High-Pressure Phase Equilibria for a Styrene/CO$_2$/Polystyrene Ternary System

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ABSTRACT: To reveal the possibility of supercritical (SC)-CO$_2$-assisted devolatilization of polystyrene, the equilibrium composition data for the CO$_2$ phase in a styrene/CO$_2$/polystyrene ternary system is determined by a semistatic experimental technique. The parameters in the lattice–fluid equation of state of Sanchez and Lacombe are determined for the investigated system. The distribution coefficients of styrene between the polymer and the supercritical fluid phases are investigated experimentally at 318 and 328 K over the pressure range of 12–20 MPa. The binary interaction parameter between styrene and CO$_2$ is obtained by regression of the vapor–liquid equilibrium data. The interaction parameter between CO$_2$ and polystyrene is calculated by using the sorption data from the literature, and the interaction parameter between styrene and polystyrene is optimized by using the measured data of this study. The investigation of the distribution coefficients indicates that styrene can be removed from polystyrene by SC-CO$_2$ at near room temperature and moderately high pressures. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1938–1944, 2002

Key words: distribution coefficient; supercritical fluid; polystyrene; phase equilibrium

INTRODUCTION

During the past two decades, supercritical fluid (SCF) techniques have received increasing attention for the purification and extraction of chemicals,[1–2] including the devolatilization[3–6] and impregnation[7–8] of polymers. In polymer processes, a variety of volatile impurities, such as monomers, solvents, byproducts, and catalysts, are involved. These impurities, if left in the polymers, can adversely affect the performance of the polymers as well as constitute both environmental and health hazards. Therefore, polymer devolatilization represents an important step for commercial polymer processes. Conventional vacuum or steam-stripping methods are normally carried out at high temperature and consume a fair amount of energy. The thermal stability of the polymers may present problems because of the long time exposures to high temperatures and the polymers may give rise to undesirable off-color effects as well as potential decomposition. The success of supercritical fluid extraction in the separation of caffeine, oils, and other compounds from the matrix[9–11] shed light on utilizing this alternative technology to produce high-purity polymers with low energy costs. A comparison of a vacuum stripping method and supercritical CO$_2$-

assisted devolatilization in the removal of toluene from polystyrene was carried out by Sasaki et al.,[12] and the results indicated that the latter took less time and the volatiles were reduced to a lower level. On the other hand, sometimes additives may be impregnated into polymers to improve their performance. With the assistance of supercritical carbon dioxide, the impregnation can be more rapid and efficient in a controlled manner.[13] Two factors of concern in these processes are the distribution coefficient of solute between the polymer and the SCF phases and the swelling degree of the polymer by the SCF. The distribution coefficient is the key to determine the behavior of SCF processes. The swelling of polymers by SCFs is the reason that SCFs can plasticize polymers and increase solute diffusivities in polymers, which could be as high as a factor greater than 10,[6] thus possibly removing mass transfer limitation in polymers.[14] Attempts on experimental techniques as well as development of equations of state were carried out to determine the behavior of polymers–SCFs.

Experimentally, Shim and Johnston[15] investigated the distribution coefficients of a solute at infinite and finite concentrations between crosslinked polymers and SCFs. Inomata et al.[16] investigated the distribution coefficients of n-hexane between polybutadiene and supercritical (SC) CO$_2$. These studies utilized a high-pressure viewable cell to determine the volume change of the polymer phase and a SCF chromatographic method was used to determine the distribution coefficients of the solute between the polymer phase and the SCF phase. Kazarian et al.[17] investigated the partitioning of solutes and cosolvents between the SCF phase and the polymer phase, in which *in situ* Fourier transform IR and UV–Vis spectroscopy were used.

With respect to equations of state for the calculation of polymer–SCF solvent phase behaviors, the Sanchez–Lacomb (SL)[18–19] and the Statistical Associating Fluid Theory (SAFT)[20–21] equations have received wide attention. The SL equation is a lattice-fluid model based on the assumption of complete randomness of the distribution of molecule segments and an appropriate number of holes in the lattice. The SAFT is a perturbation equation based on the assumption that molecules consist of covalently bonded chains of segments that may contain sites capable of forming associative complexes. A mean-field attractive term is used as a perturbation of the reference equation that consists of terms accounting for the connec-
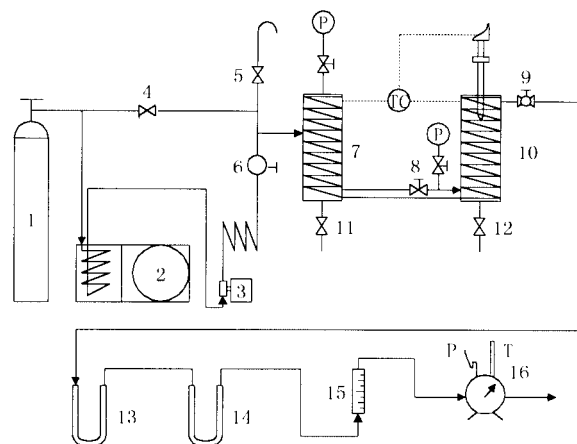

Figure 1   Schematic diagram of the experimental system. (1) CO$_2$ cylinder; (2) freezer; (3) HPLC pump; (4) reflux valve; (5) safety valve; (6, 8, 11, 12) valves; (7) surge tank; (9) heated valve; (10) extraction cell; (13, 14) collectors; (15) rotameter; (16) wet test meter.

tivity of the hard segments in the main chains, the hard-sphere repulsion of the segments, and the energy of site–site specific interactions of the segments with themselves or other segments. Further information on this can be found in the literature.[22] The SL equation has a simpler form and fewer parameters than other equations.

The understanding of the thermodynamic behavior of the solute/SCF/polymer system is essential to exploit the potential of SCF technology in polymer processes. Fundamental studies are insufficient, however, because of the expensive equipment and experimental challenges. In this study, the equilibrium composition data of CO$_2$ phase in styrene/CO$_2$/polystyrene ternary system is investigated at 318 and 328 K over the pressure range of 12–20 MPa by a simple semistatic method. The SL equation is used to correlate the results and calculate the volume change of the polymer phase. Furthermore, the distribution coefficient of styrene between the supercritical fluid phase and the polymer phase is determined.

EXPERIMENTAL APPARATUS, MATERIAL, AND METHOD

Figure 1 shows a schematic diagram of the experimental apparatus used in the present investigation to determine the equilibrium data for the SCF phase of the styrene/CO$_2$/polystyrene ternary system. This apparatus is similar to that described elsewhere.[23] The pressure is measured

at the extraction cell by using a pressure gauge with ±0.25% accuracy. The temperature is maintained to within ±0.01 K by a temperature control unit (DWK 702), made by The Sixth Automation Instrumentation Factory of Shanghai Automation Instrumentation Co., Ltd. (Shanghai, China).

Carbon dioxide provided by a local supplier with a purity of above 99.99% and styrene (analytical purity grade) with purity higher than 99.0% are used without any further purification. The polymer used is general-purpose polystyrene with $M_n = 56,599$ and $M_w/M_n = 2.836$, measured by using a Waters 150 GPC. The sample of polystyrene/styrene was prepared through adsorption[24] by enriching the polystyrene with styrene. To prepare a designed sample, a single layer of weighed polystyrene pellets were placed in a Petri dish and preheated to 343 K in a vacuum oven for 24 h. The Petri dish is then transferred to a desiccator filled with volatile liquid styrene in the lower section. The desiccator is kept at 323 K in an oven for 30 min and then allowed to stand overnight at room temperature. When the monomer concentration in the resulted sample is higher than the designed level, it will be put into the vacuum oven once again to remove the surplus volatile monomer such that a desired monomer concentration can be obtained. In this study, the polystyrene is enriched to 1 wt % styrene.

A certain amount (60 g) of prepared polystyrene pellets are deposited into a mesh stainless steel column and then placed in the 320-mL extraction cell. CO_2 from a cylinder is liquefied through a freezer and then enters a HPLC pump to be delivered to the surge tank at an elevated pressure. The pressure in extraction cell must be increased by a regulating valve (8) gradually and carefully to obtain the desired pressure at a specified temperature. About 2 h are required for the system to reach equilibrium. At that time, a heated, flow-control pressure let-down valve (9) is opened, and the solution of styrene in supercritical carbon dioxide leaves the extractor, passes through valve (9), and is expanded under the ambient pressure. Because the solubility of extracted styrene in CO_2 gas at 1 atm pressure is essentially nil, the dissolved styrene precipitates in a U-tube following the valve. A second U-tube is employed to ensure trapping of all styrene. The two U-tubes are immersed in an ice-solution bath (at about 255 K). The CO_2 gas leaves the collection system and passes through a rotameter for flow measurement and through a wet-flow meter

for flow volume integration. In this work, the flow rate is about 2.0 L/min and the sampling time is about 5 min. Because the U-tubes are initially tared, the mass of precipitated styrene is found by weighing the tubes after an experiment on an electron-optic balance (Mettler AE200) within ±0.1 mg (in the weight range 0–200 g), and the concentration of styrene in SC-CO_2 can be determined.

Determination of the equilibrium composition data of the SCF phase by using the aforesaid technique requires that the mass fraction of styrene in SC-CO_2 be maintained constant while collecting the styrene. To check whether the experimental conditions in this study satisfy this requirement, a series of experiments were conducted at a fixed pressure and temperature as well as a fixed total flow volume, but at a flow rate range of 1.0–2.0 L/min and a sampling period of 5–10 min. No difference among the results of these experiments was observed. That is, the concentration of styrene (wt %) in SCF phase during the sampling process is the same as that at the equilibrium state. This implies that in the sampling process the mass transfer of styrene between polymer and SCF phases can be neglected and the SCF phase is homogeneous. In addition, to determine the time for the ternary system to reach the equilibrium, the experiments were performed under the same temperature and pressure but sampled at 2 and 3 h, respectively. Similar results were obtained, which implies that the system reached the equilibrium between phases within 2 h.

APPLICATION OF SL MODEL TO PRESENT SYSTEM

In this study, the equation of state proposed by Sanchez and Lacombe is used to calculate the distribution coefficients because it can describe systems involving low molecular weight substances and polymers. The SL equation of state is derived from a lattice–fluid model that accounts for the compressibility of a solution, or the free-volume by introducing holes into the lattice. In reduced form, the equation of state is[13]:

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\,\tilde{\rho}] = 0 \quad (1)$$

in which

Table I   Characteristic Parameters of the SL Equation

	p^* (MPa)	T^* (K)	ρ^* (g/cm^3)	Ref.
Styrene	386.4	598	0.973	Calculation[a]
CO$_2$	574.5	305	1.510	18
Polystyrene	357	735	1.105	19

[a] Calculated according to the method proposed by ref 19.

$$\tilde{T} = T/T^*$$

$$\tilde{p} = p/p^*$$

$$\tilde{\rho} = \rho/\rho^*$$

and

$$r = Mp^*/(RT^*\rho^*) \quad (2)$$

where T^*, p^*, and ρ^* are three characteristic parameters, which can be obtained by fitting the SL equation to pure-component p-V-T data, such as saturated liquid densities and vapor pressures. M is molecular weight, ρ is density, and r is size parameter.

For mixtures, binary interaction parameters χ_{ij} are required in mixing rules:

$$p^* = \sum_j \phi_j p_j^* \sim \sum_j \sum_{i<j} \phi_i \phi_j \chi_{ij} \quad (3)$$

$$\chi_{ij} = p_i^* + p_j^* - 2(p_i^* p_j^*)^{0.5}(1 - \delta_{ij}) \quad (4)$$

where δ_{ij}, usually a small quantity, is used to adjust the deviation of the interaction from the geometric mean, and φ_i represents the closed-packed volume fraction of ith component in the mixture at the limit of zero temperature or incompressible state, and its relation to the mass fraction m_i is given by:

$$\phi_i = \frac{m_i/\rho_i^*}{\sum_j \bar{m}_j/\rho_j^*} \quad (5)$$

The chemical potential of the ith components in the mixture is

$$\frac{\mu_i}{RT} = \ln \phi_i + \left(1 - \frac{\nu_i^*}{\nu}\right) + \tilde{\rho}\nu_i^*\left(\sum_j \phi_i \chi_{ij} - \sum \sum_{i<j} \phi_i \phi_j \chi_{ij}\right)$$
$$+ r_i\left[\frac{-\tilde{\rho} + \tilde{p}_i/\tilde{\rho}}{\tilde{T}_i} + (1/\tilde{\rho} - 1)\ln(1 - \tilde{\rho})\right] + \ln \tilde{\rho} \quad (6)$$

in which $\nu^* = M/\rho^*$. When the system reaches equilibrium, the chemical potentials of each component should be equal in the two phases:

$$\mu_i^P = \mu_i^F \quad (7)$$

The superscripts P and F stand for polymer phase and supercritical phase, respectively. Then, the distribution coefficient based on mass fraction is

$$K = m_i^F m_i^P \quad (8)$$

RESULTS AND DISCUSSION

Estimation of Model Parameters

The characteristic parameters of SL model (T^*, p^*, and ρ^*) for CO$_2$ and polystyrene were reported.[18,19] The parameters for styrene are calculated according to the method proposed by Sanchez and Lacombe,[19] and the needed p-V-T data for the calculation are from the literature.[25] The calculated parameters together with those for CO$_2$ and polystyrene are listed in Table I.

For the calculations of the styrene (1)/CO$_2$ (2)/polystyrene (3) ternary system, it is assumed that polystyrene is insoluble in the fluid phase. The binary parameter δ_{12} between CO$_2$ and styrene can be determined by fitting the vapor–liquid equilibrium data from the literature.[26] The CO$_2$–polystyrene parameter is regressed from the sorption data.[27] The styrene–polystyrene parameter can be finally optimized by using the data in this study. These parameters obtained in this way are listed in Table II.

Table II   Binary Parameters

δ_{12}	δ_{13}	δ_{23}
0.033	-0.069	0.05

Styrene/CO_2 Binary System

Figure 2 shows the experimental vapor–liquid equilibrium data at two temperatures[26] and the calculated results by the SL equation based on the binary parameter obtained above. The mass fraction of styrene in CO_2 phase increases with increasing temperature (see Fig. 4). When the temperature decreases, the two-phase region becomes small and the miscibility improves. Good agreement between the experimental data and calculated results is observed and the SL equation can predict the pressure range where the one-phase region occurs.

CO_2/Polystyrene Binary System

Figure 3 shows the sorption data of CO_2 in polystyrene[27] and the calculated results by the SL equation of state based on the binary parameter obtained above. The sorption of CO_2 in polystyrene at 308 K is higher than that at 323 K. At 308 K, the state of CO_2 is closer to its critical temperature and the density of carbon dioxide becomes more liquidlike, which makes it more soluble in polystyrene. The calculation indicates that at these isotherms the amount of CO_2 sorbed in polystyrene will reach saturation levels at high pressures.
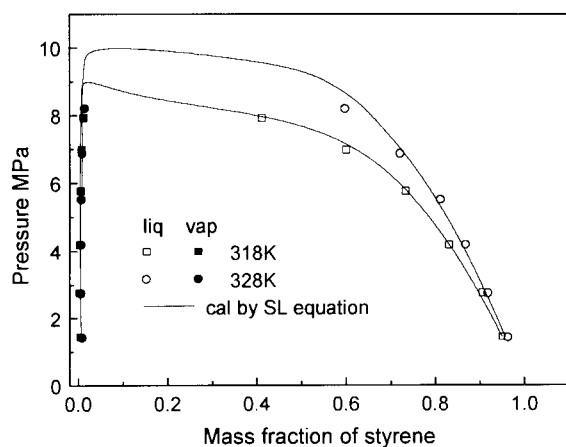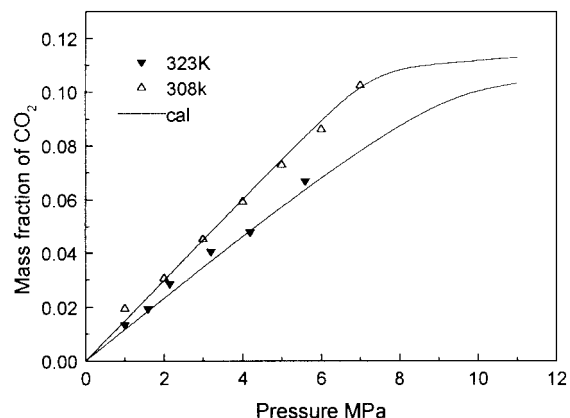

Figure 3   The sorption of CO_2 in polystyrene. Experimental data are from the literature.[27]

Styrene/CO_2/Polystyrene Ternary System

Figure 4 shows the determined equilibrium composition data of the SC-CO_2 phase at two temperatures for the present work. Also shown in Figure 4 are the predictions from the SL equation and the determined solubility of pure styrene in CO_2 from the literature.[26] The volume of the polymer phase is calculated by the SL equation and the volume change of polystyrene phase calculated is shown in Figure 5. The binary parameters of styrene-CO_2 and CO_2-polystrene are the aforesaid values in the binary systems.

In Figure 4, the mass fraction of styrene in the vapor phase in the styrene/CO_2 binary system is larger than that in the styrene/CO_2/polystyrene ternary system by about two orders of magnitude.

Figure 2   Equilibrium phase composition diagram for the styrene/CO_2 binary system. Experimental data are from the literature.[26]
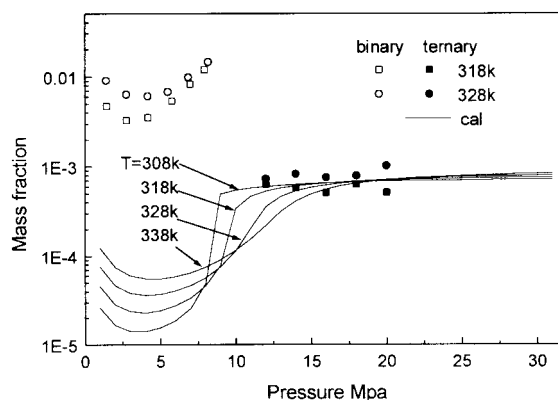
Figure 4   Mass fraction of styrene in supercritical phase. Experimental data of styrene/CO_2 binary system are from the literature.[26] Experimental data of styrene/CO_2/polystyrene ternary system are from this study.
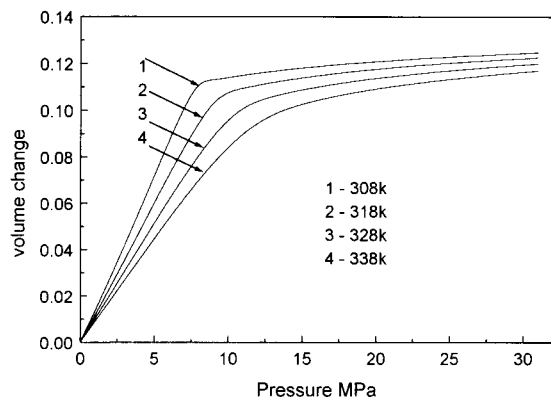
Figure 5 Volume change of polymer phase calculated by the SL equation.

This is due to phase partition control in the present ternary system. When pressures increase, the mass fraction of styrene in the CO$_2$ phase in the ternary system decreases in the low-pressure region and increases in the mediate-pressure region and reaches a limiting value at very high pressures. In the very low pressures region, the fugacity coefficient of styrene in the vapor phase is almost equal to 1, and the solubility parameter of CO$_2$ has no significant change. However, the density of CO$_2$ will increase rapidly with increasing pressure at the low-pressure region; hence, the value of mass fraction of styrene in the vapor phase decreases. At the mediate-pressures region, the solvency ability of CO$_2$ increases more rapidly than its density; therefore, the mass fraction of styrene in the CO$_2$ phase improves with increasing pressure. At high pressure, CO$_2$ becomes more liquidlike, which makes its density and solubility parameter not sensitive to pressures and hence the mass fraction of styrene in it.

There are two intersections in the isotherms in Figure 4, one at about 10 MPa and the other at about 20 MPa. The reason for these intersections is that increasing temperature in the systems influences the mass fraction of styrene in two different ways. On the one hand, higher temperature improves the volatility of styrene, thus increasing the mass fraction in the CO$_2$ phase. On the other hand, higher temperature also decreases the density and solvency ability of CO$_2$ and thus decreases the mass fraction of styrene in the CO$_2$ phase. At low and high pressures, the former is predominant; however, at mediate pressures, the latter is predominant.

The experimental data indicate that the mass fraction of styrene in the supercritical phase at

328 K is larger than that at 318 K. The possible reason for this may be that in the calculation process the polymer is assumed insoluble in CO$_2$ phase; however, experimentally, it is found that some low molecular weight polystyrene is extracted into the CO$_2$ phase, and at high temperature, more low molecular weight polymers are dissolved in SC-CO$_2$.

Therefore, the amount of styrene in the polystyrene phase (g/g polymer) at equilibrium point, M_{r1}^P, can be calculated as follows:

$$m_{r1}^P = [w_1 - (V^C - V^P)\rho^F m_1^F]/w_3 \qquad (9)$$

in which V_C is the volume of extraction cell, V_P is the volume of polymer phase, ρ^F is the density of the SCF phase, w_1 is total mass weight of styrene, and w_3 is mass weight of polystyrene. The results are shown in Figure 6, which shows that at 318 K the residual styrene in the polymer phase is less dependent on the pressure than that at 328 K for the range of experimental conditions.

Consequently, the mass fraction-based distribution coefficients of styrene between the supercritical fluid and the polymer phase can be obtained

$$m_1^P = [w_1 - (V^C - V^P)\rho^F m_1^F]w^P \qquad (10)$$

$$K = \frac{m_1^F}{m_1^P} \qquad (11)$$

where w^P is the mass weight of polymer phase calculated by the SL equation. The results are shown in Figure 7. Because the residual styrene in the polymer phase is not very sensitive to pressure and temperature, the curves of the distribu-
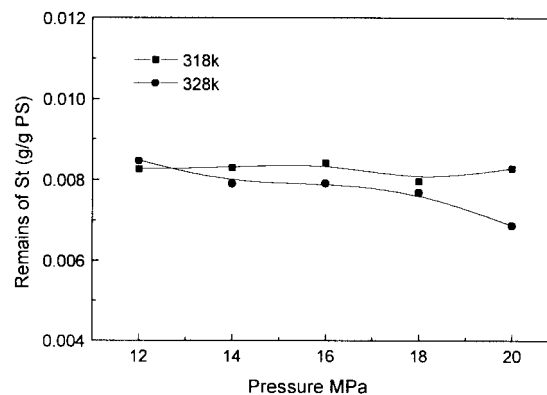

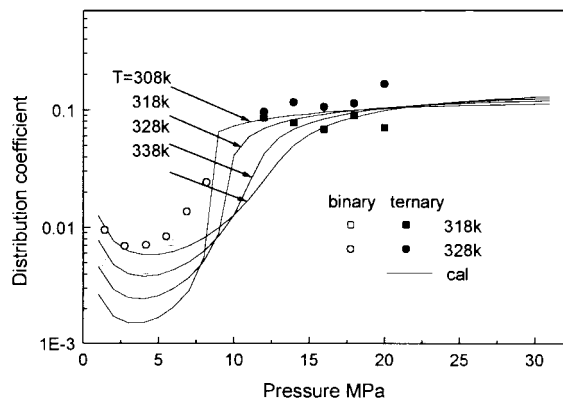
Figure 6 Residual styrene in the polymer phase.

Figure 7 Distribution coefficients of styrene between the supercritical phase and the dense phase. Experimental data of styrene/CO_2 binary system are from the literature.[26] Experimental data of styrene/CO_2/polystyrene ternary system are from this study.

tion coefficients have similar shapes to the curves of mass fraction of styrene in the CO_2 phase. Good agreement within the same order of magnitude between experimental data and calculated results was observed. More detailed investigation is required to provide necessary data for the design of devolatilization processes. However, this study has indicated that, by an appropriate design of the operation conditions, the residual styrene in polystyrene could reach a low level at near room temperatures and moderately high pressure.

CONCLUSION

A simple experimental method is used to determine the mass fraction of styrene in the supercritical phase for the styrene/CO_2/polystyrene ternary system. The model parameters of the Sanchez–Lacombe equation of state are calculated for the system involved. Furthermore, the distribution coefficient of styrene between polystyrene and supercritical fluid phases was investigated. The results suggest that the devolatilization of polystyrene assisted by SC-CO_2 could be realized at mild temperatures and moderately high pressures.

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