Solubility of Supercritical Carbon Dioxide in Polyethylene Glycol 4000

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Abstract—We present the experimental results on the solubility of supercritical carbon dioxide in polyethylene glycol of molecular weight 4000, namely, the isotherms at $T = 313$, 323, and 333 K in the pressure range of $P = 10-35$ MPa. Based on the Sanchez–Lacombe lattice model, the results of solubility are described and the empirical parameters of the binary intermolecular interaction in the system of supercritical CO_2-polyethylene glycol 4000 are obtained.

INTRODUCTION

Currently, the chemical and pharmaceutical industry is increasingly focused on the use of biodegradable polymers. This is associated with environmental aspects and the effectiveness of new pharmaceutical compounds. In some technological processes, the granulation of biodegradable polymers to micro- and nanosizes, the obtaining of porous structures, or the introduction of other substances into the polymer volume are necessary. Conventional methods of grinding, foaming, and impregnation have limitations associated with the low temperature of melting and degradation of polymers. In distinction from them, the supercritical fluid (SCF) methods are devoid of these shortcomings [1, 2]. For example, the process of preparing particles of gas-saturated solutions (PGSS) is based on the dissolution of pressurized gas in a molten material and stirring under pressure in an extractor to saturation. Typically, polymers can dissolve the compressed gas in the volume of up to 50% of their weight. Then, the pressurized gas is expanded through a microscale channel, and solid particles are formed resulting from a very rapid decrease in temperature caused by the expansion of the SCF.

The PGSS process works well for the production of polymer particles and for encapsulating active ingredients into a polymeric carrier. It can also be used to create particles filled with a liquid active substance. From a theoretical point of view, the solubility of supercritical fluid in the polymer plays a key role and affects such mechanisms in the formation of particles as nucleation and growth of particles in a supercooled liquid. When released from the polymer under normal conditions, the supercritical fluid forms a porous structure in it, thereby increasing the size and the specific surface area of the resultant particles. The existing theoretical models of PGSS do not account for this phenomenon, which leads to substantial differences between theory and experiment [3].

The phenomenon of dissolution of a SCF in a polymer can be used for introduction of ingredients like plasticizers, colorants, flame retardants, pharmaceutical substances, and others into the volume of the polymer.

To implement all the aforementioned processes based on the SCF methods, reliable data on the solubility of supercritical fluids in polymers [4, 5] and a mathematical description of these phenomena [6, 7] are required.

EXPERIMENTAL

The schematic diagram of the setup for the study of solubility is shown in Fig. 1. The solubility was determined by a static method. This setup permits experiments in the pressure range of 6–40 MPa and the temperature range from 293 to 573 K.

Before starting the experiment, the polymer was loaded into extractor *10* and then the extractor was weighed. Next, thermostat *3* is turned on to cool the heads of pump *6* and heat exchanger *4*. The process of thermosetting is continued until the coolant temperature values reaches −5°C.

The extractor temperature was set and maintained by the control unit *9*. Carbon dioxide from cylinder *1* entered the cooling heat exchanger *4* through drying filter *2* at a pressure of 5–6 MPa. Then, liquid CO_2 enters pump *6* through heat exchanger *4*, where it is compressed to a given pressure. After that, carbon dioxide is fed to extractor *10* with volume $V = 3 \times 10^{-5}$ m³, which was placed inside the air heating thermostat *13*. Carbon dioxide passes into a supercritical state upon heating and begins to saturate the test substance. Valve *8* is in the open position in order to maintain a constant pressure in the extractor.
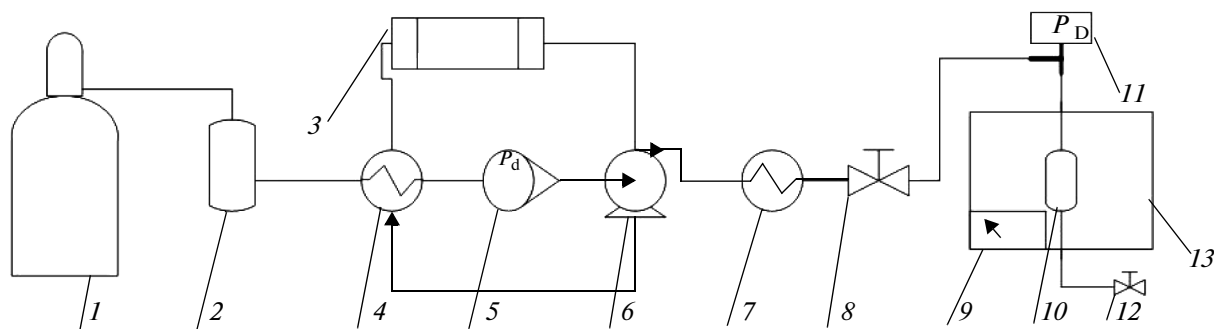
Fig. 1. Schematic diagram of the experimental setup: (*1*) cylinder with carbon dioxide, (*2*) filter-dehydrator, (*3*) thermostat, (*4*) cooling heat exchanger, (*5*) flow meter, (*6*) pump, (*7*) electric heater, (*8*) valve, (*9*) pressure and temperature control system, (*10*) extraction cell, (*11*) gauge, (*12*) throttle valve, and (*13*) heating thermostat.

The experiment lasted for at least 5 h until the complete saturation of polyethylene glycol (PEG) with carbon dioxide. The extractor with the loaded polymer was weighed on an analytical balance with an accuracy of ±0.0001 g before and after the experiment. The difference in the weight before and after the experiment shows the amount of carbon dioxide dissolved in the polymer. The solubility of supercritical carbon dioxide in polyethylene glycol is calculated by the equation

$$Y^{exp} = \frac{m_{CO_2}}{m_{CO_2} + m_{PEG}},$$

where m_{CO_2} is the weight of carbon dioxide dissolved in the polymer and m_{PEG} is the weight of PEG 4000.

For weighing the extractor before and after the experiment, we used a VIBRA HTR-220CE analytical balance (Shinko).

In this paper, we used polyethylene glycol with the molar weight of 4000 g/mol (Panreac, Spain) as a polymer. Polyethylene glycol is soluble in many organic solvents, for example, benzene, carbon tetrachloride, chloroform, dimethylformamide, and acetonitrile. It is also highly soluble in water. The solubility decreases significantly with the increasing molecular weight of the polymer. Depending on the average molecular weight, the polymer may be a viscous liquid, gel, or solid. Polyethylene glycol is nontoxic and may be included in food products and pharmaceuticals.

Carbon dioxide with a purity of 99% (*GOST* (State Standard) *8050-85*) was used as a supercritical fluid. Carbon dioxide is a colorless gas with a sour odor, heavier than air; it is a product of the complete combustion of carbon. The critical parameters of CO_2 are $T_{cr} = 303.9$ K and $P_{cr} = 7.38$ MPa. Carbon dioxide is selected for the SCF processes because it is imflammable, explosion-safe, nontoxic, and readily available [8].

RESULTS AND DISCUSSION

The investigation of the solubility of supercritical carbon dioxide in PEG 4000 was carried out at temperatures of 313, 323, and 333 K and pressures of 10–

35 MPa. The results of the study of solubility in supercritical carbon dioxide in PEG 4000 as a function of pressure and temperature are presented in Table 1.

It is seen from the table that with increasing pressure and temperature, the solubility of supercritical carbon dioxide increases. This is because with an increase in the thermodynamic parameters, the density of supercritical carbon dioxide tends to the density of liquid carbon dioxide, wherein the kinematic viscosity and the diffusion coefficient are close to those of carbon dioxide in the state of an ideal gas.

MATHEMATICAL SIMULATION OF THE SOLUBILITY OF SUPERCRITICAL CARBON DIOXIDE IN PEG 4000

To describe the thermodynamic properties of the supercritical solvent and the phase equilibria of liquid–vapor and liquid–liquid–vapor in the polymer–solvent system, the Sanchez–Lacombe lattice model can be applied [9], that is,

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0, \quad (1)$$

where $\tilde{T}, \tilde{P}, \tilde{\rho}$ are the values of the reduced temperature, pressure, and density and r is the number of occupied lattice sites. These parameters for pure sub-

Table 1. Solubility of supercritical CO_2 in PEG 4000

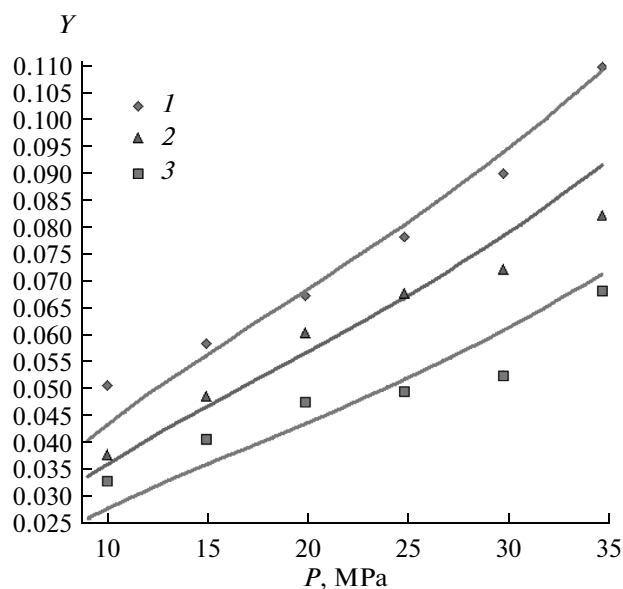| P, MPa	Y^{exp}	P, MPa	Y^{exp}	P, MPa	Y^{exp}
$T = 313$ K		$T = 323$ K		$T = 333$ K	
10	0.032	10	0.042	10	0.05
15	0.04	15	0.056	15	0.058
20	0.047	20	0.06	20	0.067
25	0.049	25	0.0675	25	0.078
30	0.052	30	0.072	30	0.09
35	0.068	35	0.082	35	0.11

Fig. 2. Solubility of carbon dioxide in PEG 4000: T = (*1*) 313, (*2*) 323, and (*3*) 333 K; lines represent the calculated data.

stances can be determined from the following equations:

$$\tilde{P} = P/P^*, \quad P^* = \varepsilon^*/\upsilon^*,$$

$$\tilde{T} = T/T^*, \quad T^* = \varepsilon^*/R,$$

$$\tilde{\rho} = \rho/\rho^*, \quad \rho^* = M/(r\upsilon^*),$$

$$\tilde{\upsilon} = \upsilon/\upsilon^* \text{ or } \tilde{\upsilon} = 1/\tilde{\rho},$$

where R is the universal gas constant, υ^* is the volume of the monomer in the convoluted state, ε^* is the interaction energy of one monomer with the solvent, and M is the molar weight.

The cross term of the reduced pressure [9] is determined as

Table 2. Characteristic parameters of substances [10]

Substance	T^*, K	P^*, bar	ρ^*, kg/m^3	r
CO$_2$	314.8	4388	1416	5.286
PEG-4000	658	485	1182	300

Table 3. Parameters of the binary interaction of the mathematical model

T, K	A_0	B_0
313	1.28	0.135
323	1.25	0.136
333	1.23	0.137

$$p_{ij}^* = \left\{ p_i^* p_j^* \right\}^{1/2} \left\{1 - \delta_{ij}\right\},$$

where p_i^* and p_j^* are the characteristic pressures of the ith and jth components, respectively, and δ_{ij} is the binary interaction parameter, which is determined as a function of temperature

$$\delta_{ij} = A_0 + B_0 T. \tag{2}$$

The parameters A_0 and B_0 are found by minimizing the deviations of the experimental data from the calculated values.

The original Sanchez–Lacombe equation (Eq. (1)) together with the above combination rules leads to the equation for the chemical potential

$$\mu_1 = RT\left\{\ln \varphi_1 + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + r_1^0 \tilde{\rho} X_1 \varphi_2^2\right\} + r_1^0 RT$$

$$\times \left\{-\tilde{\rho}/\tilde{T}_1 + \tilde{p}_1 \tilde{\upsilon}/\tilde{T}_1 + \tilde{\upsilon}[(1 - \tilde{\rho})\ln(1 - \tilde{\rho}) + \tilde{\rho}\ln\tilde{\rho}/r_1^0]\right\}.$$

The conditions of equilibrium between the two phases of the binary system can be written through the equality of the chemical potentials of the component in the two phases, that is,

$$\mu_1(T, P, \varphi_1') = \mu_1(T, P, \varphi_1''), \tag{3}$$

$$\mu_2(T, P, \varphi_2') = \mu_2(T, P, \varphi_2''), \tag{4}$$

where the prime and double prime indicate different phases. The value of the chemical potential can be expressed as a function that depends only on density $\tilde{\rho}$, which in turn depends on T, P, and φ. Density $\tilde{\rho}$ is determined by the solution of Eq. (1). The simultaneous solution of Eqs. (3) and (4) yields the volume fractions of each component in any phase, including the fraction of supercritical carbon dioxide in PEG 4000.

The optimization of the calculation model is reduced to finding adjustable parameters A_0 and B_0 in Eq. (2). For this purpose, the error function is minimized in the solubility of the SCF in the polymer as

$$F = \sqrt{\frac{\sum_{i=1}^{N}(Y^{\text{calc}} - Y^{\text{exp}})^2}{Q^{\text{exp}}}},$$

where Q^{exp} is the number of data points and Y^{calc} is the estimated weight fraction of carbon dioxide in PEG 4000, which is determined by the volume fractions φ.

This mathematical model described the solubility of supercritical carbon dioxide in the molten PEG 4000 (Fig. 2). The characteristic parameters of the substances are taken from [10] and given in Table 2, and the model parameters A_0 and B_0 are presented in Table 3.

It is seen from Fig. 2 that the Sanchez–Lacombe equation of state describes adequately the solubility in the system of CO$_2$–PEG 4000.

CONCLUSIONS

New experimental results on the solubility of supercritical carbon dioxide in PEG 4000 at a pressure of $10-35$ MPa and temperatures of 313, 323, and 333 K are obtained. It is found that with increasing temperature and pressure, the solubility of supercritical carbon dioxide in PEG 4000 grows. The empirical parameters of the binary intermolecular interaction in the system of supercritical CO_2–polyethylene glycol 4000 are obtained using the Sanchez–Lacombe equation of state. The mean square error of the deviation of the experimental data on solubility with respect to the calculated values does not exceed 6.3%.

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