Note

Application of gas chromatography for the study of precipitated calcium carbonate

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Over the past twenty years gas chromatography (GC) has become a well established technique for studying adsorption equilibria at very low surface coverage[1,2]. Thermodynamic data obtained in this manner have been reported for the adsorption of a wide range of organic vapours on graphitised carbons[1,3,4], zeolites[1,2,5] and silicas[1,2,6]. On the other hand much less attention has been given to catalysts, fillers and other materials of industrial importance. However, the few exploratory studies made with inorganic solids such as barium sulphate[7,8] and calcium carbonate[9] do provide an indication of the potential value of the technique.

Precipitated calcium carbonate is now widely used as an inexpensive white filler[10,11]. To improve its dispersibility and mechanical performance the filler is generally subjected to surface treatment, *e.g.* by coating with stearate[11]. Little is known about the changes brought about by surface treatment. Papirer *et al.*[9] reported a marked decrease in surface energy as the calcium carbonate surface was progressively coated with stearic acid and concluded that the modified surface became more uniform and less polar. The work of Schreiber *et al.*[12] also revealed that $CaCO_3$–polymer interaction could be considerably improved by surface modification.

No systematic study appears to have been made of the energetics of adsorption of selected organic vapours before and after the surface treatment of precipitated calcium carbonate. In principle, isosteric heats of adsorption can be calculated from GC retention measurements conducted at different temperatures[1,2]. It is the aim of the present paper to establish the conditions under which reproducible and reliable retention data can be obtained. Hydrocarbons of different molecular weight and polarity have been used as molecular probes. The GC retention data reported here were determined on laboratory samples of precipitated calcium carbonate. The results obtained with modified and coated samples will be presented and discussed in a subsequent paper[13].

EXPERIMENTAL

Gas chromatographic (GC) measurements were made using a Pye Unicam Model 104 gas chromatograph equipped with a flame ionisation detector. The carrier gas was nitrogen (zero grade, supplied by the British Oxygen Co.) and had a maximum

water content of < 5 vpm (volumes per million). The carrier gas was further dried and purified by passing through two molecular sieve traps and a bed of calcium carbonate before passage to the flow controller. These extreme precautions were found to be necessary after initial experiments had indicated large and random fluctuations of peak retention times for the various eluted species. The gas module was used to keep the gas pressure at the column inlet constant throughout the course of the experiments.

Glass columns of 50 cm length and internal diameters ranging from 2 to 7 mm were packed with coarse particles (44–72 mesh size) of calcium carbonate. Uniform packing was achieved by slow addition of the coarse powder into a continuously evacuated column which was at the same time subjected to gentle vibration. Before use each column was conditioned at 200°C by passing dry nitrogen gas at 20 ml min^{-1}. The pressure of the carrier gas at the column inlet was measured by a septum pressure gauge and the outlet was assumed to be at atmospheric pressure. The flow-rate of the carrier gas at the column outlet, at each temperature, was measured by a soap-bubble flow meter kept at room temperature. The measured flow-rates of the carrier gas were corrected for the gas compressibility factor, j, the saturation vapour pressure of water and the temperature difference between the ambient atmosphere and the column.

It was found necessary to inject the hydrocarbon in the form of vapour into the carrier gas stream rather than as the liquid. To generate a known amount of vapour 1 μl of the liquid hydrocarbon was introduced into a litre Pyrex glass flask, which had been purged with dry nitrogen and contained a small quantity of 3A molecular sieve (to remove any traces of water vapour). The flask was sealed with a stopper incorporating a silicone rubber injection septum. A Hamilton syringe was then used to transfer 0.02–0.5 ml of the vapour from the flask into the carrier gas stream. The amount of vapour injected was equivalent to $2 \cdot 10^{-5}$–$5 \cdot 10^{-4}$ μl of liquid hydrocarbon. The hydrocarbons were all of high purity grade supplied by Aldrich. Methane was used to determine the gas hold-up time.

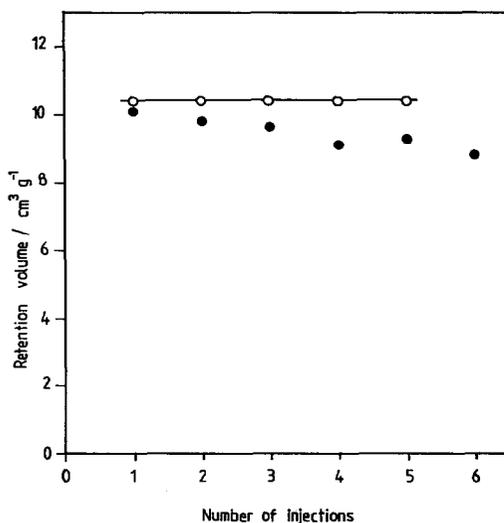The results in Fig. 1 confirm the reproducibility of the retention data when this

Fig. 1. Variation of retention volume with the number of injections for heptane at 100°C on pure calcium carbonate. $\bigcirc$ = n-Heptane vapour; $\bullet$ = n-heptane liquid < 0.05 μl.

procedure was followed —in contrast to the lack of reproducibility found with the liquid injection (*ca.* 0.05 μl) technique.

Preliminary experiments were conducted at different temperatures (over the range 130–190°C) to establish the conditions required to achieve acceptable reproducibility in the retention measurements (*i.e.* to within 2%). It was found necessary to restore the column temperature to the original level (*i.e.* 200°C) before each determination and minimum times of around 40 min and 2 h were required to remove all adsorbed non-polar molecules and polar molecules, respectively.

Values of specific retention volume, V_g, were calculated from the equation

$$V_g = (t_R - t_0)F_c \cdot \frac{273}{T} \cdot \frac{1}{\omega} \tag{1}$$

where t_R and t_0 are the retention times of the eluted hydrocarbon and of methane respectively, F_c is the corrected flow-rate, T is the column temperature and ω is the mass of calcium carbonate.

Laboratory samples of calcium carbonate were prepared by the passage of carbon dioxide through aqueous suspensions of calcium hydroxide. The reaction conditions used to prepare the pure material were as follows: pure calcium oxide was added to water to give an equivalent concentration of 0.9 M; the suspension was cooled to an initial temperature of 10°C and 40% (v/v) carbon dioxide in air passed through the suspension (total gaseous flow rate *ca.* 200 l h^{-1}) with vigorous stirring until pH 7 was attained. The product was filtered and dried at 115°C for 16 h. The levels of impurities in the calcium carbonate (w/w percentage) were: Cl, 0.01; Na, 0.026; SO$_4$, 0.024; P, 0.08. The oven-dried material had a BET nitrogen area of 29–30 m^2 g^{-1}.

RESULTS AND DISCUSSION

This work has brought to light a number of problems associated with the application of GC for surface characterisation. First, since the presence of small amounts of water vapour caused a pronounced change in the adsorptive retention time and peak shape, it was found necessary to scrupulously dry both the carrier gas and the hydrocarbon probe. Furthermore, to avoid a progressive decrease in retention time, it was necessary to recondition the column (*i.e.* by sweeping out with carrier gas at 200°C) before each measurement.

Another problem was the lack of reproducibility when small amounts of liquid adsorptive were injected into the column. This behaviour indicated that effective infinite dilution of hydrocarbon in the gas stream was not being approached —even when volumes as low as 0.05 μl were injected. This problem was overcome by the injection of small amounts of vapour equivalent to *ca.* 2 · 10^{-5} μl of liquid.

When the above procedures were followed it was found that at a given temperature the experimentally determined values of specific retention volume were independent of flow-rate and of hydrocarbon sample size. Under these conditions it could be assumed that adsorption occurred at very low surface coverage so that use could be made of the equation

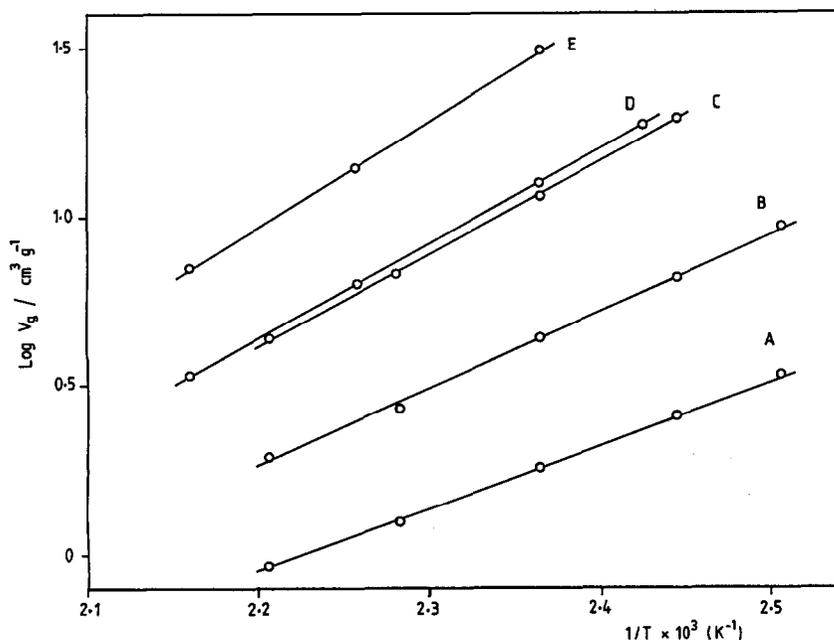$$q_0^{st} = R \frac{d(\ln V_g)}{d(1/T)} \tag{2}$$

Fig. 2. Variation of specific retention volume with temperature for various hydrocarbons on pure calcium carbonate. Plots A, B, C, D and E are for *n*-hexane, *n*-heptane, *n*-octane, hex-1-ene and hept-1-ene, respectively.

in order to calculate q_0^{st}, the isosteric heat of adsorption at zero uptake (R is the universal gas constant).

Representative plots of log V_g against $1/T$ for the pure calcium carbonate are shown in Fig. 2 and the corresponding values of q_0^{st} are given in Table I. The log V_g *vs.* $1/T$ plots were all linear over the temperature range studied in spite of the fact that the asymmetry of the alkene peaks was pronounced at the lowest temperature (150°C). Values of skew ratio (*i.e.* the ratio of the horizontal distances at half peak height from the perpendicular at the peak maximum to the leading and trailing edges of the peak) are given in Table II. Since there was no detectable effect of sample size on the retention time we may attribute the band asymmetry to slow desorption from high energy sites.

It is evident from the values of q_0^{st} recorded in Table I that there is a fairly steady

TABLE I

ISOSTERIC HEATS OF ADSORPTION FOR VARIOUS HYDROCARBONS ON PURE CALCIUM CARBONATE

Adsorptive	q_0^{st} (kJ mol^{-1})
Hexane	36.4
Heptane	44.1
Octane	52.6
Hex-1-ene	53.7
Hept-1-ene	60.3

TABLE II

SKEW RATIOS OF THE CHROMATOGRAPHIC BANDS FOR VARIOUS HYDROCARBONS AT DIFFERENT TEMPERATURES ON PURE CALCIUM CARBONATE

Adsorptive	Skew ratio			
	190°C	180°C	170°C	150°C
n-Hexane	—	0.86	0.85	0.80
n-Heptane	—	0.78	0.75	0.70
n-Octane	—	0.77	0.74	0.68
Hex-1-ene	0.78	—	0.79	0.63
Hept-1-ene	0.71	—	0.69	0.61

increase (*ca.* 8 kJ mol^{-1} per CH_2 group) in the adsorbent–adsorbate interaction energy with increase in chain length of the *n*-alkanes. This level of increment is somewhat larger than that observed by Kiselev and co-workers[1,3,6] for the interaction of *n*-alkanes with the surface of graphitised carbon black or macroporous silica, although the *n*-hexane values for the $CaCO_3$ and SiO_2 are very similar.

The most striking feature of the results in Table I is the large difference between the values of q_0^{st} for the corresponding alkenes and alkanes (*i.e.* for hex-1-ene and hexane, $\Delta q_0^{st} = 17.3$ kJ mol^{-1}; for hept-1-ene and heptane, $\Delta q_0^{st} = 16.2$ kJ mol^{-1}). Since the equivalent values of Δq_0^{st} have been found[3] to be negative and close to zero for the adsorption of these vapours on graphitised carbon, we may conclude that this contribution of *ca.* 30% to the adsorption energy is due to a strong specific interaction between the alkene molecules and certain sites on the $CaCO_3$ surface. The scale of this specific contribution is of the same order of magnitude as has been reported for NaX zeolite[1,5] and $BaSO_4$[7] and these and other findings indicate that the active sites are probably exposed cations. The evidence for this conclusion will be discussed in detail in a subsequent paper.

ACKNOWLEDGEMENTS

REFERENCES

1 A. V. Kiselev, *Adv. Chromatogr.*, 4 (1967) 113.
2 G. D. Gray and U. B. Mohlin, *J. Colloid Interface Sci.*, 47 (1974) 747.
3 O. G. Eisen, A. V. Kiselev, A. E. Pilt, S. A. Rang and K. D. Scherbakova, *Chromatographia*, 4 (1971) 448.
4 M. S. Bobyleva, A. V. Kiselev, N. S. Kulikov, E. B. Polotnyuk and K. D. Shcherbakova, *Ads. Sci. Technol.*, 2 (1985) 165.
5 A. V. Kiselev, *J. Chem. Technol. Biotechnol.*, 29 (1979) 673.
6 A. V. Kiselev, Yu. S. Nikitin, R. S. Petrova, K. D. Shcherbakova and Ya. I. Yaskin, *Anal. Chem.*, 36 (1964) 1526.

7 L. D. Belyakova, A. V. Kiselev and G. A. Soloyan, *Chromatographia*, 3 (1970) 254.
8 L. D. Belyakova, *Langmuir*, 3 (1987) 703.
9 E. Papirer, J. Schultz and C. Turchi, *Eur. Polym J.*, 20 (1984) 1155.
10 D. H. Solomon and D. G. Hawthorne, *Chemistry of Pigments and Fillers*, Wiley, New York, 1983.
11 J. Hutchinson and J. D. Birchall, *Elastomerics*, 112 (1980) 17.
12 H. P. Schreiber, M. R. Wertheimer and M. Lambla, *J. Appl. Polym. Sci.*, 27 (1982) 2269.
13 T. Ahsan, B. A. Colenutt and K. S. W. Sing, in preparation.