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Phase equilibria of methyl esters in supercritical propane

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ABSTRACT

High pressure phase equilibria measurements using a static synthetic view cell for methyl decanoate, methyl dodecanoate, methyl hexadecanoate, methyl octadecaonate and methyl docosanoate in supercritical propane were conducted between 376.6 and 412.4 K at methyl ester mass fractions between 0.0178 and 0.660. The data show a linear increase in phase transition pressure with an increase in temperature at constant composition and, within the experimental range, total solubility was achieved below 8.1 MPa for all systems. Comparing the various data sets, an increase in phase transition pressure with increasing hydrocarbon backbone is noted, indicating that propane is able to fractionate a mixture of methyl esters.

Nomenclature

A	parameter in pressure–temperature relationship
B	parameter in pressure–temperature relationship
P	pressure (MPa)
SC	supercritical
SCF	supercritical fluid
T	temperature (K)
T_r	reduced temperature (K/K)
u	standard uncertainty
u_r	relative uncertainty
w	mass fraction solute

1. Introduction

Triglycerides are the major constituent of many plant and animal oils [1–5]. These triglycerides are very often mixed, i.e. they contain two or more fatty acids. Typically, these fatty acids are linear with between 10 and 22 carbon atoms present. The fatty acid composition of the oil and the combination of the fatty acids in the triglycerides are dependent on the origin of the oil. However, triglycerides with three of the same fatty acids are very seldom encountered.

The various fatty acids present in the triglycerides have different properties and thus different uses and applications [6]. In order to obtain fractions with high concentrations of a particular fatty acid, the triglycerides need to be hydrolysed to yield fatty acids or, more often, their esters (mainly methyl or ethyl esters through hydrolysis with methanol or ethanol) [6]. These fatty acids or esters can then be fractionated according to the number of carbon atoms present to obtain the required acid or ester in high concentration [7].

Supercritical fluid (SCF) extraction has been shown to be a promising technique to fractionate fatty acids [7] or their esters [8,9], as SCFs have the ability to distinguish, within a homologous series, between the number of carbon atoms present [10,11].

Supercritical (SC) CO_2 is the most popular SC solvent due to its generally suitable critical temperature (304.12 K [12]), its non-toxicity and low cost. However, SC CO_2 is not such a good solvent for high molecular mass aliphatic components such as acids [10] and esters [13–15], and thus high pressures are required for significant solubility. Ethane has been considered as an alternative solvent to CO_2 as it has a similar critical temperature (305.32 K [12]) and improved solubility for both acids and esters [11,16,17]. However, ethane is flammable and rather costly and, while improved solubility is obtained, especially for higher molecular mass components, high pressures (>20 MPa) are at times still required.

Propane can be considered as an alternative SC solvent to CO_2 and ethane, or may even be used as a co-solvent with CO_2. While propane has a higher critical temperature than CO_2 and ethane (369.83 K [12]), and, like ethane, is flammable, high molecular mass acids and esters are considerably more soluble in propane than in ethane or CO_2. This can be seen when one compares the solubility of acids and ethyl esters in propane [11,18] with

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Table 1
Materials used.

Component	Formula	CAS number	Supplier	Product number	Minimum purity
Propane	C_3H_8	74-98-6	Air Liquide	–	99.95%
Methyl decanoate (methyl caprate)	$CH_3(CH_2)_8COOCH_3$	110-42-9	Sigma	299030	99%
Methyl dodecanoate (methyl laurate)	$CH_3(CH_2)_{10}COOCH_3$	111-82-0	Sigma	234519	99.5%
Methyl hexadecanoate (methyl palmitate)	$CH_3(CH_2)_{14}COOCH_3$	112-39-0	Sigma	P5177 and 76160	Both 99%
Methyl octadecanoate (methyl stearate)	$CH_3(CH_2)_{16}COOCH_3$	112-61-8	Sigma	85769	99.5%
Methyl docosanoate (methyl behenate)	$CH_3(CH_2)_{20}COOCH_3$	927-77-1	Sigma	11940	99%

those in ethane [11,16] and CO_2 [10,15]. However, while comprehensive studies have been conducted on the phase behaviour of acids and ethyl esters in propane, to the best of our knowledge, only data for two systems (propane/methyl tetradecanoate [19] and propane/methyl hexadecanoate [20]) have previously been published for the propane/methyl esters homologous series for methyl esters with 10 or more carbon atoms. The data for the propane/methyl tetradecanoate system encompasses a large compositional range in both the vapour-like and liquid-like region and also includes data in the mixture critical region. For the purpose of the current study the propane/tetradecanoate data [19] set is regarded as sufficient. For the propane/methyl hexadecanoate system, Rovetto et al. [20] measured data in a large temperature range but only for five mass fractions, these all being in the liquid-like region. Additional measurements to complement the work of Rovetto et al. [20] will thus be conducted and the results from the two studies compared.

The purpose of this paper is to present experimental data for the propane/methyl esters homologous series. In particular, data for the systems propane with methyl decanoate, methyl dodecanoate, methyl hexadecanoate, methyl octadecanoate and methyl docosanoate are presented. The data were measured between 378 and 408 K, which is just above the critical temperature of propane. Mass fractions of methyl ester between 0.015 and 0.65 were studied as this range encompasses the vapour-like, mixture critical and liquid-like regions. Thermodynamic modelling of the phase behaviour in this compositional range is very difficult, hence our focus on this region. Additionally, it has previously been shown that data at mass fractions higher than 0.65 can be approximated by linear interpolation between the pressure at the highest mass fraction and the vapour pressure [21], negating the need for additional experimental measurements in this region. The conditions for the measured data were selected so that, in the future, thermodynamic and process modelling, similar to that of Jaubert et al. [22] for the CO_2/fatty ester homologous series, can be done to determine the viability of fractionating methyl esters using SC propane.

The experimentally measured data is then used (1) to determine if propane can be used to fractionate methyl esters according to their hydrocarbon backbone; (2) to compare the phase behaviour of methyl esters to that of ethyl esters and acids in SC propane; and (3) to compare the phase behaviour of methyl esters in CO_2, ethane and propane.

2. Materials and methods

2.1. Experimental set-up

High pressure phase transition (bubble/dew point) measurements were conducted using a previously constructed static synthetic set-up. The set-up consists of a variable volume high pressure view cell (maximum volume of 45 cm^3) and is described in detail in previous a publication [23]. The view cell can operate between 300 and 460 K and up to 28 MPa. The pressure was measured with an Industrial Sensors Inc. pressure transducer, which was regularly calibrated in-house with a Barnett Industrial dead weight tester. The temperature was measured with a 4-wire PT100 connected to a Testo 720 display, regularly calibrated by SANAS Calibration Lab. The standard uncertainties of the measurements in the cell are as follows and further details are available in Schwarz and Nieuwoudt [23]:

- The standard uncertainty in the phase transition pressure (P), based on the combination of the measurement error of the pressure transmitter, the accuracy of the pressure calibration and the accuracy to which the phase transition is observed, is better than 0.06 MPa, i.e. $u(P) = 0.06$ MPa.
- The standard uncertainty of the temperature measurement (T), based on the temperature measurement and the range of temperature fluctuations observed, is better than 0.2 K, i.e. $u(T) = 0.2$ K.
- It is estimated that the maximum relative uncertainty in the mass fraction (w) is better than 1% of the value i.e. $u_r(w) = 0.01 \cdot w$, 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 methyl ester was loaded gravimetrically into the phase equilibrium cell, after which the cell was closed, evacuated and flushed with propane. Liquid propane was then added

Table 2
Phase equilibrium measurements for the system propane/methyl decanoate ($u(T) = 0.2$ K; $u(P) = 0.06$ MPa; $u_r(w) = 0.01$ w).

Mass fraction methyl decanoate	Experimental measurements (T in K, P in MPa) Subscripts indicate measurement sets						$P = AT + B$ (P in MPa, T in K) Valid between T_1 and T_3		
	T_1	P_1	T_2	P_2	T_3	P_3	A	B	R^2
0.648	378.4	3.13	397.2	3.88	411.2	4.73	0.04832	−15.205	0.9864
0.550	379.0	3.51	397.7	4.48	411.5	5.30	0.05481	−17.283	0.9984
0.448	378.6	3.76	397.4	4.87	411.1	5.72	0.06026	−19.060	0.9998
0.373	378.8	3.98	397.7	5.12	411.5	6.08	0.06415	−20.343	0.9986
0.303	379.2	4.13	398.3	5.37	412.4	6.33	0.06615	−20.961	0.9997
0.228	378.8	4.29	398.3	5.64	411.2	6.46	0.06690	−21.034	0.9994
0.179	378.4	4.34	397.4	5.65	411.0	6.43	0.06449	−20.039	0.9970
0.120	378.7	4.47	397.2	5.72	410.8	6.40	0.06042	−18.367	0.9931
0.0807	378.4	4.60	397.3	5.72	410.9	6.30	0.05265	−15.283	0.9921
0.0560	378.4	4.75	397.1	5.72	410.6	6.09	0.04235	−11.222	0.9746
0.0279	378.3	4.74	396.6	5.21	410.3	5.53	0.02459	−4.555	0.9995
0.0215	378.1	4.67	393.6	4.82	–	–	0.00968	1.011	–