CHROM. 11,778

INTERNAL DIFFUSION IN POROUS POLY(METHYL METHACRYLATE) COLUMN PACKINGS

H. KOPECKÁ and P. SCHNEIDER

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol (Czechoslovakia)

(Received February 6th, 1979)

SUMMARY

For describing the velocity and peak broadening of benzene in poly(methyl methacrylate) (MMA) column packings, three models were constructed, assuming adsorption (or absorption) of benzene and diffusion in the interstices between microparticles (or within these particles). For these models, relationships for the first absolute (μ_1') and second central (μ_2) moments of a chromatographic curve were derived and used to express the coefficients of a modified Van Deemter equation. This equation was applied to the analysis of experimental data for four samples of MMA differing in specific surface area (35–85 m^2/g) and pore size distribution. Although the model discrimination is not unambiguous, one model involving dissolution and diffusion of benzene within the mass of polymer microparticles seems to be the most probable.

INTRODUCTION

Recently, polymer packings have been frequently used in gas–solid chromatography[1]. In some instances the separation is affected unfavourably by slow diffusion transport in the packing particles. The aim of this work was to study the character of this transport in a series of porous poly(methyl methacrylate) (MMA) packings. The information obtained can be utilized for tailoring the optimal texture of polymer column packings.

The velocity and broadening of benzene peaks in columns with poly(methyl methacrylate) packings differing in specific surface area and pore size distribution were examined at 120°, using hydrogen as the carrier gas. The diffusion characteristics of benzene in particles of the column packings were evaluated with the use of modified Van Deemter equations which were derived for different alternatives of transport within particles on the basis of the momentum theory.

THEORETICAL

Provided that the injection of benzene can be represented as a Dirac pulse, the

first absolute moment, μ_1', of the outlet chromatographic curve, $c(L,t)$, can be expressed as

$$\mu_1' = (L/v)\,(1 + \delta_0) \qquad (1)$$

where δ_0 is defined as follows:

$$\delta_0 = [(1 - a)/a]\beta\,(1 + K) \qquad (2)$$

and K is the (constant) distribution coefficient of benzene [the ratio of the concentration of adsorbed (or absorbed) benzene to its concentration in the gas phase in the same place]. μ_1' represents the time coordinate of the centre of gravity of the outlet chromatographic curve $c(L,t)$.

The second central moment, μ_2 ($= \sigma^2$), can be expressed as

$$\mu_2 = 2(L/v)[\delta_1 + E(1 + \delta_0)^2\,(1/v^2)] \qquad (3)$$

The axial dispersion coefficient, E, characterizes the peak broadening due to the axial diffusion and flow non-idealities in the column (deviations from piston flow). The term δ_1 includes quantities characterizing rate processes within the packing particles, and the transport from the bulk of the carrier gas to the outer surface of the particle. The latter phenomenon has been disregarded.

For each chromatographic curve, $c(L,t)$, μ_1' and μ_2 can be determined by numerical integration according to

$$\mu_1' = \int_0^\infty t\, c(L,t)\,dt \Big/ \int_0^\infty c(L,t)\,dt \qquad (4)$$

and

$$\mu_2 = \int_0^\infty (t - \mu_1')^2\, c(L,t)\,dt \Big/ \int_0^\infty c(L,t)\,dt \qquad (5)$$

With regard to the small asymmetry of the peaks obtained, the retention time of the peak maximum was taken as the first absolute moment, μ_1'. For the same reason the second central moment, μ_2, was determined from the peak width (w) at 61 % of its height according to the expression

$$\mu_2 = w^2/4 \qquad (6)$$

which holds exactly for a Gaussian peak.

To describe processes within the column packing particles, it was assumed that a spherical particle of a porous column packing with radius R is composed of substantially smaller non-porous spherical microparticles (primary particles) of radius R_s; interstices between the microparticles then represent pores. Three alternative processes in a particle have been considered, as follows.

Model I. Benzene is transported from the outer surface of the particle into its interior by gas-phase diffusion in pores and adsorbs in equilibrium on the pore walls, *i.e.*, on the internal surface of microparticles. Equilibrium adsorption in the linear

part of the adsorption isotherm is expressed by the adsorption coefficient K_A (cm³/g): $K_A = c_{ads}/c$, where c_{ads} and c are benzene concentrations in the pores at the same distance from the outer particle surface. Diffusion in pores is characterized by the effective diffusion coefficient, D_g.

Model II. Gaseous benzene is transported through the particle by diffusion in pores (effective diffusion coefficient D_g), as in model I. However, it dissolves in the polymer mass of non-porous microparticles. At the same time, transport of dissolved benzene in microparticles is fast. The absorption of benzene is described by the dimensionless distribution coefficient k: $k = q/c$, where q and c hold for the same distance from the outer particle surface.

Model III. Diffusion of gaseous benzene in the pores is fast. Benzene dissolves in microparticles (analogously to model II; distribution coefficient k) and dissolved benzene is transferred by diffusion toward their centre. This diffusion is characterized by the effective diffusion coefficient D_s.

For the models presented above one can formulate differential mass balances of benzene in the column, in the packing particles and in the microparticles. The sets of partial differential equations obtained can be solved by Laplace transformation, and relationships for μ_1' and μ_2 can be obtained in the usual way[2-4]. In all instances eqns 1–3 are valid where the parameters K and δ_1 are defined as follows:

Model I:

$$K^I = (\varrho_p/\beta) K_A$$
$$\delta_1^I = (1/15) [(1 - \alpha)/\alpha]\beta(1 + K^I)^2(\beta R^2/D_g) \tag{7}$$

Model II:

$$K^{II} = k (1 - \beta)/\beta$$
$$\delta_1^{II} = (1/15)[(1 - \alpha)/\alpha]\beta(1 + K^{II})^2(\beta R^2/D_g) \tag{8}$$

Model III:

$$K^{III} = k (1 - \beta)/\beta \tag{9}$$
$$\delta_1^{III} = (1/15)[(1 - \alpha)/\alpha]\beta K^{III} (R_s^2/D_s)$$

After introducing the theoretical plate height H as $H \equiv \mu_2 L/(\mu_1')^2$, eqns. 1 and 3 can be used to express the H *versus* v dependence. In doing so, one has to specify the dependence of the axial dispersion coefficient, E, on the carrier gas velocity, v. On adopting the frequently used linear dependence

$$E = (\mathscr{D}_{BH}/\tau') + 2 Rv \tag{10}$$

where τ' is the tortuosity in the interparticle space in the column (usually $\tau' \approx 1.4$), one arrives at the Van Deemter equation:

$$H = A + (B/v) + Cv \tag{11}$$

The constants A, B and C (independent of v) are defined as

$$A = 2R \tag{12}$$

$$B = 2\mathscr{D}_{BH}/\tau'; \quad C = 2\delta_1/(1 + \delta_0)^2 \tag{13}$$

If the more realistic dependence $E(v)$ of the form[5]

$$E = (\mathscr{D}_{BH}/\tau') + \{Rv/[1 + (\mathscr{D}_{BH}\,\varphi/Rv)]\} \tag{14}$$

is considered (for the numerical coefficient φ, a value of 4.85 has been suggested[5]), eqn. 11 results again. Constants B and C are given by the same expressions as in the preceding case (eqn. 13); constant A has the following meaning[6]:

$$A = 2R/[1 + (\mathscr{D}_{BH}\,\varphi/Rv)] \tag{15}$$

From eqns. 11–15 it becomes evident that the slope of the linear asymptote of the H versus v dependence, i.e., $\lim\limits_{v \to \infty} \mathrm{d}H/\mathrm{d}v$, equals the constant C, which contains information about diffusion transport within porous particles of the column packing. Values of δ_0 and K, needed in order to determine D_g and D_s or R^2/D_g and R/D_s according to eqns. 7–9 and 13, can be obtained from the linear μ'_1 versus L/v dependences (eqn. 1).

EXPERIMENTAL

Preparation of polymer column packings

To a mixture of freshly distilled monomer (methyl methacrylate), a cross-linking agent (ethylene dimethacrylate) and a precipitating agent (decalin), an initiator [α,α'-azobis(isobutyronitrile)] were added and the reaction mixture was filtered and allowed to polymerize at 80° for 2.5 h in a temperature-controlled bath. The crushed polymer was extracted with methanol for 8 h (Soxhlet extractor) and dried. The amounts of individual components are presented in Table I, and the texture properties of the poly(methyl methacrylates) obtained are given in Table II. Pore size distributions determined by combined high-pressure mercury porosimetry (Carlo Erba Model 65a porosimeter) and physical adsorption of nitrogen at the normal boiling point of nitrogen (Carlo Erba Sorptomatic 1826 instrument) are shown in Fig. 1.

TABLE I

PREPARATION OF COLUMN PACKINGS

Packing	Amount			
	Monomer (cm^3)	Cross-linking agent (cm^3)	Precipitating agent (cm^3)	Initiator (g)
MMA 35	5	2	5	0.1
MMA 50	5	2.5	5	0.1
MMA 75	5	4	6.5	0.15
MMA 85	5	4	8	0.15

TABLE II

TEXTURE PROPERTIES OF POLYMER PACKINGS

Sample	S^* (m^2/g)	V^{**} (cm^3/g)	ϱ^{***} (g/cm^3)	$\varrho_p{}^{\xi}$ (g/cm^3)	$\beta^{\xi\xi}$ $(\%)$	$\alpha^{\xi\xi\xi}$ $(\%)$
MMA 35	35	1.13	1.24	0.52	58	36
MMA 50	50	0.89	1.23	0.59	52	44
MMA 75	75	0.68	1.24	0.67	46	51
MMA 85	85	0.73	1.24	0.65	48	51

* BET.

** Specific pore volume: $\varrho_p^{-1} - \varrho^{-\xi}$.

*** True density (by pycnometry with helium).

$^{\xi}$ Apparent density (by pycnometry with mercury).

$^{\xi\xi}$ $1 - (\varrho/\varrho_p)$.

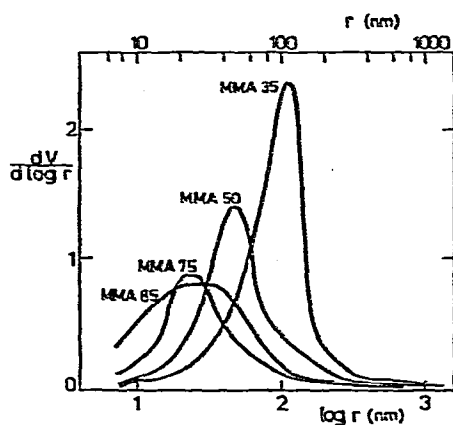$^{\xi\xi\xi}$ From column volume, packing weight and ϱ_{ξ}.

Fig. 1. Pore size distribution of polymer packings.

Apparatus

The column (200 cm × 4 mm I.D.) was packed with polymer particles of MMA having a diameter $2R = 0.3$ mm; prior to measurements the column packings were flushed with carrier gas for 48 h at 160°. Volume flow-rates of the carrier gas (hydrogen) were varied between 20 to 400 cm³/min. In calculating the linear velocity of the carrier gas, v, a correction was made for the pressure gradient along the column. Calculated quantities thus always correspond to the column mean pressure (roughly 1000 Torr). A known amount (0.3 μl) of liquid benzene was injected into the column by means of a hypodermic syringe; with regard to literature data[1] one can assume that the adsorption (or absorption) of benzene in particles takes place on the linear part of the adsorption (absorption) isotherm. Benzene concentrations in the outlet of the column (kept at 120°), $c(L,t)$, were followed with a thermal conductivity detector.

RESULTS AND DISCUSSION

The dependences obtained are illustrated in Fig. 2. It can be seen that the first
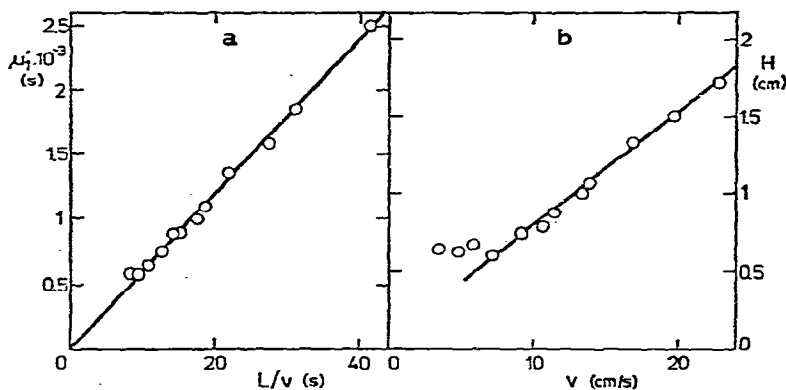
Fig. 2. (a) μ_1–L/v and (b) H–v dependences for MMA 75.

absolute moment obeys well the linear dependence according to eqn. 1; there is also a linear asymptotic part of the H *versus* v dependence (eqn. 11).

Sorption parameters for the models used (K_A for model I, k for models II and III) and diffusion times (R^2/D_g for models I and II; R_s/D_s for model III), which were evaluated from μ_1'–v^{-1} and H–v dependences according to eqns. 1, 2 and 7–9 and 3 and 6–9, respectively, are summarized in Table III.

TABLE III

SORPTION AND DIFFUSION PARAMETERS

Sample	$10^4 K_A/S$ (cm)	k	C (sec)	R^2/D_g (sec)	R^2/D_s (sec)
MMA 35	2.13	92	0.154	2.1	82
MMA 50	1.63	100	0.053	0.52	25
MMA 75	1.23	115	0.071	0.52	32
MMA 85	1.12	118	0.033	0.25	16

Provided that the samples of the polymer packings studied differ only in their structure and thus have the surface and bulk of the polymer phase of the same quality, it ought to be possible to differentiate between models I, II and III on the basis of sorption parameters which should acquire constant values. If model I is valid, *i.e.*, benzene adsorbs on the internal surface of the polymer column packing, the adsorption coefficient relative to unit column surface area (K_A/S) should be the same for all of the samples. If benzene dissolves within the polymer mass (models II and III), the distribution coefficient, k, should be constant as the actual densities of all of the samples, ϱ, are essentially identical (see Table II). As follows from Table III, none of these coefficients is strictly constant. K_A/S decreases and k increases on going from MMA 35 to MMA 85. At the same time, the average deviation from the mean value is lower for k (10%) than K_A/S (23%). This indicates that models II and III are more probable, although not too significantly.

If the determining transport step in the column particle is diffusion of benzene in the pores (models I and II), the effective diffusivities, D_g, which result from R^2/D_g

should agree with the texture properties of the samples: D_g falls in the $1 \cdot 10^{-4}$ (MMA 35) to $9 \cdot 10^{-4}$ cm²/sec (MMA 85) range. For the sake of simplicity, let us assume that the effective diffusion coefficient of benzene in the pores can be expressed as

$$D_g = (\beta/\tau)\ \mathscr{D}(\bar{r}) \tag{16}$$

where τ is the pore tortuosity ($\tau \geqslant 1$) and $\mathscr{D}(\bar{r})$ is the diffusion coefficient of gaseous benzene in a circular capillary with radius $\bar{r}$ in the diffusion transition region. The dependence of this coefficient on the capillary (pore) radius has frequently been expressed as

$$\mathscr{D}^{-1}(\bar{r}) = \mathscr{D}^{-1}(\bar{r}) + \mathscr{D}^{-1}_{BH} \tag{17}$$

where $\mathscr{D}_K(\bar{r})$ is the Knudsen diffusion coefficient of benzene in a circular capillary with radius $\bar{r}$ [$\mathscr{D}_K(\bar{r}) = (2/3)\bar{r}(8R_gT/\pi M)^{1/2}$]. At 120° and the mean pressure used in the column, the binary diffusion coefficient of the benzene–hydrogen pair is $\mathscr{D}_{BH} = 0.58$ cm²/sec. If one takes $\bar{r}$ as equal to the ratio $2V/S$, which expresses both the pore volume, V, and surface area, S, if the porous medium is regarded a bundle of identical cylindrical capillaries (for the samples studied this $\bar{r}$ lies in the range 1.7–6.5 nm), one finds that $\mathscr{D}(\bar{r})$ decreases from 0.11 cm²/sec (MMA 35) to 0.035 cm²/sec (MMA 85). These coefficients, in connection with the experimental diffusivities, D_g, would lead to unrealistically high tortuosities ($\tau = 580 \div 20$). Even worse is the situation if the most frequent radii on the pore size distribution curves (Fig. 1) are taken as $\bar{r}$; the $\mathscr{D}$ values would be about $3100 \div 30$. Only for unrealistically narrow pores with $\bar{r} \approx 0.3$–0.4 nm do the frequently found tortuosities ($\tau \approx 4$) result.

The explanation of benzene transport in terms of diffusion in pores therefore does not agree with the results obtained. Hence it is necessary to examine the validity of the decription of this transport according to model III (diffusion of dissolved benzene in polymer mass of microparticles). In this instance the effective diffusivities, D_s, calculated from R^2/D_s should be identical for all of the samples. There is no direct information about the size of the microparticles (R_s); one can, however, assume that their dimensions are inversely proportional to the specific surface area ($R_s \sim 1/S$). The validity of such an assumption and constancy of D_s are reflected in the ratio of the limiting diffusion times, R_s/D_s: $[R_s^2/D_s (MAA\ 35)]/[R_s^2/D_s (MMA\ 85)] = (2.3)^2$, which is in satisfactory agreement with the ratio $S^2(MAA\ 35)/S^2(MAA\ 85) = (2.4)^2$.

One can, however, proceed one step further and determine the size of microparticles such that their geometrical surface area is equal to the specific surface area, S, and the volume of the interstices is equal to the specific pore volume, V. Then, it holds for the microparticle size that $R_s = 3/\varrho S$. For MMA 35–MMA 85 samples this radius lies within the range 70–29 nm. These small dimensions seem to be realistic. This is indicated, e.g., by the pore size distribution curves in Fig. 1 as one can reasonably assume that the dimensions of microparticles will be similar to the dimensions of pores (i.e., interstices between microparticles). Dimensions of the same order of magnitude were also established by electron microscopy for cross-linked polystyrenes[7] and are presumed to occur also in non-cross-linked polymers having a sufficiently hig molecular weight[8].

On using these sizes of microparticles, the diffusion coefficients of benzene in

microparticle mass are as follows: $D_s = 6 \cdot 10^{-13}, 9 \cdot 10^{-13}, 3 \cdot 10^{-13}$ and $5 \cdot 10^{-13}$ cm^2/sec (for MMA 35, MMA 50, MMA 75 and MMA 85, respectively). Diffusion coefficients of this magnitude are frequent for diffusion in organic crystals[9-11], which can be considered as acceptable representatives of polymer microparticles. Diffusion coefficients in polymers reported in the literature are usually higher by several orders of magnitude; it is obvious, however, that one cannot simply compare such diffusivities derived by assuming a homogeneous polymer medium with diffusivities for the micro—macro structure considered in the present work.

Summarizing, the analysis of diffusion processes in the particles yields more reasonable results provided that transport of (dissolved) benzene within the mass of column packing microparticles (model III) is taken into account rather than the diffusion of gaseous benzene in pores (models I and II).

CONCLUSIONS

The results obtained do not allow one to discriminate unambigously between the three models proposed for explaining the sorption and transport of benzene in porous poly(methyl methacrylate) column packings. From a comparison of sorption parameters it follows that the more probable ones are models II and III based on dissolution (absorption) of benzene within the polymer mass. The analysis of diffusion times gives a preference for model III, according to which transport of gaseous benzene in the interstices between microparticles of MMA is fast and the determining step is diffusion of dissolved benzene through the polymer mass of microparticles.

LIST OF SYMBOLS

A, B, C coefficients of the Van Deemter equation.

c, c_{ads} molar concentrations of gaseous and adsorbed benzene, respectively (mole/cm^3, mole/g).

$\mathscr{D}$ diffusion coefficient of benzene in a capillary for transient diffusion region.

$\mathscr{D}_K$ Knudsen diffusion coefficient of benzene in a capillary.

$\mathscr{D}_{BH}$ binary diffusion coefficient of the benzene–hydrogen pair.

D_g effective diffusion coefficient of benzene in pores.

D_s effective diffusion coefficient of dissolved benzene in polymer mass.

E axial dispersion coefficient of benzene.

H theoretical plate height.

K, k distribution coefficients.

K_A adsorption equilibrium constant.

L column length.

M molecular weight of benzene.

q concentration of dissolved benzene in microparticle (mole/cm^3).

R radius of column packing particles.

R_s radius of polymer microparticles.

R_g gas constant.

$\bar{r}$ mean pore radius.

S specific surface area.

t time.

T	absolute temperature.
v	interstitial linear velocity of carrier gas.
V	specific pore volume.
w	peak width.
α	interparticle volume per unit column volume.
β	porosity of packing particle.
δ_0, δ_1	parameters.
μ_1', μ_2	1st absolute and 2nd central moment of chromatographic curve, respectively.
ϱ, ϱ_p	true (skeletal) and apparent density of packing particle, respectively.
τ, τ'	tortuosity of packing particle and of packed column, respectively.
φ	parameter.

REFERENCES

1 J. Lukáš, *Chem. Listy*, 72 (1978) 267.
2 M. Kubín, *Collect. Czech. Chem. Commun.*, 39 (1965) 2900.
3 E. Kučera, *J. Chromatogr.*, 19 (1965) 237.
4 P. Schneider and J. M. Smith, *AIChE J.*, 14 (1968) 762.
5 M. F. Edwards and J. F. Richardson, *Chem. Eng. Sci.*, 23 (1968) 109.
6 J. Rogut and P. Schneider, *Chem. Prům.*, 28 (1978) 108.
7 K. Jeřábek, personal communication.
8 D. H. Freeman and I. C. Poinescu, *Anal. Chem.*, 49 (1977) 1183.
9 G. Burns and J. N. Sherwood, *Mol. Cryst. Liquid Cryst.*, 18 (1972) 91.
10 A. R. McGhie and J. N. Sherwood, *J. Chem. Soc., Farad. Trans. I*, 86 (1972) 533.
11 G. Burns and J. N. Sherwood, *J. Chem. Soc., Farad. Trans. I.*, 68 (1972) 1036.