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GAS CHROMATOGRAPHIC DETERMINATION OF BINARY ADSORPTION ISOTHERMS

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SUMMARY

Gas-solid equilibrium isotherms of binary and more complex systems are of significant theoretical and practical interest, and in many cases unique physical and chemical interactions are observed in the condensed surface phases. However, the experimental difficulties encountered in the study of these complex systems have limited the store of data available compared to the immense amount of information, data, and models available for single-component adsorption systems. Volumetric and gravimetric methods for the determination of equilibrium isotherms are direct and accurate. However, the analytical requirements are often prohibitive for multicomponent systems.

Various forms of perturbation chromatography have been used for years to measure pure-component isotherms and in a few cases even binary isotherms. The present work is a compilation and review of recent work involving the use of concentration-pulse and tracer-pulse chromatography for the study of multicomponent phase equilibria. A discussion is given of the various types of perturbation chromatography, recently published experimental data, and the all too few mathematical models available for description of complex multicomponent adsorption equilibria.

INTRODUCTION

Adsorption of mixtures of gases and vapors on solids is of significant interest in many diverse areas of chemistry. The practical application of vapors as gas chromatographic (GC) carrier gases is one example of interest to the chromatographer. Similarly, analytical chemists routinely use solid adsorbents, such as graphitized carbon black (GCB) (Carbopack, Carbotrap, etc.) and polymers (Tenax-GC, XAD, Porapack, etc.) for collection and preconcentration of air and water samples. Chemical and physical interactions of the analytes in the condensed phase may influence the analytical results, and one component of a sample may significantly alter the capacity of the sampling adsorbent for a different component. Such possible interferences must be recognized by the analytical chemist. Another vitally significant area of interest is the study and control of catalytic poisons and promoters. These materials act to influence the adsorption of co-adsorbates in often bizarre ways. A large magnification is often observed for the effect of one adsorbate on the adsorption or

catalytic activity of a second adsorbate. The best-known example of this phenomenon is the observed poisoning effect of adsorbed sulfur on Fischer-Tropsch catalysts. One atom of sulfur can poison or deactivate up to ten catalytic sites^{1,2}. Conversely, adsorbed potassium often significantly enhances catalytic activity, presumably by promoting adsorption of one or more reactants³.

Cooperativity has been observed in a significant number of co-adsorption studies, especially for physical adsorption on GCB adsorbents⁴⁻⁹. Severe poisoning effects have been observed in fewer systems; however, this effect has had more economic impact and consequently has been studied in greater detail^{1-3,10-14}. Both electronic and geometric effects have been postulated to account for poisoning and promotion effects. However, neither of these phenomena is well understood, thus there is tremendous need for further experimental investigation of multicomponent adsorption, especially for well-characterized adsorbents, such as the GCBs. GCBs are commercially significant adsorbents, and they are also of theoretical interest because of the homogeneity of the surface of these adsorbents.

EXPERIMENTAL METHODS

Volumetric and gravimetric procedures have been used to investigate gas-solid equilibria for many, many years. The results are accurate and often elegant for relatively simple systems. There are, however, two major problems encountered in the application of these methods to multicomponent systems. The primary difficulty is the requirement for the analysis of both phases or exact control of the total stoichiometry of the system and analysis of one phase. Thus, the experimental procedure becomes prohibitively laborious for complex systems. The other, less significant, problem is that these methods are least accurate for low concentrations. Unfortunately, this is the experimental domain that is critical for the evaluation of most theoretical models. That is, precise determination of the limiting Henry's Law constant for each component is necessary for the accurate evaluation of the other parameters of any model.

Recently, several forms of surface spectroscopy^{1-3,10,14-16} have been used successfully for the study of the molecular details of chemisorption processes, *i.e.*, orientation, bonding, speciation, etc. These methods include thermal desorption spectroscopy^{1,2} which has been used to investigate nonequilibrium co-adsorption and the interactions of individual species chemisorbed on a surface. These studies have been extensively reviewed¹⁷, and they are especially significant for chemisorption processes, such as catalysis. However, studies of equilibrium physisorption at finite pressures are more representative of practical systems, and such studies complement the low-pressure spectroscopic investigations.

Several chromatographic methods have also been used to study complex phase equilibria. The most successful applications have involved the use of one of the several forms of perturbation chromatography.

*Perturbation chromatography*¹⁸⁻²⁰

Perturbation chromatography is a general term for any type of chromatography involving the production of small "perturbations" in a column at equilibrium. This could include concentration perturbations or isotopic perturbations, and these

methods are referred to as concentration pulse and tracer pulse, respectively. For binary systems, composed of components 1 and 2 with corrected retention times, gas phase mole fractions, moles adsorbed, and molar flow-rate given as t'_{Ri} , Y_i , n_i^{ads} , and F_m respectively, the retention volume equations are¹⁸:

$$F_m t'_R = Y_2 (dn_1^{\text{ads}}/dY_1)_{Y_1, Y_2} + Y_1 (dn_2^{\text{ads}}/dY_2)_{Y_1, Y_2} \quad (1)$$

for concentration-pulse chromatography, and

$$F_m t'_{R,i} = n_i^{\text{ads}}/Y_i \quad (2)$$

for tracer-pulse chromatography.

The mathematical complexity of the concentration-pulse method has proven to be the major deterrent for the application of this methodology^{21,22}. Several investigators have, however, used the technique to study binary isotherms. Because of the form of the differential equation relating the chromatographic parameter, t'_R , to the isotherm data, n_i^{ads} , a mathematical isotherm equation is usually assumed, differentiated, and fit to the retention data²¹⁻²⁴. Thus, the major uncertainty is the accuracy of the mathematical model. This method precludes the investigation of isotherms of unusual or complex shape, such as those with sharp inflection points. Because only one pulse appears for a two-component system, this method also requires independent knowledge of the isotherm of one component or the limiting behavior of each component at low pressure. Probably the major disadvantage of the method, however, is that it cannot be used for systems with more than two components. If there are N components in the vapor phase, there will be $N - 1$ perturbations in each experiment and it is not possible to unambiguously assign pulses to components for complex systems.

Tracer-pulse chromatography has also been used for similar studies with either radioactive or heavy, stable isotopes with specific detectors. These methods are mathematically simple, and yield an isotherm point directly for each experiment. A perturbation is observed for each component, so no additional information is required for the development of an isotherm. No mathematical model is required, and there are no inherent limitations on the shape of the isotherm, which is especially critical for the study in strongly interacting systems. Any number of components can be measured, and the method is very accurate at low concentrations. The limiting factors are the requirements for a distinguishable isotope of each adsorbate and a suitable detection system. Like any chromatography methods, perturbation chromatography is limited to systems at equilibrium. This precludes the chromatographic study of chemisorption processes and simply means that spectroscopic and chromatographic studies are excellent complementary experimental techniques.

EXPERIMENTAL RESULTS FOR BINARY SYSTEMS

The earliest work with perturbation chromatography involving multicomponent systems was carried out by Kobayashi and co-workers^{19,25-28} in the 1960's with radioactive tracers. The systems were primarily of engineering interest, *i.e.*, light gases, adsorbed on silica gels or zeolites. Industrially significant gases, such as hydrogen

sulfide and carbon dioxide were also studied in binary adsorption or solution systems²⁸.

More recently, several groups have used concentration-pulse chromatography to determine binary isotherms with the data fit to a polynomial isotherm equation. The earliest work was that of Van der Vlist and Van der Meijden²³ for mixtures of nitrogen and oxygen on a zeolite. The isotherms were almost linear, and the adsorbates did not interact. Ruthven and Kumar²⁴ later studied binary mixtures of argon, oxygen, nitrogen, methane and carbon monoxide on zeolites with similar results. In this study, the results were shown to be in excellent agreement with previous results obtained gravimetrically. Glover and Lau²¹ proposed a matrix solution for the differential equations. All of these studies involved light gases and non-homogeneous adsorbents, and no solute interactions were observed.

Danner *et al.*²⁹ also used radioactive tracer-pulse chromatography to measure pure component isotherms of carbon monoxide, ethylene, and ethane on 5 A and 13X Molecular Sieves. It was shown that the isotherms determined by tracer-pulse chromatography were in excellent agreement with previously determined static data. Binary adsorption isotherms of fixed composition mixtures of ethane and ethylene on molecular sieve adsorbents were also determined and shown to agree with static data. This work involved higher-molecular-weight adsorbates than previous tracer-pulse studies. The adsorbents were selective for ethylene; however, there was no evidence of adsorbate interaction or interference. Such interactions are difficult to observe on heterogeneous adsorbents, due to the masking effect of the wide spectrum of adsorption energies of the adsorbent sites.

The tracer-pulse methods require specific detectors; however, this also allows another type of experiment. That is the study of the retention or adsorption of small samples of any number of other solutes as a function of the surface coverage of the adsorbate. In the case of binary adsorbate systems, the retention volumes or Henry's Law constants of the infinite dilution solutes can be studied as a function of the composition as well as the surface coverage of the condensed phase. These experiments are analogous to chromatographic investigations of the effect of liquid loading with nonvolatile, pure or mixed stationary phases on the retention of solutes. The results are similar in many cases; the major difference is that the tracer-pulse methods allow the continuous variation of surface phase composition and coverage.

Bruner and co-workers^{5,30,31} carried out many of the studies of the effect of liquid phase loading on the chromatographic properties of GCBs. These studies showed many cases of cooperativity between adsorbates and nonvolatile liquids, and the expected decrease in capacity at the point of formation of a monolayer of the liquid phase. However, no magnification effects, either poisoning or enhancement, were observed. It was shown that GCBs are excellent adsorbents for the study of adsorbate interactions, due to the well-characterized chemical and physical properties and the homogeneity of the adsorbent surface.

This same type of study with volatile adsorbates on GCB by perturbation chromatography was first carried out in 1981. Berezin *et al.*³² studied the retention volumes of small samples of cyclohexane, pentane, diethyl ether, and acetone on GCB as a function of the amount of 1-propanol or *n*-hexane adsorbed. The experimental procedure was concentration-pulse chromatography with a thermal conductivity detection system. Because of the nonspecific detection system, the surface cov-

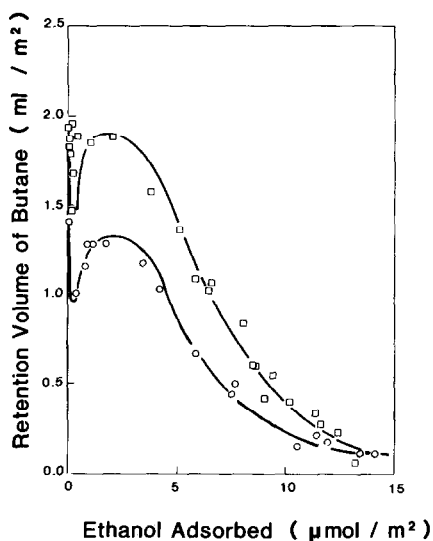


Fig. 1. Specific retention volumes of *n*-butane as a function of the amount of ethanol adsorbed on Carbopack C (\square) and Carbopack C + 0.2% CW-1500 (\circ) at 30°C. (Reproduced with permission from ref. 8.)

erage range was limited to a fractional surface coverage, θ , of $\theta < 0.6$ for hexane and $\theta < 0.2$ for propanol; however, the results clearly showed both cooperative and competitive adsorption effects. Another study of this type³³ involved only propane and butane; however, tracer-pulse chromatography with a mass-specific detection system was used. This allowed a study of a range of surface coverage up to and slightly beyond the point of formation of a monolayer of adsorbate. Significant cooperativity was observed between even the weakly interacting hydrocarbons. Extensive interference was observed at the point of completion of a monolayer.

More recently, several additional studies have been carried out, involving the study of the adsorption of infinitely dilute samples of propane³⁴, butane³³⁻³⁵, propanol, pentane, acetone, nitromethane and tetrahydrofuran^{8,9} on GCB (Carbopack C), modified by adsorption of butane, acetone, ethanol, or benzene. Figs. 1-3 show typical results for the retention of infinitely dilute solutes on these complex adsorption systems. Some cooperativity was observed in both the pure adsorption isotherms and the co-adsorption (retention volume) studies, except for the pure-component isotherm of benzene on GCB. Cooperativity is evidenced by the pronounced maxima in the retention volume plots, Figs. 1-3, and low-pressure isotherm convex to the pressure axis. These cooperative effects are caused by attractive lateral interactions between adsorbates or co-adsorbates in the condensed "two-dimensional" phase. These interactions may be specific or nonspecific. Figs. 1 and 2 show nonspecific cooperativity due to dispersion interactions between hydrocarbon solutes and different adsorbates, *i.e.*, ethanol and benzene. The point of formation of a monolayer occurred at coverages of 6 and 4 $\mu\text{mol}/\text{m}^2$ for ethanol and benzene, respectively. The initial sharp decrease in retention is due to the deactivation of small amounts of chemical or geometric inhomogeneities on the surface, and the final decrease in retention due to the formation of a monolayer is clearly shown. The effect of a small

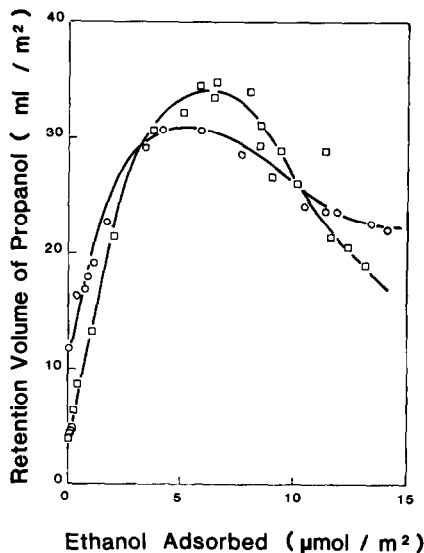
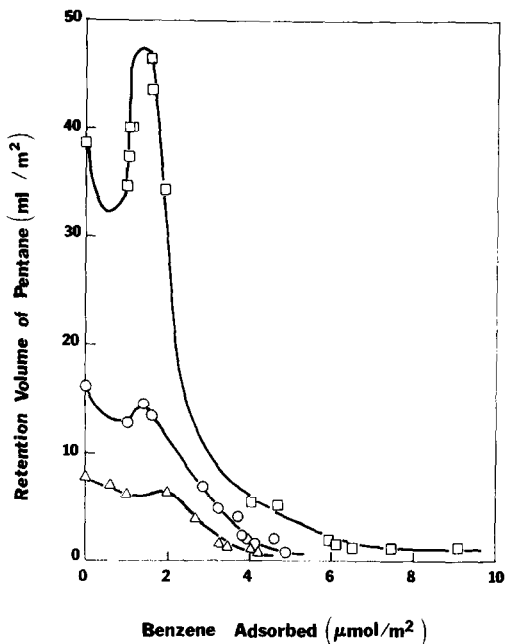


Fig. 2. Specific retention volumes of *n*-pentane on Carbpacck C at 10°C (\square), 30°C (\circ) and 50°C (\triangle)⁹. (Reprinted with permission from *Anal. Chem.*, 56 (1984) 274-278. Copyright 1984, American Chemical Society.)

Fig. 3. Specific retention volume of 1-propanol on Carbpacck C (\square) and Carbpacck C + CW-1500 (\circ) at 30°C. (Reproduced with permission from ref. 8.)

amount (0.2%) of a nonvolatile modifier (CW-1500) is shown in Fig. 1, and the effect of temperature is shown in Fig. 2. Fig. 3 shows a case of strong specific interaction between the solute, propanol and a volatile adsorbate, ethanol, as well as the non-volatile adsorbate, Carbowax. The cooperativity effect was greater in magnitude than for pentane or butane, and monolayer formation did not diminish the retention volumes as markedly.

Significantly, such interactions are not observed for pure benzene, adsorbed on GCB. This anomaly has been noted previously^{36,37} and explained by the geometric constraints imposed on the adsorbed benzene by the structure of the graphite surface. That is, the monolayer capacity is determined by the graphite hexagon structure, and the monolayer structure is not tightly packed. This is the reason that the monolayer capacity for benzene is independent of temperature over an unusually wide range^{9,36}. However, significant cooperativity was observed for small samples of several other solutes with preadsorbed benzene. Even though the adsorption of benzene on this unique adsorbent was localized, cooperativity was observed with other, more mobile adsorbates.

Benzene adsorption on GCB has been extensively studied³⁶⁻³⁹, and is probably one of the best standard or model gas-solid adsorption systems available. Investigation of this model system has been extended to binary adsorbate systems in a recent study of the adsorption of mixtures of acetone and benzene on GCB. Adsorption isotherms of benzene were determined by tracer-pulse chromatography at fixed pres-

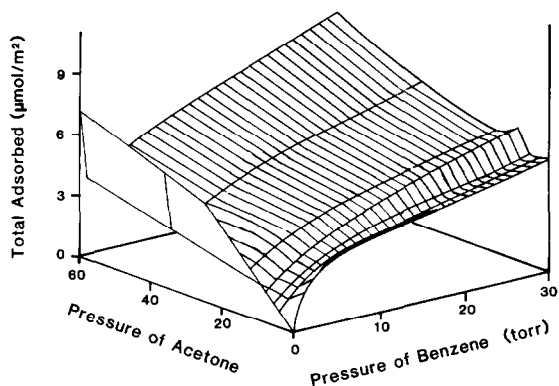


Fig. 4. Three-dimensional isotherm of benzene and acetone on Carbpac C at 20°C⁴⁰.

sures (P) of acetone. This allowed the development of full three-dimensional isotherms, *i.e.*, $n_i^{\text{ads}} = F(P_1, P_2)$, over monolayer coverage range of both adsorbates. The results of this study are shown in Fig. 4. This isotherm shows a distinct minimum in the adsorption capacity at low-surface coverages with benzene. The effect is shown for a single isotherm at fixed acetone pressure in Fig. 5. The severe poisoning effect was observed for the adsorption of acetone on a surface only partially covered with preferentially adsorbed benzene. It is not clear at present why acetone will not be adsorbed on a GCB surface if benzene is adsorbed, even at high pressures of acetone

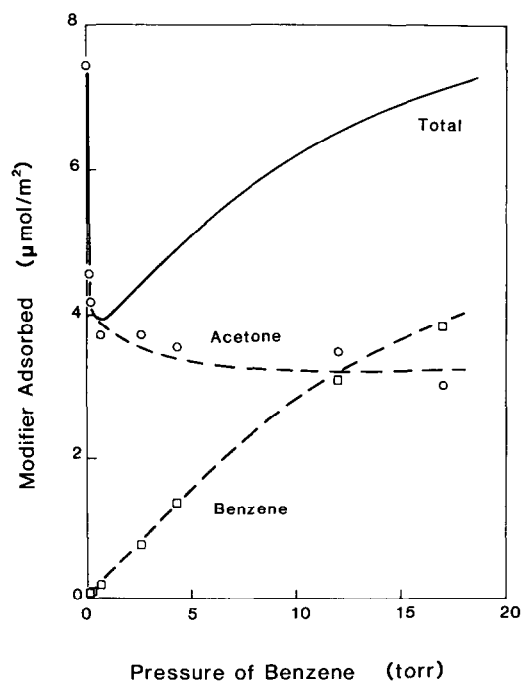


Fig. 5. Binary isotherm of benzene and acetone at a constant pressure of acetone (54 torr) on Carbpac C at 20°C.

and low-surface coverage of benzene. Both electronic and geometric interactions could account for the effect; however, further experimental studies are needed for this and other binary systems to determine the exact mechanism of such poisoning effects.

MATHEMATICAL MODELS FOR BINARY ADSORPTION SYSTEMS

There have been many isotherm models and equations developed for pure-component systems, and it is usually possible to find at least one to fit any pure-component data set. These models differ primarily in the basic assumptions used for the development of the equations. The most critical assumptions concern the type of adsorption (localized or delocalized) and the relative significance of solute-solute interactions in the condensed phase. The mathematical equations developed from these models necessarily reflect the complexity of the experimental systems.

In general, three approaches have been used for the development of theoretical models for the analysis and interpretation of experimental results of binary adsorption studies. Extension of the two-dimensional gas theory, such as the Van der Waals or virial equation of state, to binary systems has been used to interpret data for mixtures of chemically similar gases on GCBs⁴¹. Statistical thermodynamic theories have also been used for the characterization of binary systems. This method is limited to a particular type of adsorbent, such as the model for zeolites developed by Ruthven⁴².

Similarities between bulk liquid phases and two-dimensional adsorbed phases have prompted the development of adsorption theories based on well-established solution theories. Activity coefficients or interaction parameters are used to allow for the deviation of real systems from the ideal model^{43,44}. The most recent theory incorporating this approach is the "vacancy" theory of Suwanayuen and Danner^{45,46}. The model involves adsorbate solute in a solvent of equal-sized vacancies, *i.e.* holes, and two equations were used for the composition-dependence of the activity coefficients. The simplest equation was the three-parameter Margules equation. This model was mathematically tractable, but did not give satisfactory fit to the binary isotherms^{46,47}. The Wilson equation⁴⁸ was also used for the activity coefficients. This complex, four-parameter equation gave a better fit to the data. However, the mathematical solution for each point on the isotherm involved a trial-and-error solution for the activity coefficients, monolayer capacity for the mixture, and the gas-phase composition at a fixed composition of the adsorbed phase.

Simple models are accurate for nearly ideal systems involving permanent gases. On the other hand, mathematically complex models are required to describe binary adsorption and allow for solute-solute interactions. No models are currently available to describe the significant cooperativity or interference effects observed in systems, such as those shown in Figs. 1-5.

CONCLUSIONS

The study of multicomponent phase equilibria has been significantly aided by the recent application of several different experiment methods, *i.e.*, the various forms of surface spectroscopy and chromatographic methods. Chromatographic proce-

dures, especially the perturbation methods, are well suited for the investigation of complex-phase equilibria; however, the methodology has only recently been extensively employed for such studies. Efficient, sensitive ionization detectors and mass-specific detectors have been used for these studies, and the results are encouraging.

One of the most significant applications of chromatographic methods to the determination of complex phase equilibria is the investigation of the mechanisms of catalytic poisons and promoters. Catalytic processes are very complex and cannot be studied directly by any equilibrium chromatographic method. However, the initial step in any catalytic reaction involves the physisorption of reactant(s), and this is often the rate-determining step. Some catalytic poisons and promoters operate by blocking or facilitating the initial physical adsorption process as well as the chemisorption process. There is significant controversy in the literature concerning the exact mechanism for catalytic promoters and poisons, *i.e.* whether electronic effects^{15,49}, geometric effects^{2,13}, or a combination of both^{3,10} are responsible for the alteration of reactant adsorption. A convenient, accurate experimental procedure for the study of binary systems will facilitate the establishment of an improved data base and the development of useful theoretical models for such systems.

Chromatographers have long recognized the potential for control of the selectivity of chromatographic systems by external manipulation of the mobile phase composition. This method has proven invaluable for liquid chromatographic systems; however, the method has not been developed for GC, primarily due to the complex, unpredictable type of retention behavior shown in Figs. 1-3. A predictive model is needed for GC systems to allow the use of vapor programming in place of the current method of temperature programming.

Another area in which experimental determination of adsorption isotherms is of significant interest is the evaluation of the analytical sampling method for large volume samples, such as air, water, stack gas, etc. Figs. 4 and 5 show clearly that a small amount of one component in a sample may have a significant, detrimental influence on the sampling capacity and efficiency of that adsorbent for other components in the sample. Adsorbents are currently evaluated by the determination of break-through volumes of pure components. It would be far more realistic to evaluate adsorbents by measuring the break-through volumes of mixtures, rather than pure components, and chromatographic methods are the obvious choice for experiments of this type.

All of these examples point out the significance of the study of complex adsorption processes and the development of theoretical models and isotherm equations for such systems. Determination of binary isotherms for diverse mixtures on well-characterized adsorbents, such as the GCBs will provide the data base needed for the development of the models to analyze and interpret such data.

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