INVERSE GAS CHROMATOGRAPHY

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Defence Scientific Information & Documentation Centre
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PREFACE

Inverse gas chromatography (IGC) is a variation of conventional gas chromatography in which a nonvolatile material to be investigated is immobilised in the column of a gas chromatograph, as a stationary phase. The stationary phase is then characterised by monitoring the passage of volatile probe molecules as they are transported through the column by an inert carrier gas. The IGC technique can be used to determine various physicochemical properties of the stationary phase of diverse materials. Extensive use of this technique is being made by chemists, chemical engineers, and material scientists which is evident by a large volume of research publications. Reasons for IGC's popularity is because of its simplicity, convenience and rapidity. There are several centres in the country where this technique is used for studying polymers, carbon and other materials of technological importance.

An attempt has been made in this monograph to present to the readers the capability of IGC and recent research trends for the first time in a comprehensive manner. The purpose of the monograph would be served if it could stimulate additional interest in this technique.

In the introduction of the monograph, the scope of IGC has been discussed. Chapter 2 deals with basic concepts of gas chromatographic theory and Chapter 3 discusses the equipment and procedure. Thermodynamic property of solutions has been presented in Chapter 4. Studies on various thermodynamic parameters, like activity coefficient, excess quantities, solubility parameter, Flory Huggins interaction parameters of polymers, and polarity of complex materials have been included in this chapter. Till recently, compatibility study of polymer blends by IGC, was quite attractive to researchers, however, probe dependence of interaction parameter has somewhat limited the use of the method. Various authors have suggested remedial methods to eliminate the probe dependence. All these aspects have been covered

in Chapter 5 dealing with compatibilty of polymer blends. Diffusivity studies of gases and vapours through polymers using packed column, recently introduced capillary column and the validation of free volume theory has been dealt with in Chapter 6. Various methods of finite concentration gas chromatography and recent studies in the determination of adsorption isotherm and surface area has been presented in Chapter 7. Studies on phase transition of diverse materials like liquid crystals, polymers and other stationary phases has been discussed in Chapter 8. Also included in this chapter is the estimation of crystallinity of semicrystalline polymers. Recent research trend of inverse gas chromatography is the measurement of surface characteristics of materials, e.g., dispersive surface energy and acid-base properties. Such properties enable measurement of interfacial properties which are useful in the study of fibre reinforced polymer composites, dispersion of pigment in paint, batch to batch variation in pharmaceutical powders, particulate fillers, etc. The importance of the subject can be gauged by the fact that majority of papers presented in the first international conference on inverse gas chromatography held in september 2001 at London, pertained to surface studies. The various studies on surface property of materials have been discussed in Chapter 9.

The Defence Scientific Information and Documentation Centre (DESIDOC), Ministry of Defence, Government of India, has granted me a project to write a monograph on *Inverse Gas Chromatography*. I am grateful to DESIDOC for providing me this opportunity. I am also grateful to Prof. GN Mathur, Director, DMSRDE, Kanpur, for permitting me to access to the library and other facilities. I am thankful to Shri Darshan Lal of DMSRDE, and Prof. P. Guptabhaya of IIT, Kanpur for the help rendered at different stages in writing of the monograph. Above all, I am thankful for the encouragement and inspiration given by my wife Sutapa.

Kanpur AK SEN

November 2004

CHAPTER 1

INTRODUCTION

In recent years gas chromatography has become one of the most useful analytical tools. The introduction of gas liquid chromatography by James and Martin in 1952[1] stimulated rapid development of both gas liquid and gas solid chromatography. This is evidenced by the publication of numerous research papers, journals and books on the subject. The separating power has been exploited even for preparative separations in laboratory and in industry.

Another simultaneous development of gas chromatography has been as a means of studying a great variety of physical processes. One of the first workers in this area were James and Philips[2] who measured adsorption isotherms using gas solid chromatography. Later, various workers used gas liquid chromatography to measure such physical properties as boiling point, partition coefficient, and heat of solution of a volatile solute in a nonvolatile solvent. This technique was soon recognised as the earliest of all methods to study the thermodynamics of the interaction of a volatile solvent with a non-volatile solvent.

1.1 SCOPE OF INVERSE GAS CHROMATOGRAPHY

The study of physico-chemical properties of polymers and other solids by gas chromatography has emerged as an independent field of study, viz., *Inverse Gas Chromatography* (IGC). The rapid advancement in material science and the convenience of the gas chromatographic technique have contributed to the rapid development of the field. The technique involves filling a column with a stationary phase of the solid material of interest. The solid material may be in the form of thin coating on an inert substrate, a finely divided solid, strands of fibre, or a thin polymeric coating on the column wall. A volatile probe of known physicochemical property is passed through the column via an inert

mobile phase, and the output is monitored. The retention time of the probe and the shape of the chromatogram gives the physico-chemical characteristic of the stationary phase. Three types of physical properties can be measured by inverse gas chromatography[3] as has been shown in the Fig.1.1.

(a) Retention times enable measurement of equilibrium properties, like phase transitions, and measurement of distribution of a volatile solute between a mobile gas phase and a stationary phase which can be solid or liquid, i.e., thermodynamic properties of solution, sorption studies, and surface properties of solids.

(b) Kinetic and transport processes can be measured through concentration time profile of the migrating peak and the extent to which it broadens as it moves towards the column outlet. Diffusion of gases, vapours and reaction rate constants fall in this category.

(c) Miscellaneous properties like surface area, molecular weight, etc., can be measured from retention time or peak area.

Out of the three areas discussed above, equilibrium processes have been studied intensively. In the kinetic and transport areas also gas chromatographic studies find wide applicability. IGC was initially used only in the study of synthetic polymers, today it is used to study synthetic and biological polymers, copolymers, polymer blends and other solids such as glass, carbon fibres, solid foods, and pharmaceutical powders[4]. IGC is now being used to estimate various properties of the stationary phase, such as phase transition temperatures, crystallinity of polymers, thermodynamics of polymer solvent interaction, compatibility of polymer blends, solubility parameter, acid-base characteristics of solid surface, surface area, adsorption properties and diffusion coefficients.

1.2 MERITS AND LIMITATIONS

1.2.1 Advantages of IGC

IGC has significant advantages over the conventional methods[3,6]. The technique is simple, rapid, convenient, and highly sensitive. If proper precautions are taken it can furnish physico-chemical data with extremely small amount of samples. Some of the major advantages are listed below:

About the Book

Inverse gas chromatography (IGC) is a useful technique for characterising solid materials including polymers, copolymers, polymer blends, carbon, silica, pharmaceutical powders, cellulosic materials, etc. The technique involves creating within a column a stationary phase of the solid material of interest and determining its different physico-chemical properties. Extensive use of this technique is made by scientists and researchers. IGC technique is very popular because of its simplicity, convenience and rapidity. This monograph presents the entire range of capability of IGC technique and recent research trends in a comprehensive manner for the first time. The various chapters of the monograph contain gas chromatographic fundamentals, experimental procedure; and different applications such as thermodynamic properties of solutions, compatibility of polymer blends, diffusion in polymers, adsorption and surface area, phase transitions and surface properties of solids. Each application has been dealt in detail from basic theory to the current review of the research work done in the field. The book will be valuable to chemists, chemical engineers and material scientists, both in academic institutions and industry, engaged in characterisation of non-metallic materials.

About the Author

A.K.Sen obtained his M.Tech in 1958 and Ph.D in Applied Chemistry in 1963 from I.I.T Kharagpur. He was in the faculty of chemistry department of I.I.T Kharagpur from 1963-71. He was a post doctoral fellow at SUNY Stonybrook U.S.A in 1967-68. He later joined DMSRDE , Kanpur as a research scientist. He has worked in the fields of polymer science-characterisation of polymers and blends by inverse gas chromatography, chemical process development and textile and clothing. He has published several papers in international journals on various applications of inverse gas chromatography. He was awarded DRDO Technology Award in 1996. He has written a book on 'Coated Textiles Principles and Applications' in a DST project which has been'published in 2001. He is presently attached to DMSRDE as an emeritus scientist.

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