Sub-critical Fluid Phase Behaviour for n-Alkanes (C_6 to C_9) in Trifluoromethane at (273 to 313) K

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The majority of investigations into the use of supercritical fluids for separation processes entail the study of carbon dioxide, ethane or propane in their supercritical state. Carbon dioxide (CO_2) is by far the most common solvent in use, chiefly because it is a benign, stable and cheap gas that is readily available [1]. The most common difficulty experienced when using supercritical carbon dioxide as a solvent is the poor solvating power for the extraction of polar components [2].

Polar co-solvents are commonly used to overcome this problem, but they in turn cause complications in the downstream solvent recovery. The addition of these co-solvents, which are most commonly short-chained alcohols, increases the polarity of the solvent mixture, which enables the extraction of more polar solutes [3]. The downstream recovery processes are complicated because of the fact that a simple depressurisation of the fluid does not separated the co-solvent from the solute. Techniques such as distillation or crystallisation must be employed to separate the co-solvents from the product.

Trifluoromethane (fluoroform, R-23, T_c = 299.07K, P_c = 4.836 MPa) has critical properties that are closer to ambient conditions than carbon dioxide and the R-23 molecules are highly polar [4]. R-23 is also a stable, benign gas, although it does have a greenhouse warming potential that is substantially higher than that of carbon dioxide. When the extraction of polar components is desired, supercritical R-23 could possibly replace the use of supercritical carbon dioxide and a polar co-solvent. R-23 could also possibly be used to reduce the operating pressures.

Prior to analysing the solvating power of R-23 for cases involving polar solutes, an analysis of some of the more commonly measured non-polar solutes (C_6 to C_9 n-alkanes) was undertaken. This analysis was to provide a basis against which the solubilities of the polar solutes could be compared.

A static analytic, high pressure phase equilibrium cell was used to measure the isothermal binary phase equilibria for the n-alkanes. This static-analytic cell was developed by Narasigadu et al. [5]. For each of the four systems, five isotherms were measured at temperatures between (273 and 313) K, and at pressures up to the critical pressure of the mixture. Two liquid phases were observed at certain conditions, for all four binary systems.

The measured data for the four systems were regressed to obtain model parameters for two thermodynamic models. These models both consisted of the Peng-Robinson equation of state [6] with the Mathias-Copeman alpha function [7] and the Wong-Sandler mixing rules [8]. Two different liquid activity coefficient models; the NRTL model [9] and the UNIQUAC model [10]; were evaluated.

The indirect extended scaling laws of Ungerer et al. [11] were used to determine the critical loci, based upon the measured sub-critical co-existence points. The experimental data, alongside the modelled data and the extrapolated critical points are shown in Figures 1 to 4.

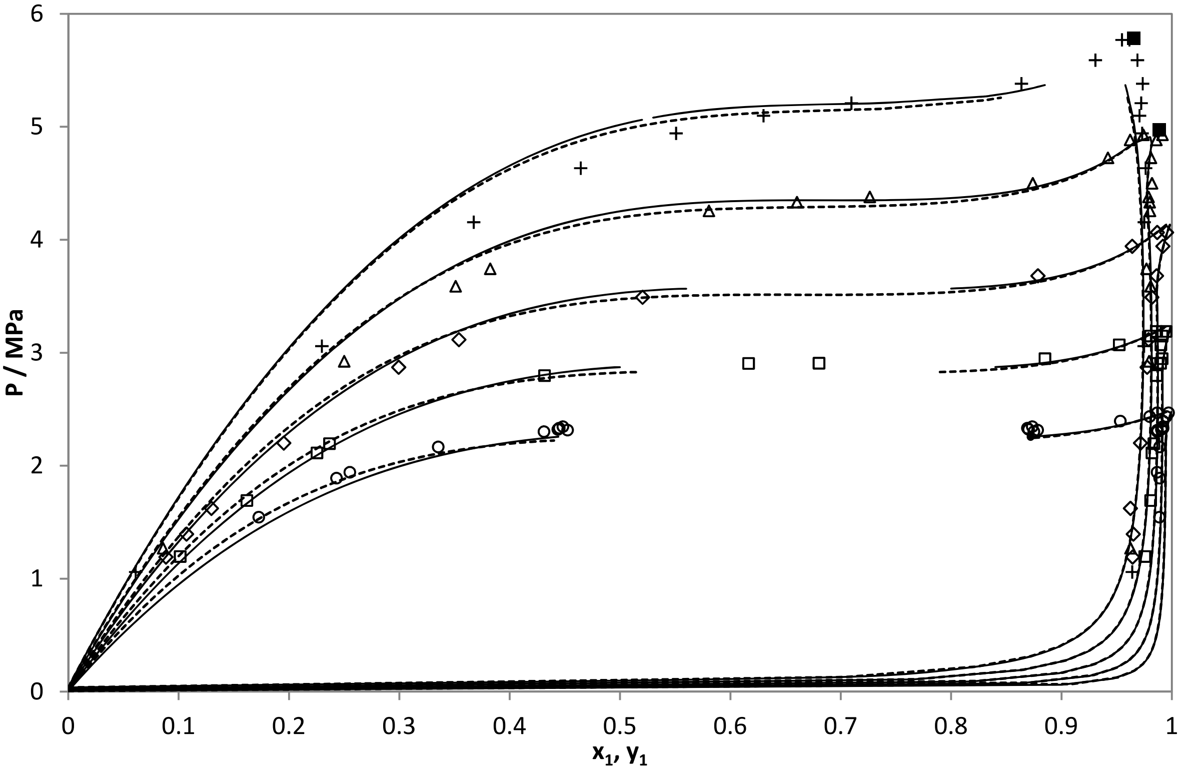

Figure 1. Plot of the P-x-y Data for the R-23 (1) + n-Hexane (2) System. ○, T = 272.9 K; □, T = 283.0 K; ◊, T = 293.0 K; Δ, T = 303.1 K; +, T = 313.2 K; ; —, PR-EoS model with NRTL liquid activity coefficient model; ---, Peng-Robinson EoS with the UNIQUAC liquid activity coefficient model; ■, critical points.

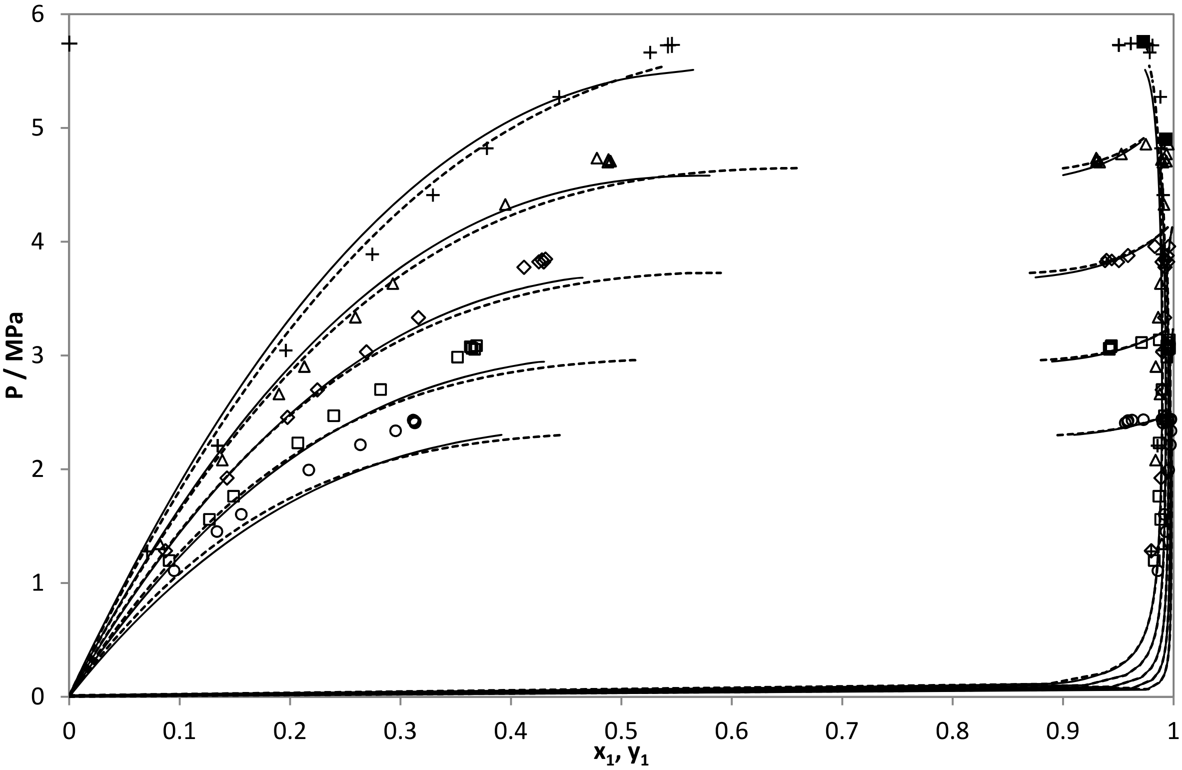

Figure 2. Plot of the P-x-y Data for the R-23 (1) + n-Heptane (2) System. ○, T = 272.9 K; □, T = 283.0 K; ◊, T = 293.0 K; Δ, T = 303.1 K; +, T = 313.2 K; ; —, PR-EoS model with NRTL liquid activity coefficient model; ---, Peng-Robinson EoS with the UNIQUAC liquid activity coefficient model; ■, critical points.

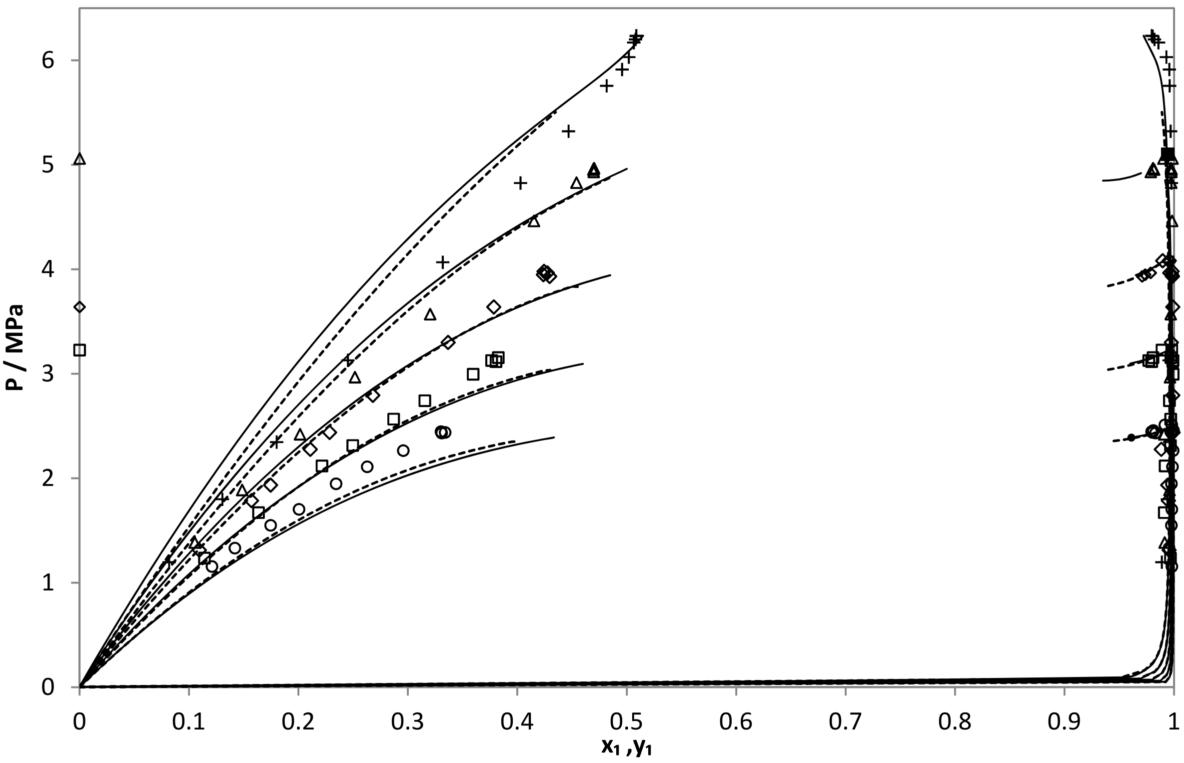

Figure 3. Plot of the P-x-y Data for the R-23 (1) + n-Octane (2) System. ○, T = 272.9 K; □, T = 283.0 K; ◊, T = 293.0 K; Δ, T = 303.1 K; +, T = 313.2 K; ; —, PR-EoS model with NRTL liquid activity coefficient model; ---, Peng-Robinson EoS with the UNIQUAC liquid activity coefficient model; ■, critical points.

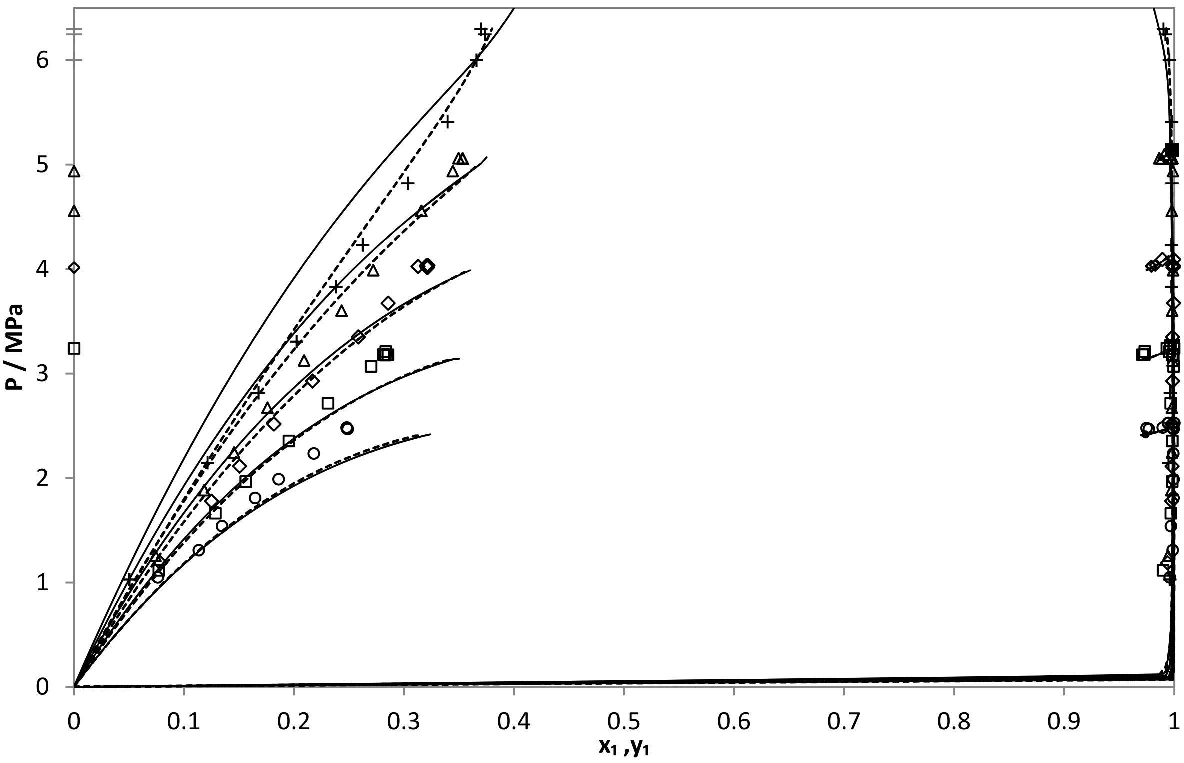

Figure 4. Plot of the P-x-y Data for the R-23 (1) + n-Nonane (2) System. ○, T = 272.9 K; □, T = 283.0 K; ◊, T = 293.0 K; Δ, T = 303.1 K; +, T = 313.2 K; ; —, PR-EoS model with NRTL liquid activity coefficient model; ---, Peng-Robinson EoS with the UNIQUAC liquid activity coefficient model; ■, critical points.

The critical points were thereafter compared with the corresponding critical points of the same solutes in carbon dioxide. The comparisons of the critical loci of carbon dioxide and trifluoromethane with n-hexane and n-heptane are shown in Figures 5 and 6.

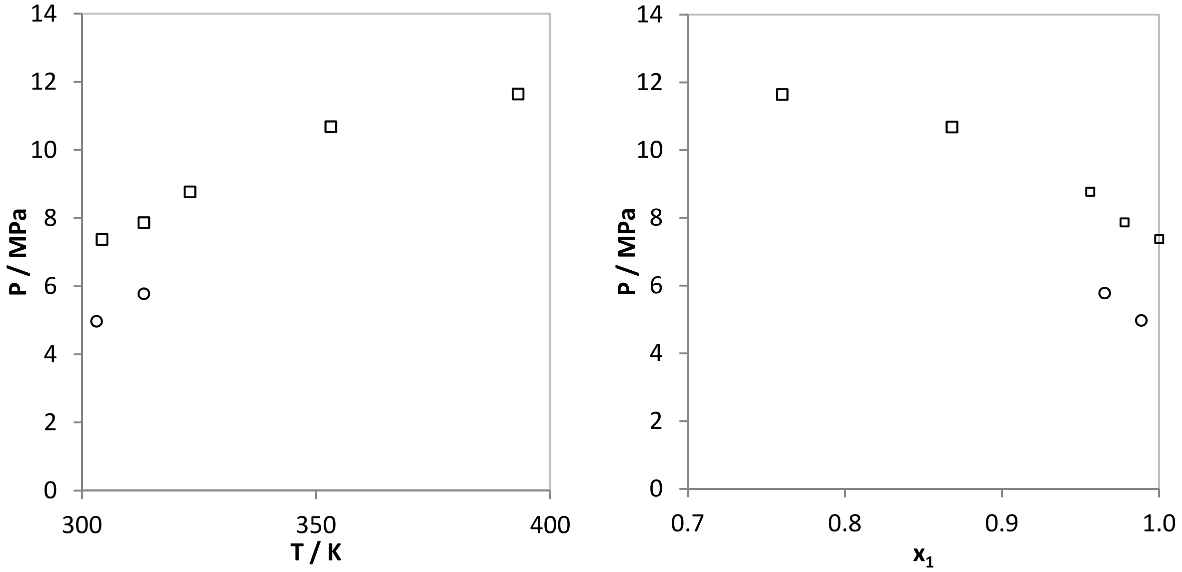

Figure 5. P-T and P-x Projections of the Critical Loci for the systems of Carbon Dioxide and Trifluoromethane with n-Hexane. □, Critical points for CO_2 (1) + n-Hexane (2), extrapolated from open literature [12-14]; ○, Experimental critical points for R-23 (1) + n-Hexane (2) (this work).

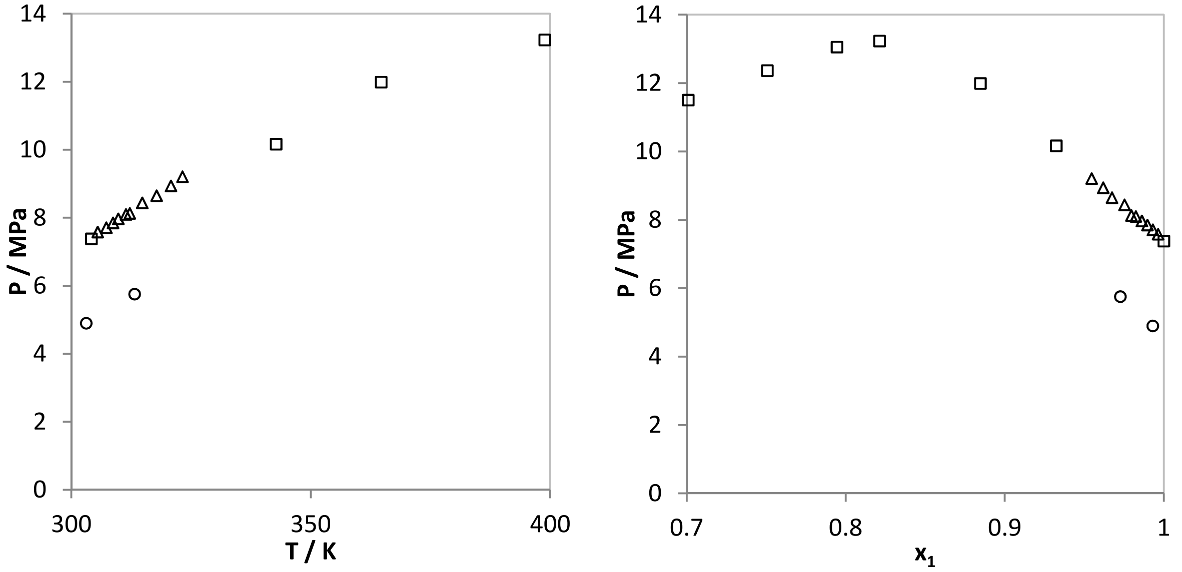

Figure 6. P-T and P-x Projections of the Critical Loci for the systems of Carbon Dioxide and Trifluoromethane with n-Heptane. □, Critical points for CO_2 (1) + n-Heptane (2), extrapolated from open literature [15, 16]; ○, Experimental critical points for R-23 (1) + n-Heptane (2) (this work).

The measured solubilities of the n-alkanes in R-23 were similar to the solubilities in CO_2, at a given temperature. However, the reduced critical pressures in the measured systems, when using R-23 as a replacement for CO_2, were immediately obvious. These reduced pressures could lead to energy savings for supercritical fluid extraction processes.

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