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Determination of gas chromatographic plate heights for hydrocarbon adsorption by superactivated carbon AX21

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ABSTRACT

Values of the height equivalent to a theoretical plate (HETP) were determined for the adsorption of several hydrocarbons by the petroleum pitch-based superactivated carbon AX21 over the temperature range 90–120°C. It was found that the HETP values were independent of both the adsorptive and the temperature of measurement. This surprising result is interpreted in terms of a very high degree of interconnectivity of the micropore structure of AX21. It is also concluded that considerable caution is required in interpreting micropore diffusivities determined from gas chromatographic measurements.

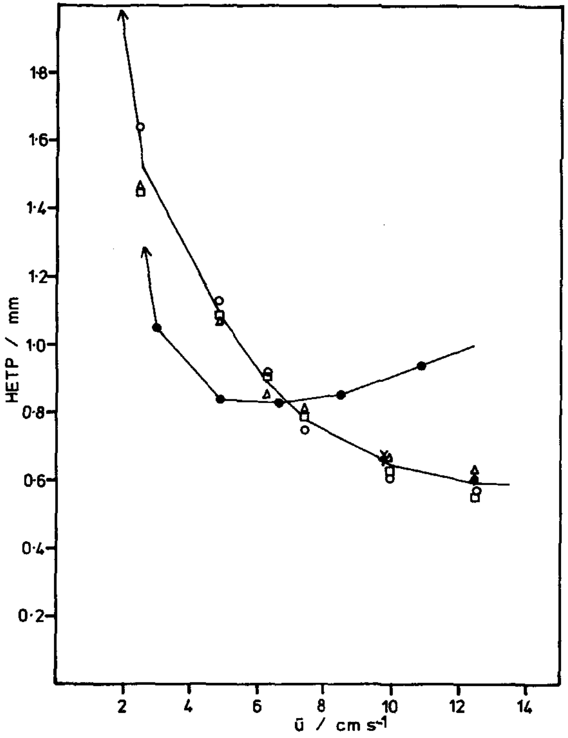
INTRODUCTION

Gas chromatography (GC) can provide a convenient and effective technique for the study of the physical adsorption of gases by microporous solids [1], provided that certain conditions are fulfilled. For instance, it is important to ensure that all contributions to band spreading arising from sources other than adsorption itself are minimized. As part of the (unpublished) preliminaries to our previous work [2–4], this was checked by making use of the well known Van Deemter equation [5]:

$$h = A + B/\bar{u} + C\bar{u} \tag{1}$$

where h is the height equivalent to a theoretical plate (HETP), defined as the peak variance per unit column length [6], and $\bar{u}$ is the linear velocity of the carrier gas. The coefficients A, B and C account for eddy diffusion, molecular diffusion and resistance to mass transfer, respectively [7]. Ideally, GC measurements at infinite dilution should be made at flow-rates corresponding to the minimum in the Van Deemter plot.

For most of the adsorbents that we studied previously, the HETP values were found to vary with flow-rate, column temperature and molecular weight of the adsorptive in the expected manner [1,7,8]. The most notable exception was the



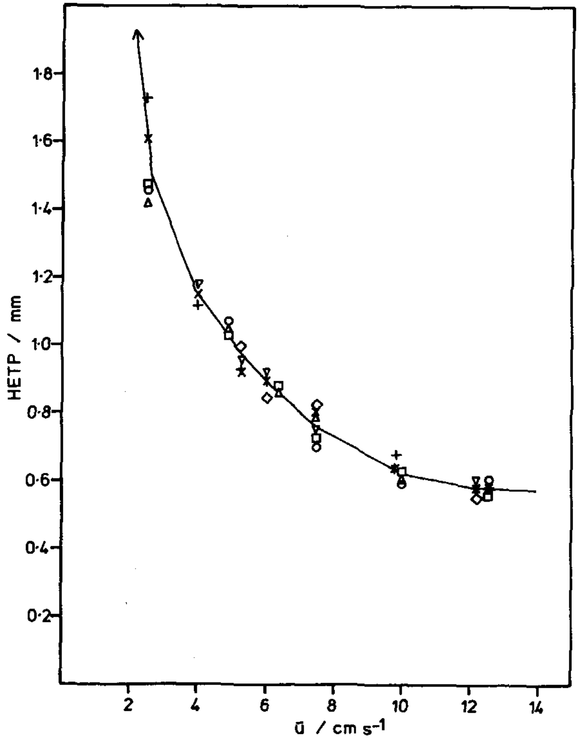


Fig. 1. Variation of HETP with linear carrier gas velocity, $\bar{u}$, for Carbosieve and AX21 at 150°C. ○ = Ethane; □ = propane; △ = butane; + = isobutane; × = neopentane; ● = methane on Carbosieve.

Fig. 2. Variation of HETP with linear carrier gas velocity, $\bar{u}$, for AX21 at 210°C. ○ = Ethane; □ = propane; △ = butane; ▽ = pentane; ◇ = hexane; + = isobutane; × = neopentane; ∗ = cyclohexane.

superactivated carbon AX21, for which the more detailed results given here were subsequently obtained.

EXPERIMENTAL

GC measurements were made using a Perkin-Elmer Model 8310 gas chromatograph fitted with a flame ionization detector. The carrier gas was helium at flow-rates of 10–50 cm^3 (STP) min^{-1}. Measurements were made mainly over the temperature range 90–210°C. More complete details of the experimental procedure were given previously [3,4]. Linear carrier gas velocities were calculated from [7]

$$\bar{u} = L/t_m \tag{2}$$

where L is the column length and t_m the gas hold-up time (determined using hydrogen). The HETP was calculated from [7]

$$h = (L/5.545)/(d/z)^2 \tag{3}$$

where d is the peak width at half-height and z is the distance to the peak maximum.

The adsorbent AX21 is a petroleum pitch-based active carbon of exceptionally high adsorption capacity manufactured by Anderson Development (Adrian, MI, U.S.A.). Its micropore volume is 1.5 cm^3g^{-1} contained in pores of width up to 2 nm [9,10]. For purposes of comparison, some results are also presented for chromatographic measurements carried out using Carbosieve, which is a polymer-based molecular sieve carbon manufactured by Supelco (Bellefonte, PA, U.S.A.) and supplied by Bioscan (Canvey Island, U.K.). Its micropore volume is 0.43 cm^3g^{-1} contained predominantly in pores of width <0.8 nm [9,10].

The chromatographic columns were made from 2 mm I.D. aluminium tubing of length 30 cm for AX21 and 29 cm for Carbosieve. The particle size and weight of adsorbent in the column were 210–360 μm and 0.6091 g for AX21 and 105–125 μm and 0.7769 g for Carbosieve.

RESULTS

Van Deemter plots for the adsorption of eight saturated hydrocarbons by AX21 at column temperatures of 150 and 210°C are shown in Figs. 1 and 2. Also shown in Fig. 1 are results obtained for the adsorption of methane by Carbosieve. The latter are in accordance with the general form of eqn. 1: as $\bar{u}$ is increased the HETP initially decreases fairly rapidly, reaches a minimum and then begins to increase again at higher flow-rates. On the other hand, it is evident that, under the conditions of the experiments carried out using AX21, only part of the curve, corresponding to the terms in A and B, was determined. The most remarkable feature of the Van Deemter plots for AX21 shown in Figs. 1 and 2, and also those obtained at other column temperatures, is that they appear to be independent of both the adsorptive and the temperature of measurement.

HETP values for AX21, averaged over all temperatures, are plotted as a function of $1/\bar{u}$ in Fig. 3. Also indicated is the spread of values obtained at different

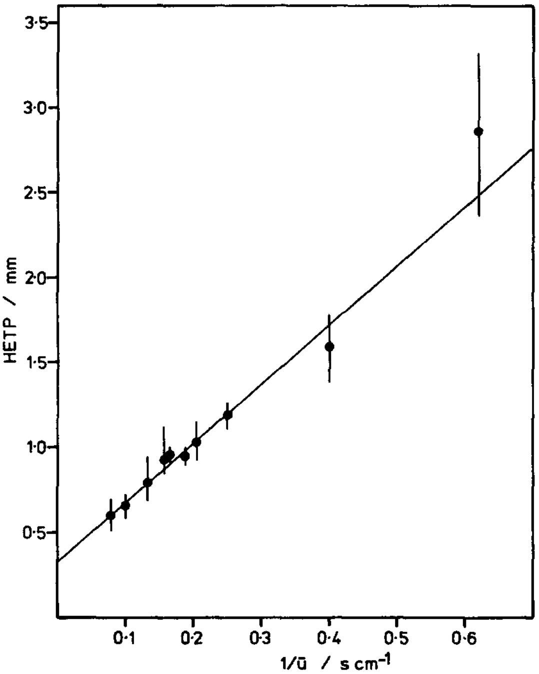


Fig. 3. Variation of HETP with reciprocal of linear carrier gas velocity, $1/\bar{u}$, for AX21 at temperatures between 90 and 210°C and for all adsorptives studied. The spread of HETP values at each temperature is indicated.

temperatures. At $1/\bar{u} = 0.62\ \mathrm{s\ cm^{-1}}$ (corresponding to $\bar{u} = 1.61\ \mathrm{cm\ s^{-1}}$ and off-scale on Figs. 1 and 2), the HETP value tends to decrease as the molecular weight of the adsorptive increases, which would be expected if gas-phase diffusion was making a significant contribution to band spreading [7,8]. At higher flow-rates, however, the spread of HETP values at each value of $1/\bar{u}$ appears to arise solely as a result of experimental uncertainty.

If the term in C in eqn. 1 is neglected, an estimate of the values of A and B can be obtained from the intercept and slope of the straight line drawn in Fig. 3. The results obtained are $A = 0.32$ mm and $B = 0.35\ \mathrm{cm^2\ s^{-1}}$. Typical values for A reported in the

TABLE I

LIMITING ISOSTERIC HEATS OF ADSORPTION, q_0^{st}, OF HYDROCARBONS BY AX21

Adsorptive	q_0^{st} (kJ mol^{-1})	Adsorptive	q_0^{st} (kJ mol^{-1})
Ethane	28	Isobutane	49
Propane	39	Neopentane	57
Butane	52	Cyclohexane	66
Pentane	63		
Hexane	75		

literature [1,7,8,11,12] are 1–2 mm. The lower value obtained here is consistent with the very low HETP values observed at all flow-rates.

Specific retention volumes were calculated from the data in the manner described previously [2–4] and were found to be independent of the flow-rate and the amount of adsorptive injected. The plots of ln V_g *vs.* $1/T$ were found to be linear and, from the slopes of the plots, the limiting isosteric heats of adsorption given in Table I were determined.

DISCUSSION

The most remarkable feature of the results is that the HETP values for AX21 appear to be independent of both the adsorptive and the temperature. This indicates that the adsorptive molecules cannot have spent much time in the gas phase and that adsorption must therefore have occurred extremely rapidly. It might be thought that the results also indicate that molecular diffusion through the micropore structure was very rapid. However, in view of the magnitude of the heats of adsorption given in Table I, it is likely that this interpretation is oversimplified.

Previous work [3,9,10] has shown that although a high proportion of the micropores of AX21 are of width between 1 and 2 nm, there are also present a significant number of narrower micropores. Little, if any, enhancement in the heat of adsorption would be expected in the wider micropores [13] and it therefore seems reasonable to assume that diffusion of molecules through these pores could occur rapidly. In narrow micropores, on the other hand, it is well known that the heat of adsorption will be enhanced [3,4,11,13,14] and, further, that elevated temperatures will generally be required to bring about complete desorption of higher molecular weight adsorptives such as neopentane or nonane [15]. Hence, even at the comparatively high temperatures used here, some restriction on the mobility of the adsorbed molecules might have been expected. It is not possible to state with certainty the reason why this effect was not detected by our GC measurements. However, it is possible that the absence of this effect may arise, in part, as a result of a very high degree of interconnectivity of the micropore structure of AX21.

Results obtained using, for example, porous silicas [1], have shown that a decrease in particle size affects the Van Deemter plot in the following ways: HETP values decrease; curves for different adsorptives come closer together; the minimum shifts to higher $\bar{u}$; and the plot tends to become flat, or nearly so, at high $\bar{u}$. Complementary results have also been obtained with, for example, steam-activated coconut shell charcoals [11]. The origin of these changes lies in an increase in the accessibility of the internal pore structure as the particles become smaller [1]. Our results for AX21 may represent a limiting case in which the combination of small particle size and a high intrinsic degree of interconnectivity result in the whole of the pore structure being freely accessible.

If this is so, then adsorption ought to occur readily in those micropores which give the highest isostetic heat of adsorption, q_0^{st}. Bearing in mind that the enhancement in q_0^{st}, in comparison with that obtained on a non-porous surface, depends on the ratio of micropore width to molecular diameter [13], it follows that adsorptive molecules of different size will tend to adsorb preferentially in slightly different parts of the micropore structure. This argument supports previous conclusions [3] that the results of GC measurements carried out at infinite dilution are not representative of the entire micropore structure, but are weighted in favour of certain groups of pores (or possibly certain active sites, in the case of specific physisorption [4]). One corollary of this is that considerable caution is required in interpreting diffusivities obtained from, for example, the coefficients of the Van Deemter equation.

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