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Super- and near-critical fluid phase behavior and phenomena of the ternary system CO_2 + 1-decanol + *n*-tetradecane

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ABSTRACT

High-pressure phase behavior of six 1-decanol + *n*-tetradecane (solute + solute) mixtures in the presence of near- and supercritical CO_2 (solvent) were experimentally studied between $T = 300$ K and $T = 358$ K using a visual static synthetic method. CO_2 free or reduced *n*-tetradecane mass fractions (w_c^{red}) of 0.2405, 0.5000, 0.6399, 0.7698, 0.8162 and 0.9200 g.g^{-1} were selected for the mixtures and the solute (i.e. combined 1-decanol + *n*-tetradecane) mass fractions (w_s) were varied between 0.015 g.g^{-1} and 0.65 g.g^{-1}. The ternary system displayed temperature inversions at $T = 308$ K and $T = 318$ K for the mixture $w_c^{red} = 0.2405$ g.g^{-1}. For all other w_c^{red} mixtures, an increase in temperature leads to an increase in pressure. A liquid-like (bubble-point) isotherm and a vapor-like (dew-point) isotherm were used to graphically define the size and range of isothermal cosolvency effects in the ternary system. The data were used to construct ternary phase diagrams from which cosolvency effects were observed for each set temperature. The large occurrence of cosolvency lead to the penetration of the liquid-liquid-gas (l_1l_2g) three-phase surface, forming a two-phase liquid-gas (l-g) hole between $w_c^{red} = 0.7698$ g.g^{-1} and $w_c^{red} = 0.9200$ g.g^{-1}. Closed isobaric miscibility windows were inferred for $w_c^{red} = 0.8162$ g.g^{-1} to classify the ternary system as Class T-IV phase behavior.

1. Introduction

The high-pressure phase behavior of numerous pure component and binary mixtures are characterized by the generation of critical points and lines. As such, binary systems have been widely studied over the last decades to find the optimum means of separation [1]. In contrast, to investigate ternary systems a composition-dependent surface must be generated. The properties of ternary mixtures are therefore much more intricate to characterize and less often considered due to its high demand in time, resources and general difficulty in measurement [1].

Ternary mixtures can be used as model systems for important industrial applications that make use of super- and near-critical fluid technology such as supercritical fluid fractionation (SFF) [2]. In SFF applications, the solutes usually consist of larger, much more complex molecules than the solvent. Complex multiphase equilibria can occur in these asymmetric mixtures, especially close to the critical point of the solvent [3]. The CO_2 + 1-decanol + *n*-tetradecane system is an important model system for the separation of detergent range alkanes and alcohols (solutes) using supercritical CO_2 (solvent). In this system the 1-alcohol has a lower boiling point than the *n*-alkane but at the same time the 1-alcohol is less soluble in CO_2 than the *n*-alkane. Interesting phenomena occur frequently in 1-alcohol + *n*-alkane systems within the temperature, pressure, and composition range of these technological processes [4]. With the correct insight into the phase behavior of multicomponent systems the phenomena can be understood, applied and controlled in the design of separation processes.

The three-phase liquid-liquid-gas (l_1l_2g) surface of several CO_2 + hydrocarbon systems contain a two-phase liquid-gas (l-g) hole that is completely surrounded by a closed-loop, critical endpoint (CEP) locus [5]. The CEP locus is formed when two liquid phases are critical in the presence of a gaseous phase ($l_1 = l_2 + g$). According to Scheidgen and Schneider [2], the physical origin of the l-g hole has to be ascribed to cosolvency effects. The phenomenon indicates that a mixture of two solute components B and C in a supercritical solvent A, (i.e. $A + B + C$), will have a lower solubility pressure than when mixed individually in A, (i.e. $A + B \text{ or } A + C$) [2]. Ternary systems exhibiting both cosolvency effects and a l-g hole in the (l_1l_2g) three phase surface could indicate the presence of closed isobaric miscibility windows, defined as a homogenous one-phase region that is completely surrounded by a two-phase region [2].

Van Konynenburg and Scott [6] classified binary mixtures throughout the entire pressure-temperature-composition range.

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Luks and co-workers [7–10] used only the (l_1l_2g) three-phase behavior in binary systems of CO_2 and 1-alcohols or *n*-alkanes to formulate a mechanism to distinguish what type of fluid phase behavior can be expected. The binary systems CO_2 + 1-decanol and CO_2 + *n*-tetradecane are reported as Type III fluids [9–11]. However, to date no equivalent classification scheme for ternary fluid mixtures has been established [12]. Bluma and Deiters [12] were able to develop a classification for ternary fluid mixtures that is based on the binary classification of Van Konynenburg and Scott [6] with the assumption of Berthelot-Lorentz combining rules for the binary interaction parameters. This assumption allows one to express all the parameters of one binary subsystems of a ternary mixture by those of the two others. For Types I and II the phase behavior of ternary mixtures has been shown to exhibit similar phenomena as that found in the constituent binary mixtures. However, the phenomena generated by ternary systems resulting from constituent Type III, IV, V, or VI binary systems will not necessarily exhibit similar phenomena observed for the respective binary mixtures and therefore completely different phase behaviors are to be expected [13]. Another classification scheme involves the use of the critical ‘points’ of a mixture [14,15]. For ternary systems the correct interpretation of phase diagrams is therefore of high importance.

The pressures of the critical loci of the two binary systems CO_2 + 1-decanol and CO_2 + *n*-tetradecane do not differ too much within the temperature range considered [12]. However, cosolvency has a strong influence on the multiphase behavior in the ternary system CO_2 + 1-decanol + *n*-tetradecane [3]. Patton et al. [5] first observed unexpected fluid multiphase behavior for the ternary system CO_2 + 1-decanol + *n*-tetradecane when they found a two-phase l-g hole in the (l_1l_2g) three phase surface. This phenomenon was later confirmed by extensive experimental investigations on related ternary systems comprising of CO_2 as the near critical solvent and 1-alcohols + *n*-alkanes as the two heavier solutes [16]. The systems were investigated in order to formulate a mechanism to distinguish what type of fluid three-phase behavior can be expected.

The current study was therefore initiated based on the two-phase l-g hole and a closed isobaric miscibility window in the ternary mixture CO_2 + 1-decanol + *n*-tetradecane, which will only occur as a result of cosolvency in the system [2]. Knowing the size and range of this phenomenon will help improve separation processes as a whole. The main aim of the present paper is to investigate the ternary system at near- and supercritical temperatures to evaluate the conditions at which cosolvency effects occur. Bubble- and dew-point pressure data at constant reduced *n*-tetradecane composition (w_c^{red}) are measured and interpreted. To date, no known study has been published containing p-T-w_c^{red} data at conditions where cosolvency will occur for the interested ternary system. Additionally, this paper aims to confirm the link to l-g holes and miscibility windows which have previously been observed.

2. Experimental

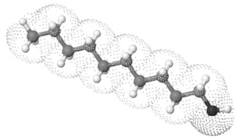
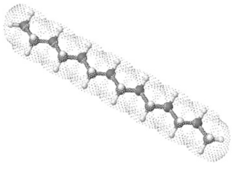
2.1. Chemicals

The chemicals used in this study are given in Table 1 along with their respective supplier and purity, as stated by the supplier. All chemicals were used without further purification.

2.2. Apparatus and procedure

Similar to Fourie et al. [17], a visual static synthetic method was used to measure the bubble- and dew-point data of the ternary mixture, including measurements in the mixture critical region.

Table 1
Specifications of chemicals used.

Chemical name	Chemical structure	Supplier	Mass fraction purity
1-decanol		Sigma-Aldrich	0.99
n-tetradecane		Sigma-Aldrich	>0.99
carbon dioxide		Air-products	>0.99

The solute mixtures (1-decanol + *n*-tetradecane) were premixed to ensure constant w_c^{red}. The components were loaded gravimetrically and the unit sealed and heated. A magnetic stirrer in the cell ensured uniform composition and temperature throughout the cell for the entire duration of the experiment. Once thermal equilibrium was reached the phase transition point was observed 3 to 4 times by noting the pressure at which a second phase formed until the phase transition pressure was repeatedly observed within the experimental limits.

The measurement uncertainties are as follows:

- The ONEhalf20 Melt pressure transducer was calibrated using a Barnet Instruments dead-weight tester to an accuracy of 0.02 MPa. The error in pressure measurement during visual observation of the phase transition point was no greater than ± 0.02 MPa. The standard uncertainty of the pressure measurement is thus no greater than 0.06 MPa, i.e. $u(p) = 0.06$ MPa, and includes all contributions towards the error in pressure measurements.
- Temperature was measured using a 4 wire Pt-100 probe, calibrated by Wika Instruments (Pty) Ltd in South Africa, with a maximum standard uncertainty of 0.1 K, i.e. $u(T) = 0.1$ K.
- Two calibrated analytical balances with precisions of 0.0001 g and 0.01 g were used to weigh the solutes (1-decanol, *n*-tetradecane) and solvent, respectively. The maximum standard uncertainties in the total solute mass fraction (w_s) is 0.01 times the value, i.e. $u(w_s) = 0.01 \cdot w_s$ g.g^{-1}.

A complete discussion of the experimental procedure is given by Schwarz and Nieuwoudt [18] and the experimental set-up has been verified several times in previous publications through comparisons of data to literature [17–19]. However, the equipment and measurement technique must be validated to ensure the credibility thereof. Reproducibility tests were conducted on the CO_2 + 1-decanol and CO_2 + *n*-tetradecane binary systems to validate the static synthetic visual view cell. Two loadings of very similar composition were measured for the binary systems and compared to literature data. The resultant data for each loading, pressure and temperature are shown in Table 2.

To validate the use of the experimental setup, the results from this work were compared to data published by other research groups. In Fig. 1(a) and (b) the 1-decanol system is compared to work conducted by Zamudio [20], Lee & Chen [21], Weng et al. [22], and Chang et al. [23]. In Fig. 2 the *n*-tetradecane system is compared to the work measured by Bonthuys [24], Gasem et al. [25] and Wang et al. [26].