid have been determined experimentally in an all-glass still of the Gillespie type with circulation of both the liquid and vapor phases [82].

Sampling through capillaries can lead to differential vaporization and scattering results, especially for mixtures containing light and heavy components when no precautions have been taken to prevent a pressure drop all along the capillary [23].

5.1.3. Isobaric-Isothermal

In isobaric-isothermal methods, sometimes called “dynamic methods”, one or more fluid streams are continuously pumped into a thermostatted equilibrium cell. The pressure is kept constant during the whole experiment by controlling an effluent stream, most commonly the vapor phase, using a back-pressure regulator [23].

This method is used to determine the solubility of a low-boiling (liquid or solid) substance in a supercritical fluid. A difficulty is to guarantee the complete saturation of the phase vapor in the output of the saturator. This method does not permit the phase transition visualization, and it is restricted to two-phase equilibrium mixtures [21].

Semi-flow, continuous flow and chromatographic methods are classified as isobaric-isothermal methods.

A semi-flow type phase equilibrium apparatus was used to investigate the solubility of ergosterol, a natural phytosterol exhibiting cholesterol-lowering properties. Ergosterol is of particular interest to the food and nutraceutical industries in supercritical carbon dioxide, where it is pumped at the head by an air-driven booster pump, to the extraction cell with a pressure rating of 70MPa housed in an oven with a temperature controller. To establish dynamic flow, an on-off valve at the cell outlet is opened to allow flow through a pressure-reducing micrometering valve [83].

Caffeine solubility in CO_2 and the co-solvents ethanol and isopropanol were measured in a semi-continuous flow apparatus [84].

When a semi-flow method is used for the measurement of vapor–liquid equilibria, the composition of the liquid phase needs to be determined. Therefore, a sample from the liquid phase is withdrawn through tubing, depressurized, and analysed [22].

The continuous-flow method was adopted using a static mixer followed by a cyclone separator that separates vapor and liquid phases of the systems CO_2+limonene+citral, and CO_2+limonene +linalool [85].

Chromatographic methods measure solute retention in a chromatographic column and connect it with the Gibbs energy of solute transfer between the stationary and the mobile phases [23].

A gas–liquid chromatography method was used to experimentally determine the vapor pressure to obtain solubilities of phenolic compounds in supercritical CO_2

using a method based on the residual chemical potential in terms of the virial coefficients and fluctuation theory [86].

5.2. Analytical Methods without Sampling

5.2.1. Spectroscopic

Non-invasive spectroscopic methods, such as in situ NIR (near infrared) or Raman spectroscopy, have been used. In the NIR region, the optical density of water is sufficiently low to measure the absorption of other compounds next to water.

However, NIR absorption requires two optical windows oriented in the line of sight (exceptions such as attenuated total reflection absorption spectroscopy are given above), while a Raman sensor operating in the back scattering configuration requires only one window. Furthermore, the Raman effect can be excited with visible laser radiation while the radiation used in the NIR absorption method is invisible [87].

Measurement of LLE for δ-tocopherol+CO_2 compositions were performed by chemical analysis of samples withdrawn from the top and bottom phases in the cell, which are taken by expansion through chromatographic valves into a small volume [88].

The solubility of caffeine, theophylline and theobromine in supercritical carbon dioxide was measured by direct coupling of an equilibrium cell to a supercritical fluid chromatographic (SFC) system [89].

The solubility of caffeine in supercritical CO_2, supercritical CO_2+water, supercritical CO_2+ethanol, and supercritical CO_2+water+ethanol were measured with a circulation-type apparatus combined with an on-line Fourier transform infrared (FTIR) spectrometer at 313.2K and 15MPa [87].

5.2.2. Gravimetric

The analytical or static gravimetric technique involves keeping the solute in a small vial where it is subjected to a pressure vessel that contains supercritical fluid. The supercritical fluid dissolves the solute in the vial and brings the dissolved material out from the vial. Eventually, an equilibrium state is achieved. Then, the vessel is depressurized, and the remaining solute is weighed gravimetrically [90].

These methods are based on the monitoring of the mass of a nonvolatile condensed phase, such as a polymer or an ionic liquid in phase equilibrium with a fluid phase. Using additional information like the phase densities, the phase composition can be determined [23].

The solubility of CO_2 and N_2O in olive oil has been measured with a gravimetric microbalance that consists of an electrobalance with sample and counterweight components inside a stainless steel pressure-vessel [91].

5.2.3. Others

Experimental methods for the investigation of phase equilibria that do not fall into the classification as described by Dohrn et al. [22] are designated as other methods. Solubility of β-carotene in the binary system was measured using a quartz crystal microbalance technique at temperatures of 313 and 323K and at pressures ranging from 12 to 20MPa [92].

6. Synthetic Methods

In this technique, no sampling is necessary to determine equilibrium compositions [93].The overall composition of the mixture is known and its behavior is observed as a function of pressure or temperature that is adjusted until a homogeneous phase is obtained.

Synthetic methods can be used when the coexisting phases have similar density [94] such as in the critical region [21].

These methods are applied when the analytical path fails, i.e., when the phase separation is difficult due to the similar densities of the two phases or in barotropic systems where, under certain conditions, the densities of the two coexisting phases have the same value

The problems associated with analyzing the composition of an equilibrium mixture are replaced by the problem of synthesizing the equilibrium mixture and effectively observing its behavior. The classification is based on the means of observation for the appearance of a new phase. Synthetic methods are based on the presence or absence of a phase transition [22].

For multicomponent systems, experiments with synthetic methods yield less information than those with analytical methods because the tie lines cannot be determined without additional experiments. Therefore, synthetic methods are used mainly for binary or pseudo-binary systems [23].

6.1. Synthetic Methods with Phase Transition

6.1.1. Visual

The appearance of a new phase is detected by visual observation from a cell provided with a transparent window resulting in a turbidity or the appearance of a meniscus in a view cell [93]. One advantage of this method is that unusual behaviors, like foaming, can be visualized.

Also called the “static synthetic” method, the main advantage is to dismiss the withdrawal of samples of the phases and, consequently, to preserve the equilibrium state. Another advantage is the least use of chemical species, reducing the cost with the experiment [95]. For iso-optic systems where the coexisting phases have approximately the same refractive index, visual observation is impossible [23]. Solubility measurements of sunflower, castor and rapeseed oils in CO_2 were performed in a variable volume high pressure cell that consists of a horizontal hollow stainless steel cylinder, closed at one end by a movable piston and at the other end by a sapphire window that allows a visual observation of the interior of the pressure cell [96].

The high-pressure phase behavior of the systems carbon dioxide + limonene + linalool [57] and ethane + orange peel oil [97] were determined using a Cailletet apparatus. At any desired temperature, the pressure is varied for a sample of constant overall composition until a phase change is observed visually.

LLE Aqueous two-phase poly (ethylene glycol)–sodium polyacrylate system, using the using the turbidimetric titration method, which poly (ethylene glycol)–stock solution (1.0g) was added to a glass tube and titrated with small aliquots of the sodium polyacrylate stock solution, approximately (0.01–0.05)g, until the solution became turbid, indicating the formation of a two-phase system [98].

The “vanishing point” method was used to measure the solubility of lycopene in mixtures of CO_2 and ethyl acetate, performed in a variable volume high pressure equilibrium cell, equipped with a stirrer to improve mixing of the phases, four sapphire windows and a heating jacket which allows adjusting a constant temperature [99].

Recently experimental data for food and pharmaceutical compound were acquired [100-102] using the synthetic visual method in a high-pressure variable-volume view cell. Briefly, the apparatus consists of a variable-volume view cell, with a maximum internal volume of 27 cm^3, with two sapphire windows for visual observations, an absolute pressure transducer, a portable programmer for the pressure data acquisition and a syringe pump. The equilibrium cell contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually through manipulation of the pressure using the syringe pump and the solvent (carbon dioxide) as a pneumatic fluid.

Figure 6 shows the experimental apparatus adapted to the reality of our research group from Lasefi (FEA/Unicamp): a HPLC pump (Thermoseparation Products, ConstaMetric, 3200 P/F Fremoni, USA) takes place the syringe pump (ISCO, 260 D, USA).

6.1.2. Non-visual

Other physical properties can be monitored to detect phase transitions, i.e., if the total volume of a variable volume cell can be measured accurately, the appearance of a new phase can be obtained from the abrupt change in the slope on the pressure-volume plot more accurately than it can be done on the basis of visual observations [93].

6.2. Synthetic Methods without Phase Transition

In synthetic methods without a phase transition, equilibrium properties like pressure, temperature, phase volumes and densities are measured and phase compositions are calculated using the material balance. They can be divided into isothermal, isobaric and other synthetic methods [104].

6.2.1. Isothermal

They are often designated as “static method” or “isothermal pTx method” and the temperature remains constant. The phase compositions are calculated through the application of a material balance. The most common application of this type of methods is in the determination of solubilities of gases in condensed phases [21].

Solubility of boldine (antioxidant compound from boldo leafs) in sub- and supercritical CO_2 was measured at 298, 308, 313, 323 and 333 K, and over a pressure range from 8 to 40 MPa [105].

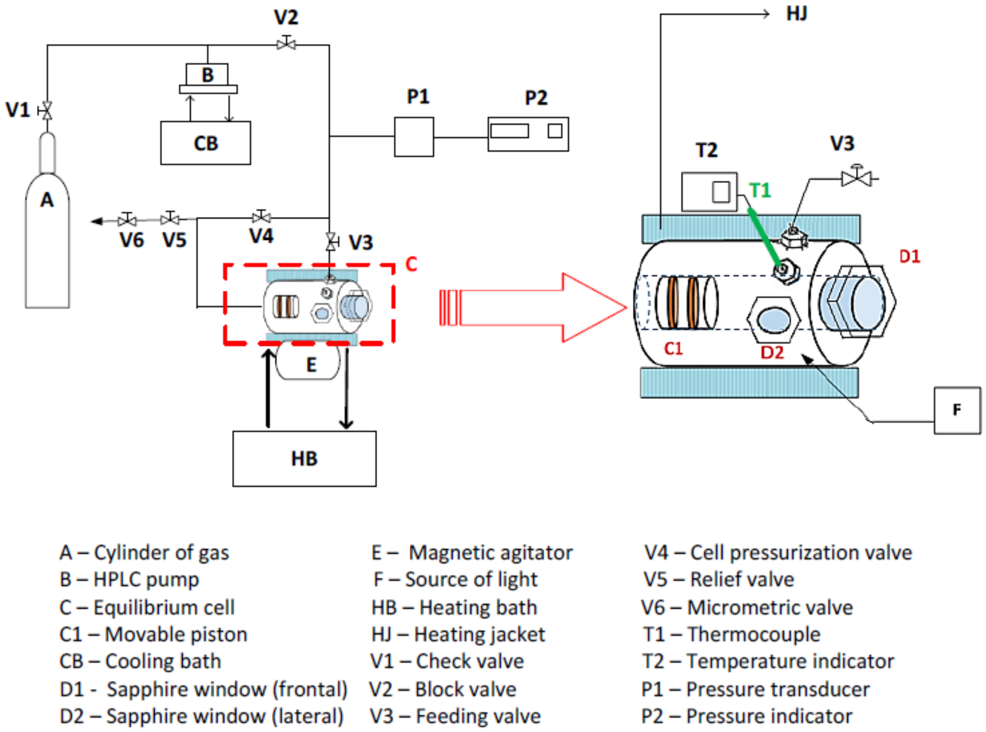

Figure 4. Schematic diagram of the experimental apparatus, adapted from Ndiaye et al. [103]

Table 4. Food systems and their used phase equilibrium measurements

System	Transition Type	Method	Reference
α-β-Ar-Turmerones (from turmeric volatile oil) + CO_2	VLE	Analytical with sampling Isothermal	[110]
α-humulene + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[111]
α-humulene + Trans-caryophyllene + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[111]
β-caryophyllene + CO_2	VLE	Analytical with Sampling Isothermal	[78]
β-Carotene + Organic Solvent +CO_2	VLE	Synthetic with phase transition Visual	[112]
δ-tocopherol + CO_2	VLE, VLLE	Analytical without sampling Spectroscopic	[113]
Borage Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Brazil nut oil + CO_2	VLE	Analytical with sampling Isothermal	[115]
Camphor (from anethole) + CO_2	VLE	Synthetic with phase transition Visual	[116]
Camphor (from anethole) + CO_2 + Propane	VLE	Synthetic with phase transition Visual	[116]
Camphor (from anethole) + Propane	VLE	Synthetic with phase transition Visual	[116]
Capsaicin + Water + Ethanol + CO_2	VLE	Synthetic with phase transition Visual	[117]
Cashew Nut Shell Liquid + CO_2	VLE	Synthetic with phase transition Visual	[7]
Cinnamaldehyde + Benzaldehyde	VLE	Analytical with sampling Isobaric	[81]
Citral + CO_2	VLE	Analytical with sampling Isothermal	[118]
Clove Oil + CO_2	VLE, LLE, VLLE	Analytical with sampling Isothermal	[56]
Cocoa butter + CO_2	VLE	Analytical with sampling Isothermal	[119]
Corn Germ Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Curcumin (from turmeric oleoresin) + CO_2 + Ethanol	VLE	Analytical with sampling Isothermal	[120]
Ethanol (from whiskey) + Water + CO_2	VLE	Analytical with sampling Isothermal	[41]
DL-α-tocopherol + Methanol	VLE	Analytical with sampling Isothermal	[121]
DL-γ-tocopherol + Methanol	VLE	Analytical with sampling Isothermal	[122]
Free Fatty Acids +Triglycerides + Squalene + CO_2	VLE	Analytical with sampling Isothermal	[123]
Fennel extract + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[124]
Fish Oil Ethyl Esters +CO_2	VLE	Analytical with sampling Isothermal Continuous flow	[125]
Fish Oil Ethyl Esters + CO_2	LLE	Analytical with sampling Isothermal	[126]
Glycerol + Olive Oil + Propane + Sodium (bis-2-ethyl-hexyl) sulfosuccinate	VLE, LLE, VLLE	Synthetic with phase transitions Visual	[125]
Grape Seed Oil + CO_2+ Ethanol	VLE, LLE, VLLE	Synthetic with phase transition Visual	[101]
l-lactic acid + CO_2 + Ethanol	LLE VLLE,	Synthetic with phase transition Visual	[102]
Lemon essential oil + CO_2	VLE	Synthetic with phase transition Visual	[127]
Lemon essential oil + C_2H_6	VLE	Synthetic with phase transition Visual	[127]
Lemon essential oil + CO_2	VLE	Analytical with sampling Isothermal	[6]
Lemon and Bergamot peel oils + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[128]
Limonene + Citral + CO_2	VLE	Synthetic with phase transition Visual	[85]
Limonene + Linalool+ CO_2	VLE	Synthetic with phase transition Visual	[85]
Limonene + Polystyrene +CO_2	LLE	Analytical with sampling Isothermal	[129]
Linoleic Acid (from banana peel oil) + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[31]
Low-Molecular Weight Triglycerides + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[130]
Menthol + CO_2	VLE	Analytical without sampling Isothermal	[131]
Menthol + Ethanol + CO_2	VLE	Analytical without sampling Spectroscopic	[132]
Oleate + Squalene (from olive oil residues) + CO_2	VLE	Analytical with sampling - Isothermal-Continuous Flow	[133]
Oleic Acid (from palm oil) + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Oleoresin Capsicum+ CO_2	VLE	Analytical with sampling Isothermal	[135]
Orange Peel Oil + Ethane	VLE	Synthetic with phase transition Visual	[135]

Orange Peel Oil + CO_2	VLE, LLE, VLLE	Synthetic with phase transition Visual	[136]
Palmitic Acid + Ethanol + CO_2	VLE, SLE	Synthetic with phase transition Visual	[137]
Palm Kernel Oil + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Palm Oil + CO_2	VLE	Analytical without sampling Spectroscopic	[134]
Propane + Chloroform + Oryzanol	VLE, SVLE, LLE, VLLE	Synthetic with phase transition Visual	[138]
Propionic acid + Caproic acid	VLE	Analytical without sampling Spectroscopic	[138]
Rapessed Oil + CO_2	VLE	Analytical with sampling Isothermal	[114]
Sunflower oil + Propane	VLE	Analytical with sampling Isothermal	[139]
Tripalmitin + CO_2	SLE	Synthetic with phase transition Visual	[140]
Ubiquinone + CO_2	SLE	Synthetic with phase transition Visual	[140]
Valeric Acid + Caproic acid	VLE	Analytical with sampling Isothermal	[141]
Vanillins (from vanilla beans) + CO_2	SLE	Analytical with sampling Isothermal	[142]
Vitamin D_2 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Vitamin D_3 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Vitamin K_2 + CO_2	SLE	Analytical with sampling Isothermal	[143]
Water + 2-Propanol + α-pinene	LLE	Analytical with sampling Isothermal	[144]
Water + 2-Propanol + β-pinene	LLE	Analytical with sampling Isothermal	[144]

Glass liquid–liquid equilibrium cells were used to measure LLE of fatty systems with emphasis on the distribution of tocopherols and tocotrienols, which samples of both phases were carefully collected with syringes with the observation of phases for quantification of the components [105].

6.2.2. Isobaric

In these methods, the boiling temperature of a synthetized mixture is measured at isobaric conditions, and the phase compositions are calculated by means of a material balance. This method is used to measure low-pressure data.

Isobaric VLE data for the mixture in the whole composition range constant pressure using an all-glass, dynamic re-circulating still, equipped with a Cottrell pump. The composition of liquid and vapor samples for the binary mixtures was determined by measuring the density whose dependence on composition at 298.15 K [106].

Similarly to analytical isobaric methods, ebulliometry is employed. Advantages of ebulliometric methods, include: data can be determined more quickly, degassing is not required, and simple apparatus and straightforward procedures are used. Specialized uses of ebulliometry include: high-pressure measurement (up to 2 MPa), measurement of infinite-dilution activity coefficients, screening of azeotropic systems, and measurement of solubility limits [107].

The corresponding disadvantages are the considerable demands on thermometry, the solubility of the buffer gas at high pressures, and thermal gradients due to pressure heads. But the greatest advantage is speed of measurement; typically, a pressure–temperature point can be obtained in an hour [23].

6.2.3. Others

Properties measured in the homogenous or heterogeneous region can be used in the calculation of phase boundaries. Here, a sample of known overall composition is placed in a vessel with constant volume, and the pressure is recorded as a function of temperature

A phase transition can be recognized from a change of the slope of the p(T) isochore [108]. Isochoric method, used for the determination of hydrate equilibrium phase diagrams, is based on a cooling/heating cycle at constant volume.

This method can be also coupled with visual observation. The advantage of isochoric method for pure gas systems in utilizing a section of hydrate phase diagram instead of the distinctive condition, at which the last piece of hydrate disappears [109]. Some food systems and their used phase equilibrium measurements are registered in Table 4.

7. Thermodynamic Modeling to Predict Phase Equilibrium Data

The development of models that can predict the behavior of thermodynamic systems is necessary to improvement and optimization of high-pressure process.

Foods are treated as aqueous mixtures that contains a wide variety of components in different phases which modeling requires a homogenous treatment for all physical (SLE, LLE, VLE) and chemical equilibria (dissociation, hydration, complexation and redox). For this purpose, it is necessary to generalize the existing models up to the prediction of equilibrium properties in a chosen reference state (generally the infinite dilution in water), and the prediction of the non−ideality (i.e., the deviation from Raoult's law) for concentrated solutions [145].

Among the many techniques of phase equilibrium calculations, the analytic combined methods (γ-ϕ and ϕ- ϕ approach) and the analytic direct methods (equation of state approach) are more widely used for performing practical fluid phase calculations than the other existing techniques [146].

Thermodynamic models can help to reduce the number of experimental data points needed for a special design problem, but very often, at least some experimental data points are needed to adjust interaction parameters of the model [22].

In the γ-φ is used the definition of the fugacity coefficient to describe the vapor phase and definition of the activity coefficient is used to describe the liquid phase. This method can be applied to a wide variety of mixtures and is accurate for low to moderate pressure calculations. As a result, applications of this method for critical and supercritical pressures become rather difficult and inaccurate [146].

In φ- φ approach is found better performance near the critical region, there is no dependence of density. When this method is used, computed solubilities are found to be sensitive to the temperature dependence of parameters in the equation of state [147].

The equation of state is a relationship between two or more functions associated with the matter (temperature, pressure, volume, or internal energy).

Equations of state are basically developed for pure components, but can be applied to multicomponent systems by employing some mixing rules to determine their parameters for mixtures. The mixing rules are considered to describe the prevailing forces between molecules of different substances forming the mixture [148].

The major advantage of this technique is its applicability for the ranges of pressures including critical and supercritical pressures. However, phase equilibrium calculations by this method will be rather lengthy except for simple equations of state. Another problem with the use of the equation of state technique is the insufficiency of information about the exact form of the equation of state of mixtures and inaccuracy of the existing mixing rules for mixtures consisting of polar and hydrogen bonding components and components with large molecular size and shape differences [146].

The van der Waals equation of state was the first equation to predict vapor-liquid coexistence. Later, the Redlich-Kwong [149] improved the accuracy of the van der Waals equation by proposing a temperature dependence for the attractive term. Soave [150] and Peng and Robinson [151] proposed additional modifications of the Redlich-Kwong [149] equation to more accurately predict the vapor pressure, liquid density, and equilibria ratios.

The virial equation of state is a power series, which expansion is, in principle, an infinite series, and such should be valid for all isotropic substances. In this case, the expansion permits to correct the ideal gas compressibility factor. However, in practice, terms above the third virial coefficient are rarely used.

8. Conclusions

Future trends for fluid properties and their phase equilibria involve research and development of convincing technologies, as for example supercritical fluid extraction, that ensures an innocuous separation process both to human health and to the environment.

Phase equilibrium data is of interest for applications to food systems in separation processes such as separating ethanol from water during distillation, the recovery of essential oils by liquid–vapor extraction or using supercritical fluids or even in liquid–liquid separation processes and there is a variety of experimental equipment and techniques designed to measure these kind of data. Phase equilibria are traditionally measured using two main approaches, depending on how composition is determined: analytical and synthetic.

In analytical method, the compositions of coexisting bulk phases are determined (often by sampling and chromatographic analysis) whereas, in the synthetic method, only the overall composition is determined experimentally (usually by metering the amounts of each pure substance introduced into the apparatus).

Each method possess its advantages and disadvantages. Therefore, there is no one ideal method, however, a specifically procedure to be used for each situation to be studied.

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