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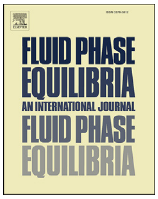

Modelling fluid phase equilibria in the binary system trifluoromethane + 1-phenylpropane

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ABSTRACT

The paper presents the results on modelling high pressure phase behaviour of the systems consisting of refrigerant, trifluoromethane (R23) and 1-phenylpropane. There were used cubic equations of state (GEOS, SRK and PR) coupled with van der Waals mixing rules in a semi-predictive approach (SPA). Based on the experimental VLE isothermal data in the range 300–330 K, binary interaction parameters (BIPs) were optimized, through regression of bubble pressure type. Unique sets of interaction parameters were estimated for each EoS, and used in the SPA to calculate the critical, subcritical and supercritical behaviour of the system.

The SPA calculations are comparatively discussed with the available experimental data in the temperature range (250–400) K and pressures up to 12 MPa. The calculations of critical line and of vapour-liquid, liquid-liquid, vapour-liquid-liquid phase equilibria, and of critical endpoints indicate a good modelling capacity of the tested EoSs and an accurate representation of the complex critical and subcritical behaviour of the investigated system.

1. Introduction

Phase behaviour knowledge and understanding of refrigerant and lubricant mixtures is essential in the optimal design of the refrigeration systems. Although the refrigerant is the key component of the working fluid, oil addition is required to lubricate the internal part of the compressor and to support sealing between its parts, thus insuring good functionality and an efficient vapour compression process [1–4].

In a typical refrigeration process, oil transport through the cycle cannot be avoided even when using an efficient oil separator, thus the two components interact affecting the physicochemical, thermodynamic and transport properties; on the other hand, phase separation is likely, mostly inside the evaporator. Therefore, selecting the efficient and effective working fluids represents a challenge and must consider the properties of the refrigerant, oil, and refrigerant-oil mixture, along with the environmental, energy and economical aspects. Properties like chemical stability in the working conditions, efficiency, low toxicity and reduced environmental impact are the most important for the refrigerant, while for oil good lubricating properties, seal compatibility, low hygroscopicity, and miscibility with the refrigerant are required.

Hydrofluorocarbons refrigerants (HFC) are used in the modern refrigeration cycles, in combination with compatible synthetic oils as: polyol esters, polyalkylene glycols, poly-alfaolefins, polyvinyleters or alkylbenzenes (phenylalkanes) [2,3,5,6]. For special biomedical or military applications at very low temperatures, mixtures consisting of HFC and phenyalkanes were recommended and successfully used [7–10]. Thus, information on the complex phase behaviour of the refrigerant-lubricant systems, the vapour-liquid, liquid-liquid, vapour-liquid-liquid phase equilibria, and the critical endpoints, are of utmost importance in the refrigeration process [7,8]. Equilibrium data can be obtained from experimental investigations, usually only for limited temperature and pressure domains; on the other hand, these experiments are time consuming and expensive. Therefore, modelling fluid phase

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equilibria, in a semi-predictive approach based on minimal experimental data, will be of importance for applications.

For the binary systems of HFC and phenyalkanes, which are of interest for this study, the experimental data on the high pressure phase equilibria are rather scarce or even are missing [9–14], comparing to systems containing the other classes of lubricants. As example, in the systems consisting of the trifluoromethane refrigerant and different members of the homologous series of the n-alkylbenzenes, the only available data are those reported by our group [11–14]. Therefore, calculations based on thermodynamic models with different complexity are needed to offer an extended view of the system phase behaviour. These models contain binary interaction parameters (BIPs) that must be adjusted, a methodology that also requires experimental data [15–18].

Models based on simple equations of state (EoS) [19,20] or on more complex thermodynamic models (e.g. based on molecular theories) were applied to describe the phase behaviour of highly non-ideal systems, with significant size difference among the molecules [6,21–23]. The advantages of developing cubic EoSs with different complexity and their limitations in predicting the critical and subcritical behaviour were previously analysed and reported [24–26]. However, despite their limitations, cubic equations remain one of the common approaches in modelling high pressure phase equilibria, with reasonable good results in reproducing the global phase behaviour.

Previous studies in similar systems of trifluoromethane and alkylbenzenes (phenyloctane, phenyltetradecane) [11,12] showed good modelling results and confirm that simple EoSs based models (PR and SRK) are reliable tools in the accurate prediction of the critical and subcritical behaviour. According to the classification of van Konynenburg and Scott, type III phase behaviour was found, specific for the asymmetric systems [27–29]. On the other hand the Cubic General Equations of State (GEOS) was successfully used for modelling asymmetric systems consisting of carbon dioxide and alcohols [30,31].

This paper aims to represent the topology of the phase behaviour for the system trifluoromethane and 1-phenylpropane using a simple model, based on cubic equations of state in a semi-predictive approach (SPA). These systems exhibit type IIIm phase behaviour as previously presented [13]. Three EoSs: Cubic General Equations of State (GEOS), the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) EoS coupled with van der Waals mixing rules and one single set of binary interaction parameters were comparatively discussed. The SPA calculation of the critical curves, LLV equilibrium, isothermal VLE and LLE, isobars, were compared with our experimental data [13] and the results showed good agreement between the model and experimental data.

2. Modelling

The Cubic General Equations of State (GEOS), the SRK and the PR EoSs coupled with conventional (van der Waals) mixing rules were used to model the global phase behaviour of the system of CHF_3+1-phenylpropane.

The good modelling capability of simple models based on EoSs for highly nonideal systems (type II–V phase behaviour) was previously justified [30–32] and confirmed (when using SRK and PR) in similar systems consisting of CHF_3 and other alkylbenzenes (phenyloctane, phenyltetradecane), [11,12].

The cubic General Equations of State (GEOS) form [32–36] is presented in relation (1):

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \tag{1}$$

where the four parameters a, b, c, d are described by following relations (2)

$$a(T) = a_c\beta(T_r) \quad a_c = \Omega_a\frac{R^2T_c^2}{P_c} \quad b = \Omega_b\frac{RT_c}{P_c} \tag{2a}$$

$$c = \Omega_c\frac{R^2T_c^2}{P_c^2} \quad d = \Omega_d\frac{RT_c}{P_c} \tag{2b}$$

The expressions of the parameters Ω_a, Ω_b, Ω_c, and Ω_d are obtained [32,36] by setting four critical conditions:

$$\Omega_a = (1-B)^3; \quad \Omega_b = Z_c - B; \quad \Omega_c = (1-B)^2(B-0.25); \\ \Omega_d = Z_c - (1-B)/2 \tag{3}$$

For the GEOS calculations, the temperature function used in the equation (2a) is:

$$\beta(T_r) = T_r^{-m} \tag{4a}$$

with reduced temperature, $T_r = T/T_c$. The B parameter of GEOS is given by equation:

$$B = \frac{1+m}{\alpha_c + m} \tag{4b}$$

where α_c is the Riedel's criterion, used as a fourth critical condition [32]. By introducing the α_c parameter in GEOS, the usual notation for the temperature function was changed to $\beta(T_r)$ in (2a). The a, b, c, d parameters of the cubic GEOS equation are calculated from the critical data (T_c, P_c, and Z_c), m, and α_c parameters.

The cubic GEOS equation is a general form for all the cubic equations of state with two, three, and four parameters [34–36]. Thus, to obtain the forms of the SRK or PR EoSs from equation (1), the following restrictions were set [34,36]:

$$c = -(b/2)^2 \text{ and } d = -b/2 \quad \text{for the SRK EoS} \tag{5a}$$

and

$$c = -2b^2 \text{ and } d = -b \quad \text{for the PR EoS} \tag{5b}$$

These restrictions lead to the well-known SRK equation:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{6}$$

with the temperature function:

$$a(T) = 0.42748\frac{R^2T_c^2}{P_c}\beta(T_r) \tag{7}$$

$$\beta(T_r) = \left[1 + m_{SRK}\left(1 - T_r^{0.5}\right)\right]^2 \tag{8a}$$

$$m_{SRK} = 0.480 + 1.574\omega - 0.176\omega^2 \tag{8b}$$

and to the PR equation:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \tag{9}$$

with the temperature function:

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