

Dilation and Solubility in Carbon Dioxide+ Poly(vinyl acetate) System at High Pressures

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Dilation and solubility in carbon dioxide + poly(vinyl acetate) (PVAc) system were measured at temperatures of 313.2 K and 323.2 K and pressures up to 9 MPa. The dilation of PVAc was measured using a high-pressure optical cell and a cathetometer. Measurement of CO₂ solubility in PVAc was performed using a pressure decay method. The solubility data were correlated using the Schotte equation of state with characteristic parameters for each component determined by best-fit-to P-v-T data or saturated properties of each pure substance. Prediction of PVAc dilation was also made using the value of a binary parameter, k_{ij} , obtained from the correlation of the solubility data. The prediction gave a fairly good agreement with the experimental data at low pressures, although some discrepancies were seen between experimental and predicted values at high pressures.

1. Introduction

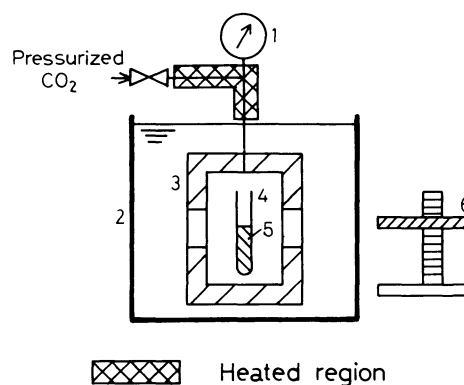
Applications of the supercritical fluid extraction techniques have become widespread in many fields. The present authors have examined the removal of low-molecular weight impurities from polymers using this technique^{1),2)}. Basic properties, such as phase equilibria and pressure-volume-temperature relationships, are needed for explaining the mechanism of this removal method and for rational design of the process. In this work, dilation and solubility in the carbon dioxide + poly(vinyl acetate) (PVAc) system were measured at temperatures of 313.2 K and 323.2 K and pressures up to 9 MPa. The experimental data were compared with calculated results by the Schotte equation of state, which is applicable to such an asymmetric system as the supercritical fluid + polymer system.

2. Experimental Apparatus and Procedure

2.1 Measurement of Dilation of PVAc Caused by the Dissolution of CO₂

The dilation of PVAc was measured by a high-pressure optical cell. In Fig. 1 is shown a schematic diagram of the experimental apparatus. A PVAc sample molded in a cylindrical shape was put into a glass tube (2 mm i.d.) mounted

vertically in the optical cell. The relationship between height and volume of a sample filled in the glass tube was calibrated by mercury, in advance, and a linear relationship was obtained. The cell was initially evacuated and then pressurized with CO₂. The PVAc sample softened by the dissolution of CO₂ and then filled up openings between the sample and the tube. The height of the PVAc sample and pressure were measured by a cathetometer and a Bourdon tube pressure gauge, respectively, until those values became constant.



1: Pressure gauge, 2: Thermostated water bath, 3: Optical cell, 4: Glass tube, 5: Sample polymer, 6: Cathetometer

Fig. 1 Schematic Diagram of the Volume Dilation Apparatus

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The volume dilation, ξ , was defined by

$$\xi = \frac{V^{P_M} - V^{P_0}}{V^{P_0}} \times 100 \quad (1)$$

where V^{P_M} and V^{P_0} are the volumes of the diluted and undiluted PVAc samples, respectively, at the system temperature and pressure.

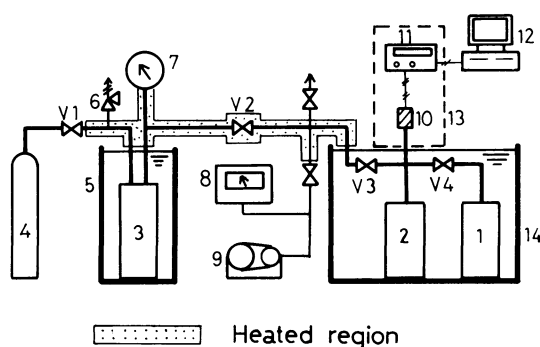
2.2 Measurement of Solubility

Measurement of CO₂ solubility in PVAc was made using a pressure decay method. In Fig. 2 is shown a schematic diagram of the experimental apparatus, which is similar to one designed by Koros³⁾. A PVAc film (100×30×0.5 mm) was placed in the solubility cell (1). After air in the apparatus was evacuated with the rotary vacuum pump, CO₂ was introduced into the solubility cell(2). The temperature and pressure were measured to evaluate the amount of CO₂ introduced. With opening of the valve between the solubility cells (1) and (2), dissolution of CO₂ into the sample polymer began. The change of pressure with dissolution of CO₂ was measured by a precise semiconductor pressure sensor (Tsukasa Sokken, Inc., type PX-1A, Precision ±5 kPa) until the pressure became constant.

The relationship between the pressure at time t , P_t , and amount of CO₂ in gas phase, n^{G_t} , is given by

$$n^{G_t} = \frac{P_t(V^I + V^{II} - V^{P_M})}{ZRT} \quad (2)$$

where V^I and V^{II} are volumes of the solubility cells (1) and (2), V^{P_M} is volume of the PVAc sample in



1: Solubility cell (1), 2: Solubility cell (2), 3: Liquefied CO₂ reservoir, 4: CO₂ cylinder, 5: Thermostated water bath, 6: Relief valve, 7: Pressure gauge, 8: Vacuum gauge, 9: Vacuum pump, 10: Precise semiconductor pressure sensor, 11: Digital multimeter, 12: Computer, 13: Thermostated air bath, 14: Thermostated water bath

Fig. 2 Schematic Diagram of the Solubility Apparatus

which CO₂ is dissolved, Z is compressibility factor of gas phase, R is gas constant and T is absolute temperature. The gas phase compressibility factor was calculated by IUPAC⁴⁾ equation of state. The volumes of the solubility cells were determined by a method used by Koros³⁾; $V^I=24.24$ ml and $V^{II}=40.70$ ml. V^{P_M} was calculated with smoothed values of the volume dilation data. The amount of CO₂ dissolved in PVAc at equilibrium state, n^{P_∞} , is determined from the change of the amount of CO₂ in gas phase, as follows:

$$n^{P_\infty} = n^{G_0} - n^{G_\infty} \quad (3)$$

where n^{G_0} is the total amount of CO₂ introduced in the apparatus and n^{G_∞} is the amount of CO₂ in gas phase at equilibrium state.

2.3 Materials

PVAc ($T_g=303$ K, $\bar{M}_v=1.58 \times 10^5$) was obtained from Aldrich Chemical Co. Inc. CO₂ (purity 99.9%) was obtained from Chugoku Teisan, Inc.

3. Results and Discussion

3.1 Experimental Results

The experimental results on the CO₂-induced dilation of PVAc and CO₂ solubility in PVAc are shown in Figs. 3 and 4, respectively. Numerical data are listed in Tables 1 and 2. The dilation of PVAc as well as CO₂ solubility was greater at 313.2 K than at 323.2 K. The broken line in Fig. 4 represents the experimental data obtained using a piezoelectric-quartz sorption method by Wang *et al.*⁵⁾ Some discrepancies between the experimental data of this work and those of Wang *et al.* were observed at high pressures. The reason for this has not become clear. However, this may be partially due to the difference in thicknesses of polymer samples; about 0.5 mm in this work and

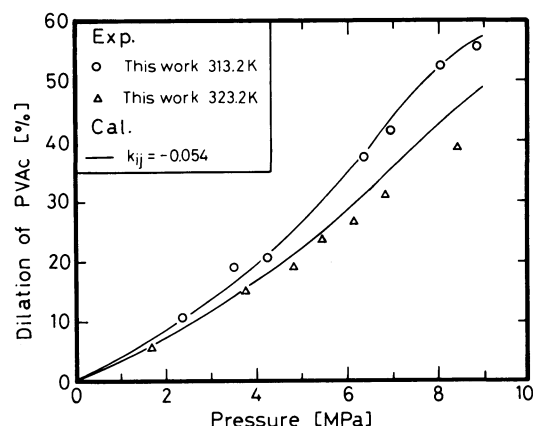


Fig. 3 Volume Dilation of PVAc with Dissolution of Carbon Dioxide at 313.2 K and 323.2 K

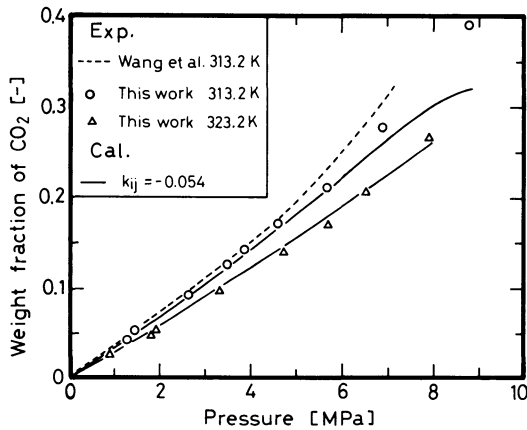


Fig. 4 Solubility of Carbon Dioxide in PVAc at 313.2 K and 323.2 K

Table 1 Volume Dilatation of PVAc

P [MPa]	ξ [%]	P [MPa]	ξ [%]
313.2 K		323.2 K	
2.374	10.09	1.725	5.99
3.522	19.36	3.793	15.21
4.210	20.69	4.804	19.12
6.364	37.22	5.444	23.97
6.955	41.88	6.187	25.85
8.020	52.74	6.850	31.18
8.893	55.44	8.403	39.01

Table 2 Solubility of Carbon Dioxide in PVAc

P [MPa]	w [-]	P [MPa]	w [-]
313.2 K		323.2 K	
1.258	0.0416	0.898	0.0254
1.449	0.0532	1.819	0.0485
2.650	0.0936	1.906	0.0533
3.467	0.1264	3.309	0.0978
3.846	0.1429	4.698	0.1397
4.583	0.1723	5.655	0.1696
5.659	0.2123	6.519	0.2073
6.885	0.2786	7.861	0.2668
8.755	0.3909		

about 0.1 μm in the work of Wang *et al.*⁵⁾.

3.2 Correlation of Solubility Data by the Schotte Equation of State

For the calculation of vapor-liquid equilibria of polymer solutions, Schotte⁶⁾ has modified the Harmony⁷⁾ equation of state, as follows:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{RT^*}{P^*Mv^*} \left\{ 1 - \frac{1}{\tilde{v}^{1/3}} \right\} + \frac{1}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (4)$$

$$\tilde{P} = P/P^*, \quad \tilde{v} = v/v^*, \quad \tilde{T} = T/T^* \quad (5)$$

where P^* , v^* , and T^* are characteristic parameters. The mixing rules used are

$$\frac{1}{Mv^*} = \sum_{i=1}^n \frac{\phi_i}{M_i v_i^*} \quad (6)$$

$$P^* = \sum_{i=1}^n \sum_{j=1}^n \phi_i \phi_j P_{ij}^* \quad (7)$$

$$\frac{P^*}{T^*} = \sum_{i=1}^n \frac{\phi_i P_i^*}{T_i^*} \quad (8)$$

$$P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{1/2} \quad (9)$$

$$\phi_i = \frac{w_i v_i^*}{\sum_{j=1}^n w_j v_j^*} \quad (10)$$

where w_i is the weight fraction of component i and k_{ij} is the interaction parameter between components i and j .

The characteristic parameters for each component, P_i^* , v_i^* and T_i^* , were determined by best-fit of Eq. (4) to saturated properties (saturated vapor pressure P^s , saturated vapor density ρ_v^s and saturated liquid density ρ_L^s) or P-v-T data of each substance, and are shown in Table 3. Although each parameter value slightly depended on temperature, for the sake of brevity, only T^* was treated as a temperature-dependent parameter in this work.

The solubility of CO₂ in PVAc was correlated using Eqs. (4)–(10), assuming that PVAc did not dissolve in gas phase. In this correlation, k_{ij} in Eq. (9) was treated as a fitting parameter. Correlated results are shown as solid curves in Fig. 4. The agreement between the experimental and correlated results was satisfactory at low pressures. However, at 323.2 K, the correlated values deviated from the experimental values at high pressures.

The prediction of PVAc dilatation was carried out using the value of k_{ij} obtained from the correlation

Table 3 Characteristic Parameters of Schotte Equation of State

	Carbon dioxide	PVAc
P^* [MPa]	328.3	378.8
T^* [K]	2,175–1,826 (1– T/T_c) +2,755 (1– T/T_c) ²	11,275–10.40 T
v^* [$\text{m}^3 \cdot \text{kg}^{-1}$]	6.425×10^{-4}	7.449×10^{-4}
Correlated properties	P^s, ρ_v^s, ρ_L^s ⁴⁾	P-v-T ⁸⁾
	250–300 K	313–373 K
	1.78–6.70 MPa	0.1–30 MPa
Error*	P^s : 1.12% ρ_v^s : 6.07% ρ_L^s : 5.03%	v : 0.020%

$$* \text{ Error} = \frac{1}{n} \sum_{i=1}^n \left| \frac{(\text{cal.})_i - (\text{lit.})_i}{(\text{lit.})_i} \right| \times 100$$

of the solubility data. The results were compared with the experimental data in Fig. 3. The predicted results were in good agreement with the experimental data at 323.2 K. However, slight deviations between the predicted and the experimental results were observed at 313.2 K. These results may indicate that the Schotte equation of state can not predict both phase equilibria and P-v-T relationships of mixtures accurately, and it is needed to develop more accurate equations of state and mixing rules.

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Nomenclatures

k_{ij}	: interaction parameter between components i and j	[—]
M	: molecular weight	[—]
M_v	: viscosity average molecular weight	[—]
n	: amount of carbon dioxide	[mol]
P	: pressure	[MPa]
R	: gas constant (8.314)	[J·mol ⁻¹ ·K ⁻¹]
T	: absolute temperature	[K]
T_c	: critical temperature of carbon dioxide	[K]
T_g	: glass transition temperature of polymer	[K]
V	: volume	[m ³]
v	: specific volume	[m ³ ·kg ⁻¹]
w	: weight fraction	[—]
Z	: compressibility factor of gas phase	[—]
ξ	: volume dilation of polymer defined by Eq. (1)	[—]

ρ	: molar density	[mol·m ⁻³]
ϕ	: segment fraction defined by Eq. (10)	[—]
<Superscripts>		
P	: polymer phase	
G	: gas phase	
S	: saturated property	
I	: solubility cell (1)	
II	: solubility cell (2)	
~	: reduced property	
*	: characteristic parameter value	
<Subscripts>		
i, j	: components i and j	
L	: liquid phase	
M	: mixture of carbon dioxide and polymer	
t	: time	
V	: vapor phase	
0	: initial state or pure polymer	
∞	: equilibrium state	

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高圧下における二酸化炭素+ポリ酢酸ビニル系の膨潤率 および溶解度の測定と相関

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著者らはポリマー中の低分子不純物の分離への超臨界流体抽出法の適用性を検討してきた^{1),2)}。この研究において除去機構を解明し, 除去実験結果を理論的に整理するためには, 超臨界流体の溶解に伴うポリマーの膨潤やポリマー中への超臨界流体の溶解度などの基礎物性が不可欠である。そこで本研究では温度 313.2 K および 323.2 K, 圧力 9 MPa 以下において二酸化炭素+ポリ酢酸ビニル系の膨潤率および溶解度の測定を行った。また, Schotte⁶⁾ の状態方程式による実験値の相関を行い, その適用性について検討した。

膨潤率の測定は, Fig. 1 に示す様な窓付き高圧セルとカセットメーターを用いて行った。また, 溶解度の測定は, Koros³⁾ の装置を参考にして製作した圧力降下法に基づく装置 (Fig. 2) を用いて行った。Table 1 および Fig. 3 に二酸化炭素の溶解に伴うポリ酢酸ビニルの膨潤率の測定結果を示す。また, Table 2 および Fig. 4 にポリ酢酸ビニル中への二酸化炭素の溶解度の測定結果を示す。膨潤率および溶解度も温度 313.2 K の方が温度 323.2 K での値よりも大きくなった。

次に, Schotte の状態方程式を用いて溶解度の相関を行った。Schotte の状態方程式中の各物質の特性パラメーター P_i^* , v_i^* , T_i^* は, 各々の物質の飽和物性あるいは P-v-T 関係を相関することにより決定した。決定されたパラメーターの値と相関に使用した物性を Table 3 に示す。溶解度の相関に際しては Eq. (9) 中の k_{ij} をフィッティングパラメーターとして取り扱った。Fig. 4 に溶解度の相関結果を示す。比較的低压においてはほぼ良好な相関が得られたが, 温度 323.2 K, 圧力 7 MPa 以上では相関値と実験値の差が大きくなった。また, 溶解度を相関して得られた k_{ij} の値を用いて膨潤率を推算した結果を Fig. 3 に示す。温度 323.2 K ではほぼ良好な推算結果が得られたが, 温度 313.2 K においては高圧領域で実験値と推算値の差異が大きくなった。これらの結果は Schotte の状態方程式では溶解度と混合物の P-v-T 関係を両者を厳密に表現するには不十分であることを示していると思われ, 今後より良い状態方程式および混合側の開発を行う必要があるものと考えられる。

Keywords

Thermodynamics, Equation of state, Dilation, Solubility, Carbon dioxide, Poly(vinyl acetate)