

MODELING THE BEHAVIOR OF BINARY MIXTURES OF SUPERCRITICAL CO₂ WITH PERFLUOROALKANES BY THE USE OF CROSSOVER soft-SAFT

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Perfluoroalkanes are synthetic fluorinated hydrocarbons formulated by substituting, on common organic compounds, the hydrogen atoms replacing them by fluorine. These compounds are used in different fields like medicine, environment and industry and their number of applications increases every year. One of their main advantages over other hydrocarbons is its high solubility potential, that make them very attractive to become cosolvents in supercritical extraction, as medium in two-phase reaction mixture and as refrigerants.

This work is intended to study the thermodynamic behavior of CO₂/perfluoroalkane mixtures with special attention to the critical region, at different temperatures from 293.15 to 353.15 K, and for different perfluoroalkanes at pressures up to 100 bar. Systems and conditions were selected in order to compare the influence of the different structures on their miscibility with carbon dioxide. A comparison with the homologous CO₂/alkane mixture is done in order to check the fluorine effect. The crossover soft-SAFT equation of state was used to study the influence of electrostatics in the solubility of carbon dioxide in perfluoroalkanes. The equation includes a quadrupolar term, to consider the quadrupole effect of CO₂, and a specific crossover treatment to take into account the fluctuations of the properties in the near critical region.

INTRODUCTION

In many supercritical fluid applications, carbon dioxide is widely used as the near-critical solvent. As an example, the formation of water in CO₂ microemulsions offers a new approach to biological processes, organic synthesis, nanoparticle chemistry and dry cleaning. Although CO₂ has many advantages, its poor solvency with respect to polar compounds can be a problem for some of its applications. Until now, attempts to find suitable hydrocarbon-based surfactants have had a limited success. One strategy that has proven quite successful for overcoming this limitation is to make use of CO₂-philic functional groups to behave as surfactants.

It has been verified that the solubility of a compound in carbon dioxide is increased if it contains a fluorinated alkyl segment, since CO₂ is more soluble in fluorinated compounds than in their hydrocarbon counterparts. Due to this fact, the solubility of carbon dioxide in perfluoroalkanes has become an attractive option for industrial and environmental applications such as the removal of carbon dioxide from gaseous effluents or the improvement of the solubility of hydrophilic substances in supercritical reaction or extraction media.

From a chemical point of view, fluorine's high ionization potential and relatively low polarizability lead to weak intermolecular forces which, together with the strong intermolecular forces give the perfluoroalkanes interesting properties, like the highest solubility known among organic liquids [1], an exceptional chemical and biological inertness, and excellent spreading characteristics.

The aim of this work concerns the study of the solubility of carbon dioxide in several selected perfluoroalkanes at supercritical CO₂ conditions, as well as a comparison with their homologous CO₂/alkane mixtures. The modeling tool is the soft-SAFT equation of state [2], which includes a

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specific contribution for considering quadrupolar interactions, as well a crossover treatment to include long-range correlations to capture the real behavior of the critical region. Next section resumes the main features of the soft-SAFT equation. Then, the main results are presented in figures and discussed in the text. The last section summarizes the main conclusions of this work.

THEORY

The modeling of the data is done through the use of a modified version of the soft-SAFT EoS [2], called the crossover soft-SAFT equation [3]. In this equation, the total free energy A of the system is written as:

$$\frac{A_0}{Nk_B T} = \frac{A^{id}}{Nk_B T} + \frac{A^{LJ}}{Nk_B T} + \frac{A^{ch}}{Nk_B T} + \frac{A^{qq}}{Nk_B T} \quad (1)$$

$$\frac{A}{Nk_B T} = \sum_{n=1}^{\infty} \left(\frac{A_{n-1}}{Nk_B T} + \frac{A_n^{cross}}{Nk_B T} \right) \quad (2)$$

where A^{id} is the ideal term contribution. A^{LJ} is the Lennard-Jones (LJ) reference term which takes into account the repulsive and attractive interactions of the monomers forming the chain. The accurate EOS of Johnson et al. [4] to calculate the free energy and derivative thermodynamic properties of the LJ reference fluid. A^{ch} , the chain term, comes from Wertheim's theory, and it is formally identical in the different versions of SAFT. A^{qq} corresponds to the quadrupole term to account for electrostatic contribution for the thermodynamic properties of a given system where at least one of the components has a quadrupole moment. The leading multipole term for fluids of linear symmetrical molecules, like carbon dioxide or perfluorobenzene is the quadrupole-quadrupole potential [5]. An expansion of the Helmholtz free energy in terms of the perturbed quadrupole-quadrupole potential with the Padé approximation was proposed by Stell et al. [6]:

$$A^{qq} = A_2^{qq} \left(\frac{1}{1 - \frac{A_3^{qq}}{A_2^{qq}}} \right) \quad (3)$$

Expressions for A_2 and A_3 , the second and third-order perturbation terms and involve the state variables, molecular parameters, and the integral J for the reference fluid. Further details can be found in references [1].

Finally, A^{cross} is the contribution obtained from a crossover treatment when the renormalization group (RG) theory [7] is applied. This term is needed to describe the long range fluctuations produced in the properties of the fluid when approaching the critical region. The treatment, based on White's work, [8],[9] is done by incorporating the scaling laws governing the asymptotic behavior close to the critical point, while reducing to the original equation of state far from the critical point. The crossover term is expressed mathematically as a set of recursive equations that incorporate the fluctuations in a progressive way (see Eq. (2)). We have confirmed [3],[10] that after five iterations ($n=5$) no further changes in the Helmholtz free energy are observed. It is important to remark that the value of A_{n-1} for first iteration correspond to the original soft-SAFT value. Details on the different terms and the implementation of the crossover term can be found in the original references.[3],[8]-[10].

Since the Helmholtz free energy is calculated by adding different terms, each of them should be expressed as a function of the composition for mixtures. As in previous works, the van der Waals one-fluid theory (vdW-1f) is used to describe the monomer contribution A^{LJ} and the crossover contribution A^{cross} , while the rest of the terms are explicitly written for mixtures. The use of this theory implies the calculation of a pure hypothetical fluid with conformal parameters σ_m and ε_m that have the same properties of the mixture. At this point, two binary adjustable parameters η_{ij} and ξ_{ij} are introduced in this calculation to correct the differences in size and energy, respectively, between the segments forming the two different compounds of the mixture. When these values are set to unity the equation is used in a pure predictive manner for mixtures. Equations and details can be found in other works [10]-[11].

RESULTS

Linear perfluoroalkanes are modeled in the same way as the linear *n*-alkanes family: homonuclear chainlike molecules, modeled as *m* Lennard-Jones segments of equal diameter σ , and the same dispersive energy ε , bonded tangentially to form the chain, plus the crossover parameters *L* and ϕ to include the long-range fluctuations in the critical region. In order to minimize the number of adjusted calculations, and considering the analogy with the *n*-alkane series, the parameter *L* was fixed to the same value as the one previously adjusted for the respective *n*-alkane. Perfluorobenzene and CO₂ are also modeled using the same parameters explained before, but they include an explicit contribution to consider the quadrupolar interactions. This term involves a new molecular parameter *Q* that represents the quadrupolar moment of the molecule. For the case of carbon dioxide and perfluorobenzene, the experimental measured values [12]-[13] are explicitly introduced in the equation, as well as the fraction of segments in the chain that contain the quadrupole (one third for carbon dioxide and one sixth for perfluorobenzene). All the parameters are optimized to the saturated liquid densities and vapor pressures for the selected compounds and presented in Table 1.

Table 1. Molecular parameters for some members of the *n*-perfluoroalkanes family

	<i>m</i>	σ (Å)	ε/k (K)	ϕ	<i>L</i> / σ	<i>Q</i>
perfluoromethane	1.025	4.152	182.0	5.00	1.04	-
perfluoroethane	1.392	4.335	203.8	5.50	1.10	-
perfluoropropane	1.750	4.400	216.0	6.12	1.16	-
perfluorobutane	2.134	4.430	222.5	6.63	1.22	-
perfluoropentane	2.471	4.460	229.0	7.10	1.27	-
perfluorohexane	2.752	4.475	234.0	7.45	1.33	-
perfluoroheptane	3.160	4.485	236.5	7.72	1.38	-
perfluorooctane	3.512	4.500	239.0	8.10	1.43	-
perfluorobenzene	3.148	3.655	257.0	7.75	1.35	$5.0 \cdot 10^{-40}$
CO ₂	1.610	3.172	160.0	5.70	1.13	$4.4 \cdot 10^{-40}$

It can be noted that the parameters are quite similar to the ones for the *n*-alkanes family [3], excepting the value of the diameter σ , which is higher because of the presence of the fluorine atom instead of the smaller hydrogen. Additionally, perfluorobenzene has been added because of their industrial interest. It is possible to establish a correlation for the previous molecular parameters of the linear perfluoroalkanes respect to the molecular weight:

$$m = 0.0352CN + 0.689 \quad (4a)$$

$$m\sigma^3 = 34.65CN + 43.05 \quad (4b)$$

$$m\varepsilon / k_B = 92.55CN + 98.29 \quad (4c)$$

$$m\phi = 3.33CN + 1.08 \quad (4d)$$

$$mL/\sigma = 0.12CN + 0.11$$

(4e)

Figure 1 shows the vapor-liquid equilibrium for the first eight members of the *n*-perfluoroalkanes. The temperature-density and the pressure-temperature diagram from perfluoromethane till perfluorooctane show excellent agreement with experimental data.

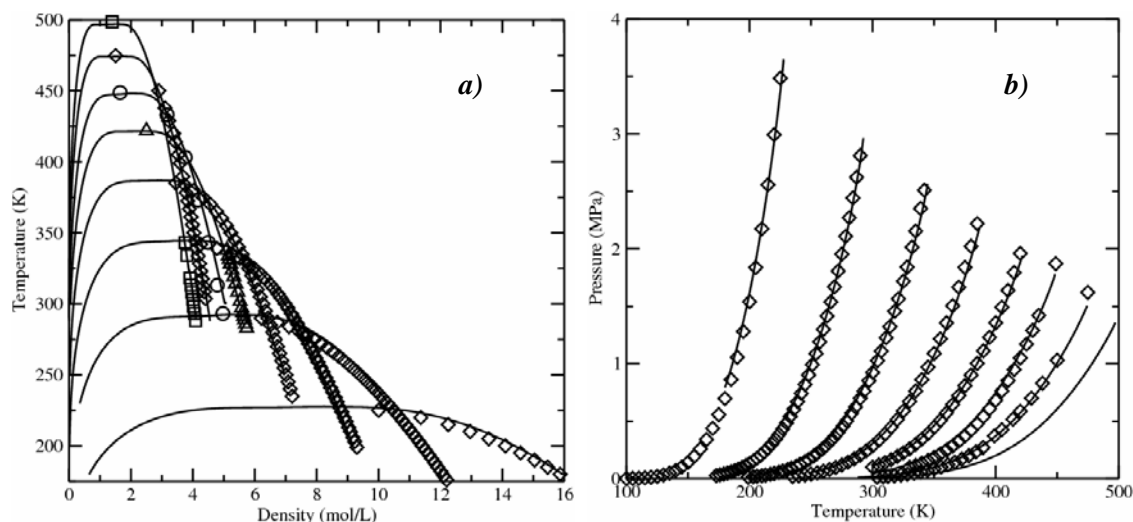


Figure 1 Phase equilibrium diagram for the light members of the *n*-perfluoroalkanes series, from perfluoromethane to perfluorooctane. **a)** Temperature-density diagram **b)** Pressure-density. Symbols represent the experimental data taken from various authors [1],[14]-[17] Lines represent crossover soft-SAFT predictions.

The crossover treatment corrects the behavior of the equation when approaching the critical point giving a good description of the critical region, without prejudicing results far away from it. Similar agreement is obtained when performing the vapor-liquid equilibrium of carbon dioxide [18].

Several diagrams are presented in this work for the evaluation of binary mixtures. Figure 2a and 2b shows the solubility of carbon dioxide in perfluorobenzene and perfluorooctane, respectively at three different temperatures from 293 till 353K. Figure 2a corresponds to the mixture CO₂-perfluorobenzene and it is a pure prediction as no adjustable binary parameters are used. Quantitative agreement is obtained at all temperatures for the whole composition range. When compared to previous works [1], the effect of the renormalization group treatment is clearly noticed in the supercritical area. Figure 2b corresponds to the CO₂-perfluorooctane mixture. Here, the use of one binary parameter has been necessary in order to obtain quantitative agreement ($\xi_{ij}=0.93$, while keeping η_{ij} equal to unity). In any case, very good agreement with experimental data is achieved for the different isotherms.

Figure 3 is devoted to a comparative study between the CO₂-perfluoroalkane mixtures and their homologous CO₂-alkanes. Figure 3a shows the vapor-liquid equilibrium at two different temperatures of CO₂-perfluorohexane, while Figure 3b shows similar isotherms for CO₂-hexane. From the experimental point of view, it is clearly seen how the solubility of carbon dioxide in perfluorohexane is superior to that in hexane. From the modeling point of view, the interesting feature is that we have used the same binary parameter value for both mixtures ($\xi_{ij}=0.96$), and quantitative agreement has been obtained in all cases. Although there are some slight deviations for CO₂-hexane at 353K, overall agreement is very good and the use of the same ξ_{ij} value increases the transferability power of the equation of state.

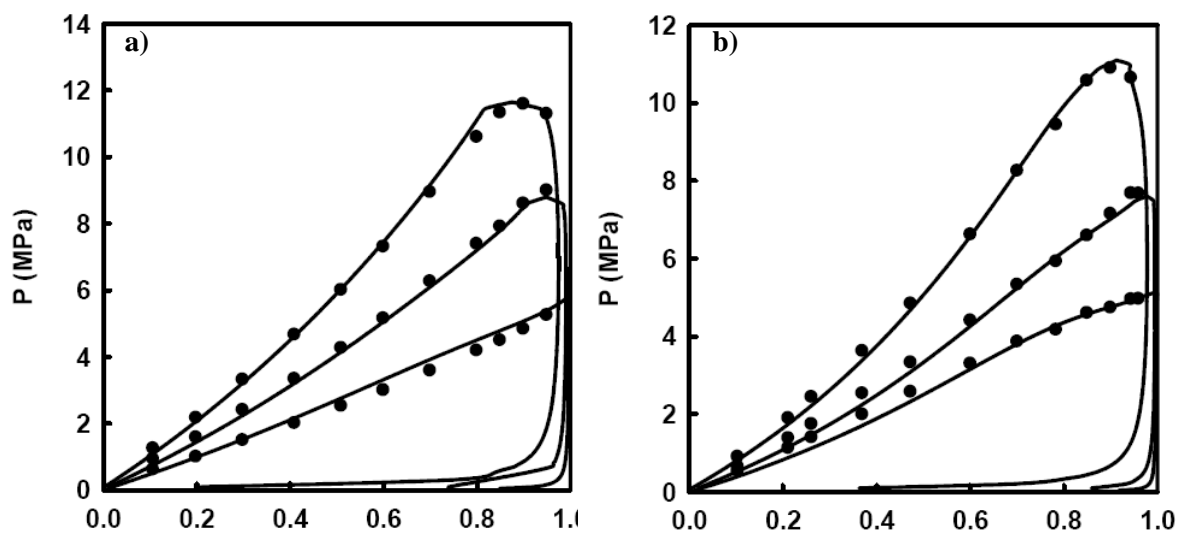


Figure 2 Vapor-liquid equilibrium of **a)** CO_2 -perfluorobenzene (293K, 323K and 353K) and **b)** CO_2 -perfluorooctane (298K, 313K and 353K). Symbols represent experimental data [1] while lines are crossover soft-SAFT predictions.

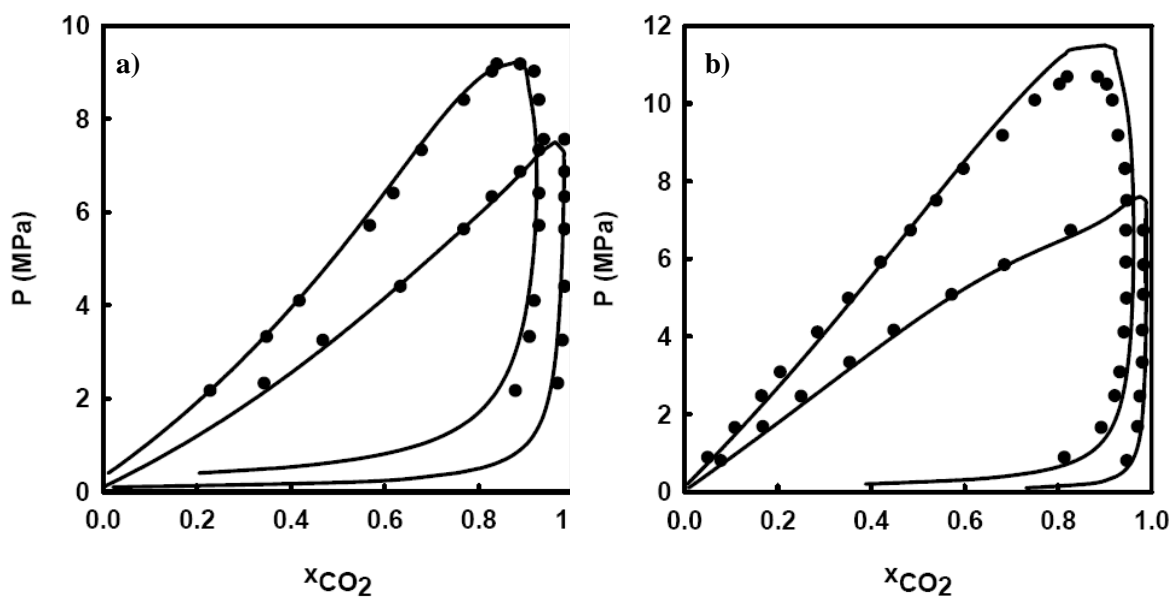


Figure 3 Vapor-liquid equilibrium of **a)** CO_2 -perfluorohexane (314K and 353K) and **b)** CO_2 -hexane (313K and 353K). Symbols represent experimental data [19]-[21] while lines are crossover soft-SAFT predictions.

CONCLUSIONS

Solubility of supercritical carbon dioxide on some selected perfluoroalkanes has been modeled through the use of the molecular-based crossover soft-SAFT equation of state. The equation includes a specific treatment to consider the quadrupolar interactions of carbon dioxide and perfluorobenzene, as well as a specific renormalization-group treatment to take into account the density fluctuations in the critical region.

The linear perfluoroalkanes have been modeled like their homologous *n*-alkanes. Vapor-liquid equilibrium calculations have given quantitative agreement in all cases. The equation has been able to capture the behavior of the compound near to and far from the critical region. Concerning the binary mixtures, crossover soft-SAFT is able to predict the solubility behavior of CO₂-perfluorobenzene mixture without any additional fitting, when considering both quadrupole interactions. Moreover, the solubility predictions of CO₂ on perfluorohexane have shown excellent agreement with respect to experimental data at two different temperatures using a unique binary parameter. Comparisons at the same temperature with the CO₂-hexane mixture corroborate the superior solubility performance of carbon dioxide on perfluoroalkanes. It is important to notice the parameters transferability between both families. Crossover soft-SAFT appears to be a powerful and robust equation of whose predictive capability permits to be applied to many different systems of industrial interest.

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