

EXPERIMENTAL METHODS FOR STUDY HIGH-PRESSURE PHASE BEHAVIOUR. PART II. RECIRCULATION METHODS

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abstract: The paper presents a review of the experimental recirculations methods used in the investigation of high-pressure phase equilibria. The main categories of these installations are described. For each case, the aspects concerning the type of experimental data, experimental conditions and experimental procedure are discussed.

Introduction

Information about high-pressure phase equilibrium is of importance for many separation processes, which are conducted at high-pressure especially supercritical fluid extraction. Applications of this technology cover the food, pharmaceuticals, chemical, coal and oil processing and production industry.

There are many experimental routs to obtain data about the phase behaviour of the fluid mixtures. Among these, the direct measurements remain an important source, though it is difficult and expensive to take accurate experimental data. On the other hand, at production level, it is expensive to use average data or to estimate data based on a thermodynamic model if literature does not offer (enough) experimental data. Thus, the understanding of the complex phenomena, which occur at high pressure in the critical region, is mainly conditioned by the quality of the experimental information [1,2].

This paper continues our previous work [3] on different techniques investigations for the high pressure phase behavior, being focused on the characterization of the *dynamic methods-recirculations methos*.

Dynamic methods

Basically, the dynamic methods consist of continuous separation of the vapour and liquid phase in a stationary regime. There are two methods that can be followed:

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- A. The components are continuous feed into the equilibrium cell and the products are simultaneously evacuated - **Continuous flow methods**.
- B. One or more phases are recirculated - **Recirculation methods**

Thus, at constant pressure, the equilibrium is achieved and the temperature is measured followed by the sampling and analysis of the equilibrium phases. This method allows obtaining complete P-T-x-y data, where x represents the composition of the liquid phase, respectively y represents the composition of the vapour phase.

Scatchard and Wilson [4] mentioned that, from the qualitatively point of view the accuracy of these data is lower than the values obtained by static methods (previously describe, [3]), because the experimental data corresponds to a stationary state, not to the real equilibrium state.

Recirculation methods

These methods are based on the recirculation of one or more (usually two) phases. According to the number of the recirculated flows and the thermodynamics conditions this installation can be:

1. Vapour recirculating equilibrium apparatus;
2. Liquid recirculating equilibrium apparatus;
3. Vapour and liquid recirculating apparatus.

1. Vapour recirculation installations (VCirc)

The method involves the continuous pumping of the vapour phase over the liquid phase in a stationary regime. In the next step, samples from the equilibrium phases are extracted using valves or capillaries, followed by their analysis.

In the beginning, VCirc installations functioned on the principle of the *pure gas recirculating method (PGR method)* [5]. The volatile component is pumped only once over the liquid, at constant temperature and pressure. The residence time of the vapour into the equilibrium cell is very short and the equilibrium state is rapidly reached. The composition of the coexisting phases can be evaluated using different physico-chemical analysis method described elsewhere [2, 3]. The schematic representation of the apparatus functioning on this method is given in Fig. 1 [5].

The accuracy of the PGR method is average, because the contact time between the vapour and the liquid phases is not always sufficient for attaining the real equilibrium state.

Literature [2, 4] presents different solutions for solving this problem. Thus, the gas can be pumped through two cells filled with liquid, serially connected. The first cell is functioning as pre-saturator; the second is the equilibrium cell. When the equilibrium is reached, the liquid phase is sampled and analyzed.

The equilibrium cell allows visualizing the process and is made of high pressure resistant glass or sapphire. But non-visual cells from stainless steel, are also used [6].

Repeated pumping of the gas over the liquid phase increases the contact time between phases and further, the accuracy. Based on this, Inglis constructed the first apparatus functioning on the continuous recirculation of the vapour phase (Fig. 2).

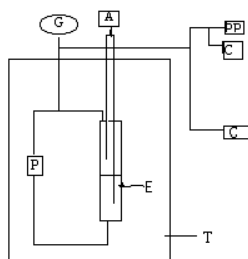


Fig. 1 Schematic representation of the pure gas recirculating apparatus [5].

(E) – equilibrium cell; (T) – thermostat; (P, PP) – pumps; (A) – capillaries for sampling the equilibrium phases; (G) – gas reservoir; (C) – compressor.

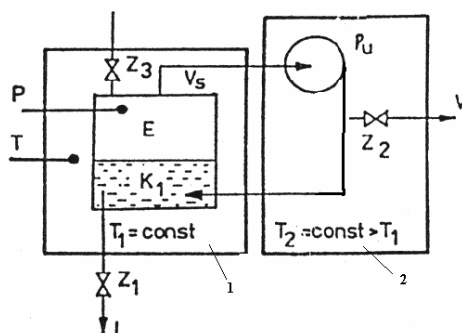


Fig. 2 Vapour recirculating apparatus proposed by Inglis [4].

(E) – equilibrium cell; (K₁) – liquid phase; (P_u) – pump; (T) – thermometer; Z₁, Z₂, Z₃ – valves.

The vapour phase is recirculated until the stationary state is reached (the separation of the phases is observed), when temperature, pressure and phases composition are determined. This equipment can be used in the low temperatures range (200 – 298 K), but also for higher temperatures and pressures (up to 200 MPa and respectively up to 458 K).

The apparatus for low temperatures is similar, but the sub-ambient temperature is obtained by circulating cold water or liquid nitrogen through a heat exchange coil, in the bath. At temperature lower than -78°C , the equilibrium cell is introduced into a cryostat using a special cooling fluid. The accuracy in temperature is ± 0.02 K and ± 0.007 MPa for pressures up to 200 MPa. The extracted samples from the liquid and vapour phases are both analyzed by chromatography [7].

Due to the vapours low densities, recirculation of the vapour phase induces pressure fluctuations, which affect the stationary state. Thus, by placing a cell [7], or a second autoclave [8] as expansion cell in the recirculation loop, the pressure drop is compensated. The composition of the equilibrium phases can be determined by different methods: titration for the liquid phase and respectively by measuring the pressure of the vapours in calibrated vessels [9], or, more accurately by chromatography [7].

The simultaneous determination of the composition of the liquid and vapour phase is proposed by Stevens and de Loos [6]. The apparatus combine the advantage of the gas saturation method with those of circulation methods. The equilibrium cell has a special design based on the air-lift bio-reactor principle. It consists of two parts: the lower part, in which the low volatile compound is present and the upper part containing a demister. The components of each part are presented in Fig. 3.

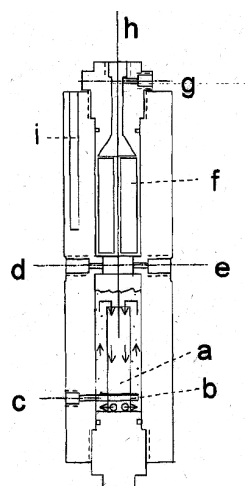


Fig. 3 Schematic drawing of the equilibrium cell based on air-lift principle [6].

- draft tube for liquid circulation;
- sieve-plate for gas dispersion;
- gas inlet;
- thermocouple;
- extra connection e.g. liquid addition;
- demister;
- gas outlet;
- liquid sampling capillary;
- thermocouple shaft.

The gas enters into the equilibrium cell through a metal filter (b), which produces very fine bubbles in the volume outside the central draft tube. The rising bubbles cause the liquid flow upwards at the outside of the central draft tube (a) and downwards at the inside of the tube. This flow pattern causes a good contact between the liquid and the gas phase and a stable equilibrium. The demister (f), positioned in the upper part of the cell prevents the entrance of the liquid droplets into the gas outlet (g). The use only of an empty space appears to be insufficient to prevent the entrainment.

In between the upper and the lower part, two connections are present: one is used as temperature indicator; the other can be used as liquid-refill inlet without level control. A pressure transducer connected with a digital pressure indicator controls the pressure. The apparatus was tested for temperature lower than 333.2 K (± 0.01 K) and pressure less than 11 MPa (± 0.01 MPa).

The composition is determined by sampling the two equilibrium phases using capillaries, followed by the on line chromatographic analysis.

The vapour recirculation method can be also applied for the study of high pressure phase equilibria of reactive mixtures, when the necessarily time for reaching the thermodynamic equilibrium is shorter than the necessarily time for chemical equilibrium. The details of the equipment are given in the work of *Arlt et al.* [10].

2. Liquid recirculating apparatus (LCir apparatus)

The functioning principle of these installations is illustrated in Fig. 4.

The liquid is pumped using a centrifugal pump, from the bottom of the absorber (equilibrium cell) to the top, where it falls in a thin film over the absorber packing. After the appropriate time, the liquid in the absorber becomes saturated with gas.

The saturation is obtained when no pressure change is observed in the gas tank [11].

The flow of the liquid over the absorber improves the contact area between the liquid and the vapour phase and insures a good mixing of the two phases.

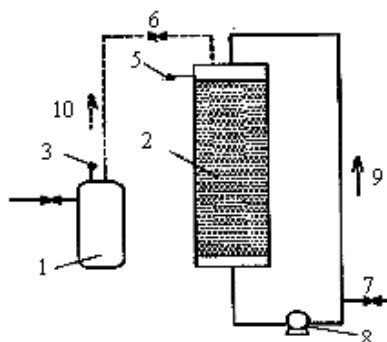


Fig. 4 Schematic representation of a LCir apparatus [11].

(1) – H₂ tank; (2) – absorber; (3, 5) – pressure gauges; (6, 7) – valves; (8) – pump; (9) – liquid flow; (10) – gas flow.

Based on the same principle the apparatus designed by Foster *et al.* [12] is equipped with special sampling valves - *eight and six - port valves*, located on the recirculation loop.

After the equilibrium state is reached, the phase are sampling by manipulating the sampling valves and injecting into the analysis compartment, containing the chromatograph.

First, the *eight and six - port valves* allow the continuous loading of the sample in one of the circuits. In the next step the sample is displaced by the mobile phase and carried into the chromatographic column. This procedure leads to a relative standard deviation for composition less than 4.4 % [12].

Literature [1,2] reports that LCir methods can be also used for measuring liquid-liquid equilibria or for gas liquid solubility's measurements.

3. Vapour-liquid recirculation installations (VLCirc)

In the beginning, the equipments based on the vapour and liquid phase recirculation were used for Bubble Point measurements.

Bassically, an ebulliometer is an one stage total reflux boiler, equipped with a vapor lift pump to spray mixture of equilibrated liquid and vapor onto thermometer walls [2].

A mixture of known composition is boiled at constant pressure. The composition of the liquid and the vapour phase change in time and will reach a steady state which should differ insignificantly from the real equilibrium state. This method yields to P-T (boiling temperature) data at constant x, but also complete P-T-x-y data can be measured. The accuracy of the data depends on the analysis method, but also on the difference in the vapour pressure of the pure components. Good results were obtained for differences in the

boiling temperatures of the components smaller than 40°C, or in the case of complete method, using refractometry or density measurements as analysis method of the equilibrium phases.

The first modified apparatus, used in the vapour liquid equilibrium was Swietoslowski ebulliometer (see Fig. 5) [5].

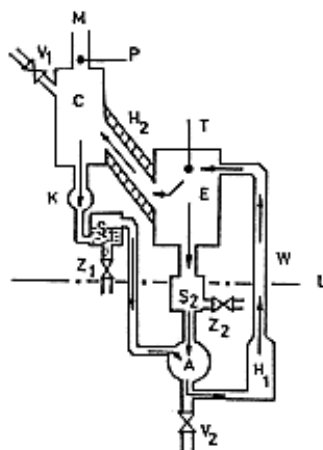


Fig. 5. Schematic representation of the Swietoslowski ebulliometer [5].

(A) – mixing vessel; (C) – condenser; (E) – equilibrium chamber; (T) – thermometer; (K) – flow meter; (S₁) – condensed vapours bottle; (S₂) – liquid tank; (V₁, V₂, Z₁, Z₂) – valves.

Usually, ebulliometry is used for low pressures ($P < 1 \text{ MPa}$), only in rare cases for pressures above 1 MPa [13, 14].

The available ebulliometers are well designed for reaching the equilibrium point, but they are not designed for optimizing the contact time between the phases. Therefore, from industrial point of view, obtaining a complete data set might require too long time (months) which is economically inefficient.

In order to reduce the measurements time, Verneau [13] equipped the thermostated ebulliometric cell, with a self-inducing turbine which insures the good contact of the liquid and vapour phase. Thus, the duration of an experiment is significantly reduced (around 2 hours), allowing the industrial applications. After the equilibrium is reach, the equilibrium phases are sampled and analyzed using an on-line chromatograph. The analysis line must be insulated to avoid condensation. The apparatus can be used for pressures up to 2 MPa in a temperature range of 273 to 423 K.

Other ebulliometric installation suitable to work at $P > 1 \text{ MPa}$, was constructed and described by Malanowski [14]. The apparatus is a typical vapour-liquid recirculating installation, but some new modified components, specially designed for the work at high pressure, are attached. So, the cell, the tubing, the sampling valves are entirely hard stainless steel made. Only the drop counter is made of thick-walled glass tubing. To insure the stability and easy regulation of pressure during the experiment, ebulliometer is attached to a pressure stabilizing system containing a nitrogen tank, a buffer tank and a set of regulation valves.

For vapour pressure measurements of the high-boiling substances, Aim [15] assembled an apparatus based on comparative ebulliometry. The equipment, based on the Cottrell pump principle, consists of two standard Swietoslowski ebulliometers: one (E_1) filled with a reference fluid of known vapour pressure, the other with the high boiling substance (E_2).

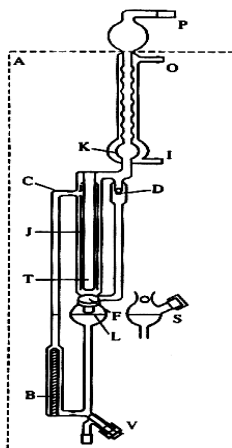


Fig. 6 Quartz ebulliometer for high-boiling substances [15]

(A – air-bath thermostated compartment; (B) – boiler with a heater placed in a hollow finger; (C) – Cottrell pump; (D) – drop counter; (F) – filling valve; (I) – cooling air input port; (J) – insulation jacket; (K) – cooler-condenser; (L) – liquid level; (O) – cooling-air output port; (P) – connection to pressure assembly; (S) – side view of the central part; (T) – thermometer; (V) – draining valve.

A few modifications were applied to the second standard ebulliometer, E_2 (see Fig. 6) [15], as it follows:

- It is all made of quartz, allowing the visual observation of the experiment and avoiding the thermal dilation.
- The boiler and the heater are inserted in a finger shaped sheath with roughened outer surface, insuring the smooth regular boiling and proper rhythmic function of the Cottrell pump.
- A filling port with vacuum tight Teflon screw cap, which makes possible to fill the apparatus directly in the operating position, inside the thermostat.
- A draining valve allows emptying the ebulliometer also in the operating position still, inside the air thermostat.

The apparatus is used only for pressure below 75 kPa, but the main advantage is the use of quartz and teflon as materials for the parts in direct contact with the substance, preventing oxidation.

In literature there are also presented other categories of VLCirc installations, where the two phases are continuously recirculated using recirculation pumps [16, 17].

The components are injected in the cell and brought to the desired temperature [16], or in other design [17], the cell is previously heated at the temperature of interest. One or two

mixing pumps insure the recirculation of both phases. Two flows are running: the vapours flow upwards through the liquid and the liquid phase flows reversely, insuring the good contact and shortening the equilibrium time. At equilibrium, the phases are sampled and analyzed using the methods previously described.

Dynamic methods based on the recirculation of one or many phases present many **advantages**:

- Can be applied in a large range of pressures and temperatures.
- May provide reliable data for industrial design.
- Recirculation of one or many phases insures a good contact between the phases, significantly reducing the equilibrium time.
- The use of circuits and valves, functioning at isobar conditions, reduces the fluctuation of pressure and differential vaporization due to the sampling procedure.

Among the **disadvantages** one can mention:

- The accuracy of the data is lower than the values obtained by the static method, because during experiments, a stationary state is obtained instead of the real thermodynamic equilibrium.
- May need expensive devices, like: special pumps to reduce the variation of pressure due to the recirculation, and respectively high precision control temperature system to avoid the secondary phenomenon: vaporization or condensation of the fluid in the recirculation loop.
- Cannot be applied in the critical region, where the equilibrium is very sensitive to the pressure or temperature variations.

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