EXPERIMENTAL METHODS FOR STUDY HIGH-PRESSURE PHASE BEHAVIOUR. PART III. CONTINUOUS FLOW METHODS

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abstract: The paper presents a review of the experimental dynamic methods-continuous flow 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

The knowledge of the phase behavior is essential for many chemical processes which are conducted at high pressure (i.e separation processes) and also for applications of this technology in different fields such as: pharmaceutical, oil processing and producing industry or geological study.

Based on experimental information it is often possible to predict the phase behaviour of the system of interest at conditions different than those studied.

The main way to collect experimental data is remain the direct measurements. But also dynamic methods are often presented in literature [1,4]. The dynamic methods consist of continuous separations of the phases in a stationary regime. Two ways can be followed: the phases are recirculated (see our previously work, [3]) or the components are continuously feed into the equilibrium cell and the products are simultaneously evacuated.

Scatchard and Wilson [4, 5] mentioned that, from the qualitatively point of view the accuracy of these data is lower than the values obtained by static methods (previously described, [3]), because the experimental data corresponds to a stationary state, not to the real equilibrium state.

This paper continues our previous work [2,3] on different techniques investigations for the high pressure phase behavior, being focused on the characterization of the continuous flow methods classified in literature as dynamic methods.

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Continuous flow methods

In a typical design of a continuous flow method (Fig. 1), the high pressure pump feed the preheated components into a mixer where the desired temperature is attained. The heated stream is separated in the equilibrium cell into vapor and liquid phase. Both phases are continually sampled, depressurized, accumulated and analyzed usually after the experiment [2]. The pressure is adjusted by controlling the effluent stream of the top phase.

The interface level between the phases is controlled with an expansion valve, positioned in the bottom part of the equilibrium cell. Its position can be visually determined, but also non-visual methods are applied for non-transparent liquids [2].

These methods can be used only in the systems that need equilibrium time shorter than the residence time of the mixture in the cell.

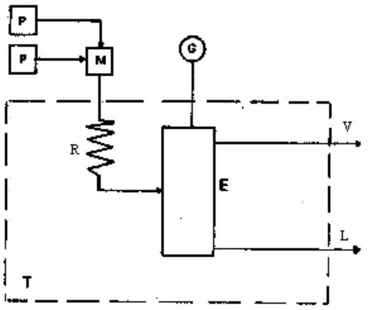

Fig. 1: *Schematic representation of a continuous flow installation* [2, 5]

(E) – equilibrium cell; (P)- high pressure pumps; (M) – mixer; (G) - valve; (T) – thermostat bath; (R) – heater; (V) – vapour sampling line; (L) – liquid sampling line.

During the pumping of the components in the cell, pressure fluctuations are produced in the system. Therefore, in Joyce and Thies [6÷8] apparatus, the components are pumped using an electronic syringe pump and a metering pump. A surge tank filled with helium was attached to dampen the fluctuations caused by the metering pump. Following the same procedure and using two high pressure liquid pumps (total rate flow: 100-300 mL/h), Kim *et al.* [9] obtained data on high pressure phase equilibria for pressure up to 35 MPa and temperatures below 673 K. Critical parameters (temperature, pressure, composition) can be also measured with these apparatus. Visual observation of the **critical phenomena** is conditioned of the flow rate. Therefore, different flow rates are tested to optimize the method.

For a better observation of the phase behavior at equilibrium conditions, Beard et *al.* [10] attached a video camera and a fluorescent light device to the equilibrium cell.

Continuous flow methods can be also applied to study three phase equilibrium (liquid-liquid-vapor) in the system containing immiscible components [11,12] (see Fig. 2), but also to the reactive mixtures or those containing thermally unstable components – ***non recycle flow still (NFS)*** **(**Fig. 3**)** [13].

In the fist case [12], the components are pumped at the desired pressure into the mixer and then in the equilibrium cell. Next, the liquid level is set by adjusting the metering valves or pump rates. The coexisting phases are sampled, could down and analyzed after at least 30 min. of steady state. Equilibrium compositions were calculated from the weight of condensable components and from the test meter volume measurements of the noncondensable component.

The working principle of the device of Jennigs şi Schucker [12] is given in Fig. 2

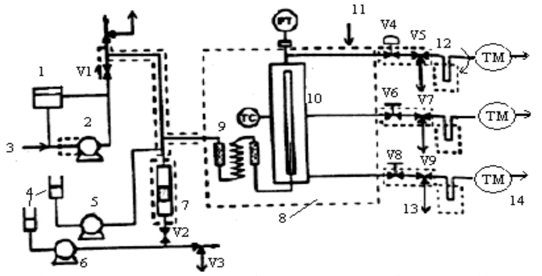

Fig. 2: *Schematic representation of the continuous flow installations used for the study of the three phase equilibria [12]*

(1) – pressure regulator; (2, 5) – Eldex pump; (6) – Milton Roy pump; (3,4) – gas feed lines; (2, 5, 6) - pumps; (7) – reactor; (8) – thermostat; (9) – mixer; (10) – view equilibrium cell; (11) – nitrogen purge; (12) – cold trap; (13) – to waste; (14) –to vent; (V1…V9) – valves; (PT) – pressure transducer; (TC) –thermocouple; (TM) – wet/dry test meters.

The NFS apparatus used for the study of the phase equilibrium in the systems containing thermally unstable substances presents the typical components of the continuous flow installations: preheater, mixer, equilibrium cell, feeding pumps The NFS installation, schematically represented in Fig. 3.

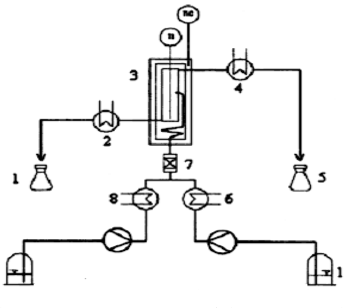

Fig. 3: *Schematic representation of the NFS installation* [13].

(1)– sample liquid phase; (2) – cooler; (3) – vapor - liquid separator; (4) – condenser; (5) – sample vapor phase; (6) – preheater; (7) – static mixer; (8) – evaporator; (9, 10) – components feeding lines; (TI) – thermometer; (TIC) – temperature controller.

An evaporator replaces the preheater on the volatile component feeding line. Special construction has the equilibrium cell, which acts as vapor-liquid separator. The main part of the cell is the Cottrell tube, where the phase equilibrium is achieved. After separation and the cooling/condensation steps, three ways ball valves-serving as flow dividers, allow the sampling of the equilibrium phases.

In this method, the components pass only once through the equipment. The phase equilibrium is established very fast under intensive mixing. Due to the short residence time in the still, the product formation is minimized. Other benefits of this technique are the low thermal impact on the component and the reduction of the necessarily lab time for phase equilibria determination. This method provides complete P, T, x, y data.

The ***advantages*** of the continuous flow methods can be conclude as it follows:

- Allow observation and measurements in of the critical parameters;
- Can be applied for the study of the low decomposition temperature substances or to the reactive mixtures, or those containing thermally unstable components
- The sampling of the phases does not significantly affect the equilibrium state. If the analysis devices need larger sample quantities, the experiment running time is prolonged until the necessarily amount of sample is accumulated.

A few ***disadvantages*** can be also mentioned for the installations functioning on continuous flow principle:

- Can be used only in the systems needing short equilibrium time (shorter than the residence time of the mixture into the cell);
- May need very expensive devices: special valves, liquid-vapour separators or high precision pump to control the flow rate of the components.

Conclusions

Experimental dynamic methods and installations for investigation of high-pressure phase behaviour are described: *Part II – Recirculation Methods* and respectively *Part III – Continuous Flow Methods.* Each category is analyzed and briefly characterized.

The experimental procedure, the description of the equipment and the improvements are presented for each type of installation. For increasing the accuracy of the experimental data obtained with dynamic techniques, different solutions presented in literature are discussed and compared.

The design and building of installations for the study of high pressure phase behaviour implies a careful analysis of the practical and economical advantages/disadvantages of the main categories of the techniques presented in the literature. It must be suited to the components type, expected equilibrium P, T values, existence/non-existence of chemical interactions.

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