

## Supercritical Carbon Dioxide Extraction of Benzene in Poly (vinyl acetate) and Polystyrene (Part 2)

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The supercritical fluid extraction (SCFE) of benzene from poly(vinyl acetate) (PVAc) or polystyrene (PS) has been examined using supercritical carbon dioxide (SC-CO<sub>2</sub>) at temperature of 313 K and pressure of 7.95 MPa. The amount of extracted benzene was quantitatively measured continuously, using ultraviolet (UV) spectrophotometer. From the experiments, it is found that when the pressure in the cell is reduced, the CO<sub>2</sub> dissolved in the polymer is quickly released with benzene, which is highly effective in benzene removal. In addition, the diffusion coefficients of benzene in PVAc and PS were calculated from correlation of the experimental data. The calculated diffusion coefficients of benzene in PVAc, which dissolved CO<sub>2</sub>, lie between the diffusion coefficients of benzene in SC-CO<sub>2</sub> and those in PVAc in the absence of CO<sub>2</sub>. The calculated diffusion coefficients of benzene in PS were about one order of magnitude below those in PVAc. These results confirm that the plasticization effect of PVAc or PS by dissolved CO<sub>2</sub> closely relates to the diffusion rate of benzene.

### 1. Introduction

Application of SCFE techniques has become widespread in many fields. Krukoniš *et al.*<sup>1),2)</sup> introduced the fractionation of low vapor pressure oils and polymers, redistribution of polymer particle size, and extraction of volatile substances from polymers, as examples of the SCFE technique, to the polymer industry. Copelin<sup>3)</sup> proposed a patent for removal of oligomeric cyclic ethers from their polymers.

The removal of volatile substances, such as unreacted monomers, reaction by-products and solvents, from polymers, is one of the most important operations in their manufacture. The impurities are usually removed by vacuum or inert gas stripping of polymer melts or polymer particles. Because the operating temperature is usually raised to accelerate the diffusion of the impurity in polymer, some degradation of the polymer can occur. Hence, the SCFE technique, which is typically carried out near room temperature, is attractive for the removal of impurities in such thermally labile polymers.

Separation of benzene from two polymers of PVAc and PS has been carried out using supercritical carbon dioxide by the authors<sup>4)</sup>, to test the applicability of the SCFE technique and examine the mechanism of the method. In this work, the

experimental apparatus was improved to measure the extraction rate; namely the UV spectrophotometer was mounted in the outlet stream from extraction cell, which enabled us to measure the gas composition continuously under high pressures. This paper outlines reports on the experimental results for benzene removal from PVAc and PS and their theoretical treatments in terms of the mass transfer model reported in the previous paper<sup>4)</sup>.

### 2. Experimental

#### 2.1 Experimental Apparatus and Procedure

A schematic diagram of the SCFE apparatus is shown in **Fig. 1**. It consists of the following sections: (a) CO<sub>2</sub> compression, (b) extraction cell, (c) UV spectrophotometer, (d) data processing, and (e) control and measurement of CO<sub>2</sub> flow rate. A polymer disk which dissolved a known quantity of benzene was placed in the extraction cell. Then, SC-CO<sub>2</sub> was passed through the cell and the benzene was extracted from the polymer disk. Average concentrations of benzene in the outlet stream from the extraction cell were quantitatively measured using the UV spectrophotometer (Japan Spectroscopic Co., Ltd., model 875-UV). After the extraction at high pressures, pressure in the cell was reduced to atmospheric pressure. Finally, the concentration of benzene in sample polymers was determined by gas chromatograph (Shimadzu Seisakusho Co., model GC-4BPTF).

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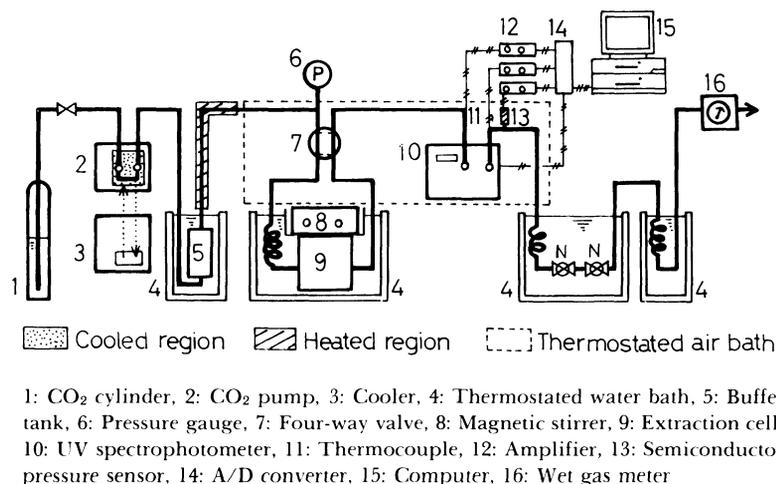


Fig. 1 Schematic Diagram of Supercritical Fluid Extraction Apparatus

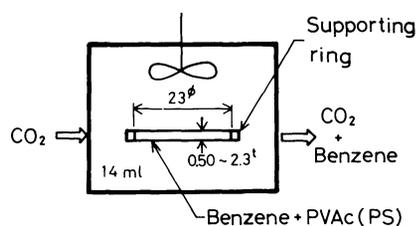


Fig. 2 Schematic Drawing of Extraction Cell

A schematic drawing of the extraction cell (internal volume 14 ml) is shown in Fig. 2. The SC-CO<sub>2</sub> phase in the extraction cell was stirred by a magnetic stirrer to minimize mass transfer resistance of benzene in the SC-CO<sub>2</sub> phase. Mass transfer of benzene in the polymer disk was limited only in direction of polymer thickness by the supporting ring.

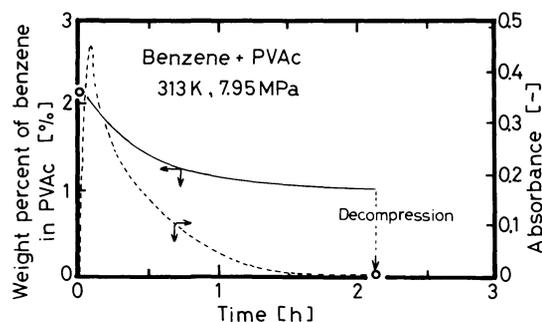
PVAc ( $T_g=303$  K,  $\bar{M}_v=1.58 \times 10^5$ ) and PS ( $T_g=373$  K,  $\bar{M}_v=2.18 \times 10^5$ ) were obtained from Aldrich Chemical Co. Inc. and from General Science Co., respectively. Benzene (Katayama Chemicals) was of special-grade purity (over 99.5%) and was used without further purification.

## 2.2 Determination of Calibration Curve for UV Spectrophotometer

The relationship between absorbance  $A$  and molar concentration of solute  $c$  is known as Lambert-Beer's law, *viz.*

$$A = \epsilon bc \quad (1)$$

where  $\epsilon$  is the absorptivity, and  $b$  is the light path length. In this work, the calibration curve was determined by a method similar to Rössling's<sup>9</sup>. Namely,  $\epsilon b$  was evaluated by the relationship



2  $l=1.25$  mm, O: analysis using GC, —: analysis using UV

Fig. 3 Typical Plots of Absorbance *vs.* Time and Concentration of Benzene in PVAc *vs.* Time at 313 K and 7.95 MPa

between benzene concentration in cyclohexane solvent and respective absorbance under temperature and pressure of the extraction condition.

## 3. Results and Discussion

All of the SCFE experiments have been carried out under the conditions, in which flow rate of CO<sub>2</sub> does not affect experimental results.

Examples of the SCFE experiments (313 K, 7.95 MPa, polymer thickness 1.25 mm) are shown in Fig. 3. The broken and solid lines represent absorbance measured by the UV spectrophotometer, and average concentration of benzene in PVAc calculated from integration of the absorbance curves, respectively. The data plotted by (O) represent the concentration of benzene in PVAc disk before and after the extraction experiments, obtained by gas chromatograph (GC) analysis.

The benzene concentration was reduced to half

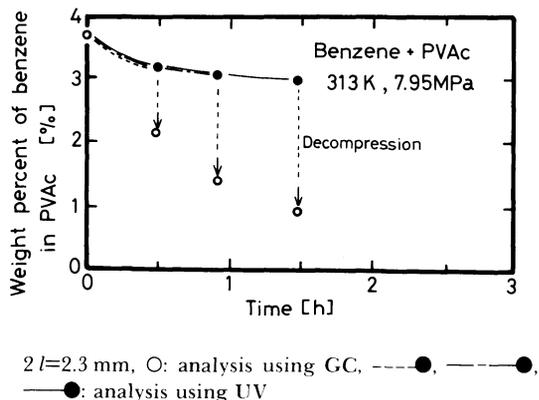


Fig. 4 Time Dependence in Extraction Experiments in Benzene+PVAc System at 313 K and 7.95 MPa

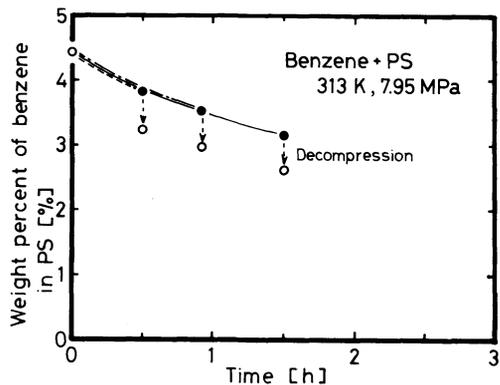


Fig. 5 Time Dependence in Extraction Experiments in Benzene+PS System at 313 K and 7.95 MPa

its initial value after two hours of extraction, which decreased slowly thereafter. After the pressure in the cell was reduced to atmospheric pressure, however, benzene content in PVAc was only 0.030 wt% by GC analysis. This indicates that the remaining benzene in PVAc was removed with quick release of  $\text{CO}_2$  dissolved in PVAc by decompression. The solubility of  $\text{CO}_2$  in PVAc has been measured by the authors<sup>6)</sup> with pressure decay method<sup>7)</sup>. The saturated solubility of  $\text{CO}_2$  went up to about 30 wt% at 313 K and 8 MPa.

From the above results, the benzene removal in this experiments can be classified into the following two mechanisms: (1) extraction of benzene in the SC- $\text{CO}_2$  phase by diffusion through the PVAc disk at high pressure, (2) decompression of the system which results in the benzene removal from PVAc. In this paper, we denote these effects as "removal by extraction" and "removal by decompression", respectively.

The results of benzene removal experiments from PVAc of thickness 2.3 mm are shown in Fig. 4. Differences were evident between analytical values by the UV spectrophotometer before decompression (●) and by the GC analysis after decompression (○). The differences increased with operating time. Namely, while the rate of removal by extraction gradually decreased with passage of time, the quantity of removal by decompression increased. This may be due to the increase in the amount of dissolved  $\text{CO}_2$  with passage of operating time.

The results for benzene removal experiments from PS of thickness 0.5 mm are shown in Fig. 5. The removals by extraction and by decompression were also observed in benzene + PS system.

The relationship between removal by extraction and removal by decompression in benzene + PVAc

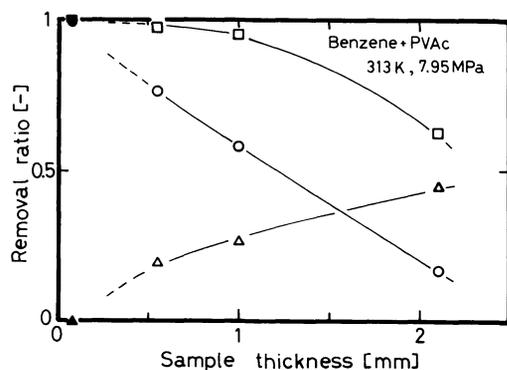


Fig. 6 Relationship between Removal by Extraction and Removal by Decompression in Benzene+PVAc System at 313 K and 7.95 MPa

system at 313 K and 7.95 MPa is shown in Fig. 6. The symbol (□) represents total amount of removed benzene obtained by GC analysis, (○) represents removal by extraction by UV analysis, and (Δ) represents removal by decompression calculated from the difference between above two values. When polymer samples are sufficiently thin, it will be possible to remove benzene from PVAc by removal by extraction only. The removal by decompression, however, becomes important with increase in polymer thickness.

#### 4. Discussion on Mass Transfer Phenomena

##### 4.1 Mass Transfer Model

In the previous paper<sup>4)</sup>, apparent diffusion

coefficients of benzene in PVAc and PS were evaluated from the amount of total benzene removal. It has been apparent, however, from our subsequent study that these calculated diffusion coefficients have less physical meaning because they contain the effect of removal by decompression.

In this work, we attempt to evaluate the diffusion coefficients of benzene in PVAc and PS, where SC-CO<sub>2</sub> is dissolved, for removal by extraction and total removal, in terms of a simple mass transfer model reported in previous paper<sup>4)</sup>. The major assumptions applied to the model are as follows:

- (1) The mass transfer phenomena of benzene in polymer are treated as the diffusion phenomena in pseudo two components system. Namely, benzene + ("transmuted" polymer by dissolution of SC-CO<sub>2</sub>) system. The concentration of CO<sub>2</sub> in the polymer disk does not change with passage of time or location in the disk.
- (2) The direction of diffusion in polymer phase is limited to the direction of thickness of the polymer disk.
- (3) The diffusion coefficient of benzene in the polymer is constant.
- (4) The thickness of the polymer disk is constant over all of the locations in it during the experimental operation.
- (5) The concentration of benzene on the surface of the disk is zero.

The unsteady state diffusion equation applied in this work is written as Eq. (2).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

The initial and boundary conditions are presented in Eqs. (3) to (5).

$$C = C_0 \text{ at } -l \leq x \leq +l, t = 0 \quad (3)$$

$$C = 0 \text{ at } x = \pm l, t > 0 \quad (4)$$

$$\frac{\partial C}{\partial x} = 0 \text{ at } x = 0, t > 0 \quad (5)$$

where  $C$  is the weight fraction of benzene in the polymer,  $C_0$  is the initial weight fraction of benzene in the polymer,  $x$  is the position variable inside the sample disk,  $l$  is a half of the sample thickness,  $t$  is time, and  $D$  is the diffusion coefficient of benzene in the polymer.

Crank<sup>8)</sup> gives the solution of these equations as follows:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-(2n+1)^2 \pi^2 \frac{Dt}{4l^2}\right] \quad (6)$$

where  $M_t$  denotes the total amount of diffusing benzene which has been extracted from the sample disk up to time  $t$ , and  $M_\infty$  denotes the corresponding quantity after infinite time, which is equivalent to the initial amount of benzene in the disk.  $D$  was determined by fitting the experimental results for the removal by extraction and the total removal, respectively.

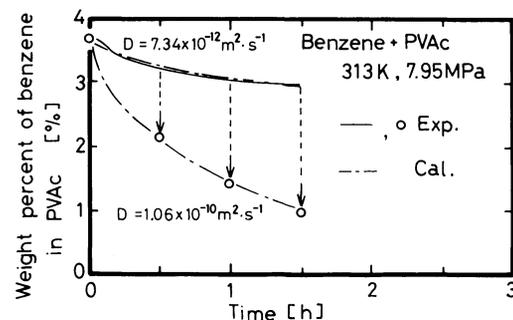
#### 4.2 Evaluation of Diffusion Coefficient of Benzene from Experimental Data

Examples of evaluation of diffusion coefficients of benzene in PVAc are shown in Fig. 7. The solid line represents experimental results measured by UV spectrophotometer, and plots (O) are the final concentrations measured by GC analysis.

Firstly, diffusion coefficients were evaluated from the experimental data for removal by extraction. Agreement between the experimental and correlated results is satisfactory. The calculated diffusion coefficient was  $7.34 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ . Secondly, diffusion coefficients were also evaluated from the experimental data for total removal. The calculated results are in good agreement with the experimental data. The apparent diffusion coefficient was determined to be  $1.06 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ . This apparent diffusion coefficient, however, has less physical meaning.

Similar evaluation in benzene + PS system are shown in Fig. 8. The calculated diffusion coefficients were  $6.05 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$  (removal by extraction) and  $1.66 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  (removal by extraction + removal by decompression), respectively.

In Table 1, the above calculated diffusion



$2l = 2.3 \text{ mm}$

Fig. 7 Evaluation of Diffusion Coefficients of Benzene in PVAc with Simple Mass Transfer Model

Table 1 Comparison between Experimental and Calculated Apparent Diffusion Coefficients of Benzene

System and condition	Data source	Diffusion coefficient [ $\text{m}^2 \cdot \text{s}^{-1}$ ]
CO <sub>2</sub> +Benzene at 313 K and 7.95 MPa	Swaid <i>et al.</i> <sup>9)</sup>	$5 \times 10^{-8}$
CO <sub>2</sub> +Benzene+PVAc at 313 K and 7.95 MPa	This work	$7.34 \times 10^{-12}$ (Removal by extraction) $1.06 \times 10^{-10}$ (Removal by extraction+removal by decompression)
Benzene+PVAc at 313 K and 0.1 MPa	Kokes <i>et al.</i> <sup>10)</sup>	$4.8 \times 10^{-17}$ (C=0 wt%) $1.7 \times 10^{-14}$ (C=10 wt%)
CO <sub>2</sub> +Benzene+PS at 313 K and 7.95 MPa	This work	$6.05 \times 10^{-13}$ (Removal by extraction) $1.66 \times 10^{-12}$ (Removal by extraction+removal by decompression)

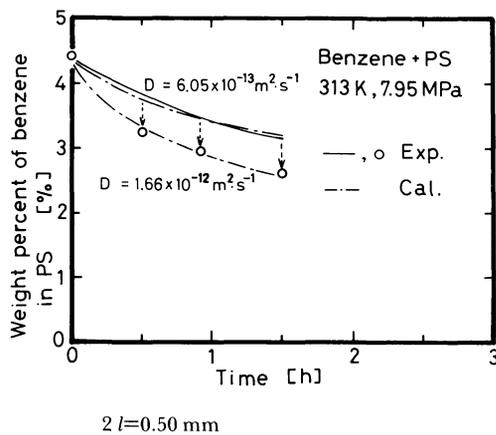


Fig. 8 Evaluation of Diffusion Coefficients of Benzene in PS with Simple Mass Transfer Model

coefficients of benzene are compared with literature values of Swaid *et al.*<sup>9)</sup> for SC-CO<sub>2</sub>+benzene and those of Kokes *et al.*<sup>10)</sup> for benzene+PVAc in the absence of SC-CO<sub>2</sub>.

It can be seen from this table that the calculated diffusion coefficients of benzene in PVAc which dissolved CO<sub>2</sub>, lie between the diffusion coefficients of benzene in SC-CO<sub>2</sub> and those in PVAc in the absence of CO<sub>2</sub>. The calculated diffusion coefficients were five orders of magnitude above those in PVAc in the absence of SC-CO<sub>2</sub>.

The investigations for sorption and dilation in gas and polymer by Kamiya *et al.*<sup>11),12)</sup> and concentration dependency of molecular motion of the polymer segment by Sefcik *et al.*<sup>13)</sup> have suggested that the plasticization effect of the polymer by dissolved molecules relates to diffusion of solute in the polymer. From these suggestions and the dissolution-diffusion theory by DiBenedetto<sup>14)</sup>, the results of the evaluation may be explained, namely, with dissolution of CO<sub>2</sub>, the polymer is gradually plasticized and polymer segments are activated. Further, the diffusion jump-frequency of benzene in the polymer increases, which accelerates the diffusion of benzene in polymers.

The diffusion coefficients of benzene in PS were about one order of magnitude below those in PVAc. It has been shown that the solubilities of CO<sub>2</sub> in PS are equal to one half of the solubilities

of CO<sub>2</sub> in PVAc at 313 K<sup>6),15)</sup>. The differences of the diffusion coefficients in PS and PVAc may be due to the differences of the plasticization with dissolution of CO<sub>2</sub> in both polymers.

In the present investigation, it was assumed that the sample polymer disk is quickly saturated with CO<sub>2</sub> and the thickness of the disk is constant. By use of these assumptions, only the diffusion of benzene in polymer was considered. Consequently, the influences of the plasticization and volume dilation of polymer with dissolution of CO<sub>2</sub> on the removal of benzene were neglected in the calculation. The authors think that the diffusion coefficients obtained in this paper are apparent values and are effective only within the limited experimental conditions established in this work. The diffusion coefficients are not suited to the rigorous expression of the mass transfer phenomena. These diffusion coefficients, however, are considered useful for evaluation of removal rate of a volatile substance from polymers by the supercritical fluid extraction technique, and design of a devolatilising unit for a polymer of which the properties pertaining to plasticization and volume dilation are not known.

To more strictly explain the mass transfer phenomena of benzene in polymer where CO<sub>2</sub> is dissolved, the solubility and diffusion coefficient of CO<sub>2</sub> in polymer and volume dilation of polymer with dissolution of CO<sub>2</sub> must be examined. Schoeber<sup>16)</sup> reported on the mathematical treatment of the diffusion in polymer when the influence of the volume dilation cannot be neglected. Research program on the influences of the plasticization and volume dilation of polymer on the removal of benzene is now in progress in our laboratory.

## 5. Conclusions

The conclusions arrived in this paper are as follows:

- 1) Removal of benzene, in conditions of this SCFE method, consists of removal by extraction and removal by decompression.
- 2) The amount of removal by decompression increases with the quantity of CO<sub>2</sub> dissolved in the

polymer.

3) The diffusion coefficients of benzene in PVAc are enhanced about five orders of magnitude by the dissolution of SC-CO<sub>2</sub>.

4) The calculated diffusion coefficients of benzene in PS are about one order of magnitude below those in PVAc.

### Acknowledgments

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### Nomenclatures

$A$	: absorbance	[ABU]
$b$	: light-path length	[m]
$C$	: weight fraction of impurity in polymer	[-]
$C_0$	: initial weight fraction or percent of impurity in polymer	[-] or [%]
$c$	: molar concentration of impurity in supercritical carbon dioxide	[mol·m <sup>-3</sup> ]
$D$	: diffusion coefficient of impurity in polymer	[m <sup>2</sup> ·s <sup>-1</sup> ]
$l$	: a half of initial sample polymer thickness	[m]
$M_t$	: total amount of diffusing impurity which has been extracted from the sample polymer up to time $t$	[kg]
$M_\infty$	: total amount of diffusing impurity which has been extracted from the sample polymer after infinite time (equals to initial amount of impurity in the sample polymer)	[kg]

$t$	: time	[s]
$x$	: distance	[m]
$\varepsilon$	: molar absorptivity	[m <sup>2</sup> ·mol <sup>-1</sup> ]

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## 超臨界二酸化炭素によるポリ酢酸ビニルおよびポリスチレン中 からのベンゼンの抽出 (第 2 報)

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著者ら<sup>4)</sup>はポリマー中からの不純物の除去操作への超臨界流体抽出法の適用性の検討および除去機構の解明を目的として, ポリ酢酸ビニル (PVAc) およびポリスチレン (PS) 中からのベンゼンの超臨界二酸化炭素 (SC-CO<sub>2</sub>) による除去実験を行ってきた。今回は実験装置に紫外分光光度計を取り付けて気相組成を連続的に分析し全除去量から脱圧時に除去される量を分離して求めることができるように装置を改造した上で, 温度 313 K, 圧力 7.95 MPa において SC-CO<sub>2</sub> による PVAc および PS 中のベンゼンの除去実験を行った。さらに前報<sup>4)</sup>で報告した物質移動モデルを用いて, 実験値の理論的な整理を行った。

実験装置の概略図を Fig. 1 に示す。抽出セル出口側流路に取り付けた紫外分光光度計によって, 抽出されるベンゼンの定量分析を操作圧力下で行い, ポリマー中のベンゼン濃度の経時変化を測定した。実験終了後に抽出セル内を大気圧まで脱圧した後, ポリマー試料をガスクロマトグラフを用いて分析し, 抽出後のポリマー中に含まれるベンゼンの濃度を決定した。Fig. 2 は本実験で用いた抽出セルの概略図である。

Fig. 3 に抽出実験の一例として試料厚さ 1.25 mm の PVAc 試料からベンゼンを抽出した結果を示す。本研究の実験法に基づくベンゼンの除去量は, SC-CO<sub>2</sub> との接触時に試料の内部から拡散して CO<sub>2</sub> 相中に抽出されるものと, 脱圧時に CO<sub>2</sub> に同伴されて除去されるものの二つに分けることができる。ここではこれらを抽出除去および脱圧除去と呼ぶことにする。

Fig. 4 は PVAc 中からのベンゼンの抽出実験を膜厚 2.3 mm の比較的厚い試料について, 抽出時間を変えて行った結果である。時間の経過と共に抽出除去量は, 次第に頭打ちになっているのに対して, 脱圧除去量は明らかに増加している。これは SC-CO<sub>2</sub> との接触時間が長いほど, PVAc 中への CO<sub>2</sub> の溶解量が増すため, 脱圧除去量が増加したものと考えられる。特に, 膜厚が 2.3 mm と比較的厚い試料の場合, 試料内部まで CO<sub>2</sub> が溶解するのに時間がかかるため, この様な傾向が顕著に現れたものと思われる。

同様な実験をベンゼン+PS 系について行った結果を Fig. 5 に示す。試料の膜厚は 0.50 mm である。ベンゼン+PS 系においても抽出除去および脱圧除去が存在することが分かる。

抽出除去と脱圧除去が全除去率に対してどの程度寄与しているのかを検討するためにベンゼン+PVAc 系について試料の膜厚を変えて抽出実験を行った結果を Fig. 6 に示す。試料が厚くなるにつれて, 全除去率および抽出除去率は低下する。また, 脱圧除去率は厚くなるにつれて上昇する。つまり, 試料の厚さを薄くすれば抽出除去のみで PVAc 中のベンゼンを十分除去することが可能である。しかし, 膜厚が厚い試料について

は抽出除去のみでは不十分であり脱圧除去が重要であることが分かる。

前報<sup>4)</sup>では物質移動モデルを作成し, 全除去を SC-CO<sub>2</sub> が溶解したポリマー中のベンゼンの見かけの拡散係数で整理した。しかしながら, その後の研究によって全除去には抽出除去に加え脱圧除去も含まれることが明らかとなったため, 拡散係数の相関値の物理的な意味は希薄であることが分かった。そこで本研究ではこれらの実験結果を踏まえ, 抽出除去および全除去について, 前報<sup>4)</sup>で報告した単純な物質移動モデルを用い, SC-CO<sub>2</sub> が溶解したポリマー中のベンゼンの拡散係数という形で実験結果を整理することを試みた。

Fig. 7 に, 試料膜厚 2.3 mm におけるベンゼン+PVAc 系の抽出実験値の相関結果を示す。また, Fig. 8 に, 試料膜厚 0.45 mm におけるベンゼン+PS 系の実験値の相関結果を示す。これらの相関によって得られた CO<sub>2</sub> が溶解した PVAc および PS 中のベンゼンの拡散係数を Table 1 に示す。

まず, ベンゼン+PVAc 系の拡散係数の相関値と Swaid ら<sup>9)</sup>による SC-CO<sub>2</sub> 中のベンゼンの拡散係数の実験値, および Kokes ら<sup>10)</sup>による CO<sub>2</sub> が存在しない場合の PVAc 中のベンゼンの拡散係数の実験値を比較する。CO<sub>2</sub> が溶解した PVAc 中のベンゼンの拡散係数の計算値は, SC-CO<sub>2</sub> 中のベンゼンの拡散係数と CO<sub>2</sub> が存在しない場合の PVAc 中のベンゼンの拡散係数の中間的な値をとることが分かる。CO<sub>2</sub> が溶解した PVAc 中のベンゼンの拡散係数は CO<sub>2</sub> が存在しない場合に比べて約 5 けた大きくなっている。ここで Kamiya ら<sup>11), 12)</sup>のポリマー中への気体収着に関する研究や, Sefcik ら<sup>13)</sup>によるポリマーセグメントの運動に対するポリマー中へ溶解した分子の濃度の依存性に関する研究から, 溶解した CO<sub>2</sub> によるポリマーの可塑化作用がポリマー中の不純物の拡散現象に密接に関連することが示唆されている。つまり, SC-CO<sub>2</sub> の溶解によりポリマーセグメントの運動が活発化し, PVAc が次第に可塑化すると共に, PVAc 中におけるベンゼンの拡散ジャンプの頻度が増加することにより, CO<sub>2</sub> が溶解した PVAc 中ではベンゼンの拡散が増進されたと説明される。

また, Table 1 より PVAc 系と PS 系の相関値を比較すると, PS 中のベンゼンの拡散係数は PVAc 中の拡散係数に比べて約一けた小さいことが分かる。この違いの要因を調べるためにポリマー中への CO<sub>2</sub> の溶解度を比較してみると, PS 中への CO<sub>2</sub> の溶解度は PVAc 中へのそれに比べて約半分であった<sup>6), 15)</sup>。この CO<sub>2</sub> の溶解度の差異に伴うポリマーの可塑化作用の違いが, PVAc および PS 系の拡散係数に大きく影響したものと考えられる。

### Keywords

Supercritical fluid extraction, Mass transfer, Carbon dioxide, Benzene, Poly(vinyl acetate), Polystyrene