

CHROM. 7216

MASS TRANSFER COEFFICIENTS IN GAS CHROMATOGRAPHY ON POROUS POLYMERS OF THE PORAPAK TYPE

N. R. RAKSHIEVA, J. NOVÁK, S. WIČAR and J. JANÁK

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

SUMMARY

The mass transfer coefficients in the gas chromatography of *n*-heptane on several kinds of Porapak, Porapak Q modified with various loadings of F-60 silicone oil, some inorganic adsorbents, and an F-60 silicone oil gas-liquid chromatographic (GLC) packing were determined at 150°. The sorbent phase mass transfer coefficients of unmodified Porapak P and Q are comparable with those of alumina and Alusil and do not differ substantially from the liquid phase mass transfer coefficient of the GLC packing. The findings indicate that there is a substantial contribution to the mass transfer resistance due to surface diffusion with all the adsorbents studied. It appears that the sorption mechanism involved in gas chromatography on Porapaks is adsorption rather than bulk dissolution.

INTRODUCTION

Much experimental work has been carried out on the dynamics of gas chromatography. However, most of the studies on sorption mass transfer were performed with gas-liquid systems. Although several theoretical papers on the dynamics of gas-solid chromatography have been published¹⁻⁴, relatively little quantitative data on solute mass transfer in gas-solid systems have been available up to now^{5,6}.

The problems of adsorption mass transfer in gas chromatography became topical after the introduction of organic porous polymers⁷. The excellent chromatographic properties of these materials on the one hand and, on the other hand, some anomalous or unexpected behaviour⁸⁻¹¹ of some kinds of these sorbents, make organic porous polymers an interesting subject for investigation.

In order to obtain a better insight into the nature of the mechanism of sorption on organic porous polymers, in the present work the coefficients of the sorbent and gas phase resistance to solute mass transfer were measured for Porapaks P and Q, some inorganic adsorbents, and an ordinary gas-liquid chromatographic (GLC) packing. The results are discussed in terms of the effects of surface diffusion¹². Attention is paid to differences in the properties of different production batches of Porapak P. A more specific aim was to ascertain whether sorption on porous polymers is due to typical surface adsorption or to dissolution in the bulk material^{7,8,13,14}. In

this respect, the mass transfer resistance coefficients of Porapak Q coated with different amounts of a stationary liquid were determined and correlated with the specific surface area and sorption capacity of the materials.

EXPERIMENTAL

Materials

Porous polymers. Porapak P (batches 550 and 411) and Porapak Q (batch 558) were obtained from Waters Ass. (Framingham, Mass., U.S.A.).

Inorganic adsorbents. Alumina (neutral) was obtained from Reanal (Budapest, Hungary) and Alusil (a sodium aluminosilicate cation exchanger) from Slovnaft (Bratislava, Czechoslovakia).

GLC packing. This consisted of 30% (by weight) of F-60 silicone oil (Carlo Erba, Milan, Italy) on Sterchamol (Sterchamolwerke, Dortmund, G.F.R.).

Modified Porapaks. Batch 411 Porapak P was extracted for several hours with benzene in a Soxhlet apparatus, and batch 558 Porapak Q was coated with 5, 30 and 50% (by weight) of F-60 silicone oil.

The particle size of all the sorbents was 100–120 mesh. Both the unmodified and modified Porapaks and the F-60–Sterchamol packing were conditioned at 150° for 8 h under a stream of nitrogen directly in the column. The alumina and Alusil were activated at 400 and 300°, respectively, for 10 h in an oven.

The model solute was *n*-heptane (Lachema, Brno, Czechoslovakia), chromatographed at 150° with argon and helium as the carrier gases (see *Processing of the results*).

Apparatus

All the measurements were carried out on a Chrom 2 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) adapted for accurate work and equipped with a flame ionization detector. A 50-cm stainless-steel column of 5 mm O.D. and 3 mm I.D. was used with all the sorbents. The excess pressure at the column inlet was measured with a high-precision tube manometer, and the volume flow-rate of the carrier gas was measured with a Mariotte flask at the column outlet.

The average forward velocity of the carrier gas was calculated from the retention time of methane, which was assumed to be virtually non-sorbed on all the sorbents at 150°. As a column of rather small volume was employed, the extra-column volumes of the instrument were fairly significant and could appreciably affect the results unless appropriate corrections were carried out. In order to determine the extra-column volumes, retention times of methane were measured on the gas chromatograph with the column replaced by capillaries of different defined volumes, at a specified flow-rate of carrier gas. The calculation of the methane retention time corresponding to zero volume of the capillary gave the extra-column gas hold-up time, which, when multiplied by the volume flow-rate, resulted in an extra-column volume of 1.17 ml. This volume was taken into account in the calculation of the forward velocity of the carrier gas.

The solute was introduced in the form of vapour containing trace amounts of methane; a few microlitres of the vapour were injected with a Zimmerman microsyringe (Zimmerman, Leipzig, G.D.R.). Very small solute charges (5–10 μ l of *n*-

heptane saturation vapour at about 20°) were injected at high sensitivity settings (sensitivity attenuation within the range 5–20) in order to obtain data corresponding to a linear part of the sorption isotherm. Fairly symmetrical peaks were obtained in all instances.

Processing of the results

The mass transfer resistance (non-equilibrium) coefficients were calculated by Giddings and Schettler's graphical method¹⁵ modified¹⁶ for processing data referred to mean column pressure and mean flow velocity of the carrier gas. The version involving the use of two different carrier gases was employed; argon and helium were used in this work. This method is based on the equation $H/f = H_m + C_s X D'_m / Pf$ where $X = Pu/D'_m$ and $f = (P_i^2 + P_o^2)/2P^2$. In these equations, H is the average plate height, H_m is the gas phase contribution to H , C_s is the sorbent phase non-equilibrium coefficient, D'_m is the diffusion coefficient of solute in the gaseous phase at unit pressure, P is the mean column pressure, f is a decompression factor¹⁷, P_i and P_o are the column inlet and outlet pressures, and u is the average forward flow velocity of the carrier gas.

Having determined H/f values with argon and helium carrier gases at a fixed value of X , the C_s coefficient can be calculated from the equation

$$C_s = [(H/f)_{Ar} - (H/f)_{He}] / X [(D'_m / Pf)_{Ar} - (D'_m / Pf)_{He}]$$

The increments of H/f and D'_m / Pf corresponding to a given value of X were read from graphs obtained by plotting the respective functions against X .

The carrier gas velocity, u , was corrected for the extra-column volume, V_e , by employing the equation

$$u = L / [t_m - (V_e/v)]$$

where L is the column length, t_m is the apparent retention time of the methane peak and v is the volume flow-rate of the carrier gas as measured under the conditions in the extra-column space.

The diffusion coefficients, D'_m , were calculated by employing the Fuller and Giddings method¹⁸. The gas phase non-equilibrium coefficients ($C'_m = \omega d_p^2 / D'_m P'$, where ω is a geometrical coefficient and d_p is the sorbent particle diameter¹⁰) were calculated from data measured in a region of higher flow velocities, by the equation

$$C'_m = [(H/f D'_m) - (C_s X / Pf)] / X$$

RESULTS AND DISCUSSION

The sorbent materials chosen for this study involve cases representing typical bulk dissolution (F-60–Sterchamol) and typical adsorption (alumina and Alusil) on the one hand and, on the other hand, a case in which the nature of the sorption process has been incompletely understood up to now, *viz.* unmodified and modified Porapak. This situation apparently offers some interesting comparisons. The results are summarized in Table I; C_s is the sorbent phase non-equilibrium coefficient,

TABLE I
SUMMARY OF THE EXPERIMENTAL RESULTS

Sorbent	C_s (sec)	$C'_m(\text{Ar})$ (sec)	$C'_m(\text{He})$ (sec)	S (m ² /g)	V_g (<i>n</i> -heptane; He) (ml/g)
30% F-60-Sterchamol	0.0051	0.0036	0.00067	83	6.0
Alumina	0.0016	0.0055	0.0015	136	18.3
Alusil	0.0033	0.0050	0.0011	84	2.7
Porapak P-550	0.0013	0.0057	0.0015	120	10.5
Porapak P-411	0.076	0.017	0.0020	104	13.5
Porapak P-411 (extracted)	0.14	0.068	0.015	65	13.9
Porapak Q-558	0.0061	0.0057	0.0015	764	68.5
Porapak Q-558-5% F-60	0.0076	0.0038	0.0010	510	47.8
Porapak Q-558-30% F-60	0.0091	0.0045	0.0012	183	23.8
Porapak Q-558-50% F-60	0.019	0.0031	0.0010	67	17.7

$C'_m(\text{Ar})$ and $C'_m(\text{He})$ are the gas phase non-equilibrium coefficients with argon and helium as carrier gas, respectively, at unit pressure, S is the specific surface area of the sorbent, and V_g is the specific retention volume of *n*-heptane at 150°. All the results (except S) are averages of several results obtained by measurement within a region of higher flow velocities; it is known that both C_s and C_m show some velocity and pressure dependence¹⁰.

Let us discuss first the C_s coefficients. The results in Table I suggest the following: (i) the C_s values of alumina and Alusil are unexpectedly large; (ii) the C_s values of Porapak P-550 and Porapak Q-558 are comparable with those of inorganic adsorbents; (iii) there are marked differences in the two different batches of Porapak P; (iv) the C_s value of Porapak Q-558 is appreciably larger than that of Porapak P-550; and (v) coating of Porapak Q-558 even with high loads of F-60 silicone oil causes only a moderate increase in the C_s coefficient, whereas the V_g and S values fall very sharply on increasing the percentage of the stationary liquid.

The C_s coefficients found for alumina and Alusil are much larger than would be expected by assuming that the sorbent phase non-equilibrium is reflected merely by the kinetic mass transfer coefficient, C_k , defined¹ by $C_k = 2R(1 - R)/k_d$, where R and k_d are the retardation factor and the first-order desorption rate constant, respectively. The theory predicts³ that C_k is of the order of 10^{-8} – 10^{-9} , and hence the contribution of the adsorption-desorption kinetics to the magnitude of the apparent C_s coefficient is negligible. In fact, the apparent C_s coefficients of the inorganic adsorbents and also Porapak P-550 and Q-558 are of the same order of magnitude as that of 30% F-60-Sterchamol. As the C_s value measured in the above manner merely reflects effects of mass transfer processes independent of the carrier gas pressure, it appears that Knudsen or surface diffusion is largely involved in the process of mass transfer in the sorbent phase. Both of these types of diffusion can occur simultaneously, but the results of MacDonald and Habgood⁵, and also our recent investigations⁶ carried out in connection with the present work, suggest that it is mainly surface diffusion that controls the solute mass transfer in the sorbent phase.

The fact that the C_s coefficients of Porapak P-550 and Q-558 are comparable with those of alumina and Alusil shows that the mechanism of sorption on both

inorganic and organic sorbents can be of the same nature. As the C_s values of both of the above types of sorbent are comparable with that of the GLC packing, the similarity in the C_s values of the inorganic adsorbents and the Porapak is, in itself, not a very strong argument for the prediction that sorption on organic porous polymers is based on surface adsorption. However, owing to the rigid three-dimensional pattern of the Porapak sorbents, the process of bulk dissolution is rather unlikely to occur. If it did occur, the C_s value of the organic polymer would have to be much larger than that of the GLC packing, as the effective path of solute diffusion would be comparable with the sorbent particle diameter, *i.e.*, it would be much larger than the diffusion path in the F-60 liquid film, the solute diffusivity in the bulk polymer being much lower than that in the F-60 liquid.

The deviation from normal behaviour found with batch 411 Porapak P was not an isolated instance, as we found several batches of Porapak P the properties of which were similar to those of batch 411. This was not found with other types of Porapak. We thought that the anomalous behaviour of some batches of Porapak P might be due to the presence of a high-viscosity liquid (lower polymers) entrapped in the pores of the material. We extracted the Porapak P-411 with benzene in order to remove the supposed liquid, but no substance was recovered from the extract. The effect of the extraction on the properties of the sorbent was rather paradoxical (*cf.* Table I): the specific surface area was somewhat decreased and the solute mass transfer was significantly worsened (C_s enlarged). It therefore seems that the anomalous properties of this Porapak P were due to a fraction of the pores having unfavourable geometry ("ink-bottle" shape) originating occasionally under certain conditions.

The larger C_s value of Porapak Q compared with that of Porapak P-550 can be considered to be due to a larger specific surface area of the former material and supports the assumption that the solute mass transfer is controlled by surface diffusion. It is interesting in this context that the ratio of the C_s coefficients of Porapak Q-558 and P-550 corresponds roughly to the ratios of the corresponding specific surface areas and specific retention volumes.

The results of the experiments with the F-60-modified Porapak Q afford independent support for the assumption that the mechanism of sorption is based on adsorption. Fig. 1 shows that the retention capacity of the coated polymer varies proportionately to the specific surface area, *i.e.*, coating the polymer with increasing loadings of the liquid results in a gradual decrease in the sorption capacity owing to a reduction in the surface by filling up the pores of the adsorbent. In Fig. 1, ΣV_g is the sum of the V_g values due to adsorption on the surface and due to dissolution in the stationary liquid, as determined on the coated polymer, V_{g1} is the specific retention volume on F-60 silicone oil alone, as measured on the 30% F-60-Sterchamol packing, and g_1 is the weight fraction of F-60 in the modified Porapak Q. If solute retention on unmodified Porapak Q were due to bulk dissolution, we would have to obtain the opposite result, *viz.* an increase in retention upon the liquid coating. Actually, the contribution to the overall V_g (ΣV_g) of the process of dissolution in the F-60 liquid phase ($V_{g1}g_1$) is negligible compared with the V_g value due to adsorption ($\Sigma V_g - V_{g1}g_1$).

The C_s coefficient increases with increasing fraction of the stationary liquid, which can be explained as a result of filling up the pores, thus lengthening the paths

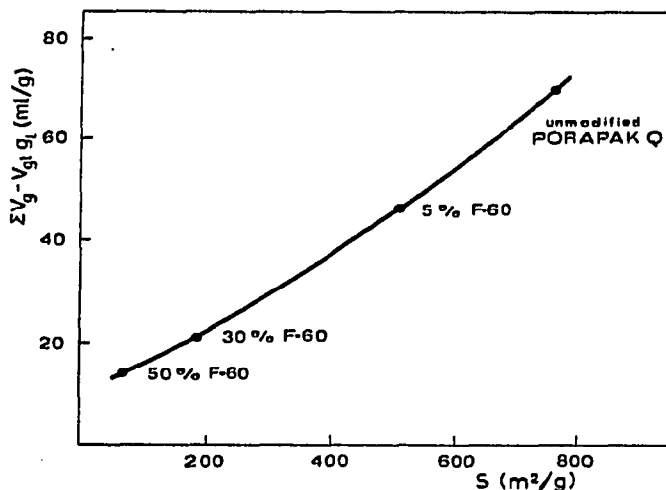


Fig. 1. Dependence of the adsorption specific retention volume of *n*-heptane on Porapak Q modified with different loadings of F-60 silicone oil on the specific surface area of the sorbent at 150°. ΣV_g is the overall specific retention volume as measured on the modified Porapak, V_{g1} is the dissolution specific retention volume as measured on an F-60 GLC packing and g_i is the weight fraction of F-60 in the modified Porapak.

through which the solute has to diffuse in the liquid. However, the increase in the C_s value is rather small; the C_s of the material with 50% F-60 is only double that of the pure Porapak Q. This result suggests that the rate of solute mass transfer along the adsorbent surface is comparable with the rate of diffusion in liquids.

The finding that the sorbent phase resistance to solute mass transfer in adsorbents is comparable with the resistance to mass transfer in liquids implies that gas-solid chromatography does not offer any great advantages, in terms of efficiency and speed of separation, over GLC. Theoretical predictions in this respect, derived from the concept that the adsorption mass transfer rate is controlled by the adsorption-desorption kinetics, give a C_s value of about 10^{-7} sec, which appears to be too optimistic. As regards the coefficients of gas phase resistance to mass transfer, it can be assumed that the C'_m values measured in this work represent the situation in the stagnant gas within the particles. According to Giddings' coupling theory²⁰, we have (neglecting the decompression factor, f):

$$H = 1/[(1/A) + (1/C'_{mc}Pu)] + B/u + C'_mPu + C_su$$

where C'_{mc} and C'_m (at unit pressure) refer to the extraparticle (mobile) and intraparticle (stagnant) gaseous phase, respectively; the other symbols have the usual meaning. As our measurements were carried out at high flow velocities, the terms $1/C'_{mc}Pu$ and B/u can be neglected and the actual situation represented by

$$H = A + C'_mPu + C_su$$

Hence, it appears that H can be reduced appreciably only by decreasing the sorbent particle diameter and the mean column pressure at higher flow velocities. Decreasing

the particle diameter should reduce the magnitude of both C'_m and C_s , if surface diffusion applies. However, a packing of smaller particles implies a higher mean column pressure at a given flow velocity, which leads to an increase in H . Hence, it follows that there are no significant differences as regards the possibilities and limitations of the separation efficiency and speed of analysis in GSC and GLC with conventional packings.

REFERENCES

- 1 J. C. Giddings, *Anal. Chem.*, 3 (1960) 443.
- 2 J. C. Giddings, *Anal. Chem.*, 34 (1962) 439.
- 3 J. C. Giddings, *Anal. Chem.*, 36 (1964) 1170.
- 4 S. J. Hawkes, *J. Chromatogr.*, 68 (1972) 1.
- 5 W. R. MacDonald and H. W. Habgood, *Can. J. Chem. Eng.*, 50 (1972) 462.
- 6 O. K. Guha, J. Novák and J. Janák, *J. Chromatogr.*, 84 (1973) 7.
- 7 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
- 8 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 9 M. Dressler, O. K. Guha and J. Janák, *J. Chromatogr.*, 65 (1972) 261.
- 10 E. N. Fuller, *Anal. Chem.*, 44 (1972) 1747.
- 11 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 506.
- 12 J. R. Dacey, *Ind. Eng. Chem.*, 57 (1965) 27.
- 13 L. Eek and T. Galcerán, *Chromatographia*, 2 (1969) 541.
- 14 O. Dufka, J. Malinský, J. Churáček and K. Komárek, *J. Chromatogr.*, 51 (1970) 111.
- 15 J. C. Giddings and P. D. Schettler, *Anal. Chem.*, 36 (1964) 1483.
- 16 J. Novák, S. Wičar and P. Boček, *J. Chromatogr.*, 53 (1970) 421.
- 17 J. C. Sternberg and R. E. Poulson, *Anal. Chem.*, 36 (1964) 58.
- 18 E. N. Fuller and J. C. Giddings, *J. Gas Chromatogr.*, 3 (1965) 222.
- 19 J. C. Giddings, *Anal. Chem.*, 35 (1963) 35.
- 20 J. C. Giddings, *Anal. Chem.*, 34 (1962) 1338.