MEASUREMENT OF PHYSICAL PROPERTIES OF REFRIGERANT MIXTURES. DETERMINATION OF PHASE DIAGRAMS.

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ABSTRACT

Accurate knowledge of high pressure phase equilibrium is of utmost interest in designing chemical processes and separation units operating at high pressures. Moreover, these data are essential to develop optimized models in order to provide continuous representation of high pressure phase equilibrium. The best models are required to permit process simulators to be the most accurate as possible. There are many experimental ways to obtain information about the phase behaviour of fluid mixtures. They can be classified into two main categories open and closed circuit methods. Closed circuit methods are composed of two main categories: the synthetic methods where compositions are known a priori and analytic methods where samplers are needed. The laboratory has published several data sets concerning refrigerant systems (binaries and ternaries). The more recent are:

The binary and ternary systems with 1,1,1,2,3,3,3-Heptafluoropropane (R227ea), Difluoromethane (R32) (two hydrofluorocarbons) and propane.

The binaries of R227ea or R32 with CO_2 and an old refrigerant SO_2. The ternary system composed of Dimethyl Ether (DME), Pentafluoroethane (R125) and 1,1,1,2-Tetrafluoroethane (R134a)

Two binary systems involving DME with R134a and R32

In this paper we have focused our attention on two types of models:

The first one is a thermodynamic model implying Equations of State and several mixing rules

The second one is neural network model. It's not a "thermodynamic" model, but it can be used to calculate thermodynamics properties like enthalpy, entropy from density values. It has been used to represent density data of the R134a + R125 + DME ternary system.

INTRODUCTION

Information about high-pressure phase equilibrium is essential for many chemical processes and separation operations but also for the simulation of petroleum reservoirs, the transportation of petroleum fluids and the refrigeration industry. First, we will present some experimental techniques to obtain high pressure VLE data. The next step will consist in modelling and validating the experimental data. For high pressure calculations, the best method is a symmetric approach with isofugacity criterion. In this way, the mixture critical point is conveniently predicted. We have chosen a static-analytic method to measure PTxy data for the R227ea + Propane, R32 + Propane, R227ea + R32, CO_2 + R32 and CO_2 + R227ea, SO_2 + R227ea, SO_2 + R32, R134a + DME, R32 + DME systems. The 1,1,1,2,3,3,3,-Heptafluoropropane (R227ea), Difluoromethane (R32), 1,1,1,2-Tetrafluoroethane (R134a) and Pentafluoroethane (R125) are alternative refrigerants used for air conditioning and also as propellants for pharmaceutical aerosols and as fire extinguishing agents. These refrigerants have a zero Ozone Depletion Potential (ODP) but a significant Global Warning Potential (GWP). Propane is a hydrocarbon, carbon dioxide is an "old" refrigerant first used in marine refrigeration, DME can be considered as a solvent, as an extraction agent, as a propellant in aerosols, and as a fuel in welding, cutting and brazing. Sulphur dioxide (SO_2) is an "old" refrigerant first used by Raoul Pierre Pictet (1846-1929) in industrial scale. It has zero ODP and zero GWP.

EXPERIMENTAL TECHNIQUES AND MODELLING

Experimental techniques.

Experimental methods for the investigation of high-pressure phase equilibrium belong either to

closed or open circuit methods (see xxx for more details).

Closed circuit methods:

They can be divided into two main classes, depending on how the composition is determined: static-analytic methods and static-synthetic methods. For the analytic methods, the composition of each phase is obtained by analyses after sampling (direct sampling method). For the synthetic methods, the global composition of the mixture is known a priori. No sampling is necessary. The composition of each phase is determined by solving mass balance equations (indirect methods) or the system is brought to its bubble or dew point. The variable volume cell technique can be cited as a static-synthetic method (Meskel-Lesavre et al., 1981; Fontalba et al., 1984). The components of the mixture are introduced separately and the composition is known by weighing procedure. The volume of the cell is modified with a piston to study bubble or dew points. At fixed temperature, saturating properties (pressure and saturated molar volume) of the mixture are determined through the pressure vs volume curve recorded that display a break point. With the static methods, the chemical system reaches equilibrium state with a good agitation either through the use of a magnetic stirrer or through circulating one or several phases with pumps. At equilibrium (constant temperature and pressure) samples of phases are withdrawn and analysed leading to PTxy data determination. Two categories can be distinguished:

- Dynamic-analytic methods with one or more circulating phases using pumps. With these methods special care must be taken to ensure the circulating phase is in equilibrium. Samples are directly taken in the circulation line with valves and analysed, generally by chromatographic analysers.

- Static-analytic method with a sampler system. The mixture is enclosed in a equilibrium cell. An internal stirring system permits to reach fast equilibrium. When this latter is reached, small quantities of the phases are sampled and analysed through chromatographic analysers. Laugier and Richon (1986) develop such an apparatus with samplers based on capillary sampling. With this procedure, sampling is the important point where analyses are necessary. Our laboratory is specialised in the development of reliable tools (Guilbot et al., 2000) in order to obtain the most representative sampling.

Open circuit methods: There are several different techniques based on this principle. Only the densimeter technique developed by Galicia Luna et al. (1994), and Bouchot and Richon (1998) which is a synthetic method is considered here. A mixture with known composition circulates through a vibrating U-tube. Density is deduced from the Forced Path Mechanical Calibration Model developed in the laboratory (Bouchot and Richon, 1998). This model linked the density to the acquired data (vibration period of U-tube, temperature and pressure). This apparatus can be used to obtain ($P\rho T$) data of compressed phases and to estimate saturating properties.

Modelling.

One of the goals with the experimental data is to develop models to represent and calculate thermodynamics properties of studied systems. According to theory, at equilibrium and for a mixture, the Gibbs energy is minimal. Consequently there is equality between the component fugacities in each phase.

We can choose two different models (dissymmetric approach or γ-Φ approach), one for the vapour phase (an equation of state) and a second for the liquid phase (an activity coefficient model). Unfortunately, this method is limited to the low or moderate pressures and can not accurately calculate the critical point of mixtures.

At high pressures, it is recommended to use a symmetric (Φ-Φ) approach. The same model is used for both the liquid and the vapour phases. This approach needs an equation of state (EoS) with an alpha function. This alpha function permits to calculate more precisely pure component vapour pressures. Mixing rules are necessary to calculate the parameters of the equation of state for the mixtures. Two types of mixing rules are frequently used:

- The van der Waals mixing rules (known as quadratic mixing rules).

- Excess function type mixing rules: they combine an EoS with an activity coefficient model. The first mixing rules belonging to this approach were developed by Huron and Vidal (1979) with an infinite pressure reference. Wong and Sandler (1992) develop more accurate mixing rules at high pressures. Other authors use zero pressure reference for low pressure VLE.

Non theoretical models like neural network can perform the representation of experimental data with very high precision. However, these kinds of model need a lot of data (> 500) during the learning step where the parameters are adjusted on the experimental values. This is used in the laboratory for representation of ($P\rho T$) data (Laugier and Richon, 2003). The uncertainties obtained enable to calculate derived properties like: enthalpy, entropy, or heat capacities. Artificial neural networks (ANN) consist of large numbers of computational units connected in a massively parallel structure (Fig. 1). The processing units (neurons) from each layer "n" are linked to all of the other processing units appearing in layer "$n+1$" by weighted connections.
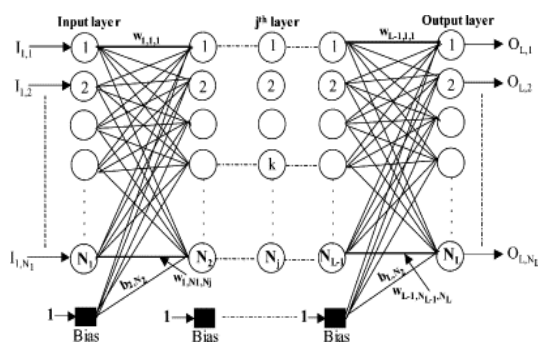
Figure 1. Artificial neural network architecture.

REFRIGERANTS SYSTEMS

Experimental method.

The apparatus used for the study of the R227ea + R32, R227ea + propane, R227ea + CO_2, R227ea + SO_2, R32 + propane, R32 + SO_2, R32 + CO_2, R134a + DME systems is based on a static-analytic method with liquid and vapour phase sampling. This apparatus (Fig. 2) is similar to that described by Valtz et al. (2002) and Valtz et al. (2003). The equilibrium cell is inside a regulated liquid bath. Temperatures are measured thanks to two platinum resistance thermometer probes (Pt100) directly inside the walls of the equilibrium cell. Pressures are measured through a pressure transducer (Druck, type PTX611, range: 0 - 6 MPa). The resulting uncertainties on T and P are respectively: ± 0.02 K and less than 0.001 MPa.

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system (BORWIN ver 1.5, from JMBS). The analytical column is HAYSEP T model, 100/120 Mesh (1/8" silcosteel tube, 1.6 m length, from Resteck France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe in the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses, resulting uncertainties on vapour and liquid mole fractions are estimated to be less than ± 1 %.

At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded with liquid of less volatile component (about 5 cm³). Equilibrium temperature is assumed to be reached when the two Pt100 probes give equivalent temperature values within their temperature uncertainty for at least 10 minutes. After recording the vapour pressure of the heavier component at equilibrium temperature, the two-phase envelopes are described with at least six P, x, y points (liquid and vapour): the lighter component is introduced step by step, leading to successive equilibrium mixtures of increasing overall lighter

component compositions. Equilibrium is assumed when the total pressure remains unchanged within ± 1.0 kPa during a period of 10 min under efficient stirring.

For each equilibrium condition, at least five samples of both vapour and liquid phases are withdrawn using the pneumatic samplers ROLSI™ (Guilbot et al., 2000) and analysed in order to check for measurement repeatability.
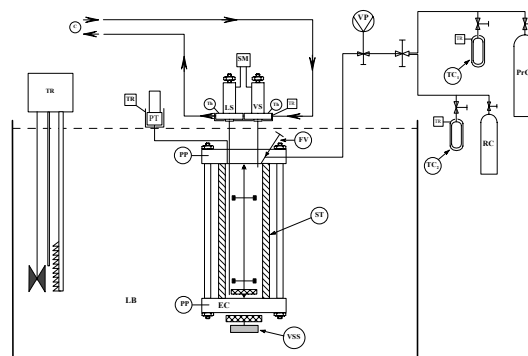

Figure 2. Vapour Liquid apparatus. C : Carrier Gas; EC : Equilibrium Cell; FV : Feeding Valve; LB : Liquid Bath; LS : Liquid Sampler; PP : Platinum resistance thermometer Probe; PrC : CO_2 Cylinder; PT : Pressure Transducer; RC : Refrigerant Cylinder; SM : Sampler Monitoring; ST : Sapphire Tube; TC_1 and TC_2 Thermal Compressors; Th : Thermocouple; TR : Temperature Regulator; VS : Vapor Sampler; VSS : Variable Speed Stirrer; VP : Vacuum Pump.

The apparatus used to measure vapour liquid equilibrium data of the ternary system composed of R32 + propane + R227ea is based on a static-synthetic method with a variable volume cell. This apparatus is similar to that described by Fontalba et al. (1984). With this apparatus, we can measure the bubble pressure for a given composition at a given temperature. The overall composition of the mixture is determined by accurate weighing of the cell before and after successive loadings of each species in the cell.

The apparatus used to measure *(PρT)* data and to estimate limits of VLE equilibrium of the ternary system composed of R134a + R125 + DME, is based on the dynamic-synthetic vibrating tube method. This apparatus, presented on Fig. 3, is mainly composed of the DMA 512 P Cell (Anton Paar) linked to a frequency meter. The Forced Path Mechanical Model (Bouchot and Richon, 2001) was used to link the density to U-tube vibrating period, temperature and pressure. The parameters of this model are determined, at each temperature, by measuring the vibrating period under a vacuum ($< 10^{-4}$ MPa) and vibrating periods of U-tube filled with a reference fluid of accurately known density along pressures. .

Figure 3. Vibrating tube densimeter. (1) Loading Cell ; (2a,b) Valve; (3) rupture disc; (4) Heat exchanger ; (5) DMA 512 P Cell (Anton Paar) linked to an Electronic unit to measure vibrating tube periods ; (6) circuit of temperature regulating fluid ; (7) Pressure sensors regulated at fixed temperature (373 K); (8) vacuum pump; (9) Vent ; (10) Liquid bath; (11) Vibrating cell temperature probe; (12) Bath temperature probe.

The mixture is introduced into the loading cell (1) and maintained over its bubble pressure at ambient temperature. The baths are regulated at fixed temperature with a difference of about 0.3 K between the circuit and the U-tube to be sure that the first step of changing of phase will take place inside the U-tube. Then, the gas and liquid densities are measured at different pressures respectively from the vacuum up to the dew point and (after a purge procedure of U-tube) from high pressures down to the bubble point. The global uncertainties of data are about ± 0.002 MPa, ± 0.02 K and ± 0.05% in density with a limit of ± 0.2 kg/m^3 at lowest densities.

Correlations and modelling.

The experimental data were correlated by means of in house software, developed by Armines, Ecole des Mines de Paris. We have used the Peng and Robinson (1976) Equation of State (PR EoS) and Redlich and Kwong (1949) Equation of state (RK EoS) in a symmetric (Φ-Φ) approach. The Mathias Copeman (1983) (MC) alpha function was selected to have accurate representation of vapour pressures of each component. Three mixing rules, the Huron Vidal mixing rules, the MHV1 mixing rules (Michelsen, 1990) (zero pressure reference) and the Wong Sandler mixing rules (WS) were used. The excess Gibbs energy is obtained through the NRTL (Renon and Prausnitz, 1968) local composition model. Parameters are adjusted directly to VLE data through a modified Simplex algorithm (Åberg and Gustavsson, 1982) using an objective function:

Neural network model was used to represent ($P\rho T$) data of the R134a + R125 + DME ternary system. Sigmoid functions were chosen for the hidden layers and linear function for the output layer. The weights of the network are adjusted on experimental data (about 600) during the training step. Then the network is validated on other experimental data.

EXPERIMENTAL RESULTS AND MODELLING

The R32 + R227ea + propane system.

All binary systems were studied prior to the study of the ternary system composed of R32, R227ea and propane. The R32 + R227ea (Coquelet et al., 2003) system can be considered as ideal.. The propane + R227ea (Valtz et al., 2002) and R32 +propane (Coquelet et al., 2003) systems exhibit an azeotrope (Fig. 4). These systems were represented with the RK EoS, involving MC alpha function and MHV1 mixing rules with the NRTL excess Gibbs energy model.
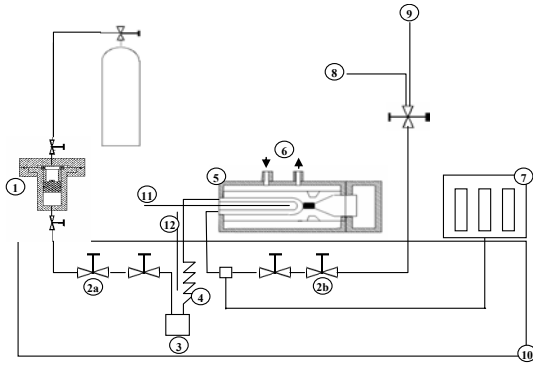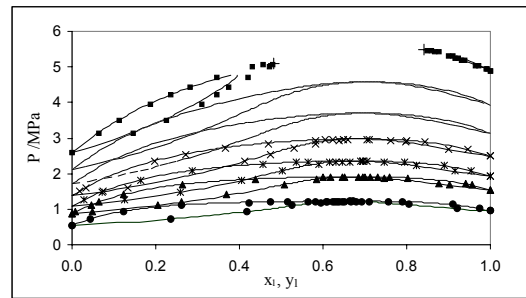

Figure 4: VLE for the R32 (1) + propane (2) system at different temperatures: ●, 278.10 K; ▲, 294.83 K; *, 303.23 K; ×; 313.26 K ; ■; 343.26 K; +; graphical end points; solid lines, calculated with RK EoS and MHV1 mixing rules ; dashed lines ---, calculated at 323 K; dashed lines _ _ _, calculated at 333 K

According to the Fig. 4, the previous model is not capable to represent the region close to the mixture critical points. The PR EoS with the Wong Sandler mixing rules, which proposed a supplementary adjustable parameter were preferred. Consequently, the critical line could be calculated for the R32 + propane system (Fig. 5).
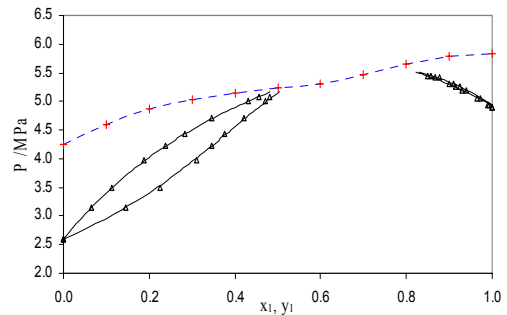

Figure 5: Pressure vs R32 mole fraction in the R32 (1) - propane (2) system at 343.26 K. Solid lines are calculated with PR EoS and Wong-Sandler mixing rules. Dashed line is the line of critical point.

Thanks to these binaries system and the experimental data obtained with the variable volume cell, the corresponding ternary system (Coquelet et al., 2003) can be predicted. Three mixtures were studied. We have plotted the experimental data in a *PT* diagram in which we have calculated bubble and dew pressures for each experimental composition.

The prediction of the ternary system (Fig. 6) with the binary parameters determined from the study of each binary system is accurate in the whole temperature range even outside the temperature range in which the binaries were studied.
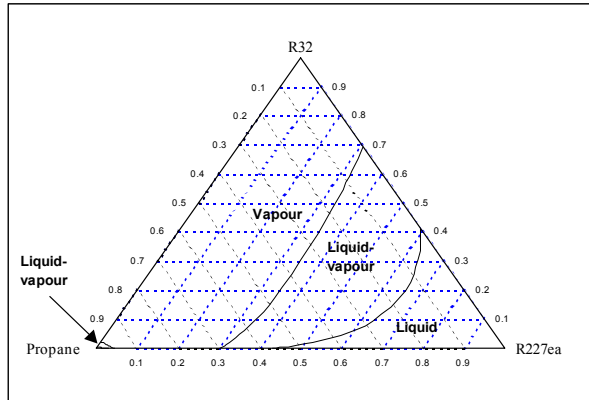

Figure 6: Ternary phase diagram: The system R32 (1) + R290 (2) + R227ea (3) at $T = 293$ K and $P = 0.85$ MPa.

Systems with old refrigerants

Two old refrigerants were considered: the CO_2 which is no toxic and commonly used, and the SO_2 which is toxic but used in the past in industrial refrigeration. Moreover, systems with SO_2 exhibit some very interesting aspects.

Two binaries systems including CO2 were studied with the static-analytic apparatus (figure 2). These two systems are R32 + CO_2 (Rivollet et al., 2004) and R227ea + CO_2 (Valtz et al., 2003). They do not present azeotropic behaviour. Two other binary systems including SO_2 were studied also with the static-analytic apparatus. These two systems are R32 + SO_2 (Valtz et al., 2004) and R227ea + SO_2 (Valtz et al., 2004). The R227ea + SO_2 system exhibits an azeotrope while the R32 +SO_2 system does not. For temperatures below the R227ea critical temperature, the composition of the azeotrope decreases with temperature increase. At the critical temperature of R227ea, it appears a drastic change in the slope of the T vs x azeotropic line. For temperatures above the R227ea critical temperature, a special behaviour of the azeotropic compositions was observed.

The R134a+R125+DME refrigerant mixture

This mixture has been studied at different temperatures and pressures. Other VLE data for systems containing DME are available: R32 + DME (Valtz et al., 2004) and R134a + DME (Valtz et al., 2004) . The peculiarity of the R134a + DME system is to present minimum pressure azeotropes, which disappear around 350 K. The isothermal P, x, y data are well represented with the RK EoS using the Mathias Copeman alpha function and the Huron-Vidal mixing rules involving the NRTL model.
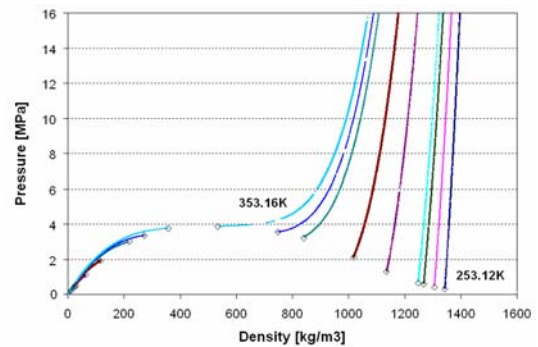

Figure 7: 9 isothermal ($P\rho T$) data of R134a + R125 + DME mixture (253.12, 263.10, 273.18, 278.30, 303.18, 323.15, 343.12 and 353.16 K). ($\diamond$) represent estimated VLE limits.

($P\rho T$) data of compressed phases, measured with the vibrating tube method are represented on the Fig. 7. The data cover a range from 253.12 K up to near the critical point estimated at about 357 K. These data were used to represent the limits of the liquid-vapour region.

Moreover, a neural network presented before was developed to represent both vapour and liquid phase with uncertainties closed to the experimental results.

CONCLUSION

The study of vapour liquid equilibrium systems needs an adequate experimental technique. Several techniques involving synthetic or analytic methods, open circuit methods or closed circuit methods exist. Refrigerant mixtures are very interesting from the point of view of thermodynamics and phase diagrams. Binary systems including "old" refrigerant generate different shapes of phase envelops.

Two types of modelling were performed: one with a physical model based on thermo dynamical considerations and another with a mathematical model using artificial neural networks.

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