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Note

Obstruction factors are not always flow dependent

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When a static method or theoretical model is used to determine the value of the obstruction factor γ in a bed of randomly packed solid spheres, the value of 0.60 ± 0.02 is obtained[1–4]. If a dynamic method is used, the value of 0.73 ± 0.02 is reported[5–9]. With this discrepancy in reported values, Hawkes[10] used a dynamic method and reported that γ is velocity dependent, having a value of 0.60 at or near zero velocity and 0.73 ± 0.02 at higher velocities. Tadmor[11] also has shown a velocity dependence of γ with unabsorbed gases in Idaho Falls regolith soil. In order to extend and substantiate the results reported by Hawkes, a similar method was developed to show the velocity dependence of γ using an 1/8 in. O.D., 1/18 in. I.D. copper column packed with 60–80 mesh glass beads, with some improvements in the apparatus.

EXPERIMENTAL

The chromatograph consisted of a coiled copper column 736.6 cm in length with an 1/8 in. outside diameter and 1/18 in. inside diameter packed with 60–80 mesh glass beads. To ensure a consistent environment, post- and pre-columns 173.9 cm in length packed with 60–80 mesh glass beads were placed between the reference side of the detector and the injection port, and after the sample side of the detector to atmosphere (Fig. 1). The instrument was placed in a $50 \pm 0.5°$ water-bath and a 762-cm empty coiled column was placed before the detector to ensure a constant temperature of 50° in the helium carrier before the gas entered the column. The methane sample was injected through an injection port of minimal dead volume with a gas-tight syringe. A Carle microkatharometer detector with special outlet fittings to reduce dead volume was used and peaks were recorded on a Heathkit Model SR-255B recorder, except at higher velocities, where an Esterline-Angus E110S recorder was used.

The inlet pressure was varied to obtain velocities from 0.1–17 cm/sec average linear velocity, and by using the recorded peaks at the various velocities, γ was calculated from eqn. 1 using the higher velocities to determine ω as in the previous work[10].

$$H = \frac{2\gamma D_{go} jf}{\bar{v}} + \frac{\omega d_p^2 f \bar{v}}{D_{go} j} \quad (1)$$

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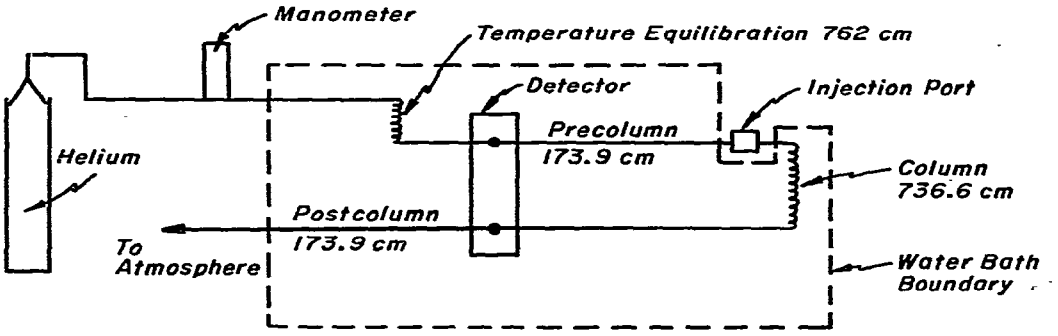

Fig. 1. Diagram of chromatograph.

where H is the column dispersivity (the so-called "plate height"), D_{go} the diffusivity of the sample in the carrier gas at the column outlet, j and f are the James–Martin and the Giddings compressibility factors, $\bar{v}$ the time-averaged gas velocity (column length/elution time), d_p the particle diameter, and ω an ill-defined geometrical constant.

The diffusion coefficient of methane in helium at 50° was calculated to be 0.7754 cm^2/sec using the value of 0.6735 cm^2/sec at 25° of Yang *et al.*[12] and correcting for temperature by proportion to $T^{1.75}$.

RESULTS AND DISCUSSION

In the previous paper by Hawkes[10], the peaks were significantly skewed. The cause was found to be the empty tube that followed the detector to lead effluent gases to atmosphere: back-diffusion from this tube was asymmetric with forward diffusion from the packed column. The post- and pre-columns used in the present system corrected this skewness. The peaks were symmetrical except at the slowest velocities and even at the slowest velocity the front-to-back ratio was never less than 0.87. Hartung and Dwyer[13] have pointed out that this skewness at slow velocity is due to the fact that the peak is measured at a single point on the column but recorded over a period of time. The latter half of the peak spends a longer time in the column, thus causing the latter half to diffuse longer than the front before reaching the detector, causing a tailed peak. Because tailed peaks could cause an error in the determination of H and $\bar{v}$, Sternberg's[14] method was used at the slowest velocities, to determine τ^2, the variance of the peaks in time units, translating to σ^2 assuming $\sigma^2 = \tau^2\bar{v}^2$, an assumption which causes a negligible error in τ even at the slowest velocities assuming Kučera's equation[15] for the second moment. The result obtained using Sternberg's method showed only a 1.0% difference in the measured values of H and $\bar{v}$ from those obtained from the recorded peaks, using the standard method measuring the width at half the height.

The intention of this work was to investigate the effect of column geometry on the variation of γ with velocity. However, no such variation was found. γ remained constant at 0.74 $\pm$ 0.02 over a velocity range from 0.1–8.0 cm/sec (the maximum velocity at which uncertainty in ω caused negligible uncertainty in γ).

Since no dependence of γ on $\bar{v}$ was found, it is not plotted in this paper as in ref. 10 but H is plotted against $jf/\bar{v}$ in Fig. 2 and the slope was used to obtain the mean value of $\gamma = 0.74$ in agreement with the individual values. It may be noted that the single point at the lowest velocity in Fig. 2 is significantly below the line and may perhaps represent a trend to lower values of γ, but if so it is at velocities 30 times lower than those previously reported[10].

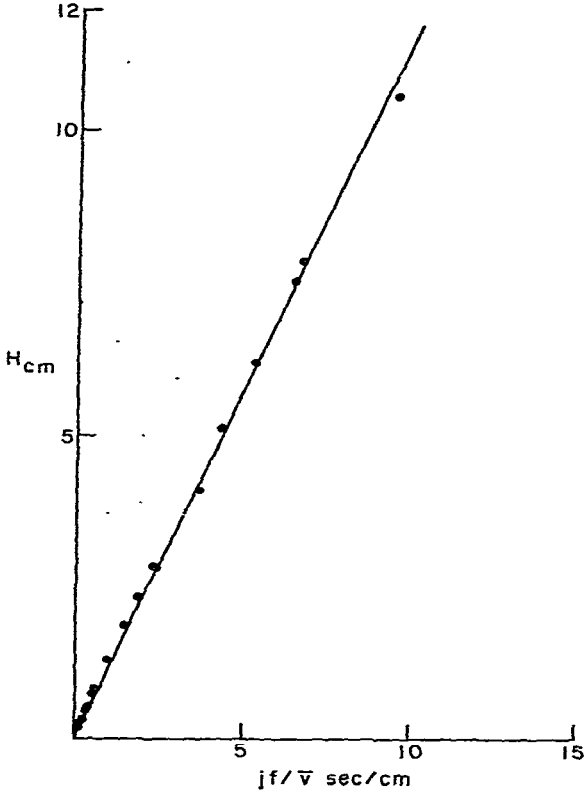

Fig. 2. Plot of measured column dispersivity H against compressibility $\times$ reciprocal of corrected zone velocity.

CONCLUSION

The value and interpretation of γ are still doubtful. In the previous paper[10] a column of larger diameter was used than in the present work (1/4 in. O.D.), as well as larger glass beads (40–50 mesh). It is possible that with the size of beads and column diameter used here γ varies at velocities lower than 0.1 cm/sec, the lowest we were able to try. The velocities at which Tadmor[11] reported variation in the value of γ were very slow, 0.08–0.3 cm/sec. Alternatively, Knox and Parcher[16] have shown that there is a transition in the packing structure in a circular column when the ratio of the column and particle diameters is between 6 and 8. The present work is on a column just in this region (ratio = 7) so that a dramatic difference from the previous results is feasible.

The other possibility is that the earlier data used by Hawkes are not valid. With the back diffusion problem and significantly skewed peaks, the values obtained from the recorded peaks could possibly be erroneous.

The prediction of Deininger[17] that $\gamma = 1.0$ for non-porous spheres is not fulfilled: although his correction of D_g for particle porosity is doubtless sound, it is evident that γ has other causes beside this, as indeed is evident from the work of Knox and McLaren[1].

However, the 25% discrepancy between static values of γ, determined by two different experimental systems[1,2] and one computer-simulated analysis[3] and the most careful dynamic values such as those reported here is still not satisfactorily explained. Unsupported theory has been offered by Hawkes and Steed[5] and Hawkes[10] and a mathematical analysis has been given by Knox and McLaren[1], but the discrepancy is greater than either theory would predict. Further elucidation probably will be possible only with digital analysis of peaks at much slower velocities even than those reported here.

Such a discrepancy between measurements in static and dynamic systems suggests that our present understanding of combined diffusion and flow in packed beds has some fundamental misconception, and this work has ramifications beyond the elucidation of a trivial constant.

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