SOLUBILITY OF HIGH MOLECULAR MASS METHYL ESTERS IN SUPERCRITICAL ETHANE

C.E. Schwarz, M.L. Hahn, J.H. Knoetze*
Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa, *e-mail: jhk@sun.ac.za, Tel: +27 21 808 4488, Fax: +27 21 808 2059

Abstract

This paper presents trends in the high pressure solubility measurements of long chain saturated methyl esters (methyl decanoate, methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate, methyl octadecanoate and methyl docosanoate) in supercritical ethane between 313 K and 353 K and for mass fractions between 0.65 and 0.018. The data shows generally a linear relationship between the solubility pressure and the temperature with complete solubility below 17 MPa. No three phase regions or temperature inversions were observed while maxima in the solubility pressures were found for methyl ester mass fractions usually between 0.2 and 0.3. When the solubility pressure is plotted as a function of carbon number at constant temperature and mass fraction methyl ester, a linear relationship is realised. When the measured solubility of the methyl ester is compared to that of the corresponding alkane, all in supercritical ethane, it was found that the methyl ester requires higher pressures for total solubility. The difference between the solubility of the methyl ester and the alkane in supercritical ethane is larger than in supercritical propane.

Keywords

Methyl esters, ethane, supercritical, solubility, phase equilibrium

Introduction

Long chain aliphatic compounds with functional groups have attracted a lot of interest in recent years. These compounds, particularly fatty acids, occur in many natural oil products and are highly sought after. However, processing with traditional methods is difficult due to the low thermal stability and high boiling points of the long chain aliphatic compounds. Supercritical fluid extraction is an attractive alternative method for the fractionation of high molecular mass compounds. However, for high molecular mass saturated acids supercritical fluid extraction is not necessary realistic due to the low solubility of the acids [1-3] in supercritical solvents. In order to overcome the low solubility of high molecular mass fatty acids, these acids are often transesterfied to methyl or ethyl esters, which usually have a higher solubility than the corresponding acid and are thermally more stable.

A number of studies have been conducted on the solubility of long chain saturated acids [4] and their corresponding methyl [5,6] and ethyl esters [2,7] in supercritical carbon dioxide. The data shows total solubility of methyl and ethyl esters at moderate pressures while pressures in excess of 25 MPa are usually required for total solubility of the acids. Rovetto et al. [8] studied the solubility of methyl hexadecanoate (C16 hydrocarbon backbone) in sub- and supercritical propane and their results indicate that the solubility is considerably higher in propane than in carbon dioxide. However, the higher solubility of propane compared to carbon dioxide is often at the cost of selectivity and the use of higher operating temperatures. Ethane has been suggested as an alternative supercritical solvent to carbon dioxide for other processes. The critical temperature of ethane (305.4 K) is very similar to that of carbon dioxide (304.1 K) [9] and studies comparing supercritical ethane with carbon dioxide for the fractionation of paraffin wax [10] and separation of alkanes and alcohols [11] have indicated that ethane has similar if not superior selectivity while at the same time allowing for lower operating pressures. Ethane thus shows promise for the processing of products containing high molecular mass esters and acids yet no phase behaviour studies for any of these compounds in supercritical ethane have been published to date.

The aim of this paper is to investigate some of the aforementioned phase behaviour by considering the solubility of a range of methyl esters in supercritical ethane. The solubility of methyl esters between methyl decanoate (C10 hydrocarbon backbone) and methyl docosanoate (C22 hydrocarbon backbone) was measured at temperatures between 313 and 353 K ($T_r = 1.02$ to $T_r = 1.16$) for methyl ester mass fractions between 0.65 and 0.018.

Materials and Method

A static synthetic method, using two previously constructed setups, 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 [12,13] and are very similar, the main difference being the volume: 45 cm^3 [13] versus 80 cm^3 [12]. The view cells are used interchangeably and measurements can be conducted on either. Generally, higher methyl ester concentration measurements were conducted on the smaller cell to limit the cost associated with the methyl ester while lower methyl ester 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 27.5 MPa. The accuracy of the measurements in the cell are the same and can be summarised as follows [12,13]:

- The uncertainty in the phase transition pressure is approximately 0.06 MPa.
- 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.

A schematic representation of the experimental setup is shown in Figure 1.

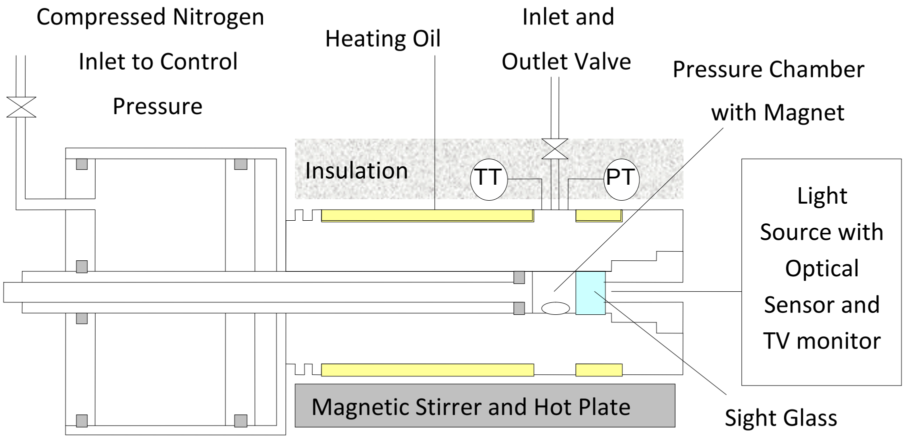
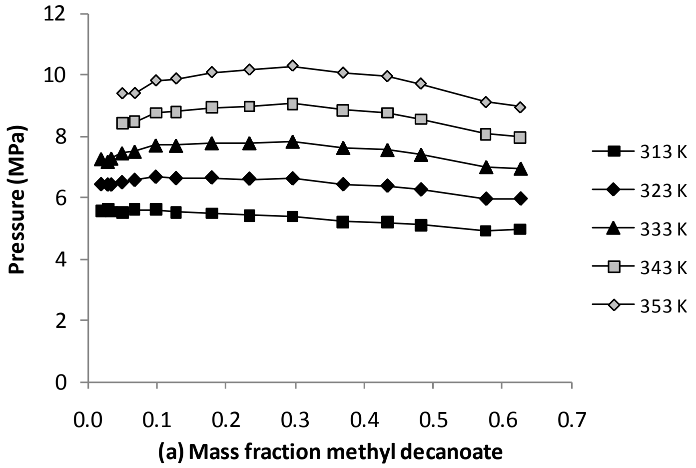


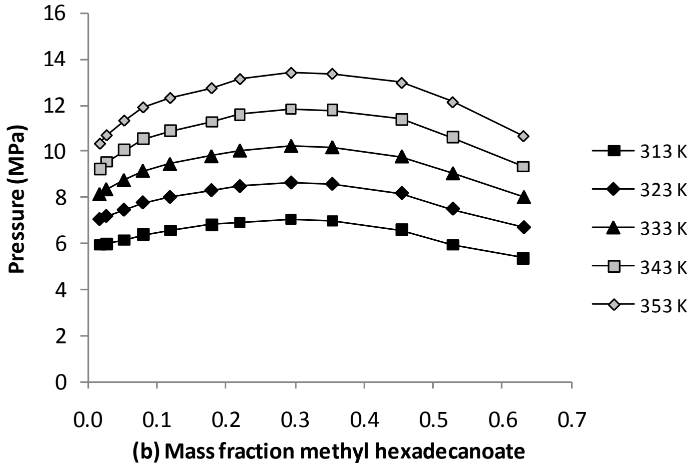
Figure 1: Schematic representation of the experimental setup

The experimental procedure can be summarised as follows: A known amount of the methyl ester is loaded into the phase equilibrium cell, after which the cell is closed, evacuated and flushed with ethane. Liquid ethane is then added quantitatively and the inlet valve is securely closed. The cell is now heated to the required temperature using circulating heating water and the cell contents is stirred with a magnetic stirrer to ensure proper mixing. Once the cell contents reaches thermal equilibrium the pressure is increased until the cell contents is in the one phase region. The pressure is now slowly reduced until the transition point between the one and the two phase region is observed and logged. The procedure is repeated at a number of temperatures. 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 [12,13].

Experimental Results

Solubility measurements were conducted for methyl decanoate (C10), methyl dodecanoate (C12), methyl tetradecanoate (C14), methyl hexadecanaote (C16), methyl octadecanoate (C18) and methyl docosanoate (C22) in supercritical ethane between 313 and 353 K. For low methyl decanoate mass fractions (< 0.05) no measurements were conducted above 338 K due to a steep pressure gradient / total solubility in this region. In addition, measurements for methyl docosaoate were only conducted above 326 K as methyl docosanoate is a solid below this temperature. Although the temperature is constant throughout the experiment, not all the data could be measured at exactly the same temperature due to variations in the ambient conditions and the fact that the temperature controller controls the heating fluid temperature, which in turn regulates the temperature of the cell contents. It is known that for these type of systems a linear relationship exists between the solubility pressure and the temperature [12,14,15] and this linear relationship can be used to interpolate between measurements to obtain isothermal data. The R^2 values of the linear pressure – temperature relationships (0.975 – 1.000) indicate that the assumption of the linear pressure – temperature relationships holds true in the desired temperature range. Figure 2 shows the phase behaviour for methyl decanoate, methyl hexadecanoate and methyl docosanoate in ethane at various temperatures between 313 and 353 K.





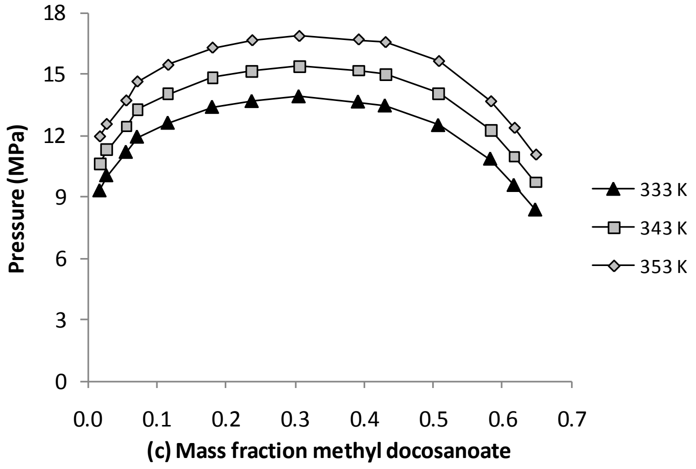
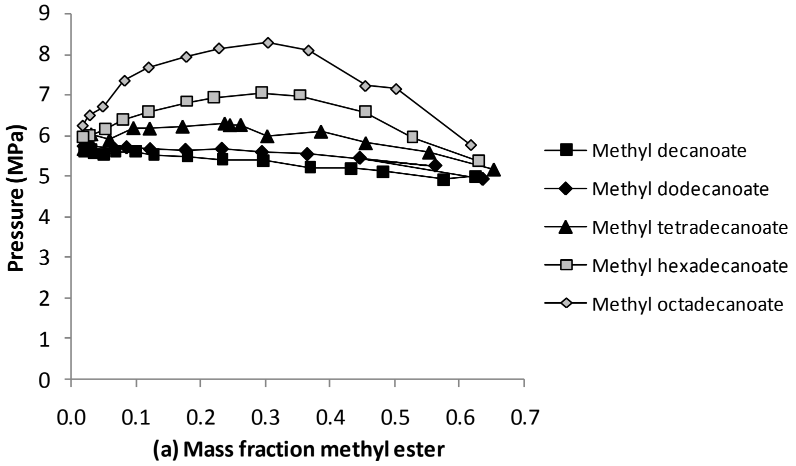
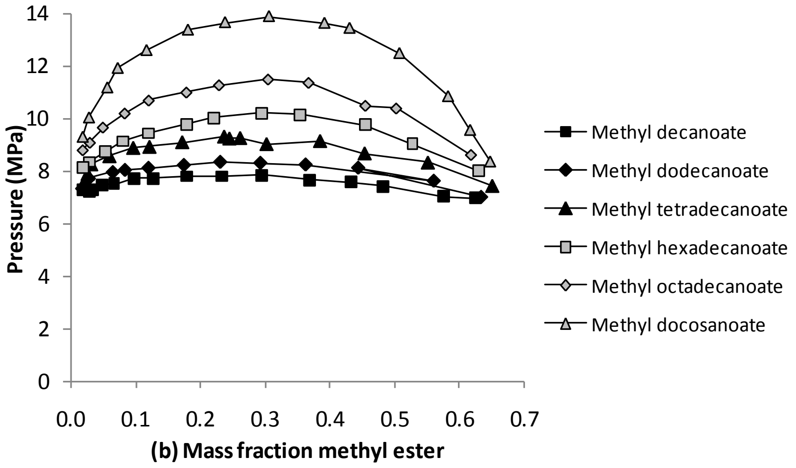


Figure 2: Phase behaviour of (a) Methyl decanoate, (b) Methyl hexadecanoate and (c) Methyl docosanoate in ethane at 313 to 353 K

The experimental measurements, as shown in Figure 2, indicated that in all cases an increase in temperature leads to an increase in the pressure required for solubility. No three phase regions or temperature inversions were observed and neither did the experimental measurements indicate the presence of either of these phenomena. A comparison of the solubility pressure for the various methyl esters in ethane at 313 K, 333 K and 353 K is given in Figure 3 (a), (b) and (c) respectively.





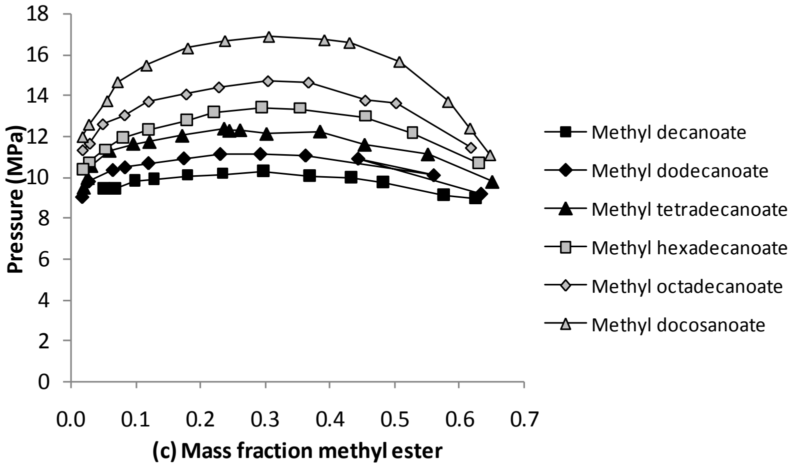


Figure 3: Comparison of phase transition pressure for various methyl-esters in ethane at (a) 313 K, (b) 333 K and (c) 353 K

As seen, an increase in the number of carbon atoms leads to an increase in the solubility pressure. This increase is more noticeable at higher temperatures: The difference between the solubility pressures of methyl decanoate and methyl octadecanoate at 313 K is approximately 2.6 MPa while the difference at 353 K is 4.4 MPa. It is also noted that a maximum exists for the solubility pressures. The maximum, or mixture critical point, is mostly between methyl ester mass fractions of 0.2 and 0.3, with lower mass fractions being observed at the lower temperatures and for lower carbon number homologues. Specifically, for methyl decanoate and methyl docosanoate the mixture critical points are at very low mass fractions at 313 K. The location and movement of the mixture critical point may assist in shedding light on the type of phase behaviour observed.

As no information is available for these systems in the literature, and due to a lack of data at very low mass fractions (below 1.5 mass % methyl ester) and below the critical temperature of ethane, there is insufficient information available for classification according to the method of van Konynenburg and Scott [16]. However, literature information can be used to obtain an indication of the type of phase behaviour. Systems of propane – 1-alcohols are widely regarded as being either type III, type IV or type V [14,18,19] and as the homologous series ethane – 1-alcohols is less symmetric than propane – 1-alcohols it is expected that they should also be type III, IV or V. At the same time the systems ethane – n-alkanes are generally type I for lower homologues and type V for higher homologues; the transition occurring at approximately octadecane (C18) [17]. From a comparative study of the solubility of compounds with various functional groups, all containing a hydrocarbon backbone of 14 carbon atoms, in supercritical propane [3] it is expected that the behaviour of methyl esters in supercritical ethane will be between that of n-alkanes and 1-alcohols. Indications are thus that the systems ethane – methyl esters are either type III, type IV or type V with the possibility of type I for the lower members. However, further experimental results are required before classification can be made with any surety.

Pressure – Carbon Number Relationship

Previous studies on the phase behaviour of alkanes in ethane [15] and propane [12,20] as well as 1-alcohols in propane [14] have shown that a linear relationship exists between the solubility pressure and the number of carbon atoms at constant mass fraction heavy component. The question now arises as to whether this relationship also holds true for methyl esters in ethane. Although it may seem as if this linear relationship may simply be arbitrarily applied, the concept is based on the idea of group contribution: The addition of a $–CH_2–$ group to an existing methyl ester results in, at the same temperature and mass fraction, the same increase in pressure, irrespective of whether it is added to a molecule with a hydrocarbon backbone of 10 or of 20 carbon atoms. Typical linear relationship plots are shown in Figure 4 (a) and (b) for mass fractions 0.100 and 0.350 respectively at various temperatures.

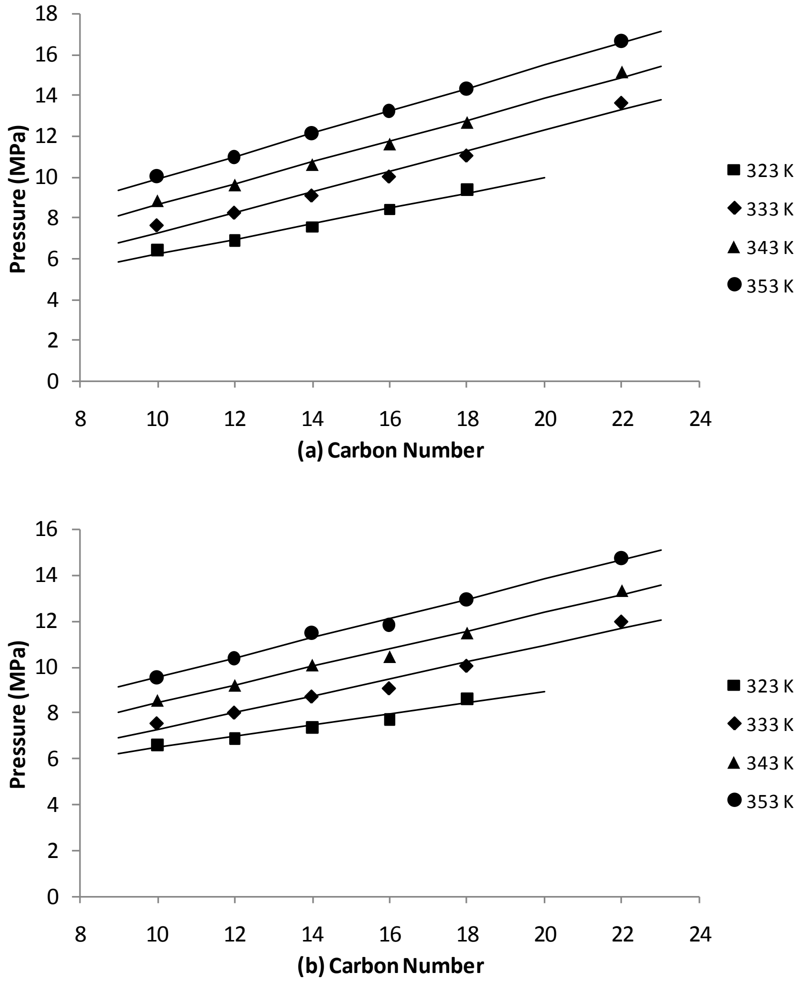
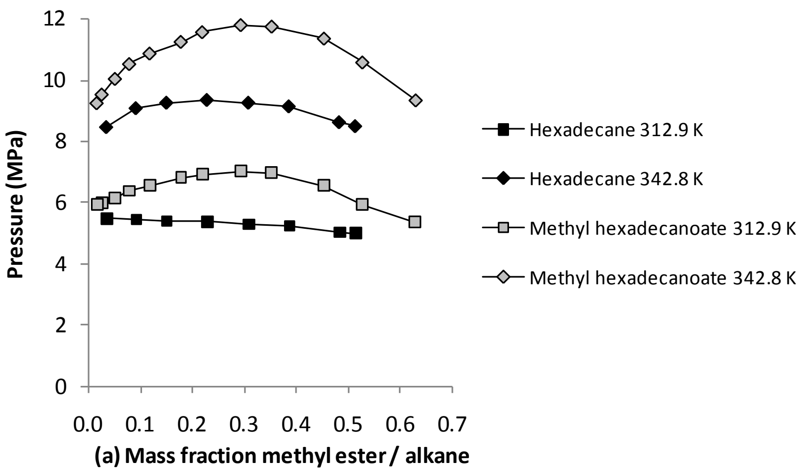


Figure 4: Pressure-carbon number plot at mass fraction at 323 K, 333 K, 343 K and 353 K for (a) x = 0.100 and (b) x = 0.350

Typically the linear relationships fit the data with an average R^2 value of 0.98 and the average absolute deviation is 0.14 MPa while the average absolute percentage deviation is 1.5 %. Schwarz et al. [21] showed that limited extrapolation of the data to higher and lower carbon numbers is possible yet this should be done with care, especially at high heavy component mass fractions. A different type of phase behaviour may be present and the larger the degree of extrapolation, the larger the potential error. The relationships can, however, be used for a good first order approximation of the phase behaviour for systems outside the range measured.

The effect of the methyl ester group

The effect of the methyl group is investigated by comparing the phase behaviour of a methyl ester with the corresponding alkane. Figure 5 (a) compares the phase behaviour of methyl hexadecanoate and n-hexadecane in ethane while Figure 3 (b) compares methyl tetredecanoate and n-tetradecane in propane.



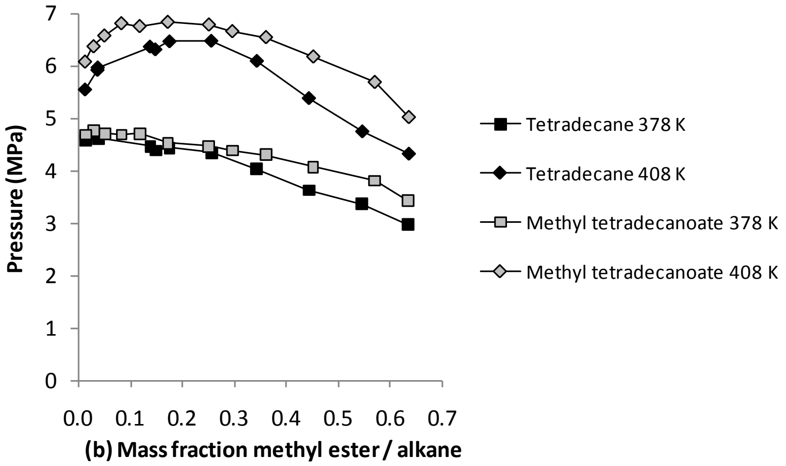


Figure 5: Comparison of phase transition pressure for an alkane and its corresponding methyl ester in (a) ethane [22] and (b) propane [3]

The methyl ester group definitively has a significant effect on the phase behaviour, with the effect being larger in ethane than in propane. The methyl ester group is polar and the addition of the polar group results in a decrease in solubility. The larger difference of solubility in ethane may be due to higher asymmetry of the system with ethane as supercritical solvent due to a larger absolute as well as relative difference in molecular mass. Figure 4 (b) shows that ethane has improved ability to distinguish between the alkane and the methyl ester and indicates that ethane is more selective in separating these two compounds.

Conclusions and future work

High pressure solubility measurements for a range of methyl esters (methyl decanoate through methyl docosanoate) have been conducted in supercritical ethane at temperatures between 313 and 353 K for methyl ester mass fractions between 0.018 and 0.65 . In this range no three phase regions or temperature inversions were observed and the data showed a generally linear relationship between the solubility pressure and the temperature at constant composition. The experimental results allowed for the construction of pressure – carbon number plots, these showing a linear relationship with an average R^2 value of 0.98. The results show that there is a significant difference in the phase behaviour of methyl ester and n-alkanes in supercritical ethane, indicating that ethane is able to separate these two, and possibly other compounds, according to the functional group present. However, save the ethane-n-alkane homologous series [15], very little other phase equilibrium data is available for ethane as supercritical solvent and measurements with other functional groups, such as ethyl ester, acids and alcohol needs to be done. These measurements will indicate if ethane can be used as a supercritical solvent to separate these types of molecules. In addition, in the future detailed thermodynamic modelling with state of the art equations of state needs to be conducted to allow for quantitative prediction of the phase behaviour and modelling of possible separation processes.

Acknowledgements

The financial assistance of Sasol Technology (Pty) Ltd and the Department of Trade and Industry (DTI) of South Africa through the Technology and Human Resources for Industry Programme (THRIP) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the sponsors. The assistance of Mr. J. Batt with some of the experimental measurements is hereby acknowledged.

References

1. M. Zou, Z.R. Yu, P. Kashulines, S.S.H. Rizvi, J.A. Zollweg, J. Supercrit. Fluids 3 (**1990**) 23-28.
2. C. Crampton, G. Charbit, E. Neau, J. Supercrit. Fluids 16 (**1999**) 11-20.
3. C.E. Schwarz, G.J.K Bonthuys, J.H. Knoetze, A.J. Burger, J. Supercrit. Fluids 46 (**2008**) p. 233-237.
4. Y. Iwai, Y. Koga, H. Maruyama, Y. Arai, J. Chem. Eng. Data 38 (**1993**) p. 506-508.
5. H. Inomata, T. Kondo, S. Hirohama, K. Arai, Y. Suzuki, M. Konno, Fluid Phase Equilib. 46 (**1989**) p. 41-52.
6. C.A. Lockemann, S. Muñoz de Soto-Soliz, E.-U. Schlünder, Chem. Eng. Process. 34 (**1995**) p. 561-564.
7. R. Bharath, H. Inomata, K. Arai, K. Shoji, Y. Noguchi, Fluid Phase Equilib. 50 (**1989**) p. 315-327.
8. L.J. Rovetto, S.B. Bottini, C.J. Peters, J. Supercrit. Fluids 31 (**2004**) p. 111-121.
9. R.C. Reid, J.M. Prausnitz, B.E. Poling, The properties of gases and liquids, 4th Edition, McGraw-Hill Book Company, USA, **1987**.
10. I. Nieuwoudt, J.C. Crause, M. du Rand, J. Supercrit Fluids 24 (**2002**) p. 47-55.
11. G.J.K. Bonthuys, Separation of 1-dodecanol and n-tetradecane through supercritical extraction, Master Thesis in Chemical Engineering, University of Stellenbosch, South Africa, **2008**.
12. C.E. Schwarz, I. Nieuwoudt, J. Supercrit. Fluids 27 (**2003**) p. 133-144.
13. F.C.v.N. Fourie, C.E. Schwarz, J.H. Knoetze, J. Supercrit. Fluids 47 (**2008**) p. 161-167.
14. C.E. Schwarz, J.H. Knoetze, Fluid Phase Equilib. 258 (**2007**) p. 51-57.

15. C.E. Schwarz, I. Nieuwoudt, J.H. Knoetze, J. Supercrit. Fluids 46 (**2008**) p. 226-232.
16. P.H. van Konynenburg, R.L. Scott, Trans. R. Soc. Lond. A 298 (**1980**) p. 495-540.
17. M.A. McHugh, V.J. Krukonis, Supercritical Fluid Extraction Principles and Practice, 2nd Edition, Butterworth-Heinemann, USA, **1994**.
18. H. Gardella, K. Fischer, J. Gmehling, Ind. Eng. Chem. Res. 41 (**2002**) p. 1051-1056.
19. E. Brunner, J. Chem. Therm. 17 (**1985**) p. 871-885.
20. C.E. Schwarz, I. Nieuwoudt, J. Supercrit. Fluids 27 (**2003**) p. 145-156.
21. C.E. Schwarz, I. Nieuwoudt. J.H. Knoetze, J. Supercrit. Fluids 41 (**2007**) p. 327 -334.
22. M. du Rand, I. Nieuwoudt, J. Supercrit. Fluids 21 (**2001**) p. 181-193.