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Needs of thermodynamic properties measurements and modeling in the frame of new regulations on refrigerants

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Abstract: In 1987, the Montreal Protocol prohibited the worldwide use and production of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) and hydro fluorocarbons (HFCs) were proposed as alternative refrigerants. Unfortunately, HFCs have non negligible global warning potential and therefore new refrigerants must be proposed or old refrigerants must be used associated with HFC. Accurate experimental thermodynamic data and predictive techniques are required for better understanding of the performance of the newly proposed refrigerants. In this communication, experimental techniques based on either analytic or synthetic methods are first described. Data are reported. Then two newly developed predictive models based on thermodynamic approach with the isofugacity criterion and artificial neural network method are presented. The results can provide better evaluation of refrigerants, especially with the aim of studying global warning effects.

Key words: Refrigerants, Experimental apparatus, Thermodynamic, Modeling, Vapor-liquid equilibria (VLE), Phase diagram, Density
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INTRODUCTION

CFCs and HCFCs were the most frequently used materials in the refrigeration and air conditioning industry. At the end of 1970s, it was shown by the scientific community that these fluids were a source of ozone layer depletion. Ozone layers absorb certain wavelength of ultraviolet radiation from the sun. The presence of chlorine in CFCs and HFCs molecules is one of the reasons of their stability, which allows them not to be destroyed by solar radiations in the atmosphere, whereas the presence of chlorine radicals sets off a reaction that may destroy hundred thousands of ozone molecules. In 1989, 29 countries ratified the Montreal Protocol. CFCs and HCFCs were completely prohibited and new generations of refrigerants, namely the HFCs, were adopted, which are safe for the ozone layer (zero Ozone Depletion Potential, ODP). However, their Global Warming Potentials (GWPs) are not negligible and they contribute to greenhouse effects. In 1992, the decision to prohibit progressively the HFCs was taken at the Kyoto Protocol, where a *TEWI* (Total Equivalent Warming Impact) factor was introduced, which is defined below as:

$$TEWI=GWP\times L\times n+GWP\times m(1-\alpha)+n\times E\times\beta, \qquad (1)$$

where, GWP is the global warming potential (CO_2 related), L represents leakage rate per year (kg), n stands for system operating time (year), m indicates refrigerant charge (kg), α is recycling factor, E represents energy consumption per year (kW·h) and β stands for CO_2-emission per kW·h. This factor takes into account the direct effect due to emission and the indirect effects due to energy requirement. In fact, cold production is costly. Electricity, obtained from combustion of fossil fuels is required for using refrigeration facilities.

There are many possibilities to reduce the value of the *TEWI* factor: the first one is reducing refrigerant losses; the second one is improving efficiency of processes reducing energy consumptions; the last one would come from use of new generation of fluorinated fluids with the lowest possible GWP. Ammonia is an example of fluids used in refrigeration without any GWP but with special application criteria. Whatever the fluid, it is necessary to rely on the most accurate possible representation of their thermodynamic properties.

In this work, we first review and present various experimental techniques for obtaining high pressure Vapor-liquid equilibria (VLE) data with the aim of enhancing our knowledge to generate the required experimental data for developing models. The best modelling technique for high pressure phase equilibria calculations is a symmetric approach with equality of fugacities concept. A review is then made on this method through which, the mixture critical point is also predicted. Application of other modelling techniques, such as artificial neural networks is also discussed. A static-analytic method is used to measure the *PTxy* value 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. It should be mentioned that the R227ea (1,1,1,2,3,3,3-heptafluropropane), R32 (difluoromethane), R134a (1,1,1,2-tetrafluoroethane) and R125 (pentafluoroethane) are alternative materials used for air conditioning, pharmaceutical aerosols (as propellants) and fire extinguishing. These chemicals have zero ODP. However, their significant GWP should not be neglected. Propane is a hydrocarbon, carbon dioxide is an "old" refrigerant used in marine refrigeration, dimethylether (DME) is used as a solvent, as an extraction agent, a propellant in aerosols, and 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 investigation of high-pressure phase equilibrium belong to either closed or open circuit methods. We consider here only the closed circuit methods, which can be divided into two main classes, depending on how the composition is determined: analytical methods and synthetic methods. For the analytical methods, the composition of each phase is obtained by analysing 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. For the static methods, temperature, global composition and volume (or pressures) are constant. The system reaches equilibrium state with a good agitation through either the use of a magnetic stirrer or circulating one or several phases with pumps.

1. Open circuit methods

The densimeter technique developed by Galicia-Luna *et al.*(1994), and Bouchot and Richon (1998) is a synthetic method. 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, 2001). This model links the density to the acquired data (vibration of tube, temperature and pressure).

This apparatus can be used to obtain ($P\rho T$) data of compressed phase and to estimate limits of VLE equilibrium.

Another example is with the stripping of a solute from a solution (dilutor technique, Legret *et al.*(1983)). An equilibrium cell contains non-volatile solvent and infinitely dilute solute. As the solute is carried away through a stripping gas flow, the decrease of the solute concentration enables to obtain the value of the limiting activity coefficient or Henry constant using a mass balance and equilibrium equations.

2. Closed circuit method

The variable volume cell technique can be cited as a static method (Meskel-Lesavre *et al.*, 1981; Fontalba *et al.*, 1984). It is a static-synthetic method, no sampling is needed. The components of the mixture are introduced separately and the composition is known by a 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 verses volume curve recorded that displays a break point.

3. Analytic method

Two categories can be distinguished:

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

(2) Static method with a sampler system. The mixture is enclosed inside an equilibrium cell. An internal stirring system permits reaching fast equilibrium. When the latter is reached, small quantities of the phases are sampled and analysed through chromatographic analysers. Laugier and Richon (1986) develop this apparatus with samplers based on capillary sampling. With this procedure, sampling is the important point where analyses are necessary. CEP/TEP laboratory at Ecole Nationale Supérieure des Mines de Paris (Paris School of Mines) is a well known and well equipped laboratory for developing reliable tools (Guilbot *et al*., 2000) to obtain the most representative sampling.

Modeling

One of the objectives of generating experimental data is to develop and validate models which could permit representing and calculating thermodynamics properties of studied systems. At equilibrium conditions, the Gibbs free energy of the system is minimal and fugacities of the components through all the existing phases are equal:

$$f_i^{\mathrm{V}}(T,P,y) = f_i^{\mathrm{L}}(T,P,x), \tag{2}$$

where f stands for fugacity. Superscripts 'V' and 'L' represent vapour and liquid phases, respectively. T, P and x are temperature, pressure and mole fraction, respectively. There are two main methods for calculating fugacity and therefore solving Eq.(2). The first method employs dissymmetric or γ-Φ approach, in which an equation of state (EoS) is used for calculating fugacity in vapour phase and an activity coefficient model is employed for calculating fugacity in liquid phase. This method can be especially used for studying interactions between molecules on phase equilibra. However, it is limited to low and moderate pressures and cannot accurately calculate the critical point of the mixture.

At high pressures, it is better to use a symmetric (Φ-Φ) approach, in which an EoS with an alpha function is used for calculating fugacities in both liquid and vapour phases. The alpha function permits more precise calculation of the pure component vapour pressures. Mixing rules are necessary to calculate parameters of EoS for the mixtures. Two types of mixing rules are normally used: (1) The van der Waals type mixing rules; (2) g^E type mixing rules, which combine an EoS with an activity coefficient model. The latter was originally developed by Huron and Vidal (1979) with an infinite pressure reference. Wong and Sandler (1992) developed more accurate mixing rules at high pressure. Other authors use zero pressure reference for low pressure VLE.

Non theoretical based models such as artificial neural network (ANN) can perform the representation of experimental data with very high precision. For information about neural network used in our laboratory we suggest reading papers (Laugier and Richon, 2003; Chouai *et al*., 2002; Scalabrin *et al*., 2002; 2006a; 2006b) ANN models need a lot of data (>500) during the learning step where the parameters are adjusted on the experimental values. The accuracy of volumetric properties (PVT) representations (within experimental uncertainty) enables calculating derivative properties like enthalpy, entropy, or calorific capacities. ANNs consist of large numbers of computational units connected in a massively parallel structure. The processing units (neurones) from each layer "n" are linked to all of the other processing units appearing in layer "n+1" by weighted connections. Collectively, these connections (as well as the transfer functions of the processing units) form more or less good distributed representations of relationships between input and output data. Neural networks do not need an explicit formulation of the mathematical or physical relationships of the handled problem. The input layer of the network does not perform any processing, but acts as a means to introduce scaled data to the network.

The data from the input neurones are propagated through the network via the interconnections. Every neurone in a layer is connected to every neurone in adjacent layers. A scalar weight is associated to each connection. The neurones within the hidden layer perform two tasks: they sum the weighted inputs connected to them and then pass the resulting summations through a non-linear activation function to the output neurone or adjacent neurones of the corresponding hidden layer (in case of more than one hidden neurone layer). The sigmoid function: $f(x)=1/(1+e^{-x})$ is often used as activation function. A bias term is associated with each interconnection in order to introduce a supplementary degree of freedom. Thus, the expression of the weighted sum to the kth neurone in the jth layer ($j\geq2$) is given by

$$S_{j,k}=\sum_{i=1}^{N_{j-1}}\left(w_{j-1,i,k}I_{j-1,i}\right)+b_{j,k}, \tag{3}$$

where $I_{j-1,i}$ is the information from the ith neurone in the ($j-1$)th layer, $b_{j,k}$ stands for the bias term and N_{j-1} is the number of neurones in the layer $j-1$. The output of the kth neurone in the layer j ($j\geq2$) is, for a sigmoid function,

$$O_{j,k}=1/[1+\exp(-S_{j,k})]. \tag{4}$$

REFRIGERANTS SYSTEMS

Experimental method

The apparatus used for studying 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 phases sampling. This apparatus (Fig.1) is similar to that described by Valtz *et al.*(2002; 2003). The equilibrium cell is inside a regulated liquid bath. Temperatures are measured by two platinum resistance thermometer probes (Pt100) directly inside the walls of the equilibrium cell. These Pt100 probes are calibrated against a 25 Ω reference probe (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the International Temperature Scale 1990 protocol. Pressures are measured through a pressure transducer (Druck, type PTX611, range: 0~6 MPa). This sensor is calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot). Pressure and temperature data acquisition is performed with a computer linked to an HP unit (HP34970A). The resulting uncertainties on T and P are respectively ±0.02 K and ±0.0015 MPa.

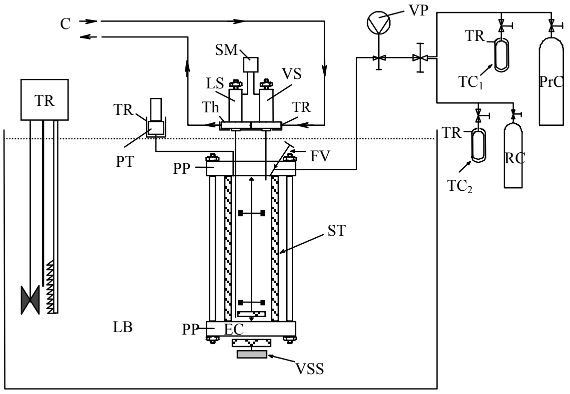

Fig.1 Vapour liquid apparatus

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: thermal compressors; Th: thermocouple; TR: temperature regulator; VS: vapor sampler; VSS: variable speed stirrer; VP: vacuum pump

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 cm^3). Equilibrium temperature is assumed to be reached when the two Pt100 probes give equivalent temperature values within their temperature uncertainty for at least 10 min. After recording the vapour pressure of the heavier component at equilibrium temperature, the two-phase envelopes are described with about 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^{TM} (Guilbot *et al.*, 2000) and analysed in order to check for the measurement repeatability.

The apparatus used to measure VLE data of the ternary system composed by R32+propane+R227ea is based on a 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 thermocouples are periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY Precision Instruments). The resulting uncertainty is ±0.1 K. The 25 Ω reference platinum resistance thermometer was calibrated by the Laboratoire National d'Essais (Paris) based on the 1990 International Temperature Scale (ITS 90). Pressures are measured by means of a pressure transducer (Sedeme, France, range: 0~25 MPa) directly connected to the equilibrium cell. The pressure uncertainty is estimated to be ±0.002 MPa, after a careful calibration against a dead weight balance (Desgranges and Huot 5202S, CP 0.3~40 MPa, Aubervilliers, France) at different temperatures. We determine the composition of the mixture by accurate weighing of the cell before and after successive loadings of each species in the cell. The uncertainty of the liquid composition is given below as Eq.(5) and its value is less than 0.2 mol% for each component:

$$\Delta x_i = x_i\left[\frac{\Delta m_i}{m_i}+\left(\Delta m\sum_i\frac{1}{M}\right)\Big/\sum_i\frac{m_i}{M_i}\right], \tag{5}$$

with Δm_i=Δm=2×10^{-3} g.

The apparatus used to measure ($P\rho T$) data and to estimate limits of VLE equilibrium of the ternary system composed by R134a+R125+DME, is based on the synthetic dynamic vibrating tube method. This apparatus, described in Fig.2, is mainly composed of 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 vibrating period, temperature and pressure. The parameters of this model are determined by measuring the vibrating period at a very low pressure (<5×10^{-4} MPa) and liquid phase period of a reference fluid.

The mixture is introduced to the cell (1) in Fig.2 and maintained at a pressure above the bubble point ambient temperature. The baths are regulated at fixed temperature with a difference about 0.3 K between the circuit and the Vibrating tube to be sure that the first step of changing of phase will be placed in the U-tube. Then, the gas and liquid phases are measured at different pressures respectively from the vacuum up to the dew point and from the upper limit 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 in lower density of 0.2 kg/m^3.

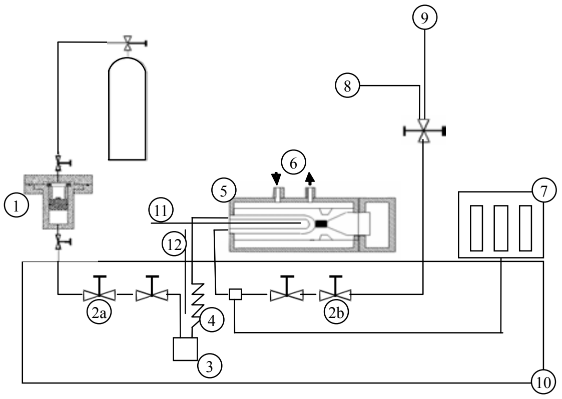

Fig.2 Vibrating tube densimeter

(1) components cell; (2) valve; (3) bursting disc; (4) heater ; (5) DMA 512 P Cell (Anton Paar) linked to an electronic unit to measure vibrating tube periods; (6) links with a liquid bath for vibrating tube; (7) pressure sensors regulated at fixed temperature (373 K); (8) access to vacuum pump; (9) extraction; (10) liquid bath; (11) vibrating cell temperature sensor; (12) bath temperature sensor

Correlations and modeling

The experimental data were correlated by means of in-house software, developed at Ecole des Mines de Paris. Two equations of state, namely the Peng and Robinson Equation of State (PR EoS) (Peng and Robinson, 1976) and Redlich and Kwong Equation of State (RK EoS) (Redlich and Kwong, 1949) have been used in a symmetric (Φ-Φ) approach. The Mathias Copeman (MC) alpha function (Mathias and Copeman, 1983) was selected to have an accurate representation of vapour pressures of each component. Three mixing rules, the Huron Vidal mixing rules (Huron and Vidal, 1979), the MHV1 mixing rules (Michelsen, 1990) (zero pressure reference) and the Wong Sandler (WS) mixing rules (Wong and Sandler, 1992) were used to perform the representation of the mixture. The excess Gibbs free energy is obtained through the NRTL (Renon and Prausnitz, 1968) local composition model, shown as Eq.(6):

$$g^E(T,P,x_i)/(RT)=\sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{j,i}\tau_{j,i}/(RT)\right)}{\sum_k x_k \exp\left(-\alpha_{k,i}\tau_{k,i}/(RT)\right)}\tau_{j,i},$$

$$\tau_{i,i}=0 \text{ and } \alpha_{i,i}=0, \qquad (6)$$

where $\alpha_{j,i}$, $\tau_{j,i}$ and $\tau_{i,j}$ are adjustable parameters. It has been recommended (Renon and Prausnitz, 1968) to use $\alpha_{j,i}$=0.3 for systems with polar component. $\tau_{j,i}$ and $\tau_{i,j}$ 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 ternary system R134a+R125+DME. Fig.3 presents an example of the architecture of a unique network to represent both phases. Sigmoid functions are used for the hidden layers and linear function was chosen as the output layer.

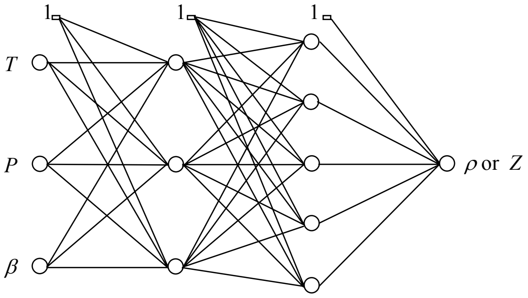

Fig.3 Architecture of a neural network used to represent liquid and vapour ($P\rho T$) data of FX90 mixture. β is a coefficient equal to 1 for the vapour phase and equal to 0 for the liquid phase

The weights of the network are adjusted on experimental data (about 600) during the training step. Then the network is approved on other experimental data.

EXPERIMENTAL RESULTS AND MODELLING

The R32+R227ea+propane system

Before studying the ternary system composed by R32, R227ea and propane, each binaries system was studied. The R32+R227ea (Coquelet *et al.*, 2003a) system can be class ideal VLE (Fig.4).

However, the propane+R227ea (Valtz *et al.*, 2002) and R32+propane (Coquelet *et al.*, 2003b) systems exhibit azeotropic behavior (Figs.4 and 5).

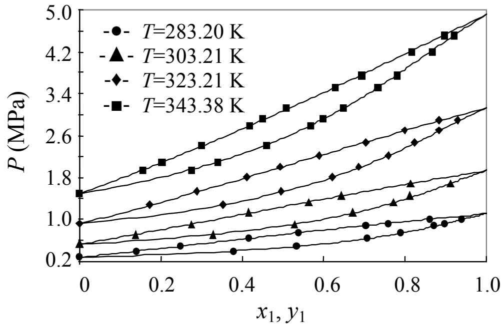

Fig.4 Vapour liquid equilibrium data for the R32 (1)–R227ea (2) system at different temperatures, calculated with RK EoS and MHV1 mixing rules

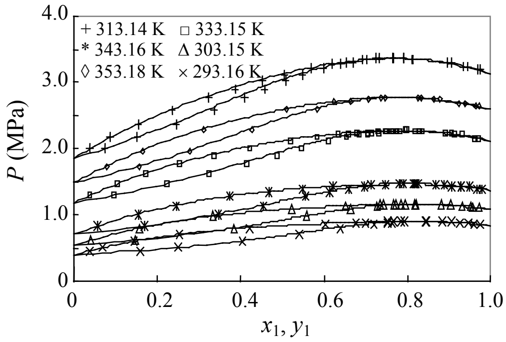

Fig.5 Pressure as a function of propane mole fraction in the propane (1)–R227ea (2) mixture at different temperatures, calculated with RKS EoS and the MHV1 mixing rules

Concerning these systems, the RK EoS, with the MC alpha function and the MHV1 mixing rules involving the NRTL excess Gibbs energy model was used to correlate the data.

According to Fig.6, the previous model cannot represent the region close to the mixtures critical points. This is due to incapability of the EoS and particularly of the MHV1 mixing rules. EoS parameters (molar co-volume and energy parameter) are not well calculated. The PR EoS with the WS mixing rules, which proposed a supplementary adjustable parameter was preferred. Consequently, the critical line could be calculated for the R32+propane system (Fig.7). The calculation of critical points was proposed by Heidemann and Khalil (1980) and Michelsen and Heidemann (1981). They assumed that the stability criterion for an isothermal variation (between an initial state and a very close new one) corresponds to a minimum of the molar Helmholtz free energy A, shown as Eq.(7):

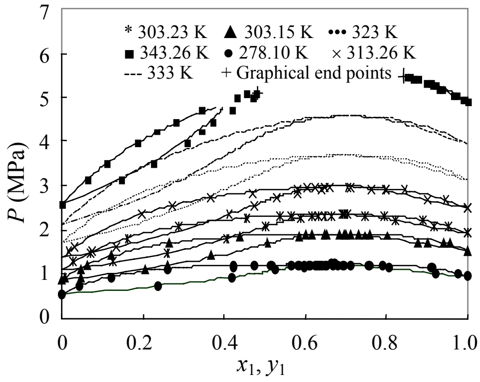

Fig.6 VLE for the R32 (1)+propane (2) system at different temperatures (solid lines calculated with RKS EoS and MHV1 mixing rules)

$$A - A^0 - \sum_i \mu_i^0 \Delta n_i \ge 0, \qquad (7)$$

where μ and n stand for chemical potential and mole, respectively. The critical point corresponds to the limit of stability. They developed an algorithm to calculate the critical point with a van der Waals type EoS, associated to the classical mixing rules. Stockfleth and Dohrn (1998) improved this method by generalizing the previous algorithm. The latter was chosen here to calculate the critical line using the PR EoS and WS mixing rules involving the NRTL model.

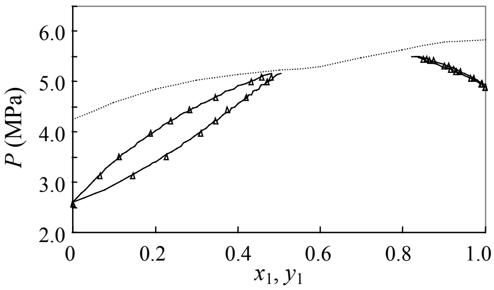

Fig.7 Pressure vs R32 mole fraction in the R32 (1)–propane (2) system at 343.26 K. Solid lines are calculated with PR EoS and WS mixing rules; Dashes line is the line of critical point

With the binaries system and the experimental data obtained with the variable volume cell, the corresponding ternary system (Coquelet *et al.*, 2004) could be predicted. Three mixtures were studied. We plotted the experimental data in a PT diagram in which we have calculated bubble and dew pressures for each experimental composition (Fig.8). The prediction of the ternary system 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. Consequently, a ternary phase diagram can be determined precisely (Fig.9) for a given temperature and a given pressure.

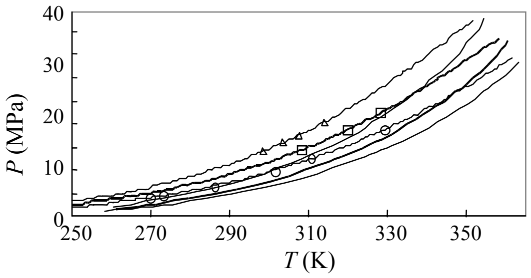

Fig.8 The system R32 (1)+R290 (2)+R227ea (3). Pressure versus temperature diagram for each composition

Mixture 1: x_1=0.322, x_2=0.123, □: Experimental bubble points, thick line: calculated with RKS EoS and MHV1 mixing rules;
Mixture 2: x_1=0.135, x_2=0.174, ○: Experimental bubble points, solid line: calculated with RKS EoS and MHV1 mixing rules;
Mixture 3: x_1=0.493, x_2=0.127, Δ: Experimental bubble points, dashed line: calculated with RKS EoS and MHV1 mixing rules

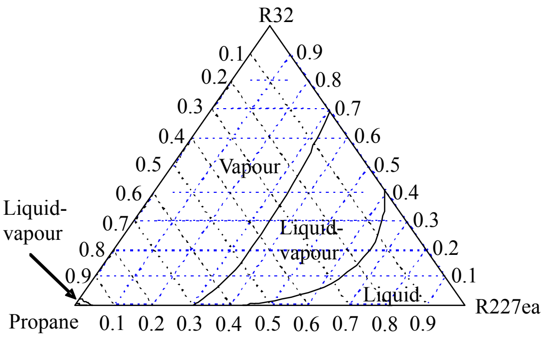

Fig.9 Ternary phase diagram of the system R32 (1)+R290 (2)+R227ea (3) at *T*=293 K and *P*=0.85 MPa

Systems with old refrigerant

Two old refrigerants were considered: CO_2 which is not toxic and commonly used, and SO_2 which is toxic but used in the past in industrial refrigeration. Moreover, systems with SO_2 exhibit some very interesting aspects.

Two binary systems including CO_2 were studied with static analytic apparatus. These two systems are R32+CO_2 (Rivollet *et al.*, 2004) and R227ea+CO_2 (Valtz *et al.*, 2003). They do not present any azeotropic behaviour. For these systems the mixture critical points line was calculated (Figs.10 and 11).

Two binaries system including SO_2 were studied with static analytic apparatus. These two systems are

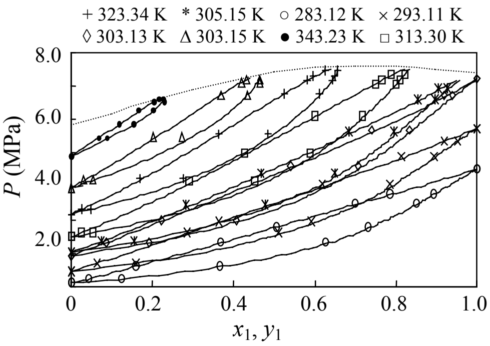

Fig.10 Pressure as a function of CO_2 mole fraction in the CO_2 (1)–R32 (2) mixture at different temperatures

Solid lines: calculated with PR EoS, WS mixing rules and NRTL activity coefficient model; dashes line: mixture critical points line

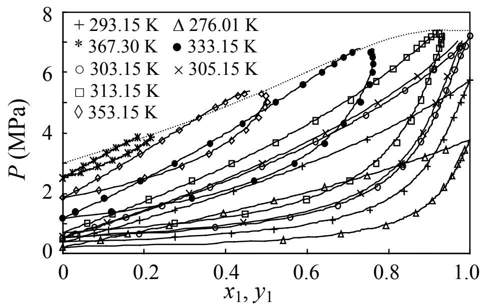

Fig.11 Pressure as a function of CO_2 mole fraction in the CO_2 (1)–R227ea (2) mixture at different temperatures

Solid lines: calculated with PR EoS, WS mixing rules and NRTL activity coefficient model; dashes line: mixture critical points line

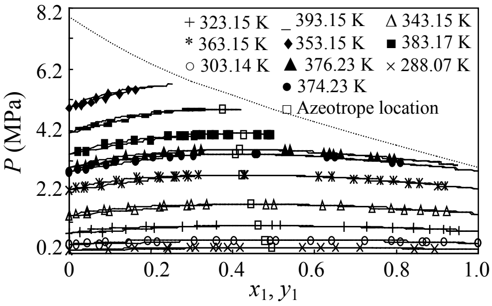

Fig.12 Pressure as a function of R227ea mole fraction in the R227ea (1)–SO_2 (2) mixture at different temperatures

Solid lines: phase envelopes calculated with PR EoS, WS mixing rules and NRTL activity coefficient model; dashes line: critical point line

R32+SO_2 (Valtz *et al.*, 2004a) and R227ea+SO_2 (Valtz *et al.*, 2004b). The R227ea+SO_2 system exhibits azeotropic behavior whereas R32+SO_2 system does not (Fig.12). The azeotrope location was calculated at each temperature and plotted in Fig.12. For temperatures below the R227ea critical temperature, the composition of the azeotrope decreases while temperature increases. At the critical temperature of R227ea, a drastic change appears in the slope of the *T* vs *x* azeotropic line.

For temperatures above the R227ea critical temperature, a special behaviour of the azeotropic composition was observed. At temperatures below the critical temperature of the lightest component the same type of trend was already reported by Gmehling *et al.*(1994), for the 2-propanone+tetrachloromethane system and 2-propanol+2-methyl-2-propanol systems. In each case, the vapour pressures of the two components are very close. When the vapour pressures of the two components become identical for one temperature, we have a Bancroft point. At this point, there will be at least one azeotrope. The vapour pressures of R227ea (1) and SO_2 (2) are very close to each other and if we extrapolate the R227ea vapour pressure above R227ea critical temperature, a Bancroft point appears. It may be one reason of the strange behaviour of the azeotrope (temperature vs composition).

The FX90 refrigerant mixture

The FX90 refrigerant mixture was studied for different temperature and pressure. Previously, the R32+DME (Coquelet *et al.*, 2005) system and the R134a+DME (Valtz *et al.*, 2005) system were studied. Experimental data and modelling of the R32+DME system are presented in Fig.13.

The peculiarity of the R134a+DME system is to present an azeotrope with a minimum pressure which disappear around 350 K (Fig.14). The isothermal *P*, *x*, *y* data are well represented with RK EoS using MC alpha function and the Huron-Vidal mixing rules involving the NRTL model.

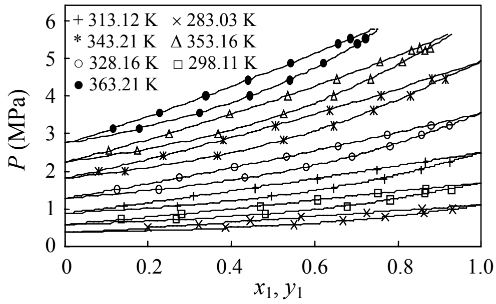

Fig.13 Pressure as a function of R32 mole fraction in the R32 (1)+DME (2) mixture at different temperatures, calculated with PR EoS, WS mixing rules and NRTL activity coefficient model

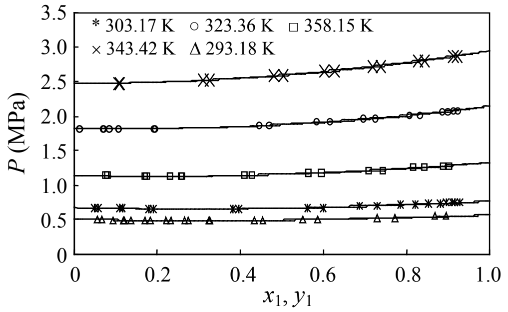

Fig.14 Pressure as a function of R134a mole fraction in the R134a (1)+DME (2) mixture at different temperatures, calculated with RK EoS, Huron-Vidal mixing rules and NRTL activity coefficient model

($P\rho T$) data of compressed phase, measured with the vibrating tube method are represented in Fig.15. 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.

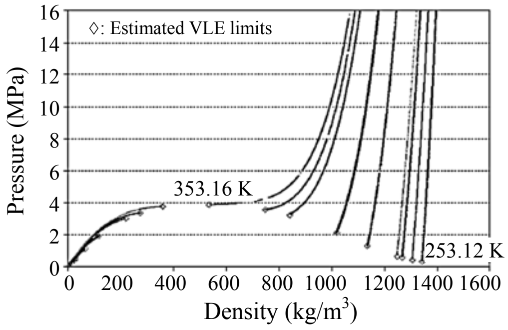

Fig.15 9 isothermal ($P\rho T$) data of FX90 mixture (253.12, 263.10, 273.18, 278.30, 303.18, 323.15, 343.12 and 353.16 K)

Moreover, a neural network presented before was developed to represent both vapour and liquid phase with uncertainties closed to the experimental results. This could be used to calculate derived properties like enthalpies if the vaporization enthalpies of the mixture are known.

CONCLUSION

A quick review was made on experimental techniques for measuring VLE, including synthetic or analytic methods, open circuit methods or closed circuit methods, to enhance our knowledge for selecting reliable experimental methods. Refrigerant mixtures are very interesting from the thermodynamics and phase diagrams point of view. Several mixtures that are good candidates for their future use in refrigerating systems have been studied and data treated herein. Two types of modelling have been used: physical models based on thermo dynamic aspects and mathematical based models such as neural networks. These two types of models permit accurate representation of VLE and volumetric properties, which has been shown in this paper. However, although the neural networks based models are very powerful for representing data in the range of data used for adjustment of their weights, they must not be used for prediction outside this range as they have no physical basis.

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