Comparison of the Phase Behaviour of Alkanes and Acids in Supercritical Fluids

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ABSTRACT

The phase behaviour of acids and n-alkanes in supercritical CO_2, ethane and propane is compared. Literature data was assembled and, where necessary, additional phase behaviour measurements were conducted, specifically for ethane with dodecanoic acid and tetradecanoic acid. The results show that propane and ethane behave in a similar manner with CO_2 showing different trends. The phase transition pressure in propane and ethane for an acid with N carbon atoms is similar or slightly higher than that of an n-alkane with 2N+2 carbon atoms. For CO_2 the phase behaviour of an acid is considerably lower than that of an n-alkane with 2N+2 carbon atoms. The difference in the phase behaviour of n-alkanes and acids in CO_2 compared to that in propane and ethane can, in all probability, be attributed to the presence of the quadrupole moment in CO_2 atoms.

INTRODUCTION

A recent study on the high pressure phase behaviour of propane – long chain acids (more than 8 carbon atoms) revealed that, in the presence of supercritical (SC) propane, two acid molecules appear to associate to form a dimer [1]. On molecular scale, the hydroxyl group of one molecule associates by means of hydrogen bonding with the double bonded oxygen of the other molecule, and vice versa. This hydrogen bonded (not chemically bonded) double acid now behaves very similar to an alkane with double the number of carbon atoms. Due to the central position of the newly formed functional group, it has a limited effect on the phase behaviour. The doubled bonded acid is observed experimentally where, in SC propane, the phase behaviour of an acid with N carbon atoms is similar to that of an alkane with 2N carbon atoms. The question now arises as to whether this association of acids is a general phenomenon in SC fluids or only limited to certain solvents.

This question leads to the aim of this study, namely a comparison of the phase behaviour of n-alkanes and acids in various SC solvents. By comparing the phase behaviour of both n-alkanes and acids in SC fluids and then comparing the phase behaviour of acids and n-alkanes with 2N carbon atoms the above mentioned question can be answered, namely if the phase behaviour of an acid mimics that of an n-alkane with 2N carbon atoms in all SC fluids.

The study will be conducted with three popular SC solvents: CO_2, propane and ethane. CO_2 is the most popular SC solvent while propane and ethane are attractive alternatives due to their improved solubility and selectivity compared to CO_2. The study will limit itself to the phase behaviour of acids of 8 or mole carbon atoms. The phase behaviour will be considered at temperatures just above the critical temperature of the solvent (range 378 to 408 K for propane and 313 to 370 K for ethane and CO_2). This temperature range is considered as it is typical of industrial processes.

PUBLISHED PHASE EQUILIBRIUM DATA

Phase behaviour data for n-alkanes in all three SC solvent have previously been published [2-5] and the data are sufficient for the purposes of this paper. Recently [1,6] data has been published for the phase behaviour of acids in propane and in CO_2. However, data for acids in ethane is limited to that of C8COOH at three temperatures. A summary of the data used in this work is given in Table 1.

Table 1: Summary of literature data used in this work

Homologous series	Acids/n-alkane	Ref.
n-alkanes – propane	nC32, nC36, nC38, nC38, nC40, nC44, nC54 and nC60	[2,3]
n-alkanes – ethane	nC16, nC24, nC28	[4]
n-alkanes – CO_2	nC12, nC16, nC20, nC24, nC28, nC36	[5]
acids – propane	C7COOH, C9COOH, C10COOH, C13COOH, C15COOH, C17COOH, C19COOH, C21COOH	[1]
acids – ethane	C8COOH	[1]
acids – CO_2	C7COOH, C9COOH, C10COOH, C11COOH, C13COOH, C15COOH, C17COOH	[7,8]

Additional measurements for at least two acids with ethane are thus required. nC11COOH and nC13COOH were selected for additional measurements to facilitate a good comparison.

EXPERIMENTAL METHOD AND RESULTS

A static synthetic method, using two previously constructed setups, each consisting of a variable volume high pressure view cell, was used to measure the phase equilibria data. The view cells have been described in detail in previous publications [3,9] and a description of the experimental method specifically applicable to the phase behaviour of acids in SC fluids has also previously been published [1,6]. High pressure phase equilibria measurements of C11COOH and C13COOH in SC ethane were measured and the results are shown in Figure 1.

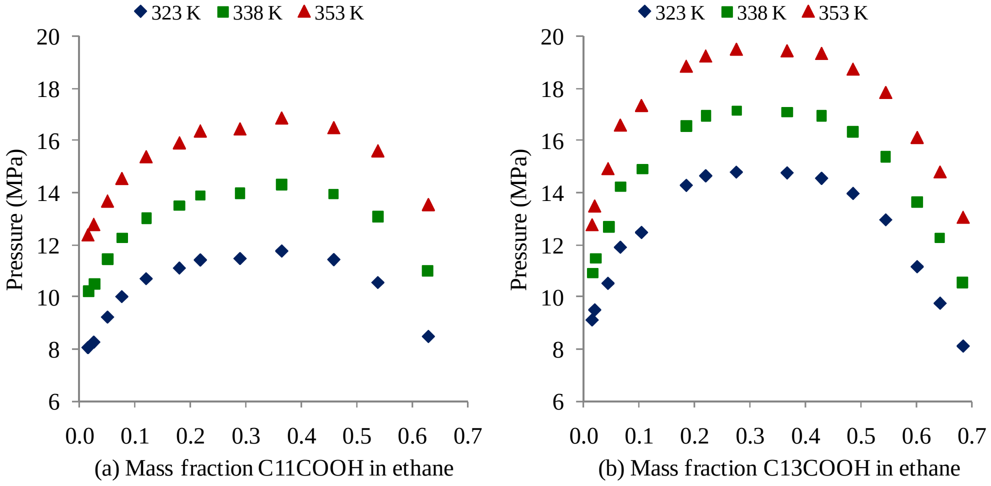
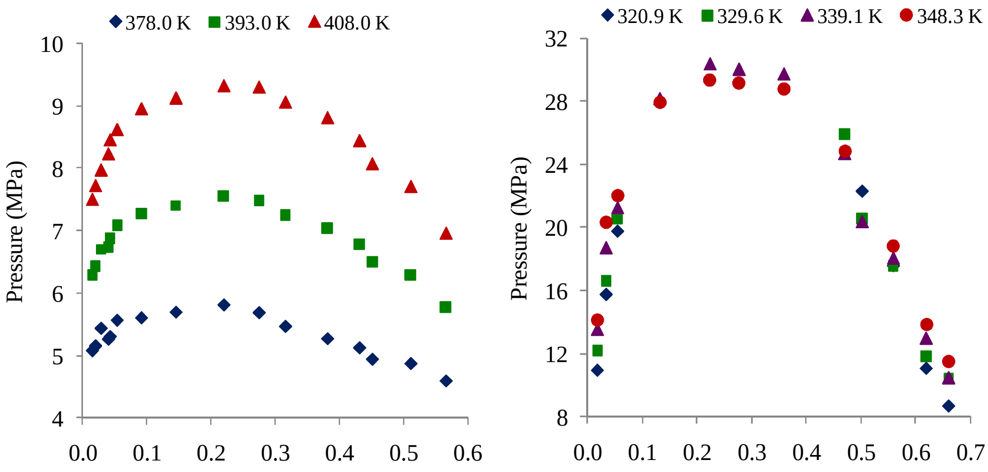


Figure 1: Measured phase equilibria data for (a) C11COOH and (b) C13COOH in SC ethane

As for the case of propane, an increase in system temperature leads to an increase in phase transition pressure. This oberservation is in agreement with the work of Buyn et al. [7]. Additionally, it is noted that the phase transition pressure of C11COOH is lower than that of C13COOH at the same temperature and both these components have a higher phase transition pressure than C8COOH, as measured by Buyn et al. [7]. However, further measurements are required to quantify the exact relationship between the number of carbon atoms and the phase transition pressure.

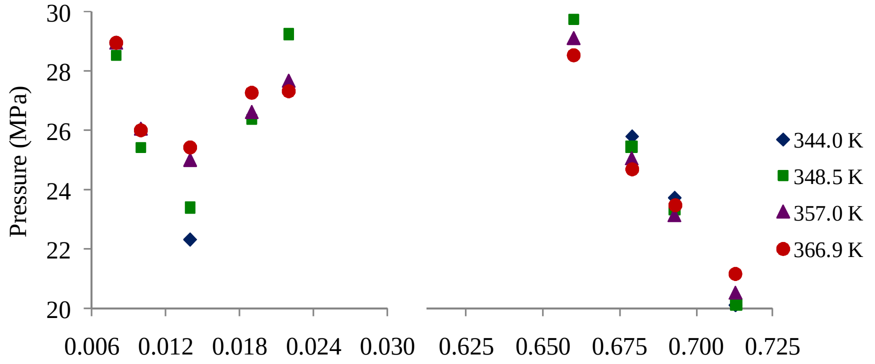
COMPARISON OF THE PHASE BEHAVIOUR OF ALKANES IN SC FLUIDS

A comparison of the phase behaviour of nC32 in propane and nC20 and nC36 in CO_2 is given in Figure 2 and typical relationships between the system temperature and the phase transition pressure are given in Figure 3 for nC36 in propane and in CO_2.



(a) Mass fraction nC32 in propane

(b) Mass fraction nC20 in CO_2



(c) Mass fraction nC36 in CO_2

Figure 2: Phase behaviour of (a) nC32 in propane [3], (b) nC20 in CO_2 [5] and (c) nC36 in CO_2 [5] at various temperatures

The phase behaviour seen in Figure 2 (a) is typical of that of n-alkanes in propane and ethane with total solubility being achieved at moderate pressure (< 30 MPa for nC36 – ethane [10] and < 20 MPa for nC60 – propane [2]). Figure 3 (a) shows that a general linear relationship exists between the system temperature and the phase transition pressure. As temperature increases so does the phase transition pressure. This linear relationship between temperature and the phase transition pressure has previously been proven for both ethane [10] and propane [2] and can be used to determine the phase transition pressure at temperatures other than those for which measurements were conducted with an accuracy similar to that of experimental measurements.

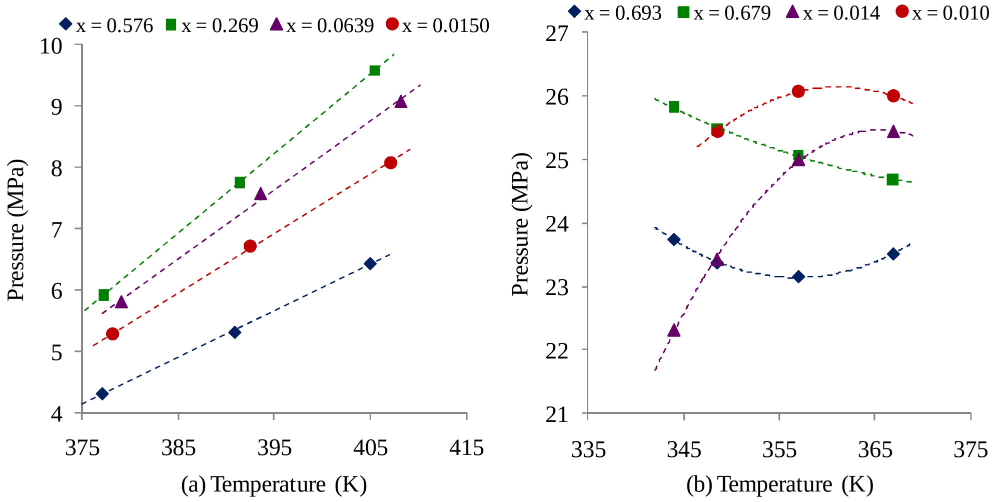
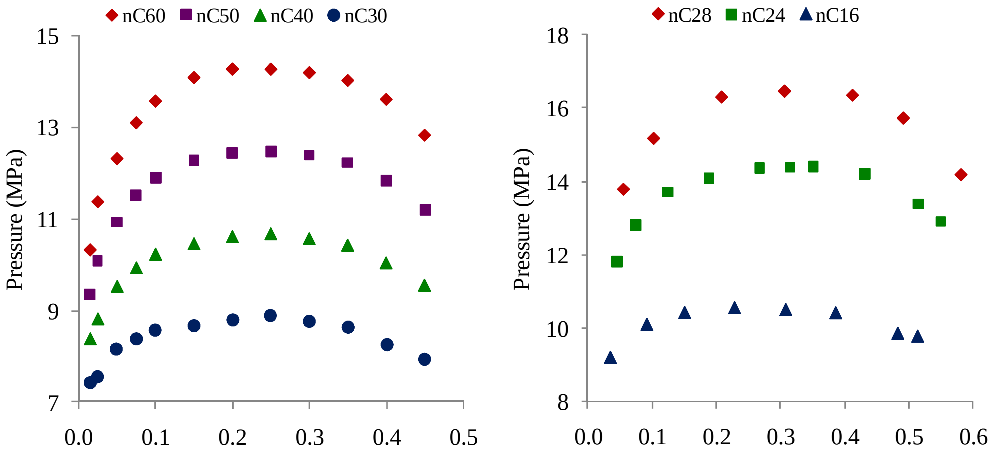


Figure 3: Pressure-temperature plots at various constant composition for nC36 in (a) propane [2] and (b) CO_2 [5]

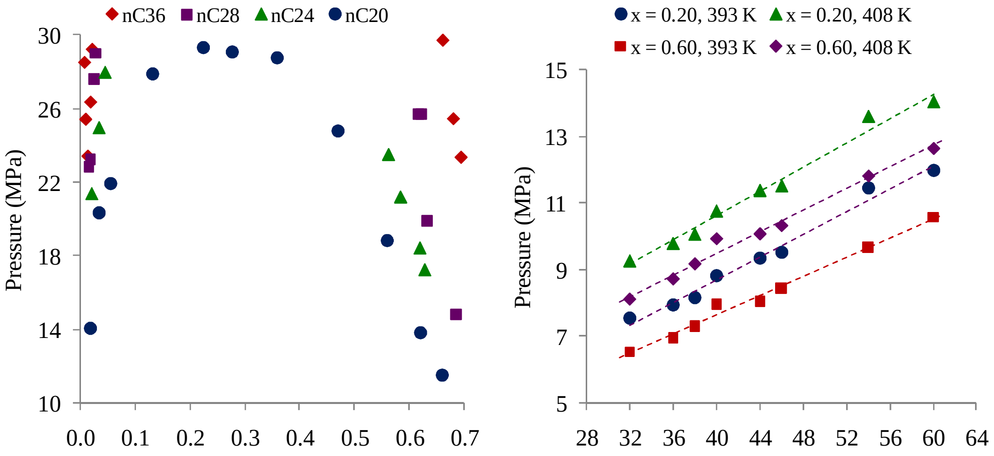
The phase behaviour of n-alkanes in CO_2 differs significantly from that of n-alkanes in propane and ethane. Figure 2 (b) and (c) shows that for lower n-alkanes (nC20 and lower) total solubility can be achieved but at considerably higher pressures, while for higher n-alkanes a miscibility gap appears in the mixture critical region. Figure 3 (b) shows that the relationship between the system and the phase transition pressure is no longer linear. In fact, the data suggests the presence of temperature inversions i.e. an increase in system temperature leads to a decrease in system pressure at certain conditions. These temperature inversions are typical of symmetric systems where the SC fluid is not a good solvent of the solute. Figure 2 (c) shows the existence of a three phase region for the system nC36 – CO_2 over the entire temperature range investigated and such three phase regions are present for a range of n-alkanes in this homologous series. The literature shows that three phase regions are also present for n-alkanes in propane [11] and in ethane [12] but at lower temperatures, below those considered in this work.

Figure 4 shows how the phase behaviour of n-alkanes in propane, ethane and CO_2 changes with a change in the number of carbon atoms of the n-alkane.

For propane and ethane as SC solvent Figure 4 (a) and (b) shows that an increase the number of carbon atoms leads to an increase in the phase transition pressure. Previous studies have shown that for both propane [2] and ethane [10] this increase is linear and this linear increase can be used by means of interpolation to predict the phase behaviour of systems not measured. Typical linear relationships between the phase transition pressure and the number of carbon atoms for propane are shown in Figure 4 (c). On the other hand, for CO_2, while the phase transition pressure increases with increasing carbon number, the increase is not linear; the gradient increases as the number of carbon atoms increases.



(a) Mass fraction n-alkane in propane (b) Mass fraction n-alkane in ethane



(c) Mass fraction n-alkane in CO_2 (d) Number of carbon atoms

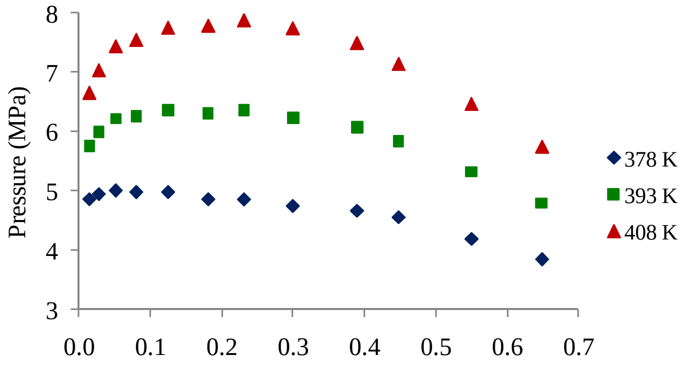
Figure 4: Phase behaviour of alkanes in (a) propane at 408 K [2], (b) ethane at 353 K [4] and (c) CO_2 at 348 K [5] and pressure – carbon number plot for alkanes in propane x = 0.20 and x = 0.60 [2]

Generally, propane and ethane, having a similar structure, behave in a similar manner while CO_2 behaves totally differently. CO_2 is a poorer solvent of n-alkanes, most probably due to the presence of the quadrupole and interactions associated therewith.

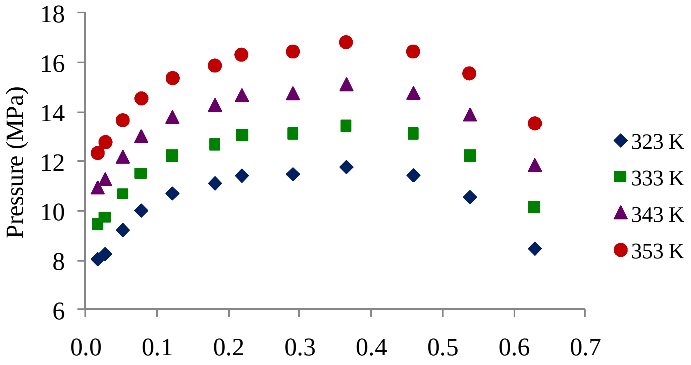
COMPARISON OF THE PHASE BEHAVIOUR OF ACIDS IN SC FLUIDS

A comparison the phase behaviour of C13COOH in propane, ethane and CO_2 is given in Figure 5 while selected relationships between the system temperature and the phase transition pressure are shown in Figure 6. For all three SC solvents an increase in temperature leads to an increase in phase transition pressure for C11COOH. This increase has also been noted for higher and lower acids between C7COOH and C21COOH for propane [1], ethane (this work) and CO_2 [6].

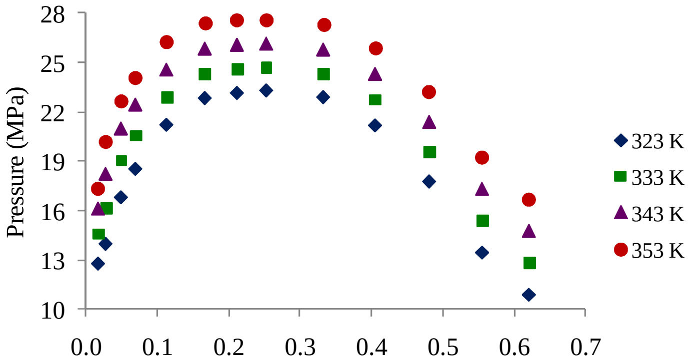
As seen in Figure 6, the increase in phase transition pressure with increasing temperature is generally linear with exceptions only at acid mass fractions of lower molecular weight acids in CO_2 – see x = 0.0180 and to a lesser extent x = 0.0500 in Figure 6 (c). Neither the experimental measurements conducted in this work or the data used here provide evidence of three phase regions. However, Peters [11] suggests the presence of a three phase region for the homologous series acid – propane. As the homologous series acid – ethane and acid – CO_2 are less symmetrical, these systems may also display three phase regions but further experimental measurements are required.



(a) Mass fraction C11COOH in propane



(b) Mass fraction C11COOH in ethane



(c) Mass fraction C11COOH in CO_2

Figure 5: Phase behaviour of C11COOH in (a) propane [1], (b) ethane (this work) and (c) CO_2 [6] at various temperatures

A comparison of the phase behaviour of various acids in propane and CO_2 is shown in Figure 7 while typical pressure – carbon number plots for the homologous series propane – acids and CO_2 – acids are shown in Figure 8.

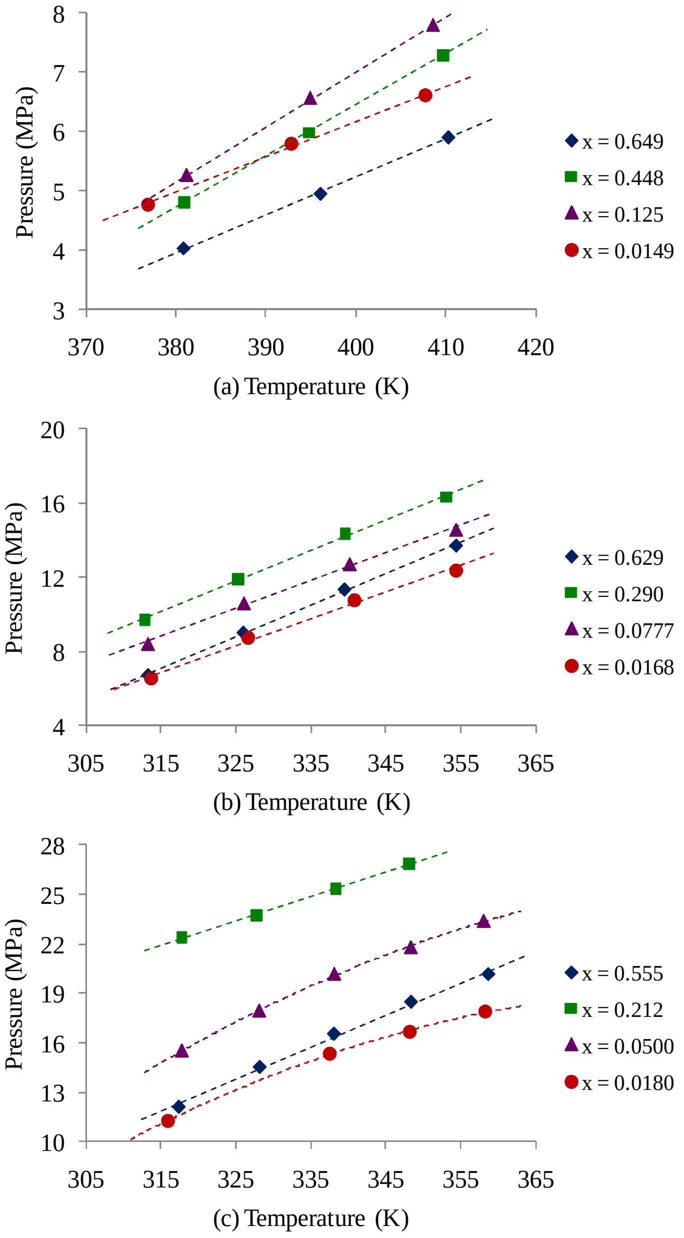


Figure 6: Pressure-temperature plots at constant composition for C11COOH in (a) propane [1], (b) ethane (this work) and (c) CO_2 [6]

Figure 7 (a) shows that an increase in the number of carbon atoms leads to a regular increase in phase transition pressure, with Figure 8 (a) as well as the work of Schwarz et al. [1] confirming that the relationship is linear. The data presented in this work, together with that of Buyn et al. [7] indicates that such relationships also hold true for ethane. However, further data is required to confirm the linear relationships.

At first appearance the relationship between the phase transition pressure and the number of carbon atoms for CO_2 appears to be linear. However, Figure 8 (b) reveals that the relationship displays an increasing gradient as the phase transition pressure increases. This increasing gradient is more prominent at lower mass fractions acids and lower temperatures.

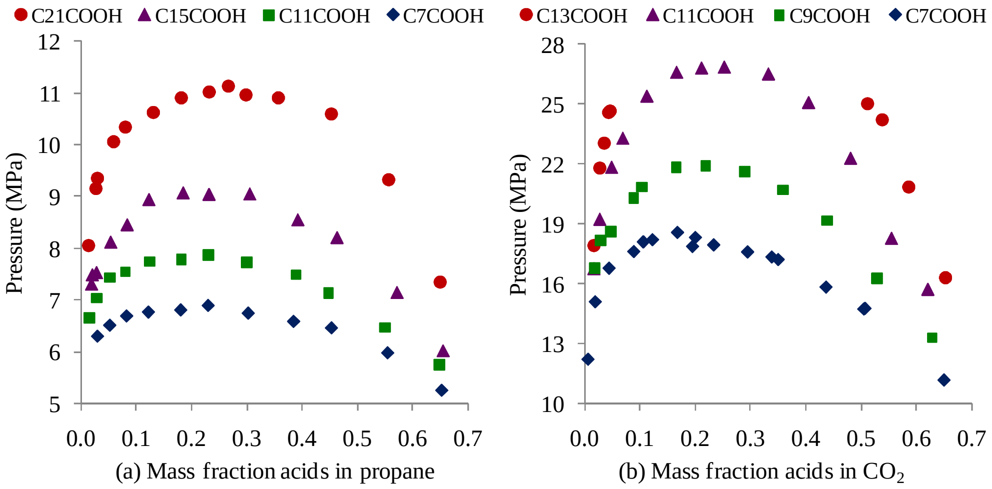


Figure 7: Phase behaviour of acids in (a) propane at 408 K [1] and (b) CO_2 at 353 K [6,8]

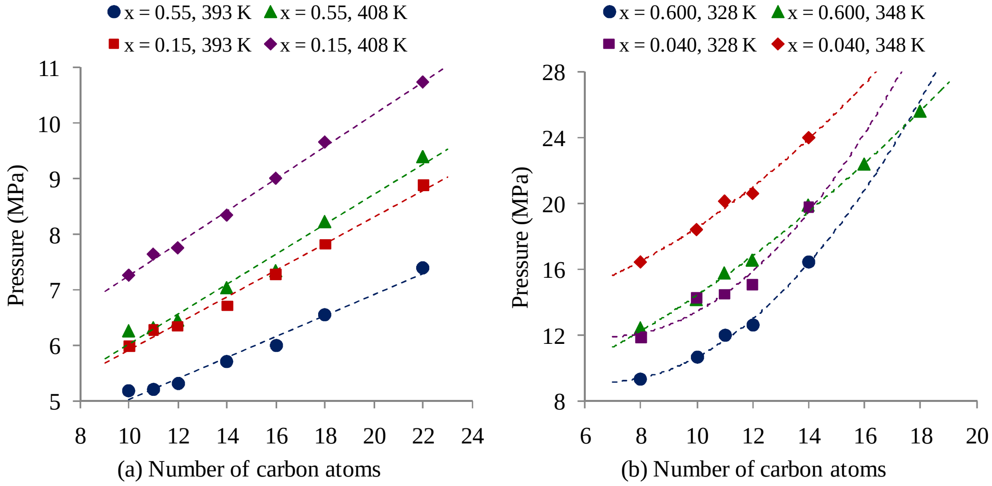


Figure 8: Pressure – carbon number plots for acids at various mass fractions for (a) propane at 393 K and 408 K [1] and (b) CO_2 at 328 and 348 K [6]

COMPARISON OF THE PHASE BEHAVIOUR TRENDS OF N-ALKANES AND ACIDS

From the discussion presented above, the phase behaviour of n-alkanes and acids can now be compared. The results show that in the temperature range considered, for individual systems of all homologous series except that of n-alkanes in CO_2 an increase in temperature leads to an increase in phase transition pressure. This increase is generally linear with exception of the low mass fraction region of lower acids in CO_2. On the other hand, temperature inversions are present in the n-alkane – CO_2 homologous series.

With regard to the presence of three phase regions, insufficient information exists to provide clarity with regard to three phase regions for the acid – ethane and acid – CO_2 homologous series. The literature does, however provide evidence of three phase regions for all other homologous series considered in this paper [5,11-13]. It is therefore highly likely that for the homologous series acids – ethane and acid – CO_2 three phase regions are also present, only outside the measured region. However, only high molecular weight n-alkanes in CO_2 show three phase regions in the temperature ranges considered.

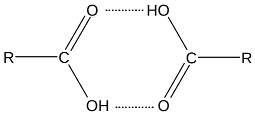
Comparing the behaviour of various compounds in the SC solvents, it is seen that generally an increase in the number of carbon atoms of the molecule leads to an increase in the phase transition pressure for each homologous series. For the series of n-alkanes and acids in propane and ethane a linear relationship exists between the phase transition pressure and the number of carbon atoms. However, for CO_2 as solvent the relationship is not linear; the gradient increases with increasing carbon number with the increasing gradient being more prominent for n-alkanes than for acids.

Comparing the behaviour of the various solvents it is seen that in all cases the phase transition pressure of propane is the lowest, followed by that of ethane and CO_2 has the highest phase transition pressure. In many cases for the higher homolog members miscibility gaps exist for CO_2. In all cases, the phase transition pressure of the acid is higher than that of the corresponding n-alkane, indicating that all three SC solvents can be used to separate n-alkanes and acids with the same number of carbon atoms.

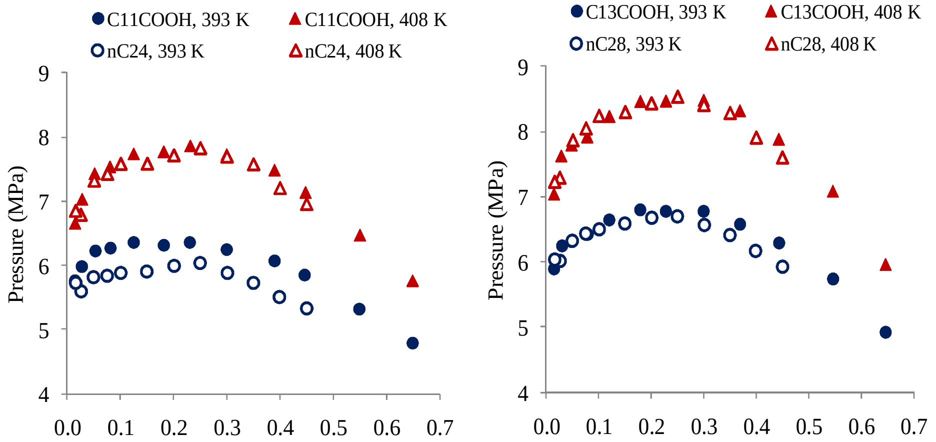
This work has shown that generally the phase behaviour of n-alkanes and acids in propane and ethane is similar with exception that the phase transition pressures for ethane are higher than those of propane. The lower phase transition pressures of propane are most probably due to the decreased asymmetry of the systems due to the increased molecular mass of the solvent. CO_2 as SC solvent behaves differently, most probably due to the presence of the quadrupole. Although CO_2 is not a polar molecule, the quadrupole creates regions of varying polarity around the molecule thus decreasing its solubility in non-polar n-alkanes and in the mainly non-polar acids (due to the long hydrocarbon backbone).

COMPARISON OF THE PHASE BEHAVIOUR OF ACIDS WITH ALKANES OF DOUBLE THE NUMBER OF CARBON ATOMS

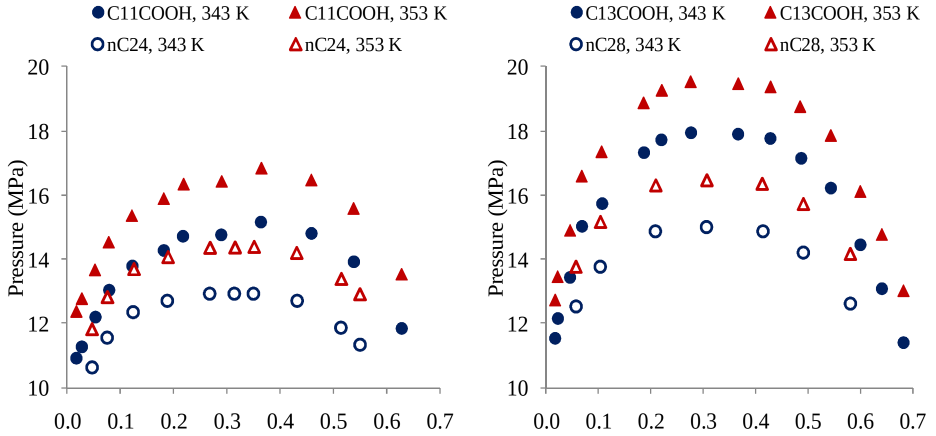
A previous study on the phase behaviour of acids in propane [1] showed that for propane the phase behaviour of acids is very similar to that of n-alkanes with double the number of carbon atoms. The reason for this observation can be traced back to the formation of acid dimers in SC solution. The dimer is formed through a hydrogen bond between the hydroxyl group of one molecule with the double bonded oxygen of the other molecule and vice versa. This association, often encorporated in state of the art equations of state such as those of the SAFT family [14], can be represented schematically as follows:



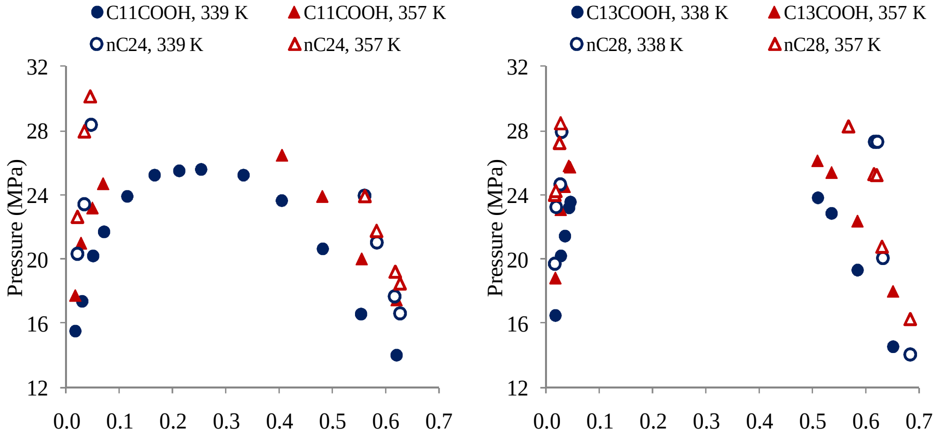
The question now arises whether such relationships hold true for ethane and CO_2, and where differences are observed what the origin of these differences may be. Figure 9 shows a comparison of the phase behaviour of C11COOH and nC24 as well as C13COOH and nC28 in propane, ethane and CO_2. In all cases, experimental data or pressure – temperature interpolation of experimental data is used except for n-alkanes in propane. Here pressure – carbon number extrapolations to lower carbon number have been used to generate the phase equilibrium data. Although it has been proven that these relationships can be extrapolated to lower carbon numbers [4], the results are more of an indication of the phase behaviour rather than an accurate prediction.



(a) Mass fraction acid/alkane in propane (b) Mass fraction acid/alkane in propane



(c) Mass fraction acid/alkane in ethane (d) Mass fraction acid/alkane in ethane



(e) Mass fraction acid/alkane in CO_2 (f) Mass fraction acid/alkane in CO_2

Figure 9: Comparison of the phase behaviour of an acid with an alkane with double the number of carbon atoms (a) C11COOH [1] and nC24 [2] in propane at 393 and 408 K, (b) C13COOH [1] and nC28 [2] in propane at 393 and 408 K, (c) C11COOH (this work) and nC24 [2] in ethane at 343 and 353 K, (d) C13COOH (this work) and nC28 [4] in ethane at 343 and 353 K, (e) C11COOH [6] and nC28 [5] in CO_2 at 338 and 357 K and (f) C13COOH [6] and nC28 [5] in CO_2 at 339 and 357 K

As mentioned above, seen in Figure 9 (a) and (b) and discussed by Schwarz et al. [1], for propane the phase behaviour of the acid mimics that of an alkane with double the number of carbon atoms. Schwarz et al. [1] showed similar results to those presented in Figure 9 (b) for comparisons between C15COOH and nC32, C17COOH and nC36, and C21COOH and nC44. The slight deviations observed for C11COOH and nC24 at lower temperatures can in all probability be attributed to the method of generation of the nC24 data.

Figure 9 (c) to (f) shows that the same trends are not observed for ethane and CO_2 as SC solvent. Considering the comparison of the phase behaviour in ethane shown in Figure 9 (c) and (d) it is noted that the phase transition pressure of the acid is higher than that of the n-alkane with double the number of carbon atoms. If the phase behaviour of C11COOH and nC28 are compared at the same temperature it is seen that the phase behaviour is rather similar. The postulation of Schwarz et al. [1] does not take the effect of the oxygen atoms into account and the dimer should rather be regarded as an alkane with 2N+2 carbon atoms. Considering this effect, together with the polarity of the oxygen the experimental observation of C11COOH mimicking nC28 can be explain. With regard to propane, it should be remembered that the phase behaviour is at higher temperatures and the effect of the oxygen atoms will thus be lower due to diminished influence free electrons of the oxygen atoms. In addition, for propane the difference between the phase behaviour of two n-alkanes differing with only one carbon atom is smaller than for ethane (compare gradients of pressure – carbon number plots for propane [1] with those for ethane [10]). The phase behaviour of an acid with N carbon atoms will thus still be similar to an n-alkane with 2N+2 carbon atoms.

On the other hand, CO_2 shows totally different trends. The acid is considerably more soluble than the n-alkane with double the number of carbon atoms. As mentioned by Schwarz and Knoetze [6], the difference may be due to the quadrupole moment of the CO_2 molecules interacting with the oxygen atoms of the acid. The acid, in all likelihood, still forms the dimer, only now CO_2 is able to dissolve the acid better than n-alkanes with double (or 2N+2) the number of carbon atoms due to the interaction between the CO_2 molecule and the oxygen group in the middle of the dimer.

CONCLUSION

The aim of this paper is to compare the phase behaviour of n-alkanes and acids in SC propane, ethane and CO_2. Experimental data and interpretation thereof has shown that in general the n-alkanes and acids do not behave very differently in propane or ethane with an acid having N carbon atoms behaving similarly to an n-alkane with 2N+2 carbon atoms. In propane and ethane the relationship between the system temperature and phase transition pressure at constant composition is linear for both the acid and the n-alkane. Similarly, a linear relationship exists between the phase transition pressure and the number of carbon atoms at constant mass fraction alkane or acid and constant temperature for these solvents. However, for CO_2 neither the relationship between the system temperature and the phase transition pressure nor the relationshop between the number of carbon atoms and the phase transition pressure at constant acid or alkane mass fraction and constant temperature is linear. Additionally, an acid having N carbon atoms behaves differently to an n-alkane with 2N+2 carbon atoms when the supercritical solvent is CO_2. Therefore for CO_2 as SC solvent the presence of the quadrupole moment and its interaction with the acids molecule has a significant effect on the phase behaviour.

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NOMENCLATURE

CNCOOH	Linear carboxylic acid with a total of N + 1 carbon atoms
nCX	Normal alkane with N carbon atoms

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