

Binary solid–liquid–gas equilibrium of the tripalmitin/CO₂ and ubiquinone/CO₂ systems

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Received 14 October 2005; received in revised form 12 December 2005; accepted 12 December 2005

Available online 20 January 2006

Abstract

A conventional method was used to measure the melting points of the natural lipid tripalmitin and of the coenzyme ubiquinone (coQ10) under high pressure carbon dioxide. The pressure–temperature behavior of the binary three-phase solid–liquid–gas (SLG) equilibrium for these and other systems, namely naphthalene and biphenyl with carbon dioxide, ethylene and ethane, were investigated using the Peng–Robinson equation of state (PR-EoS) with the van der Waals one fluid (vdw-1) mixing rules and with the NRTL equation to calculate the solute activity in the liquid phase. When the interaction parameter in the vdw-1 mixing rules could be determined by the PR-EoS through the correlation of the solid–fluid phase equilibrium data, the two NRTL parameters were used as adjustable parameters. The results showed that fairly good correlations could be achieved for the experimental pressure–temperature data of all the asymmetric systems studied here, indicating that the NRTL parameters are crucial for describing the pressure–temperature behavior but have little effect on the phase compositions at the SLG equilibrium.

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Keywords: Solid–liquid–gas equilibrium; Tripalmitin; Ubiquinone; Supercritical

1. Introduction

One of the largest scientific achievements of Prausnitz and coworkers were the activity coefficient models (UNIFAC, NRTL and UNIQUAC) that are widely used by the industrial and research worlds to model the liquid phase behavior. There are abundant examples in the literature describing applications of such models in a wide range of chemical engineering problems, namely VLE of multicomponent mixtures, LLE of aqueous polymer solutions, reactive azeotropy, protein solubility, etc. This work illustrates one further application of the activity coefficient model proposed by Renon and Prausnitz in 1968 – the NRTL equation – that combined with Peng–Robinson equation of state, is used to describe the binary SLG line of systems involving CO₂ with rather complex molecules, i.e. systems composed of species with large differences in size, shape and molecular interactions.

When compressed gases are dissolved in liquids (such as polymers or lipids), the gas-saturated solution formed can be expanded through a nozzle to produce very small particles. This is the basis of the PGSS process reported by several authors for polymers [1] and lipids [2,3] and that has been intensively investigated because it offers some notorious advantages over other similar processes. Because in a PGSS process a compressed gas is dissolved in a liquid phase, its main feature from a thermodynamic point of view is the correct description of the solid–liquid–gas (SLG) phase equilibrium, as required for the design of any particle formation process. In the crystallization model for the PGSS process reported earlier [4], the liquid–gas phase equilibrium between the CO₂-rich phase and the hydrogenated palm oil (HPO)–CO₂ mixed phase was described using the Peng–Robinson equation of state; this model did not take into account the pressure dependence of the HPO melting point led by the dissolved CO₂ into HPO and the depressurization of the system through the nozzle. Later, in another work [5], it was shown that using the pressure–temperature behavior of HPO into a melt crystallization model for a PGSS process, the particle distribution becomes narrower compared to the case where is neglected the influence of the pre-expansion pressure

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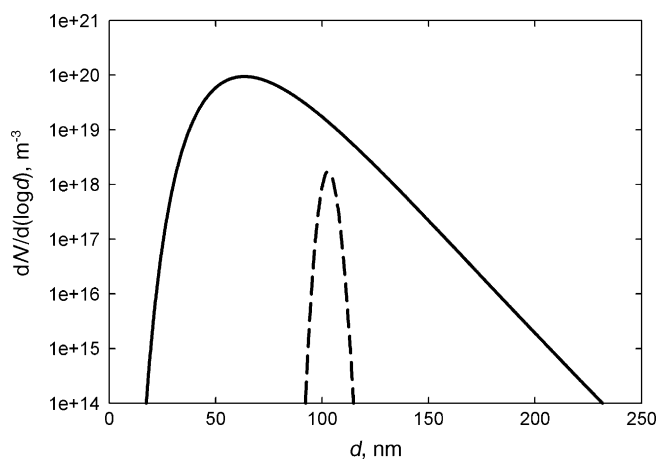


Fig. 1. Effect of SLG-line on the simulated particle size and particle size distribution for the HPO/CO₂ system at 359 K and 18 MPa pre-expansion temperature and pressure. With constant (normal) HPO melting point (—); with the SLG line calculated by the PR-EoS (---). N is the particle density (particles/m³) and d is the particle size (nm).

on the melting point of HPO, as Fig. 1 illustrates. Therefore in our recent crystallization and atomization model [6], we used the SLG equilibrium data in the modeling and more reasonable simulation results have been obtained.

Tripalmitin (C₅₁H₉₈O₆, $M = 807.3 \text{ g mol}^{-1}$) is a convenient choice as the encapsulating material for a hydrophobic drug such as coenzyme Q10 (coQ10, ubiquinone or ubiquinone, C₅₉H₉₀O₄, $M = 863.4 \text{ g mol}^{-1}$), a fat-soluble, vitamin-like substance found in the cells of many organisms that is involved in key biochemical reactions that produce energy in cells and acts as an antioxidant. There are reports of the preparation of microparticles of ubiquinone/tripalmitin by a traditional method to form solid–lipid nanoparticles [7]. For comparison, it should be interesting and also reasonable to produce ubiquinone/tripalmitin microparticles through the supercritical fluid based PGSS process that involves no liquid organic solvents.

The aim of this work is to study experimentally and theoretically the effect of pressure on the melting points of ubiquinone and tripalmitin, namely the effect of pressure on the temperature of the solid–liquid–gas (SLG) coexistence line, as required for further particle formation investigations.

2. Experimental and results

The SLG line can be obtained by different experimental techniques. The traditional “first melting point” method is simple and fast to access the desired data and was adopted here. The SLG line was located by finding either the first melting temperature due a change of pressure or the first melting pressure due a change of temperature. Uncertainties in the SLG temperatures were estimated to be below 0.5 K. Our experimental apparatus is similar to that used before to measure high pressure isothermal vapor–liquid equilibrium data through the synthetic method using a view cell [8]. It is composed by a stainless steel high pressure view cell with a movable piston (pressurized by water) used to change the pressure inside the cell. The working pressures were measured with an uncertainty of $\pm 0.01 \text{ MPa}$ by a

Table 1

Experimental SLG coexistence data for the tripalmitin/CO₂ and coQ10/CO₂ systems

Tripalmitin/CO ₂		coQ10/CO ₂	
Pressure (MPa)	Melting point (K)	Pressure (MPa)	Melting point (K)
0.10	337.4	0.10	322.5
1.98	334.3	0.71	321.5
3.19	332.7	1.80	319.4
4.61	329.6	2.84	316.0
5.96	327.4	4.16	314.2
7.39	326.0	5.15	312.7
8.70	323.7	5.86	310.3
92.8	322.9	6.11	308.4
10.87	322.7	7.03	306.3
13.65	322.7	7.41	305.4
16.15	322.5	8.93	305.8
18.29	322.4	10.45	306.2
19.67	322.5	12.40	306.3
		15.00	306.7
		17.65	306.9
		19.20	307.2

pressure transducer (Setra, model 204) coupled to a digital indicator (Setra, Datum-2001 model) and controlled by the water-pressurized moving piston inside the visual cell. The cell was placed in a Plexiglas thermostated air bath whose temperature was maintained by a digital temperature controller (BTC-9200, ROC) and a thermocouple (Omega, type T) with an uncertainty of $\pm 0.1 \text{ K}$. The cell contents were mixed with a Teflon coated stir bar. The normal enthalpies of fusion of tripalmitin and coQ10 (presented in Table 2) were measured with a Setaram DSC121 differential scanning calorimeter (Caluire, France) with continuous purge of the reference and sample compartments with argon. The calorimeter was periodically calibrated for temperature and heat-flow measurements with indium as reference at a scanning rate of $1 \text{ }^\circ\text{C/min}$, according to the standard procedures described in the user’s manual.

Carbon dioxide (99.998% pure) was supplied by Air Liquido, Portugal; tripalmitin (Dynasan 116) was bought from Sasol GmbH, Germany; and coQ10 was kindly provided by Labor Qualitas, Portugal.

Table 1 presents the measured SLG-coexistence data for the tripalmitin/CO₂ and coQ10/CO₂ systems. Most of pressures (or melting temperatures) presented in Table 1 are averaged results of three experimental data. For the coQ10/CO₂ system, we found out that the minimum melting temperature occurs around the pure CO₂ critical point.

3. Modeling

For solid–liquid–gas equilibrium, the equality of the component’s fugacities in solid, liquid and gas phases is required to calculate the SLG-line. Previous works, such as those of McHugh et al. [9] and of Zhang et al. [10], used an equation of state (namely the modified PR-EoS or the SRK-EoS) approach to deal with the binaries solid–gas and gas–liquid equilibria to address the solid–liquid–gas equilibria. Yet, the limitations of an equation of state to describe a liquid solution are well known

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