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ADSORPTION OF MIXTURES OF ACETONE AND BENZENE VAPORS ON GRAPHITIZED CARBON BLACK

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SUMMARY

Further description and interpretation of a previously determined set of adsorption isotherms of mixtures of acetone and benzene on Carbopack C at 20°C are presented. The individual and combined isotherms are represented as three-dimensional plots covering a full range of surface coverage up to, and slightly beyond, monolayer coverage. A limited set of isotherm data is also presented for hydrogen-treated Carbopack C.

The experimental procedure was a chromatographic method, mass spectrometric tracer pulse chromatography, which allowed the determination of the isotherm of one component at a fixed partial pressure of the second component. This protocol permitted the development of full isotherms, rather than the more restricted isotherms obtained with classical experiments at fixed gas phase composition or fixed total pressure.

The adsorbent was selective for benzene at 20°C, and the isotherms of benzene were not significantly affected by adsorbed acetone. However, the isotherms of acetone were critically dependent on the partial pressure of benzene. Very low surface coverages of benzene prevented the adsorption of disproportionately large amounts of acetone (up to a ratio of 1:100). This amplification effect was similar to that observed for poisoning and promotion effects on Fischer–Tropsch catalysts.

The experimental results are discussed in terms of two possible adsorption mechanisms. Both models emphasize the significance of a small number of high energy sites (mostly chemisorbed oxygen or sulfur) on the surface of the Carbopack C. These "key" sites may anchor segregated adsorption of acetone clusters stabilized by direct lateral interactions, or they may influence the work function or ionization potential of the surface adjacent to the site by influencing the electron density in the delocalized pi orbital of the graphite surface. Removal of the hot sites by treatment with hydrogen at high temperature reduced the adsorption of acetone and the poisoning effect of benzene.

INTRODUCTION

Adsorption isotherms of mixtures of vapors often deviate significantly from

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the isotherms of the pure components at the same relative pressures. Such deviations may be caused by direct or indirect solute interactions in the condensed phase on the surface of the adsorbent. The strengths of such interactions depend upon many diverse factors, such as the nature of the adsorbates and the physical and chemical characteristics of the adsorbent, as well as the primary factors of pressure and temperature. In addition, non-ideality of the binary isotherms may be caused by changes in the electronic properties of the adsorbent surface or by geometric factors such as the formation of segregated clusters or ensembles of one or more adsorbates.

Enhanced adsorption or cooperativity has been observed for several adsorbate mixtures[1–4] on graphitized carbon blacks (GCBs) and for solutes on GCB partially covered with a non-volatile liquid[5–8]. Such effects have primarily been observed by chromatographic methods with one or more components present only at very low pressure (infinite dilution). Most of these studies were done with GCBs because these adsorbents have very homogeneous surfaces which facilitate the observation of such enhancement effects. The general explanation for cooperativity in these systems is that direct lateral solute–solute interactions produce enhanced adsorption, and this effect dominates over the loss of available surface area.

On the other hand, severe poisoning or interference has been observed for other vapor mixtures[9–11] on GCBs. This effect is most commonly observed when both adsorbates are present at finite pressures. Interference is usually pronounced at the point of completion of a monolayer on the surface, although diminished adsorption has often been observed at low surface coverages[9,10].

Similar interference and enhancement effects have been extensively studied for coadsorption on metal catalysts where small amounts of one adsorbate or additive may poison or promote the catalytic activity of a second component, often by an order of magnitude or more[12–14]. Chemisorption of mixtures on catalysts is far more complex than physisorption on GCBs. However, physical adsorption is an integral part of any catalytic process, and accurate models are needed for the description of such multicomponent adsorption processes. Theories have been developed[15–18] for adsorption of mixtures; however, these models were derived for relatively ideal systems, such as mixtures of permanent gases, and are not adequate for systems in which pronounced cooperativity or interference effects occur. The lack of adequate and appropriate experimental data for binary adsorption systems is the primary reason for the lack of practical isotherm models for complex systems.

Classical gravimetric and volumetric methods for the determination of adsorption isotherms are laborious and time-consuming, and the analytical requirements are prohibitive for multicomponent systems. However, chromatographic methods have recently been used to study complex systems with one or more components at finite concentrations[1–4]. These methods are fast, accurate, and relatively simple. In one recent investigation[19], coadsorption of acetone and benzene on a GCB was studied and all three phenomena, cooperativity, interference, and magnification, were demonstrated for the physical adsorption of these solutes. The present work is an extension and interpretation of this earlier investigation.

EXPERIMENTAL

The experimental procedure used[20] to determine the binary adsorption isotherms involved the use of a fixed-bed column at equilibrium conditions. The adsorbed phase composition was determined from the residence times of small plugs of isotopically labeled adsorbate. In this case the isotopic solutes were [$^2H_6$]benzene and [$^2H_6$]acetone. Small correction (*ca.* 5%) were made for the isotope effect on the retention of the perdeuterated solutes.

The experiments were carried out with fixed pressures of acetone and variable pressures of benzene. This procedure was used with eight different pressures of acetone, so that full three-dimensional isotherms could be developed. This experimental protocol was significantly different from the normal static methods which are usually limited to either fixed gas phase composition or fixed total pressure.

The Carbopack C and C-HT (Supelco) had measured surface areas of 8.9 and 11.3 m^2/g, respectively, as determined from the BET parameters for benzene. All of the experiments were carried out at 20°C.

RESULTS

The single-component isotherms of benzene and acetone have been determined previously[3,21], and the isotherms of mixtures of these adsorbates are given in a previous publication[19]. Both adsorbates have also been studied previously[2,3] in mixtures with one component at infinite dilution. In these studies, the retention volumes (Henry's Law constants) of small samples of one component were determined as a function of the surface coverage with the other component. The retention volume of benzene

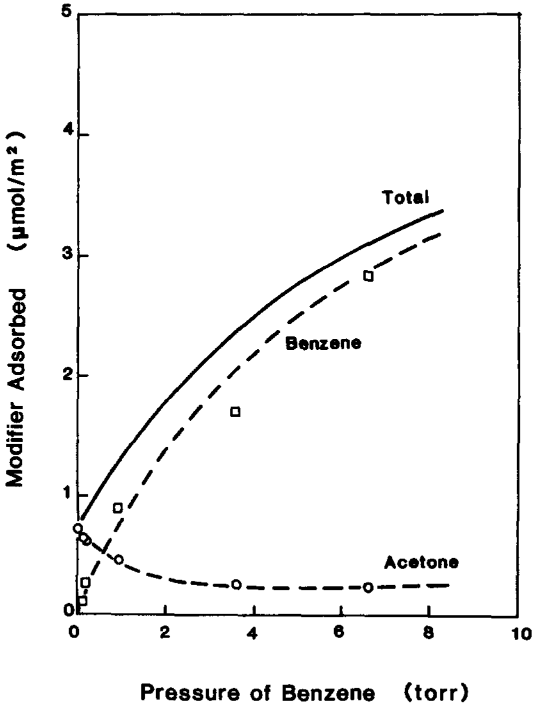

Fig. 1. Adsorption isotherms of acetone and benzene on Carbopack C at 20°C; acetone pressure, 4.0 torr[19].

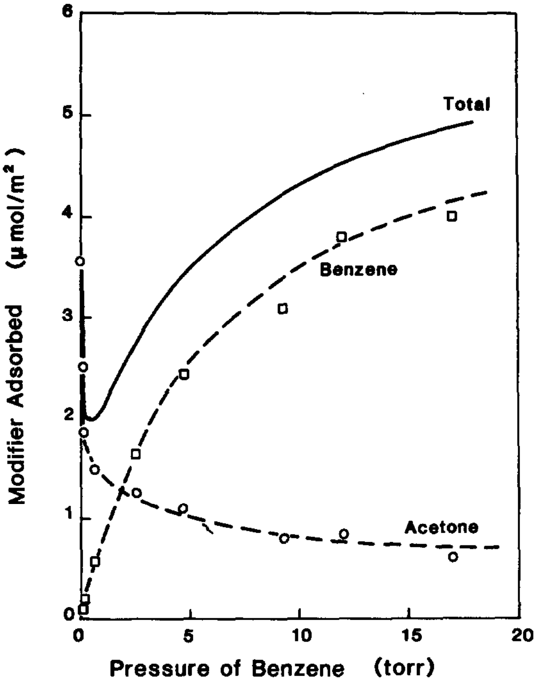

Fig. 2. Adsorption isotherms at 14 torr of acetone.

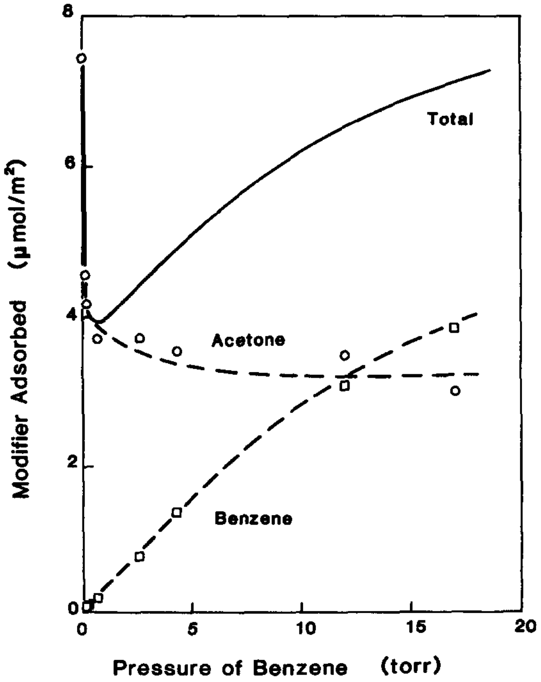

Fig. 3. Adsorption isotherms at 57 torr of acetone.

simply decreased monotonically with surface coverage of acetone. No clear enhancement effects were observed because of the stronger, localized adsorption of benzene compared with acetone. On the other hand, cooperative (enhanced) adsorption of acetone was observed at intermediate surface coverage with benzene owing to the lateral interactions of benzene with the weakly adsorbed acetone.

The isotherms of binary systems with both components at finite pressures are also very complex. Some of these isotherms at different acetone pressures are given in Fig. 1–3. At low acetone pressure, benzene is preferentially adsorbed, and the amount of acetone adsorbed at fixed acetone pressure decreased with the fractional surface coverage of benzene, Θ_B. Fig. 2 shows that the isotherm of benzene is almost the same at higher acetone pressures; however, a significant decrease in the amount of acetone adsorbed occurred at very low benzene pressures. A minimum was observed in the total isotherm at a benzene pressure of 1 torr. The fractional surface coverage of benzene was less than 0.2, and the total fractional surface coverage, $\Theta_A + \Theta_B$, was *ca.* 0.5. This interference effect was even greater at higher acetone pressures (Fig. 3). Adsorption of 0.02 μmol/m^2 of benzene reduced the amount of acetone adsorbed from 7.4 to 4.6 μmol/m^2. This represents an amplification factor of 140.

The isotherms of benzene were fit to the BET[22] equation, and the results are given in Table I. The values of the *C* term, which is proportional to the net heat of adsorption, decreased significantly with acetone pressure. However, the monolayer capacity, v_m, is relatively constant at 3.8–4.0 μmol/m^2. Slightly higher values were calculated at intermediate pressures of *ca.* 9 torr and at the highest acetone pressure, 57 torr. The latter value was not reliable because the isotherm was nearly linear and did not fit the BET equation well. The high v_m values at 9 torr were confirmed by duplicate experiments at 8.8 and 9.3 torr.

The parameters in Table I were used to generate continuous isotherms of benzene at fixed acetone pressures, and the resultant complete isotherm is given in Fig. 4. In general, the magnitude of the benzene adsorption was surprisingly independent of the amount of acetone adsorbed. Interference was observed only at the highest acetone pressures.

The isotherms of acetone in the same experiments were significantly different in shape and magnitude from the isotherm of pure acetone on the GCB. These continuous isotherms are shown in Fig. 5. At fixed pressures of benzene from 2 to 30

TABLE I

BET PARAMETERS FOR THE ISOTHERMS OF BENZENE ON CARBOPACK C AT 20°C

Pressure of acetone (torr)	*Monolayer capacity n_m (μmol/m^2)*	*C*
0.0	3.8	83
4.0	3.7	25
5.3	3.6	25
8.8	4.5	15
9.3	4.1	16
14	3.7	23
27	3.6	29
35	4.0	11
57	4.9	5

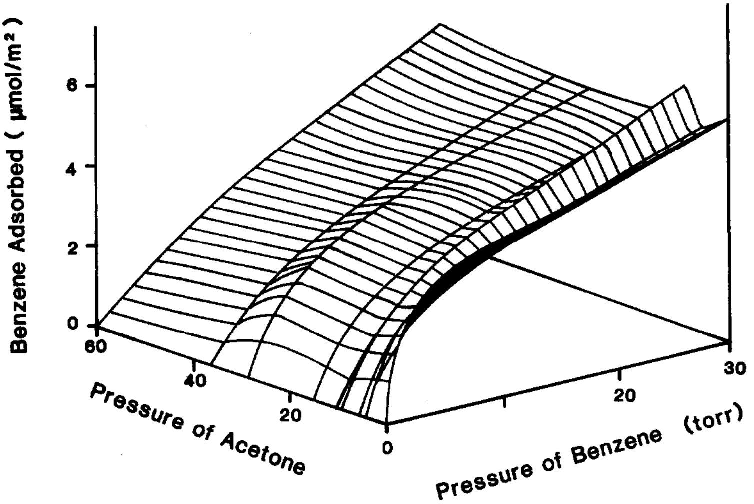

Fig. 4. Complete adsorption isotherm of benzene on Carbopack C at 20°C.

torr, the acetone isotherms are linear, essentially independent of the amount of benzene adsorbed, and lower in magnitude than the pure acetone isotherm. The sharp decrease in acetone adsorption at the lowest pressures of benzene is evident. This antagonistic effect is shown in a different manner in Fig. 6, which is a plot of the surface coverage with acetone as a function of the surface coverage with benzene at fixed acetone pressures. The significant interference and magnification effects occur at the highest acetone pressures and the lowest benzene pressures. This plot is very similar to those observed by Erley and Wagner[13] for sulfur poisoning and by Chen

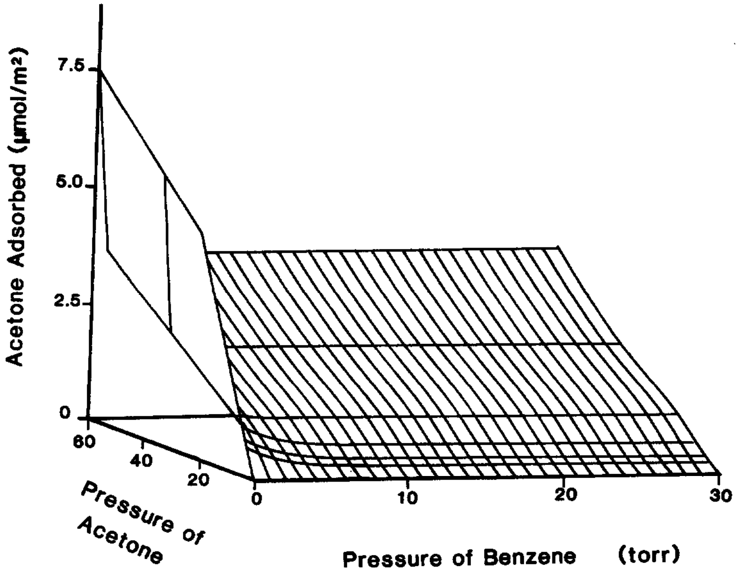

Fig. 5. Complete adsorption isotherm of acetone on Carbopack C at 20°C.

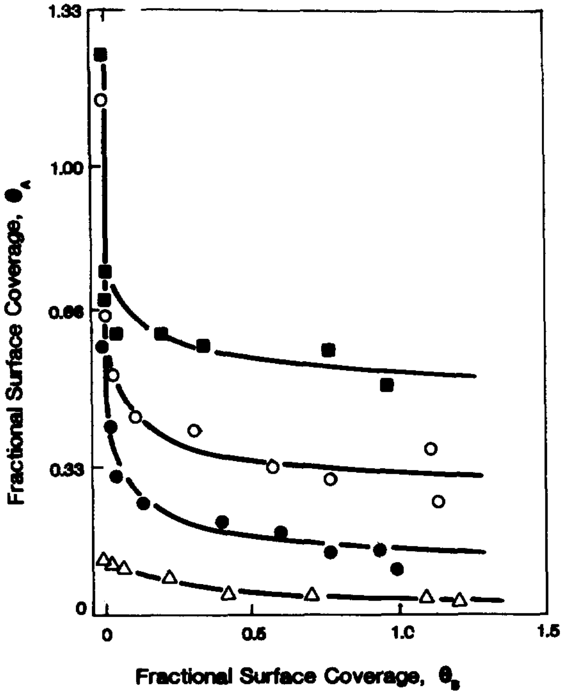

Fig. 6. Variation of fractional surface coverage with acetone as a function of surface coverage with benzene at fixed acetone pressures. Curves: △ = 4.0 torr; ● = 14 torr; ○ = 35 torr; ■ = 57 torr.

and White[23] for the effect of adsorbed potassium on chemisorption of hydrogen.

Fig. 7 is the combined isotherm for acetone and benzene on the GCB. The plot emphasizes the effect of the composition of the binary vapor phase upon the adsorption capacity of an adsorbent and the non-stoichiometric nature of the physical adsorption of mixtures on homogeneous adsorbents.

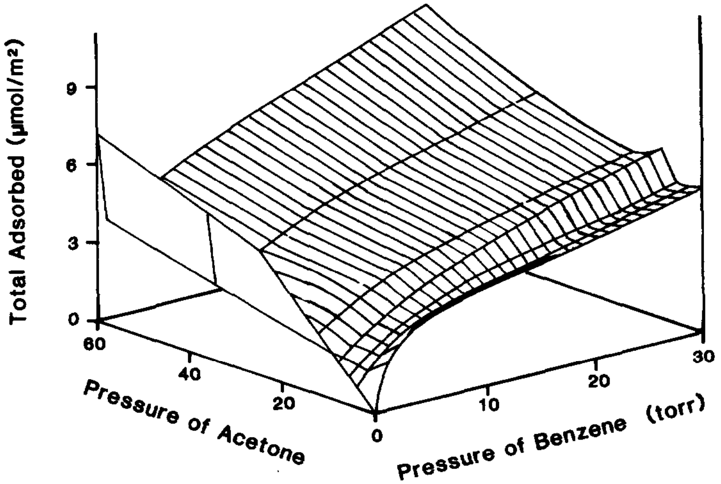

Fig. 7. Combined adsorption isotherm of benzene and acetone.

DISCUSSION

Mass spectrometric tracer pulse chromatography is a unique experimental procedure for the investigation of complex multicomponent adsorption systems. Determination of the isotherm of one component at fixed pressure of another component allows the accurate determination of isotherm surfaces or hyperplanes, such as those shown in Figs. 4, 5 and 7. These three-dimensional isotherms show the full scope of the complex interactions of adsorbates and the resultant effect on the adsorbent capacity.

The isotherms show that benzene is preferentially adsorbed at 20°C, and the benzene isotherms are not complex or unusual. However, the acetone isotherms have two unexpected features. One is the strong poisoning effect of benzene at very low surface coverage, and the other is the apparent absence of interference effects at higher benzene surface coverages. Increased benzene adsorption should produce statistically diminished adsorption of acetone at fixed acetone pressure.

The poisoning effect at very low surface coverages is similar to that observed for chemisorbed sulfur and oxygen atoms on metal catalysts. This effect is most commonly interpreted in terms of a model proposed by Blyholder[24] for adsorption of carbon monoxide. This model has been used for many other systems[25-28] to explain both promotion and poisoning effects. The general explanation is that chemisorbed electron-withdrawing groups cause an increase in the work function or ionization potential of the adjacent surface by decreasing the electron density of the *d*-level orbitals of the metal catalysts. This effect would impair the adsorption of an adsorbate, such as carbon monoxide, that requires back-donation of electrons from the surface for bond formation. Enhanced adsorption would result for adsorbates which utilize an electron-donation adsorption mechanism. Chemisorbed sulfur and oxygen atoms on GCB could have the same type of electronic effect on the delocalized pi orbital of the graphite surface. The region of surface adjacent to the "hot" spot would have adsorption properties different from those of the free surface. The observed poisoning effect of benzene on the adsorption of acetone would be caused by

TABLE II

ADSORPTION DATA FOR ACETONE ON CARBOPACK C-HT AT 20°C

Relative pressure of acetone (p/p^0)	*Acetone adsorbed* ($\mu mol/m^2$)
0.010	0.28
0.087	2.02
0.099	2.32
0.114	2.66
0.138	3.20
0.143	3.10
0.174	3.87
0.202	4.87
0.215	5.35
0.230	5.23
0.231	5.33
0.243	5.08
0.244	5.68
0.268	5.95

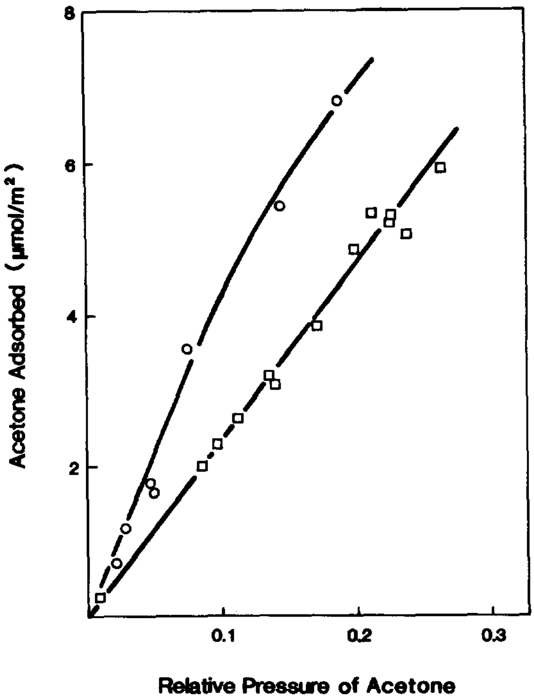

Fig. 8. Adsorption isotherms of acetone on Carbopack C (○)[19] and Carbopack C-HT (□) at 20°C.

the neutralizing effect of benzene preferentially adsorbed on the hot spots to decrease the effect of the heteroatoms on the electronic structure of the surface.

The chemisorbed heteroatoms could also support the formation of ensembles or clusters of adsorbates, such as acetone, which can interact directly and strongly. The clusters would not be supported as well by interactions with benzene preferentially adsorbed on the heteroatom sites, thus benzene would prevent the formation of acetone clusters. Segregated adsorption of this type has been observed frequently[29-31], and the existence of sulfur and oxygen atoms on the surface of Carbopack C has also been proven[5,32,33]. The number of such high energy sites is small; however, their effect may be unexpectedly significant.

The chemisorbed species may be partially eliminated by treatment with hydrogen at high temperature[5] or acid washing[33]. Adsorption isotherm data for acetone on hydrogen-treated Carbopack C is given in Table II, and Fig. 8 shows the acetone isotherms for the treated and untreated GCB. The HT material adsorbs significantly less acetone than the untreated material, and removal of the oxygen or sulfur complexes from the surface eliminates the poisoning effect of benzene. Unfortunately, this would be the anticipated result for either of the proposed models.

The lack of interference between the two adsorbates at high surface coverage of benzene is due to two offsetting effects. Benzene is preferentially adsorbed, so the surface area available for adsorption of acetone decreases with increasing Θ_B. However, preadsorbed benzene supports additional adsorption of acetone by a direct interaction mechanism[3]. This effect would be weaker than that for pure acetone, yet strong enough to offset the loss of surface area. The two effects apparently cancel in this system, and at high benzene pressures the amount of acetone adsorbed at fixed acetone pressure is relatively independent of the surface coverage with benzene.

The mechanisms of adsorption of acetone and benzene on GCB are significantly different. Benzene adsorption is localized; the adsorbed molecules are relatively far apart; and there are only weak interactions between adsorbed molecules[29]. Acetone is not as strongly adsorbed as benzene, and the adsorbate forms segregated islands or clusters on the surface. These ensembles form preferentially around chemisorbed heteroatoms or other physical and chemical inhomogeneities, and the adsorbate clusters are held together by direct lateral interactions or indirectly by the influence of the heteroatoms on the adsorption energy of the adjacent surface.

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