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GAS CHROMATOGRAPHY OF PURE AND SURFACE-MODIFIED PRECIPITATED CALCIUM CARBONATE

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SUMMARY

Precipitated calcium carbonates, either pure or coated with stearic acid, are materials of major industrial importance. Gas chromatographic measurements of specific retention volumes have been used to derive isosteric heats of adsorption for various hydrocarbons on both pure and modified calcium carbonate samples. Significant differences in the heats of adsorption and peak skew ratios have been observed with the different samples. The results are explained by the presence of exposed polar cationic species at the surface of pure calcium carbonate. Modification by stearate coating masks these sites and so reduces specific interaction. Gas chromatography is shown to be a valuable tool for probing the nature of the calcium carbonate surface.

INTRODUCTION

Finely divided calcium carbonate is extensively used as a filler or extender in many industries, the rubber and plastics industry being particularly important[1]. Precipitated calcium carbonate is produced on the industrial scale by passing a stream of carbon dioxide through a suspension of calcium hydroxide. The solid product may be given a stearate coating as part of the production process. A stearate coating makes the material more easily wetted and so improves the incorporation and dispersion characteristics[2].

It is thought that strong filler–polymer interactions are required for good reinforcement[3], but although stearate coated calcium carbonate is readily dispersible it has a reduced degree of reinforcement. However, the lack of understanding of calcium carbonate reinforcement may be partially attributed to a lack of fundamental knowledge about the properties and surface characteristics exhibited by the pure and modified surfaces. It is in probing and elucidating the surface properties of calcium carbonates that gas chromatography (GC) may be a valuable tool. GC provides a unique means of studying the adsorption characteristics of surfaces at low coverage[4]. We have already reported that GC can be used as a convenient and effective technique to assess adsorbent–adsorbate interaction parameters such as heats of adsorption on calcium carbonate at low surface coverage provided that certain conditions such as stringent drying of the carrier gas and careful adsorbent conditioning are fulfilled[5].

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There are few accounts in the literature of previous GC studies of calcium carbonate. These have revealed the existence of polar sites at the surface[6–8]. In a recent study[8] a comparison was made of the entropy and heats of adsorption of some saturated hydrocarbons on pure and stearate coated calcium carbonate. To date little has been reported on the characterization of the surface and particularly its behaviour towards molecular probes of varying polarity.

Here we report the isosteric heats of adsorption of various hydrocarbon molecular probes on the surfaces of pure and modified calcium carbonates and compare the nature of the surfaces with those of other solid adsorbents such as graphitized thermal carbon black (GTCB) and silica gel using data from the literature.

EXPERIMENTAL

Gas chromatography

Comprehensive experimental detail and the necessary precautions have been described and discussed previously[5]. Thus to obtain reproducible and reliable data it is vital to remove all water from the carrier gas and to recondition the columns after injections have been made. This prevents build-up of adsorbed substances which might modify the surface during the study and is particularly vital in dealing with uncoated calcium carbonate.

Gas chromatography measurements were made on a Pye Model 104 gas chromatograph equipped with a flame ionization detector. Calcium carbonate particles were packed in 50 cm × 3 mm I.D. glass columns. Vapour samples of the hydrocarbon molecular probes were introduced into the nitrogen carrier gas stream by means of a Hamilton gas-tight 1-ml syringe. Each injection was equivalent to between 1 and 50 nmol of the compound. The hydrocarbons (Aldrich) were of high purity (better than 99%) and gave a single peak in the chromatogram. Sequences of injections were made until retention volumes were reproducible to within 2% for at least four consecutive injections. Injections were made over a range of oven temperatures between 70 and 190°C.

Preparation of calcium carbonate

The finely divided calcium carbonate was prepared by a precipitation process starting from granular calcium carbonate. The raw calcium carbonate (AnalaR grade, BDH) was heated to 1100°C and the resulting calcium oxide was added to water to produce a 0.9 *M* suspension. Calcium carbonate was precipitated by passing 40% carbon dioxide in air at a flow-rate of 200 l/h with continous stirring. This was continued until a pH of 7 was reached when the product was filtered and dried at 115°C for 16 h.

One sample (acetone washed) of the colloidal calcium carbonate collected at pH 7 was mixed with an equivalent volume of acetone, filtered and washed three times with more acetone. This product was also dried at 115°C for 16 h.

A further sample (Calgon treated) of the colloidal calcium carbonate was mixed with a 500 ppm (w/v) aqueous solution of Calgon S (sodium hexametaphosphate) and stirred for 10 min. The calcium carbonate was filtered and dried as described above.

A final sample (stearate coated) of the calcium carbonate was coated with 2.6% (w/w) of stearic acid by a proprietary method and once again dried at 115°C for 16 h.

TABLE I

SURFACE AREA OF CALCIUM CARBONATE SAMPLES

Type of sample	*BET surface area (m^2/g)*
Pure uncoated material	29.4
Acetone washed	34.1
500 ppm Calgon S impurity	44.2
2.5% (w/w) Ammonium stearate	30.0

The treatments with acetone and Calgon S were intended to reduce Ostwald ripening and so prevent aggregation. These products would be expected to have higher surface areas than the other two samples. The BET nitrogen surface areas of the samples were measured and are given in Table I.

RESULTS AND DISCUSSION

When the precautions described previously[5] are adopted it is possible to determine values of specific retention volume, V_g, from the expression

$$V_g = (t_R - t_o)\,F_c \cdot \frac{273}{T} \cdot \frac{1}{w}$$

where t_R and t_o are the retention times at the peak maxima of the hydrocarbon and methane, respectively, F_c is the corrected carrier gas flow-rate, T is the absolute column temperature and w is the mass of calcium carbonate.

The values of V_g are independent of any variables such as sample size. Under these conditions the isosteric heats of adsorption at low or essentially zero coverage, q^{st}, can be calculated using the equation

$$q^{st} = \frac{R\ \mathrm{d}(\ln V_g)}{\mathrm{d}(1/T)}$$

where R is the universal gas constant.

Fig. 1 shows examples of the linear plots which were obtained when log V_g was plotted against $1/T$. The heats of adsorption for the hydrocarbon probes on the four calcium carbonate samples calculated from the plots are given in Table II.

Comparisons can be made between the heats of adsorption in Table II and those reported for the same hydrocarbon molecular probes on GTCB[9] and macroporous silica[4].

Fig. 2 shows the plots of heat of adsorption against carbon number for the adsorption of a range of normal alkanes on various adsorbents. From this it is possible to compare the magnitude of the non-specific adsorbent–adsorbate interactions. It can be seen that the increase in the interaction energy is linear with the carbon number in all cases. The position of the plot for GTCB may be explained by its non-specific surface

TABLE II

ISOSTERIC HEATS OF ADSORPTION (kJ/mol) OF VARIOUS HYDROCARBONS ON CALCIUM CARBONATES

Adsorbate	*Adsorbent*			
	Unmodified	*Acetone washed*	*Calgon S treated*	*Stearate coated*
n-Hexane	36.4	35.5	37.3	35.3
n-Heptane	44.1	40.5	43.2	41.1
n-Octane	52.6	46.5	49.3	47.7
Cyclohexane		32.1	33.4	33.4
But-1-ene		46.9	41.1	34.7
Hex-1-ene	53.7	51.4	52.3	42.6
Hept-1-ene	60.3	56.9	58.5	47.0
Benzene			64.3	
Toluene			68.0	42.4

and the surface density of the carbon atoms[9]. The plots for calcium carbonate and macroporous silica start at a nearly common point at a carbon number of six but the individual slopes are very different. The greater slope for the calcium carbonate samples may be explained by the presence of cationic sites at the surface which undergo specific polarization interactions[10] with adsorbate molecules. Since the polarizability

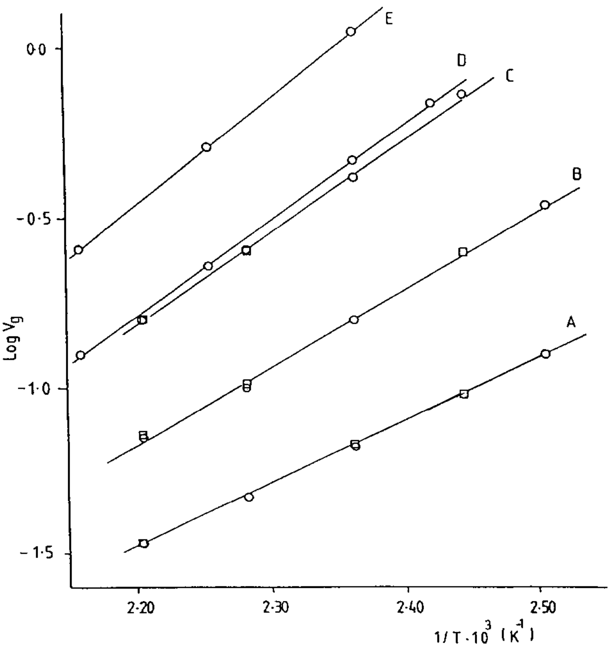

Fig. 1. Plots of log V_g against $1/T$ for hydrocarbons on pure calcium carbonate. (A) *n*-hexane; (B) *n*-heptane; (C) *n*-octane; (D) hex-1-ene; (E) hept-1-ene. Circles and squares indicate measurements made on different occasions on the same adsorbent after reconditioning.

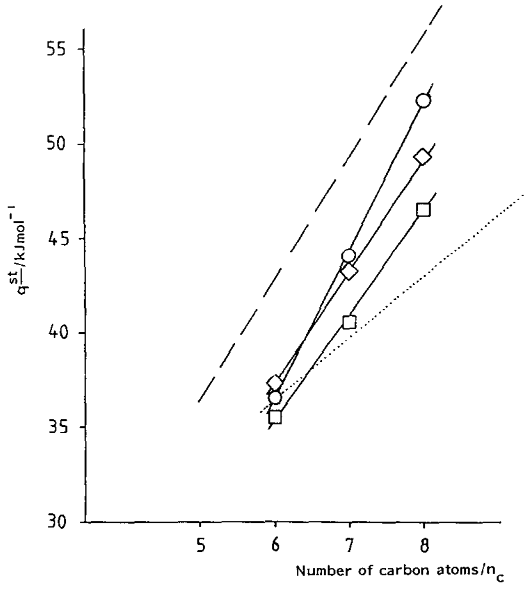

Fig. 2. Heats of adsorption of *n*-alkanes against carbon number for various adsorbents. ○ = Unmodified; ◇ = Calgon treated; □ = stearate coated; -------- = GTCB; ······ = macroporous silica[4].

of the hydrocarbons increases with increasing molecular weight, an enhancement of this interaction energy for the higher hydrocarbons in the homologous series would be expected and this is observed. Furthermore, the strongest interaction is apparent with the pure calcium carbonate surface as would be expected if the surface modification involves masking or reaction at the exposed cationic sites.

Fig. 3 shows the plots of heat of adsorption against carbon number for the normal alkanes and certain alkenes on various calcium carbonates. It can be seen that the corresponding plots for the alkanes and alkenes are nearly parallel for the unmodified and Calgon-treated calcium carbonates, but that this is not the case with the stearate coated sample. The greater rate of increase in heats of adsorption for the alkenes are due to the contribution made by the specific interactions between the π-bonds of the alkene molecules and the polar cationic sites on the surface of the pure calcium carbonate.

The skew ratios (the ratio of the horizontal distances at half peak height from the perpendicular at the peak maximum to the leading and trailing edges) were calculated from the chromatographic bands observed with unsaturated hydrocarbons on calcium carbonate samples at two different temperatures. The values are given in Table III. The skew ratios of the bands increase and approach unity, representing a completely symmetrical peak, as the high energy cationic sites are progressively masked as a result of the different treatments given to the calcium carbonate surfaces. The effect becomes most pronounced in the case of the stearate-coated sample where the coating has evidently played an important role in masking the polar catonic sites. This conclusion is supported by the calculated differences between the corresponding heats of adsorption of unsaturated and saturated C_6 and C_7 hydrocarbons on the calcium carbonate samples given in Table IV. The smallest difference, reflecting the least contribution by specific interactions, is given by the stearate coated sample.

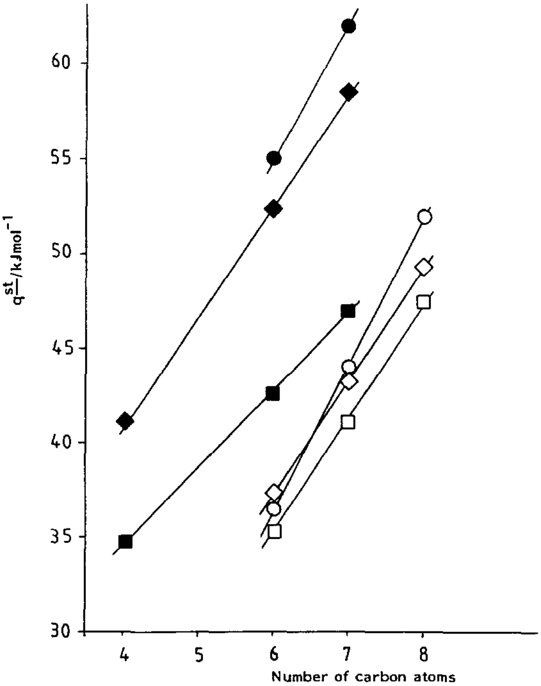

Fig. 3. Heats of adsorption against carbon number in hydrocarbons for various calcium carbonate samples. ○ = Unmodified; ◇ = Calgon treated; □ = stearate coated. Open symbols: *n*-alkanes. Filled symbols: alk-1-enes.

Table V shows the difference between the corresponding heats of adsorption for benzene and *n*-hexane on Calgon treated precipitated calcium carbonate, two barium sulphate samples, hydroxylated silica and GTCB. The data for the latter four adsorbents have been obtained from the literature[4,9,11]. The differences in heats of adsorption decrease in the order calcium carbonate, barium sulphate and hydroxylated silica, eventually becoming zero for GTCB. Thus the strongest specific

TABLE III

SKEW RATIOS OF THE CHROMATOGRAPHIC BANDS FOR POLAR HYDROCARBONS AT TWO DIFFERENT TEMPERATURES ON CALCIUM CARBONATES

Calcium carbonate	*Hex-1-ene*		*Hept-1-ene*	
	150°C	*170°C*	*150°C*	*170°C*
Unmodified	0.63	0.79	0.61	0.69
Acetone washed	0.77	0.77	0.65	0.73
Calgon S treated	0.83	0.86	0.68	0.69
Stearate coated	0.90[a]	0.99[b]	0.90[a]	0.91[b]

[a] At 100°C.
[b] At 120°C.

TABLE IV

DIFFERENCES BETWEEN THE ISOSTERIC HEATS OF ADSORPTION OF *n*-ALKANES AND ALKENES ON CALCIUM CARBONATE SAMPLES

Calcium carbonate	*Difference between hex-1-ene and hexane (kJ/mol)*	*Difference between hept-1-ene and heptane (kJ/mol)*
Unmodified	17.3	16.2
Acetone washed	15.9	16.4
Calgon treated	15.0	15.3
Stearate coated	7.3	5.9

interactions are observed on the calcium carbonate with phosphate covering about 10% of the surface. In fact the value of the heat of adsorption for benzene on pure calcium carbonate was probably larger but it could not be measured because of the greater asymmetry of the chromatographic band and problems of irreproducible retention data. The two sets of values for the barium sulphate samples are puzzling but could be explained by the effect of impurities, even at trace levels, at the surface.

The difference between the corresponding heat of adsorption values for calcium carbonate and barium sulphate may be explained by differences in cationic radii. The values for Ca^{2+} and Ba^{2+} ions are 0.099 and 0.139 nm respectively[12]. Since the positive charge for Ca^{2+} is concentrated over a smaller ionic radius it is likely that it interacts more strongly with the π electrons of the benzene ring than is the case with Ba^{2+}. It is evident that the specific contribution in the case of hydroxylated silica is considerably less than either of the other two adsorbents discussed above.

Recently heats of adsorption for *n*-alkanes from pentane to nonane on coated and uncoated calcium stearate have been reported[8]. The results for *n*-hexane, *n*-heptane and *n*-octane are directly comparable with the data reported here. Schmitt *et al.*[8] examined calcium carbonate coated with 8% stearate rather than the 2.6% used in this study. However, their results of 28, 37 and 46 kJ/mol for *n*-hexane, *n*-heptane and

TABLE V

HEATS OF ADSORPTION (kJ/mol) OF BENZENE AND HEXANE ON VARIOUS ADSORBENTS

Adsorbent	*Adsorbate*		
	Benzene	*n-Hexane*	*Difference between benzene and n-hexane*
Calgon treated calcium carbonate	64.3	37.3	27.0
Barium sulphate-1 (11)	70.3	46.8	23.5
Barium sulphate-2 (11)	50.6	30.5	20.1
Hydroxylated silica[4]	42.6	30.9	11.7
Graphitised thermal carbon black[9]	41.0	41.0	0

n-octane, respectively, are within a few kilojoules of the values we report here despite the difference in the degree of surface coating.

The effect of modifying surfaces with essentially non-volatile or chemically bound liquids has been demonstrated for the silica–polyethylene glycol system[13] and comparisons can be made with the coating of calcium carbonate. Papirer *et al.*[13] has shown that the heats of adsorption are related to the degree of surface coverage, effectively ranging from the heat of adsorption onto the solid to the heat of solution into the coating liquid. On that basis we would expect the heat of adsorption measured in the calcium carbonate–stearic acid system to vary with the degree of coating and the differences between the two sets of results might be explained in this way.

However, the calcium carbonate surface is clearly heterogeneous and treatment with stearic acid is unlikely to result in a uniform coating. Stearate will concentrate at the high energy sites and the effect of various degrees of coating cannot be predicted with confidence. Thus the apparent differences in the heats of adsorption for calcium carbonates with differing surface coatings is significant. The industrial scale production of calcium carbonate generally involves a stearate coating in the range 2.5–3.0%, a range which has developed for empirical reasons. The observation that an increase in loading produces relatively little change in the heat of adsorption indicates that although 2.6% may not be the optimum loading it has virtually eliminated the influence of the high energy cationic sites and increased loadings above that level would have relatively little effect.

So far as uncoated calcium carbonates are concerned there is poor agreement between the values of heats of adsorption we report here and those of Schmitt *et al.*[8]. Their values of 11, 15 and 17 kJ/mol for *n*-hexane, *n*-heptane and *n*-octane, respectively, are remarkably low, being less than half of the values of the corresponding heats of condensation. Such values are similar to those we obtained in experiments before taking all the precautions we eventually found to be necessary[5]. There may be problems with water adsorption from the carrier gas and, equally important, if columns are not repeatedly reconditioned between injections, trace amounts of hydrocarbon probe may adsorb at polar cationic sites modifying the surface during the analysis. This results in variable retention volumes and poor linearity of the plots of log V_g against $1/T$. Hence it is possible that Schmitt *et al.* were in fact studying a modified calcium carbonate surface rather than the uncoated one which was assumed. In such circumstances the nature of the surface would probably be changing during the determinations so that reliable results would be difficult to achieve. The relatively good agreement between our two sets of results for coated calcium carbonate suggests that there are no fundamental differences of chromatographic technique which could account for the differences in the uncoated calcium carbonate.

CONCLUSIONS

Gas chromatographic measurements of the specific retention volumes for various hydrocarbons have provided a means of characterizing the surfaces of different precipitated calcium carbonate samples. For each homologous series the derived values of isosteric heat of adsorption at very low surface coverage show a linear dependency on carbon number. For a given hydrocarbon the highest value of heat of adsorption has been obtained with the pure calcium carbonate sample and the lowest with a stearate coated sample. The differences may be explained by the presence of exposed polar cationic sites on the surface of the pure material giving rise to specific interactions. These cations are masked by the stearate coating and there is thus less specific interaction in this case. There is some evidence that a coating of 2.6% stearate is sufficient to mask all of the cationic sites and that higher loadings have little effect.

The magnitude of the specific adsorbent–adsorbate interaction has been estimated as the difference between the corresponding values for unsaturated and saturated linear hydrocarbons. The pure sample again gives the highest value of heat of adsorption. The effect is further emphasized by the calculation of skew ratios for the various band since the value approaches unity, a symmetrical peak, on the stearate modified sample but is much lower on other samples.

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