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ADSORPTION OF ACETONE AND BUTANE ON LIQUID-MODIFIED GRAPHITIZED CARBON BLACKS

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SUMMARY

Gas–liquid, gas–solid, and gas–liquid–solid equilibrium isotherms were determined for acetone and butane on graphitized carbon black (Carbopack C) and liquid-modified graphitized carbon black (Carbopack C plus 0.2 % Carbowax 1500). The measurements were carried out over the range of temperatures from 30 to 75°C by mass spectrometric tracer pulse chromatography with stable isotopic solutes. Studies of the gas–liquid systems show that the bulk liquid undergoes a phase transition (wax → liquid) at 40°C and that the equilibrium isotherms vary significantly with temperature for the wax form. The temperature of the phase transition is shifted to 50–55°C for the same liquid coated on Carbopack C as a thin film.

The adsorption isotherms of acetone on the coated and uncoated Carbopacks were interpreted by means of a model of simultaneous competitive and cooperative adsorption effects. The Carbowax-modified adsorbent generally adsorbed as much, if not more, acetone at any given pressure than the uncoated adsorbent. This effect was attributed to specific lateral interactions between the solute and liquid or wax modifier. The magnitude of the enhanced capacity was much greater than could be accounted for by bulk solubility of acetone in the Carbowax.

The effect of preadsorbed acetone on the adsorption and retention of other solutes was also investigated. The specific retention volumes of small samples of butane were measured as a function of the surface coverage by acetone or acetone plus Carbowax 1500. Small amounts of preadsorbed acetone had little or no effect on the retention volume of butane, and the retention volumes were greater on the uncoated adsorbent. However, at surface coverages close to a monolayer, the retention volume of butane decreased dramatically with increased acetone adsorption. Also, at higher surface coverages, the retention volumes were the same for the coated and uncoated adsorbent at any fixed amount of acetone adsorbed. These "interference plots" were also explained in terms of the model previously discussed.

INTRODUCTION

Graphitized carbon blacks (GCBs) are unique adsorbents which have been used extensively as trapping material for water and air analysis and as chromato-

graphic stationary phases for the separation of a wide variety of samples[1-3]. These adsorbents have relatively homogeneous surfaces; however, many investigators have found that the chromatographic properties of these adsorbents could be improved by the addition of small amounts of a normal chromatographic liquid phase, presumably to block and deactivate high-energy, specific adsorption sites on the GCB surface[2,4-6].

Numerous investigations have been carried out to determine the exact effect of these high-molecular-weight, non-volatile liquids on the chromatographic properties of the adsorbents. The experiments usually involved the measurement of the isosteric heats of adsorption or some chromatographic retention parameter as a function of the amount of liquid phase coated on the adsorbent. Kiselev et al.[7] studied polyethylene glycols of different molecular weights coated on GCB and found that the retention volumes of all of the solutes studied decreased dramatically at the point of formation of a monolayer of the liquid. Bruner and co-workers[5,6] found that the isosteric heats of adsorption of alkanes and substituted benzenes increased slightly (1-3 kcal/mol) with surface coverage by high-molecular-weight hydrocarbons, such as squalane, up to the coverage corresponding to the formation of a monolayer. A sharp (4-6 kcal mol) decrease in the heats was observed at the point of formation of a monolayer. These same general results were obtained[4,5] for alkane solutes on GCB coated with a polar liquid, such as glycerol or Carbowax (PEG). The results for polar solutes (alcohols) were similar; however, the increase in the heats of adsorption at low surface coverage was greater (3-6 kcal/mol) and the decrease in the isosteric heats at coverages of a monolayer or greater was less dramatic (0-2 kcal·mol). It was also observed[4] that much more of the liquid was required to form the initial monolayer than was required for the formation of any subsequent layer.

These observations have been discussed[4-8] in terms of a model incorporating both competitive and cooperative adsorption. This latter effect is enhanced adsorption caused by lateral interactions between the adsorbate and the liquid "modifier" on the adsorbent surface[8]. All of the previously mentioned investigations were carried out with solutes at very low pressures ($P \rightarrow 0$). Under other conditions, there are additional sorption mechanisms which may operate, especially at finite solute concentrations. These are (i) adsorption of the solute on the surface of the liquid, (ii) solution of the solute in the adsorbed liquid, (iii) adsorption of the solute on the liquid-modified surface of the GCB, and (iv) cooperative adsorption caused by solute–solute interactions in addition to solute–liquid phase interactions. Another factor which must be considered is the magnitude of the modifier–adsorbent interactions which control the type of adsorption (localized or mobile) of the polymeric liquid.

In addition, the properties of the adsorbed liquid and the liquid-modified surface may differ significantly from the properties of the bulk liquid and the uncoated solid surface. Kern et al.[9] found that n-alkanes exhibited "prefreezing" (ordering) on the surface of graphite at temperatures above the normal freezing point of the bulk liquid, and several authors[9,10] have reported that the vapor pressures of liquids are diminished near a solid surface. Serpinet[12] has shown that docosane exhibited unusual melting phenomena when coated on the surface of GCB. Shifted melting points and significant hysteresis effects were also observed for this system. This author[12] suggests that docosane does not exhibit normal solvent properties at the melting point of the bulk liquid if it is coated on GCB, even in thick multilayers.

In previous investigations[13,14], the interactions of solutes at finite concentrations on the surface of GCBs with different surface areas have been studied. The effect of a liquid modifier. Carbowax 1500 (CW-1500). on these interactions was also investigated for non-polar solutes. In general. it was found that the polar liquid modifier did. indeed. decrease the capacity of the adsorbent for alkane solutes and that the isotherms of the alkanes were linear and segmented for the Carbowax-modified adsorbents. Significant cooperative adsorption was observed between the non-polar adsorbates. but no cooperative adsorption effects were observed for the non-polar adsorbates with the polar liquid. The primary role of the liquid in these systems was to deactivate the surface and diminish the surface area available for adsorption of the alkanes.

The mechanisms of retention and adsorption for these alkane systems are fairly well understood. On the other hand. polar systems. especially with solutes at finite pressures. are not as well characterized or understood. In this study. an investigation of the interactions of polar solutes with other solutes and with adsorbed liquids on the surface of GCB was undertaken. Other objectives were to clarify the role of the liquid modifier in these adsorption systems and to test the significance of each of the possible mechanisms which may operate in these polar systems. especially at high solute concentrations and at temperatures close to the normal melting point of the liquid "modifier".

EXPERIMENTAL

The instrumentation and mass spectrometric tracer pulse techniques have been described elsewhere[13-15]. The isotopic solutes used were [^{2}H$_6$]acetone (99.8 "$_o$) (Commissariat Pour l'Energie Atomique. France) and [^{2}H$_2$]butane. which was synthesized from butan-2-one by condensation with tosylhydrazide to give the tosylhydrazone which was subsequently reduced with sodium cyanoborodeuteride.

Mixtures of helium and unlabeled acetone were used as the carrier gases. The analysis of these mixtures was carried out on a Hewlett-Packard 5840A gas chromatograph by comparison of the gas mixture with standard samples from a gas stream saturated with acetone at different temperatures. The GCBs were commercial chromatographic adsorbents (Carbopack C and Carbopack C plus 0.2 "$_o$ CW-1500) (Supelco. Bellefonte. PA. U.S.A.).

The solubility studies were carried out with conventional packed columns. The solid support was Chromosorb P AW DMCS (Johns-Manville. Denver. CO. U.S.A.) coated with 21 "$_o$ CW-1500. Acetone was injected as a vapor with an effective sample size of less than 5 μg. The dead time of the column was determined from the retention time of the C_1–C_4 alkanes[16] or from the retention time of methane if the alkane peaks were unresolved.

RESULTS

Carbopack C with 0.2 "$_o$ Carbowax is a popular chromatographic adsorbent. Unfortunately the liquid modifier is not pure, but rather a mixture of equal amounts of CW-300 (PEG-300) and CW-1540 (PEG-1540). The material is a liquid at temperatures above 40°C and a wax at the lower temperatures studied. Most practical

TABLE I

COMPARISON OF ISOTHERM AND ELUTION DATA FOR ACETONE IN CARBOWAX 1500

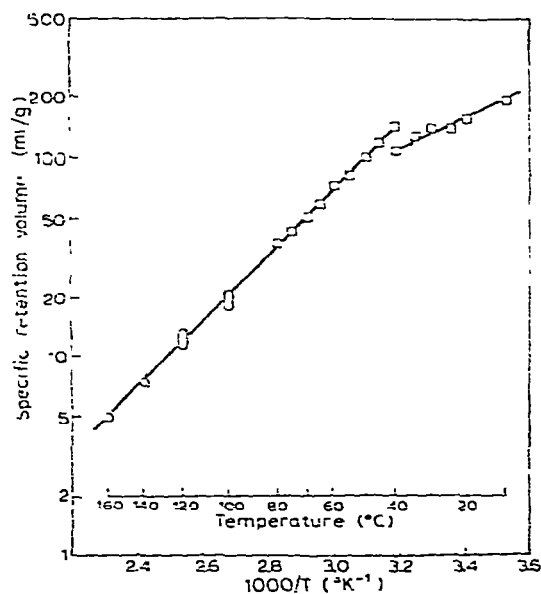| Temperature (°C)	Specific retention volume, V_g^0 (ml/g)	Calculated limiting slope of isotherm (mmol)
10	191	6.49
20	155	8.40
25	137	9.25
30	141	11.8
35	129	13.1
40	144	17.8
45	119	17.8
50	101	18.2
55	81.5	17.4
60	72.0	18.3
65	58.5	17.4
70	50.1	17.5
75	43.1	17.5
80	37.2	17.5
Average calculated limiting slope of isotherm (temperature range 40–80 °C)		17.7
Observed limiting slope of isotherm (temperature range 40–75 °C)		17.9

Fig. 1. Specific retention volume of acetone in Carbowax 1500. O, Literature data[1]; □, this work.

TABLE II

THE SOLUBILITY OF ACETONE IN CARBOWAX 1500

Relative pressure (P/P°)	Acetone dissolved (mmol/g)	Relative pressure (P/P°)	Acetone dissolved (mmol/g)
30°C		35°C	
0.023	0.044	0.006	0.012
0.033	0.065	0.030	0.072
0.092	0.187	0.061	0.151
0.134	0.291	0.110	0.289
0.193	0.456	0.159	0.471
0.283	0.750	0.222	0.703
0.369	1.106		
40°C		45°C	
0.023	0.065	0.032	0.103
0.066	0.223	0.080	0.279
0.115	0.413	0.138	0.486
0.166	0.600	0.199	0.764
0.231	0.929	0.268	1.139
60°C		75°C	
0.016	0.049	0.012	0.039
0.041	0.141	0.034	0.112
0.069	0.242	0.055	0.192
0.108	0.397	0.080	0.288
0.151	0.582		
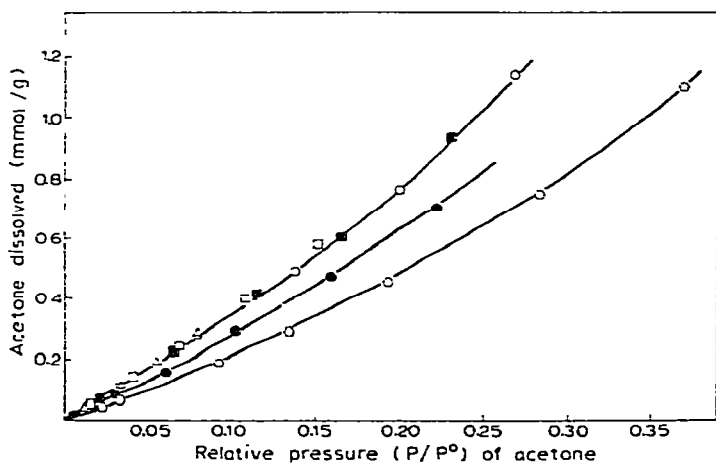
Fig. 2. Equilibrium isotherms of acetone in Carbowax 1500. ○, 30°C; ●, 35°C; ■, 40 C; ○, 45°C; □, 60°C; △, 75°C.

chromatographic applications of this adsorbent system require high temperatures, so the phase transition is not commonly a problem. However, sampling procedures are usually carried out at ambient temperatures, and the lower temperature regions are of more interest for a study of solute interactions on an adsorbent surface.

The low pressure ($P \to 0$) solubility of acetone in bulk CW-1500 over a range of temperatures from 30 to 75°C was determined by normal elution chromatography with the liquid coated on a deactivated (DMCS-treated) support. These data are presented in Table I. and Fig. 1 is a plot of the data in the form of ln V_g^o vs. 1000/T. The break in Fig. 1 at 40°C is due to the phase transition. The plots are linear at both high and low temperatures; however, at temperatures close to 40°C a significant hystersis effect was observed. If the column was equilibrated at room temperature and then heated to 40°C, the measured retention volumes initially agreed with the extrapolated value for the wax. Over a period of hours, the retention volume eventually increased to the extrapolated value for the liquid and remained at that value. For this reason two data points are shown in Fig. 1 for 40°C.

McReynold's[17] data at higher temperatures are also shown in Fig. 1. The agreement between the two data sets is very good, especially in view of the fact that the literature data is for a series of different molecular weight Carbowaxes. The heat of solution for acetone in liquid CW-1500 was determined from the slope of the plot and found to be -7.5 kcal/mol and the heat of "sorption" of acetone on the wax form of CW-1500 was only -2.7 kcal/mol.

The solubility isotherms were also determined over a range of temperatures and pressures by mass spectrometric tracer pulse chromatography (MSTPC)[15]. These data are given in Table II and Fig. 2. The plots of the amount of acetone dissolved as a function of the relative pressure (P/P^0) are congruent for the temperatures greater

TABLE III

THE SPECIFIC RETENTION VOLUMES OF INFINITE DILUTION SAMPLES OF BUTANE AND ACETONE ON GRAPHITIZED CARBON BLACK

Temperature (°C)	Specific retention volume (ml/m²)			
	Carbopack C		Carbopack C with 0.2% CW-1500	
	Butane	Acetone	Butane	Acetone
10	3.08	—	1.63	—
30	1.10	0.810	0.804	0.900
35	—	—	0.674	0.785
40	—	—	0.536	0.638
40	0.83	—	0.600	—
45	0.579	0.436	0.454	0.540
50	—	—	0.395	0.475
55	—	—	0.355	0.450
60	0.360	0.265	0.297	0.376
65	—	—	0.253	0.324
70	0.28	—	0.220	0.279
75	0.211	0.157	0.189	0.237
80	—	—	0.158	0.194
100	0.111	—	0.094	—

than 40°C. This is indicative of a liquid polymeric system in which the athermal or configurational contribution to the activity coefficient is predominant. On the other hand, the isotherms at 30 and 35°C are more typical of solid adsorption isotherms. The limiting slopes of each of the isotherms agree well with the value calculated from the limiting elution data as shown in Table I. No hystersis effects were observed in the MSTPC experiments at any of the temperatures used. This set of solubility data was obtained in order to quantitatively evaluate the liquid solubility contribution to the retention (adsorption) mechanisms for the liquid-modified GCB adsorbents.

The limiting ($P \rightarrow 0$) retention data for butane and acetone on Carbopack C and liquid-modified Carbopack C are given in Table III as specific retention volumes. These data were obtained by normal elution GC. however. the values are given in units of ml/m^2. rather that the normal units of ml/g. Fig. 3 is a plot of ln V_g^0 vs. 1000/T for the acetone data. There is an obvious irregularity in the range from 50 to 55 C. This is indicative of the wax $\rightarrow$ liquid transition. which has been shifted to higher temperatures by adsorption of the liquid on the GCB surface[12]. This transition occurs at ca. 40°C for the bulk liquid. but is shifted to 50–55 C when the liquid is present as a monolayer on the adsorbent.

Fig. 3 also shows that there is a small contribution to the specific retention volume from the solubility of acetone in CW-1500. or more likely from some other mechanism which operates when the modifier is in the liquid form. The limiting heats of adsorption for these systems were ca. −7.5 kcal/mol for acetone on both the GCB and liquid-modified GCB at temperatures above 40°C. The corresponding data for butane was ca. −6.5 kcal/mol.

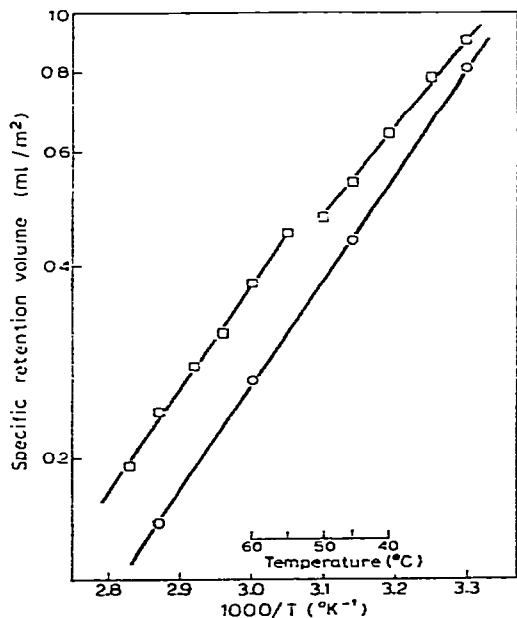Adsorption isotherms of acetone on the two adsorbents were determined at

Fig. 3. Specific retention volumes of acetone and on Carbopack C (O) and Carbopack C with 0.2"₀ Carbowax 1500 (□).

TABLE IV

ADSORPTION DATA FOR ACETONE AND RETENTION DATA FOR [²H₆]-ACETONE AND n-BUTANE ON GRAPHITIZED CARBON BLACKS

Temperature (°C)	Carbopack C				Carbopack C with 0.2% Carbowax 1500			
	Relative pressure (P/P^0)	Acetone adsorbed $(\mu mol/m^2)$	Specific retention volume (ml/m^2)		Relative pressure (P/P^0)	Acetone adsorbed $(\mu mol/m^2)$	Specific retention volume (ml/m^2)	
			Acetone isotope	Butane			Acetone isotope	Butane
75	0.008	0.13	0.205	0.245	0.0050	0.09	0.255	0.155
	0.033	0.50	0.188	0.204	0.020	0.36	0.218	0.154
	0.045	0.79	0.216	0.213	0.029	0.57	0.243	0.161
	0.053	0.91	0.209	0.197	0.042	0.90	0.260	0.156
	0.069	1.25	0.222	0.190	0.054	1.15	0.261	0.141
	0.086	1.72	0.239	0.185	0.072	1.57	0.268	0.131
	0.100	1.75	0.214	0.184	0.091	1.96	0.263	0.120
60	0.005	0.07	0.269	0.322	0.0065	0.15	0.445	0.336
	0.021	0.34	0.313	0.329	0.029	0.72	0.476	0.342
	0.042	0.73	0.328	0.344	0.045	1.21	0.517	0.333
	0.047	0.91	0.377	0.348	0.063	1.75	0.530	0.264
	0.068	1.26	0.380	0.267	0.086	2.13	0.475	0.185
	0.070	1.40	0.418	0.281	0.116	2.41	0.393	0.125
	0.099	2.05	0.408	0.217	0.131	2.67	0.392	0.115
	0.124	2.30	0.368	0.162	0.154	2.74	0.340	0.089
	0.155	2.56	0.324	0.123	0.163	2.91	0.341	0.087

45	0.009	0.15	0.522	0.571	0.017	0.25	0.585	0.427
	0.020	0.33	0.513	0.567	0.045	1.14	0.796	0.434
	0.037	0.76	0.736	0.552	0.066	1.73	0.831	0.343
	0.046	1.04	0.718	0.518	0.095	2.36	0.792	0.237
	0.074	1.78	0.767	0.406	0.127	2.82	0.709	0.185
	0.083	2.01	0.776	0.326	0.135	3.05	0.720	0.180
	0.112	2.36	0.679	0.272	0.167	3.27	0.624	0.142
	0.173	3.08	0.573	0.163	0.193	3.59	0.595	0.121
	0.217	3.35	0.494	0.112	0.247	3.98	0.516	0.098
	0.290	3.78	0.419	0.095	0.274	4.30	0.501	0.092
30	0.015	0.22	0.817	0.961	0.023	0.36	0.881	0.691
	0.033	0.55	0.951	0.954	0.037	0.71	1.082	0.714
	0.063	1.49	1.334	0.791	0.081	1.74	1.225	0.675
	0.144	3.04	1.203	0.314	0.130	2.88	1.262	0.347
	0.233	3.61	0.879	0.168	0.202	3.79	1.065	0.231
	0.373	4.35	0.663	0.096	0.310	4.41	0.810	0.132
	0.500	5.04	0.574	0.064	0.454	5.28	0.665	0.079
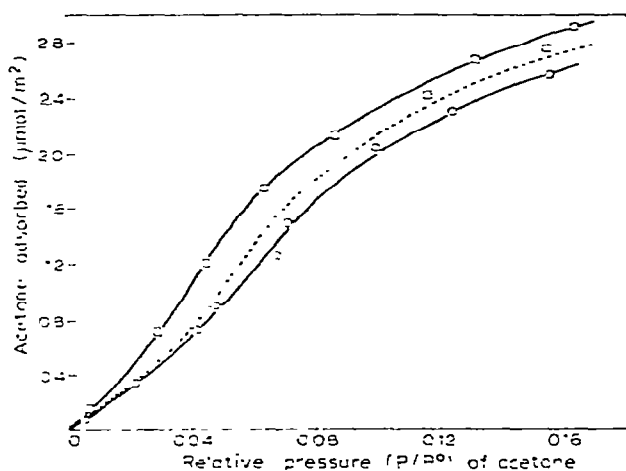
Fig. 4 Adsorption isotherms of acetone at 60 C. O. Carbopack C: □. Carbopack C with 0 2"₀ Carbowax 1500; ----. Carbowax 1500.

several temperatures using MSTPC and these data are given in Table IV. The first two columns for each adsorbent represent the adsorption isotherm for acetone. and this data is plotted in Figs. 4–6. The plot at 75°C is not shown; however, it has the same general form as the plot for 60°C. At these higher temperatures, the liquid-modified adsorbent adsorbed more acetone than the uncoated GCB at all pressures. On the other hand, there was little or no difference between the isotherms of the two sorbents at low temperatures and low pressures (Figs. 5 and 6. $P/P^0 \leqslant 0.1$). At higher pressures, the capacity of the liquid-modified GCB was again greater than that of the bare GCB.

This finite concentration data shows that several different adsorption mechanisms are operative in these systems. The relative contribution of each mechanism is a
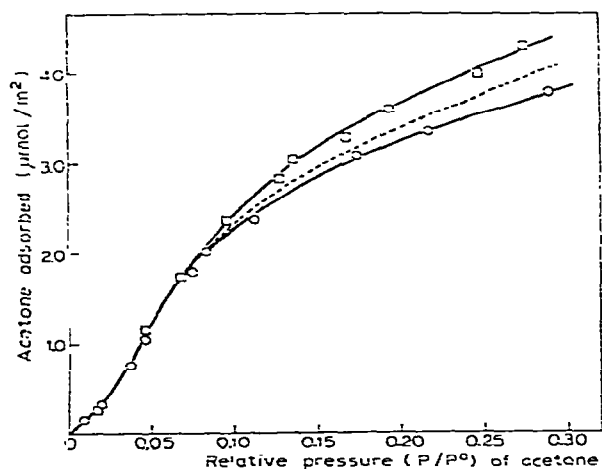

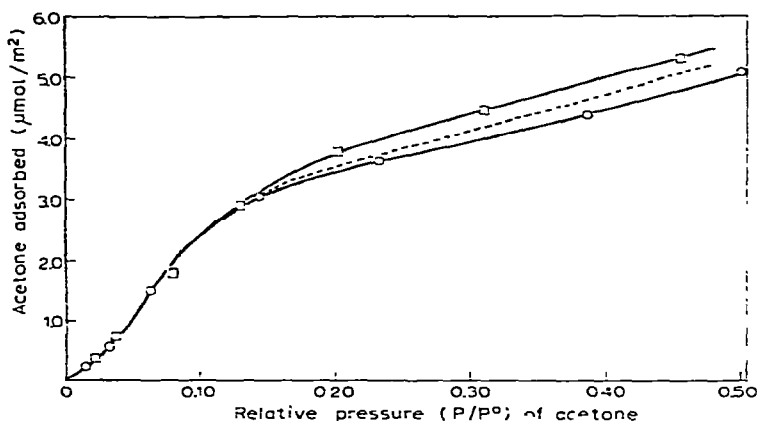Fig. 5. Adsorption isotherms of acetone at 45°C. Legend same as Fig. 4.

Fig. 6. Adsorption isotherms of acetone at 30 C. Legend same as Fig. 4.

function of temperature. pressure. surface condition (bare or liquid-modified). and the condition of the liquid or wax modifier.

DISCUSSION

In general, the results of this investigation agree with previous work. The liquid modifier (CW-1500) blocks some of the surface sites. This is indicated by the decreased adsorption of non-polar solutes, such as propane and butane, on the liquid-modified adsorbents[14]. The amount of surface blocked by the liquid cannot be determined exactly, but is *ca.* 1/3 to 1/2 of the total surface area. However, this blocking effect is only apparent for solutes which cannot specifically interact with the non-volatile liquid modifier.

Solutes such as acetone which can interact with the polar liquid modifier exhibit enhanced adsorption on the liquid-modified adsorbent in spite of the blocking effect of the liquid. This enhanced adsorption is due to lateral interactions on the adsorbent surface. The specific interactions are solute–modifier at low pressures and solute–solute at higher pressures. Cooperative adsorption effects are also observed for non-polar solutes for polar liquid-modifiers, but only at high pressures indicating only solute–solute interactions. Cooperative adsorption of non-polar solutes with non-polar liquids has been observed previously[6] at low solute pressures.

The significance of bulk solubility effects in these systems is not clear because of the small amount of liquid (0.2 %) and the monolayer character of the liquid film. The solubility of butane in CW-1500 was too low for an accurate assessment at the temperature used in this study; however, the solubility of acetone was significant and was dependent upon the physical state of the modifier as shown in Fig. 1.

The specific retention volumes of infinite dilution samples of butane and acetone on the GCB and liquid-modified GCB show that a phase transition occurs for the CW-1500 on the GCB but at elevated temperatures. In this case the transition occurs in the range 50–55°C, as indicated by both the acetone and butane data (Figs. 3 and 7). At higher temperatures, the heats of adsorption of acetone are equal for the coated and uncoated adsorbents; however, the retention is greater on the liquid-

modified adsorbent. The same is true for butane as a solute, except that the retention is greater on the uncoated adsorbent. For both solutes, the heats of adsorption at lower temperatures are significantly less than at high temperatures where CW-1500 is a liquid. This decrease in heats and retention for the wax phase could be caused by a change in the retention mechanism from solution to adsorption, as observed for the bulk liquid, or by a change in the magnitude of the cooperative and competitive adsorption processes on the liquid and wax coated adsorbents.

The modified adsorbents were studied at finite solute pressures in order to examine further the retention mechanisms. At temperatures above the transition temperatures for the CW-1500 on the GCB surface, the liquid-modified adsorbent consistently adsorbed more acetone at the same pressure than the uncoated GCB. This could possibly be due to the solubility of acetone in CW-1500. To determine the magnitude of this effect, the maximum possible solubility contribution to the sorption isotherms at each temperature was calculated from the data given in Table II and plotted in Figs. 4–6 as the dotted line. This represents the enhancement in the isotherm that would be expected *if the CW-1500 did not block any of the surface and the CW-1500 had bulk solubility properties*.

The increased capacity if the liquid-modified adsorbent is due to the cooperative (solute–liquid and solute–solute) adsorption effects which are significant for these systems when the modifier is a liquid. On the other hand, the wax-modified GCB (at temperatures less than 50°C) showed enhanced adsorption of acetone at very low pressures (Fig. 3) and high pressures (Figs. 5 and 6), but little or no effect at intermediate pressures. At intermediate pressures, *i.e.* $0 < P/P^0 \leqslant 0.10$–0.15, the amount of acetone adsorbed by the modified and uncoated GCBs are the same within the limits of the measurements. This observation cannot be explained by changes in the solubility of acetone in CW-1500. More likely, there is a significant difference in the relative magnitudes of the cooperative and competitive adsorption effects between the two modified surfaces (wax-modified and liquid-modified).
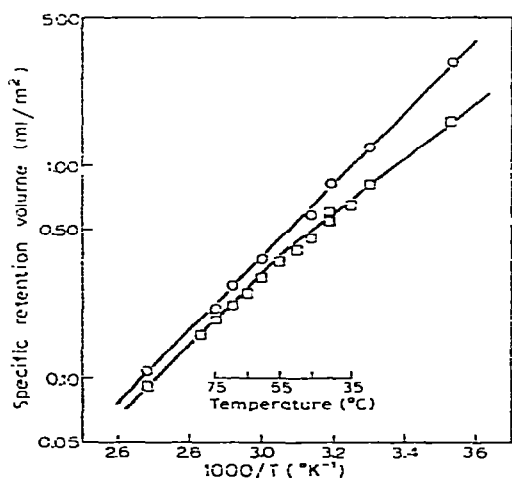

Fig. 7. Specific retention volumes of butane on Carbopack C (O) and Carbopack C with 0.2 % Carbowax 1500 (□).
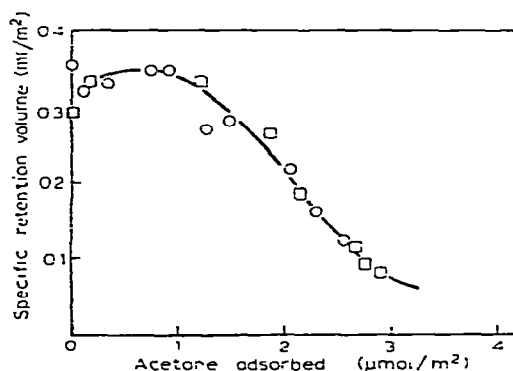
Fig. 8. Specific retention volumes of butane on Carbopack C (O) and Carbopack C with 0.2 % Carbowax 1500 (□), as a function of amount of acetone adsorbed at 60°C.
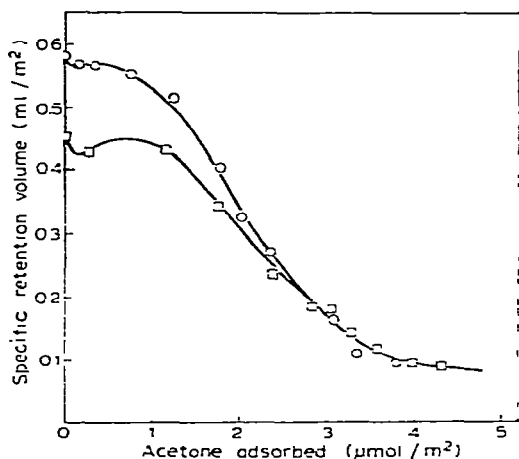
Fig. 9. Specific retention volumes of butane on Carbopack C (O) and Carbopack C with 0.2"" Carbowax 1500 (□) as a function of amount of acetone adsorbed at 45 C.
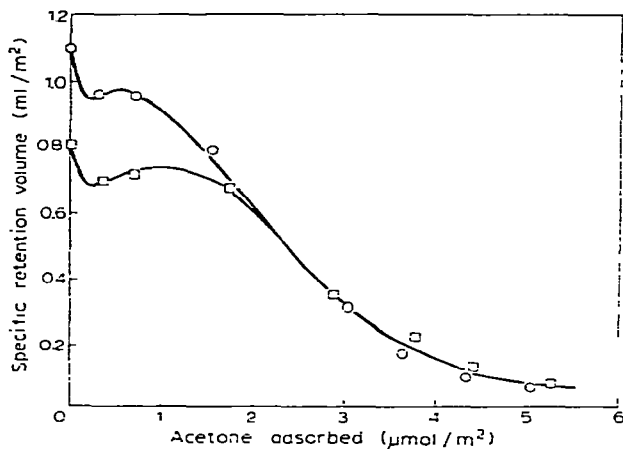
Fig. 10 Specific retention volumes of butane on Carbopack C (O) and Carbopack C with 0 2"" Carbowax 1500 (□) as a function of amount of acetone adsorbed at 30 C.

Localized adsorption of the wax form, as opposed to delocalized (mobile) adsorption of the liquid form could account for the diminished magnitude of solute–modifier cooperative adsorption at the lower temperatures and pressures. Decreased mobility of the modifier on the surface would result in less accommodation of the solute molecules, diminished cooperative adsorption and enhanced competitive adsorption (blocking). At very low pressures of the solute, the mobility of the modifier is not critical so the usual cooperative adsorption effects are observed. At higher pressures, multilayer adsorption of the acetone is observed and the liquid simply provides a better surface for adsorption than the acetone itself in the form of multilayers on uncoated GCB. The same phenomenon is observed at high pressures for all of the temperatures investigated. That is, the physical state of the modifier (wax or liquid) (localized or delocalized adsorption) does not influence the adsorption of acetone after the formation of a monolayer.

This model was tested for additional solutes at infinite dilution, by measuring the effect of adsorbed acetone on the specific retention volumes of small samples of butane. This data is given in the fourth and last columns of Table IV for the two types of adsorbent. The results are also shown in Figs. 8–10. The curves all have the same general form as previously observed for butane and propane adsorption[14]. At low acetone pressures, the blocking effect of the CW-1500 is predominant. Increased amounts of acetone adsorbed on the surfaces result in decreased retention (adsorption) of the infinite dilution samples of butane. The sharp decrease in the retention volume with 1–3 μmol/m^2 of acetone adsorbed corresponds to the formation of a monolayer of acetone or acetone plus CW-1500. Significantly, the presence of CW-1500 has little or no effect on the amount of acetone required to block out the butane samples. This indicates that the acetone, unlike butane, is not preferentially adsorbed on the solid (GCB) surface, but is adsorbed on regions of the surface "covered" by the CW-1500 polymer. That is, there exist regions on the surface that are inaccessible to butane because of competitive adsorption, but accessible to acetone due to cooperative adsorption effects.

CONCLUSIONS

CW-1500 present as a thin layer on the surface of GCB has significantly different physical properties. *e.g.* phase transition temperature and solubility. from the bulk liquid. This confirms the results of previous investigations of similar systems[12].

Cooperative adsorption due to solute–solute interactions was observed for both acetone and butane at finite concentrations on both adsorbents. However. solute–modifier interactions were observed only for solutes with polarity similar to that of the modifier. These cooperative adsorption effects differed in magnitude for the same system depending upon the mobility of the non-volatile modifier on the surface of the GCB.

Adsorption of a component from the carrier gas can significantly alter the adsorption properties of the system for other solutes. The exact effect of the adsorbed component depends upon the amount adsorbed and on the polarity and chemical characteristics of the adsorbed component and the other solutes. The influence of a non-volatile modifier is similar to that of a volatile component. except that the type of adsorption (localized–delocalized) of the non-volatile modifier may significantly alter the balance of the cooperative and competitive adsorption equilibria.

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