# LINEAR VARIATION OF ISOCHORIC LINES AND DETERMINATION OF PHASE TRANSITIONS IN SIZE ASYMMETRIC MIXTURES

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## Abstract

The study of isochoric lines for the determination of densities of reactive mixtures provided strong evidence that the change in the slope of the pressure vs. temperature lines can be used to determine the phase boundaries of size asymmetric mixtures. It was found that isochoric pressure vs. temperature lines, in the gas-liquid region, are virtually linear. This method can be applied to binary or multicomponent mixtures. Based on this a methodology was developed to determine phase transition conditions when rather extreme values of pressure and temperature must be investigated. The observed experimental behavior is also supported by the computation of pressure vs. temperature variation of isochoric flashes for asymmetric mixtures, using different equations of state.

*Keywords:* phase transitions, asymmetric mixtures, supercritical reactors, isochoric experiments

## Resumen

**Variación lineal de líneas isocóricas y determinación de transiciones de fase en mezclas asimétricas.** El estudio de líneas isocóricas para la determinación de densidades en mezclas reactivas, muestra que el cambio de la pendiente de las líneas presión vs. temperatura puede ser usado para determinar los limites de transición de fases. Este fenómeno se ha observado en mezclas de compuestos con importante asimetría en tamaño. Dichas mezclas son de especial importancia en procesos sustentables que utilizan fluidos supercríticos como solventes no contaminantes. Se encontró que las líneas isocóricas presión vs. temperatura, en la región gas-líquido, son prácticamente rectas. Este método puede ser aplicado a mezclas binarias o multicomponentes y su principal ventaja es su aplicación a casos donde condiciones extrema de temperatura o presión dificulta el uso de metodologías clásicas. El comportamiento experimental observado es también confirmado por el cómputo de *flashes* sobre las líneas isocóricas presión vs. temperatura usando diferentes ecuaciones de estado.

*Palabras clave*: transiciones de fases, mezclas asimétricas, reactores supercríticos, experimentos isocóricos

## Introduction

An interesting behavior of the pressure vs. temperature lines was observed during the study of the volumetric (PVT) properties of a reacting system. This behavior was ascribed to phase transitions in the mixture under study. Therefore the technique was further refined in order to develop a procedure to find the boundaries of phase transitions of complex mixtures. This method allows the study of mixtures under rather extreme conditions of pressure and temperature in an indirect way. The systems studied in a previous work of PVT measurements[1] of reacting mixtures were the trans esterification of different vegetable oils to fatty esters using supercritical alcohols like methanol or ethanol.

The problem of finding the conditions of pressure, temperature and composition that give rise to a homogeneous phase during the operation of a chemical reactor is of great interest from a theoretical and practical point of view. In the particular case of gas-liquid heterogeneous catalytic reactions, the operation under homogeneous conditions reduces the mass transfer and solubility limitations that many times hinder this kind of processes[2]. One approach to achieve a homogeneous operation is to use a supercritical co-solvents in reactions like hydrogenation, hidrogenolysis, hydroformilation, etc. van den Hark et al.[3] have shown that homogeneous hydrogenation of vegetable oils can be carried out with the use of propane as a supercritical co-solvent. Depending on the reactants and reaction conditions other solvents can be chosen to operate the system in a single fluid phase; a systematic procedure to find solvents to achieve homogeneous conditions has been developed by Pereda et al.[4],[5]. Several authors have stressed the need to know the phase condition for the interpretation of the kinetics and conversion of chemical processes. The knowledge of the phase behavior of a reaction process can help to understand the results of experimental studies and to plan and design experimental runs. This topic has been recently discussed by Grunwald et al.[6] and Novitsky et al.[7], who extensively reviewed the experimental techniques applied in monitoring the phase behavior. When the reactions are carried out under fairly extreme conditions of pressure and temperature the direct observation of the phase condition may result in technical difficulties and require the use of indirect methods like the one discussed in the present work.

**Phenomenological behaviour**

As it was mentioned before, the experiments that motivated the present work were the reactions of supercritical methanol and ethanol with different vegetable oils (transesterification) to obtain fatty esters and glycerol[1]. The study of the volumetric properties of these mixtures was carried out at temperatures that ranged from 480 to 630 K and pressures between 50 and 250 bar. The density measurements were used to compute the actual residence time of reacting mixtures in a continuous transesterification reactor. The pressure and temperature conditions investigated in the density studies of transesterification mixtures were in a range of values for which no commercial densitometer was available. Therefore the measurement of the volumetric properties under homogeneous conditions was carried out in a constant volume cell. The cell was charged

with a known amount of the mixture and the variation of pressure with temperature in the desired range was recorded. The size asymmetric nature of the mixture charged into the cell - methanol+triglyceride or methanol+methyl oleate - should be pointed out. Previous studies on the triolein+methanol binary[8] indicate that there is liquid – liquid immiscibility up to a temperature close to the critical temperature of methanol. Van Konynenburg and Scott[9] have shown that the fluid phase behavior observed in binary mixtures can be classified in five main types. In type I phase behavior, complete liquid miscibility is observed at all temperatures. When there is partial miscibility at low temperatures the system is of type II. The behavior of the methanol+triolein system can be classified as type II. Liquid-liquid immiscibility is quite common in size asymmetric mixtures; for instance, mixtures of a heavy substrate like triglycerides with $CO_2$ exhibit strong liquid-liquid immiscibility up to the $CO_2$ critical point. In this type of mixtures the locus of their critical points starting from that of the heavy subtract diverges at higher pressures and liquid-liquid immiscibility can be observed up to very high pressures. These types of mixtures are classified as type III. When the main feature of the binary mixture is difference in size, but not in chemical nature, like with propane-heavy hydrocarbons, liquid-liquid immiscibility is observed near the critical point of the lighter component. In the case of propane, immiscibility is observed starting with paraffins of carbon number 35 and with ethane of carbon number 17. These binary mixtures are classified as types V or IV, depending whether liquid–liquid immiscibility is observed or not at low temperatures.

The selection of suitable operating conditions for supercritical gas-liquid reactions starts with the search of a co-solvent with a critical temperature above the recommended operation temperature for the reaction. In this way the gaseous reactants and the co-solvent are completely miscible. At this temperature the pressure at which the co-solvent and the heavy subtract are completely miscible should be obtained experimentally or by calculation. If we have two miscible pairs in a ternary mixture there will be a region of composition where the system will be homogeneous for any ratio of the reactants (see Figure 1). The investigation of complete miscibility in the supercritical region of these asymmetric binaries is of great interest and the experimental data available are, in general, scarce [10]. The experimental technique proposed in the present work can be useful to find the pressures that yield complete miscibility at various temperatures for these types of asymmetric mixtures.
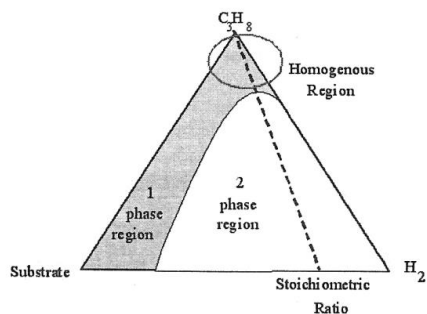
Fig.1. Conditions of homogeneous operation in a gas-liquid reaction using a supercritical cosolvent
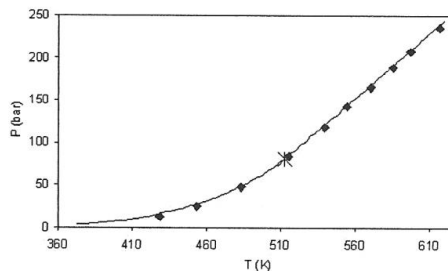


Fig. 2. Comparison of experimental values with NIST data for methanol in the liquid vapor region and in the supercritical isochoric region of density=0.28 g/cc. (♦): Experimental data, (—): NIST data for Methanol (density = 0.28 g/cc), (*): Critical Point of Methanol.

*Experimental procedure*

The constant volume cell is a stainless steel 3/8 inch nominal diameter tube, 64 cm long, closed at both ends. The cell volume at room temperature was 26.1 cc. This cell was used in all the density related experiments. The pressure was measured with a Dynisco melt pressure gauge PG4 series, suitable for measurements at elevated temperatures with accuracy of 2%. Temperature was measured with a PT-100 platinum resistance thermomether with accuracy of 0.1°C. The cell was placed in an electric oven with temperature control and covered with aluminum foil to isolate the cell from the electric oven radiation.. The cell temperature was increased at a slow rate up to a desired temperature level and then it was kept constant until no variation in the system pressure was observed. The accuracy of the pressure measurements was checked against the vapor pressure of methanol. The experimental measurements were contrasted against data from the NIST tables[11] (see Figure 2). This comparison covers the vapor-liquid and supercritical region of methanol. In the supercritical region the experiments with pure methanol give the isochoric pressure vs. temperature line at the chosen density. The intersection between the isochoric line and the vapor pressure curve corresponds in this case to the critical point because the cell was charged with the critical density of methanol. The experimental pressure–temperature relation in the supercritical region was in good agreement with the values from the NIST tables at the chosen density.

*Isochoric experiments*

Figure 3 depicts the typical evolution of pressure vs. temperature of an experimental run
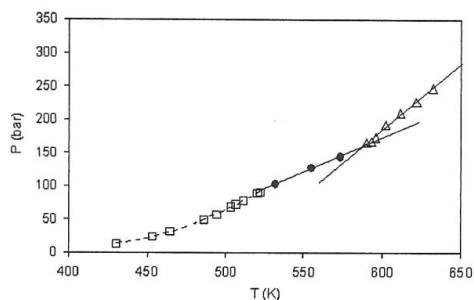


Fig.3. Pressure vs.Temperature for Methanol – Sunflower Oil (Molar Ratio : 40, density 0.44 g/cc). (☐) and (●): LLV and LV Region, (△): Single Phase Region

for a binary mixture. In this case, the cell feed consists of sunflower oil+methanol at a density of 0.44 gr/cc and with a molar ratio of methanol/oil of 40. The pressure vs. temperature line has three different sections. In the first section, at the lower temperature range (dashed line), the liquid phase of the methanol+oil system is heterogeneous and a liquid-liquid-vapor (LLV) equilibria is obtained. Under these conditions, given that the reaction start up above 500 K, there is only one degree of freedom in a binary system and the vapor pressure line will be unique at any system density or methanol/oil ratio. The complete miscibility in the liquid phase of the vegetable oil with methanol is achieved at conditions of pressure and temperature close to the critical values of methanol[8].

Above the critical temperature of methanol a linear relation of pressure vs. temperature, of lower slope than the vapor pressure line, is observed (solid line). In this region, depending on the mixture global density, either the liquid phase or the vapor phase increases up to a point in which the whole mixture becomes homogeneous. At this point a high conversion to fatty esters and glycerin of the sunflower oil starts to take place. This supercritical phase is of almost constant composition and displays a linear relationship typical of the isochoric variation of pressure with temperature of homogeneous systems. The point of intersection between the two high-temperature linear sections are considered to be the dew or bubble point values for the reaction product mixture. The linear relation of the third section (solid-dashed line) is observed up to the highest temperatures studied (around 630 K).

This type of experiments were carried out for several global densities and molar ratios for methanol/sunflower oil by Velez et al.[1] and the same behavior was observed in all cases. The variation of pressure vs temperature at constant volume conditions was also studied for a non reacting system: methanol + methyl oleate. Figure 4 shows that the same behavior of pressure vs. temperature relation is observed with an intermediate linear region above the critical temperature of methanol and a change in the isochoric slope at the transition point from heterogeneous to homogeneous system.

In the case of a homogeneous phase (gas or liquid) under isochoric conditions it is a common observation that a linear pressure vs. temperature relation is obtained. This behaviour can not be justified on thermodynamic grounds but it is related to the usual behavior of fluids and follows the predicted behavior of all commonly used equations of state[12]. The almost linear relation between P and T indicates that:

$$\left(\frac{\partial^2 P}{\partial T^2}\right) = 0$$

Using the classic van der Waals equation of state:

$$P = \frac{R.T}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right) = \frac{R}{V - b}$$

Therefore at constant volume the linear relation is justified if the attractive energy parameter "$a$" is considered independent of temperature. We can conclude that the slope of the isochore is a function of the repulsive term and the curvature deviation is due to the attractive term.

The intermediate region, at lower temperatures but above the critical point of the more volatile component, corresponds to a vapor–liquid phase equilibrium at different temperatures but at constant volume. This type of flash computation corresponds to a minimum in the Helmholtz function of the mixture at specified T and V. Even though in this case we are dealing with a heterogeneous vapor-liquid mixture at constant volume, an almost linear variation of pressure with temperature is again observed. In the experiments carry out in this work, that behavior covers the temperature range from the critical point of the lighter component to the condition of phase transition to a homogeneous phase. Again this result cannot be justified on a thermodynamic basis. The modeling with an equation of state, of a constant volume flash at various temperatures, can be useful to check the linear variation of pressure versus temperature.

The product of the transesterification reaction is a mixture of methyl oleate+methanol+glycerine. This mixture has been modeled with the GCA-EoS[13] equation of state. The computation of a series of flashes at constant volume for various temperatures is shown in Figure 5 for a global density of 0.19 g/cc. Again a linear relation of temperature vs. pressure is obtained. The evolution of the phase behavior from the heterogeneous condition at low temperature to conditions close to the phase saturation point is indicated by the variation of the mixture compressibility factors as shown in Figure 6. Above
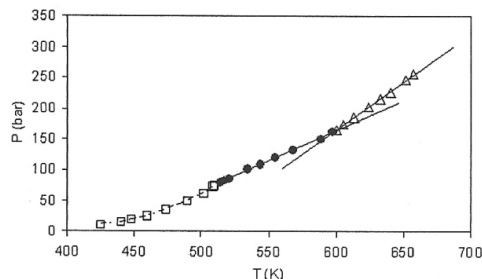


Fig. 4. Pressure vs.Temperature for Methanol – Methyl Oleate (Molar Ratio: 12.37), density = 0.37 g/cc. (□) and (●): LLV and LV Region, (△): Single Phase Region
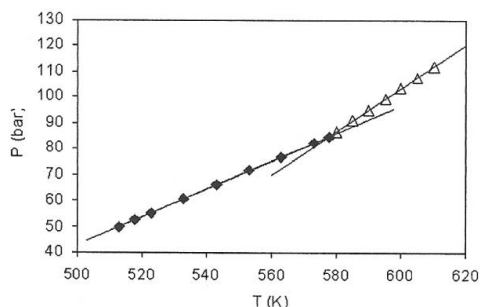
Fig. 5. Pressure vs temperature variation for a constant volume flash of a mixture of Methyl Oleate-Methanol-Glycerol (molar fraction = 0.073-0.904-0.022) at constant density of 0.19 g/cc. GCA-EOS model. (◆): LLV and LV Region, (△): Single Phase Region
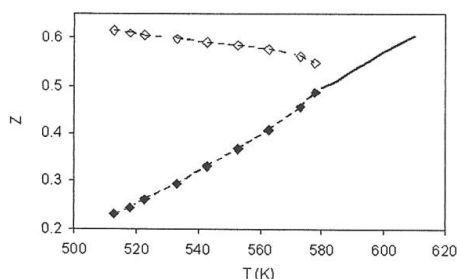


Fig. 6. Vapor and liquid compressibility factors as a function of temperature for the mixture of methanol – methyl oleate + glycerine at constant density of 0.19 g/cc. GCA-EoS model: ◇vapor phase compressibility factor, ◆liquid phase compressibility factor —single phase compressibility factor at the experiments constant volume

the phase saturation point the normal linear variation of pressure vs. temperature is observed. The compressibility factor plot indicates that the phase that disappears in the transition poiunt (at a 0.19 g/cc global density) is the vapor phase.

The experimental and simulation results indicate that the conditions of phase transition for the compositions and global densities charged into the cell are obtained from the intersection of the two linear relations of pressure vs. temperature observed above the critical point of the lighter component.

The phenomenon that is taking place in these experiments can be illustrated using a phase envelope diagram for the composition charged into the cell. If we consider a non-reactive and size-asymmetric binary system, for the composition of interest a phase envelope as shown in Figure 7 can be simulated with GCA-EoS. Also some lines of constant vapor fractions are indicated. Inside the phase envelope curve we can draw, starting from the bubble point line, the pressure–temperature trajectory obtained at a given density. This almost straight line will cross different vapor fraction values to reach again a phase boundary at the intersection of the pressure vs. temperature line with the phase envelope curve. Experiments at different global densities with the same composition will give conditions for the phase transitions that could correspond to bubble or dew point curves of the phase envelope. In Figure 7 two isochoric lines of different densities reach the saturation line at different conditions of pressure and temperature. In each case there is an isochoric line in the homogeneous region of different slope to the one corresponding to the heterogeneous region of the phase envelope [14].

**Conclusion**

The variation of pressure with temperature in constant composition isochoric experiments can be used to determine the phase boundaries of multicomponent systems. Experimental evidence indicate that almost linear relations are observed in isochoric two phase flashes and the same result is obtained by simulation with different equations of state. The phase boundaries are identified by a sudden change in the slope of the pressure vs. temperature lines. The phase envelope region of a mixture of a given composition
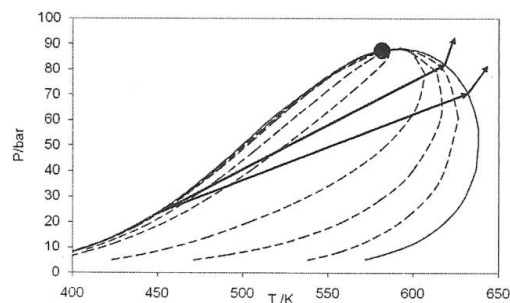


Fig. 7. Phase envelope and isochoric lines. Light solid line: phase envelope; dashed lines: mixtures of different vapor fractions. ●Critical point.

can be explored by the study of the pressure vs. temperature lines at different global densities.

### References

[1]  A. Vélez, S. Espinosa, P. Hegel & E.A. Brignole, Proceedings of VIII Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design - EQUIFASE 2009, Portugal.

[2]  A. Baiker, *Chem. Rev.* **99**, 453 (1999).

[3]  S. van den Hark & M.Härrod, I*nd. Eng .Chem. Res.* **40**, 5052 (2001).

[4]  S. Pereda, S. B. Bottini & E. A. Brignole, *AIChE J,* **48**, 2635 (2002).

[5]  S. Pereda, S. B. Bottini & E.A.Brignole, *Applied Catalysis A General* **281**, 129 (2005).

[6]  J.D. Grunwaldt, R. Wandeler & A. Baiker, *Cat. Rev. Sci. Eng.* **45**, 1 (2003).

[7]  A. A. Novitskiy, E. Pérez, W.  Wu, J. Ke & M. Poliakoff, *J. Chem. Eng. Data* **541**, 580 (2009).

[8]  Z. Tang, Z. Du, E. Mihn,. L. Gao, T. Jiang & B. Han *Fluid Phase Equilib.* **239**, 8 (2006).

[9]  P. H. van Konynenburg & R. L. Scott, *Phil. Trans.* **298**, 495 (1980).

[10]  L. J. Rovetto, S.B.Bottini, E.A.Brignole & C.J.Peteres, *J. Supercrit.Fluids* **25**, 165 (2003)

[11]  National Institute of Standards and Technology, http://webbook.nist.gov/chemistry/

[12]  M.M. Abbot, *Chem. Eng.Prog.* **85**, 25(1989).

[13]  P. Hegel, A. E. Andreatta, S.Pereda, S.B.Botttini & E.A. Brignole, *Fluid Phase Equilibria* **266**, 31 (2008).

[14]  J.C. Holste, K.R. Hall, P.T. Eubank K.N. Marsh, *Fluid Phase Equilibria* **29**, 116 (1986).