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Phase equilibria of 3-methylstyrene, 4-methylstyrene, alpha-methylstyrene and a methylstyrene mixture in supercritical CO_2

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ABSTRACT

Phase equilibria of 3-methylstyrene, 4-methylstyrene, alpha-methylstyrene and a methylstyrene mixture (mainly 3-methylstyrene (60% mol) and 4-methylstyrene (40% mol)) in supercritical CO_2 were measured using high-pressure variable-volume view cells based on the static synthetic method. The systems were investigated between 308 and 353 K, with mass fractions of solute ranging continuously from 0.0275 to 0.65 and pressures up to 15 MPa. The experimental data shows a linear relationship between the phase transition pressure and the system temperature at constant composition. When the solubilities are compared, the methylstyrene isomers show little yet significant differences between them with the methylstyrene mixture being the most soluble. As the temperature increases, a decrease in the difference between the phase transition pressures of the methylstyrene structural isomers were observed. Lastly, the experimental data were correlated with the Peng-Robinson cubic equation of state using one temperature-independent binary interaction parameter and satisfactory results were obtained in both low and high solute concentration regions.

1. Introduction

The major population growth encountered during the last decades directly results in increasing use of automobiles around the world. This continuous society development comes with an environmental and health concern regarding the end of life of automotive tyres. It is estimated that approximately 1.5 billion tyres reach the end of their life cycle annually worldwide [1]. Only limited disposal of tyres is conducted and they are often illegally dumped or stocked to landfill [2,3]. This situation leads to pollution issues such as uncontrolled leaks of degraded tyre rubber into the soil and groundwater, or into the atmosphere since combustion of tyres produces toxic gases, which also contain carcinogenic and mutagenic compounds [4]. As a consequence, legislation on waste tyres has become more stringent in many countries, leading to a favourable conjuncture for the valorisation and recycling of the tyres.

Tyres are derived from natural and synthetic rubber and contain mainly long-chain hydrocarbons, making them a recyclable resource for energetic and chemical purposes. Nowadays, pyrolysis is a popular technique to convert waste tyres into valuable materials. In this process, materials are thermally decomposed into simpler constituents when subjected to high heat, in an oxygen free atmosphere. Total conversion of waste tyres can be achieved by pyrolysis at 773 K under atmospheric pressure and results in three main products: gas with a high calorific value, char that can be used as fuel or carbon source and pyrolytic oil or Tyre Derived Oil (TDO) [1,4]. The latter is a complex mixture of C_5–C_{20} aliphatic and aromatic compounds with a wide boiling range of 343–673 K [5]. The TDO composition and distribution depends on the processing conditions and tyres composition. Thereafter, further purification of TDO is needed for commercial valorisation as a fuel or feedstock to produce chemicals.

Significant concentrations of valuable chemicals with wide industrial applications, like limonene, benzene or toluene, have been identified in TDO [5–7]. Since these components have similar vapour pressures and are sensitive to thermal degradation, separation of these components by distillation and liquid–liquid extraction would require, respectively, a large number of stages and high energy consumption. Supercritical fluid fractionation (SFF) has been shown to be able to fractionate complex mixtures such as bio-oil derived from biomass pyrolysis, as well as heavy aromatic

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Nomenclature

CO_2	Carbon dioxide
EoS	Equation of state
PR	Peng-Robinson
SFF	Supercritical fluid fractionation
TDO	Tyre derived oil
a	Energy parameter
b	Co-volume parameter
$c_{1,i}$ $c_{2,i}$, and $c_{3,i}$	Parameters for the component i in Twu alpha function
k_{ij}	Binary interaction parameter between two components i and j
n	Total number of data points
P	Pressure
P_c	Critical pressure
T	Temperature
T_c	Critical temperature
T_r	Reduced temperature
u	Standard uncertainty estimation
x_{iA} and x_j	Molar fraction of the components i and j
w_i and w_j	Mass fraction of the components i and j
V_m	Molar volume
α_i	Twu alpha function for equation of state the components i

streams in the food and petroleum industry at relatively low temperatures combined with high selectivity and low solvent residue [8–10]. Therefore, isolating TDO components by SFF may be viable. CO_2 could be used for this purpose as it is a non-toxic inert fluid, readily soluble in many organic liquids, with low critical pressure (7.38 MPa) and low critical temperature (304.2 K), making it a popular solvent for SFF.

The solubility of a component in a supercritical fluid provides a first indication of the technical feasibility of any SFF process. Thus, a detailed literature investigation of phase equilibria studies on the components present in TDO at high concentrations is needed. Selected phase equilibria data of limonene [11,12], ethylbenzene [12–14], styrene [13,15–17], and toluene [13,18] in supercritical CO_2 are available in the open literature over a large composition range. Amongst the valuable components of TDO, methylstyrene is the one with limited phase behaviour data in CO_2 [19,20], particularly at low solute concentrations.

Therefore the aim of this paper is threefold, firstly to present phase equilibrium experimental data of a methylstyrene mixture and three methylstyrene isomers, i.e. 3-methylstyrene, 4-methylstyrene and alpha-methylstyrene in supercritical CO_2. Secondly, comparisons of the phase behaviour in supercritical CO_2 of a methylstyrene mixture and 4-methylstyrene with other main valuable components of TDO are presented. Lastly, this paper aims to determine whether accurate thermodynamic modelling of the studied systems could be obtained by using commercial simulation software with the widely used Peng-Robinson equation of state (EoS).

2. Experimental

2.1. Experimental set-up and measurement method

Two high-pressure variable volume view cells, each based on a piston-cylinder set-up, with maximal internal volumes of 45 cm^3 and 80 cm^3, were used to measure the phase equilibrium data reported in this study. The view cells are able to operate at pressures up 28 to MPa within a temperature range of 300–460 K. A detailed description of the view cells has been reported previously by Schwarz and Nieuwoudt [21] and Fourie et al. [22], respectively. The utilization of the small or larger cell is related to the accuracy of the mass solute weighed and its cost. Generally, the large cell was used to measure the low solute concentration phase transition points to ensure accurate determination of the mass fraction while measurements with high solute concentration were conducted on the small cell to limit the quantity of compound and the cost associated.

The measurement method and comparison of its results with high quality literature data has been described in detail in previous publications [21–23] and can be summarise as follows. The experimental procedure started with gravimetrically loading a known amount of solute into the view cell. The cell was closed, evacuated and flushed with CO_2. A quantitative amount of liquid CO_2 was then added gravimetrically and the inlet valve securely closed. After completion of loading, the sample was heated to the selected temperature of investigation. Thermal regulation was ensured by recirculating water in a thermostat bath. Once equilibrium was reached in the cell at the required temperature, the pressure was slowly increased until the system became homogeneous. Due to supersaturation effects, the phase transition point was reported as the pressure at which the system moves from a single to a two-phase region at constant temperature. During the heating procedure, as well as while conducting the measurements, the cell content was stirred with a magnetic stirrer to ensure and maintain good mass and energy transfer as well as equilibrium.

2.2. Uncertainty estimation

The main factors which affect the accuracy of the measurements are the pressure, the temperature and the weighing of the materials [21]. The uncertainty associated with the phase transition pressure resulted from the measurement error of the pressure transmitter combined with the accuracy of the pressure calibration over the studied temperature range. The pressure was measured with Industrial Sensors Inc. pressure transducers, which was calibrated in-house with a Barnett Industrial deadweight tester between 307 and 363 K. Thus, the standard uncertainty of the phase transition pressure measurement was found to be 0.05 MPa, i.e. $u(P) = 0.05$ MPa. The uncertainty associated with the temperature resulted from the temperature measurement and the range of temperature fluctuations observed. Temperature calibrations were performed by WIKA Instruments (Pty) Ltd on the probes (4-wire PT-100) and showed a standard uncertainty in temperature measurement of 0.2 K, i.e. $u(T) = 0.2$ K. The relative standard uncertainty in the mass fraction was based on the accuracy of the balances used to measure the loaded compounds and was estimated to be better than 1% of the mass fraction value, i.e. $u(w_i) = 0.01 \times w_i$.

2.3. Chemicals

The methylstyrene isomers and mixture were obtained from Sigma–Aldrich and used without further purification. Their molar purities, supplier, CAS registry numbers (CAS RN) and chemical structures are listed in Table 1. CO_2 used as a solvent was supplied from Air Products at a purity level of 99.99%.

3. Results and discussions

3.1. Measured phase equilibrium data

The phase transition pressures of 3-methylstyrene, 4-methylstyrene, alpha-methylstyrene and the methylstyrene mixture in supercritical CO_2 were measured at four temperatures, approximatively 308, 323, 338 and 353 K, for solute mass fractions