PHASE BEHAVIOUR OF VARIOUS LINEAR OCTANOLS IN SUPERCRITIAL CO_2

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1   INTRODUCTION

To date a number of studies have been conducted to determine the phase behaviour of alcohols in supercritical fluids [1]-[4]. While the aforementioned studies have shown that the hydroxyl group influences the phase equilibria of alcohols in supercritical fluids, comparative studies investigating the effect of the position of the hydroxyl group on the phase behaviour are lacking.

Elizalde-Solis et al. [5] studied the phase behaviour of 1- and 2-propanol in CO_2 at temperatures between 344 and 397 K. They found that the phase transition pressure of 1-propanol is higher than that of 2-propanol. Byun and Kwak [6] and Chen et al. [7] studied the phase behaviour of 1- and 2-butanol in CO_2 and their results show that 2-butanol has a lower phase transition pressure than 1-butanol. These studies have indicated that the position of the hydroxyl group is important in the phase behaviour of alcohols in supercritical carbon dioxide. However, due to the short hydrocarbon backbone, only alcohols with the hydroxyl group in the 1- and 2-position were investigated. A longer alcohol where the hydroxyl group has a choice of at least 4 carbon atoms would assist in determining the effect of the position of the hydroxyl group on the phase behaviour.

In light of the above, it was decided to investigate the phase behaviour of linear octanols. Octanols have a long enough hydrocarbon backbone to allow for an investigation of a linear alcohol with the hydroxyl group in 4 different positions. In addition, the hydrocarbon backbone is not so large that it becomes dominant. Due to its popularity and wide application, carbon dioxide was selected as supercritical solvent.

The aim of this work is thus to compare the phase behaviour (pressure, density, temperature) of 1-, 2-, 3- and 4-octanol in supercritical carbon dioxide to determine the effect of the position of the hydroxyl group on the phase behaviour.

2   HIGH PRESSURE PHASE EQUILIBRIUM AND DENSITY DATA

A number of sources provide high pressure phase equilibrium data of octanols in carbon dioxide. This study focused on the phase envelope region where only two co-existing phases exist and in a temperature range of 303 to 365 K ($T_r \approx 1 - 1.2$). The data in question will thus typically be used in supercritical processes. Three phase data and data outside this temperature range was not considered in this work. The data used have been listed in Table 1. The data from the various sources agreed well with one another and was used for comparative purposes.

Table 1: **Sources of phase equilibrium data for octanols in supercritical carbon dioxide for T_r = 1.0 – 1.2 (composition in mass fraction octanol)**

Octanol	Temperature Range	Pressure Range	Composition Range	Reference
1-Octanol	313 –353 K	29.3 – 189 bar	0.0969 – 0.913	[6]
	313 – 348 K	40.0 – 190 bar	0.00112 – 0.920	[8]
	348 K	10.0 – 50.0 bar	0.00168 – 0.00244 and 0.896 – 0.983 [*]	[9]
	308 – 328 K	21.7 – 151 bar	0.000 – 0.154 and 0.452 – 0.961 [*]	[10]
	308 – 348 K	68.1 – 180 bar	0.0163 – 0.712	[11]
2-Octanol	308 – 348 K	68.1 – 147 bar	0.0166 – 0.626	[11]
	303 – 323 K	30 – 91 bar	0.00443 – 0.896	[12]
3-Octanol	308 – 348 K	67.8 – 143 bar	0.0164 – 0.626	[11]
4-Octanol	308 – 348 K	71.5 – 143 bar	0.0172 – 0.517	[11]

[*] No data in the mixture critical region

The data listed provides a relationship between the pressure and temperature at the phase boundary. Sufficient information was available and no additional measurements were required. However, none of the aforementioned published data provides any indication of the density at the phase boundary, prompting experimental work. However, simultaneous to measuring the phase equilibrium pressure [11], Fourie and co-workers also measured the density at the phase boundary. These, to date unpublished, measurements will be used to determine if the hydroxyl group has any effect on the density of the fluid mixture at the phase boundary. Details regarding the measurement technique is given by Schwarz [13].

3 EFFECT OF THE POSITION OF THE HYDROXYL GROUP

3.1 Phase equilibrium

The data listed in Table 1 is used to illustrate effect of the position of the hydroxyl group on the phase behaviour and is shown in Figure 1 (a) and (b) for 313 and 328 K respectively. As seen, there is a marked difference in the phase behaviour of the 1-octanol in comparison to 2-, 3 and 4-octanol. It is believed that this difference is due to a difference in polarity of the molecule. The primary hydroxyl group of 1-octanol results in greater polarity than is the case for 2-, 3- and 4-octanol. The higher polarity of 1-octanol results in a higher polarity difference between the solvent and the solute, and the authors believe that it is this higher polarity that causes the increased pressure required for total solubilisation.

Considering Figure 1, very little difference exists between 2-, 3- and 4-octanol, especially at low temperatures. However, Fourie et al. [11] have shown that this difference increases with an increase in temperature with 4-octanol requiring the lowest pressure and 2-octanol the highest pressure. The decrease in pressure required for solubility as the hydroxyl group moves to the centre of the molecule may be attributed to the increasing shielding effect of the hydrocarbon backbone and thus decreasing polarity. 2-, 3- and 4-octanol behave in a similar manner with respect to increasing temperature: As temperature increases, the phase equilibrium pressure increases, generally linearly. The increase is greater the further the

hydroxyl group is from the centre of the molecule. For 2-, 3- and 4-octanol, the effect of the position of the hydroxyl group is thus greater at higher temperatures.
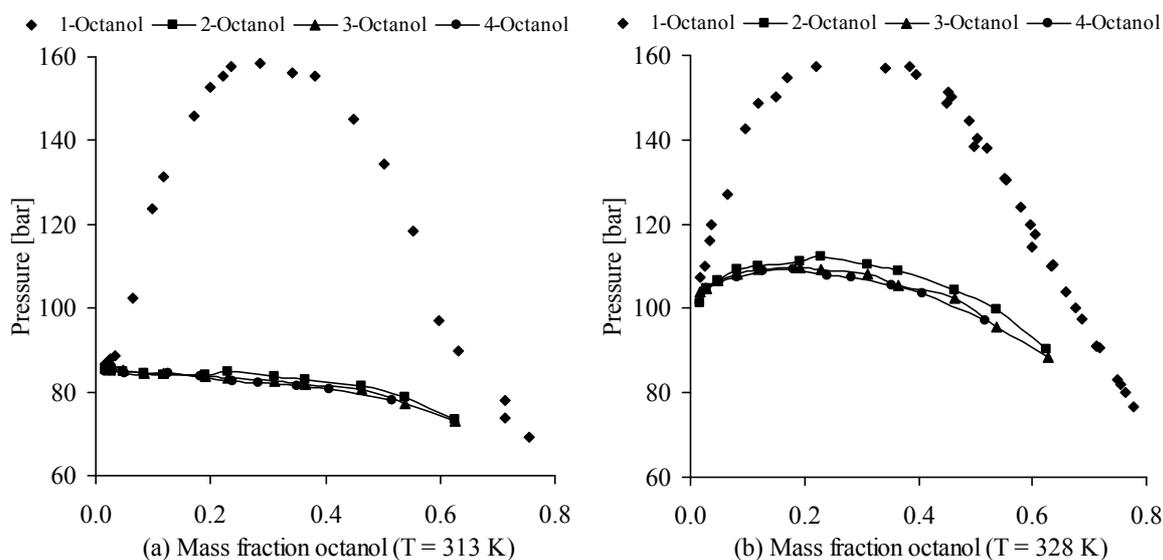

Figure 1: **Phase equilibrium pressure as a function of composition for 1-, 2-, 3- and 4-octanol in CO_2 at (a) 313 K and (b) 328 K**

If one compares the behaviour of 1-octanol versus the other octanols considered in this study, one sees that 1-octanol behaves differently. As temperature increases, the difference in the pressure required for solubility between 1-octanol and 2-, 3- and 4-octanol decreases. This decrease can be seen in the entire temperature region investigated. One should also note that the curves of 2-, 3- and 4-octanol are a lot flatter than that of 1-octanol, resulting in a much larger mixture critical region. The difference in phase behaviour for 1-octanol can be explained if one considers the relationship between pressure and mass fraction as a function of temperature as well as the relationship between pressure and temperature at constant mass fraction. Figure 2 (a) and (b) show a plots of pressure versus composition at 308, 328 and 348 K for 1-octanol and for 2-octanol respectively (3- and 4-octanol behave in a similar manner to 2-octanol) [11]. In Figure 3 (a) and (b) a number of the isopleths for the data given by Fourie et al [11] have been generated for the system 1-octanol and 2-octanol respectively.

Figure 2 indicates that for 1-octanol in the mixture critical region ($x_{1\text{-octanol}} \approx 0.20$ to 0.55) a temperature inversion occurs. On the other hand, for 2-octanol (and similarly 3- and 4-octanol) no such temperature inversions occur. This temperature inversion contributes to the large difference in phase transition pressure between 1-octanol and 2-, 3- and 4-octanol experienced at low temperatures. However, even in the temperature region where no temperature inversion occurs, the difference between 1-octanol and 2-, 3- and 4-octanol becomes less with increasing temperature. This can be seen by comparing the gradient of the isopleths at mass fractions of approximately 0.3 octanol between 340 and 350 K (See Figure 3 (a) and (b)): the gradient for 1-octanol is less than that of 2-octanol.
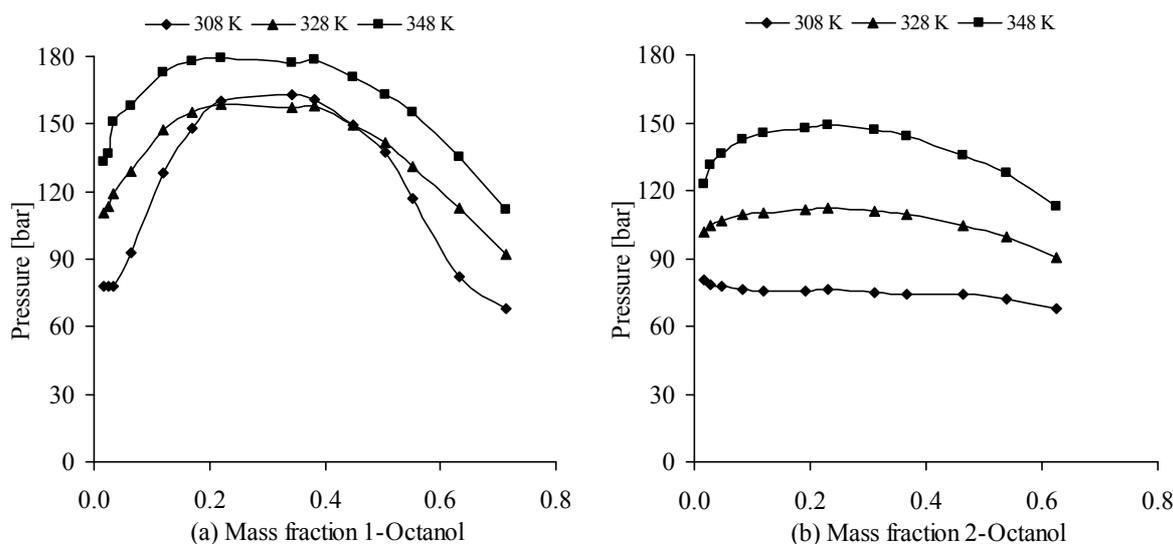
Figure 2: **Phase equilibrium pressure as a function of composition for (a) 1-octanol and (b) 2-octanol in CO_2 at 308 K, 328 K and 348 K**
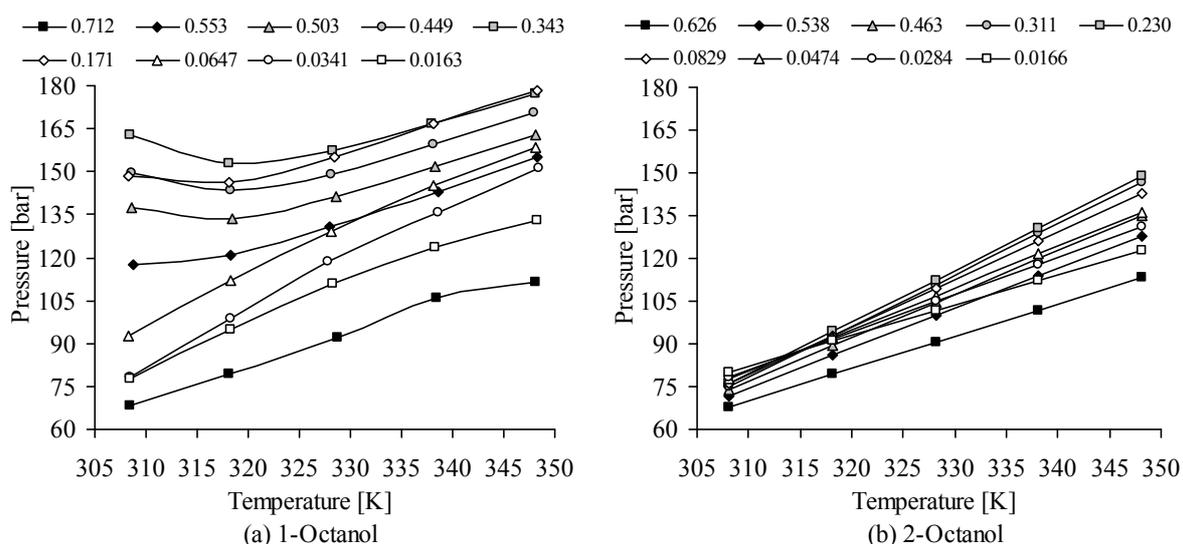

Figure 3: **Phase equilibrium pressure as a function of temperature at constant composition for (a) 1-octanol and (b) 2-octanol in CO_2 at various mass fractions**

Although 2-, 3- and 4- octanols do not exhibit such temperature inversions in the region studied, temperature inversions are not unique to 1-octanol. The phase behaviour of higher octanols in carbon dioxide, such as 1-hexadecanol [14] and 1-eicosanol [15], also exhibit such behaviour, the region of temperature inversion increasing with increasing hydrocarbon backbone length.

3.2   Density

As seen in the aforementioned section, a difference exists between the phase equilibrium pressure for the various octanols, depending on the position of the hydroxyl group. The

question now arises as to the effect of the hydroxyl group on the density of the phase at the phase boundary. Generally, very little information is available concerning the density of the fluid at the phase boundary. Specifically, for the systems 1-, 2-, 3- and 4-octanol in supercritical carbon dioxide no such information could be obtained, thus, prompting experimental work. Simultaneous to measuring the phase equilibria [11], Fourie and co-workers measured the density of the phase at the phase transition. Figure 4 (a) shows a plot of the density at the phase equilibrium boundary as a function of composition for 1-, 2-, 3- and 4-octanol at 348 K while Figure 4 (b) compares the density of 1- and 4-octanol at 308 K and 348 K.
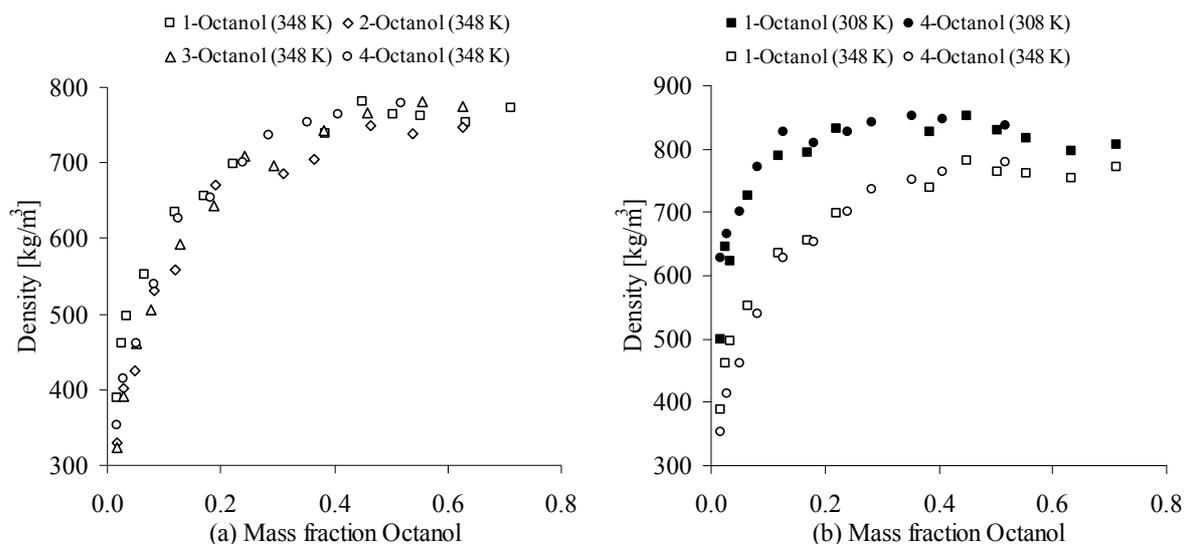

Figure 4: Density at the phase equilibrium boundary as a function of composition for 1-, 2-, 3- and 4-octanol in CO_2 at 308 and 348 K

From the density measurements it can be seen that there is no clear trend with regard to a difference in density due to the position of the hydroxyl group. Any separation technique based on density alone would not be able to distinguish between the isomers and can thus not be applied. The density measurements do, however, show a dependence on temperature. In all cases, the density decreases as temperature increases. On the other hand, there is no indication of the temperature inversion, observed for 1-octanol in carbon dioxide, on the density-composition plots.

4   CONCLUSIONS AND FUTURE WORK

The aim of this work was to consider the phase behaviour of linear octanols in supercritical carbon dioxide in order to investigate the effect of the position of the hydroxyl group on the supercritical phase behaviour (PvT).

The results showed that an increase in temperature generally leads to an increase in phase transition pressure at constant composition with exception of the low temperature region of 1-octanol in CO_2 for mass fractions near the mixture critical region, where a temperature inversion was observed. The results also showed that the phase transition pressure of 1-octanol is significantly higher than that of 2-, 3- and 4-octanol. 2-Octanol has a slightly higher phase transition pressure than 3-octanol, which in turn has a marginally higher phase

transition pressure than 4-octanol. The difference between 1-octanol and the other isomers is larger at lower temperatures while the difference between 2-, 3- and 4-octanol is higher at higher temperatures. It may be possible to explain these effects if one considers the polarity and shielding of the hydroxyl groups: Shifting the hydroxyl group further from the terminal position results in greater shielding thereof and a reduction in polarity. Since less polar molecules are more soluble in CO_2, moving the hydroxyl group away from the terminal position may effect an increase in solubility and a reduction in solubility pressure.

An investigation of the effect of the hydroxyl group on the density at the phase boundary failed to show any clear trend with regard to the position of the hydroxyl group, However, as expected, it was found that an increase in temperature results in an decrease in the density at the phase transition pressure.

This work showed that the phase behaviour of linear octanol isomers in supercritical carbon dioxide differs. The effect of side branching as well as the hydrocarbon backbone length needs to be investigated and similar studies should be conducted in other supercritical solvents, such as ethane and propane. In addition, thermodynamic modelling needs to be conducted. This will aid in predicting these and similar systems and may shed light as to the exact reason why the phase behaviour differs between various isomers.

5   ACKNOWLEDGEMENTS

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