

Phase Behavior of strongly associating systems

A. Belkadi^{1,2}, *M.K. Hadj-Kali*¹, *F. Llovell*^{2,3}, *V. Gerbaud*¹, *L. F. Vega*^{2,3,4}

¹ Université de Toulouse, LGC (Laboratoire de Génie Chimique), CNRS, INP, UPS, 5 rue Paulin Talabot, F-31106 Toulouse Cedex 01 – France.

² MATGAS Research Center, Campus UAB. 08193 Bellaterra, Barcelona Spain.

³ Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas, Campus UAB, 08193 Bellaterra, Barcelona, Spain.

⁴Carburos Metálicos-Grup Air Products. C/Aragón 300. 08009 Barcelona. Spain

Abstract

The modeling of associating fluids has been an active area of research for several decades. Attention has gradually shifted from the so called chemical theories, where molecular association is treated as a chemical reaction, to molecular models where association naturally arises from strong attractive intermolecular forces; among the last ones the Statistical Associating Fluid Theory (SAFT) and related approaches are becoming very popular. We will present calculations performed with the soft-SAFT EoS [F.J. Blas and L.F. Vega, *Ind. Eng. Chem. Res.* 37 (1998) 660-674.] to simulate the equilibrium thermodynamic properties of the acetic acid and the nitriles family (two classes of strongly associating compounds) as well as their mixtures [K. Jackowski and E. Wielogorska, *Journal of Molecular Structure* 355 (1995) 287-290.]. Carboxylic acids form stable double hydrogen bridged dimers which in the gas phase exist in equilibrium with the monomers. Molecular association in liquid phase of the nitriles family is interesting as they are important organic solvents which are soluble in water without any limits. Pure-component molecular parameters are obtained by fitting the equation to available experimental data. The equation enables to search for physical trends, allowing the transferability of the parameters. The complex behavior of these mixtures is also investigated with the same approach.

Key words: soft-SAFT, Nitriles, Acetic Acid, NO₂/N₂O₄

1. Introduction

Over the past decades accurate methods have been developed for describing the thermodynamics behavior of fluids composed of simple molecules. By simple we mean molecules for which the most important intermolecular forces are repulsion and dispersion (van der Waals attractions). Many hydrocarbons, natural gas compounds, simple organic molecules (e.g. methyl chloride, toluene) and simple inorganics (N_2 , CO, N_2O , NO_2 , etc.) fall within this category. Depending on one's taste and desired application, we can use an equation of state (e.g. cubic equation of state such as Redlich-Kwong), corresponding state theory, or group contribution methods. Nevertheless, a great many fluids, and particularly mixtures, do not fall within this simple class – electrolytes, polar solvents, hydrogen bonded fluids, liquid crystals, plasmas, etc. In this work we consider complex fluids composed of molecules that associate to form relatively long-lived dimers and higher-mers and where hydrogen bonding can occur: the reacting system NO_2/N_2O_4 , compounds of the nitriles family and acetic acid. The associative force can be strong or moderate [1]. We note that the acetic acid was modeled successfully by Tsangaris et al. by using Bond – Bias Monte Carlo simulation [2] which coupled the conventional Gibbs ensemble with the strong intermolecular potential accounting for the association effects.

In recent years, the advent of models based on molecular approaches such as the Statistical Associating Fluid Theory (SAFT) [3-4] has opened new possibilities in the modeling of complex molecules. Having a strong statistical mechanics basis, SAFT equations of state have been used to describe a wide variety of compounds, including associating fluids and complex mixtures. Its formulation allows the systematic addition of new terms in order to consider particular physical effects, such as polarity, ring structures, etc, when this is necessary.

We use a molecular based equation of state, namely the soft-SAFT EoS, developed by Blas and Vega [5-6] to investigate the phase behavior of nitriles and acetic acid. Unlike classical PR or SRK equations of state that require molecule properties (critical temperature, critical pressure and acentric factor) to model the PVT properties of compounds, molecular based EoS require to describe the gross chemical structure of molecules in terms of molecular parameters, enabling to find suitable correlations between compounds from the same homologous series.

The present paper is organized as follows: a brief background of the soft-SAFT EoS is exposed. Then, details on former published models and the proposed model are provided. Finally, molecular parameters are regressed for the three lightest nitriles of the linear nitrile family and their transferability is validated for heavier compounds of the same family, in a pure predictive manner.

2. The soft-SAFT approach

The soft-SAFT EoS is a variant of the original SAFT equation proposed by Chapman and co-workers [3-4] and Huang and Radosz [7-8] based on Wertheim's first order Thermodynamics Perturbation Theory (TPT) [9-10]. Since the SAFT equation and its modifications have been extensively revised elsewhere [11], only the main features of the equation are retained here.

SAFT-type equations of state are written in terms of the residual Helmholtz energy:

$$a^{res}(T, P, N) = a(T, P, N) - a^{id}(T, P, N) \quad (1)$$

Where $a(T, V, N)$ and $a^{ideal}(T, V, N)$ are the total Helmholtz energy per mole and the ideal gas Helmholtz energy per mole at the same temperature and density, respectively. The residual Helmholtz energy is the sum of the microscopic contributions to the total free energy of the fluid, where each term in the equation represents different microscopic contributions to the total free energy of the fluid:

$$a^{res} = a^{LJ} + a^{chain} + a^{assoc} \quad (2)$$

The main difference between the soft-SAFT equation and the original equation [3-4] is the use of the Lennard–Jones (LJ) intermolecular potential for the reference fluid (with dispersive and repulsive forces into the same term), instead of the perturbation scheme based on a hard-sphere reference fluid plus dispersive contributions to it. This difference also appears in the chain and association term, since both terms use the radial distribution function of the reference fluid. The LJ potential includes a dispersive term in r^{-6} and a repulsive term in r^{-12} . It exhibits an energy minimum versus the interaction distance and is thus more realistic than the HS + dispersion potential.

The accurate LJ EoS of Johnson et al. [12] is used for the reference term. The chain term in the equation comes from Wertheim's theory, and it is

formally identical in the different versions of SAFT. In our case, it is expressed as:

$$a^{chain} = k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (3)$$

Where ρ is the molecular density of the fluid, T is the temperature and k_B is the Boltzmann constant. In the soft-SAFT case, it is applied to tangent LJ spheres of chain length m that are computed following the pair correlation function g_{LJ} , evaluated at the bond length σ .

The association term comes from the first-order Wertheim's TPT for associating fluids. The Helmholtz free energy change due to association is calculated from the equation

$$a^{assoc} = k_B T \sum_i x_i \sum_{\alpha} \left(\ln X_i^{\alpha} - \frac{X_i^{\alpha}}{2} \right) + \frac{M_i}{2} \quad (4)$$

Where M_i is the number of associating sites of component i and X_i^{α} the mole fraction of component i not bonded at site α which accounts for the contributions of all associating sites in each species:

$$X_i^{\alpha} = \frac{1}{1 + N_{avog} \rho \sum_j x_j \sum_{\beta} X_j^{\beta} \Delta^{\alpha;\beta_j}} \quad (5)$$

3. Results and discussion

The soft-SAFT EoS needs a minimum of three pure compound parameters to model any non spherical molecule: m , the chain length, σ the diameter of the LJ spheres forming the chain, and ε the interaction energy between the spheres. For associating molecules, the association volume κ^{HB} and the association energy ε^{HB} of the associating sites of the molecule should be considered. All parameter values are obtained by fitting the saturated liquid densities (ρ^{liq}) and vapor pressures (P^{sat}), by the minimization of the objective function:

$$F_{obj}^{corps} = \frac{1}{N^p} \sum_{i=1}^{Np} \left(\frac{Y_i^{cal} - Y_i^{exp}}{Y_i^{exp}} \right)^2 \quad (1)$$

Where Y represents the property data used for the regression, namely ρ^{liq} and P^{sat} .

3.1. The reacting system NO₂/N₂O₄

NO₂ is a strongly associating molecule, mostly appearing with its dimer in the liquid phase. The NO₂/N₂O₄ molecule was already studied by De Souza and Deiters [13] modeling its VLE by the use of two different molecular based EoS: the Hard Sphere Attractive (HSA) EoS and the Semi empirical EoS (SES). In the first equation HSA, molecules were modeled as single hard spheres / beads with a mean field – type attraction. Two adjustable parameters were needed: the hard sphere diameter and the attractive interaction parameter. The second formulation, SES, had three adjustable molecular parameters (molecule size, attractive energy, and anisotropy parameter). Unsurprisingly, SES, with its adjustable anisotropic parameter, gave better overall results.

In our case the molecule of NO₂ was modeled as an associating molecule with one site of association located at the N atom. From the observations of Huang and Radosz [11] about the relation between the association strength ε^{HB} and volume κ^{HB} value, NO₂ can be classified as a strong associating fluid, in agreement with experimental observations. In our modeling approach this translates into a large ε^{HB} value and a small κ^{HB} value. The association volume is significantly smaller than for moderately associating fluids (alkanols) modeled with the soft-SAFT equation [14] (see also table 1). Contrary to the association in alkanols, or even in carboxylic acid dimers that corresponds to loose hydrogen bonds from 2.1 to 2.8 Å, chemical association in the NO₂ corresponds to a shorter and stronger bond (1.78 Å according to Chesnut and Crumbliss [15]).

The soft-SAFT parameters are listed in table 1. The figure 1 depicts the vapor-liquid equilibrium of NO₂ computed with these parameters. Figure 1.a) shows the temperature-density diagram while figure 1.b) is devoted to the pressure-temperature diagram. The experimental density data in the vapor-liquid coexistence region was taken from the work of Reamer

and Sage [16]. Additional low temperature liquid density data were taken from Gray and Rathbone [17] and saturated pressure data at low temperature was taken from Giaupe and Kemp [18].

| molecule | m | σ (\AA) | ε/k_B (K) | ε^{HB}/k_B (K) | κ^{HB} (\AA^3) |
|--|--------|---------------------------|-----------------------|----------------------------|----------------------------------|
| NO ₂ /N ₂ O ₄ | 1.29 | 3.17 | 247.8 | 6681 | 1 |
| CO ₂ [21] | | | | | |
| <u>1-nitriles</u> | | | | | |
| acetonitrile | 1.45 | 3.70 | 268.0 | | 69 |
| propionitrile | 1.55 | 3.97 | 272.0 | | |
| butyronitrile | 1.65 | 4.22 | 279.3 | 8425 | 49 |
| valeronitrile | Eq. 2a | Eq. 2b | Eq. 2c | | |
| hexanonitrile | Eq. 2a | Eq. 2b | Eq. 2c | | |
| <u>acids</u> | | | | | |
| Acetic acid | 1.55 | 3.73 | 290.7 | 7701 | 75 |
| <u>1-alkanols</u> | | | | | |
| methanol | 1.48 | 3.39 | 227.4 | 3193 | 4907 |
| ethanol | 1.71 | 3.66 | 240.0 | 3470 | |
| 1-propanol | 1.94 | 3.82 | 249.8 | | |
| 1-butanol | 2.21 | 3.93 | 266.5 | | |
| 1-pentanol | 2.47 | 4.02 | 279.5 | 3600 | 2300 |
| 1-hexanol | 2.69 | 4.11 | 291.0 | | |
| 1-heptanol | 2.92 | 4.17 | 299.5 | | |
| 1-octanol | 3.15 | 4.21 | 306.0 | | |

Table1: Molecular parameters of the molecules investigated in this work (alkanol parameters are from [REF])

In addition to obtaining accurate phase diagrams, the use of soft-SAFT enables to evaluate the fraction of dimerization in the NO₂ molecule, since the association term, leading to the dimer formation, is built into the theory. Experimental monomer NO₂ fractions in the liquid phase data is scarce and concerns only the low temperature range 246.65 – 295.95 K [19]. The soft SAFT predicts up to 56% of NO₂ monomer at 430 K (Figure 1c). Indeed, the maximum mole fraction of monomer NO₂ in the mixture is not achieved at the critical temperature. It is observed that a high temperature favors the monomer NO₂ (from the non-interacting, ideal part of the energy change upon reaction) whereas high pressure favors N₂O₄ (because of the stoichiometry N₂O₄:NO₂). The balance between those two forces is

observed in Figure 1c. The curves are similar to those obtained by De Souza and Deiters [13] for their SES and HSA EoSs. Those authors also computed the theoretical monomer fraction assuming ideal gas and liquid and taking densities from the SES EoS. The shape of all curves is similar but the effect of non-ideality is evident in the liquid phase, where it contributes to a lower mole fraction of NO_2 than what would be expected from purely ideal calculations. A zoom on the experimental monomer fraction (Figure 1d) shows a discrepancy with the predictions at low temperature. Calculations and experimental points of James and Marshall [19] differ by an order of magnitude but the absolute value of the non bonded NO_2 remains extremely small and is equivalent to other modelling efforts [13].

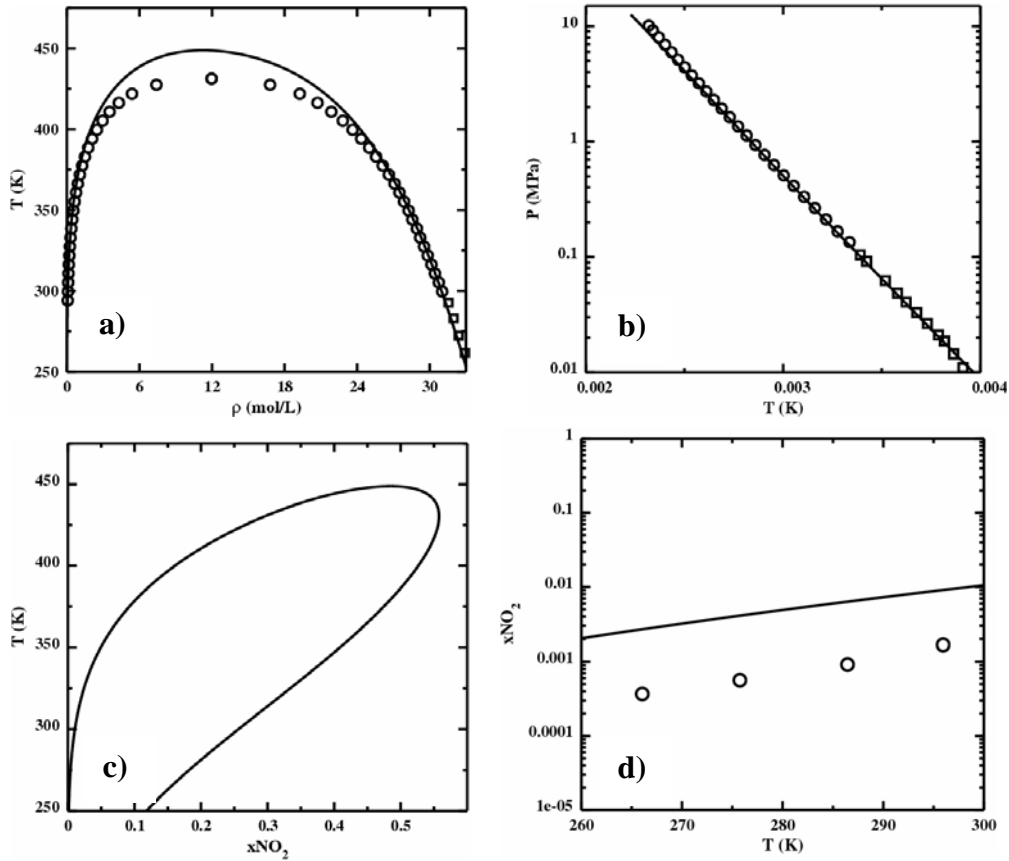


Figure 1. a) Temperature – density diagram for the light members of the reacting system $\text{NO}_2 / \text{N}_2\text{O}_4$. b) Pressure – density diagram for the light members of the reacting system $\text{NO}_2 / \text{N}_2\text{O}_4$. c) Temperature dependence of the mole fraction of NO_2 in the $\text{NO}_2 / \text{N}_2\text{O}_4$ reactive mixture. d) Liquid phase at low temperature. The full line is the performance of the equation with the crossover treatment. The symbols are the experimental data, Circles are from [16,17]. Squares are from [19].

We mention that all the calculations are with good agreement with the experimental data except near the critical point. This was expected, since we are using an analytical equation of state, in which the density fluctuations occurring near the critical region are not explicitly expressed. Additional mathematical treatments like renormalization group theory have been shown to correct effectively the VLE near the critical point [20] but, since for the applications we are interested in are far from the critical region and the calculations with crossover only improve the region near the critical point,

they are not considered here. Crossover modeling was presented elsewhere [21].

3.2. Nitriles

Light nitriles like acetonitrile often display peculiar behaviour because of the short radical bonded to the $-\text{CN}$ group, which dominates the interactions. In UNIFAC group contribution method, acetonitrile is indeed considered as a unique group while other nitriles can be constructed from $-\text{CH}_x$ and $-\text{CH}_2\text{CN}$ groups. In the comprehensive work of Spuhl et al. [22], acetonitrile (ACN) was modelled by three different schemes: the first considers ACN as a chain of hard spheres, the second as an associative molecule with one associating site on the nitrile contribution CN, and the third one takes into account the dipolar moment of the ACN. Results show that the model which considers the dipolar moment is better than the two others although the associative model also showed good results. Earlier, Jackowski's experimental studies of the propionitrile by NMR [23] lead to the presumption that self association interactions must be considered in these systems.

We apply the one association site approximation in this study and find that acetonitrile requires a larger association volume than other nitriles, a fact also observed for the alkanol family (table1). Propionitrile association parameters are then kept constant for the rest of the nitrile family compounds (table1).

We mention in this work the great advantage of the use such a molecular based EoS: The molecular parameters with physical meaning are that their physical trend can be investigated within the same family. Therefore, as in previous works, we have linearly correlated the three molecular parameters m , $m\sigma^3$ and $m\varepsilon$ with the molecular weight of the compounds within the same chemical family [24, 25]. This allows obtaining a set of transferable parameters as a function of the molecular weight. These correlations are established from the optimized parameters with a correlation coefficient greater than 0.98.

$$m = 0.0083M_w + 1.1083 \quad (2.a)$$

$$m\sigma^3 = 2.1143M_w - 13.878 \quad (2.b)$$

$$m\varepsilon / k_B = 3.025M_w + 263.53 \quad (2.c)$$

Using these correlations, VLE properties of heavier linear nitriles of the same family are predicted, without any further fitting on supplementary experimental data. From the observations of Huang and Radosz [7] about the relation between the association strength ε^{HB} and volume κ^{HB} value, we can classify nitriles as an associating fluid stronger than alkanols but with a smaller association volume, hinting at the fact that associated nitriles may interact at distances smaller than H-bonds (typically 2.8 Å) found in alkanols (see also table 1). Experimental vapour pressure and density-temperature data are plotted along with the description of the soft-SAFT model in Figure 2. The absolute average deviation on density and vapour pressure is below 1% and in the 2-4% range respectively.

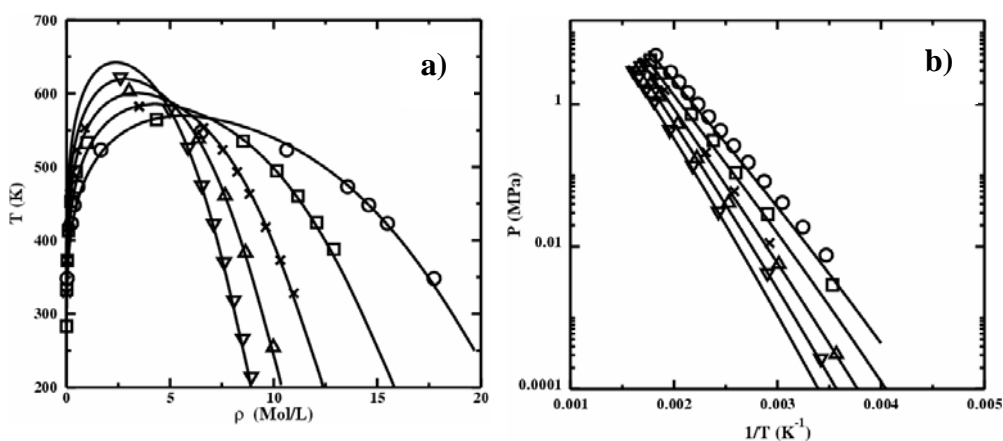


Figure 2. a) Temperature – density diagram for the light members of the n-nitriles, series from acetonitrile to n-hexanonitrile. b) Pressure – density diagram for the light members of the n-nitriles, series from acetonitrile to n-hexanonitrile. Solid lines represent the soft-SAFT predictions and the symbols are from the DIPPR data base [26].

3.3. Acetic acid

We give a last example of a strongly associating fluid: the acetic acid presenting a particular interest in the chemical industry. Acetic acid has a place in the organic chemical industry that is comparable to sulfuric acid in the inorganic chemical industry. A large percentage of acetic acid is used for vinyl acetate production which is the raw material used in the manufacture of polymers, e.g. poly(vinyl acetate) and copolymers. Furthermore, acetic

acid is used as solvent, like in the liquid phase oxidation of *p*-xylene to terephthalic acid [27].

Carboxylic acids are known to exhibit strong intermolecular attraction in the gas phase resulting in ring dimers in equilibrium with monomers even at sub-atmospheric pressures. This phenomenon is attributed to the formation of hydrogen bonding between the two monomers of carboxylic acids and this behaviour seems to be unique for acids. As far as the liquid state is concerned, it has been shown by Raman spectroscopy [28] that acetic acid may form cyclic dimers, open dimers, trimers or even higher *n*-mers. However, the distribution or the extent of polymerisation of the different *n*-mers species is difficult to deduce from single spectroscopic experiments. Further experimental investigation has shown that the acid crystalline phase is composed of linear chains [29, 30]. Thus, some researchers [31] believe that the liquid state of acids contains linear chains, which cannot be accounted for by the monomer–dimer model.

Huang and Radosz [7] acetic acid model uses a one site approximation, as suggested when the value of the association energy is very large and the association volume is very small comparing with the molecular parameters of the alkanols. S. O. Derawi et al. [32] have used the CPA equation of state extended to systems containing carboxylic acids. Among several possibilities of the association scheme, the one-site association (1A) scheme provided the best results and so we chose it. Figure 3 depicts the vapor- liquid equilibrium, good agreement is obtained.

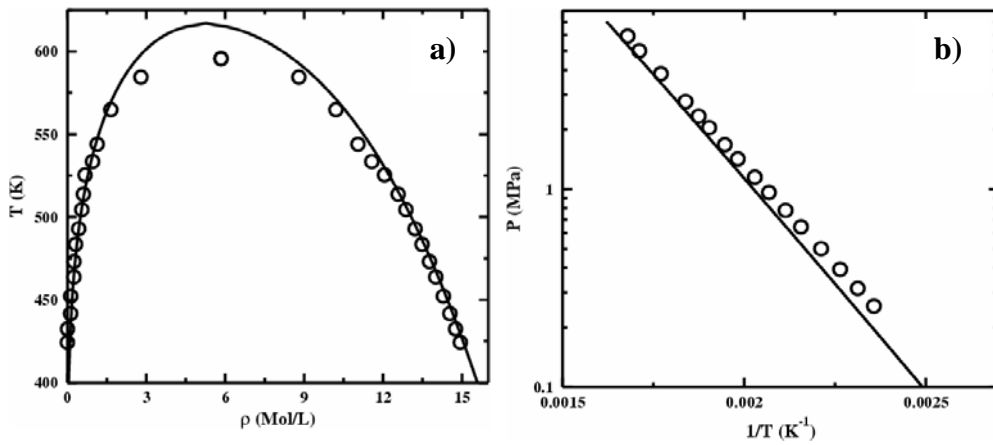


Figure 2. a) Temperature – density diagram for acetic acid. b) Pressure – density diagram for acetic acid. Solid lines represent the soft-SAFT predictions and the symbols are the experimental data [33].

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3.4. Mixtures

The next step in this work concerned the evaluation of the mixture CO_2 + associating fluids. The previously mentioned pure compound parameters were used to predict the vapor – liquid coexistence of the mixture; we choose the acetic acid and the acetonitrile for this section. Figure 4 show some isotherms at several temperatures. All calculations are done without the use of the binary parameters. The agreement with the experimental data is very good.

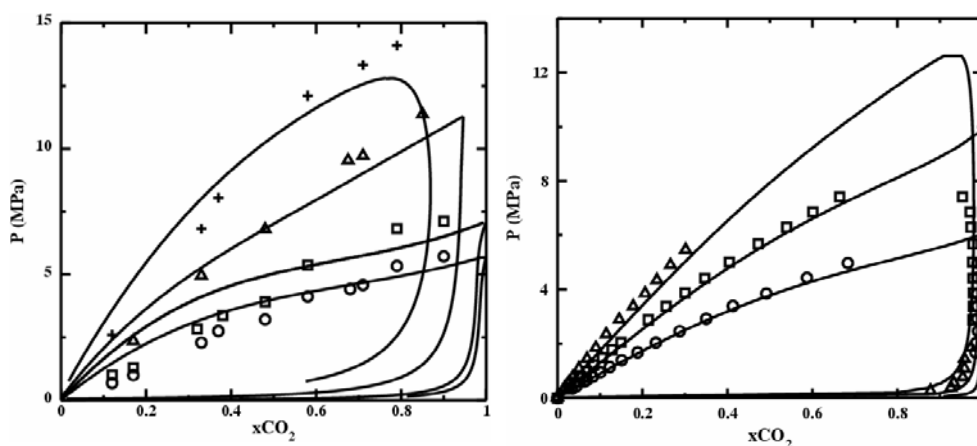


Figure 4. a) mixture acetone nitrile/carbon dioxide, solid lines represent the soft-SAFT predictions, while symbols from [34]. (○) 298K, (□) 308K, (△) 343K, (+) 373K. b) mixture acetic acid/carbon dioxide, solid lines represent the soft-SAFT predictions, and the experimental provided from [17], (○) 298K, (□) 323K, (△) 348K, (+) 373K.

4. Conclusion

The soft-SAFT equation of state has been used to successfully describe the vapor – liquid equilibrium for strongly associating fluids, these classes of these molecules are treated as a self associating compound with a single association site. Compared to other self associating fluids, the large ϵ^{HB} and small κ^{HB} optimized values defined as a strong associating fluid, in agreement with the experimental observations. The association volume κ^{HB} found is significantly smaller than that used for moderately associating fluids (alkanols) modelled with the same soft-SAFT equation.

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