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Experimental determination and association model for the solubilities of methyl 10-undecenoate with methyl ricinoleate in supercritical carbon dioxide

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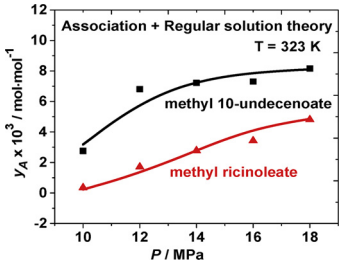
GRAPHICAL ABSTRACT



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ABSTRACT

The mixture solubilities of methyl 10-undecenoate (M10U) + methyl ricinoleate (MR) in supercritical carbon dioxide ($SCCO_2$) were determined at temperatures from 313 to 333 K, and pressures from 10 to 18 MPa. At constant pressure, the solubilities decreased with an increase with temperature for the investigated range of operating conditions. The maximum solubility enhancement for the current mixture was observed to be 32% for the MR in a mixture of M10U + MR. The maximum selectivity of $SCCO_2$ was 12 towards M10U in a mixture of M10U + MR. The experimental data obtained was internally consistent, as verified by Mendez-Teja model. A new association theory based model was derived and used to model the solubilities of the investigated mixture in $SCCO_2$ along with the literature data.

1. Introduction

The fossil fuels are depleting rapidly as the demand for energy is continuously increasing [1]. Therefore, sustainable renewable energy sources based on non-edible oils are being explored as a viable option as they do not compete with the food commodities [2]. Oils such as castor oil are rich in fatty acids and thus can be used for the synthesis of biodiesel, bio-lubricants, and many fine industrial chemicals [3,4]. There are several processes available for the synthesis of different products obtained from castor oil [5]. One such process is the transesterification of castor oil that results in a mixture of fatty acid methyl esters (FAMEs) primarily consisting of methyl 10-undecenoate (M10U) and methyl ricinoleate (MR). After the successful synthesis of these esters, there is a need for the separation of these two FAMEs from the product mixture. A detailed description about these FAMEs and their applications has been reported previously [6].

The traditional separation processes such as distillation and liquid-liquid extraction are not a viable option for the separation of the high boiling point compounds such as FAMEs from the oil as they require large number of stages making the process complex and energy

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Nomenclature

AARD	Average absolute relative deviation
EOS	Equation of state
FAMEs	Fatty acid methyl esters
MT	Mendez-Teja
M10U	Methyl 10-undecenoate
MR	Methyl ricinoleate
SE	Solubility enhancement
$SCCO_2$	Supercritical carbon dioxide
a	Interaction parameter
E	Enhancement factor
F	Degrees of freedom
f	Fugacity
H	Enthalpy
K	Equilibrium constant
N	Number of experimental data points
N_C	Number of components
N_P	Number of phases
P	Pressure
R	Universal gas constant
S	Selectivity
T	Temperature
y	Solubility in terms of mole fraction
Z	Compressibility factor

Greek symbols

β, δ, η	Virial coefficients
γ	Activity coefficient
λ, κ	Association numbers
ρ	Density
ϕ	Fugacity coefficient

intensive. In addition, the final product obtained using liquid-liquid extraction contains traces of solvent in the end product that reduces the purity of the desired compound. Hence, there is a need for alternative separation processes that can overcome the limitations associated with the traditional processes. In this regard, the separation of high boiling compounds using supercritical fluids has been found to be a suitable option [7]. There are several supercritical fluids available of which supercritical carbon dioxide ($SCCO_2$) is the frequently used solvent. The main advantages of using $SCCO_2$ as a solvent are that it is inert, non-flammable and non-toxic. A preliminary requirement for designing any separation processes using $SCCO_2$ is the solubility or phase equilibrium data.

There are nearly ~1000 studies on the solubilities of solids in $SCCO_2$ [8–10] and nearly ~100 studies on the solubilities of solid mixtures in $SCCO_2$. These have been suitably summarized [11] and modeled [12]. Similarly, there are several studies on the phase equilibria and solubilities of $SCCO_2$ in various liquids. However, the literature on the solubilities of liquid solutes in $SCCO_2$ is limited with ~30 studies, as summarized and modeled elsewhere [13,14]. Further, there are only four studies that are available on the solubilities of mixtures of two liquid solutes in $SCCO_2$ [15–18]. Recently, the liquid mixture solubilities of 10-undecenoic acid with M10U and MR in $SCCO_2$ have been determined [18]. In the current study, the solubilities of the mixture of M10U + MR in $SCCO_2$ were determined for the first time. This solubility data can be helpful in the designing of the separation processes for the products obtained from the transesterification reaction of castor oil.

It is important to have empirical or semi-empirical models to correlate the solubilities in $SCCO_2$ at different operating conditions along with the experimental determination of solubilities in $SCCO_2$. These models are either equations of state (EOS) or density based correlations. In the earlier studies, the liquid mixture solubilities in $SCCO_2$ have been modeled using appropriate mixing rules with Peng-Robinson EOS [7,16]. However, the EOS based models are tedious and require pure component properties such as critical temperature, critical pressure, acentric factor, and binding interaction parameters that are difficult to obtain. On the other hand, the density based models do not have such limitations, and thus are easier to use. Typically, these density-based semi-empirical models can be obtained using two fundamental theories: solution and association theories. Further, the non-ideality of the solutes in supercritical phase can be expressed with activity coefficients. Recently, a solution theory based model was developed to correlate the solubilities of liquid mixtures in $SCCO_2$ [18]. In the current study, a new association theory based correlation has been developed to predict the solubilities of liquid solutes mixture in $SCCO_2$.

The objectives of the current study are three-fold: i) the measurement of the mixture solubilities of M10U + MR in $SCCO_2$ experimentally at different pressures and temperatures, ii) development of an association theory based model to predict the solubilities of liquid mixtures in $SCCO_2$ and iii) compilation of all the existing data and semi-empirical models on mixture solubilities; and compare the ability of the new model with the existing models to correlate the solubilities of all compounds reported in the literature.

2. Materials and methods

2.1. Materials

The chemicals, methyl 10-undecenoate (> 96% purity, CAS 111-81-9, TCI chemicals, Japan), methyl ricinoleate (> 95% purity, CAS 141-24-2, TCI chemicals, Japan), n-heptane of HPLC grade (Sigma Aldrich, Bangalore, India), butyl laurate (> 99% purity, Merck, India), and carbon dioxide (99% purity, Noble Gases, Bangalore, India). Further, the carbon dioxide was purified to 99.9% by passing the gas through a silica bed. The impurities present in the investigated compounds are primarily the castor oil fatty acids as reported by the manufacturers that have similar solubilities as the parent compounds in $SCCO_2$. Due to the chemical and physical similarity of the impurities, these impurities will not have any significant effect on the solubility of the liquid mixtures in $SCCO_2$. Therefore, the chemicals have been used as obtained without any further purification

2.2. Experimental procedure

The equilibrium solubilities of a liquid mixture in $SCCO_2$ were determined by flow saturation technique (Jasco International Company, Japan). The detailed procedure about the experimental setup has been reported earlier [19]. Carbon dioxide was sent to a chiller and this was pumped into the 50 ml column having an optimized amount of 30 ml of the solute mixture. The optimized volume was determined by varying the volume of the liquid solute mixture from 20 to 40 ml, as discussed in our earlier work [18]. This column was placed inside a thermostat maintained at the desired temperature within ± 1 K. The back pressure regulator maintained the pressure within ± 1 bar. All the experiments were performed at a constant flow rate of 0.10 ml/min as the solubilities were invariant below 0.20 ml/min [18]. A glass collection trap was used for collecting the sample mixture every hour for at least 8 h after the saturation was reached after 2 h [18]. The collected sample mixture was then analyzed using the gas chromatography. The weight of the mixture was obtained gravimetrically and the individual weights of the solutes in the mixture was obtained using the gas chromatographic analysis. The solubility of a solute in a mixture (y_i) in $SCCO_2$