JOURNAL OF CHEMICAL & ENGINEERING DATA

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Solubility of Mesquite Gum in Supercritical Carbon Dioxide

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ABSTRACT: The solubility of mesquite gum (MG) in supercritical carbon dioxide (SC-CO_2) was determined for the first time at T = (313, 323, 333, and 343) K and with pressures ranging from (138 to 345) bar. The solubility values of MG in SC-CO_2 in mole fraction ranged from $2.622 \cdot 10^{-9}$ to $4.189 \cdot 10^{-9}$, $2.768 \cdot 10^{-9}$ to $6.365 \cdot 10^{-9}$, $3.442 \cdot 10^{-9}$ to $7.570 \cdot 10^{-9}$, and $4.194 \cdot 10^{-9}$ to $11.886 \cdot 10^{-9}$ at (313, 323, 333, and 343) K, respectively. This biomaterial showed low solubility in SC-CO_2 based on the MG molecule polarity and high molecular weight. The experimental solubility data were successfully correlated with the Bartle and Méndez-Santiago and Teja models. Using correlation results, the MG enthalpy of sublimation was ΔH_{sub} = 57.63 kJ·mol^{-1}.

INTRODUCTION

Supercritical fluid (SCF) technology has been recently used in the formulation of natural substances along with a biocompatible or biodegradable carrier material to form composites or encapsulates that have a great relevance for the pharmaceutical, cosmetic, and food industries.[1] Several coatings or carrier materials could be used for this purpose. One of them is the mesquite gum (MG). MG is classified as an arabinogalactan with a protein fraction that ranges from (0.7 to 5.8) %.[2,3] It belongs to the proteoglycans which covalently bound to protein polysaccharides. Its structure consists of a central chain of D-galactose units and branches of L-arabinose, D-glucuronic acid, and 4-*O*-methyl-glucuronic acid.[4] MG has physicochemical properties similar to those from Arabic gum and is extensively used in food applications such as a coating biomaterial in microencapsulation and as a binder in the drink industry.[5]

The design of the SCF processes requires any material solubility knowledge in a selected SCF. Carbon dioxide is commonly used as a SCF because of its nontoxicity, nonflamability, low cost, moderate critical pressure, high critical density, and critical temperature close to ambient temperature properties.[6] The SCF advantages compared with conventional liquid solvents include: low surface tension, high diffusivity, low viscosity, and high compressibility. In addition, the density, dielectric constant, diffusion coefficient, and solubility parameter can be continuously tuned by varying pressure and temperature. For such reasons SCF has become an attractive solvent for many industrial process.[7]

One of the most important thermophysical parameters considered in the application of the SCF technology is the compound solubility in SC-CO_2.[8] Generally, the solubility depends on the solute vapor pressure which is related to the intermolecular interactions, polarity, molecular weight, and the solution temperature and pressure.[9,10]

The solubility of many compounds has been reported in recent literature,[11] but the MG solubility in SC-CO_2 has not been reported yet.

In the present study, the MG solubility was measured in SC-CO_2 at different temperatures and pressures, and the values were correlated using the Bartle model.

EXPERIMENTAL SECTION

Materials. Carbon dioxide (99.99 purity) was purchased from INFRA (México) and MG hand-collected in the form of tear drops from *Prosopis laevigata* trees in the Mexican State of San Luis Potosí and purified as indicated by Vernon-Carter et al.[12]

Equipment. A schematic representation of the experimental device built on stainless steel which was used to determine the solubility is shown in Figure 1.

Experimental Procedure. A static phase equilibrium device was used to determine the experimental MG solubility in SC-CO_2. The typical experimental procedure is described below.

A high-pressure equilibrium cell, equipped with sapphire windows and an internal volume of approximately 30 cm^3, is loaded with 0.1 g of MG along with a magnetic stirrer. The cell is connected to the device tubing lines and immersed in a water bath equipped with a temperature controller (TECHNE 02026). This controls the operational temperature within (0.1 K). Carbon dioxide is compressed using a high-pressure liquid pump (LabAlliance A19284). When the water bath reaches the experiment temperature, the cell is pressurized with CO_2 until the desired experimental pressure is attained. Pressure is measured

Received: January 6, 2011
Accepted: February 12, 2011
Published: March 01, 2011

dx.doi.org/10.1021/je2000155 | *J. Chem. Eng. Data* 2011, 56, 2449–2452

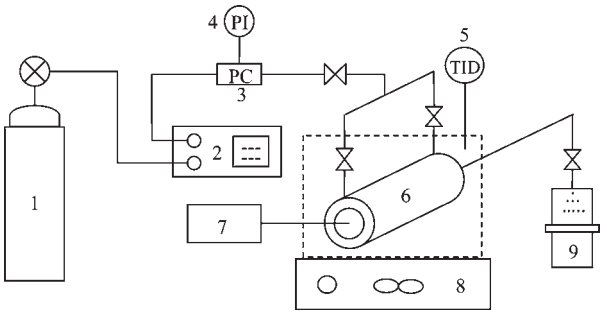

Figure 1. Schematic diagram of experimental setup. 1, carbon dioxide cylinder; 2, high pressure pump; 3, pressure transducer; 4, pressure indicator; 5, temperature indicator driver; 6, high-pressure vessel (equilibrium cell) 7, turbidimeter; 8, magnetic stir device; 9, expansion cell.

with a high-pressure transducer (Sensotec THE/7093-03). After pressure and temperature stabilization, the magnetic stirring plate, positioned under the equilibrium cell, is switched on, and the GM + CO_2 mixture is left to stir for 90 min (the period of time found to be necessary to attain equilibrium and complete fluid phase saturation). The procedure is followed by a 20 min period, without stirring, to allow mixture stabilization. This sample is then quickly depressurized and expanded into previously calibrated expansion cell. During expansion, the formerly dissolved solid precipitates and is retained by a filter paper placed just half of the expansion cell. The amount of solubilized GM was determined by gravimetric measurements performed on an analytical balance with an uncertainty of ± 0.1 mg. Each experimental solubility data point is the average of, at least, three replicate measurements.

The cloud point for this system was determinated with the turbidimeter connected to the same equipment.[13]

Correlation of Experimental Solubility Data. Empirical and semiempirical correlations based on the density of the pure SC-CO_2 are widely used for the correlation of solid−SCF equilibrium mainly due to their simplicity and easy application. In the present study, the experimental data were correlated using the Bartle et al. model[14] and Méndez-Santiago and Teja model.[15]

Bartle and co-workers[16] proposed a simple density-based semiempirical model to correlate the solubility of solids in SC-CO_2

$$\ln \frac{yP}{P_{ref}} = A + b_1(\rho - \rho_{ref}) \quad (1)$$

where

$$A = b_0 + \frac{b_2}{T} \quad (2)$$

and

$$\ln \frac{yP}{P_{ref}} = b_0 + b_1(\rho - \rho_{ref}) + \frac{b_2}{T} \quad (3)$$

where y is the equilibrium mole fraction of the solute in SC-CO_2, P_{ref} is assumed as a standard pressure of 0.1 MPa, ρ_{ref} is a reference density assumed as 700 kg·m^{-3}, and b_0, b_2, A, and b_1 are empirical constants. From the experimental solubility data, each isotherm is fitted using eq 1 to obtain the values of A and b_1. The values of b_1 are averaged, and these values are then used to recalculate the A values for the various isotherms. The A constants are then plotted against $1/T$ and correlated with eq 2, to determine constants b_0 and b_2. Finally, the values b_0, b_1, and b_2 are used to predict the solubility, applying eq 3. In this model, the parameter b_2 is related to the enthalpy of sublimation of the solid solute, by the expression $\Delta H_{sub} = -Rb_2$. The parameters b_0, b_1, and b_2 obtained from the eqs 1, 2, and 3, where determined by a linear regression analysis with Origin version 8.5 Scientific Graphing and Analysis Software (OriginLab Corp., Northampton, MA, USA). The MG molecular weight was reported as 2 120 864 g·mol^{-1}.[17]

The Méndez-Santiago and Teja model is based on the theory of dilute solutions and relates the solubility of a solid with the density of SC-CO_2. In this model Méndez-Santiago and Teja proposed to plot the so-called enhancement factor as a function of the density of the solvent in the form of eq 4:

$$T \ln E = T \ln\left(\frac{yP}{P_{ref}}\right) = A + B\rho \quad (4)$$

where T is the absolute temperature; E is the enhancement factor; y is the solute mole fraction; P is the total pressure; P_{ref} is the reference pressure; ρ is the density of the SCF, and A and B are temperature-independent constants.

Density Determination. The density of SC-CO_2 was calculated with the equation:

$$\rho = \frac{M}{V} \quad (5)$$

where M is the molar mass of CO_2 and V is the molar volume obtained from Peng−Robinson (P-R) equation of state. The P-R equation gives an appropriate qualitative description and higher accuracy of quantitative calculation for the phase behavior of supercritical carbon dioxide.[7]

Experimental Solubility Determination. Solubility expressed as mole fraction y^{exp} of MG in pure SC-CO_2 is given by

$$y^{exp} = \frac{n_{MG}}{n_{SC\text{-}CO_2} + n_{MG}} \quad (6)$$

where n_{MG} represents the MG moles dissolved and $n_{SC\text{-}CO_2}$ represents the moles of SC-CO_2 fed.

RESULTS AND DISCUSSION

The solubility of MG was determined at (313, 323, 333, and 343) K, in the pressure range from (138 to 345) bar. The results are summarized in Table 1.

The average absolute relative deviations (AARDs) were determined for each experiment using the following equation

$$\text{AARD} = \frac{1}{n}\sum \frac{|y_i^{cal} - y_i^{exp}|}{y_i^{exp}} \quad (7)$$

where n is the number of data points, y_i^{exp} is the experimental solubility of the MG for experimental point i, and y_i^{cal} is the calculated solubility corresponding to the point i.

The optimal fitting parameters are presented in eq 7 which correlates the experimental solubility values measured in this paper.

$$\ln \frac{y^{cal}p/\text{MPa}}{0.1} = 7.1673 + 0.005325(\rho/\text{kg·m}^{-3} - 700) - \frac{6931.7}{T/\text{K}} \quad (8)$$

where y^{cal} is the equilibrium mole fraction of the solute in

Table 1. Mole Fraction Solubility[a,b] of Mesquite Gum in $SCCO_2$

T	P	ρ	$y \cdot 10^9$	$y \cdot 10^9$	AARD
K	bar	$kg \cdot m^{-3}$	exp	cal	%
313	138	722.02	2.62 ± 0.06	2.55	8.57
	207	840.15	3.42 ± 0.05	3.18	
	276	910.12	3.90 ± 0.07	3.47	
	345	960.8	4.19 ± 0.11	3.63	
323	138	619.33	2.77 ± 0.08	2.93	6.82
	207	775.54	4.66 ± 0.05	4.48	
	276	859.05	5.67 ± 0.09	5.24	
	345	917.29	6.37 ± 0.11	5.72	
333	138	513.65	3.44 ± 0.05	3.17	8.78
	207	708.91	5.72 ± 0.09	5.99	
	276	806.98	6.95 ± 0.09	7.57	
	345	873.18	7.57 ± 0.11	8.61	
343	138	426.83	4.19 ± 0.10	3.67	6.20
	207	642.84	8.26 ± 0.11	7.72	
	276	754.85	10.59 ± 0.10	10.52	
	345	828.99	11.89 ± 0.08	12.49	

[a] Average values of mole fraction taken from triplicate runs. [b] ± uncertainties refer to standard deviation.

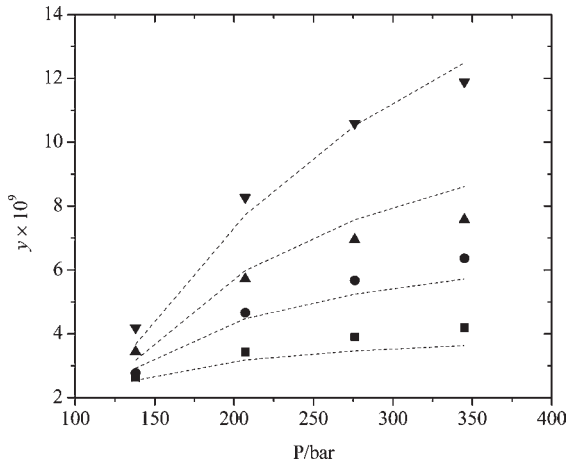

Figure 2. Effect of pressure on mole fraction solubility for MG in $SCCO_2$ at different temperatures. ■, 313 K; ●, 323 K; ▲, 333 K; ▼, 343 K; (experimental values), - - -, Bartle model prediction.

$SC\text{-}CO_2$, P is the pressure, ρ is the density of $SC\text{-}CO_2$, and T is the absolute temperature.

Figure 2 shows the experimental and calculated isothermal mole fraction of MG measured in this study as a function of equilibrium pressure. As in most solute supercritical carbon dioxide systems, the solubility increases with increasing temperature and pressure.[8] The solubility of organic compounds increases with pressure due to a $SC\text{-}CO_2$ higher density at higher pressures as a result of higher molecular interactions between the solute and the $SC\text{-}CO_2$ molecules. It also increases with temperature according to the high volatility at high temperatures.[8] In this case, pressure effect is higher than the temperature effect on the solubility of MG. The solubility of this biomaterial can be considered as low, compared with other polar but smaller compounds,[18,19] and it is similar to fatty acid solubility.[20]

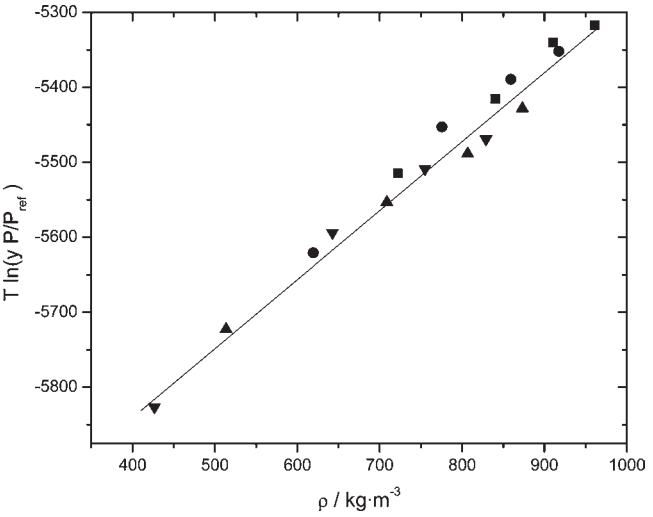

Figure 3. Experimental solubility data of MG in $SCCO_2$ at different temperatures. ■, 313 K; ●, 323 K; ▲, 333 K; ▼, 343 K; solid lines, calculation based on the Méndez-Santiago and Teja model.

The cloud point for this system was observed and determined at 413.6 bar, 343 K, and 0.1 g of MG in 17.68 g $SC\text{-}CO_2$ at 90 min. The maximum MG solubility obtained in the cloud point expressed in mole fraction in supercritical carbon dioxide was $1.173 \cdot 10^{-7}$.

In Figure 3 the data consistency is verified by the Méndez-Santiago and Teja model wherein the experimental solubility data of MG at different temperatures collapse onto a single straight line.[19] The values of A and B are equal to −6096.2 K and 0.797 $m^{-3} \cdot kg$, respectively. In this work the Méndez-Santiago and Teja model correlates the experimental solubility of MG in $SCCO_2$ with an average absolute deviation value of 46.3 %. For the regression analysis, P, ρ, and T were expressed in MPa, $kg \cdot m^{-3}$, and K, respectively.

CONCLUSIONS

The MG solubility in supercritical carbon dioxide ($SC\text{-}CO_2$) was determined for the first time through a static method at T = (313, 323, 333, and 343) K with pressures ranging from (138 to 345) bar. The solubility values in mole fraction of MG in $SC\text{-}CO_2$ ranged from $2.622 \cdot 10^{-9}$ to $4.189 \cdot 10^{-9}$, $2.768 \cdot 10^{-9}$ to $6.365 \cdot 10^{-9}$, $3.442 \cdot 10^{-9}$ to $7.570 \cdot 10^{-9}$, and $4.194 \cdot 10^{-9}$ to $11.886 \cdot 10^{-9}$ at (313, 323, 333, and 343) K, respectively. This biomaterial showed low solubility in $SC\text{-}CO_2$ based on the MG molecule polarity and high molecular weight. The experimental solubility data were successfully correlated with the Bartle and Méndez-Santiado and Teja models. Using correlations results, the MG enthalpy of sublimation was ΔH_{sub} = 57.63 $kJ \cdot mol^{-1}$. The cloud point for this system was observed and determined at 413.6 bar, 343 K, 90 min of equilibrium contact time, and 0.1 g of MG in 17.68 g $SC\text{-}CO_2$. The maximum MG solubility in $SC\text{-}CO_2$ obtained in the cloud point expressed in mole fraction was $1.173 \cdot 10^{-7}$.

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Funding Sources

This work was supported by the National Council for Science and Technology (CONACyT) of Mexico under Project 83842.

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