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Phase equilibria of linear saturated high molecular mass acids in supercritical ethane

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ABSTRACT

High-pressure phase equilibria of the ethane/acid homologous series for linear saturated acids with between 10 and 22 carbon atoms are investigated. Measurements for ethane with decanoic, undecanoic, dodecanoic, tetradecanoic, hexadecanoic, octadecanoic and docosanoic acid were conducted between 308 and 353 K in the acid mass fraction range of 0.016–0.68. Higher phase transition pressures were measured at higher temperatures and no three-phase regions, or indications thereof, were observed. The measurements revealed that as the number of carbon atoms increased, so the phase transition pressure increased linearly, prompting the compilation of a set of linear pressure–carbon number plots. The observed phase transition pressures for the ethane/acid systems are also lower than that of the CO_2/acids systems, suggesting that ethane is an alternative supercritical solvent to or co-solvent with CO_2 for processes involving high molecular mass acids.

1. Introduction

Long chain acids (10 or more carbon atoms) and/or their triglycerides are found in a range of natural products such as palm oil, algae oil and fish oil [1]. Due to their ever-increasing value both as, amongst others, an alternative energy source and as food supplements purification of these oils is becoming increasingly important [2,3]. Due to their high melting and boiling points and low vapour pressures, traditional separation techniques such as distillation and crystallisation are very difficult, if not impossible to employ. While liquid organic solvent extraction can be applied, it is very difficult, if not impossible to remove the solvent residue to acceptable levels. Supercritical fluid processing is thus an alternative technique that can be used to separate or fractionate mixtures containing long chain fatty acids [4].

CO_2 is traditionally the supercritical solvent of choice as it is non-toxic and non-flammable. However, CO_2 is not a very good solvent for long chain acids. High-pressures (greater than 30 MPa) are required for total solubility of acids with 13 and more carbon atoms in supercritical CO_2 [5]. In order to increase the solubility and therefore reduce the phase transition pressure either an alternative supercritical solvent to or co-solvent with CO_2 can be used. Low molecular mass alkanes (mainly ethane and propane) are popular alternative supercritical solvents and can also be used as co-solvents. A previous study [6] has shown that propane is able to achieve total solubility at much lower pressures than CO_2 (less than 12 MPa at 408 K for docosanoic acid). However, while significantly lower phase transition pressures are attained, in order to optimally utilise the solvent behaviour around the critical point, temperatures in excess of 370 K are required. These higher temperatures (compared to 310–360 K for CO_2) result in high-energy costs as well as an increase in the degree of thermal degradation. On the other hand, ethane has a critical temperature close to that of CO_2 ($T_{c,\text{ethane}} = 305.12$ K vs $T_{c,CO_2} = 304.12$ [7]) yet due to the absence of the quadrupole present in CO_2, it is generally a better solvent for high molecular mass compounds with a long hydrocarbon chain (compare for example the ethane/n-alkane [8] and the CO_2/n-alkane [9] homologous series data of du Rand and Nieuwoudt). Ethane is thus a possible alternative solvent to or co-solvent with CO_2 for the processing of high molecular mass acids.

A literature survey showed that, to the best of our knowledge, no data has to date been published on the phase behaviour of the ethane/acid homologous series. The primary aim of this paper is to present measured data on the phase behaviour of selected systems of the ethane/acid homologous series for saturated acids with 10–22 carbon atoms. The results of phase transition measurements at temperatures between 308 and 353 K are presented for acid mass fractions between 0.016 and 0.68. Measurements were conducted at 15 K intervals in the aforementioned temperature range. Where the normal melting point of the acid is above 308 K the temperature range has been adjusted and the number of temperatures

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included in the measurements and/or the temperature intervals was reduced, provided a minimum of three temperatures were studied.

After presentation of the experimental results and discussion thereof, the phase behaviour of various functional groups in ethane as well as a comparison between the two solvents is included. Finally the article investigates whether the previously published hypothesis applicable to the propane/acids homologous series [6], where the phase behaviour of an acid mimics that of an n-alkane with double the number of carbon atoms, is also applicable to the ethane/acid homologous series.

2. Materials and methods

2.1. Experimental set-up

High-pressure phase transition (bubble/dew point) measurements were conducted using a static synthetic method. Two previously constructed set-ups, each consisting of a variable volume high-pressure view cell, were used to measure the phase equilibria data. These view cells have been described in detail in previous publications [10,11] and are very similar, the main difference being the volume: 45 cm^3 [10] versus 80 cm^3 [11]. The view cells are used interchangeably and measurements can be conducted on either. Generally, higher acid concentration measurements were conducted on the smaller cell to limit the cost associated with the acid and the ethane while lower acid concentration measurements were conducted in the larger cell to ensure accurate determination of the mass fraction. Both view cells are able to operate between 300 and 460 K and up to 28 MPa. In the small cell the pressure was measured with an Industrial Sensors Inc. pressure transducer and in the large cell with a ONEhalf20 pressure transducer. The pressure transducers are regularly calibrated in-house with a Barnett Industrial dead weight tester. In both cells the temperature was measured with a 4-wire PT100 thermocouple connected to a Testo 720 display. The thermocouples are calibrated by SANAS Calibration Lab regularly. The accuracy of the measurements in the cell was the same in both cell and can be summarised as follows [10,11]:

- The uncertainty in the phase transition pressure is approximately 0.1 MPa, i.e. $u(P) = 0.1$ MPa. This value is slightly higher than in previous works (approximately 0.06 MPa) but the measurements were complicated by a higher viscosity and surface tension of the compounds being investigated, thus decreasing the accuracy slightly.
- The accuracy of the temperature measurement is better than 0.2 K, i.e. $u(T) = 0.2$ K.
- It is estimated that the maximum error in the mass fraction is approximately 1% of the value i.e. $u(x) = 0.01x$, based on the accuracy of the balances used to measure the loaded compounds.

The experimental procedure can be summarised as follows: A known amount of the acid was loaded gravimetrically into the phase equilibrium cell, after which the cell was closed, evacuated and flushed with ethane. Liquid ethane was added quantitatively (gravimetrically) and the inlet valve securely closed. The cell was then heated to the required temperature using circulating heating fluid. Once the cell content reached thermal equilibrium, the pressure is increased until the cell content was in the single-phase region. The pressure was then slowly reduced until the transition point between the single and the two-phase region was observed and temperature and pressure were logged. The procedure was repeated at a number of temperatures. During the heating procedure, as well as while conducting the measurements, the cell contents were stirred with a magnetic stirrer to ensure proper mixing. Further 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 [10,11].

2.2. Materials used

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

3. Results

High-pressure phase transition measurements were conducted for decanoic, undecanoic, dodecanoic, tetradecanoic, hexadecanoic, octadecanoic and docosanoic acid with supercritical ethane in the temperature range 307.8–359.3 K for acid mass fractions of 0.0161–0.684. The experimental measurements can be seen in Tables 2–8.

For the entire composition and temperature range total miscibility was observed with phase transition pressures between 10.39 and 27.28 MPa. No temperature inversions or three-phase regions, or indications thereof, were observed in the composition and temperature range studied. Such phenomena may, however, be present beyond the experimental range studied.

Although the temperature remained constant throughout the experiment, not all data could be measured at exactly the same temperature, predominantly due to variations in the ambient conditions. Previous studies on the propane/acid [6], ethane/1-alcohol [12], ethane/methyl ester [13] and ethane/n-alkane [14] homologous series, amongst others, have shown that in most cases a linear expression can be used to describe the relationship between the temperature and the phase transition pressure at constant composition. Where such an expression does not suffice, a second or third order polynomial can be used. The same concept was applied to the systems studied here. A linear expression was regarded as acceptable should the error in pressure be smaller than 0.1 MPa and the R^2 value of the fit be larger than 0.98. In all cases where a linear fit did not suffice, a second order polynomial provided an acceptable fit (same constraints as for the linear fit). The expressions derived and the R^2 value of the fit have been included in Tables 2–8. In general, second order polynomials were used for systems with the lower molecular mass acids (dodecanoic acid and lower) while linear expressions sufficed for the higher molecular mass acid systems (tetradecanoic acid and higher).

4. Discussion

4.1. Pressure–composition relationship

Pressure–composition plots for the systems ethane/decanoic acid and ethane/tetradececanoic acid at 308, 323, 338 and 353 K are shown in Fig. 1(a) and (b), respectively. The data was generated using the pressure–temperature relationships given in Tables 2 and 5. The ethane/tetradecanoic acid system is not shown at 308 K as this temperature is below the normal melting point of tetradecanoic acid and outside the measurement and pressure–temperature correlation range. Similar plots can be compiled for the other systems studied.

In agreement with the experimental observations, an increase in temperature leads to an increase in phase transition pressure. By implication a higher pressure is required for total miscibility at higher temperatures. The maximum phase transition pressure is observed between approximately 0.2 and 0.4 mass fraction acid and thus indicates the presence of a critical line in this mass fraction range in the temperature range studied. Due to the flat nature