PHASE DIAGRAM OF METHANOL AND ALKANE BINARY SYSTEMS IN THE FIELD OF NATURAL GAS FRACTIONATORS: EXPERIMENTAL WORK AND MODELING

Xavier Courtial, *Centre d'Énergétique, École Nationale Supérieure des Mines de Paris CEP/TEP, Fontainebleau, France*

Chien-Bin Soo, *Centre d'Énergétique, École Nationale Supérieure des Mines de Paris CEP/TEP, Fontainebleau, France*

Christophe Coquelet, *Centre d'Énergétique, École Nationale Supérieure des Mines de Paris CEP/TEP, Fontainebleau, France*

Patrice Paricaud, *Laboratoire de Chimie et Procédés, ENSTA, ParisTech, Paris Cedex 15, France*

Deresh Ramjugernath, *Thermodynamic Research Unit, School of Chemical Engineering, University KwaZulu Natal, Durban, South Africa*

Dominique Richon[1], *Centre d'Énergétique, École Nationale Supérieure des Mines de Paris CEP/TEP, Fontainebleau, France*

Abstract

Natural gas is normally saturated with water inside reservoirs. The presence of water can lead to formation of gas hydrates, with high probability of serious operational, economic, and safety problems in production, transportation, and processing. In order to avoid gas hydrate formation, methanol is injected as a traditional inhibitor into natural gas lines. Therefore, down-stream of pipelines, natural gases contain non-negligible quantities of water and methanol. Water is classically removed from natural gases using dehydration units. However, methanol remains in natural gas streams, which may cause problems in optimizing the operating conditions of hydrocarbon fractionators.

Accurate data and modelling of vapor-liquid equilibria for methanol-hydrocarbon mixtures are necessary to provide requested information for the design and optimization of natural gas processing units. In this communication, we first report the details of an experimental apparatus based on the ″static-analytic″ technique, which

[1]Corresponding author: dominique.richon@mines-paristech.fr

allows us to measure new vapour-liquid-equilibrium (VLE) data, including the propane + methanol binary system at 313.2 K, and n-butane + methanol binary system at six temperatures above and below the n-butane critical temperature, from 323.22 to 443.19 K. The new experimental results and some selected literature data of binary hydrocarbons–methanol VLE are modeled by a phi-phi approach, using the Peng-Robinson equation of state combined with the Wong-Sandler mixing rule. These data are also represented using the SAFT-VR and PC-SAFT models, which take into account self-association between methanol molecules. A comparison between the modeling approaches is presented herein.

Introduction

The phase behavior of the system hydrocarbon + methanol is very interesting due to the combination of unlike species formed of a non-polar and a polar component, presenting both vapor-liquid-liquid-equilibrium (VLLE) and azeotropic behavior depending on the hydrocarbon species. The modeling of such binary mixtures is often a challenge due to self-association between the polar methanol molecules, which makes the behavior of the mixture highly non-ideal.

These types of mixtures present also an important industrial interest in the field of natural gas processing. Methanol is widely used as a hydrate inhibitor due to its performance and its ability to be used at lower temperatures than other hydrate inhibitors such as glycols. Even if methanol is almost entirely removed with water in dehydration units, small quantities are found elsewhere with natural gas and accurate phase equilibrium determinations can be important in predicting methanol behavior in natural gas processes, such as fractionators.

Extensive sets of VLE and VLLE data for these binary mixtures are found in the literature, especially with lower carbon number hydrocarbons. Literature data were usually in relatively good agreements among themselves, whenever comparison is possible. Our preference was to use isothermal *PTxy* data sets with an objective function based on *P* and *y*, although *PTx* and *PTy* data sets were also used with an objective function based on pressure only.

The aim of this paper is to present accurate modeling of VLE data for hydrocarbon + methanol binary mixtures using different models at temperatures below, and where possible, above the hydrocarbons' critical temperatures. In addition, new isotherms for the propane and n-butane + methanol binary mixtures are presented and treated in this paper. The new data sets were determined by an apparatus based on the static-analytic method, which takes advantage of two ROLSI[TM] capillary samplers [1] for analysis in a gas chromatograph.

Three different models are chosen for the treatment of the new data. The Peng-Robinson (PR) [2] is a cubic equation of state (EoS), well-established in the oil industry for its simplicity and accuracy in describing the behavior of hydrocarbon systems. However, as with most cubic EoS, association interactions between molecules (hydrogen bonding) remain unaccounted for. In recent years, the use of statistical thermodynamics has provided a sounder, more rigorous theoretical basis to fluid models. This has led to the development of a new family of EoS, which is able to describe associating interactions of polar systems, at the expense of mathematical complexity and computational time, although this is rarely an issue with current computer advancements. Within this context, we employ two SAFT-type equations which have been widely accepted, namely SAFT-VR (Variable Range) [3,4] and PC-SAFT (Perturbed-Chain) [5,6], to represent the phase equilibria for the hydrocarbon + methanol binary systems. This work is a follow-on of the extensive modeling studies on the n-alkane + n-alcohol mixtures done by Yarrison and Chapman [7], Tamouza et al. [8], von Solms et al. [9] and Lymperiadis et al. [10], with either PC-SAFT or SAFT-VR. The SAFT-like molecular-based EoS are not without flaws, particularly in the critical region [11], and comparisons with a cubic EoS (PR) are made to justify whether or not extra complexity implies better accuracy.

Apparatus Presentation

The apparatus used in this work is based on a static-analytic method with fluid phase sampling. This apparatus is similar to that described originally by Laugier and Richon [12]. Cell temperature is measured at two locations corresponding to the vapor and liquid phases through two 100 Ω platinum resistance thermometer devices (Pt100) connected to an Hewlett-Packard (HP) data acquisition unit (HP34970A) with

a resulting uncertainty not higher than ± 0.015 K. Pressures are measured by means of a Druck pressure transducer connected to the HP data acquisition unit with uncertainties estimated to be within ± 0.4 kPa in the 0.1 – 6 MPa range. The HP on-line data acquisition unit is connected to a personal computer allowing real time readings and storage of temperatures and pressures throughout the different isothermal runs. The average deviations on temperature and pressure recorded during isothermal runs are about 0.16 K and 2.3 kPa for the propane + methanol mixture, and 0.015 K and 4 kPa for the n-butane + methanol mixture, giving a global uncertainty of 0.2 K and 2.7 kPa, and 0.03 K and 4.4 kPa respectively. For each equilibrium condition, at least four reproducible samples of both liquid and vapor phases are withdrawn using the pneumatic samplers ROLSI^{TM} [1] and analyzed in order to check for measurement repeatability. The analytical work was carried out using a gas chromatograph (PERICHROM model PR-2100) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system fitted with WINILAB III software (ver. 4.0, from Perichrom, France). The analytical column is Porapak Q column (length: 2 m, diameter: 1/8 in., 80/100 Mesh) for n-butane + methanol binary mixture and HayeSep T column (1.5 m length, 100/120 mesh, Silcosteel^{TM} 1/8 inch) for propane + methanol, both maintained at 393 K with a helium flow rate of 25 mL.min^{-1}. The TCD was used to quantify all compounds, with uncertainties on the calculated moles of each component are estimated to be within ± 2 %. In addition, average deviations on mole fractions due to the repeatability measurements are about 0.0031 for the liquid and about 0.0013 for the vapor, for both binary systems.

One isotherm at 313.2 K was measured for the propane + methanol binary system using the above set-up, and six isotherms at 323.22, 373.19, 403.13, 423.09, 433.16 and 443.19 K for the n-butane + methanol binary system. The n-butane data have been submitted for a future publication.

Literature Review

Several authors present experimental data for the hydrocarbon + methanol binary system. In this work, we will focus primarily on isothermal *PTxy* data sets. This

extended abstract covers only a small section of the modelling that is currently being finalized for the conference.

The propane + methanol *PTxy* data is taken from Leu *et al.* [13] at 352 K and 393 K, and from Galivel-Solastiouk *et al.* [14] at 313.1, 343.1 and 373.1 K. Measurements from both authors were performed using a static analytical technique with GC analysis. We further process a new set of data from our laboratory at 313.2 K. Propane's critical temperature is 369.8 K [15], and it can be seen that maximum pressure azeotropes exist until the critical temperature, above which critical points prevail.

For the n-butane + methanol mixture, we first proceed to treat new *PTxy* data from our laboratory at 323.22, 373.19, 403.13, 423.09, 433.16 and 443.19 K. Data from Leu *et al.* [13] at 323.2 and 372.5 K are used for experimental azeotrope loci comparison. This mixture behaves similarly to propane with respect to VLE, except for the azeotrope loci being found at higher methanol compositions, as is the case with increasing carbon numbers. At 423.09 K, just below the n-butane's critical temperature (425.12 K), we present experimentally the phenomenon of two phase envelopes coexisting with two critical points and a critical area between them.

Thomas *et al.* [16] provides *PTx* data at 303.15 K by the total pressure measurement method, and Wilsak *et al.* [17] *PTxy* data at 372.7, 397.7 and 422.6 K using a static analytical technique with GC analysis, for the n-pentane + methanol mixture. The isotherms are all well below the n-pentane critical temperature of 469.7 K [15], and present maximum pressure azeotropes.

For n-hexane + methanol mixtures, we have selected *PTx* data from Choi *et al.* [18] at 313.15 K, *PTxy* data from Hongo *et al.* [19] at 298.15 K, who used a flow-type apparatus with GC analysis of vapor phase, and data from Zawisza [20] presenting both *PTx* and *PTy* data at 398.15, 423.15 and 448.15 K. The isotherms are subcritical with respect to the n-hexane critical temperature (507.6 K, [15]), with only vapor-liquid equilibrium specified.

Theoretical Background

Thermodynamic models

The Peng-Robinson EoS [2] is still possibly the most used cubic equation of state for industrial and simulation purposes to date. The expression, in terms of critical parameters, is given by,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \qquad .$$ (1)

In this study, the alpha function in the term *a(T)* is given by Mathias and Copeman [21]. We employ the Wong and Sandler mixing rule [22] coupled with the NRTL composition model [23] for extending Eq. (1) to binary mixtures.

The original molecular-based SAFT EoS was first formalized by Chapman *et al* [24], and consisted of four Helmholtz free energy terms: the ideal term, the segment (or monomer) term, and the chain and association terms,

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{seg}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \qquad .$$ (2)

Gil-Villegas *et al.* [3] later modified the dispersion contribution A^{seg} of Eq. (2) by using a square-well intermolecular potential. Because of the ability of this potential to represent different ranges of molecular interactions, this approach was known as the SAFT-VR EoS. The A^{seg} term draws its basis from the second order Barker-Henderson (BH) perturbation theory [25]. In 2001, Gross and Sadowski [5] developed the PC-SAFT equation of state which included the chain-length dependence of the attractive interactions in the dispersion contribution. While the dispersion term is still based on the BH perturbation theory, the derivation is somewhat different to its predecessors, but the result was an equally accurate and practical equation of state.

Pure component parameters

The pure component critical parameters and Mathias-Copeman constants for use in the PR-EoS can be found in the works of Poling [15]. For the SAFT-VR, pure component parameters used for n-butane are readjusted to experimental liquid densities and vapor pressures, while the remaining hydrocarbons are taken from Paricaud *et al.* [26]. Gross and Sadowski [5,6] give the pure component parameters used for the PC-SAFT EoS.

Data Treatment

Every set of VLE data selected, regardless of its completeness, is subject to data treatment by readjusting the appropriate interaction parameters to minimize an objective function. The general form of this equation is given as,

$$F \;=\; \frac{100}{N_{exp}}\left[\sum_1^{N_{exp}}\left(\frac{U_{cal}-U_{exp}}{U_{exp}}\right)^2 + \sum_1^{N_{exp}}\left(\frac{W_{cal}-W_{exp}}{W_{exp}}\right)^2\right] \qquad (3)$$

where we have allocated dummy variables, *U* and *W*, as the two variables to be optimized. In the presence of *PTxy* data, the two variables in Eq. (3) are replaced by *P* and *y*, i.e., a bubble-point pressure type calculation is applied. If only *PTx* or *PTy* data is at hand, the second term in Eq. (3) is dropped and only pressure is used as an optimized variable.

In this work, we have avoided treating isobaric data. One of the objectives of this paper is to observe the evolution of the interaction parameters with temperature, and not pressure.

Results and Discussion

The results presented in this extended abstract represent only a portion of the complete study to be presented in the 2008 AIChE meeting. Although the procedures of data treatment are similar to that submitted to another publication, a different objective function is employed in this work, with distinct results.

In Fig.1, methanol azeotrope compositions are plotted against azeotrope reduced pressures, from propane to n-hexane + methanol mixtures, where appropriate literatures were available. Azeotropes occur at higher methanol molar compositions with an increase in the alkane chain length, for a specified reduced pressure. Azeotropes in shorter hydrocarbon + methanol systems require only a small fraction of methanol to exist, particularly at temperatures away from the respective hydrocarbon critical temperature. Furthermore, an increase of temperature leads to an increase of the azeotropic composition of methanol and this effect is more pronounced for the longer chain alkanes than for propane and butane. Since the azeotropes are found at a maximum in pressure for the studied alkane + methanol

mixtures, the methanol-alkane cross interactions are unfavorable compared to the methanol-methanol and alkane-alkane interactions, and the azeotrope composition corresponds to the most volatile liquid mixture. This difference between like and unlike interactions is mainly due to hydrogen bonding between the methanol molecules. On one hand, as the carbon number increases, and so does the concentration of the alkyl groups, the methanol hydroxyl molecules (OH group) are subjected to dilution and form a small minority of the fluid. On the other hand, as the temperature is increased, the thermal agitation of the OH groups leads to less hydrogen bonding. As a result, the maximum pressure (azeotrope) of the isotherm corresponds to higher mole fractions of methanol in the liquid phase when the alkyl chain of the alkane is increased, or when temperature is increased. There is also a possibility of an entropic effect relating to molecular size, although this requires further validation beyond the scope of this work.

The experimental azeotropes estimated from our measurements occur at a lower methanol composition than those of literature, due to a slight under-prediction of pressure in our data in comparison to literature at similar temperatures. The n-hexane azeotrope compositions cover the widest range while increasing temperature up to the n-hexane critical temperature. This allows industries to separate methanol from longer hydrocarbons in conventional distillation units by operating at different temperatures to pass from one side of the azeotrope to the other. There is not the same degree of freedom for manipulating azeotrope locations, when dealing with shorter hydrocarbons.

In order to compare the performance between a cubic and non-cubic EoS, we have presented binary phase diagrams modeled by both the PR and PC-SAFT EoS with parameters fitted to data, in Figs. 2 and 3 for the propane + methanol and n-butane + methanol system respectively. Figure 2 contains a new isotherm measured in this work (T = 313.2 K), and Fig. 3, the six new isotherms. For the propane + methanol system, the main discrepancy lies in the azeotrope and critical point regions, and becomes more significant as the temperature increases, for both types of models. In general, at subcritical temperatures (T < 370 K), there is very little difference between the two models, until the onset of the propane azeotrope. At 313 K, both the PR and PC-SAFT EoS predict the propane azeotrope composition prematurely compared to the experimental data. Thereafter, the PC-SAFT EoS tends

to over-predict the propane azeotrope, while the PR EoS continues to detect this value in advance.

At 373 K, which is just above the propane critical temperature, the PR EoS is more applicable due to its ability to predict a critical point, rather than an azeotrope as seen with the PC-SAFT EoS. This was expected as the former is based on critical parameters of the components, while SAFT-type EoS employs parameters of molecular nature. At supercritical temperatures, the PR EoS deviates significantly from literature in the liquid phase, although it remains the more accurate of the two in the vapor phase. An explanation for the deterioration of accuracy in the PR EoS could be attributed to the value of the non-randomness parameter α_{ij}, used in the NRTL model. A value of 0.3 is generally acceptable with this model and has been selected for all the binary systems. However, from the paper of Renon and Prausnitz [23], the value of α_{ij} can be adjusted for a system of polar and non polar component such as methanol and a hydrocarbon, and the value should be found in the range between 0.4 and 0.5. This may have resulted in a deficiency observed at temperatures near the hydrocarbon critical temperature where the PR EoS coupled to the NRTL model cannot represent well the pressure deviation between maximum pressure azeotrope and pure hydrocarbon vapor pressure without vapor-liquid-liquid equilibrium representation. In addition, the value of the interaction parameter for the WS mixing rule was adjusted manually to avoid liquid-liquid equilibrium, despite it resulting in a significantly lower azeotrope pressure. At a temperature well above the propane critical temperature, the PC-SAFT EoS becomes unreliable as it completely over-predicts the phase envelope.

For the n-butane + methanol system, both the models tend to over-predict the pressure, with lower propane azeotrope compositions compared to the experimental data. Up to the n-butane critical point of 425 K, the PC-SAFT EoS is more accurate than the PR, even if it does predict an azeotrope at 423 K, where in fact two critical points were observed experimentally. Unfortunately, neither of the two models was able to represent this phenomenon. The value of the α_{ij} parameters in the PR EoS would have an effect in this regard as well. Once again, the interaction parameter value of the WS mixing rule is adjusted manually to avoid LLE. Similarly, at supercritical temperatures, the PR EoS improves significantly over the PC-SAFT EoS, which once again over-predicts the size of the phase envelope.

Temperature-dependant binary interaction parameters for the two models are presented in Figs. 4 and 5, for hydrocarbons from propane to n-hexane, and temperatures up to but not exceeding their respective critical temperatures. The purpose of plotting reduced temperatures is to facilitate comparison between the systems. The general trend observed in Figs 4 and 5 is similar to the works of Yarrison and Chapman [7] and Asadi Malekshah et al. [27], where values of k_{ij} are an increasing function of temperature, or of temperature and molecular weight, with a function order of two or less. On the graph, we have shown the linear tendency of the k_{ij} parameters, without giving the constants of the function. The parallel nature of the trendlines is for graphical purpose, and does not represent an optimized function. We felt that, unless the deviation exhibited between the trendline and the actual values was less than 5%, which it was not, interpolation will generally lead to misinterpretation of the VLE. This is particularly so for SAFT-type EoS, in which only small changes in interaction parameter value are required over a relatively large range of isotherms. In addition, close to the components' critical points, interaction parameters tend to increase exponentially, and the trend is better described by a second-order function. The behavior of the interaction parameters in the supercritical region is shown in Valtz et $al.$ [28]. Two points were omitted in the Fig 5, that of 423 K for n-butane as it is a near-critical condition and will not conform to a linear behavior; and that of n-pentane at 372 K from Wilsak et $al.$ [17], which deviated significantly from the other interaction parameters. This linear behavior is observed only for the k_{ij} parameters for the PR EoS, while τ_{12} and τ_{21} energetic parameters do not show any distinct trends when viewed individually, as seen in Fig 6.

In Fig. 7, k_{ij} interaction parameters for the SAFT-VR and PC-SAFT EoS are given as a function of hydrocarbon length, at approximately constant temperature (± 380 K). Numerically, both models follow an increase-decrease pattern for the parameter; although the behavior of PC-SAFT is more distinct, but this may be misleading due to the same deviated point mentioned above (for n-pentane + methanol). Nevertheless, the range of values, and the slope of the two linear trends are somewhat similar.

Conclusion

In this short communication, some preliminary results of the VLE study on the phase diagram of methanol and alkane binary systems were covered. New VLE data have been measured for the propane and n-butane + methanol systems, using a "static-analytic" VLE still fitted with two ROLSI^{TM} online samplers. The experimental results are given with the following uncertainties: 0.2 K and 2.7 kPa for propane + methanol, and 0.03 K and 4.4 kPa for n-butane + methanol, and 4 % for vapor and liquid mole fractions of both binary mixtures studied. Relevant binary interaction parameters for isotherms for the new experimental data, as well as literature data from propane to n-hexane, were determined for the PR and PC-SAFT EoS, and partially for the SAFT-VR EoS. A brief comparison between the performance of a cubic and non-cubic EoS is given, outlining areas of strength and weakness of the two distinct models. A few remarks on the evolution of the interaction parameters with temperature for both SAFT-type EoS are also provided.

List of symbols

A	Helmholtz free energy (J)
a	attractive term in PR EoS (Pa.m^6.mol^{-2})
b	co-volume term in PR EoS (m^3 .mol^{-1})
F	objective function
k	Boltzmann constant (J.K^{-1})
k_{ij}	binary interaction parameter
N	number of molecules in the system
N_{exp}	number of experimental points
P	pressure (MPa)
P_r	reduced pressure
R	universal gas constant (J.(mol.K)$^{-1}$)

T	temperature (K)
U, W	dummy variables for optimized variables used in Eq. (3)
v	molar volume ($m^3.mol^{-1}$)
x	liquid phase mole fraction
y	vapor phase mole fraction

Greek letters

τ_{ij}	binary interaction parameter in NRTL model in the PR EoS
ω	acentric factor

Subscripts

az	azeotropic condition
cal	calculated property
exp	experimental property

Superscripts

assoc	association contribution in SAFT equations
chain	hard sphere chain contribution in SAFT equations
ideal	ideal gas mixture contribution in SAFT equations
seg	segment contribution in SAFT equations

Acknowledgment

References

[1]   Guilbot, P., Valtz, A., Legendre, H. and Richon D. (2000), "Rapid on-line sampler injector: a reliable tool for HT-HP sampling and on-line GC analysis," *Analusis*, pp. 28426–431.

[2]   Peng, D.Y. and Robinson, D.B. (1976), "A new two constant equation of state," *Ind. Eng. Chem. Fundam.*, 15, pp. 59–64.

[3]   Gil-Villegas, A., Galindo, A., Whitehead, P.J., Mills, S.J., Jackson, G. and Burgess, A.N. (1997), "Statistical associating fluid theory for chain molecules with attractive potentials of variable range," *J. Chem. Phys.*, 106, pp. 4168–4186.

[4]   Galindo, A., Davies, L.A., Gil-Villegas, A. and Jackson, G. (1998), "The thermodynamics of mixtures and the corresponding mixing rules in the SAFT-VR approach for potentials of variable range," *Mol. Phys.*, 93, pp. 241-252.

[5]   Gross, J. and Sadowski, G. (2001), "Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules," *Ind. Eng. Chem. Res.*, 40, pp. 1244-1260.

[6]   Gross, J. and Sadowski, G. (2002), "Application of the Perturbed-Chain SAFT Equation of State to Associating Systems," *Ind. Eng. Chem. Res.*, 41, pp. 5510-5515.

[7]   Yarrison, M. and Chapman, W.G. (2004), "A systematic study of methanol + n-alkane vapor–liquid and liquid–liquid equilibria using the CK-SAFT and PC-SAFT equations of state," *Fluid Phase Equilib.*, 226, pp. 195–205.

[8]   Tamouza, S., Passarello, J.-P., Tobaly, P. and de Hemptinne, J.-C. (2005), "Application to binary mixtures of a group contribution SAFT EOS (GC-SAFT)," *Fluid Phase Equilib.*, 228, pp. 409-419.

[9]   von Solms, N., Jensen, L., Kofod, J.L., Michelsen, M.L. and Kontogeorgis, G.M. (2007), "Measurement and modelling of hydrogen bonding in 1-alkanol plus n-alkane binary mixtures," *Fluid Phase Equilib*., 261, pp. 272-208.

[10] Lymperiadis, A., Adjiman, C.S., Galindo, A. and Jackson, G. (2007), "A group contribution method for associating chain molecules based on statistical associating fluid theory (SAFT-gamma)," *J. Chem. Phys*., 127(22):234903.

[11] von Solms, N., Kouskoumvekaki, I.A., Michelsen, M.L. and Kontogeorgis, G.M. (2006), "Capabilities, limitiations and challenges of a simplified PC-SAFT equation of state," *Fluid Phase Equilib*., 241, pp. 344-353.

[12] Laugier S. and Richon, D. (1986), "New apparatus to perform fast determinations of mixture vapor-liquid equilibria up to 10MPa and 423K," *Rev. Sci. Instrum*., 57, pp. 469–472.

[13] Leu, A.-D., Robinson, D.B., Chung, S.Y.-K. and Chen, C.-J. (1992), "The equilibrium phase properties of the propane-methanol and n-butane-methanol binary systems," *Can. J .Chem. Eng*., 70, pp. 330-334.

[14] Galivel-Solastiouk, F., Laugier, S. and Richon, D. (1986), "Vapor-liquid equilibrium data for the propane-methanol and propane-methanol-carbon dioxide system," *Fluid Phase Equilib*., 28 pp. 73-85.

[15] Poling, E. (1988), "The Properties of Gases and Liquids," *McGraw-Hill Book Company*, 4th Edn.,

[16] Thomas, S., Bhethanabotla, V.R. and Campbell, S.W. (1991), "Total pressure measurements for n-pentane-methanol-2-butanol at 303.15 K," *J. Chem. Eng. Data*, 36(4), pp. 374-378.

[17] Wilsak, R.A., Campbell, S.W. and Thodos, G. (1987), "Vapor-liquid equilibrium measurements for the n-pentane-methanol system at 372.7,397.7 and 422.6 K," *Fluid Phase Equilib*., 33, pp. 157-171.

[18] Choi, J.S., Park, D.W. and Rhim, J.N. (1985), *J. KIChE*, 23, pp. 89.

[19] Hongo, M., Tsuji, T., Fukuchi, K. and Arai, Y. (1994), "Vapor liquid equilibria of methanol + hexane, methanol + heptane, ethanol + hexane, ethanol + heptane, and ethanol + octane at 298.15 K," *J. Chem. Eng. Data*, 39, pp. 688-691.

[20] Zawisza, A. (1985), "High-pressure liquid-vapour equilibria, critical state, and $p(V_m, T, x)$ to 448.15 K and 4.053 MPa for $\{xC_6H_{14} + (1-x)CH_3OH\}$, *J. Chem. Thermodyn*., 17, pp. 941-947.

[21] Mathias, P. M. and Copeman, T. W. (1983), "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of Various Forms of the Local Composition Concept," *Fluid Phase Equilib.*, 13, pp. 91-108.

[22] Wong, D.S.H. and Sandler, S.I. (1992), "A theoretically correct mixing rule for cubic equations of state," *AIChE J.*, 38, pp. 671–680.

[23] Renon, H. and Prausnitz, J.M. (1968), "Local Composition in Thermodynamic Excess Function for Liquid Mixtures," *AIChE J.*, 14, pp. 135–144.

[24] Chapman, W.G., Gubbins, K.E., Jackson, G. and Radosz, M. (1990), "New Reference Equation of State for Associating Liquids," *Ind. Eng. Chem. Res.*, 29, pp. 1709-1721.

[25] Barker, J.A. and Henderson, D. (1967), "Perturbation theory and equation of state for fluids: The square-well potential," *J. Chem. Phys.*, 47, pp. 2856 -2861.

[26] Paricaud, P., Galindo, A. and Jackson, G. (2004), "Modeling the cloud curves and the solubility of gases in amorphous and semicrystalline polyethylene with the SAFT-VR approach and flory theory of crystallization," *Ind. Eng. Chem. Res.*, 43, pp. 6871-6889.

[27] Asadi Malekshah, V., Taghikhani, V., Ramazani S.A., A. and Ghotbi, C. (2005), "Application of a new simplified SAFT to VLE study of associating and non-associating fluids," *Fluid Phase Equilib*., 233, pp. 110-121.

[28] Valtz, A., Coquelet, C., Baba-Ahmed, A. and Richon, D. (2003), "Vapor–liquid equilibrium data for the CO_2 + 1,1,1,2,3,3,3,-heptafluoropropane (R227ea) system at temperatures from 276.01 to 367.30 K and pressures up to 7.4 MPa," *Fluid Phase Equilib*., 207, pp. 53-67.
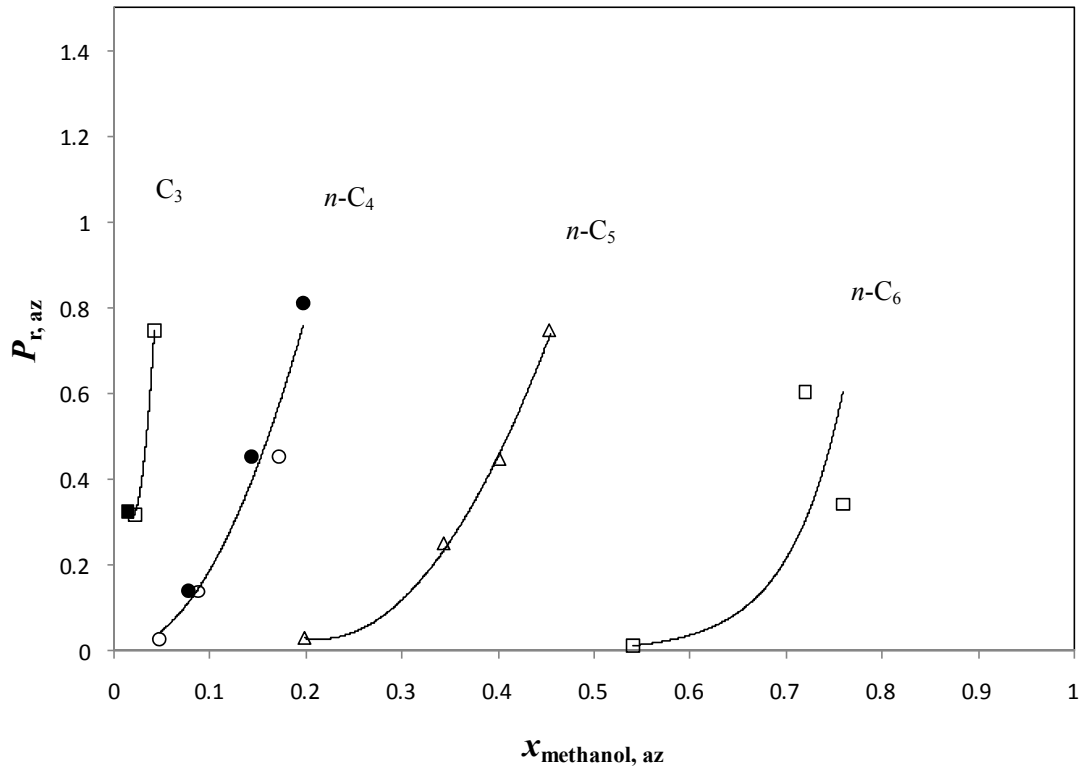
butane, n-pentane and n-hexane in methanol. Literature data are given as open symbols, while closed symbols represents new experimental data from this work.
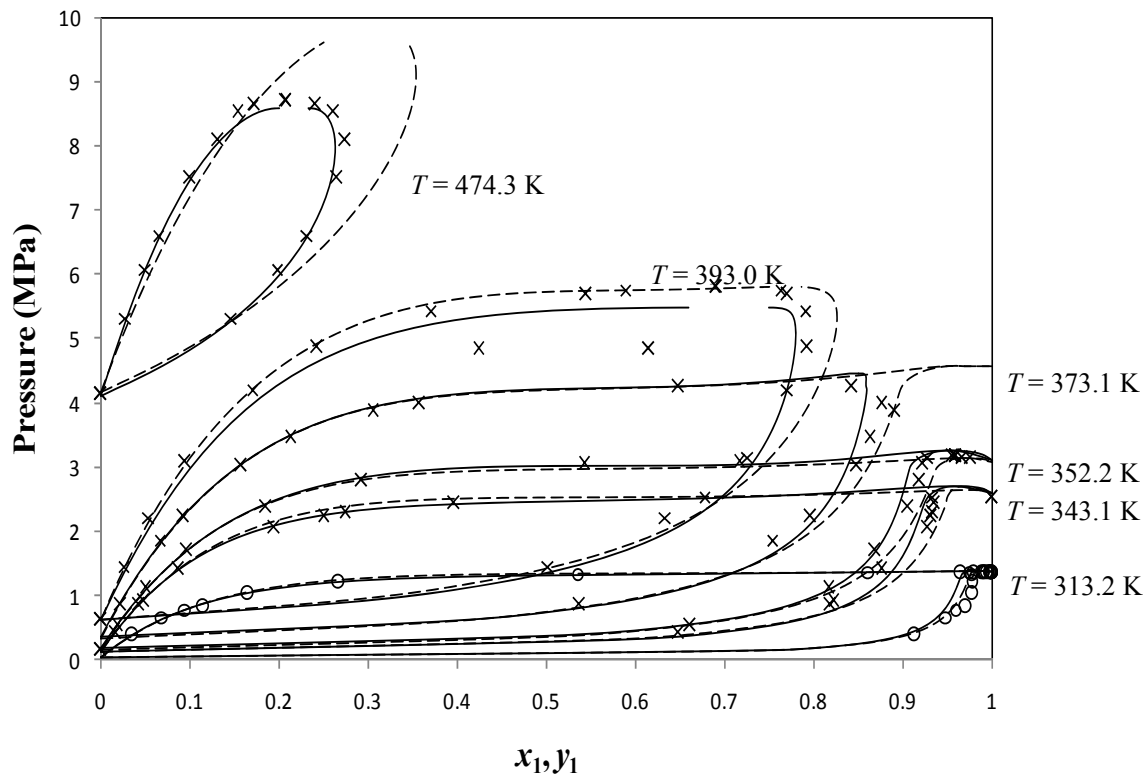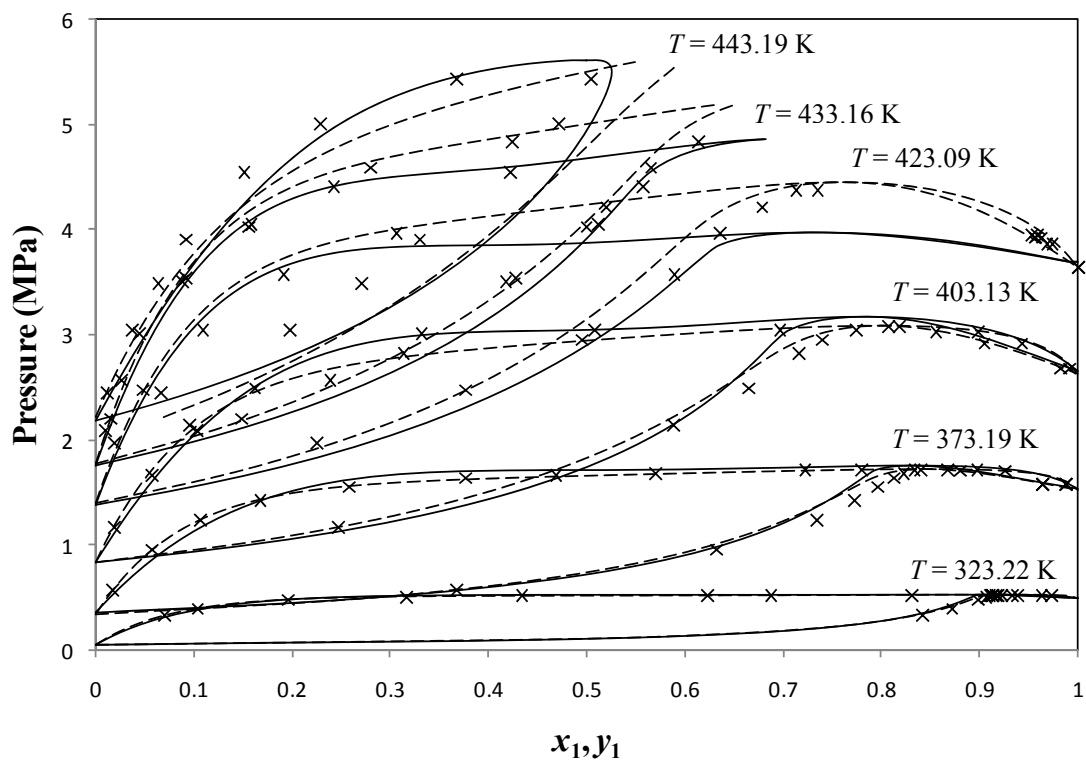
Fig. 2. Pressure vs. liquid and vapor phase mole fraction for propane (1) + methanol (2) at six isotherms. Experimental data from this work are shown as ○, and from literature ×. Results obtained from the PR EoS are shown as solid lines, and as dotted lines for PC-SAFT EoS.
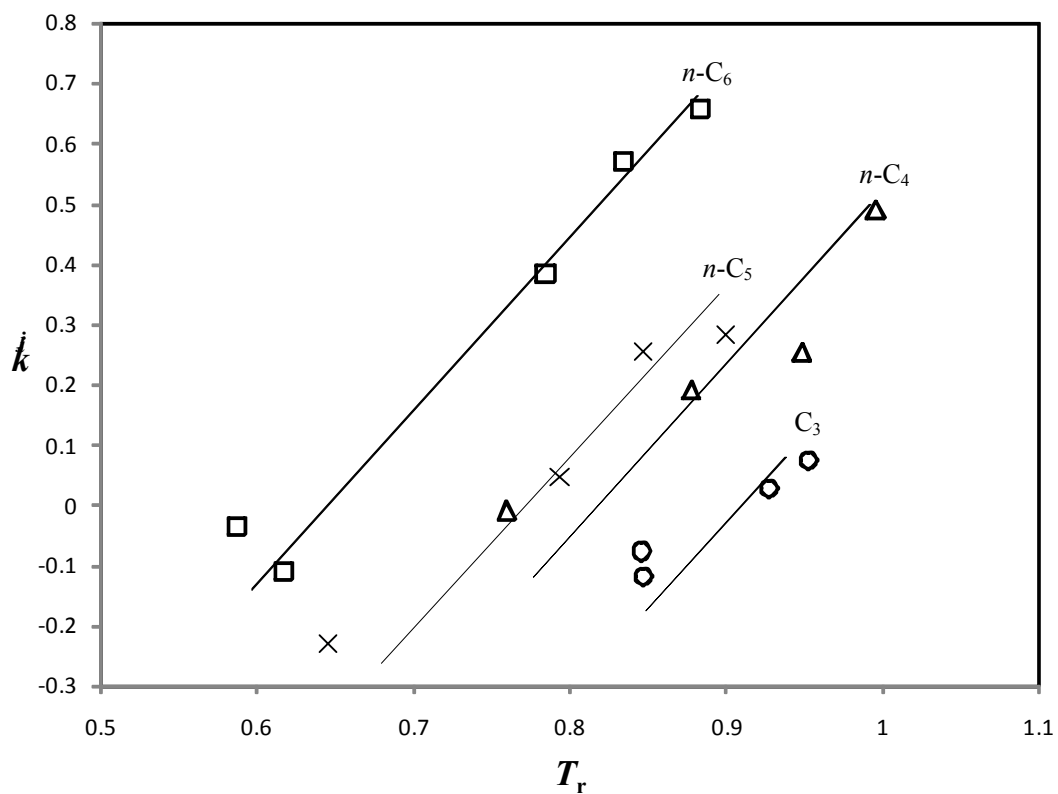
Fig. 3. Pressure vs. liquid and vapor phase mole fraction for n-butane (1) + methanol (2) at six isotherms. Experimental data from this work are shown as ×. Results obtained from the PR EoS are shown as solid lines, and as dotted lines for PC-SAFT EoS.
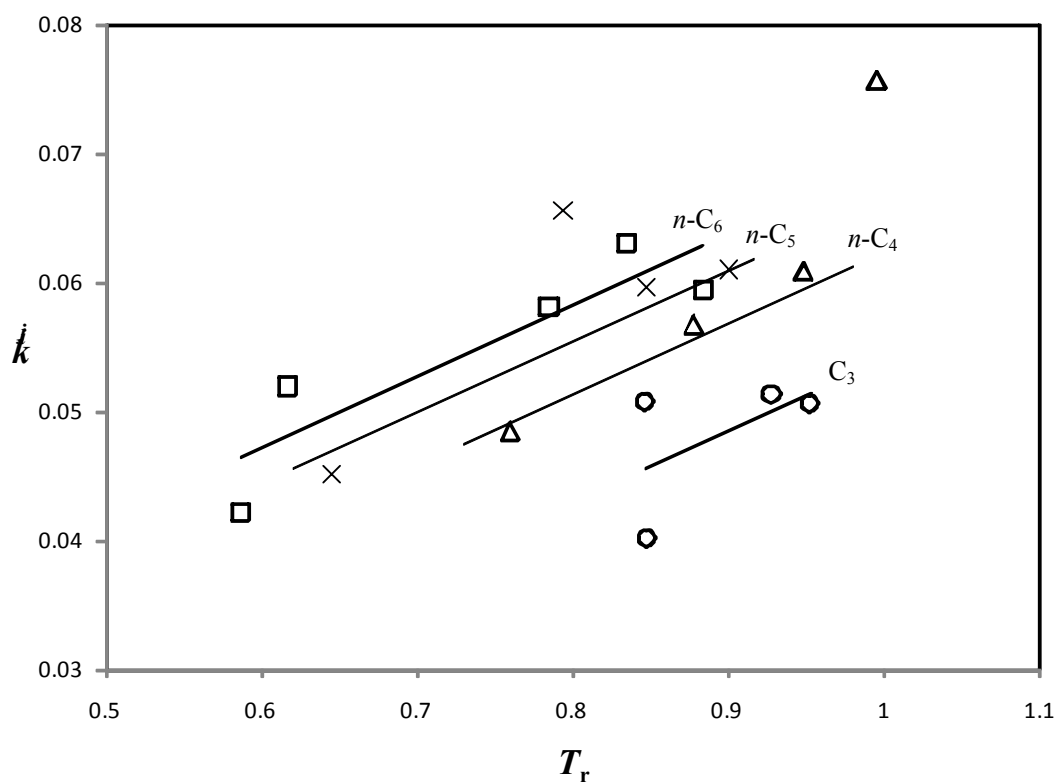
Fig. 4. Binary interaction parameters k_{ij} for the PR EoS plotted as a function of the hydrocarbon reduced temperature for four hydrocarbon + methanol VLE systems: ○ for propane, △ n-butane, × n-pentane, and □ n-hexane.

Fig. 5. Binary interaction parameters k_{ij} for the PC-SAFT EoS plotted as a function of the hydrocarbon reduced temperature for four hydrocarbon + methanol VLE systems: ○ for propane, △ n-butane, × n-pentane, and □ n-hexane.
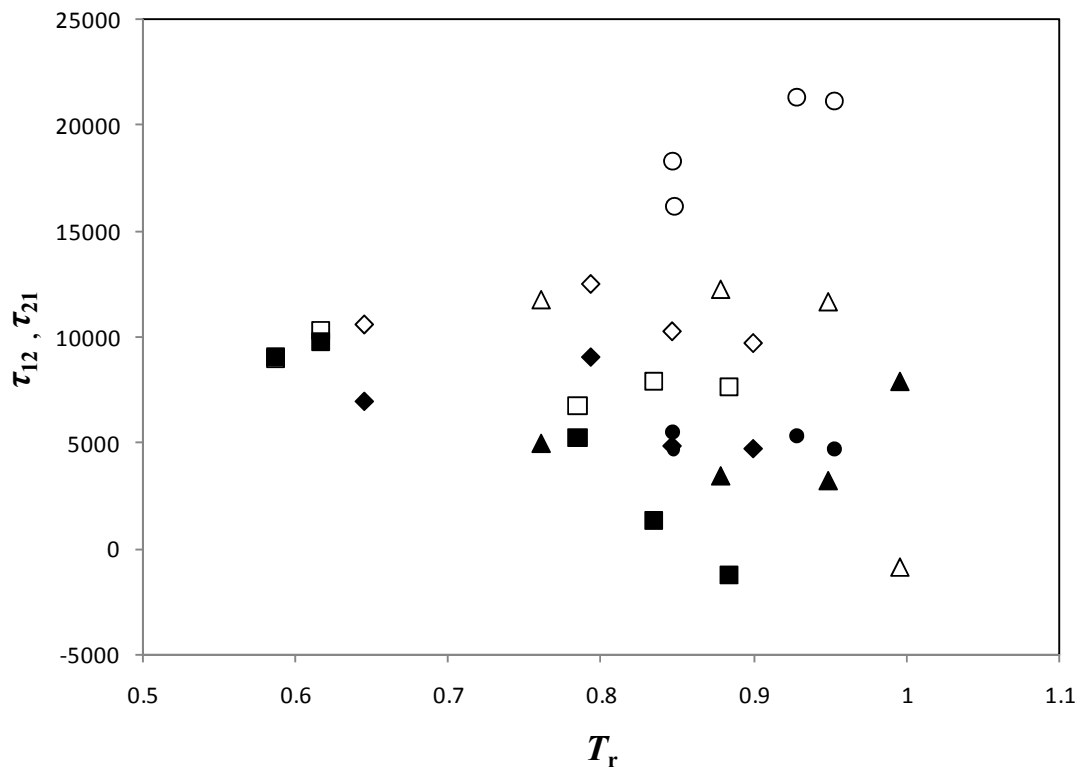
Fig. 6. Binary interaction parameters τ_{12} (open symbols) and τ_{21} (closed symbols) for the PR EoS plotted as a function of the hydrocarbon reduced temperature for four hydrocarbon + methanol VLE systems: ○/● for propane, △/▲ n-butane, ◇/◆ n-pentane, and □/■ n-hexane.
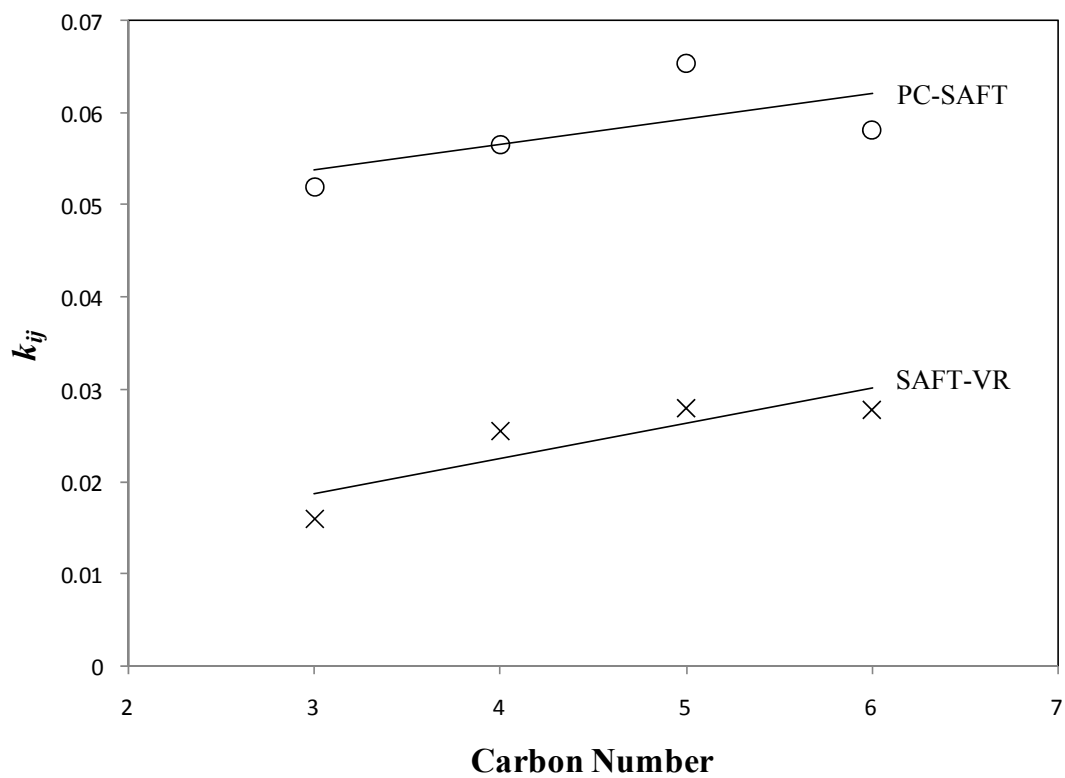
Fig. 7. Binary interaction parameters k_{ij} for the SAFT-type EoS for propane to n-hexane + methanol systems at an approximate constant temperature: around 373 K for propane, n-butane and n-pentane and 398.15 K for n-hexane.