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PEAK SHAPES AND ADSORPTION KINETICS: GAS-SOLID CHROMATOGRAPHY WITH A COATED ANATASE STATIONARY PHASE

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SUMMARY

Experiments are described with a novel gas-solid stationary phase consisting of anatase coated with a carbonaceous material resulting from the disproportionation reaction of 1,3-butadiene. At 204°C, tailing peaks are observed for branched-chain paraffins while the peaks of straight-chain isomers are symmetrical. Changes of peak shape and of the adsorption coefficient with gas flow-rate are accounted for in terms of variations in the kinetics of adsorption and desorption on different surface sites.

INTRODUCTION

In the course of a study¹ of the reaction of 1,3-butadiene on the surface of anatase (TiO₂), it was found that large quantities of a non-volatile material, very rich in carbon, were deposited on the surface. The resulting "coated anatase" was investigated for its potential as a novel gas-solid chromatographic stationary phase. Preliminary experiments showed that adsorption coefficients for straight and branched-chain paraffin hydrocarbons were very different. However, good analytical separations were not achieved as the branched isomers showed considerable peak tailing and broadening, even when very small quantities were used. The changes in the peak shapes with temperature and with gas flow-rate were investigated. The experimental results were then compared with those predicted by a model which assumed that there were adsorption sites on the surface which could be kinetically distinguished.

EXPERIMENTAL

A 7.9-g amount of anatase (Tioxide International Ltd. CLDD 1195/1) was packed in a 5-cm bore tube. 1,3-Butadiene was then passed through the anatase at 1 ml min⁻¹ for 12 h at 410°C. By weighing the anatase before and after coating it was found that 0.90 g of non-volatile material had been deposited, *i.e.*, 11.4% by weight. This had an empirical composition of CH_{0.63} as calculated from the weight increase and the gaseous reaction products. The material was then packed into a 1-m glass column (3 mm I.D.) in a Pye 104 gas chromatograph fitted with a flame ionization detector.

RESULTS AND DISCUSSION

The general chromatographic characteristics of the coated anatase may be summarised as follows:

(1) The surface area ($26 \text{ m}^2 \text{ g}^{-1}$), as measured by the BET low temperature nitrogen adsorption method, was very similar to that of the uncoated anatase ($23 \text{ m}^2 \text{ g}^{-1}$).

(2) The retention times of alkanes were much greater than on uncoated anatase.

(3) There was a larger separation of straight and branched paraffin hydrocarbons than on uncoated anatase.

(4) The retention times of hexane and benzene were similar, whereas on the uncoated anatase benzene was retained very much longer than hexane.

(5) The adsorption isotherms of alkanes no longer fit the Langmuir model as they do on uncoated anatase.

(6) Retention times were not dramatically reduced by the presence of water in the carrier gas as is the case with uncoated anatase¹.

These results suggested that the non-volatile material had essentially covered the surface of the anatase.

However, the most remarkable features of the modified anatase column were the distinctions between the behaviour of branched and straight-chain isomers at 204 and 300°C.

(a) Branched- and straight-chain isomers gave peaks of similar width (*i.e.*, similar height equivalent to a theoretical plate, HETP) at 300°C, but at 204°C the peaks of the branched-chain isomers were very much broader than those of the straight-chain isomers.

(b) At 300°C all peaks were symmetrical as were those for straight-chain isomers at 204°C, but the peaks of branched-chain isomers tailed significantly at 204°C.

(c) The retention volumes of peak maxima for the branched-chain isomers varied with flow-rate at 204°C but not at 300°C.

These distinctions were marked even at the very low vapour concentrations ($< 10^{-10} \text{ mol ml}^{-1}$) in the experiments and were not affected by further reduction in concentration. We shall discuss them in more detail by concentrating in particular on the behaviour of *n*-hexane and 2,2-dimethylbutane.

The first distinction, (a), may be illustrated by the HETP plots shown in Figs. 1 and 2, which at first sight appear to conform to the simple Van Deemter equation. In terms of this equation, there is, on lowering the temperature, a marked increase in the mass-transfer term, *C*, for 2,2-dimethylbutane, and an even more marked increase in the *A* term, for which it is difficult to find a rational explanation. We believe that the traditional interpretation of peak shape is no longer valid for 2,2-dimethylbutane on the coated anatase at 204°C and that all the distinctions (a)–(c) may be accounted for by a model in which there is a variety of adsorption sites which are kinetically distinguished. In particular, a very reasonable fit for the data may be obtained by taking into consideration just three types of site involving fast, medium and slow adsorption–desorption kinetics, the last being of real significance only at the lowest of the three gas flow-rates which we investigated.

The theory of chromatographic peaks arising from two kinetically-distinguishable sorption sites has been worked out by Giddings². On the first type of site (“nor-

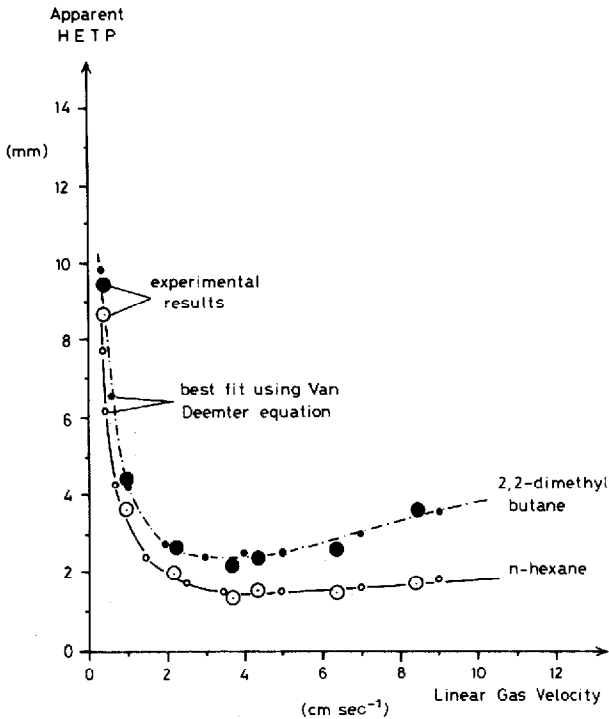


Fig. 1. Apparent HETP values at 300°C on coated anatase.

mal" site) molecules are sorbed and desorbed rapidly. On the second type ("tail-producing" site) the sorption processes are slow so that molecules often fail to be captured by such sites. However, those that are sorbed are also desorbed slowly, so that a molecule may then be held for some considerable time and be desorbed only when the bulk of the peak has passed. This results in peak tailing.

Assuming that the first-order rate constants for adsorption and desorption on the tail-producing sites are k_a and k_d , Giddings showed that the elution profile for molecules which had been adsorbed at least once on tail-producing sites is

$$P(y) = \left(\frac{a_1 a_2}{y} \right)^{\frac{1}{2}} \cdot \exp(-a_1 - a_2 y) \cdot I_1(\sqrt{4a_1 a_2 y}) \tag{1}$$

where

$$y = \frac{t_s}{t_0} = \frac{\text{time spent on "tail-producing" sites}}{\text{dead time}}$$

$$a_1 = k_a t_0$$

$$a_2 = k_d t_0$$

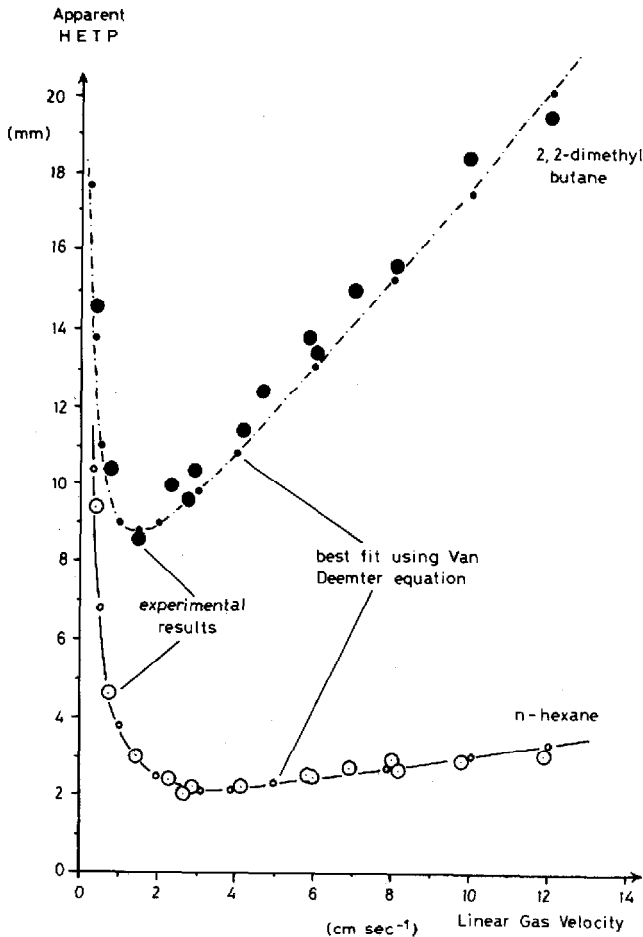


Fig. 2. Apparent HETP values at 204°C on coated anatase.

$$I_1(x) = \frac{x}{2} + \frac{x^3}{2^3 2!} + \frac{x^5}{2^5 2! 3!} + \frac{x^7}{2^7 3! 4!} \quad (\text{Bessel function})$$

The fraction of molecules eluted through the column without being adsorbed on tail-producing sites is:

$$F = \exp(-a_1) \quad (2)$$

This is added to eqn. 1 to produce the total elution profile

$$P'(y) = \left(\frac{a_1 a_2}{y}\right)^{\frac{1}{2}} \cdot \exp(-a_1 - a_2 y) \cdot I(\sqrt{4a_1 a_2 y}) + \exp(-a_1) \cdot \delta(y) \quad (3)$$

where $\delta(y)$ is an infinitely thin pulse at $y = 0$.

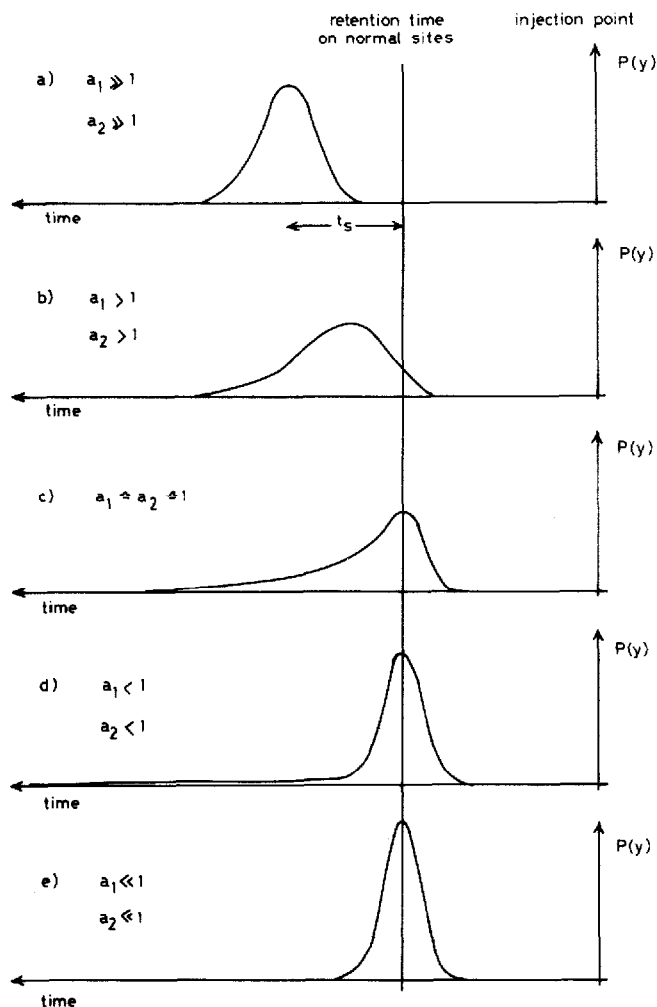


Fig. 3. Peak shapes as a_1 and a_2 are decreased.

This undisturbed profile must now be modified to allow for the zonespreading by various (Van Deemter) diffusion processes. Under the conditions used for our experiments, data from the eluted profiles of non-tailing (straight-chain) molecules were used as a first approximation to calculate this zone spreading. The undisturbed profile was divided into strips and each strip was then assumed to undergo the zone spreading of non-tailing molecules. The final profile was then obtained by summing all the diffused profiles.

The general effects of such a model may be illustrated by considering the position and shape of a peak as a_1 and a_2 are decreased, *i.e.*, as adsorption-desorption on the tail-producing sites becomes progressively slower and therefore less significant, as is shown in Fig. 3. At very low values of a_1 and a_2 (Fig. 3e) virtually all molecules are adsorbed and desorbed only on "normal" sites and a normal symmetrical peak results. At very large values of a_1 and a_2 all molecules are adsorbed on both normal

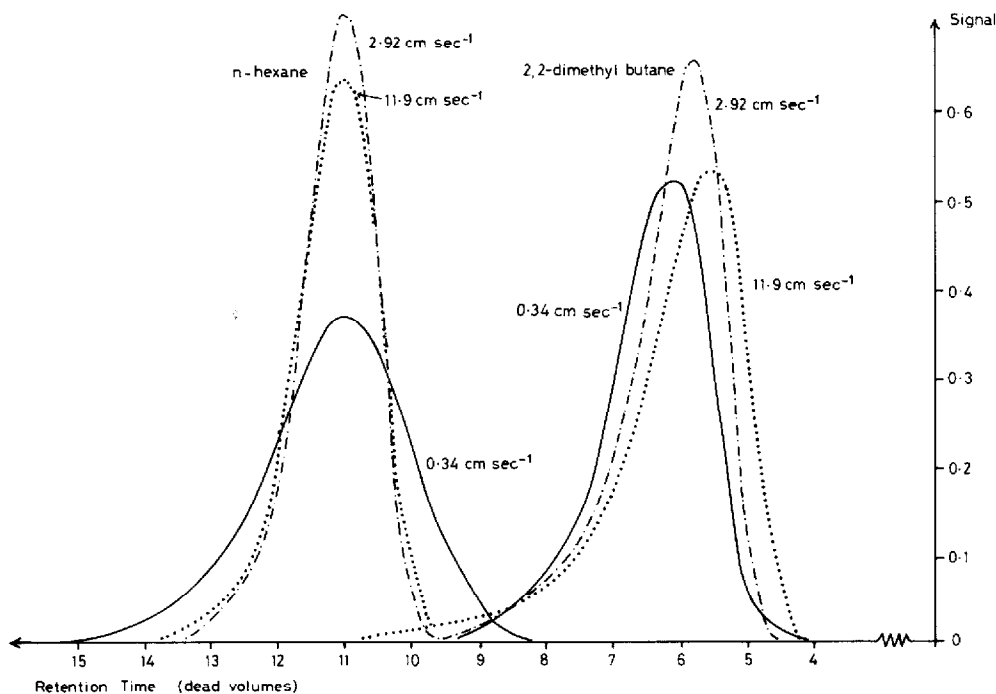


Fig. 4. Normalised chromatograms for *n*-hexane and 2,2-dimethylbutane at 204°C and at three different gas flow-rates.

and "tail-producing" sites to give again a symmetrical peak but with the tail-producing sites contributing t_s to the total retention time, where $t_s = t_0 k_a / k_d$. At intermediate values of a_1 and a_2 the peaks will become broader and less symmetrical, the contribution of the tail-producing sites to the positions of the peak maximum decreasing with decrease of a_1 and a_2 .

The chromatograms of *n*-hexane and 2,2-dimethylbutane at 204°C and at three different flow-rates are illustrated in Fig. 4. In each case the peak areas have been normalised. It is seen that the *n*-hexane peak is symmetrical with a constant retention volume for the peak maximum, while the peak for 2,2-dimethylbutane shows considerable tailing and the retention volume of the peak maximum changes with flow-rate. The three peaks for 2,2-dimethylbutane (at flow-rates of 0.34, 2.92 and 11.9 cm sec^{-1}) may be considered as fitting approximately to the first three peaks of Fig. 3(a, b, c). The corresponding a_1 and a_2 values (see below) are calculated as 21.0 and 28.0, 2.45 and 3.25 and 0.60 and 0.80.

The method of calculation used was as follows. At the fastest flow-rate (11.9 cm sec^{-1}) the fraction of molecules which have been adsorbed at least once on tail-producing sites can be estimated as this is given by the area A_1 under the tail, see Fig. 5. The fraction of molecules which are eluted without being adsorbed on tail-producing sites is therefore $F = 1 - A_1$, and by themselves these molecules would produce a symmetrical peak. Hence a_1 is calculated from eqn. 2 to be 0.60. The length and shape of the tail is governed by a_2 and for the results at 11.9 cm sec^{-1}

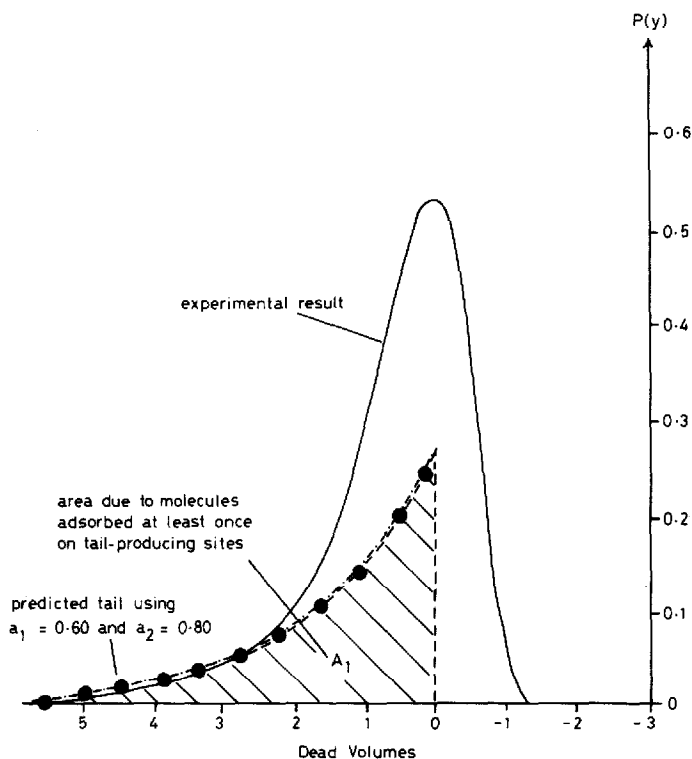


Fig. 5. Area due to molecules which have been adsorbed at least once on tail-producing sites (2,2-dimethylbutane, 204°C, flow-rate 11.9 cm sec⁻¹).

the best fit is obtained when $a_2 = 0.80$. At this flow-rate, $t_0 = 8.4$ sec, so that:

$$k_a = a_1/t_0 = 0.71 \text{ sec}^{-1}$$

$$k_d = a_2/t_0 = 0.95 \text{ sec}^{-1}$$

Hence for flow-rates of 2.92 cm sec⁻¹ ($t_0 = 34.4$ sec) and 0.34 cm sec⁻¹ ($t_0 = 298$ sec), a_1 and a_2 are 2.45 and 3.25 and 21.0 and 28.0 respectively. As the flow-rate approaches zero we would expect to approach the condition of Fig. 3a and the extra retention arising from adsorption on the "slow" sites would be at a t_s value equivalent to k_a/k_d or 0.75 dead volumes. This gives a retention time for the peak of 2,2-dimethylbutane relative to that of *n*-hexane of 0.57 which agrees exactly with that estimated from extrapolation of the values obtained over a series of flow-rates. Similarly, we can calculate from eqn. 3 the relative maximum positions at 11.9, 2.92 and 0.34 cm sec⁻¹ as 0.50, 0.53 and 0.56 which are again in agreement with the experimental values, 0.50, 0.53 and 0.56 respectively.

The above values were also found, using eqn. 3, to give a good fit for the whole of the peak shape of 2,2-dimethylbutane at the flow-rate of 2.92 cm sec⁻¹ using the *n*-hexane HETP results at the same flow-rate to derive the zone-spreading effect of the various (Van Deemter) diffusion processes, as outlined above. However, a better

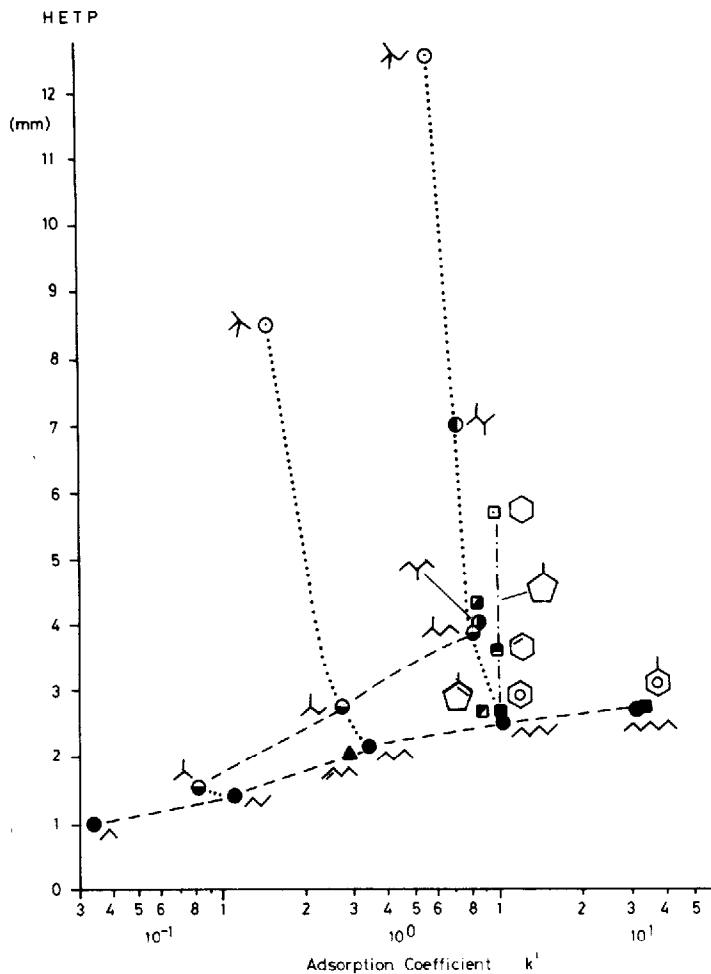


Fig. 6. HETP values and molecular shape at 204°C and a flow-rate of 5.5 cm sec⁻¹.

fit of the peak shape at 11.9 cm sec⁻¹ was obtained if the HETP used was larger than that for *n*-hexane by a factor of 2, suggesting that the normal *C* term for the "faster" sites was greater for the branched than for the straight-chain molecules. This is not unreasonable in view of the results obtained for the symmetrical peaks at 300°C, see Fig. 1.

The shape of the peak produced at a flow-rate of 0.34 cm sec⁻¹ was also in good agreement with the calculated value except that the experimental results showed slightly more tailing. This could be completely accounted for by postulating a third type of site with even slower adsorption kinetics, $k'_a = 1.7 \times 10^{-3}$ sec⁻¹ and $k'_d = 3.5 \times 10^{-3}$ sec⁻¹, from which values of A_1 (fraction of molecules adsorbed at least once on these sites) would be 0.4, 0.06 and 0.02 at flow-rates of 0.34, 2.92 and 11.9 cm sec⁻¹ respectively. This model with three quite distinct and sharply-defined kinetic sites is likely, of course, to be a considerable simplification of the real situation in which there must surely be a spread of kinetic sites.

It is also possible that there could exist adsorption sites with even slower kinetics, whose presence would not be observed experimentally as the tailing of the elution peak. In other words, the tail thus produced would be so small as to escape detection in the normal chromatogram. Such sites may however be observed by using stopped-flow chromatography^{3,4}, in which the gas flow is stopped for a period long enough for a significant number of molecules to be adsorbed on the "very slow" sites. The adsorption from these sites can then be monitored, after restarting the gas flow and eluting the main bulk of sample, by further short stops each of which produces a sharp peak originating from the position in the column of the original long stop. However, in the case of the modified anatase column we were not able to observe effects resulting from such "very slow" sites. This is in line with the absence of tailing at 300°C when presumably the activated adsorption-desorption effects which we have been discussing are subsumed into the normal *C* term of the Van Deemter equation.

Investigations were also carried out at 204°C with a variety of hydrocarbons of different molecular shapes: the results are summarised in Fig. 6 for a flow-rate of 5.5 cm sec⁻¹. It is seen that there is a general increase in peak breadth with increase in chain branching and also on hydrogenation of a benzene ring. The effect of branching must, we assume, be associated with some activated change in the surface structure of the adsorbent in order to accommodate more effectively the branched molecules or possibly an activated passage of the molecules through a narrow pore mouth through which the straight-chain molecules pass easily.

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