

## Book Reviews

**Chromatographic Separations Based on Molecular Recognition.** Edited by Kiyokatsu Jinno (Toyohashi University of Technology). Wiley/VCH: New York, 1997. \$95.00. xiv + 426 pp. ISBN 0-471-18894-8.

This book deals with different aspects of the molecular interactions involved in chromatographic separations. This book is of interest to scientists involved in separation science for analytical purposes, and to scientists interested in the effects of synthetic and natural polymers able to interact selectively with biologically active molecules. The synthesis of efficient chromatographic beads and the use of molecular complexes for gas chromatographic separations are also reported.

The first two chapters stress the steric effects which permit polycyclic aromatic hydrocarbon (PAH) separations on reversed phase supports. Chapter 1 from S. A. Wise and L. C. Sander emphasizes the role of the shape of solutes and the structure of sites on retention. Concerning the solutes, a planarity criterion is based on the length-to-breadth ratio (L/B ratio) which can be linked satisfactorily to retention. The role of stationary phase characteristics, monomeric or polymeric layers, pore size effects, bonding density, and grafted chain length, is described in detail. These results support an interpretation of recognition based on a slot model allowing a more or less deep solute penetration giving good separations. A comparison with a statistical thermodynamic analysis evidences very similar retention predictions. Chapter 2 from K. Jinno reviews the same topic but outlines the effects of stationary phase structure by giving detailed information on the grafted alkyl chains. NMR relaxation measurements explain the role of solvent composition on separations. The role of temperature is analyzed by NMR and DSC (differential scanning calorimetry) techniques, and this approach gives a very convincing interpretation of the retention using the configurational constraints of the different chain structures. Other types of structures are reported: liquid crystal bonded phases and multilegged sites bearing phases which improve the PAH recognition through weak differences in planarity. The properties of fullerene C<sub>60</sub> materials (pure or grafted) are reported on and exhibit retention orders very different from octadecylsilanized silica (ODS) phases, which is explained by the occurrence of  $\pi$ - $\pi$  interactions. These two chapters give exhaustive information on PAH separations and are of a major interest for scientists involved in fundamental studies on molecular interactions and for workers who analyze these species for environmental purposes.

Chapter 3 from K. Jinno is devoted to fullerene separations by chromatography. As most of the preparative methods lead to mixtures containing mostly C<sub>60</sub> and C<sub>70</sub> but also higher molecules up to C<sub>98</sub>, careful purification and analysis is needed to isolate definite species. A complete description of the ODS capabilities is reported with mention of the role of monomeric and polymeric structures and temperature. The experimental observations are interpreted from NMR measurements. Other types of efficient phases have been evaluated: alkyl-phenyl, multiphenyl, liquid crystal bonded phases, multilegged phases, copper-phthalocyanine phases, and C<sub>60</sub> bonded phases. Molecular modeling has permitted valuable interpretations. From a comparison of the tested materials, it is concluded that molecular recognition based on molecular fitting between solutes and shape sites is essential for separation. The multilegged phases are highly recommended to achieve complete separations. All scientists concerned with fullerene separations and identification can take advantage of the information gathered in this chapter.

Chapter 4 from Y. Okamoto and E. Yashima deals with enantiomer separations from chiral polymers. The authors have summarized a lot of papers concerning the use of natural (proteins, polysaccharides) native or chemically modified and synthetic polymers (polyamides, polymethacrylates, polymethacrylamides) associated or not with silica or polystyrene beads. The main interest of this part concerns the properties of polysaccharides and derivatives that are the most common materials for preparative separations. Despite numerous citations, it should be noticed that the most recent reference dates from 1992 and some important points are lacking such as the molecular aspects of the recognition, as well as molecular imprinting techniques.

Chapter 5 from R. Kalistan and I. M. Wainer brings a more original overall view of molecular recognition since it concerns the relationships among chromatographic retention of drugs, solute molecular structure, hydrophobic character, and biological activity. The first part includes immobilized artificial membrane (IAM) based supports introduced by C. Pidgeon which give a good estimation of the hydrophobic character of different solutes allowing comparisons with the water-octanol partition coefficient. The use of immobilized serum albumin columns offers larger possibilities for interaction studies: drug binding, selective enantiomer interactions, influence of a second drug, etc. The different types of interference occurring with two ligands (cooperative, noncooperative, anticooperative) can be easily identified from retention properties. Moreover, using quantitative structure-retention relationships (QSRR), the authors have shown good correlation between solute molecular parameters and retention. This analysis leads to identification of the kind of binding area sites involved in retention. Similar results concerning  $\alpha$  glycoproteins are reported. This chapter is indeed very informative because it brings a good overview of drug-protein interaction and its role in separation processes and in some biological phenomena. His interest in the pharmacological field is evident.

Chapter 6 from K. Hosoya moves away from the question of molecular recognition since it focuses on the synthesis of uniform and pore-controlled chromatographic beads. Processes derived from J. Ugelstad's work are carefully described in order to optimize the chromatographic performance. Several special supports are reported such as restricted-access supports (for drug assays) or temperature-responsive polymer-based supports. These last materials exhibit variations of porosity and hydrophobicity with temperature which permit the selectivity to be improved. Chiral supports based on polymethacrylamides introduced for the first time by G. Blaschke can be achieved with uniform size beads. A too brief mention of molecular imprinted materials extends the field of this polymerization method. This chapter is of interest for polymer chemists who can find here ideas for new separation materials synthesis. This part completes Chapter 4 on chiral polymers in a fruitful manner.

The last chapter by V. Schurig is a very important part of the book since it concerns the separation by gas chromatography based on molecular complex formation. An excellent thermodynamic analysis of the connection between complexation strength and retention is presented. The role of solute concentration is emphasized, and the difference between apparent and absolute parameters is clearly justified. Thus, separation factor variations with the experimental conditions are rigorously predicted. Several examples of complexes allowing chromatographic separations are reported: rhodium-olefins with mention of deuterated compounds and enantiomers-transition metal complexes. The different thermodynamic contributions which govern the separations are clearly connected to the peak parameters, and this approach is illustrated by several experimental examples. The role of temperature leading sometimes to coalescence phenomena is predicted from the thermodynamic parameters. The occurrence of enantiomerization in the course of analysis is also taken into account. Particular aspects such as kinetic resolution and broadening effects are reported and commented upon. The author distinguishes four enantioselective processes and six coalescence situations which bring a complete description of the phenomena encountered by the experimenters. Inclusion chromatography is briefly presented, and the difficulty to define a reference material devoid of interaction between selector and matrix is outlined.

Finally, molecular recognition is a subject for which chromatography is both a tool of study and a field of application. This book is of great interest both for chromatographers and for all scientists concerned with specific molecular interactions in the fields of chemistry and biology.

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JA975691M

10.1021/ja975691m