STUDY of the SURFACE PROPERTIES of CERAMIC MATERIALS
by CHROMATOGRAPHY

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FINAL REPORT

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ABSTRACT

This report summarizes the progress made on the subject project from its beginning up to near the end of the last project year (3/1/94 to 10/1/94) and describes our plans for the end of the year.

During the grant period, we have (i) developed a theoretical model permitting the calculation of the adsorption energy distribution from the isotherm without making any assumptions regarding the experimental isotherm, by contrast with what current methods do; (ii) coded, tested and validated the calculation procedures developed, which involved solving serious computational difficulties; (iii) carried out a systematic investigation of the propagation of the experimental and model errors made in the chromatographic measurements to the energy distribution derived from these data; (iv) prepared series of columns with silica particles of various origins, virgin or bonded with different groups; (v) determined the adsorption energy distributions of diethylether, methanol, ethanol, n-heptane, pyridine, and tetrahydrofuran on the surfaces of several of these adsorbents.

Plans for the remaining third of the last project year include finishing the evaluation of experimental data already collected, calculation of the energy distributions, interpretation of the results, and completion of two additional papers.

Study of the Surface Properties of Ceramic Materials by Chromatography

Final Report, April 1995

INTRODUCTION

In this report, we first review briefly the aim of the proposal and our research plan for the grant period, in order to provide a perspective for the work carried out. Then, we describe the theoretical and experimental work performed, the results achieved and the present status of the project. Finally, the research plan for the rest of the period is described.

In summary, we have not achieved our original objectives but we have made a significant contribution to the understanding of the fundamentals of adsorption on actual surfaces. We have shown how the errors of measurements, the experimental constraints, and the model errors limit drastically the range of surface energies within which meaningful results are accessible. The distribution can be calculated only for systems in which the majority of the adsorption energy is 10 kJ/mol greater than the heat of vaporization of the probe-adsorbate used, which restricts considerably the usefulness of the method. Otherwise, the adsorption energy distributions (AED) are divergent at low energies and artifactual peaks are observed at high energies, peaks which change widely with minor adjustments in the experimental conditions.

I - SCIENTIFIC OBJECTIVES OF THE ORIGINAL PROPOSAL

Our original research grant supported investigations of the surface properties of raw ceramic powders by inverse gas chromatography. Specialty ceramic products have achieved a great importance, notably in the production of high temperature materials for aeronautic engines and of materials with unusual dielectric, magnetic or electric properties for electronic devices.

Considerable difficulties are met when molding and firing ceramic parts. The raw material is a fine powder (particle size between 0.2 and 1 μm) of the desired oxide, nitride or carbide. After mixing with other powders (flux), a binding agent (usually polymeric), a solvent and a dispersant (surface active agent), the powder is agglomerated and molded, then fired. During the thermal process, the parts or green bodies (originally porous, unconsolidated agglomerates) shrink, and their porosities decrease from about 40% to almost zero. During the firing, the organic compounds introduced to facilitate the molding of the green body and to give it the strength to withstand handling stress are vaporized and/or pyrolyzed. If vaporization is too slow,

this may result in the deposition of traces of carbon and the loss of mechanical strength of the parts, or the loss of other performance (e.g., electrical). Ceramic raw powders having the same origin and the same bulk properties behave differently, some giving satisfactory products, others not.

Growing evidence has accumulated that this phenomenon is due to differences in the surface chemistry of the particles which are not shown by conventional tests, e.g., titration curves, zeta potential, pH of a suspension of the powder, etc. Because major changes in the chemical properties of atoms or group of atoms on the surface involve relatively minor changes in their bonding energy to the solid, physical methods using irradiation with high energy particles to abstract these atoms from the surface and analyze them are not well suited to compare lots of similar particles of different origins. Thus, other methods of studying the chemical properties of the surface appear to be necessary.

A. Aim of the Research.

The aim of our research in this field is the development of a general method of characterization of surface heterogeneity based on (i) the determination of the isotherms of adsorption of carefully selected probe components on the surface of the studied material, for a series of appropriate probes; (ii) the derivation of the distribution function of the adsorption energy of these probes and of the energy of formation of their monolayers; and (iii) the use of correlations between adsorption energy distributions and chemistry of the adsorbent surface. Previous results had shown that the first step is simple and that very accurate isotherm data can be obtained. They also suggested that the more difficult second step was also solved.

The goal of our research during the current grant period was the systematic investigation of the surface heterogeneity of finely pulverulent materials in relation to the chemical properties of their surface using the method developed previously. A considerable amount of knowledge has been developed in liquid chromatography on the relationship between the nature of the groups bonded to silica surfaces and their physical properties as adsorbents. A wide variety of such chemically bonded silica materials are easily available, either commercially or through simple synthesis. Thus, it was proposed to use these adsorbents for our investigation of the relationship between surface chemistry, surface heterogeneity and adsorption energy distributions.

B. Proposal Objectives.

Our original objectives were:

- 1 - An understanding of how the characteristics of the adsorption energy

distribution of a number of probe compounds is related to the chemical composition of the surface, and more particularly the identification of the atoms, ions, or chemical groups whose presence on the surface causes the experimentally observed heterogeneity.

2 - The identification, among the atoms, ions, or groups of atoms found to be responsible for the surface heterogeneity, of those which cause problems in the production processes of ceramics.

3 - The design of analytical tests permitting the selection of satisfactory lots, based on the identification of the undesired chemical features found at the surface of pulverulent or fibrous materials and of the relationship between these features and the adsorption energy distribution.

These objectives are compared to our results at the end of the second part. As indicated above, we have met our first objective in part. We have also shown that, most probably, the method of AED determination cannot be used to develop simple analytical tests.

II - REPORT OF TECHNICAL PROGRESS

A. Adsorption Isotherm and the Energy Distribution Function.

Adsorption isotherms are derived from chromatograms obtained with large samples (ECP method) or from the decay of large concentration steps (FACP method)¹. The determination of accurate isotherms is the necessary step in the determination of the adsorption energy distributions (AED).

1. Accuracy of Isotherms Derived from Chromatographic Data.

Both the ECP and the FACP methods assume that the column efficiency is infinite (ideal model of chromatography). So, these methods are not accurate because the exact profile of the rear part of a band eluted from an actual column depends on the kinetics of mass transfer and on axial dispersion¹. This problem is illustrated in Figure 1 which shows how the column efficiency influences the measured isotherm. Calculations show that the error made on the isotherm is almost inversely proportional to the column efficiency and becomes negligible when the column has more than

¹ G. Guiochon, S. Golshan-Shirazi and A.M. Katti, "Fundamentals of Preparative and Nonlinear Chromatography", Academic Press, Boston, MA, 1994, Chapter 3.

5000 theoretical plates². The columns used in our work have between 20 000 and 30 000 plates. This is one of the great advantages of using porous layer open tubular columns. Nevertheless, errors made due to the finite mass transfer kinetics accumulate in the calculation of the isotherms and make them less accurate at low partial pressure, in the range corresponding to high adsorption energy.

2. Theoretical Model of Adsorption Energy Distribution.

Adsorption energy distributions of solute probes on heterogeneous surfaces have been determined from their nonlinear chromatographic band profiles for the last twenty years as a method of inverse chromatography. The general problem of obtaining distribution functions from adsorption isotherm data has proceeded for a substantially longer period of time, with many of the nagging fundamental obstacles being delineated and characterized along the way^{3,4}. The basic fundamental hurdle is centered around the solution of the linear Fredholm integral of the first kind:

$$q(p) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \theta(\epsilon, p) f(\epsilon) d\epsilon \quad (1)$$

where $q(p)$ is the experimentally measured global adsorption isotherm, function of the solute partial pressure, p ; $\theta(\epsilon, p)$ is the local model of adsorption for each adsorption site of energy, ϵ , and $f(\epsilon)$ is the distribution function of interest. The solution of this equation for the function $f(\epsilon)$ is mathematically ill-posed, which is to say that any error in data, $q(p)$, is unbounded upon inversion to the solution, $f(\epsilon)$.

In order to accelerate research in this area, chromatographic retention volumes may be used to obtain the adsorption isotherm through⁵:

$$q(p) = \frac{1}{M_s} \int_0^y \frac{j(V_R - V_M)}{1 - \psi} dc \quad (2)$$

where M_s is the mass of stationary phase or adsorbent under study, y is the mole

² H. Guan, B.J. Stanley and G. Guiochon, *J. Chromatogr.*, 659 (1994) 27.

³ W. Rudzinski and D.H. Everett, "Adsorption of Gases on Heterogeneous Surfaces", Academic Press, New York, 1992.

⁴ M. Jaroniec and R. Madey, "Physical Adsorption on Heterogeneous Solids", Elsevier, Amsterdam, The Netherlands, 1988.

⁵ J.R. Conder and C.L. Young, "Physicochemical Measurement by Gas Chromatography", Wiley, New York, 1979; Chapter 9.

fraction of solute at partial pressure p , j is the James-Martin correction term, ψ is a correction term for nonideal gas behavior and the sorption effect⁶, and c is the concentration of solute at partial pressure p . In this way, an adsorption isotherm can be obtained in one chromatographic run and potentially possesses hundreds of data points. Use of a highly linear detector such as the flame ionization detector (FID) allows an isotherm segment covering five orders of magnitude in partial pressure.

The critical problem is in the derivation of a numerical procedure for the AED determination. The problem is arduous because any error of experimental origin or any information not germane to the data introduced by any simplifying assumption will cause major artifacts in the adsorption distribution. This a direct consequence of the ill-posed nature of the problem.

3. Numerical Solution of the Problem.

Many authors have introduced considerable simplifications by assuming that the experimental isotherm, $q(C)$, can be fitted to one of the classical models or that the solution, $f(\epsilon)$, can be represented by a classical distribution, e.g., Gauss or Gamma function. This is profoundly wrong. We have shown that each of these approaches introduces a profound bias in the solution which becomes artifactual and loses its physical meaning^{7,8}.

Numerical estimation of $f(\epsilon)$ assuming only the measured $q(p)$ and a local model $\theta(\epsilon, p)$ necessarily results in artifactual information since perfect noise-free data may never be obtained. The nature of solution inaccuracy may be dictated, however, by the algorithmic approach of the solution estimation. A tradeoff typically exists: resolution versus smoothness. For this class of problems one may increase the resolution by approaching the minimum squared variance of the data, $q(p)$, from the estimated data, $q_{\text{est}}(p)$. Unfortunately, this condition is not equivalent to that of the estimated solution, $f_{\text{est}}(\epsilon)$, being minimally close to the true distribution, $f(\epsilon)$. In order to minimize the latter deviation, it is common practice to incorporate some form of smoothing into the solution with the estimation algorithm. This practice increases the estimation variance, and the concomitant loss of inherent resolution is justified by assuming that a smooth solution is closer to the true distribution in all probability than a possibly artifactual, highly curved one.

We have developed and implemented an iterative maximum-likelihood method

⁶ M. Pyda, B.J. Stanley, M. Xie and G. Guiochon, *Langmuir*, 10, 1994, 1573.

⁷ S. Golshan-Shirazi and G. Guiochon, *J. Chromatogr.*, 670, 1994, 1.

⁸ B.J. Stanley and G. Guiochon, *Langmuir*, In Press.

called expectation-maximization (EM) to obtain a statistical robust estimate of $f(E)$ ⁹. The algorithm yields smoother estimates than those of regularization methods commonly used for the solution of similar problems. Requiring no prior knowledge of the error distribution, the EM solution appears to be the most prudent choice in terms of guarding against artifactual information. The major disadvantage of the technique is the long computation times it requires if a fine energy grid is used in connection with hundreds of data points and several thousands iterations. The method has been successfully implemented on the massive parallel computer (MasPar MP-2) available at the University of Tennessee (in cooperation with the Joint Institute for Computer Research). This reduces typical run times to a few minutes.

4. Main Causes of Errors on the Adsorption Energy Distributions.

The above numerical problem has been observed in simulations with well-defined functions, correct assumed models, $\theta(\epsilon, p)$, and well-behaved noise (truly random or Gaussian) [1]. The problem of ill-defined noise or systematic error present in the data is less well known, and presents a further challenge in this research area. We have discussed in section II.A.1 how the finite efficiency of chromatographic columns affects the isotherm data. The effect on the isotherm is that it is biased high (Figure 1). The effect on the estimated distribution is a divergent function at the low-energy side of the distribution. This is apparently because the kinetic or diffusional information imprinted on the isotherm due to the finite efficiency resembles adsorption on a lower-energy site not yet sufficiently sampled by the data. We have shown that in order to sufficiently sample an adsorption isotherm, approximately 70% of the monolayer must be present⁸. Thus a significant amount of isotherm curvature at the lowest energy site present on the surface must be sampled in order for that site to be confirmed with respect to the model. Diffusional processes appear to be adsorption processes still in the linear range of coverage.

Another obstacle in solving Eq. 1 for the distribution function is the problem of assuming the correct local model of adsorption. The effect of an incorrect local model has been investigated and shown to influence the accuracy of the obtained distribution⁴. One of the primary decisions that must be made in choosing a local model is the presence and nature of lateral adsorbate-adsorbate interactions on the surface. If these interactions can be neglected, either the Langmuir or the Jovanovic model may be chosen, with the Langmuir model being the most popular. These models also assume static adsorption and no multilayer effects. If lateral interactions are to be modeled, the Fowler-Guggenheim model is the most popular choice.

In order to model the lateral interactions properly, a further assumption about the surface topography must be chosen in order to depict the relevant θ correctly.

⁹ B.J. Stanley and G. Guiochon, J. Phys. Chem., 97 (1993) 8098.

The extreme cases are those of a patchwise and a random surface. The patchwise surface contains adsorption sites of the same energy in discrete patches with complete correlation of the lateral interactions to the neighbors within that patch. The random surface assumes a random distribution of adsorption energy across the entire space of adsorption sites with no correlation of neighbors to the same adsorption energy. As with many cases in physical theory, a situation in between most likely exists. However, an extreme must be chosen for practical reasons of model simplicity and tractability. For the patchwise surface, θ is taken as the local coverage within the energy patch under consideration. For the random surface, θ is taken as the global coverage across the entire surface. The interaction parameter is estimated from theory. For a rigorous estimation, a statistical mechanical estimate should be developed. At the very least, the number of nearest interacting neighbors and the interaction energy between two adsorbates should be known. Considering the problems and assumptions associated with the AED estimation alluded to so far, it seems overzealous to pursue the evaluation of molecular interactions in any complicated sort of manner.

The effect of lateral adsorbate-adsorbate interactions is to increase the adsorption as the partial pressure and surface coverage increases. Thus as the higher energy sites become saturated, lower energy adsorption becomes influenced by these lateral interactions. The deconvolution of the lateral interactions from the low energy adsorption can only succeed if the accuracy of the model and the quality of the data (signal-to-noise ratio) are very high. If the model is not accurate, or if the modeled response of lateral interactions is similar to that of low energy adsorption, it is impossible to estimate the lower energy adsorption. The intermolecular interactions sustain continued adsorption and the sites appear never to saturate. Compounding this impasse is the onset of multilayer effects. It cannot be assumed that a full monolayer (100%) is adsorbed before another one begins, and it cannot be assumed that 70% of a monolayer is present before another one begins at the high energy sites either. Therefore from a theoretical standpoint, it is a challenging task to accurately estimate an adsorption energy distribution due to the error incurred in the low energy region of the distribution, resulting from an adsorption isotherm that does not appear sufficiently sampled.

B. Experimental Determination of the Isotherm Data.

Two gas chromatographs have been used in this study. The first one is the Perkin Elmer 8500 used in our previous work in this field. The second one is a Hewlett-Packard HP5840 of similar performance made available to us by the Chemical and Analytical Sciences Division at ORNL. The technique used to prepare the open tubular columns and coat their inner wall with a thin layer of adsorbent was developed during the previous grant period and was not modified. The pressure drop of the column at the standard flow rate (3 - 4 mL/min) is ca 2 psi, which has the great

advantage of making the James and Martin pressure correction factor very close to unity and making practically negligible the consequences of a small variation of the column permeability on the experimental data. The inconvenient of the technique is the limited accuracy on the determination of the mass of adsorbent in the column, this mass being derived from the weight of the column before and after coating.

C. Data Acquisition and Analysis.

The data is acquired via a D/A board installed in the gas chromatograph and an A/D board installed in a microcomputer. A Peaksimple II software was used. Acquisition is performed at 10 Hz sampling rate, with 19 bits of resolution for 5 orders of magnitude of signal output. When data acquisition proceeds beyond 15 min, the frequency of acquisition is reduced. The data is then uploaded to the computer system of the University of Tennessee Computing Center for further processing.

The experimental isotherm is calculated using Eq. 2. The AED is derived using the EM method, with the Langmuir model for the local isotherm¹⁰. The Jovanovic and the Fowler-Guggenheim models have not given improved results. The use of a massive parallel computer permits the computation of large size problems (e.g., up to 1000 data points, 500 energy points and 20 000 iterations) in a matter of minutes. The ends of the energy range are derived from the minimum and maximum pressure points measured by use of the condensation approximation:

$$E_{\min} = -RT \ln\left(\frac{P_{\max}}{K}\right) \quad (3)$$

$$E_{\max} = -RT \ln\left(\frac{P_{\min}}{K}\right) \quad (4)$$

Goodness of fit is estimated by the root-mean-squared deviations of the estimated data from the raw isotherm data. The distribution function is analyzed by the method of moments to yield the total amount adsorbed (0th moment), the mean adsorption energy (1st moment), and the variance (2nd moment) for each peak as well as for the total solution.

¹⁰ B.J. Stanley and G. Guiochon, submitted to Langmuir.

D. Analysis of Our Results.

1. Experimental Data.

The chromatograms obtained consistently show band profile overlap, a result explained by the high column efficiency. This ensures that the effect of axial apparent dispersion on the results will be minimum. The few exceptions, in the case of pyridine, ethanol, and THF at low temperatures, are due to a slow rate of mass transfer kinetics. This is in agreement with the theory of nonlinear chromatography¹¹. A typical example is given in Figure 2 (left side of the previous page) which shows the chromatograms obtained for three samples of diethylether (bp = 34.6C, $E_{\text{vap}} = 25$ kJ/mol) on Davisil silica¹⁰ at 60C. A small discrepancy is observed near the maximum for the smaller sample. Figure 3 shows the isotherms derived from the profiles. The first two overlap exactly. The third one appears to be biased high. The isotherm was sampled up to a high coverage ratio with the large injections, as demonstrated by the low slope of the isotherm at the high pressure end and by the retention time of the front, which is close to the holdup time (difference of 3.5 s for the 20 μ L injection). Similar results were obtained in almost all cases^{6,10}.

2. Adsorption Energy Distributions.

Figure 4 shows the AED distributions derived from the isotherms in Figure 3. The reproducibility appears to be high in this case. The curve corresponding to the smallest sample is in error because of incomplete sampling of the isotherm. A systematic study showed that the sample size should amount to about 60% of a monolayer to provide sufficient sampling⁸. A similar result, with quantitative differences explained by the markedly lower specific surface area, was obtained for IMPAQ, a silica widely used in preparative liquid chromatography¹⁰.

Particularly noteworthy is the convergent nature of the distribution, a marked difference with most similar curves published in the literature. Our results indicate that the divergence of the distribution is most often due to insufficient sampling of the isotherm at high partial pressures. This conclusion, originally based on simulation results⁸, was confirmed by experimental results¹⁰. It is illustrated by the distribution reported in Figure 5, for methanol on Davisil silica at 50C. Although the chromatograms overlap almost exactly, as well as those in Figure 2, and the isotherms show the same kind of agreement as those in Figure 3, the AED calculated for the two smallest samples are divergent, while the one obtained for the largest sample is convergent. The difficulty in sampling the high pressure range of the isotherm and determining the AED is due to the relatively small difference between the energy of vaporization of methanol ($E_{\text{vap}} = 36.1$ kJ/mol) and the low end of the range of

¹¹ Ref. 1, Chapter 14.

adsorption energies sampled in Figure 5, 6.7 kJ/mol. The determination of a convergent adsorption energy distribution is easier for ethanol, which has a higher vaporization energy and lower molecular interactions.

By contrast, a convergent AED could not be obtained for n-heptane on Davisil at 40C, for diethylether on Vydac, a silicagel which appears to have the majority of its adsorption energy in a lower range than Davisil or IMPAQ, nor for alcohols on Vydac at 40 and 50C. In this last case, a slow rate of mass transfer, causing divergence in the chromatograms and difficulties in the calculation of the AED, was the source of the problem. Poor results were also observed with a series of chemically bonded phases prepared specially for this experiment¹⁰. The adsorption energy is markedly reduced. The surface heterogeneity is probably reduced also. The main peak in the adsorption energy distribution moves close to the heat of vaporization, precluding any accurate measurement with our method.

3. Isotherm Data at Very Low Partial Pressures.

A paradox has been observed at low partial pressures, in the range of data points just above the noise. The first points of the isotherm are on an exact straight line, which is expected in principle but should not be observed in this range. If an injection is made within this concentration range, a highly skewed peak is observed on the screen of the gas chromatograph terminal, which shows the filtered response of the flame ionization detector. Our A/D system does not permit detection in this range. The decay of the elution profile into the noise looks linear upon ECP integration because of the lack of A/D resolution bits. Gaining the two orders of magnitude in sensitivity required to acquire data at these low concentrations (i.e., high adsorption energy) would require a major transformation of our gas chromatographs and work in detector technology which is beyond our current possibilities.

E. Summary of Project Status.

In summary, our results show that our initial objectives have not been met. They probably could not have been met. In most cases, it is impossible to obtain an adsorption energy distribution which is meaningful. Difficulties arise at both ends of the energy range. Because of the mathematical nature of the problem, these difficulties affect the entire distribution calculated.

At low energies (high partial pressures), the detector response is no longer linear; the retention time of the band front becomes very close to the holdup time and the accuracy of the determination of the isotherm vanishes; the adsorbate concentration becomes important, so simple models of local isotherm become inadequate; the injection of large samples cannot be instantaneous and the profile of the injected band is not rectangular, causing perturbation in the elution band profile.

Our data show that the AED become poorly reproducible when the adsorption energy becomes less than 10 kJ/mol higher than the heat of vaporization of the probe.

At high energies (low partial pressures) the detection limit sets the upper end of the accessible range. Our data show that a significant amount of adsorption energy is not properly sampled, explaining the differences observed at high energies between the AED's derived from isotherm data acquired at different temperatures. In spite of the sensitivity of the flame ionization detector, data are needed at lower partial pressures than those accessible with good commercial instruments. These problems could be solved with the development of a dedicated instrument which would meet the specifications for wide dynamic linear range, accuracy and short response time.

It is our opinion that this combination of problems precludes the development of a practical method of analysis of the surface heterogeneity of pulverulent or fibrous materials. The technical problems which remain, essentially an improvement of the signal/noise ratio of the detector, do not seem difficult to overcome in a research laboratory. The practicality of an analytical method which cannot be implemented with commercial instruments is, however, doubtful.

ANNEX I

LIST of PUBLICATIONS SUPPORTED by GRANT

DE-FG05-88ER13859

- (1) **Experimental Determination of Adsorption Isotherm Data for the Study of the Surface Energy Distribution of Various Solid Surfaces by Inverse Gas-Solid Chromatography.** J. Roles and G. Guiochon. *Journal of Chromatography*, 1992, 591, 233-243.
- (2) **Precision and Accuracy of Gas-Solid Adsorption Isotherms Derived by ECP.** J. Roles and G. Guiochon. *Journal Chromatography*, 1992, 591, 245-265.
- (3) **Validity of the Model Used to Relate the Energy Distribution and the Adsorption Isotherm.** J. Roles and G. Guiochon. *Journal of Chromatography*, 1992, 591, 267-272.
- (4) **Prediction of the Elution Profiles of High Concentration Bands in Gas Chromatography.** J. Roles and G. Guiochon. *Journal of Chromatography*, 1992, 589, 223-230.
- (5) **Analysis of the Surface Heterogeneity of Different Samples of Aluminum Oxide Ceramic Powders.** J. Roles and G. Guiochon. *Analytical Chemistry*, 1992, 64, 25-32.
- (6) **Study of the Surface Heterogeneity of Chromatographic Alumina.** J. Roles and G. Guiochon. *Analytical Chemistry*, 1992, 64, 32-35.
- (7) **Numerical Estimation of Adsorption Energy Distributions from Adsorption Isotherm Data with the Expectation-Maximization Method.** B.J. Stanley and G. Guiochon, *Journal of Physical Chemistry*, 1993, 97, 8098-8104.
- (8) **Comparative Evaluation of Adsorption Energy Distribution Functions Obtained by Analytical and Numerical Methods.** S. Golshan-Shirazi and G. Guiochon. *Journal of Chromatography*, 1994, 670, 1-14.
- (9) **Analysis of the Surface Heterogeneity of Unmodified and Modified Silica by Capillary Inverse Gas-Solid Chromatography at Finite Dilution.** M. Pyda, B.J. Stanley, M. Xie and G. Guiochon, *Langmuir*, 1994, 10, 1573-1579.

(10) Importance of the Accuracy of Experimental Data in the Nonlinear Chromatographic Determination of Adsorption Energy Distributions. B.J. Stanley and G. Guiochon, *Langmuir*, 1994, 10, 4278-4285.

(11) Using Parallel Supercomputers to Calculate Surface Energy Distributions. B.J. Stanley, C. Halloy and G. Guiochon, *J. Chem. Inf. Comput. Sci.*, 1995, 35, 110-114.

(12) Calculation of the Adsorption Energy Distributions of Silica Samples using Nonlinear Chromatography. B.J. Stanley and G. Guiochon, *Langmuir*, In Press.

(13) Surface Properties of some Silica Materials Determined by Inverse Capillary Gas Chromatography. M. Pyda, B.J. Stanley and G. Guiochon. In preparation.