



## Phase equilibria of alcohols in supercritical fluids Part II. The effect of side branching on C<sub>8</sub> alcohols in supercritical carbon dioxide

C.E. Schwarz, F.C.v.N. Fourie, J.H. Knoetze\*

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

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### ABSTRACT

This paper is a continuation of a previous study and investigated the phase equilibria of six C<sub>8</sub> alcohols (2,2,4-trimethyl-1-pentanol, 2,4,4-trimethyl-1-pentanol, 2-ethyl-1-hexanol, 2-propyl-1-pentanol, 4-methyl-3-heptanol and 6-methyl-2-heptanol) in supercritical carbon dioxide. Data has been measured between 308 and 348 K for alcohol mass fractions between 0.660 and 0.0162. The results show that the position, size and quantity of side chains have a significant effect on the phase behaviour by changing the shape of the molecule and the effect of the hydroxyl group on the polarity of the molecule. The pressure required for total solubility increases in the following sequence: 4-methyl-3-heptanol < 2,2,4-trimethyl-1-pentanol < 6-methyl-2-heptanol < 2,4,4-trimethyl-1-pentanol < 2-propyl-1-pentanol < 2-ethyl-1-hexanol < 1-octanol. The difference in phase behaviour is believed to be a result of a difference in shielding of the hydroxyl group. Greater shielding of the hydroxyl group results in a less asymmetric system, and this, in turn, results in higher solubility of the molecule.

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### 1. Introduction

Supercritical fluids are attracting increasing interest in the processing of high molecular mass petrochemical, natural and other products. These products often contain functional groups, such as hydroxyl and carboxyl groups, and thus a need exists to investigate the effects of functional group type, functional group position and side branching on the phase behaviour of these compounds together with supercritical fluids. This paper is a continuation of a previous paper [1], which focused on the phase behaviour of linear C<sub>8</sub> alcohols and investigated the position of the hydroxyl group along the hydrocarbon backbone. The aim of this paper is to extend the previous paper by investigating the influence of structural isomerisation on the phase behaviour.

C<sub>8</sub> alcohols are particularly suited to the study of the effect of structural isomerisation. The presence of 8 carbon atoms allows for a large variety of structural isomers and a significant amount of these isomers are available commercially in sufficient quantities (20 g) at high enough purities (>98%). At the same time, C<sub>8</sub> alcohols generally show sufficient solubility for the desired investigation. In addition, part I of this series studied the influence of the position of the hydroxyl group on the phase behaviour using C<sub>8</sub> alcohols and thus the effect of the hydroxyl group position

can be explained for the molecular mass alcohol investigated. By predominantly limiting the study to C<sub>8</sub> alcohols, the effect of molecular mass is eliminated. Carbon dioxide is selected as the supercritical fluid due to the total solubility of 1-octanol below 200 bar at 348 K [1] and from the results seen in part I it is expected that the structural isomers will be more soluble than 1-octanol.

Fig. 1 contains information on all the molecules studied in this paper. Part I of this study published the phase behaviour of 1-, 2-, -3 and 4-octanol in supercritical carbon dioxide. Due to a lack of published data, the phase behaviour of the remainder of the molecules with carbon dioxide will be measured in this work. Ideally, supercritical processes should operate just above the critical point of the solvent. In this region, small changes in temperature and/or pressure result in large changes in density. As solubility is a function of density, a small change in temperature and/or pressure can result in a large change in solubility. In addition, most of the interesting and important phase behaviour phenomena (temperature inversions, three phase regions, etc.) generally occur near the critical temperature and it is in this region where thermodynamic modelling is most difficult and most likely to fail. From both a practical and thermodynamic point of view, the phase behaviour should thus be measured just above the critical temperature of the solvent. Carbon dioxide has a critical temperature of 304.1 K [2] and measurements will thus be conducted between 308 and 348 K (i.e. at reduced temperatures between 1.01 and 1.15) at intervals of 10 K.

\* Corresponding author. Tel.: +27 21 808 4488; fax: +27 21 808 2095.  
E-mail address: [jhk@sun.ac.za](mailto:jhk@sun.ac.za) (J.H. Knoetze).




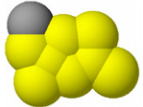
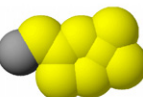
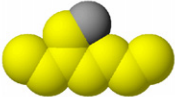

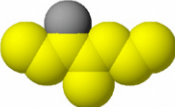
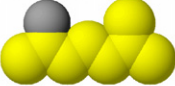
Compound	Molecular Structure	3D Representation
1-Octanol	$\text{OH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	
2-Octanol	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	
3-Octanol	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	
2,2,4-Trimethyl-1-Pentanol	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{OH}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	
2,4,4-Trimethyl-1-Pentanol	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{OH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	
2-Ethyl-1-Hexanol	$\begin{array}{c} \text{CH}_2-\text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	
2-Propyl-1-Pentanol	$\begin{array}{c} \text{CH}_2-\text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	
4-Methyl-3-Heptanol	$\begin{array}{c} \text{OH} \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	
6-Methyl-2-Heptanol	$\begin{array}{c} \text{OH} \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	

Fig. 1. Schematic representation of the molecules investigated in this study.

## 2. Experimental procedure, set-up and accuracy

A static synthetic method, using two previously constructed set-ups, each consisting of a variable volume high pressure view cell, was used to measure the solubility data. The view cells have been described in detail in previous publications [1,3] and are very similar, the main difference being the volume: 45 cm<sup>3</sup> [3] versus 80 cm<sup>3</sup> [1]. The view cells are used interchangeably and measurements can be conducted on either. Generally, higher alcohol concentration measurements were conducted on the small cell to limit the cost associated with the alcohol while lower alcohol concentration measurements were conducted in the large cell to ensure accurate determination of the mass fraction. Both view cells are able to operate between 300 and 460 K and up to 275 bar. The accuracy of the measurements conducted in the cell is the same and can be summarised as follows [1,3]:

- The uncertainty in the phase transition pressure is approximately 0.6 bar.

- 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.

Details pertaining to the experimental procedure as well as comparison with high quality data from other reputable research groups have been described in previous publications [1,3].

## 3. Materials

The suppliers, purity and catalogue numbers of the materials used are given in Table 1.

## 4. Experimental results

Due to variations in the ambient temperature it is not possible to measure all data isothermally. However, isothermal data is required for comparative purposes. Various techniques can be used

**Table 1**  
Materials used in this study.

Component	Purity	Supplier	Catalogue number
Carbon dioxide	99.95%	Afrox	340101
2,2,4-Trimethyl-1-pentanol	~95% <sup>a</sup>	Aldrich	S444049
2,4,4-Trimethyl-1-pentanol	98%	Aldrich	186678
2-Ethyl-1-hexanol	>99%	Fluka	04050
2-Propyl-1-pentanol	99%	Aldrich	277312
4-Methyl-3-heptanol	99%	Aldrich	M48171
6-Methyl-2-heptanol	99% +	Aldrich	48309

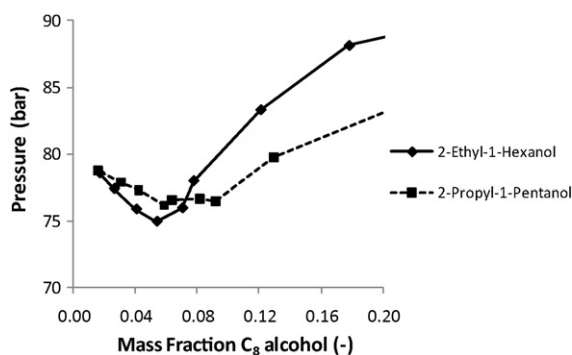
<sup>a</sup> Obtained from Sigma–Aldrich Library of Rare Chemicals. GC analyses estimates maximum impurities of 5%.

to obtain isothermal data. Previous studies [1,3–5] have shown that in many cases, within a limited temperature range, a linear relationship exists between the phase transition pressure and the temperature. However, this is not always true for carbon dioxide systems, as seen for 1-octanol in part I of this series [1]. Where the linear relationship does not hold true, previous studies have described the phase transition pressure as a second or third degree polynomial expression in temperature [1,6]. These relationships work well within the temperature range studied, yet importantly, irrespective of their form should not be extrapolated beyond their range of application. In this paper, where possible, the relationship between the phase transition pressure and temperature was described with a linear expression. Should the  $R^2$  value of the linear fit be smaller than 0.95, a second degree polynomial was used.

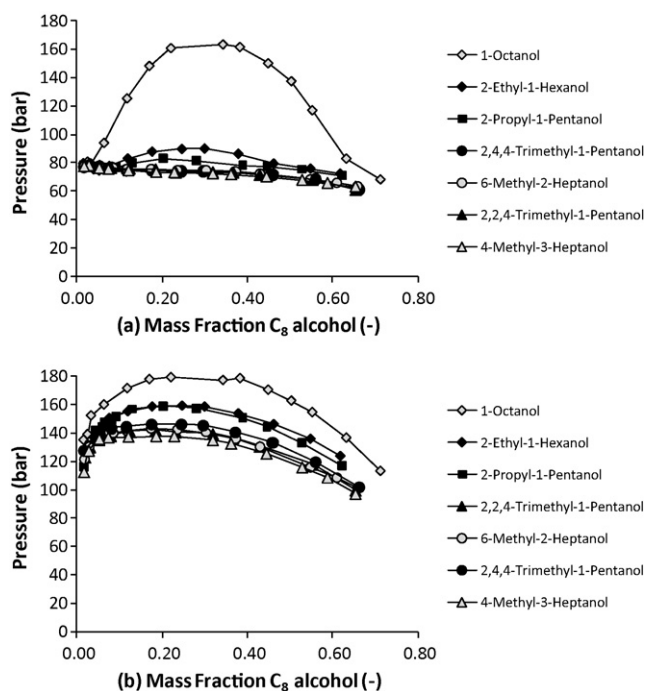
The parameters for the pressure–temperature relationships as well as the values of the phase transition pressures at three temperatures (308, 328 and 348 K) are given in Table 2 through Table 7. The pressure–temperature relationships describe the phase behaviour with an average  $R^2$  value of 0.995 with only five mass fractions having an  $R^2$  value less than 0.98.

## 5. Discussion of results

Throughout the entire range of experimental measurements, for all systems measured in this work, an increase in temperature leads to an increase in phase transition pressure with no observed temperature inversions. The phase behaviour also does not hint towards temperature inversions close to the measured temperature range. However, for the systems 2-ethyl-1-hexanol and 2-propyl-1-pentanol in carbon dioxide there are strong indications for the existence of a three phase region at low temperatures. This can be seen if one considers the data for these systems at 308 K for mass fractions below approximately 0.20, as shown in Fig. 2. Although no three phase points were observed, the existence of a minimum indicates the potential occurrence thereof. In



**Fig. 2.** Low mass fraction detail of phase transition pressure as a function of mass fraction at 308 K for the systems 2-ethyl-1-hexanol and 2-propyl-1-pentanol in carbon dioxide.



**Fig. 3.** Comparison of the phase behaviour of the measured  $C_8$  alcohols including 1-octanol [1] in carbon dioxide at (a) 308 K and (b) 348 K.

addition, between alcohol mass fractions of approximately 0.05 and the mixture critical point, dew point measurements were observed. At alcohol mass fractions below 0.05 bubble point measurements were observed, similar to those at very high mass fractions. This region of dew point data between regions of bubble point data, together with the observed minima, indicates the possibility of a three phase region at an alcohol mass fraction of  $\pm 0.05$ . Using the pressure–temperature correlations for the phase behaviour it can be estimated that for 2-ethyl-1-hexanol three phase behaviour occurs up to a temperature of  $\pm 313$  K and for 2-propyl-1-pentanol up to  $\pm 310$  K. Three phase regions are not uncommon in phase behaviour near the critical point of the solvent and have been observed in the carbon dioxide – 1-alcohol homologous series [7] as well as other homologous series [8–11] and their existence may provide insight as to the type of phase behaviour present. However, for all the systems studied, insufficient information is available to allow for complete classification according to van Konynenburg and Scott [12] and additional measurements nearer to and below the critical region are required.

The aim of this article is to determine the influence of side branching on the phase behaviour of alcohols in supercritical carbon dioxide. A comparison of the various  $C_8$  alcohols studied, together with 1-octanol as reference, at 308 and 348 K is given in Fig. 3. As seen, the structural isomers behave differently with the changes more pronounced at higher temperatures. The following sequence of increasing phase transition pressure is observed (It should be noted that very little difference exists between 2,2,4-trimethyl-1-pentanol and 6-methyl-2-heptanol):

- 4-methyl-3-heptanol < 2, 2, 4-trimethyl-1-pentanol  
 < 6-methyl-2-heptanol  
 < 2, 4, 4-trimethyl-1-pentanol  
 < 2-propyl-1-pentanol  
 < 2-ethyl-1-hexanol < 1-octanol

**Table 2**

Experimental bubble- and dew point pressures for 2,2,4-trimethyl-1-pentanol in carbon dioxide.

Mass fraction 2,2,4-trimethyl-1-pentanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.655	–	0.9632	–235.63	0.999	61.0	80.3	99.6
0.554	–	1.247	–315.87	0.999	68.1	93.0	118.0
0.429	–	1.480	–384.30	1.000	71.5	101.1	130.7
0.368	–	1.591	–417.07	1.000	73.0	104.9	136.7
0.319	–	1.659	–437.70	1.000	73.3	106.5	139.7
0.233	–	1.696	–449.47	0.999	73.0	106.9	140.8
0.185	–	1.676	–441.00	0.999	75.3	108.8	142.4
0.124	–	1.644	–430.50	0.999	75.9	108.8	141.6
0.0799	–	1.541	–398.38	0.998	76.4	107.2	138.0
0.0526	–	1.435	–364.18	0.997	77.8	106.5	135.2
0.0308	–	1.282	–315.93	0.991	78.9	104.6	130.2
0.0194	–0.01143	8.635	–1497.89	0.998	77.5	104.8	123.0

**Table 3**

Experimental bubble- and dew point pressures for 2,4,4-trimethyl-1-pentanol in carbon dioxide.

Mass fraction 2,4,4-trimethyl-1-pentanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.660	–	1.019	–252.52	0.999	61.3	81.7	102.1
0.558	–	1.278	–324.97	1.000	68.6	94.1	119.7
0.459	–	1.539	–402.54	0.999	71.5	102.3	133.1
0.372	–	1.679	–443.54	1.000	73.6	107.2	140.8
0.297	–	1.783	–475.10	0.998	74.1	109.8	145.4
0.245	–	1.803	–481.24	0.999	74.0	110.1	146.1
0.176	–	1.783	–474.64	0.999	74.7	110.3	146.0
0.116	–	1.740	–461.23	0.997	74.7	109.5	144.3
0.0819	–	1.670	–437.88	0.996	76.5	109.9	143.3
0.0539	–	1.555	–401.72	0.996	77.3	108.4	139.5
0.0185	–0.01253	9.488	–1656.18	0.998	77.2	107.6	127.9

**Table 4**

Experimental bubble- and dew point pressures for 2-ethyl-1-hexanol in carbon dioxide.

Mass fraction 2-ethyl-1-hexanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.619	–	1.276	–320.37	0.999	72.7	98.2	123.8
0.549	–	1.494	–383.78	0.998	76.3	106.2	136.1
0.463	–	1.670	–434.72	0.996	79.8	113.2	146.6
0.380	–	1.691	–434.21	0.999	86.6	120.4	154.3
0.301	–	1.718	–438.70	0.999	90.3	124.7	159.0
0.248	–	1.743	–446.75	0.998	90.0	124.8	159.7
0.178	–	1.772	–457.66	0.997	88.2	123.6	159.0
0.121	–	1.806	–473.01	0.995	83.3	119.5	155.6
0.0777	–0.01101	9.046	–1663.75	1.000	78.0	118.9	150.9
0.0704	–0.01390	10.88	–1958.02	1.000	76.0	116.9	146.7
0.0540	–0.01160	9.252	–1673.96	0.997	75.0	112.4	140.6
0.0407	–0.01773	13.16	–2296.83	0.998	75.9	113.7	137.2
0.0265	–0.01532	11.37	–1971.16	0.999	77.4	109.9	130.2
0.0170	–0.01287	9.657	–1674.41	0.993	78.6	107.9	127.0

**Table 5**

Experimental bubble- and dew point pressures for 2-Propyl-1-Pentanol in Carbon Dioxide.

Mass fraction 2-propyl-1-pentanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.623	–	1.146	–281.89	0.998	71.0	93.9	116.9
0.529	–	1.439	–367.86	0.998	75.4	104.2	133.0
0.446	–	1.681	–440.39	0.999	77.5	111.1	144.7
0.389	–	1.807	–477.91	0.997	78.5	114.7	150.8
0.281	–	1.894	–501.58	0.996	81.8	119.6	157.5
0.202	–	1.901	–502.37	0.996	83.2	121.2	159.3
0.129	–	1.934	–515.96	0.995	79.7	118.4	157.1
0.0918	–0.01314	10.51	–1913.38	1.000	76.5	119.5	152.0
0.0819	–0.01122	9.165	–1681.80	1.000	76.7	117.2	148.8
0.0637	–0.01427	11.15	–2004.98	1.000	76.6	118.2	148.3
0.0587	–0.01227	9.763	–1766.43	0.999	76.2	115.3	144.7
0.0424	–0.01114	8.935	–1617.59	1.000	77.3	114.3	142.3
0.0308	–0.01050	8.232	–1461.62	1.000	77.9	109.0	131.7
0.0162	–0.01491	10.71	–1805.42	0.997	78.8	103.3	115.9

**Table 6**

Experimental bubble- and dew point pressures for 4-methyl-3-heptanol in carbon dioxide.

Mass fraction 4-methyl-3-heptanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.654	–	0.8575	–201.04	0.999	63.1	80.2	97.4
0.588	–	1.077	–265.93	1.000	65.7	87.2	108.7
0.529	–	1.198	–301.26	1.000	67.8	91.8	115.8
0.445	–	1.382	–355.41	1.000	70.2	97.8	125.4
0.362	–	1.517	–395.58	1.000	71.7	102.1	132.4
0.319	–	1.564	–409.53	1.000	72.3	103.6	134.8
0.228	–	1.609	–422.42	0.999	73.2	105.4	137.5
0.186	–	1.606	–421.28	0.999	73.4	105.5	137.6
0.121	–	1.564	–406.98	0.999	74.6	105.9	137.2
0.0737	–	1.528	–394.89	0.999	75.6	106.2	136.7
0.0524	–	1.488	–381.86	0.999	76.3	106.1	135.8
0.0278	–	1.229	–300.47	0.990	78.2	102.8	127.3
0.0166	–0.01393	10.01	–1685.81	0.997	77.5	100.6	112.6

**Table 7**

Experimental bubble- and dew point pressures for 6-methyl-2-heptanol in carbon dioxide.

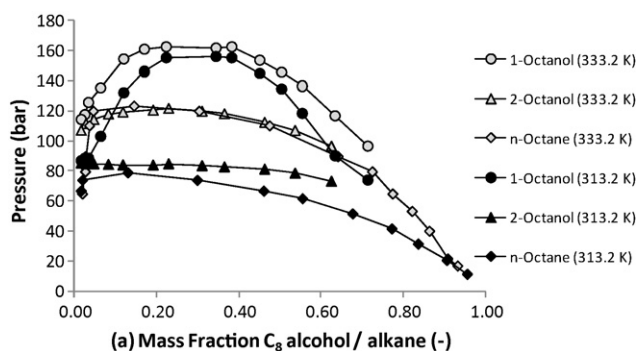
Mass fraction 6-methyl-2-heptanol	$P(\text{bar}) = A \times T^2 + B \times T + C$ (T in K for 308–348 K)				Pressure (bar)		
	A	B	C	$R^2$	308 K	328 K	348 K
0.658	–	0.9492	–228.94	0.999	63.4	82.4	101.4
0.608	–	1.058	–259.93	0.999	66.1	87.2	108.4
0.546	–	1.185	–296.58	0.999	68.3	92.0	115.7
0.430	–	1.453	–375.19	0.999	72.2	101.3	130.3
0.372	–	1.578	–412.68	1.000	73.4	105.0	136.5
0.303	–	1.665	–438.75	0.999	74.2	107.5	140.8
0.235	–	1.701	–449.47	0.999	74.5	108.6	142.6
0.175	–	1.704	–449.16	0.999	75.6	109.6	143.7
0.118	–	1.663	–436.97	0.998	75.2	108.5	141.7
0.0856	–	1.601	–417.05	0.998	76.0	108.1	140.1
0.0535	–	1.456	–371.12	0.994	77.2	106.3	135.4
0.0304	–	1.299	–321.64	0.990	78.5	104.5	130.5
0.0185	–0.01240	9.241	–1592.25	0.998	77.4	104.5	121.6

Since the molecular mass of all the components are identical, the difference in the phase equilibria must be due to a difference in the structure of the molecule, i.e. the position of the hydroxyl group, the presence and shielding effect of the side chains and the shape of the molecule. The effect of shielding of the hydroxyl group can be seen in Fig. 4. Here the phase behaviour of 1-octanol, 2-octanol [1] and n-octane [13] are compared. The hydroxyl group in 2-octanol is considerably more shielded than the hydroxyl group in 1-octanol and thus the phase behaviour of 2-octanol is much closer to that of n-octane. Similarly, with regard to the components studied in this paper, consider, for example, 4-methyl-3-heptanol and refer to the structure and three-dimensional representation, as shown in Fig. 1. Here the methyl group as well as the hydrocarbon backbone shield the hydroxyl group well and thus the molecule is not very polar compared to, for example, 1-octanol. Due to this lower polarity, as

a result of the shielding of the hydroxyl group, 4-methyl-3-heptanol is thus more soluble in carbon dioxide, which is non-polar. Similar arguments can be made for the other molecules with respect to one another, with the phase transition pressure increasing with increasing polarity of the molecules.

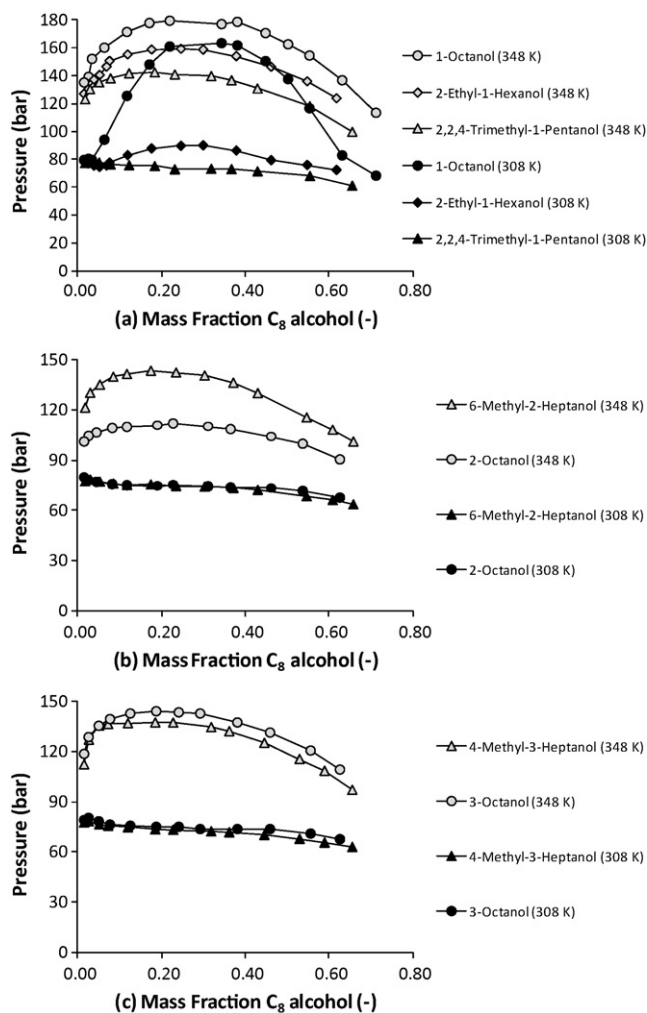
Schwarz et al. [14] studied the phase behaviour of long chain molecules with various functional end groups in supercritical propane and suggested a link between temperature and the functional group. They suggested that, as temperature increases, the repulsion forces between the polar functional groups and the non-polar solvent increase thus leading to an increase in the difference in polarity, which in turn results in an increase in phase transition pressure. The increase in repulsion forces is more pronounced for a larger difference in polarity. Similarly, with application to the systems studied here, as temperature increases, the polarity difference between the alcohol and the solvent increases, this increase being more pronounced the more polar a group is. The larger polarity difference at higher temperatures results in, as shown in Fig. 3, larger differences in phase behaviour. The only exception to this trend is that of 1-octanol, which displays a region of temperature inversion near the critical temperature of carbon dioxide.

The question now arises as to the magnitude of the influence the side groups have on the phase behaviour. Fig. 5 shows the effect of structural isomerisation. As seen in Fig. 5(a), the methyl groups of 2,2,4-trimethyl-1-pentanol and the ethyl group of 2-ethyl-1-hexanol have a significant effect on the phase behaviour. The three-dimensional representations in Fig. 1 show that these side groups shield the hydroxyl group and also change the shape of the molecule. 2,2,4-Trimethyl-1-pentanol is much more spherical and less polar than 1-octanol and the structural isomerisation results in a solubility increase to such an extent that the systems possibly exhibit different types of phase behaviour altogether.



**Fig. 4.** Effect of shielding of the hydroxyl group on the phase behaviour at 313.2 K (solids) and 333.2 K (grey fill)—comparison of 1-octanol [1], 2-octanol [1] and n-octane [13].

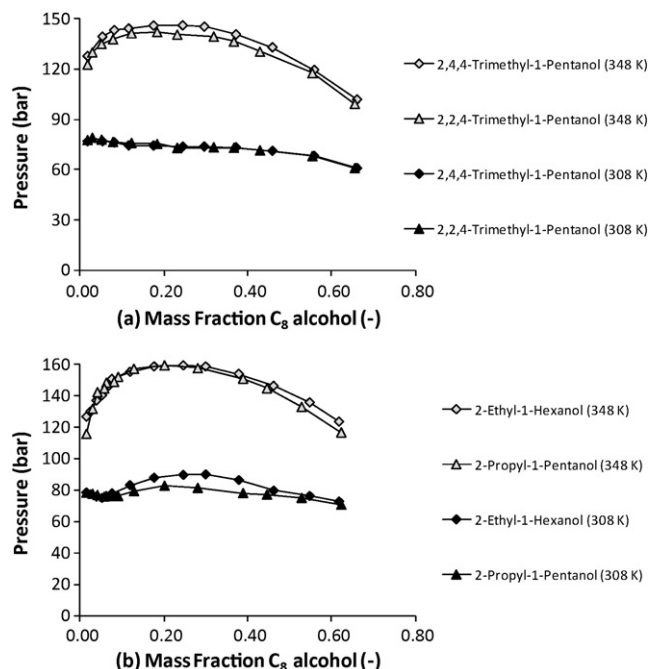




**Fig. 5.** Effect of side groups on the phase behaviour at 308 K (solids) and 348 K (grey fill): (a) 2,2,4-trimethyl-1-pentanol, 2-ethyl-1-hexanol and 1-octanol [1]; (b) 6-methyl-2-heptanol and 2-octanol [1]; (c) 4-methyl-3-heptanol and 3-octanol [1].

The methyl group isomerisation of 2-octanol and 3-octanol to 6-methyl-2-heptanol and 4-methyl-3-heptanol, as seen in Fig. 5(b) and (c), respectively, also has an influence. The result of the influence of the methyl group isomerisation is not as significant, possibly due to the fact that in both 2- and 3-octanol the hydroxyl group is already shielded and the main effect of the methyl group isomerisation is effectively a shortening of the hydrocarbon backbone.

Further it can be seen that even the change in position of a single functional group has an effect on the phase behaviour. This is evident when comparing 2,2,4-trimethyl-1-pentanol and 2,4,4-trimethyl-1-pentanol as well as 2-ethyl-1-hexanol and 2-propyl-1-pentanol, as seen in Fig. 6(a) and (b), respectively. As seen in Fig. 1, the difference in molecular structure between 2,2,4-trimethyl-1-pentanol and 2,4,4-trimethyl-1-pentanol is the position of 1 methyl group, which is in the 2 position in the former and in the 4 position in the later. The methyl groups in 2,2,4-trimethyl-1-pentanol thus shield the hydroxyl group better thus resulting in lower pressures required for total solubility. Similarly, consider the structures of 2-ethyl-1-hexanol and 2-propyl-1-pentanol, as illustrated in Fig. 1. The only difference in structure is that in 2-ethyl-1-hexanol the  $-CH_2-OH$  group is on the 3rd position of the 7 carbon chain while in 2-propyl-1-pentanol it is on the 4th position. The latter thus shields the hydroxyl group better thus resulting in lower phase transition pressures, as seen in

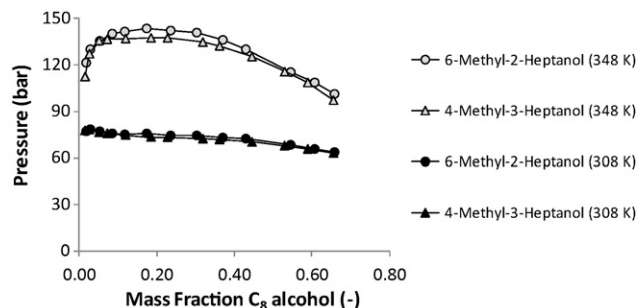


**Fig. 6.** Effect of position of the side groups on the phase behaviour at 308 K (solids) and 348 K (grey fill): (a) 2,2,4-trimethyl-1-pentanol and 2,4,4-trimethyl-1-pentanol; (b) 2-ethyl-1-hexanol and 2-propyl-1-pentanol.

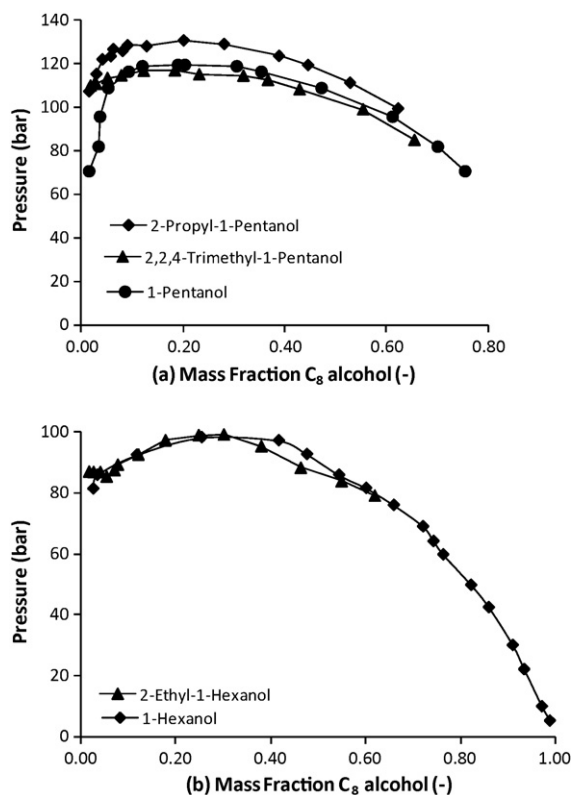
the observed measurements. However, similarities in the structure still ensure similar phase behaviour.

Fig. 7 shows the combined effect of changing the position of the hydroxyl group as well as the methyl group. In 4-methyl-3-heptanol the hydroxyl group is further away from the end of the molecule and the methyl group is closer to the hydroxyl group compared to 6-methyl-2-heptanol. Both changes result in increased shielding of the hydroxyl group and thus a reduction in the polarity of the molecule. This, in turn, results in an increase in the solubility and thus the lower observed phase transition pressures.

The measurements conducted in this study indicate that the type and quantity of the side branching in a molecule influence the phase equilibria. So far this study has been conducted without any variation in the molecular mass, to eliminate the effect thereof. It is well known that an increase in the number of atoms, specifically the number of carbon atoms, leads to an increase in the phase transition pressure [15] and now one should question whether the addition of a side branch, which increases the solubility by increasing the shielding of the hydroxyl group, is able to counteract the additional atoms present. Fig. 8(a) compares 2,2,4-trimethyl-1-pentanol and 2-propyl-1-pentanol with 1-pentanol [16], all with a hydrocarbon backbone of 5 carbon atoms. The



**Fig. 7.** Combined effect of side groups and hydroxyl position on the phase behaviour at 308 K (solids) and 348 K (grey fill).



**Fig. 8.** Effect of the addition of a side branch to a primary alcohol: (a) 2,2,4-trimethyl-1-pentanol, 2-propyl-1-pentanol and 1-pentanol [15] at 333.08 K and (b) 2-ethyl-1-hexanol and 1-hexanol [16] at 313.15 K.

methyl groups in 2,2,4-trimethyl-1-pentanol shield the hydroxyl group to such an extent that the shielding more than counteracts the effect of the additional atoms present thus leading to lower solubility pressures. However, the shielding effect of the propyl group in 2-propyl-1-pentanol is insufficient to counteract the added atoms. A comparison of 2-ethyl-1-hexanol and 1-hexanol [17] is shown in Fig. 8(b). Both the alcohols have a hydrocarbon backbone of 6 carbon atoms and, as seen, in this case the two effects basically counteract one another. The shielding of the hydroxyl group with the ethyl side chain in 2-ethyl-1-hexanol thus compensates for the additional atoms present and thus the solubility of 2-ethyl-1-hexanol is similar to that of 1-hexanol. The comparisons shown in Fig. 8(a) and (b) were conducted at 333.08 and 313.15 K, respectively, and comparisons at other temperatures may result in different trends. However, one can conclude that the addition of side branches, especially near the hydroxyl group, is able to compensate, either wholly or in part, for an increase in the number of atoms present, the exact magnitude thereof depending on the systems and temperatures being investigated.

## 6. Conclusions and further work

Phase equilibrium measurements in supercritical carbon dioxide for a range of C<sub>8</sub> alcohols with varying degrees of side branching and positions of the hydroxyl group have been performed at temperatures from 308 to 348 K. No temperature inversions were observed and only the systems 2-ethyl-1-hexanol and 2-propyl-1-pentanol indicated the possible presence of a three phase region at temperatures below  $\pm 313$  K and  $\pm 310$  K, respectively. The phase equilibrium measurements indicate that the degree and position of side branching has a significant effect on the phase behaviour, with

the phase transition pressure increasing in the following sequence:

4-methyl-3-heptanol < 2, 2, 4-trimethyl-1-pentanol  
 < 6-methyl-2-heptanol < 2, 4, 4-trimethyl-1-pentanol  
 < 2-propyl-1-pentanol < 2-ethyl-1-hexanol < 1-octanol

The side chains change the shape of the molecule and assist in shielding of the hydroxyl group. The shielding in turn decreases the polarity, which decreases the asymmetry of the system. The more symmetric the system, the lower the pressure required for total solubility.

This work has assessed the influence of side branching on the phase behaviour of C<sub>8</sub> alcohols in supercritical carbon dioxide in the mixture critical region and complements a previous paper on the influence of the position of the hydroxyl group, also on C<sub>8</sub> alcohols in supercritical carbon dioxide. However, to date the study has concentrated on the mixture critical region for practical and thermodynamic reasons and other parts of the phase envelope should also be investigated. It is recommended that in the future, data should be measured for these systems at other temperatures and pressures. This will complement data presented in this paper and may assist in classification of the type of phase behaviour present. Future work should also include an investigation of the position and effect of side branching in different supercritical solvents (e.g. ethane and propane) as well as an investigation of the effect of the size of the hydrocarbon backbone.

In addition, to complement experimental work, thermodynamic modelling needs to be conducted. Thermodynamic modelling may shed light on the exact effect of the side groups, position of the hydroxyl group and hydrocarbon backbone length and ultimately assist in predicting the phase behaviour. State of the art equations of state, such as SAFT, have versions that may account for branching in molecules (e.g. the Banaszak et al. [18] version of SAFT) and such an equation of state may provide insight as to the effects at play in the systems discussed in this work. However, these versions are new and have generally not been implemented into process simulators and other readily available phase equilibria software. Future work may also include simulation studies with these type of equations of state.

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