J. of Supercritical Fluids 47 (2008) 161–167

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Phase equilibria of alcohols in supercritical fluids
Part I. The effect of the position of the hydroxyl group for linear C_8 alcohols in supercritical carbon dioxide

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

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

ARTICLE INFO

Article history:
Received 1 February 2008
Received in revised form 26 June 2008
Accepted 1 July 2008

Keywords:
Hydroxyl
Alcohol
Solubility
Supercritical
Carbon dioxide
Octanol

ABSTRACT

The ability to model and predict the behaviour of high-pressure alcohol and carbon dioxide mixtures is important for industrial purposes. The phase equilibria behaviour of four 8-carbon alcohols in supercritical carbon dioxide are measured to determine the effect of the hydroxyl group position on alcohol solubility. Experimental bubble- and dew point data are generated on a high pressure phase equilibrium cell for the systems 1-octanol, 2-octanol, 3-octanol and 4-octanol in supercritical carbon dioxide between 35 °C and 75 °C. 1-Octanol is shown to be the least soluble and, at 35 °C, exhibits a phase transition pressure 85 bar higher than that of 2-octanol. 1-Octanol also exhibits a temperature inversion near the critical temperature of carbon dioxide in the mixture critical region. 2-Octanol possesses marginally higher phase transition pressures than 3-octanol which, in turn, possesses marginally higher phase transition pressures than 4-octanol. This difference in phase equilibria is believed to result from a difference in polarity. Shifting the hydroxyl group from the first to the second carbon atom causes a large decrease in polarity and increase in solubility. Further movements toward the molecule centre result in progressively smaller polarity reductions and solubility increases, producing phase boundaries that coincide or differ minimally.

1. Introduction

The use of supercritical fluids in the petroleum, oil and natural gas industries is enjoying ever increasing popularity as a medium for extraction and chromatography processes [1]. Supercritical mixtures of carbon dioxide and alcohols are often encountered in these industries and, as such, these mixtures have been and will be studied extensively in years to come [1–17]. Given the intricate nature of molecular interactions in supercritical mixtures, experimental work forms an integral part of these studies. The bubble-, critical- and dew point data generated from these experiments enable the design and operation of separation equipment and processes. In addition, thermodynamic modelling applied to these data can be used to predict behavioural patterns in different, yet similar and related mixtures.

It has been shown that the hydroxyl group of a primary alcohol reduces solute solubility relative to the corresponding alkane due to an increase in polarity [18]. Barring a few studies on 2-alcohols, limited work has been done on systems containing a non-terminal alcohol and carbon dioxide. As such, limited knowledge concerning the effect of the hydroxyl group position exists. This study aims to address this shortcoming in determining the effect of the hydroxyl group position on alcohol solubility in supercritical carbon dioxide.

The alcohol of choice, octanol, is chosen for a number of reasons. Firstly, the existence of 3- and 4-substituted isomers allows sufficient differentiation to enable the detection of a definite pattern (refer to Fig. 1). The low vapour pressures of octanols at ambient conditions ensure a small uncertainty in octanol mass during the loading procedure. Moreover, 3-octanol and 4-octanol are among few 3- and 4-substituted alcohols commercially available in significant quantities (20 g) at sufficient purity (>97%). The existence of 1-octanol data for validation purposes, the scarcity of 2-octanol data as well as the lack of any 3-octanol or 4-octanol data confirms the choice of solute. CO_2 is selected because total solubility of 1-octanol can be achieved below 200 bar at 75 °C [11].

The phase equilibria behaviour of 1-octanol, 2-octanol, 3-octanol and 4-octanol in supercritical carbon dioxide are measured in a high-pressure, piston-cylinder equilibrium cell of the static type. Experiments are conducted at temperatures of 35, 45, 55, 65 and 75 °C and solute mass fractions ranging between 0.017 and 0.712.

---

* Corresponding author. Tel.: +27 21 8084488; fax: +27 21 8082059.
E-mail address: jhk@sun.ac.za (J.H. Knoetze).

0896-8446/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2008.07.001

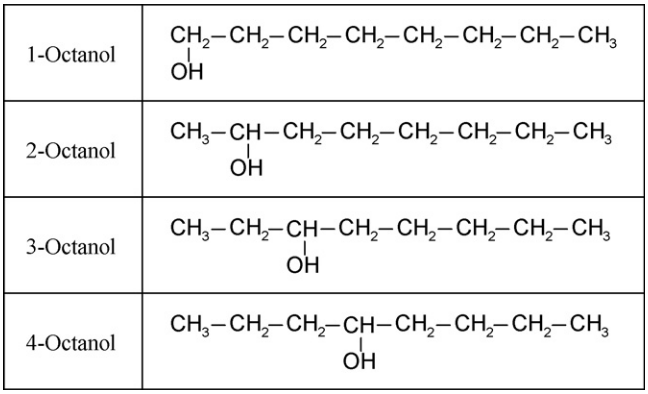

Fig. 1. Difference in hydroxyl group position between the four straight-chain C_8 alcohols.

2. Published data

The effects of different functional groups on the solubility of a molecule in a supercritical solvent have been studied previously. The work by Schwarz et al. [19], Weng and Lee [4,20] as well as Schwarz et al. [21] indicate that the addition of a primary hydroxyl group reduces solute solubility relative to the alkane. To date, however, little comparative research has been conducted to determine the effect of the position of a functional group on the solubility of a molecule. This is also the case for binary systems containing an alcohol and CO_2.

Studies on the phase equilibria behaviour of 1-propanol and 2-propanol in CO_2 have been conducted by Elizalde-Solis et al. [16], Secuianu et al. [13] and Suzuki et al. [22]. In addition, Byun and Kwak [11], Secuianu et al. [1] and Chen et al. [12] have conducted studies on the phase equilibria behaviour of 1-butanol and 2-butanol in CO_2. Owing to the relatively small difference in hydroxyl group position between these 1- and 2-substituted alcohols, results could not provide an unambiguous understanding of the effect of the hydroxyl group.

The phase equilibria behaviour of 1-octanol in CO_2 has been studied by Lam et al. [3], Weng and Lee [4], Lee and Chen [5], Weng et al. [6], Chiehming et al. [10] and Byun and Kwak [11]. Selected data from these studies enable the validation of the newly generated experimental results. Gamse and Marr [23] published phase equilibria data for the 2-octanol-CO_2 binary system but without any accompanying 1-octanol data, thus, negating the possibility of a direct comparison.

In conclusion, the phase equilibria behaviour of alcohols in CO_2 is important for industrial applications and yet, insufficient data are available to determine the positional effect of the hydroxyl group. This study provides the necessary data to achieve this objective and is therefore justified.

3. Materials and methods

3.1. Apparatus and experimental procedure

A variable volume, high-pressure phase equilibrium cell of the static type, with a maximum operating temperature and pressure of 200 °C and 275 bar, respectively, is used to conduct all experiments. This newly constructed equipment is similar in design to the device used by Schwarz and Nieuwoudt [24], but for an increase in internal volume to 80 cm^3. The larger volume allows for increased accuracy of the composition, especially in the high solvent mass fraction region (>95%). In addition, a Unitemp Testo 720 thermometer with an accuracy of ±0.2 °C and resolution of 0.1 °C, a ONEhalf20 Melt pressure transducer with an accuracy of 0.5% over the measurable range of 0 to 350 bar, a Precisa 3100C balance with a readability of 0.01 g and an Ohaus Precision Plus TP200S balance with a readability of 0.001 g are utilised.

The experimental procedure, which incorporates loading the cell, the measurement procedure itself as well as unloading and cleaning the cell, is explained in detail in Schwarz and Nieuwoudt [24], and Schwarz [25]. In brief, this process can be described as follows: a measured quantity of octanol is loaded into the cell. The cell is then rid of air by means of the vacuum pump and flushed with CO_2. These procedures are repeated four and six times respectively, after which a measured quantity of CO_2 is transferred to the cell. The cell is heated to the first of five temperatures and pressurised into the single-phase region. Pressurisation is achieved by means of nitrogen backpressure and is based on the concept of pressure intensification. While gradually reducing the pressure at constant temperature, the phase transitions are visually observed through a sight glass by means of an optical sensor, light source and monitor. This process is repeated until the pressure at phase transition is determined to within 0.2 bar. Thereafter, the content is once again pressurised into the single-phase region and the procedure repeated at each of the remaining four temperatures. During unloading, care is taken to recover as much of the octanol as possible while cleaning is performed with xylene, cyclohexanol and methanol. If one considers CO_2 impurities to be negligible, the amount of octanol recovered has no effect on the accuracy of subsequent measurements.

3.2. Accuracy of measurements

The accuracy of the measurement procedure has been shown by Schwarz and Nieuwoudt [24] and Schwarz [25] to be as follows:

- The uncertainty in the phase transition pressure is approximately 0.2 bar.
- The accuracy of the temperature measurement is better than 0.2 °C.
- The maximum error in mass fraction is estimated to be approximately 1% of the value.

However, the larger volume of the new high-pressure cell increases the possibility of significant solute losses during the loading procedure. As a result, the following analyses are performed:

The vapour pressure of 1-octanol at the maximum loading temperature of 25 °C is approximately 14 Pa [26–31]. Given the maximum cell volume of $7.9 \times 10^{-5}\,m^3$, the maximum mass of gaseous octanol contained in the cell is estimated to be 5.9×10^{-5} g. Since the minimum mass of 1-octanol added is 0.273 g, 10 octanol extractions (four vacuum extractions and six CO_2 flush operations) translate to a maximum loss in 1-octanol of 0.2%. The losses in 2-octanol, with a vapour pressure of 30 Pa at 25 °C [32–34], can also be shown to be negligible. Even though 3-octanol and 4-octanol display marginal increases in volatility (normal boiling points between 174 and 176 °C compared to 179 °C for 2-octanol), similar results are expected for these species.

3.3. Materials

The materials used in this study, as well as their respective purities, suppliers and catalogue numbers are given in Table 1. Shown in Fig. 1 are the molecular structures of each of the four straight chain C_8 alcohols clearly indicating the different hydroxyl group positions. Moving the hydroxyl group toward the molecule centre increases the shielding it experiences. This reduces the polarity of said molecule resulting in the follow-