

COMPARISON OF THE PHASE BEHAVIOUR OF HIGH MOLECULAR MASS ALCOHOLS IN VARIOUS SUPERCRITICAL FLUIDS

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Abstract

Supercritical fluid processes show an ever increasing promise as an alternative separation technique for the separation of high molecular mass compounds, both from natural sources as well as those from a synthetic feed stock. These compounds usually include alkanes, alcohols, esters and carboxylic acids. Carbon dioxide is by far the most popular supercritical fluid. However, low molecular weight alkanes, such as ethane and propane, are becoming increasingly popular due to their improved solubility of high molecular mass compounds compared to carbon dioxide. The aim of this paper is to compare the phase behaviour of one of the series of high molecular mass compounds, namely 1-alcohols, in carbon dioxide, ethane and propane to highlight similarities and differences.

The results show that the phase behaviour of 1-alcohols in the various solvents differ. Propane requires the lowest pressure for total solubility, followed by ethane while carbon dioxide requires the highest pressure. Phase behaviour of propane and ethane show an increase in the phase transition / solubility pressure with an increase in temperature, the temperature and pressure having a generally linear relationship. On the other hand, the phase behaviour of 1-alcohols in carbon dioxide shows a region of temperature inversion, this region being larger for higher 1-alcohols. The isopleths are also non-linear with some having gradients of varying sign. Propane and ethane show an approximate linear relationship between the phase transition pressure and the number of carbon atoms at constant temperature and composition while carbon dioxide shows an increasing gradient as the number of carbon atoms increases. The investigation shows that propane and ethane behave in a similar manner and both demonstrate relatively simple phase behaviour. On the other hand the carbon dioxide phase behaviour is different and considerably more complicated, most probably due to complicated intermolecular interactions.

Keywords

1-alcohols, carbon dioxide, ethane, propane, phase behaviour

Introduction

Over the last number of years supercritical fluid processing has become an attractive alternative separation method, especially for mixtures that can not be separated with traditional techniques. These mixtures often include, but are not limited to, high molecular weight petrochemicals and natural product extracts. Typical compounds present in these

mixtures include alkanes, alcohol, esters and carboxylic acids and may be linear or have a degree of branching.

Historically carbon dioxide has pioneered supercritical fluid extraction and is often the first option as a supercritical fluid extraction medium due to its non-toxicity and non-flammability. However, carbon dioxide is not a very good solvent of high molecular mass compounds. Recent studies have revealed that low molecular weight alkanes, especially ethane and propane, are attractive alternative solvents to carbon dioxide due to their improved solubility characteristics compared to carbon dioxide.

The aim of this paper is to compare the ability of carbon dioxide, ethane and propane as supercritical solvents for high molecular weight linear primary alcohols by considering their phase behaviour. Specifically this paper will focus on the pressures required for solubility as well as the manner in which the solubility changes with temperature and with molecular mass. Linear primary alcohols were selected as they can be produced synthetically, yet also occur naturally. In addition, as discussed below, a certain amount of literature data is available and 1-alcohols are probably the most widely available group of high molecular mass compounds with functional end groups. As most supercritical fluid extraction processes usually operate at reduced temperatures of 1.0 to 1.2, the focus of this study will be in this temperature range. Additionally, only fluid-liquid phase behaviour will be studied and phase behaviour involving the solid phase is beyond the scope of this paper.

Available literature data

A number of studies involving the phase behaviour of high molecular mass liquid phase alcohols in supercritical fluids have been conducted and a summary is provided in Table 1. However, as the data shows, to date no comparative study has been conducted, hence the impetus for this paper.

From Table 1 it is clear that sufficient data exists to study the phase behaviour of liquid phase 1-alcohols in ethane and propane. However, upon careful inspection it becomes clear that for carbon dioxide, particularly at higher molecular masses, more data may be required. For the purpose of this investigation additional liquid phase bubble point measurements of nC16-OH in carbon dioxide is measured to complement the literature data.

Table 1: Summary of available literature data for phase behaviour data of liquid phase 1-alcohols in supercritical fluids

Solvent	Alcohol	Temperature Range (K)	Pressure Range (MPa)	Type of Data	Reference
Carbon dioxide	1-C8-OH	308 – 348	6.77 – 17.94	Bubble/Dew point	[1]
		313.15 – 348.15	4 – 19	Equilibrium	[2]
		348.15	1 – 5	Equilibrium	[3]
		308.15 – 328.15	1.51 – 15.11	Equilibrium	[4]
		313 – 393	2.93 – 21.87	Bubble/Dew point	[5]
	1-C9-OH	308.15 – 328.15	2.23 – 15.60	Equilibrium	[4]
	1-C10-OH	348.15 – 453.15	1 – 5	Equilibrium	[3]
		308.15 – 328.15	2.23 – 15.17	Equilibrium	[4]
		348.15 – 453.15	7 – 19	Equilibrium	[6]
	1-C12-OH	293 – 393	25 MPa	Equilibrium	[7]
		353.2	10 – 25.2	Equilibrium	[8]
		310 – 355.5	8.3 – 17.01	Bubble/Dew point	[9]
	1-C16-OH	328 – 338	14.18 – 41.59	Vapour phase solubility	[10]
Ethane	1-C10-OH – 1-C22-OH	307.9 – 356.0	5.77 – 23.99	Bubble/Dew point	[11]
Propane	1-C10-OH – 1-C22-OH	378 – 408	3.70 – 8.37	Bubble/Dew point	[12]

Additional Phase Equilibrium Measurements: Materials, Method and Data Measured

A static synthetic method, using a previously constructed setup consisting of a variable volume high pressure view cell, was used to measure the solubility data. The view cell has been described in detail in a previous publications [13]. The view cells is able to operate between 300 and 460 K and up to 27.5 MPa. The accuracy of the measurements can be summarised as follows [13]:

- The uncertainty in the phase transition pressure is approximately 0.06 MPa.
- The accuracy of the temperature measurement is better than 0.2 K.
- It is estimated that the maximum error in the mass fraction is approximately 1 % of the value.

Further details pertaining to the experimental procedure as well as comparison with high quality data from other reputable research groups has been described in a previous publication [13].

1-Hexadecanol obtained from Sigma-Aldrich (Catalogue number 52240) with a purity of > 99.0% and carbon dioxide obtained from Afrox (Catalogue number 340101) with a purity of 99.95 % was used without further purification. The experimental data is given in Table 2.

Table 2: Experimental bubble point measurements for 1-hexadecanol in carbon dioxide

Mass Fraction nC16	Temperature (K)	Pressure (K)
0.741	329.4	10.42
	337.7	11.38
	348.1	12.43
	358.1	13.39
0.692	329.2	13.20
	338.7	13.98
	349.0	14.83
	358.7	15.36
0.640	329.1	18.35
	334.1	17.90
	338.9	17.87
	343.5	17.90
	346.4	18.27
	352.7	18.27
	358.7	18.13
0.593	325.9	26.11
	329.5	24.39
	334.4	22.52
	338.8	21.79
	348.5	21.15
	358.5	21.15
0.547	343.3	25.76
	348.7	24.83
	353.4	24.35
	358.0	24.21

Comparison of temperature dependence behaviour

The temperature dependence of the phase pressure-composition plots for selected alkanes in carbon dioxide (1-octanol and 1-hexadecanol), ethane (1-hexadecanol) and propane (1-hexadecanol) are given in Figure 1 while selected isopleths (constant composition plots) for 1-octanol and 1-hexadecanol in carbon dioxide as well as 1-hexadecanol in propane is given in Figure 2.

Firstly compare Figure 1 (b), (c) and (d): here the phase behaviour of 1-hexadecanol in carbon dioxide, ethane and propane is illustrated. Notably it can be seen that pressures in excess of 40 MPa are required for total solubility of 1-hexadecanol in supercritical carbon dioxide while total solubility in ethane and propane is obtained at pressures below 21 and 8 MPa respectively. Ethane and propane are thus significantly better solvents than carbon dioxide.

Figure 1 (a) and (b) show typical phase behaviour of 1-alcohols in carbon dioxide. Generally an increase in temperature leads to an increase in phase transition / solubility pressure. However, there are exceptions. In both these cases, as well as that of 1-dodecanol seen in the work of Bonthuys [9], a temperature inversion is noted. In 1-octanol the range of temperature inversion is very small, i.e. only at temperatures close to the critical

temperature and for a small composition range, while the inverted temperature range was observed in 1-hexadecanol for the entire temperature range investigated in this work. These temperature inversions can also be seen in Figure 2 (a) and (b) where the isopleths show a change in the sign of the gradient. This temperature inversion is a common phenomena in the phase behaviour of high molecular weight compounds in carbon dioxide and is also noted in the phase behaviour of high molecular weight alkanes in carbon dioxide [14]. Although temperature inversions were observed, no three phase region was observed and the data does not hint towards any three phase behaviour. This does not, however, eliminate the existence of a three phase region at temperatures outside the range studied here. The information presented in this paper only describes a limited region of the phase envelope and thus insufficient information is available to classify the systems according to the types of Scott and van Konynenburg [15]. However, the trends observed may assist in future classification of the systems.

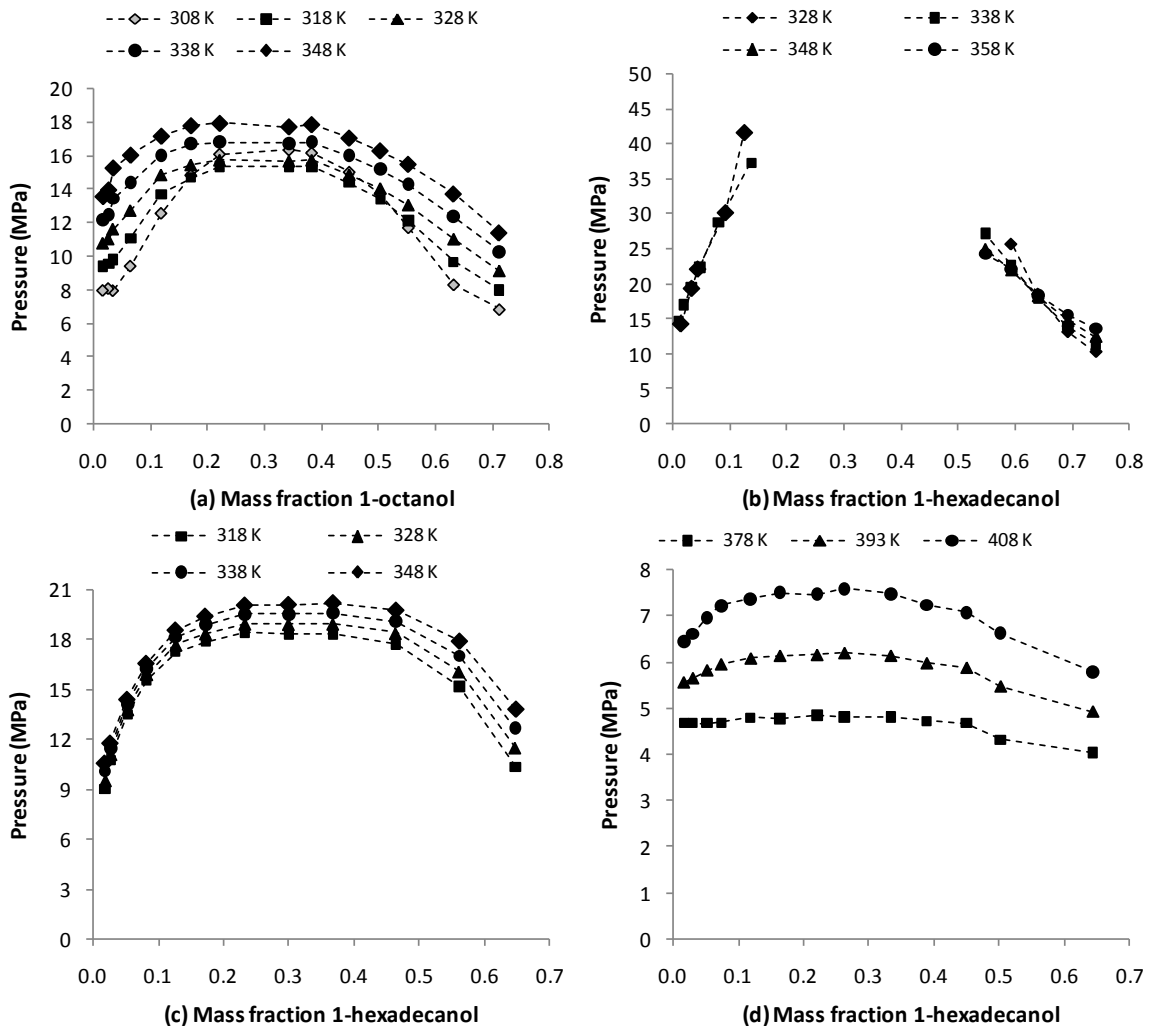


Figure 1: Pressure-composition plot at various temperatures for (a) 1-octanol in carbon dioxide [1], (b) 1-hexadecanol in carbon dioxide (mass fractions less than 0.2 taken from Kramer and Thodos [10], (c) 1-hexadecanol in ethane [11] and (d) 1-hexadecanol in propane [12]

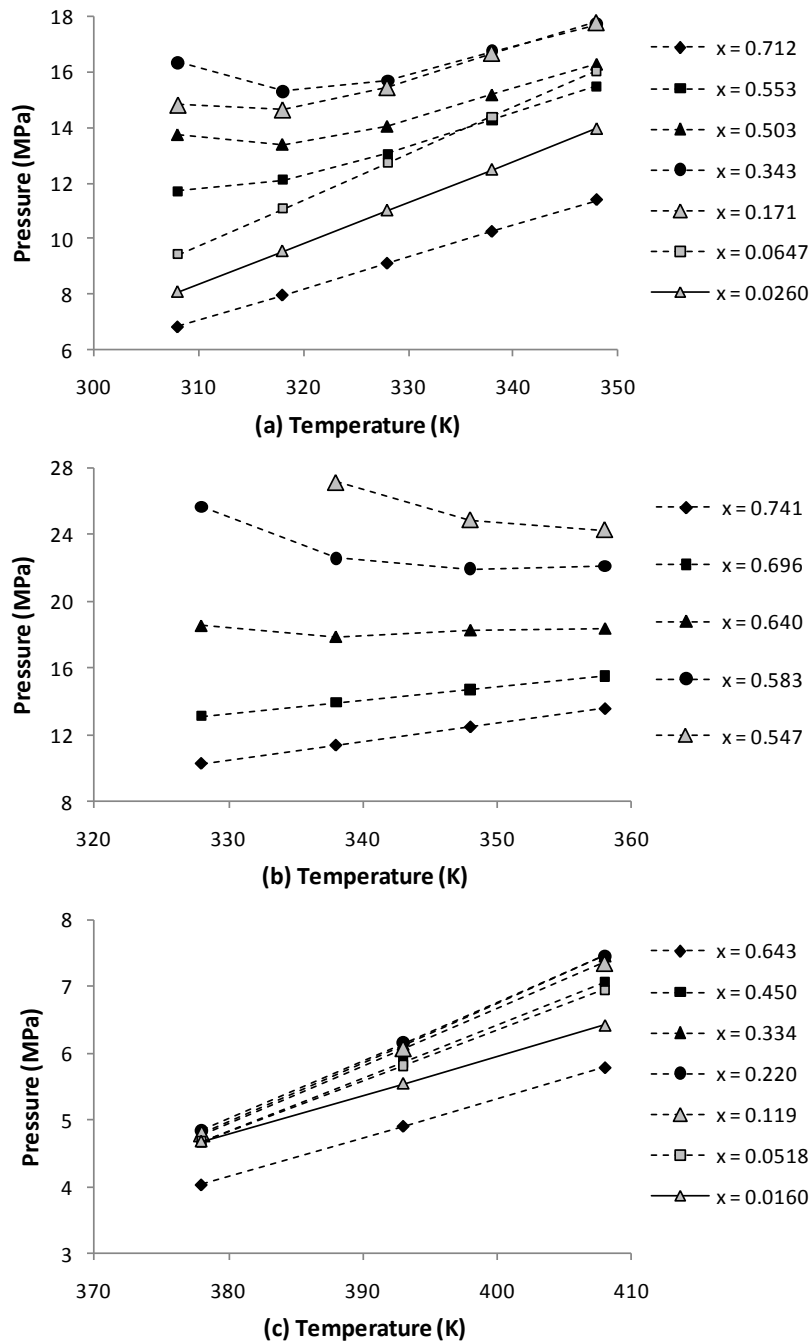


Figure 2: Isopleths for the systems (a) 1-octanol in carbon dioxide [1], (b) 1-hexadecanol in carbon dioxide (this work) and (c) 1-hexadecanol in propane [12]

The phase behaviour of 1-hexadecanol in ethane and in propane is presented in Figure 1 (c) and (d) and a set of typical isopleths are shown in Figure 2 (c) for 1-hexadecanol in propane. Isopleths for ethane show similar trends to that of propane. The phase behaviour presented is typical of these two homologous series. No temperature inversions or three phase regions were observed and the data does not indicate the presence of any of these phenomena. As seen, an increase in temperature leads to an increase in phase transition

pressure and the isopleths indicate that this relationship is linear. This linear relationship seems to be common in systems with ethane and propane as solvents and is also seen for alkanes in propane [16], alkanes in ethane [17] as well as other functional end groups in propane [18]. However, as in the case of carbon dioxide, insufficient information is available to classify the systems according to van Konynenburg and Scott [15] yet the phase behaviour trends observed may provide insight into future classification of these systems.

Comparison of trends in homologous series

Figure 3 compares the phase behaviour of various 1-alcohols in carbon dioxide, ethane and propane while Figure 4 shows pressure-carbon number plots for selected mass fractions for the three solvents being investigated.

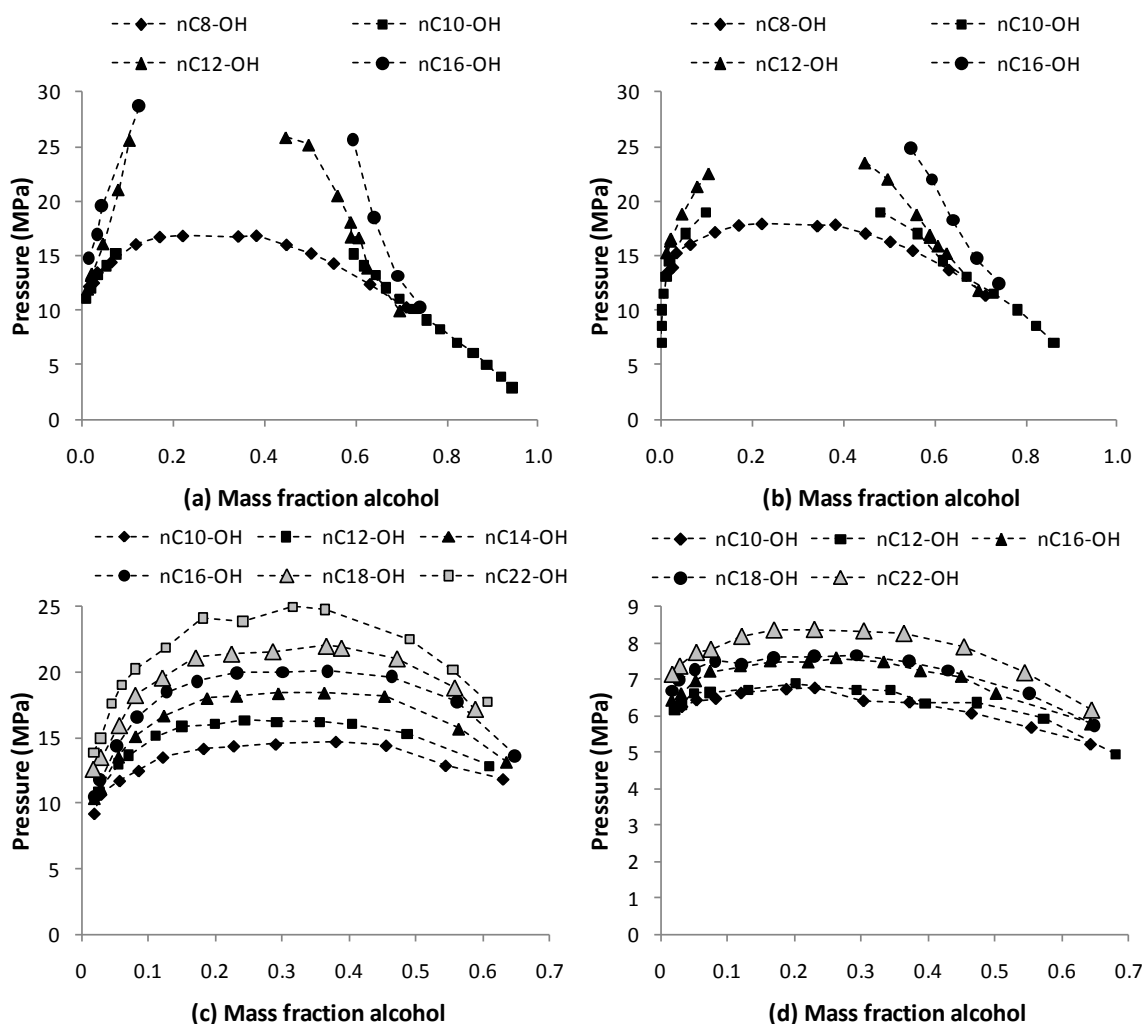


Figure 3: Pressure-composition plot for a range of alcohols in (a) carbon dioxide at 328 K [1,6,9,10], (b) carbon dioxide at 348 K [1,6,9], (c) ethane at 346 K [11] and (d) propane at 408 K [12]

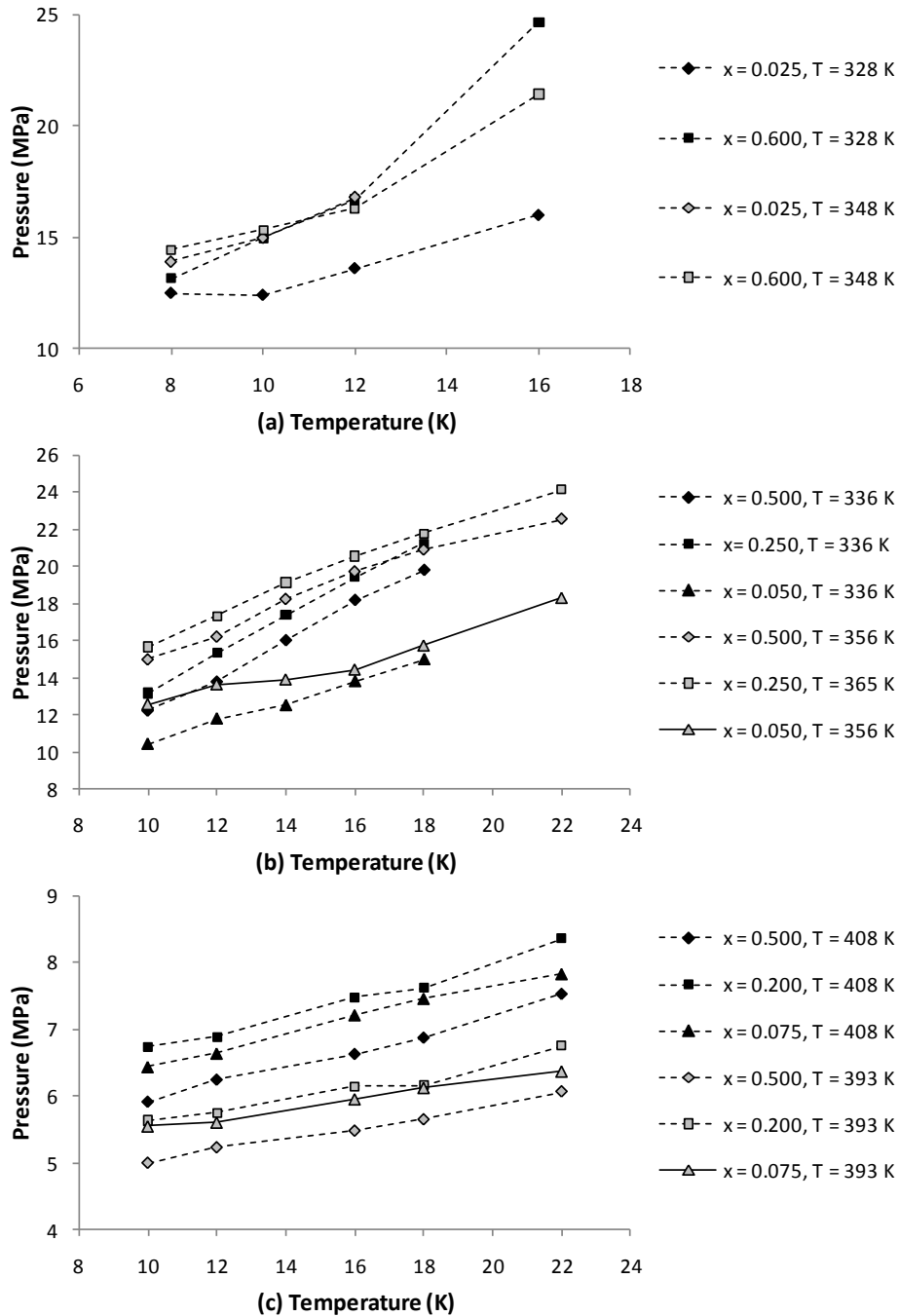


Figure 4: Pressure-carbon number plots at constant composition and temperature for alcohols in (a) carbon dioxide [1,6,9,10], (b) ethane [11] and (c) propane [11]

The plots presented in Figure 3 and Figure 4 show that carbon dioxide behaves different to ethane and propane.

Figure 3 (a) and (b) shows that for carbon dioxide, especially in the mixture critical region, the phase behaviour is very much dependent on the number of carbon atoms present. Considering Figure 4 (a) it is seen that the relationship between the number of carbon atoms and the phase transition pressure at constant temperature and composition is not linear for carbon dioxide as solvent but the gradient increases with increasing carbon

number. Comparing Figure 3 (a) and (b) it can be seen that as temperature increases the difference between the 1-alcohols becomes less, possibly due to the increased effect of the region of temperature inversion observed at higher 1-alcohols. However, an increase in the number of carbon atoms still results in a non-linear increase in the phase transition / solubility pressure. Although the gradient and change in gradient is different at different temperatures, this trend is true throughout the entire composition and temperature range studies and indicates that supercritical fluids can be used to fractionate 1-alcohols in the temperature range studied here, albeit at relatively high pressures. Taking the decreasing difference in the solubility pressure at higher temperatures into account there are indications that at temperatures higher than those being considered here, the pressure – carbon number plots may no longer have an increasing gradient throughout the entire region and under these conditions carbon dioxide may not be able to separate a mixture of alcohols successfully.

Figure 3 (c) and (d) shows that phase behaviour of 1-alcohols in ethane and propane is very similar. Together with the pressure – carbon number plots given in Figure 4 (b) and (c), and data presented by Schwarz and Knoetze [12] as well as McClune [11], it is seen that an increase in carbon number leads to a nearly linear increase in phase transition pressure for the entire temperature range studied here. Both supercritical ethane and propane should thus be able to separate mixtures of 1-alcohols according to the number of carbon atoms and should be able to achieve this separation at much lower pressures than those when using carbon dioxide as solvent.

Conclusions and future work

This paper has shown that the phase behaviour of 1-alcohols in supercritical carbon dioxide differs considerably from that in supercritical propane and ethane. Supercritical carbon dioxide requires much larger pressures and shows a non-linear pressure – temperature (at constant composition) as well as pressure – carbon number relationship. In addition, for all alcohols investigated (1-octanol through 1-hexadecanol) a region of temperature inversion exists, this region increasing in temperature and mass fraction range with an increase in the number of carbon atoms. On the other hand, ethane and propane show a linear pressure – temperature (at constant composition) and pressure – carbon number relationship and, in the region investigated in this work, do not display any temperature inversions.

The analysis presented in this work was somewhat limited by a lack of data for 1-alcohols in carbon dioxide, especially for high molecular weight alcohols. Additional measurements would aid in such an investigation. In addition, a similar investigation should be conducted for alkanes and the findings compared. This comparison may assist in shedding light on the underlying phenomena dominating the phase behaviour.

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