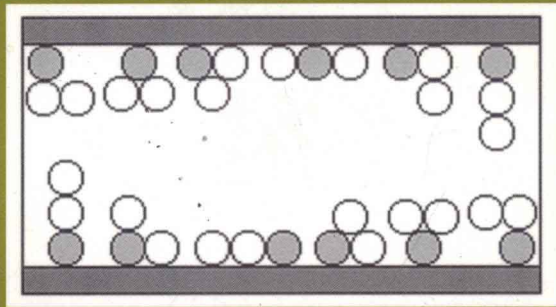


surfactant science series
volume **80**

INTERFACIAL PHENOMENA IN *CHROMATOGRAPHY*



edited by
Emile Pefferkorn

INTERFACIAL PHENOMENA IN CHROMATOGRAPHY

edited by
Emile Pefferkorn

*Institut Charles Sadron
Strasbourg, France*



MARCEL DEKKER, INC.

NEW YORK • BASEL

ISBN: 0-8247-1947-6

This book is printed on acid-free paper.

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Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
tel: 44-61-261-8482; fax: 44-61-261-8896

World Wide Web

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Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

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Preface

Chromatography is largely employed in characterization and separation methods in the biomedical, industrial, and environmental domains, and the technical development has called for diversified detection and analysis procedures. Concerning principles, the major efforts to improve separation efficiency have been directed to (1) the establishment of specific interactions between groups of the stationary phase and groups belonging to molecules present in the mobile phase and (2) the elimination of all specific interactions between constituents of the stationary phase and those of the mobile phase. A great number of books and reviews have been devoted to the improvement of chromatographic stationary phases.

The present book is aimed at the presentation of different chromatography methods in which interactions between the stationary and mobile phases are employed to enhance and/or control separation selectivity. Obviously, separation requires the stationary phase to be well characterized from the physicochemical and structural viewpoints.

The principles of gas chromatography are presented first to show the multiplicity of information on the gas–solid interaction provided by the use of the virial coefficient theory. Since efficient separation requires the best adhesion (adsorption, retention, etc.) of the solute in the stationary phase, inverse gas chromatography has been directed toward the optimization of the properties of fibers and fillers for reinforced materials, but it may serve as a convenient technique for characterization of stationary phases used in liquid chromatography. Inverse gas chromatography has been applied to fibers and fillers in order to determine the different components of their surface free energy. It has been employed to determine the modifications resulting from chemical surface treatments of natural and

synthetic fibers as well to detect the particularities of amorphous and crystalline powders. General and particular results are presented and discussed in Part I.

Interaction phenomena in liquid chromatography have been found to be efficient in the separation of colloids and solutes as a function of size and chemical nature. Interfacial interactions between silica and solutes have been suppressed through adsorption and grafting methods to allow for the use of silica beads in size exclusion chromatography. The separation efficiency of the inverse method, which is based on the development of strong or solvent-modulated solid–solute interactions, has been tested. In Part II, as in Part I, general and particular aspects of the different methods are presented.

The book presents results related to the less explored possibilities offered by establishing and/or designing interfacial phenomena in chromatography. Separation processes in industrial and biomedical applications are expected to benefit greatly from these new methods, and environmental areas requiring better determination of the multiple selective interactions of gaseous and liquid species with soil constituents should also benefit.

Emile Pefferkorn

Contributors

Henri Balard Institute of Chemistry of Surfaces and Interfaces, French National Center of Scientific Research, ICSI–CNRS, Mulhouse, France

Mohamed Naceur Belgacem Department of Paper Science and Technology, University of Beira Interior, Covilhã, Portugal

Halim Chtourou* Department of Wood Science, CERSIM, Laval University, Quebec City, Quebec, Canada

Yoram Cohen Department of Chemical Engineering, University of California, Los Angeles, Los Angeles, California

Paul L. Dubin Department of Chemistry, Indiana University—Purdue University, Indianapolis, Indiana

Abdelhamid Elaissari Chemistry of Supports, CNRS–Biomérieux (UMR-103), Lyon, France

Ron S. Faibish Department of Chemical Engineering, University of California, Los Angeles, Los Angeles, California

* *Current affiliation:* Rétec Inc., Granby, Quebec, Canada.

Christian-Herbert Fischer Department of Solid State Physics, Hahn-Meitner-Institut Berlin, Berlin, Germany

Alessandro Gandini Department of Polymeric Materials, Ecole Française de Papeterie et des Industries Graphiques, St. Martin d'Hères, France

Clarisse Huguenard Laboratoire RMN et Chimie du Solide, Université Louis Pasteur, Strasbourg, France

S. N. Lanin Department of Chemistry, M. V. Lomonosov State University of Moscow, Moscow, Russia

Yu. S. Nikitin Department of Chemistry, M. V. Lomonosov State University of Moscow, Moscow, Russia

Eugène Papirer Institute of Chemistry of Surfaces and Interfaces, French National Center of Scientific Research, ICSI-CNRS, Mulhouse, France

Harald Pasch Department of Polymer Analysis, German Plastics Institute, Darmstadt, Germany

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Bernard Riedl Department of Wood Science, CERSIM, Laval University, Quebec City, Quebec, Canada

Montserrat Rovira-Bru Department of Chemical Engineering, University of California, Los Angeles, Los Angeles, California

Thomas R. Rybolt Department of Chemistry, University of Tennessee at Chattanooga, Chattanooga, Tennessee

Howard E. Thomas Department of Chemistry, Erskine College, Due West, South Carolina

Yingfan Wang Department of Chemistry, Indiana University—Purdue University, Indianapolis, Indiana

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1

Henry's Law Behavior in Gas-Solid Chromatography: A Virial Approach

THOMAS R. RYBOLT Department of Chemistry, University of Tennessee at Chattanooga, Chattanooga, Tennessee

HOWARD E. THOMAS Department of Chemistry, Erskine College, Due West, South Carolina

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I. INTRODUCTION

Changes in the distribution of molecules between the gas and adsorbed phases as a function of pressure and temperature have been used for many years to study surface area, surface structure, and gas–solid interactions. Gas–solid chromatography provides a useful alternative to conventional adsorption experiments and can serve as a method to study these aspects of physical adsorption.

In the virial coefficient treatment of physical adsorption, the moles of gas adsorbed per gram of adsorbent, n_a , are related to the second gas–solid virial coefficient, B_{2s} , which is a measure of the interaction of isolated gas molecules with a solid surface. Adsorption isotherms or gas chromatographic retention times measured in the Henry's law region of low adsorption can be used to provide values of second gas–solid virial coefficients. In this chapter we will explore the theoretical basis of the second gas–solid virial coefficient, how these values are determined from gas–solid chromatography experiments, and how an analysis of these values and their temperature dependence for various adsorbate gases can provide adsorbent structural information, solid surface areas, and measures of gas–surface interactions. In addition, we will examine how retention times and B_{2s} values can be correlated with other physical or structural properties.

In the pulse flow technique, a gas or vapor is injected into a flowing carrier gas. The adsorbate flows through a powder-packed column, and molecules are distributed between an adsorbed form and the gas phase. The retention time depends on the magnitude of the equilibrium between the adsorbed and free forms of the adsorbate. As we shall see in the theory section, the second gas–solid virial coefficient depends on the corrected flow rate of the carrier gas through the column, the retention time of the sample gas measured relative to a noninteracting reference gas, and the mass of powder in the column.

The virial coefficient treatment of physical adsorption was developed primarily by Steele and Halsey [1] and others [2–4], discussed by Steele [5], and thoroughly reviewed by Pierotti and Thomas [6] who covered the exact statistical thermodynamic basis of this approach. The importance of a Henry's law approach to studies of surface heterogeneity has been discussed by Bakaev and Chelnokova [7]. An excellent review of the historical background and approaches used in a virial analysis of adsorption is provided by Rudzinski et al. [8]. Although most early work used volumetric or gravimetric adsorption techniques, chromatographic studies included work by Boucher and Everett [9], Rudzinski et al. [10], and Ross et al. [11].

Since the introduction of the virial coefficient theory [1–4], continued attention has been given to physical adsorption and the application of the virial coefficient theory [8,12–14]. Adsorption in micropores has been studied at various pressures and temperatures [15,16], and the size and shape of the micropores

[17–20], as well as their formation and structure [21,22], have also been studied. Virial coefficients have been used to analyze experimental data [23,24], and calculations have been carried out to compare the adsorption in slit-like pores to flat surfaces and to find surface areas and volumes of the solids [25]. Other studies have been conducted to analyze Henry's law constant [7] and the energy aspects of adsorption [24,26,27].

A variety of studies have used gas–solid chromatography to determine second or second and third virial coefficients for gases interacting with solid surfaces [10,28–37]. Other studies have examined the theoretical basis of the virial approach or used traditional adsorption experiments to determine virial coefficients or Henry's law constants [8,24,38–52]. The use of gas chromatography to determine equilibrium properties and second virial coefficients for gases was reviewed by Conder [45]. Gas–solid chromatography has been used by Rybolt and Thomas to determine B_{2s} values, find powder surface areas, specify the gas–solid interaction energies, determine structural parameters for microporous solids, determine the relative amounts of higher and lower energy surfaces on two-surface solids, and correlate B_{2s} values or adsorption energies obtained from B_{2s} values with other molecular physical properties [28,29,32,37,53].

II. THEORETICAL BACKGROUND

A. Adsorption and the Second Gas–Solid Virial Coefficient

A virial approach to physical adsorption and gas–solid chromatography is based on the following equation:

$$n_a = \sum_{i=1} B_{i+1,s}(f/RT)^i \quad (1)$$

where n_a is the moles of gas (adsorbate) adsorbed per gram of solid adsorbent, f is the fugacity, R is the gas constant, T is the temperature, and $B_{i+1,s}$ is the $(i + 1)$ th gas–solid virial coefficient [6]. B_{2s} represents the interaction of one adsorbate molecule with the surface, B_{3s} represents a pair of gas molecules interacting with each other and the surface, B_{4s} represents a triplet of adsorbate molecules, and so forth. In the Henry's law region of adsorption where only a small portion of the surface is covered with adsorbate, the adsorbate–adsorbate interaction is negligible and the higher order terms drop out of the power series in the previous equation.

As the pressure, P , approaches zero, Eq. (1) may be simplified and written as [6]:

$$n_a = B_{2s}(P/RT) \quad (2)$$

B_{2s} values vary with temperature and contain information about the structure of the solid as well as the strength and nature of the gas–solid interactions. The probably more familiar Henry’s law constant, K_H , relates pressure to moles adsorbed as $n_a = K_H P$ where $B_{2s}/RT = K_H$. As we shall show in this chapter, B_{2s} values have an exact definition based on statistical thermodynamic considerations that make them useful in analyzing gas–solid interactions.

In order to extract the maximum amount of information about a solid, it is necessary to have adsorption data or gas chromatographic data for several different adsorbates over a range of temperature. Sets of B_{2s} –temperature pairs for varied gases on a particular adsorbent can be generated from careful experimental measurements of corrected retention times, corrected flow rates, and the mass of the powder in the packed column.

Experimental values of B_{2s} are related to the surface structure and gas–solid interaction through the integral expression:

$$B_{2s} = \int_V [\exp(-u_{1s}/kT) - 1] dV \quad (3)$$

u_{1s} is the gas–solid interaction potential, k is the Boltzmann constant, and dV is the volume element in the gas phase [5]. Note that B_{2s} values may be calculated from Henry’s law constants but have the useful feature of being related to the gas–solid interaction potential by an exact statistical thermodynamic derivation [5,6]. Approximations enter into the equation only as one develops specific equations to represent u_{1s} .

Given the functional form of u_{1s} and the appropriate parameters to characterize the solid surface and gas–solid interaction, one can calculate B_{2s} values and predict adsorption and chromatographic data. However, the approach discussed below is based on the availability of experimental B_{2s} data and the desire to extract gas–solid molecular parameters from these data. In the following sections, we will show how B_{2s} is related to chromatographic retention times and focus on four different models that have been used to represent the gas–solid interaction. These models are by necessity simplified versions of the surface structure but can nevertheless provide useful data and insights into unique methods to calculate surface area, surface structural parameters, and gas–solid interaction parameters. The theoretical equations for the flat single-surface, flat two-surface, cavity, and parallel plate models are presented in this section while applications are presented later, in the analysis section.

B. Gas–Solid Chromatography

The diffusion of an adsorbate pulse transported through an adsorbent packed column by an inert carrier gas stream is given by [11,54–56]:

$$n_{gc}/n_{ac} = L/tv \quad (4)$$