

THE LIQUID CHROMATOGRAPHY OF AROMATIC  
DIAMINES: ANALYTICAL AND PREPARATIVE

By

Philip R. Young

Dissertation submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

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APPROVED:

H. M. McNair, Chairman

N. J. Johnston

J. G. Mason

J. P. Wightman

J. F. Wolfe

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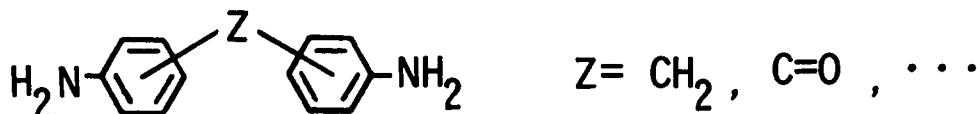
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THE LIQUID CHROMATOGRAPHY OF AROMATIC  
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INTRODUCTION

Isomeric aromatic diamines are becoming increasingly important in studying the effects of chemical structure on the properties of polyimides (1, 2), polyamides (3), epoxies (4), and urethanes (5). For example, glass transition temperatures can be significantly reduced without sacrificing thermal stability by polymerizing aromatic dianhydrides and diacid chlorides with meta- and perhaps ortho-oriented monomers (1, 2). Glass transition temperatures are of vital concern if these polymers are to be fabricated into useful materials.



The importance of the reactivity or basicity of the amino group to the molecular weight of the resultant polymer has also been noted (1, 3, 6). As a general rule, the more basic the amino group, the more reactive it is toward other monomers. Seven isomeric diamines have recently been synthesized in our laboratory where  $\text{Z} = \text{C}=\text{O}$  and five isomers where  $\text{Z} = \text{CH}_2$ . Additional series are being studied having a wide range of interconnecting Z groups. This activity poses two questions for the analyst: (1) Are these diamines sufficiently reactive to form useful polymer, and (2) Can enough high purity monomer be obtained to allow meaningful polymer characterization?

The direct measurement of  $K_b$  values for all these isomers is not

always satisfactory or possible because the measurements are often time consuming and lack specificity. Thus, other techniques are needed which will help establish the relative basicity for series of aromatic diamines differing only in the point of attachment of the amino group or the interconnecting Z group. The classical recrystallization and sublimation techniques for purification are also often inadequate since many of these diamine isomers have similar solubilities and vapor pressures. New methods for purification are required. These two problems are confronted in this study through the use of high pressure liquid chromatography. This technique was employed because of its separative capability, potential for sample scale up, and because it provides a low temperature, gentle environment for these reactive species.

It is generally accepted that the adsorption of many basic organic compounds on silica gel may be treated as bases interacting with an acidic surface. In this research, a chromatographic investigation was conducted to determine if the adsorption of weakly basic aromatic amines on slightly acidic silica gel adsorbents could be used to study their relative basicity. The effect of chemical structure on chromatographic behavior has been extensively studied (7). However, a review of the literature revealed that the correlation of sample basicity with retention has received limited attention. Before the complex diamines used in polymer synthesis could be studied, the adsorption of some simple aromatic amines on silica was investigated. Retention data was



correlated with respective  $pK_b$  values and under the proper conditions, a linear correlation between  $pK_b$  and log of the capacity factor was observed. The extension of this concept to the aromatic diamines of interest was then pursued.

The preparative aspects of the liquid chromatography of aromatic diamines were also investigated. A literature search showed that several pertinent chromatographic parameters had been studied in a number of reports. However, no single comprehensive evaluation directed toward the preparative high pressure liquid chromatography of a specific class of organic compounds has been made. In this study, the effect of the column packing technique, flow rate, column internal diameter and length, adsorbent surface area and particle size, and column capacity were evaluated as they pertain to the preparative separation of aromatic diamine isomers. It is shown that adequate separations can be made on milligram quantities of diamine monomers used for polymer synthesis.

### NOTATION

$d_c$	= internal diameter of the column
$d_p$	= particle diameter of the adsorbent
HETP	= height equivalent to a theoretical plate
$k'$	= capacity factor
L	= column length
n	= number of measurements
N	= number of theoretical plates
$R_s$	= resolution
$t_r$	= retention time of a peak measured from the start
$t_o$	= retention time of a non-sorbed species (hold-up time)
v	= volume
w	= peak width
x	= measured value
$\bar{X}$	= arithmetic mean
$\text{\AA}$	= angstrom
$\eta$	= inherent viscosity
$\sigma$	= standard deviation of a Gaussian band
$\sigma_{rel}$	= relative standard deviation
$\Sigma$	= summation
$\mu$	= micrometer
$\mu\text{g}$	= microgram
$\mu\text{l}$	= microliter

## SURVEY OF LITERATURE

Basicity from Chromatographic Retention. - There is a continuing interest in the chromatographic separation of amines. One of the early papers by James was concerned with the gas-liquid separations of aliphatic amines and homologs of pyridine (8). A search of the literature revealed many amine separations. However, these were primarily thin layer, ion exchange, or gas chromatographic analyses of aliphatic amines. A review of these types of separations is not within the scope of the present work although they do provide a background for modern high pressure liquid chromatography (HPLC). A literature search of HPLC separations of aromatic amines was not nearly as fruitful, primarily due to the newness of the technique.

The effect of sample structure on chromatographic behavior has been extensively investigated (7). With very few exceptions, however, the correlation of sample acidity or basicity with retention has received limited attention. Brown states that "in liquid chromatography the order of elution does not follow  $pK_a$  values" (9). Although this statement pertained to ion exchange separations, the two supporting references given by Brown were the earliest found on the subject. Unfortunately, neither the article by Volkin and Cohn (10) nor the article by Sober and Peterson (11) mentioned the correlation of solute acidity with chromatographic retention on the cited pages. A thorough review of both articles failed to find any reference to the subject.

In several instances, Snyder notes that the adsorption of many basic organic compounds on silica gel may be treated as based inter-

acting with an acidic surface and states that "group adsorption energies increase with increasing electron density or increasing group basicity" (12). However, no definitive statement concerning the direct correlation of sample basicity with chromatographic retention appears in his comprehensive text on adsorption chromatography.

Several articles by Soczewinski on the relationship between molecular structure and chromatographic parameters (13-16) have been published since Dr. Snyder's book appeared in 1968. In the most pertinent of these (14), thin layer chromatography was used to determine  $R_m$  values of ten methyl derivatives of aniline. The experimental data were plotted against  $pK_a$  values for the bases and fairly linear results were observed in some cases. This suggested that their chromatographic behavior in acidic systems was determined by the basicity of the amino group, steric effects, and the molecular structure of the solutes. Basicity played only a minor role in neutral systems.

Yasuda examined the thin layer chromatographic behavior of several aromatic amine isomers on regular silica gel and silica gel impregnated with cadmium sulfate and cadmium acetate (17, 18). Improved separations were observed on the salt impregnated layers. In acidic mobile phases, retention was found to be related to the basicity of the amines. Further, it was established that a correlation existed when  $pK_a$  values were plotted as a function of retention. The special adsorption phenomenon on metallic salt-impregnated layers was assumed to be due to a complex formation between the metallic salt and the amine (19). The relationship between the amine basicity and retention

seemed to support this assumption.

More recently, Kunzru and Frei extended Yasuda's work by studying the retention characteristics of several aniline isomers on cadmium-impregnated silica gel columns by HPLC (20). Since the amines contained a lone pair of electrons, they were expected to act as electron donors with the impregnated cadmium acting as electron acceptors. As the column loading on the silica gel increased, the efficiency of the separation of o-, m-, and p-chloroaniline and toluidine isomers decreased but the relative retention increased. Kunzru concluded that the basicity of the amine was very important but not the sole factor determining chromatographic behavior since no direct correlation between  $pK_a$  and retention could be established.

Although the separation of aromatic amines has received more than casual attention and the predominant separation mechanism is well known, a direct correlation between amine basicity and chromatographic retention was not demonstrated until the preliminary phases of the present research was published (21). The development of this concept is one of the primary objectives of this research problem.

Preparative Liquid Chromatography. - Preparative scale liquid chromatography may be defined as the practice of using a chromatographic separation to prepare a purified sample for future use. The demands placed on the amount of sample collected vary depending on the ultimate use. Small amounts are usually required for identification purposes and thin layer or paper chromatographic techniques may suffice. If larger samples are necessary, gas chromatography, gel permeation, or liquid chromatography are usually considered. Preparative gas chromatography has been extensively reviewed (22, 23). Gel permeation chromatography is usually reserved for high molecular weight materials such as polymers and has also been reviewed (24). A further discussion of these techniques is not within the scope of the present work.

Unfortunately, reports on the use of preparative HPLC are somewhat limited although it is probably widely practiced. This apparently reflects the loss of research interest in preparative capabilities with the increase in interest in using HPLC procedures for analytical purposes. Also, many researchers have a greater concern for the use of the purified product than in reporting on the preparative technique itself. Four recent publications (25-28) where preparative liquid chromatography was used as a means to achieve an end result illustrate this conjecture.

Several systematic studies on parameters which effect preparative efficiency have been made. Sie and van den Hoed studied the preparation and performance of chromatographic columns (29). This study demonstrated that columns with 10 mm i.d. could be used with high

efficiency. Knox and Parcher studied the effect of column to particle diameter ratio on the dispersion of unsorbed solutes and presented the infinite-diameter concept (30). A column which is free from wall effects was termed an infinite diameter column. In such a column, a centrally injected sample at the head of the column would fail to reach the disturbed packing region close to the walls by the time it reached the foot of the column. The minimum column internal diameter which would produce the "infinite-diameter" effect could be calculated using the equation

$$d_c = (2.4 d_p L)^{1/2}$$

where  $d_c$  is the internal diameter of the column,  $d_p$  is the adsorbent particle diameter, and  $L$  is the column length. This study concluded that infinite-diameter columns offered advantages over conventional columns and experimental evidence was presented to support this conclusion.

DeStefano and Beachell reported on the performance of large diameter columns in a series of articles. In the first of these (31), five 50 cm columns having internal diameters of 1.6 mm, 2.1 mm, 4.76 mm, 7.94 mm, and 10.9 mm were evaluated under a number of conditions. These columns were packed with a <37 micron controlled surface porosity support similar to the commercially available "Zipax" adsorbent (32). HETP was studied as a function of carrier velocity and the volume and weight of sample injected. An effort was made to verify the "infinite-diameter" column effect of Knox and Parcher (30). Large

diameter columns were shown to have superior performance in some cases over narrow-bore analytical columns. Large volume injections of dilute solutions were also shown to be more effective than small volume injections of concentrated solutions.

In their second study (33), DeStefano and Beachell investigated the effects of support particle size on the performance of large diameter columns. Controlled surface porosity supports having 20-37 $\mu$ , 37-44 $\mu$ , 44-53 $\mu$ , 53-63 $\mu$ , and 63-74 $\mu$  diameters were used to dry-pack 50 cm x 7.94 mm i.d. columns. Slurry packing techniques were said to be necessary for particles having smaller diameters. HETP was evaluated as a function of carrier velocity and particle size. The influence of particle size on column permeability was also investigated. The results of this study showed that column performance increased as the particle diameter decreased. It also suggested that even higher efficiencies could be obtained from particles smaller than those available at the time of their study. This has subsequently been proven with the appearance of the 5 $\mu$  totally porous adsorbents (34, 35).

In their third paper (36), DeStefano and Beachell again studied the effect of flow rate, injection volume and weight, and sample concentration on chromatographic performance. For this study, 50 cm x 2.1 mm i.d. and 49.3 cm x 10.9 mm i.d. columns were packed with Porasil A. Many of the conclusions of an earlier study (31) were verified. Two applications on the preparative separation of optically active compounds and aniline derivatives were also presented. Large diameter columns packed with Porasil A were shown to have greater



efficiency than smaller narrow-bore analytical columns packed with the same adsorbent. Several observations on preparative chromatography were also offered in this study. A 1 mg of sample per gram of adsorbent loading did not exceed the capacity of the column. Although capacity could be increased by increasing column length, a greater advantage was expected to be realized by increasing column diameter. However, no supporting experimental evidence for this was offered. Some of the disadvantages of preparative chromatography such as increased retention times and mobile phase volumes were also noted.

Other investigations have included an analysis of through-put and band overlap in preparative chromatography (37) as well as additional research on large diameter columns (38, 39). Wolf (38) pointed out that the "infinite-diameter" concept could not be used to explain the improved performance of his large diameter columns over that observed for analytical columns. To be "infinite" in diameter, it is necessary for the sample to be injected at a point on the column axis so that it will not reach the walls before it exits the column. The column end-fittings for his study were designed to transpose a slug of solute in the carrier stream into a uniform disk over the entire cross section of the packing. Thus, a necessary condition was not satisfied and yet his columns exhibited improved efficiency. Bombaugh described the system requirements for the use of recycle in high efficiency liquid chromatography (40).

Studies have also been made on the vitally important subject of scaling from analytical to preparative practices (41-43). An automated

low pressure (30 psi) system has been described in which the sample is injected, monitored, and collected and then the solvent is distilled and reused (44). An example of the use of this system was also reported (45).

Thus, a review of preparative HPLC reveals that many pertinent chromatographic parameters have been studied and several examples of its use have been reported. However, it appears that the effect of column length and adsorbent surface area has not been investigated. These two parameters were evaluated in the present study as well as a re-examination of many of the parameters discussed in this summary. It is also apparent from a review of the literature that a comprehensive investigation directed toward the preparative separation of a specific class of organic compounds has not been made. This also was an objective of the present study.

## EXPERIMENTAL

Apparatus. - A Waters Associates Model ALC 202/R401 Liquid Chromatograph (Waters Associates, Milford, MA) equipped with a Model 6000 Solvent Delivery System was used throughout this study. The 254 nm fixed wavelength ultraviolet detector was employed during the analytical phase of this research while both the ultraviolet and differential refractometer detectors were employed during much of the preparative study. The chromatograph was operated under ambient temperature conditions. A 25 $\mu$ l Series "B-110" Pressure-Lok Liquid Syringe (Precision Sampling Corp., Baton Rouge, LA) was used to inject the analytical samples. A Model U6K Universal LC Injector (Waters Associates), capable of injecting volumes from 1 $\mu$ l to 2 ml, was used to inject the preparative samples. This injection system has been previously described (46). The chromatograms were recorded on a Hewlett-Packard 7100 Strip Chart Recorder at a 0.2 in/min chart speed.

### A. ANALYTICAL

Adsorbents. - The Corasil I, Corasil II, Porasil A, Porasil B, and Porasil C adsorbents were obtained from Waters Associates. The Zorbax-SIL adsorbent was obtained in a pre-packed stainless steel column from E. I. DuPont de Nemours & Co. (Inc.), Instrument Products Division, Wilmington, DEL.

Columns. - Only the 25 cm x 2.1 mm i.d. stainless steel Zorbax-SIL column was obtained pre-packed. Special end-fittings were fabricated to make this column compatible with the chromatograph. The re-

mainder of the columns were hand-packed. Each column was prepared for packing by cutting 1/8 in. (2.4 mm i.d.) stainless steel tubing into 2 ft. (61 cm) lengths. Since the cutting process can deform the ends of the column, both ends were filed to a flat surface and reopened to their maximum diameter with a circular file. The columns were than washed with hot soapy water using a pipestem cleaner and rinsed with distilled water, methanol, distilled water, and acetone in that order. They were dried by a nitrogen-purge. A 5 micron stainless steel frit was fitted on the detector end of each column.

Packing Procedure. - The columns were dry-packed using the modified tap-fill technique described by Kirkland (32). Approximately 100 mg additions were made to the vertically held column. This was followed by one minute of light rapping on the side of the column at the appropriate level with a wooden ruler and then three minutes of tapping on the floor. The tapping was continued for one hour after the column appeared to be full. The injection port end of the column was then plugged with a piece of silanized glass wool. Approximately 3.2 g of Corasil and 1.2 g of Porasil were required to pack the columns. No attempt was made to optimize column performance by altering the packing procedure.

Materials. - The o-, m-, and p-bromoaniline, chloroaniline, and toluidine isomers and the m-phenylenediamine isomer were used as received from the supplier. The o- and p-phenylenediamine isomers were recrystallized with decolorizing charcoal treatment from ethanol and water, respectively.

The two series of diaminobenzophenone and methylenedianiline

isomers as well as the other aromatic diamines studied were obtained from Dr. Vernon L. Bell, NASA-Langley Research Center, Materials Division, Hampton, VA. They were either synthesized in-house, on grants to Virginia Commonwealth University (NGR 47-002-041) and the University of Southern Mississippi (NGR 25-005-005), or obtained from commercial sources. Reference 1 gives the synthesis of many of the diamino-benzophenone isomers. The  $K_a$  values for the diaminobenzophenone and methylenedianiline isomers were measured by Dr. John G. Mason, Department of Chemistry, Virginia Polytechnic Institute and State University under NASA Master Agreement NAS1-10,646-7.

The reagent grade mobile phases were filtered prior to use.

#### B. PREPARATIVE

Adsorbents. - The Porasil A, Porasil B, and the Porasil C adsorbents were obtained from Waters Associates. The 20 $\mu$ , 30 $\mu$ , and 40 $\mu$  Li-Chrosorb SI 60 adsorbents were obtained from E. M. Laboratories, Inc., Elmsford, N.Y.

Columns. - The 1/8 in. (2.4 mm i.d.), 1/4 in. (4.57 mm i.d.), and 3/8 in. (7.75 mm i.d.) stainless steel tubing for the preparative columns were stock items. They were cut into 2 ft. (61 cm) lengths, prepared for packing by the previously described procedure, and fitted on the detector end with 5 micron stainless steel frits. The 1 in. (21.13 mm i.d.) stainless steel column was obtained from Waters Associates, cut into a 2 ft. length, cleaned, and fitted with a 10 micron stainless steel frit assembly.

Packing Procedure. - An apparatus was constructed for packing the

columns for this study which allowed repeatable packing conditions. It was patterned after the automatic dry-packing device depicted on p. 75 of reference 47. A 110 volt, 60 rpm, 1/1500 h.p. Bodine electric motor was bolted to the base of a ringstand and fitted with a special cam which elevated and dropped a lever arm at the rate of two cycles per second. A hinged adapter which retained the bottom of the column during the packing process was attached to the end of the lever arm. The column was held in the vertical position by guides attached to the ringstand. When activated, the column was dropped under its own weight approximately 1.5 cm. The adsorbent was manually added at one minute intervals through a small funnel attached to the top of the column. Continuous tapping was maintained while the column was being packed and the tapping was continued for one hour after the column appeared to be full. This entire packing procedure was adopted in an effort to minimize variations from column to column due to the manner in which they were packed.

This device was used to pack the 1/8 in., 1/4 in., and 3/8 in. columns. Approximately 20 mg, 115 mg, and 225 mg additions were made to these columns, respectively. After packing, the 1/8 in. and 1/4 in. columns were plugged on the injection port end with silanized glass wool. The 3/8 in. columns were fitted with a second stainless steel frit. The 1 in. x 2 ft. column did not fit the packing apparatus and had to be packed manually. Approximately 1.10 g additions were made followed by approximately 15 sec of rapping on the side and then 1 min of tapping on the floor. The injection port end was fitted with a second stainless steel frit.

Materials. - The materials used in the preparative study were the same as those used for the analytical study.

## CALCULATIONS

The formulas used to calculate the various performance parameters are given in this section. Their derivations may be found in most general textbooks on chromatography. Figure 1 shows a chromatogram which illustrates the definitions of retention time ( $t_r$ ), hold-up time ( $t_o$ ), and band width ( $w$ ).

$$\text{Resolution:} \quad R_s = \frac{2(t_{r2} - t_{r1})}{w_2 + w_1} \quad (1)$$

$$\text{Theoretical Plates:} \quad N = 16 \left( \frac{t_r}{w} \right)^2 \quad (2)$$

Height Equivalent to Theoretical Plate:

$$\text{HETP} = \frac{L}{N} \quad (3)$$

$$\text{Capacity Factor:} \quad k' = \frac{t_r - t_o}{t_o} \quad (4)$$

$$\text{Standard Deviation:} \quad \sigma = \sqrt{\frac{(x - \bar{X})^2}{n - 1}} \quad (5)$$

Relative Standard Deviation:

$$\sigma_{\text{rel}} = \frac{\sigma}{\bar{X}} \times 100 \quad (6)$$



## ANALYSIS

### A. ANALYTICAL

The chromatographic conditions which provided a satisfactory separation in a reasonable time for each mixture were determined by changing the polarity of the mobile phase for one of the adsorbents and then, if necessary, repeating the process with an adsorbent of higher or lower surface area as appropriate. A description of each adsorbent is included in Table I. A further description may be found in references 35, 48, and 49.

Procedure. - Satisfactory separations were obtained on approximately 50 aromatic diamines using several silica gel adsorbents with chloroform and cyclohexane mobile phases. These monomers were chromatographed on a routine basis in order to determine their purity prior to polymer synthesis. Table II summarizes the diamines studied and lists the chromatographic conditions for each study. The conditions for the separation of several amine precursor aromatic dinitro compounds are also included in Table II.

In order to study amine basicity, approximately 1 mg of each isomer within a series was dissolved in 1 ml of mobile phase. The concentrations were adjusted to maintain approximately equal peak heights. Injections of 2-3 $\mu$ l of each mixture were made and the identity of each peak was established from retention time data. The capacity factor ( $k'$ ) for each isomer was then calculated from the retention time and the hold-up time. The hold-up time for each column was determined by

injecting carbon tetrachloride into the mobile phase. Isomer  $k'$  values were then correlated with their respective  $pK_b$  values obtained from reference 50 or with measured  $pK_a$  values.

#### B. PREPARATIVE

In general, the same chromatographic conditions which yielded a separation on an analytical basis also allowed a separation on a preparative basis. However, higher flow rates had to be employed to reduce analysis time. More economical adsorbents also had to be used to pack the larger preparative columns. While these adsorbents were not always as efficient as the pellicular and 5 micron totally porous adsorbents, they exhibited higher loading levels. A description of each adsorbent is included in Table I.

Procedure. - The procedure for the preparative study varied depending on the particular variable being studied. However, to insure that consistency was maintained from one experiment to the next, a 50/50 (w/w) mixture of 2,2'- and 2,4'-methylenedianiline dissolved in chloroform was always used as the standard mixture. The concentration and size of each sample injected depended on the column size. The mobile phase was chloroform at various flow rates. Sufficient carbon tetrachloride was added to each sample to allow a determination of column hold-up time or dead volume. The least retained peak, that for 2,2'-methylenedianiline, was used to calculate  $N$ , HETP, and  $k'$ . Both peaks were used to calculate  $R_s$ .

Several experiments were designed to evaluate particular parameters. These will be described separately.

1. Column Packing Technique. - Ten 1/4 in. (4.57 mm i.d.) x 2 ft. columns were packed with Porasil C by the previously described method. Precautions were taken to insure that the adsorbent used to pack these columns came from the same batch of silica gel from the supplier so that reproducible conditions could be achieved. Thus, all of the silica gel used to pack these columns should have the same activity. Three separate days were required to obtain the data for this evaluation. Therefore a 1/4 in. x 2 ft. Porasil C column was also run each day as a check on instrument performance. The adsorbent used to pack this column came from a different batch of silica gel.

Injections of 5 $\mu$ l at a concentration of 5 $\mu$ g of each isomer per  $\mu$ l of solution were made. A 3.0 ml/min flow rate (1100-1500 psi) was employed. Calculations were made to determine  $N$ ,  $R_s$ ,  $k'$ ,  $\sigma$ , and  $\sigma_{rel}$ .

2. Effect of Carrier Velocity. - The separation of the standard mixture was made at various flow rates on 2 ft. sections of 1/8 in. (2.4 mm i.d.), 1/4 in. (4.57 mm i.d.), 3/8 in. (7.75 mm i.d.), and 1 in. (21.13 mm i.d.) Porasil C columns. Variable sample size injections at a concentration of 5 $\mu$ g of each isomer per  $\mu$ l of solution were made depending on the column size. Each flow rate was converted to a carrier velocity by dividing by the column internal diameter in  $cm^2$ . HETP was calculated for the 2,2'-methylenedianiline peak and the classical HETP versus carrier velocity plots were then made.

3. Effect of Column Internal Diameter. - The data for this evaluation was obtained from the preceding experiment for the 6.0 ml/min flow rate.  $N$ , HETP,  $R_s$ ,  $k'$ , and  $t_r$  were calculated. These parameters were

also calculated at all the flow rates run so that the performance of each column size could be determined as a function of flow rate.

4. Effect of Adsorbent Particle Diameter. - Three 1/8 in. (2.4 mm i.d.) x 2 ft. columns were dry-packed with 20 $\mu$ , 30 $\mu$ , and 40 $\mu$  Li-Chrosorb SI 60, a closely sized, irregularly shaped silica gel with a 60 Å mean pore size. The standard mixture, 5 $\mu$ l at a concentration of 2.5 $\mu$ g/ $\mu$ l, was injected at a 2.0 ml/min flow rate.  $N$ , HETP,  $k'$ , and  $t_r$  were calculated from the resultant chromatograms. Because of the poor resolution observed with the chloroform mobile phase, an 80/20 (v/v) chloroform/cyclohexane mobile phase was also used.  $R_s$  as well as  $N$ , HETP,  $k'$ , and  $t_r$  were calculated for this solvent.

5. Effect of Column Length. - Four 3/8 in. (7.75 mm i.d.) x 2 ft. column sections were packed with Porasil A. The four sections were then mounted parallel in a holder designed to keep them stationary and connected in series by 0.25 mm i.d. x 6 cm capillary tubing. The standard mixture, 10 $\mu$ l at a concentration of 1 $\mu$ g/ $\mu$ l, was injected at a 6.0 ml/min flow rate. Two foot sections were successively removed and the injection repeated until 8 ft., 6 ft., 4 ft., and 2 ft. column lengths had been evaluated. The entire procedure was then repeated with series of Porasil B and Porasil C columns.  $N$ , HETP,  $R_s$ ,  $k'$ , and  $t_r$  were calculated for each adsorbent at each column length.

6. Effect of Adsorbent Surface Area. - Porasil A, Porasil B, and Porasil C, with respective surface areas of 350-500 m<sup>2</sup>/g, 125-250 m<sup>2</sup>/g, and 50-100 m<sup>2</sup>/g, were studied in this evaluation. The effect of the surface area of these adsorbents on column performance was derived from

the data obtained in the preceding experiment.

7. Column Capacity. - The flow rates which provided a convenient constant retention time for the 1/8 in., 1/4 in., and 3/8 in. Porasil C columns were determined from plots of retention time versus flow rate for those columns. The 1 in. column could not be evaluated in this experiment because the required flow rate exceeded the pumping capacity of the solvent delivery system. The standard mixture, at a concentration of  $5\mu\text{g}/\mu\text{l}$ , was repetitively injected in increasing amounts on each column. A plot of resolution versus  $\mu\text{g}$  of each isomer injected was then made and the point at which the resolution had decreased to 90% of its maximum value was arbitrarily taken as the capacity of that column. A constant retention time insured that each sample spent the same amount of time undergoing the partitioning process.

## RESULTS AND DISCUSSION

### A. ANALYTICAL

The first part of this research was devoted to developing methods for determining the purity of diamine monomers prior to polymerization. A recently published text would have been beneficial in this early work (51). In general, these compounds were found to separate nicely on various silica gels with chloroform and cyclohexane mobile phases. Table II gives the chromatographic conditions and  $k'$  values for the separation of approximately 50 aromatic amines. Figures 2 and 3 show typical chromatograms obtained.

Due to the method of synthesis of these compounds, often the impurity in a particular diamine was an isomer of that amine. A constant UV detector response could be expected under this condition and a 0.1% impurity could easily be detected. There was no problem detecting other impurities as long as they possessed a UV chromophore. Although the initial objective of this research was realized with minimum difficulty, other interesting results emerged.

Figure 4 gives the overall reaction scheme which leads to polyimide polymers. The importance of the reactivity or basicity of the amino group to the molecular weight of the resultant polymer has been noted in a number of studies (1, 3, 6). Techniques are needed which will help establish relative orders of basicity for series of amines differing only in the point of attachment of the amino group or the interconnecting Z group. It is generally accepted that the adsorption of many

basic organic compounds on silica gel may be treated as a base interacting with an acidic surface. This is illustrated for an amine in figure 5. The free pair of electrons associated with the amine nitrogen interacts with the slightly acidic hydroxyl proton. The strength of this interaction determines how long the amine is retained in the column. The stronger the base, the more it interacts with the adsorbent, and the longer it takes the amine to elute from the column. A primary objective of this research was to determine whether the adsorption of weakly basic amines on slightly acidic silica gels could be used to study their relative basicity.

Figure 6 shows two chromatograms obtained early in this research which supported this concept. Tetrafluoro-p-phenylenediamine is expected to be less basic than p-phenylenediamine because the electronegative fluorine atoms would tend to withdraw the two amine electrons. Thus, the fluorinated diamine should interact less with the active sites on the silica gel and elute before the unfluorinated compound. This behavior is observed in figure 6. Similarly, octafluorobenzidine is predicted to be less basic than benzidine and does indeed elute before the unfluorinated species.

Before complex diamine monomers could be investigated, it was necessary to study the adsorption of simple aromatic amines on silica. Four series of amines, o-, m-, and p-bromoaniline, chloroaniline, toluidine, and phenylenediamine were chromatographed under various conditions on several silica gel supports. The chromatogram obtained for the phenylenediamine isomers is given in figure 7. This figure is

typical of all other chromatograms obtained with chloroform and cyclohexane as the mobile phases. In each case, the order of elution was ortho-, meta-, para-.

This order of elution is also the order of increasing basicity for these amines. This is probably explained on the basis of weakly basic amino groups interacting with the slightly acidic silica adsorbent. The more basic the amine, the greater this acid-base interaction and the longer the retention time. Therefore, the least basic ortho-isomer elutes first, followed by the intermediate basic meta-isomer, and finally, the most basic para-isomer elutes last.

It was found that this relationship could be put on a quantitative basis by plotting  $pK_b$  versus log of capacity factor for a series of amine isomers. Table III lists  $pK_b$  values (50) and summarizes the retention data for the four series of aromatic amines studied here. Figure 8 gives a plot of  $pK_b$  versus log of capacity factor for the toluidine isomers on Porasil A, B, and C. It also gives the chromatographic conditions for the separation. Figure 9 gives a similar plot for the bromo- and chloroaniline isomers on Corasil I. Very small differences are noted in  $pK_b$  values or capacity factors for corresponding aniline isomers and a straight line fits all six points. Figure 10 gives the plot of  $pK_b$  versus log of capacity factor for the phenylenediamine isomers on Corasil I and II and Zorbax-SIL.

The linear and so far empirical correlation between  $pK_b$  and log  $k'$  observed in figures 8, 9, and 10 was not totally anticipated. All of this suggests that the relative basicities between similar diamine



isomers can be established simply from chromatographic retention data. The order of elution is the order of increasing basicity. Also, if two  $pK_b$  values within a series of amine isomers were known, the other values could be obtained chromatographically. This assumes, of course, that the amino groups are the only parts of the molecule to enter into the partitioning process. It should also be noted that this correlation appears to hold equally well with the  $pK_a$  values of these amines.

This work did not clearly establish whether a correlation exists between different series of amines. The bromo- and chloroaniline isomers were separated under similar conditions while an entirely different set were required to separate the more basic toluidine isomers. This indicates that monoamines with similar basicities should be separated under similar conditions. The phenylenediamine isomers, which have two active sites for interaction with the adsorbent, require a third set of chromatographic conditions. However, other isomeric diamines with similar basicities should separate under the same conditions.

Except for the toluidine isomers on Porasil B, the retention was also related to adsorbent surface area. For example, in figure 10, it is noted that the phenylenediamine isomers take longer to elute on Corasil II than on Corasil I. This can be understood since there are more active -OH sites available on the higher surface area Corasil II. The Zorbax-SIL curve would undoubtedly lie far beyond the Corasil curves had all columns been the same size. Both Corasil columns were 2.4 mm i.d. x 61 cm while the Zorbax-SIL column was only 2.1 mm i.d. x 25 cm.

The toluidine isomers, figure 8, were not retained on Corasil I or II or Zorbax-SIL with chloroform as the mobile phase. However, the high surface area Porasil adsorbents and a less polar solvent (75/25 chloroform/cyclohexane) allowed these isomers to be separated. Finally, the bromo- and chloroaniline isomers, figure 9, would not elute in a reasonable time on Corasil II, Zorbax-SIL, or the Porasils. Corasil I, a low surface area adsorbent, and a cyclohexane mobile phase were required. Separations can therefore be made by selecting the proper adsorbent surface area or by changing the mobile phase polarity. These two variables are most important in determining the slopes of the lines in figures 8-10 and can be manipulated to improve resolution.

An exception to this linear correlation of basicity and chromatographic retention was observed when ethyl acetate was used as the mobile phase. When the phenylenediamine isomers were chromatographed on Corasil II, the order of elution was meta-, ortho-, para-. Apparently this more polar solvent competed for sites on the adsorbent and altered the adsorption process. Under the proper liquid-liquid conditions, the order can be made to be ortho-, para-, meta- (52). This type of behavior is not uncommon (7) and emphasizes that there are conditions where a linear correlation between basicity and retention will not hold. However, it does hold for the amines studied here when chloroform and cyclohexane are the mobile phases.

With this understanding of simple aromatic amine behavior, the more complex diamine monomers were then investigated. Thus, the five methylenedianiline (MDA) and seven diaminobenzophenone (DABP) isomers

given in figure 11 were studied in detail. The results of this study are summarized in Table IV.

The third column in Table IV gives an index value based on the capacity factor for each isomer within a series. This column was calculated by giving the least retained species a value of 1.000 and then making each isomer for that series relative to the least retained species. For example, the 1.304 index value for the *o,p'*-MDA isomer was obtained by dividing the  $k'$  for that isomer by the  $k'$  of *o,o'*-MDA, the least retained species. These index values are arranged to give the relative order of increasing chromatographic basicity. It is interesting to compare index values with measured  $pK_{a_1}$  and  $pK_{a_2}$  values for these diamines. The overall correlation with the DABP isomers is good. The least acidic 3,5-DABP isomer is the most basic chromatographically. The *o,o'*-DABP isomer was too acidic to be measured and was found here to be the least basic. The remaining isomers correlate accordingly. The most acidic *o,o'*-MDA isomer was found to be the least basic chromatographically. However, the least acidic *p,p'*-MDA isomer was found to be of intermediate basicity. Finally, the most basic *m,m'*-MDA isomer did not correlate with measured  $pK_a$  values.

The last column in Table IV gives the inherent viscosity obtained when these isomers are polymerized with 3, 3', 4, 4'-benzophenone tetracarboxylic acid dianhydride (BTDA) in dimethylacetamide (53). The magnitude of the viscosity gives an indication of the molecular weight of the polymer.

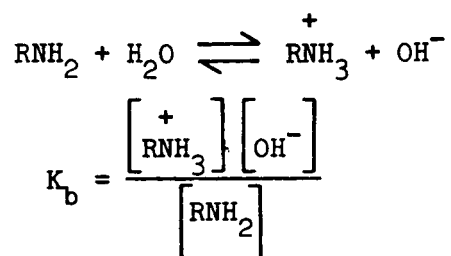
The chromatographic basicity index appears to correlate well with viscosity measurements. For example, the p,p'-,m,p'-, and m,m'-MDA isomers yielded higher molecular weight polymer than the o,o'- and o,p'-MDA isomers. It should be noted that the p,p'-, m,p'- and m,m'- isomers had the highest index values. The DABP isomers are even more striking. The four isomers which yielded high molecular weight polymer had high chromatographic index values. The o,o'-, o,p'-, and o,m'-DABP isomers were too weakly basic to form good polymer. This could have been predicted from their chromatographic index values. This may prove to be a useful rapid screening procedure for future diamine studies.

An additional observation can be made which suggests that the chromatographic basicity may yield information where measured  $pK_a$  values cannot. The p,p'-DABP isomer ( $pK_a = 3.09$ ) yielded good polymer. Based on this, the o,p'-isomer ( $pK_a = 3.08$ ) would be expected to also yield polymer. The fact that it does not form good polymer can be predicted from index values. Thus, it appears that this approach complements  $pK_a$  measurements and, in some cases, predicts polymer behavior better than  $pK_a$  values. Finally, relative basicities for series of amine isomers can be obtained chromatographically in as little as five minutes whereas  $pK_a$  measurements usually take longer.

When the data in Table IV were plotted, some encouraging although somewhat confusing results were obtained. Figure 12 gives a plot of  $pK_a$  versus  $\log k'$  for the methylenedianiline isomers. Both  $pK_{a_1}$  and  $pK_{a_2}$  are shown for these isomers. Linearity is observed in this figure but in two distinct regions. This behavior is not understood and

cannot be rationalized at the present time. Figure 13 gives a similar plot for the diaminobenzophenone isomers. Straight lines could not be drawn with any confidence. The o,o'- isomer was too strongly acidic to allow a  $pK_a$  measurement. This isomer was by far the least basic and had a  $\log k'$  of -0.471. If the  $pK_a$  for this isomer were known, perhaps it would be around 2.00 and then linearity would be established between the o,o'-, o,p'-, m,m'- and 3, 5- data points. The apparent randomness observed in figure 13 may indicate that the interconnecting carbonyl group is entering into the adsorption process. Under this condition, a simple acid-base separation mechanism may not apply and the proposed correlation could not be expected to hold.

Several items caused concern during much of this research. One was the effect of the solvent. The basicity of an amine is defined by how easily it accepts a proton from water according to the equation



The measurement of the hydroxide ion concentration formed in solution provides a means for comparing the basicities of different solutions of amines in water. For various reasons,  $K_b$  measurements cannot always be made in water. The solvents used for measuring the basicity of the simple aromatic amines are unknown. The solvent used for the methylenediamine and diaminobenzophenone isomers was 90% acetonitrile-10%

water. More importantly, the solvent used for determining the chromatographic basicity was chloroform and/or cyclohexane. Considering the definition of basicity and the wide range of solvents involved, the fact that linear correlations between  $pK$  and  $\log k'$  were observed was difficult to rationalize.

Bell notes that his survey of a wide number of solvents suggests the generalization that "the relative strengths of acids of the same charge and chemical type are independent of the solvent" (54). He also shows that a plot of  $pK_a$  measured in cresol versus  $pK_a$  measured in water for both anilinium ions and carboxylic acids is linear (55). Thus,  $pK$  values for the amines studied here should exhibit the same relative change regardless of solvent. This being the case, the solvent should have little effect on the linear correlation observed in this research.

Other possible correlations might also have been attempted. These included an analysis of such areas as steric effects, dipole moments, polarizability, and the Hammett equation. Many of these could not be considered except in theory due to the lack of pertinent experimental data on the aromatic amines studied here. Often, theoretical rationalizations after the fact can be biased to prove just about anything. However, the Hammett equation does offer some interesting possibilities.

The Hammett equation (56-58), originally defined for benzoic acid derivatives, allows a quantitative treatment of the relationships between structure and reactivity. However, the equation is not generally applicable to ortho-substituted benzene derivatives. Therefore, it cannot offer information on the simple ortho-, meta-, and para-

substituted aromatic amines studied in this research. However, the Hammett equation has been found to correlate with such diverse data as half-wave potentials from polarographic reductions, infrared adsorption frequencies, and nuclear magnetic resonance-adsorption frequencies associated with the fluorine nuclei in substituted fluorobenzenes (59). Thus, a logical extension of the present research might be to study the liquid-solid adsorption chromatography of some benzoic acid derivatives and determine if  $\log k'$  values will correlate with published Hammett substituent constants for those derivatives.

The approach taken in the present research appears to provide the most information of use to the polymer chemist. This approach also allows a better understanding of the liquid-solid separation mechanism of basic organic compounds on slightly acidic silica gels.

#### B. PREPARATIVE

The chromatographic conditions which yielded a separation on an analytical scale, in general, also yielded a separation on a preparative scale. Thus, large quantities of sample and mobile phase could be saved by determining the conditions first on analytical columns and then, transferring them with increased flow rate to preparative columns. For economic reasons, Porasil adsorbents were substituted for Corasil and Zorbax-SIL in the larger preparative columns. Before the ultimate goal of prepping selected diamines for polymer synthesis could be realized, it was necessary to make a systematic study of the variables which can effect preparative separations.

Experiments were designed to yield information on six column para-

meters: the effect of flow rate, column diameter, adsorbent particle size, column length, adsorbent surface area, and column capacity. These parameters were initially judged to play dominant roles in determining the efficiency of preparative columns. A typical mixture of aromatic diamine monomers, 50/50 (w/w) 2, 2'- and 2, 4'-methylenedianiline, was selected as the test sample for these experiments. The separation of this test sample then showed how a particular column parameter would apply to other diamine monomers of immediate interest. In some cases,  $N$  may appear to be low. This probably would not be the case had the test sample been selected to maximize column performance.

Before data from the preparative study could be interpreted with confidence, an evaluation of the technique used to pack the various columns had to be conducted. The results of this evaluation are summarized in Table V. The overall reproducibility for the control column was good. Therefore, data for the individual columns should not be biased by instrument performance on the three days required to perform this analysis. The relative standard deviation calculated for  $N$ ,  $R_g$ , and  $k'$  was approximately 8, 9, and 10% respectively. Values of 4, 8, and 9% can be calculated by arbitrarily discarding the one data point for each data set with the greatest difference from the mean value. These values are probably acceptable, especially since an independent evaluation yielded a 6% relative standard deviation for  $N$  based on repetitive injections of o-phenylenediamine on a 1/8" Corasil II column under analytical conditions. The column packing technique employed in this research was concluded to yield columns which were as reproducible



as could be expected. Further, an analysis of the various parameters should not be greatly influenced by the manner in which the columns were packed.

The effect of flow rate on column performance for the 1/8 in. (2.4 mmi.d.), 1/4 in. (4.6 mm i.d.), and 3/8 in. (7.75 mm i.d.) columns is shown in figure 14. Figure 15 shows higher resolution on the 3/8 in. column and includes data on the 1 in. (21.13 mm i.d.) column. These figures are typical of the type of behavior observed in liquid chromatography. This behavior differs significantly from that observed in gas chromatography because the contribution of the  $B$  or molecular diffusion term of the Van Deemter equation (60) is negligible in the liquid phase. Thus, Van Deemter plots in liquid chromatography do not necessarily suggest the optimum flow rate for a particular separation as they do in gas chromatography. Since carrier velocity does not have a large influence on column performance, the flow rate is usually dictated by the time allotted to the analysis.

Table VI gives data on the effect of column internal diameter on performance. This data was obtained at a constant 6.0 ml/min flow rate for all columns. While this was obviously too fast for the 1/8 in. column, the overall trend of improving  $N$ , HETP, and  $R_g$  with increasing internal diameter, suggests that column performance is not sacrificed by going to larger diameter columns. Thus, the concept that optimum column efficiency is obtained by using narrow-bore columns, tightly packed with small, regularly shaped particles, is not necessarily true. However, longer retention times and larger volumes of mobile phase are

required for larger diameter columns.

The effect of internal diameter on column performance is more easily seen by plotting various parameters as a function of flow rate for each column. This is illustrated in figure 16 where resolution is plotted versus flow rate. Again a steady improvement in  $R_s$  is noted with increasing internal diameter. This also emphasizes that performance is not necessarily sacrificed by going to larger columns.

The enhanced performance of the 1 in. column over that observed for smaller diameter columns in figures 14, 15, and 16 and Table VI could easily be explained by invoking the infinite-diameter theory (30). Only this column calculates to be infinite in diameter. However, Wolf gave a convincing rebuttal of this theory (38). The column end-fittings for his study were designed to transpose a slug of the solute in the carrier stream into a uniform disk over the entire cross-section of the packing. To prove this, Wolf injected a dye, stopped the development of the chromatogram, and sectioned the column. The dye was found to be in contact with the column walls. Thus, a necessary condition for being an infinite-diameter column was not met and yet improved performance was observed. The end-fittings used in the present study were essentially the same as those used by Wolf. By Wolf's reasoning, the infinite-diameter theory cannot apply to this column either. However, it is difficult to disagree with the theory, especially when photographs are used to visually record the elution of a colored solute through an infinite-diameter column (61). In the photographs, the solute never comes in contact with the column walls. Regardless of why large diameter

columns exhibit better performance, the fact remains that they do. It is apparent that the entire infinite-diameter effect is not completely understood and needs to be studied in greater detail.

The effect of particle size on performance is shown in Table VII for a 1/8 in. column. The trend to be noted in this table is that  $N$ ,  $R_s$ , and  $t_r$  improve with decreasing particle size. This is the same type of behavior observed by Beachell and DeStefano for particles having a wider range of sizes (33). This suggests that even smaller diameter particles should exhibit much better performance and, indeed, as many as 2550 plates per foot have been observed for m-phenylenediamine on 5 $\mu$  Zorbax-SIL. The capacity factor takes dead volume into account. The decrease in  $k'$  with decreasing particle size probably reflects the increased difficulty of packing small diameter particles. Snyder found that 50-60 $\mu$  particles were the smallest size that could be effectively dry-packed into columns (62). Perhaps the 20 $\mu$ , 30 $\mu$ , and 40 $\mu$  particles used here are too small to be dry-packed effectively and should be slurry-packed.

The effect of column length on performance was also investigated. Figure 17 gives a plot of  $N$  versus column length for 3/8 in. columns packed with Porasil A, B, and C. The number of theoretical plates appears to increase almost linearly. Each two foot section was evaluated individually prior to being evaluated in series with other columns. The number of theoretical plates were found to be approximately additive. Thus, if two column sections each had 500 plates, they would have 1000 plates when connected in series.

Figure 18 shows how resolution varies with column length for the three adsorbents. Since resolution is known to increase as the square root of the number of theoretical plates (63, 64), a doubling of column length would double  $N$  but would only improve  $R_s$  as the square root of  $N$ . Thus, the slope of the curves in figure 18 must necessarily be less than the slope of the curves in figure 17. The capacity factor remains almost constant with increasing column length as shown in figure 19. When column length is doubled as in this experiment, retention time and dead volume must also approximately double. Therefore, the fraction  $\frac{t_r - t_o}{t_o}$  must remain essentially constant.

It might appear that if more plates and better resolution are required for a particular separation, all that is necessary is to increase the length of the column. Figure 20 shows the penalty that is paid by following this approach. The time required for an analysis increases rapidly with column length. A penalty is also paid in the volume of mobile phase required with longer columns.

The effect of column length on performance has not been previously experimentally investigated. DeStefano observed that column capacity could be increased by increasing column length but that the option should be evaluated in terms of the longer retention times, decreased permeabilities, and increased pressures associated with longer columns (36). While noting that coupled columns would probably be required, he concluded that it appears more advantageous to increase column capacity by increasing column diameter rather than column length. However, Conder concluded in his study that an order of magnitude improvement in

throughput could be obtained at the expense of only a 50-100% increase in column length by operating in the overload condition (37).

Table VIII compares column diameter and length and summarizes data for the 1 in. x 2 ft. column and the three 3/8 in. x 8 ft. column banks. Surprisingly,  $N$ ,  $R_s$ ,  $t_r$ , and elution volume are almost identical for the 1 in. Porasil C and 3/8 in. Porasil A columns. Many parameters for the other columns are also similar. The pressure drop across the eight foot columns did not present any problems. Thus, it is difficult to tell from these data whether an increase in column diameter or in length leads to the better performance. Column capacity probably would be the determining factor. These measurements were not made in this study but capacities may also turn out to be quite similar. From an economic viewpoint, about half as much adsorbent is required to pack four 3/8 in. x 2 ft. columns as is required to pack a 1 in. x 2 ft. column. Eight 3/8 in. end-fittings cost about 25% less than two 1 in. end-fittings. Also, 3/8 in. stainless steel tubing costs considerably less than 1 in. stainless steel pipe. Thus, the 3/8 in. column bank would be less expensive to pack. Further work should be conducted in the area of column length versus column diameter.

The experiment on column length was also expected to yield information on the effect of adsorbent surface area on performance. These columns were packed with Porasil C, Porasil B, and Porasil A, which are 37-50 $\mu$  particle size silica gels having 50-100, 125-250, and 350-500  $m^2/g$  surface areas, respectively. Due to its larger surface area, Porasil A was expected to have more active sites available for adsorp-

tion than Porasil C. Other factors being equal, the more active sites available to the adsorption process, the more efficient it should be. Therefore, a C B A sequence for the improvement of performance parameters was anticipated for columns packed with Porasils A, B, and C. Figures 17 and 18 show this is not the case. In figure 17, the highest surface area Porasil A gave values of  $N$  which were intermediate to Porasil B and Porasil C. The sequence here for increasing  $N$  is C A B. In figure 18, Porasil A exhibits the poorest resolution and the sequence for increasing  $R_s$  is A C B. However, plots of  $k'$  and  $t_r$  versus column length, figures 19 and 20, follow the anticipated C B A sequence.

This unpredictable surface area effect might be more easily rationalized by noting that two factors, solvent efficiency and/or column efficiency, determine column performance (65). Under a given set of conditions, the mobile phase or solvent efficiency determines peak maximum position while column efficiency determines peak width. Thus,  $t_r$  and  $k'$ , which are calculated from the peak maximum position, are determined by solvent efficiency and do not depend on the efficiency of the particular separation. In contrast to this,  $R_s$  and  $N$  are a function of column efficiency since both parameters are related to the base widths of the individual peaks. Every parameter except surface area was held constant for this study. Hopefully, the C B A sequence observed in figures 19 and 20 for  $k'$  and  $t_r$  is a true reflection of the effect of surface area. Since  $N$  and  $R_s$  in figures 17 and 18 do not follow the same sequence, the efficiencies of the Porasil A, B, and C columns

must be different.

All of this poses the question of why should the column efficiency vary for these three adsorbents. For this particular experiment, the mobile phase, flow rate, column diameter, adsorbent particle size, and respective column lengths were all held constant. Only the adsorbent surface area varied. However, as this work progressed, it became apparent that the activity of the Porasil A, B, and C adsorbents was not the same. In fact, the activity for the same adsorbent could vary from batch to batch as shown in Table V for Porasil C. The control column was packed from one batch of silica gel while the 10 test columns were packed from another batch. The control column is obviously the best column.

The relative adsorption of a sample can be controlled by changes in solvent strength rather than changes in adsorbent activity. Thus, activity is not usually considered when designing a separation. However, when every condition is held constant, as in this experiment, activity must be considered. Surface activity can be referred to as the relative tendency of a unit surface to adsorb different samples (66). Active surfaces are characterized by greater site concentrations and/or sites of greater average strength, and perhaps differing degrees of surface regularity or crystallinity (67).

For silica gel, surface activity is also intimately related to water content. The addition of water to dry or partially dehydroxylated silica normally results in the selective adsorption of molecular water upon the stronger surface hydroxyl sites. Deactivating techniques,

which hopefully yield 50-75% of a monolayer, have been covered in detail (68). No effort was made to standardize the activities of the Porasil A, B, and C adsorbents prior to packing the preparative columns. This may have been an error in judgement.

Finally, an experiment was conducted to determine the capacity of these preparative columns. The results of this study are summarized in Table IX. Flow rates of 0.5, 1.6, and 5.1 ml/min were required to produce a constant 720 sec retention time for the 1/8 in., 1/4 in., and 3/8 in. Porasil C columns, respectively. A constant  $t_r$  insured that the time spent undergoing the adsorption process was the same for all columns. The 1 in. column could not be evaluated because the required flow rate, >40 ml/min, exceeded the pumping capacity of the solvent delivery system.

The last column of Table IX gives the mg of each isomer which caused an arbitrary 10% loss in resolution for each column. The 3/8 in. column appears to have about 4.5 times the capacity of the 1/8 in. column and the 1/4 in. column had about 3 times the capacity. The capacity tends to increase as the square root of the column internal diameter. This correlation probably would not hold had all columns had the same efficiency. A review of figure 14 shows that the efficiency of these columns was different.

When this research began, there was a desire to derive a master equation or curve into which various chromatographic parameters could be inserted so that the optimum conditions for a particular preparative separation could be determined. At this stage, it is concluded that



this is not possible. An appreciation of all the variables is necessary and compromises made between them in order to achieve the desired effect. With the appreciation obtained from this study, preparative separations of diamine monomers for polymerization studies are currently being made.

## CONCLUSIONS

A study was made of the analytical and preparative liquid chromatography of aromatic diamines. From this study it is concluded that:

1. The chromatographic conditions which will allow a determination of diamine purity have been established. These compounds separate satisfactorily on various silica gels using chloroform and/or cyclohexane mobile phases.
2. A linear correlation between  $pK_b$  and log of the capacity factor was demonstrated for four series of simple aromatic amines. This correlation allows a better understanding of the separation mechanism of aromatic amines on silica gel.
3. A chromatographic basicity index for two series of aromatic diamines was proposed and correlated with the inherent viscosity of the polyimides obtained when these monomers were polymerized.
4. An appreciation of several parameters as they pertain to the preparative separation of diamine monomers was obtained. These parameters include the effect of the column packing technique, flow rate, column length and diameter, adsorbent size and surface area, and column capacity.
5. Milligram quantities of aromatic diamine monomers can be readily prepped with high purity for use in polymer synthesis.

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TABLES  
AND  
FIGURES



Table I. - Properties of Column Packing Materials

Name	Particle Form	Particle Size ( $\mu$ )	Surface Area ( $m^2/g$ )
Corasil I	Porous pellicular layer	37-50	7
Corasil II	Porous pellicular layer	37-50	14
Zorbax-SIL	Porous microspheres	6-8	200+
Porasil A	Porous beads	37-75	350-500
Porasil B	Porous beads	37-75	125-250
Porasil C	Porous beads	37-75	50-100
Li Chrosorb SI60	Porous, irregular shape	20	500
Li Chrosorb SI60	Porous, irregular shape	30	500
Li Chrosorb SI60	Porous, irregular shape	40	500

TABLE II - CONDITIONS FOR SEPARATION OF AROMATIC AMINES


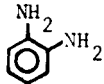
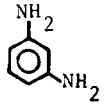
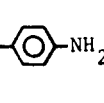
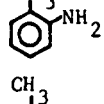
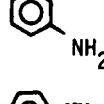

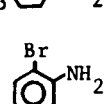
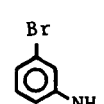
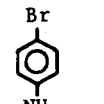


STRUCTURE	COLUMN	MOBILE PHASE	FLOW RATE (ml/min) [PSI]	k'
	} Corasil II	CHCl <sub>3</sub>	1.0 [500]	0.40
				
	} Corasil I Corasil II Zorbax-SIL	} CHCl <sub>3</sub> CHCl <sub>3</sub> 0.7% MeOH/CHCl <sub>3</sub>	} 0.5-2.0 [325-1000] 0.5 [2000]	} 0.82-6.92 5.70-15.09
				
				
	} Porasil A Porasil B Porasil C	} 75/25 CHCl <sub>3</sub> / 	} 0.5/[400] 0.5/[350] 0.5/[350]	} 0.89-1.52 0.75-2.16 0.38-0.72
				
				
	} Corasil I	cyclohexane	} 2.0 [1300]	} 2.42 7.52 11.68
				
				

TABLE II - CONTINUED

STRUCTURE	COLUMN	MOBILE PHASE	FLOW RATE (ml/min) [PSI]	k'
	Corasil I	cyclohexane	2.0 [1300]	2.77
				7.70
				12.35
	Corasil II	CHCl <sub>3</sub>	1.0 [700]	0.44
				0.38
	Zorbax-SIL	90/9.7/0.7 CHCl <sub>3</sub> /[3]/MeOH	0.5 [2000]	7.26
				6.50
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	1.61
				2.10
				2.66
				2.92

TABLE II - CONTINUED

STRUCTURE	COLUMN	MOBILE PHASE	FLOW RATE (ml/min) [PSI]	k'
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	3.23
	Corasil II	CHCl <sub>3</sub>	1.0 [600]	0.34
	Corasil II	CHCl <sub>3</sub>	1.0 [600]	3.14
	Corasil II	CHCl <sub>3</sub>	1.0 [600]	3.44
	Corasil II	CHCl <sub>3</sub>	1.0 [600]	3.63
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	5.04
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	0.13
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	0.54
	Corasil II	CHCl <sub>3</sub>	0.5 [350]	0.54

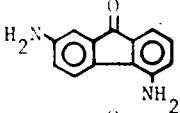
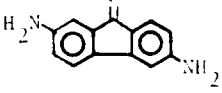
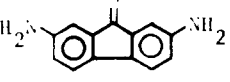
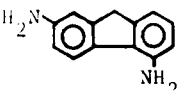
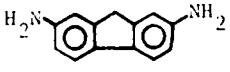
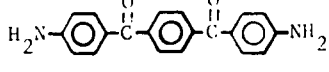
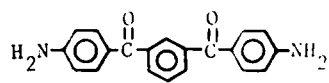
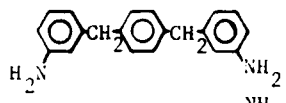
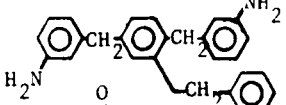
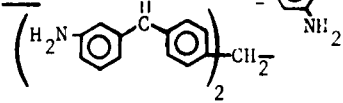
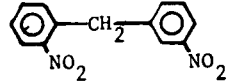
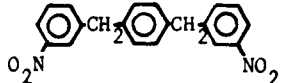
STRUCTURE	COLUMN	MOBILE PHASE	FLOW RATE (ml/min) [PSI]	k'
	Zorbax-SIL	90/9.3/0.7 CHCl <sub>3</sub> /[5]/MeOH	0.5 [2000]	9.80
				12.07
				9.80
	Corasil II	CHCl <sub>3</sub>	0.5 [800]	2.02
				1.54
	Corasil II	CHCl <sub>3</sub>	1.0 [1000]	3.11
				4.46
	Zorbax-SIL	90/9.3/0.7 CHCl <sub>3</sub> /[5]/MeOH	0.5 [2000]	4.33
				22.96
	Corasil II	CHCl <sub>3</sub>	1.0 [600]	3.62
	Zorbax-SIL	82/17.3/0.7 CHCl <sub>3</sub> /[5]/MeOH	0.6 [2500]	3.08
	Zorbax-SIL	90/9.3/0.7 CHCl <sub>3</sub> /[5]/MeOH	0.5 [2000]	13.78

Table III. - Summary of Capacity Factor Data and  $pK_b$  Values  
for Simple Aromatic Amines

Isomer	$pK_b$	Log of Capacity Factor		
		<u>Corasil I</u>	<u>Corasil II</u>	<u>Zorbax-SIL</u>
<u>o</u> -phenylenediamine	9.523	-0.085	0.489	0.756
<u>m</u> -phenylenediamine	9.000	0.025	0.616	0.886
<u>p</u> -phenylenediamine	7.854	0.301	0.840	1.179
<u>o</u> -bromoaniline	11.523	0.383	- - -	- - -
<u>m</u> -bromoaniline	10.398	0.876	- - -	- - -
<u>p</u> -bromoaniline	10.155	1.067	- - -	- - -
<u>o</u> -chloroaniline	11.301	0.442	- - -	- - -
<u>m</u> -chloroaniline	10.523	0.886	- - -	- - -
<u>p</u> -chloroaniline	10.000	1.092	- - -	- - -
		<u>Porasil A</u>	<u>Porasil B</u>	<u>Porasil C</u>
<u>o</u> -toluidine	9.585	-0.051	-0.126	-0.425
<u>m</u> -toluidine	9.301	0.058	0.081	-0.305
<u>p</u> -toluidine	8.921	0.182	0.334	-0.143

Table IV.  
 Index Data for Methylenedianiline (MDA) and  
 Diaminobenzophenone (DABP) Isomers

Isomer	$k'$	Index	$pK_{a_1}$	$pK_{a_2}$	$*r_{inh}$
o,o'-MDA	1.61	1.000	4.86	2.97	0.20
o,p'-MDA	2.10	1.304	5.33	3.52	0.62
p,p'-MDA	2.66	1.652	5.82	4.65	0.96
m,p'-MDA	2.92	1.814	5.56	4.17	0.99
m,m'-MDA	3.22	2.000	5.29	4.01	0.80
o,o'-DABP	0.34	1.000	-	-	0.09
o,p'-DABP	1.13	3.324	3.08	-	0.22
o,m'-DABP	1.14	3.353	-	-	0.09
p,p'-DABP	3.14	9.235	3.09	-	0.79
m,m'-DABP	3.44	10.118	3.98	2.84	0.70
m,p'-DABP	3.63	10.676	3.94	-	0.64
3,5-DABP	5.04	14.824	4.52	-	0.74

\*Polymerized with BTDA in DMAc

Table V. - Evaluation of Column Packing Technique

Column Number	Test Date	N	$R_s$	$k'$
Control	1-17	297	1.621	1.658
Control	1-23	317	1.628	1.704
Control	1-30	298	1.712	2.072
1	1-17	178	0.767	1.115
2	1-17	148	0.769	1.366
3	1-17	178	0.753	1.074
4	1-23	183	0.913	1.298
5	1-23	199	0.956	1.326
6	1-23	183	0.861	1.298
7	1-30	188	0.928	1.384
8	1-30	188	0.816	1.188
9	1-30	193	0.783	1.059
10	1-30	174	0.839	1.273
Average value		181	0.839	1.288
$\sigma_{rel}$		7.66%	8.77%	9.72%

Conditions :

Size: 1/4 in. x 2 ft.

Adsorbent: Porasil C

Flow Rate: 3.0 ml/min

Mobile Phase:  $\text{CHCl}_3$ Sample: 2,2'-methylenedianiline (+2,4'-methylenedianiline  
for resolution test)



Table VI. - Effect of Column Diameter On Performance

o.d. (in.)	i.d. (mm)	N	HETP, cm	R <sub>s</sub>	k'
1/8	2.4	39	1.563	0.556	1.500
1/4	4.6	110	0.554	0.647	1.349
3/8	7.75	211	0.289	1.067	1.184
1	21.13	1220	0.050	2.038	1.061

Conditions :

Length: 2 ft.

Adsorbent: Porasil C

Flow rate: 6.0 ml/min

Mobile Phase: CHCl<sub>3</sub>Sample: 2,2'-methylenedianiline (+2,4'-methylenedianiline  
for resolution test)

Table VII. - Effect of Particle Size on Performance

Particle Size, $\mu$	N	$R_s$	$k'$	$t_r$ , sec.
20	156	0.473	9.214	676
30	130	0.410	9.745	698
40	109	0.432	11.059	726

Conditions :

Size: 1/8 in. x 2 ft.

Adsorbent: LyChrosorb SI 60

Flow Rate: 2.0 ml/min

Mobile Phase: 80/20  $\text{CHCl}_3$ /cyclohexaneSample: 2,4'-methylenedianiline (+2,2'-methylenedianiline  
for resolution test)

Table VIII. - Comparison of Column Length and Diameter

Column	N	R <sub>s</sub>	HETP	k'	t <sub>r</sub> (sec)	Elution Volume (ml)	gram of Adsorbent
1" x 2' Porasil C	1220	2.038	0.050	1.061	3558	356	104.80
3/8" x 8' Porasil A	1154	1.817	0.211	2.530	3632	363	53.72
3/8" x 8' Porasil B	1240	3.524	0.197	1.719	2881	288	50.10
3/8" x 8' Porasil C	815	2.154	0.299	1.154	2335	234	46.50

Conditions :

Column: As noted

Flow Rate: 6.0 ml/min

Mobile Phase: CHCl<sub>3</sub>

Sample: 2,2'-methylenedianiline (+2,4'-methylenedianiline for resolution test)

Table IX. - Column Capacity Evaluation

o.d. (in.)	i.d. (mm)	<sup>1</sup> flow rate	<sup>2</sup> capacity
1/8	2.4	0.5 ml/min	8 mg
1/4	4.6	1.6 ml/min	24 mg
3/8	7.75	5.1 ml/min	36 mg
1	21.13	-	-

1-flow rate required for constant  $t_r = 720$  sec

2- $\mu$ g of each isomer for a 10% loss in resolution

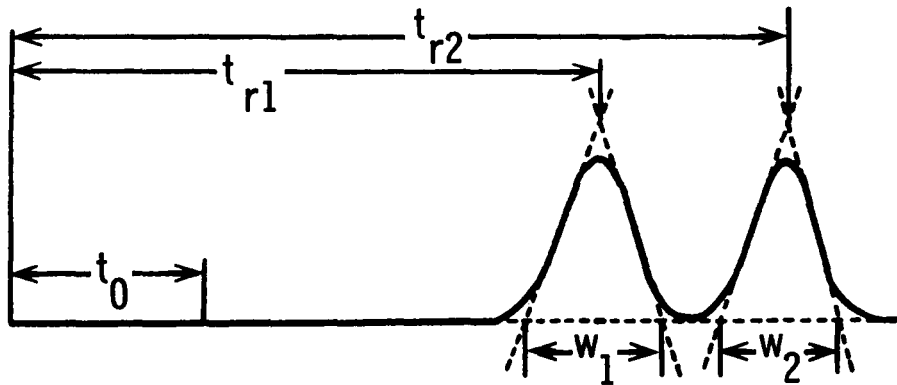


Figure 1. - Chromatogram illustrating the definitions of retention time,  $t_r$ ; hold-up time,  $t_0$ ; and band width,  $w$ .

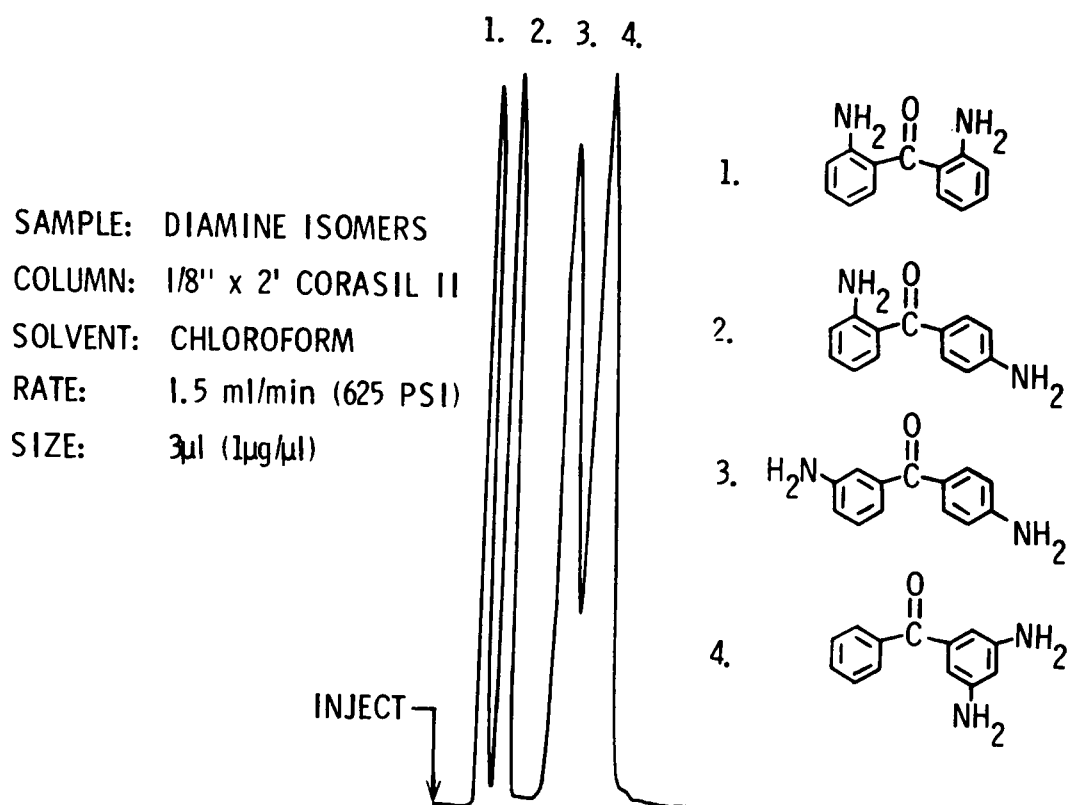


Figure 2. - Analytical chromatogram of diaminebenzophenone isomer mixture.

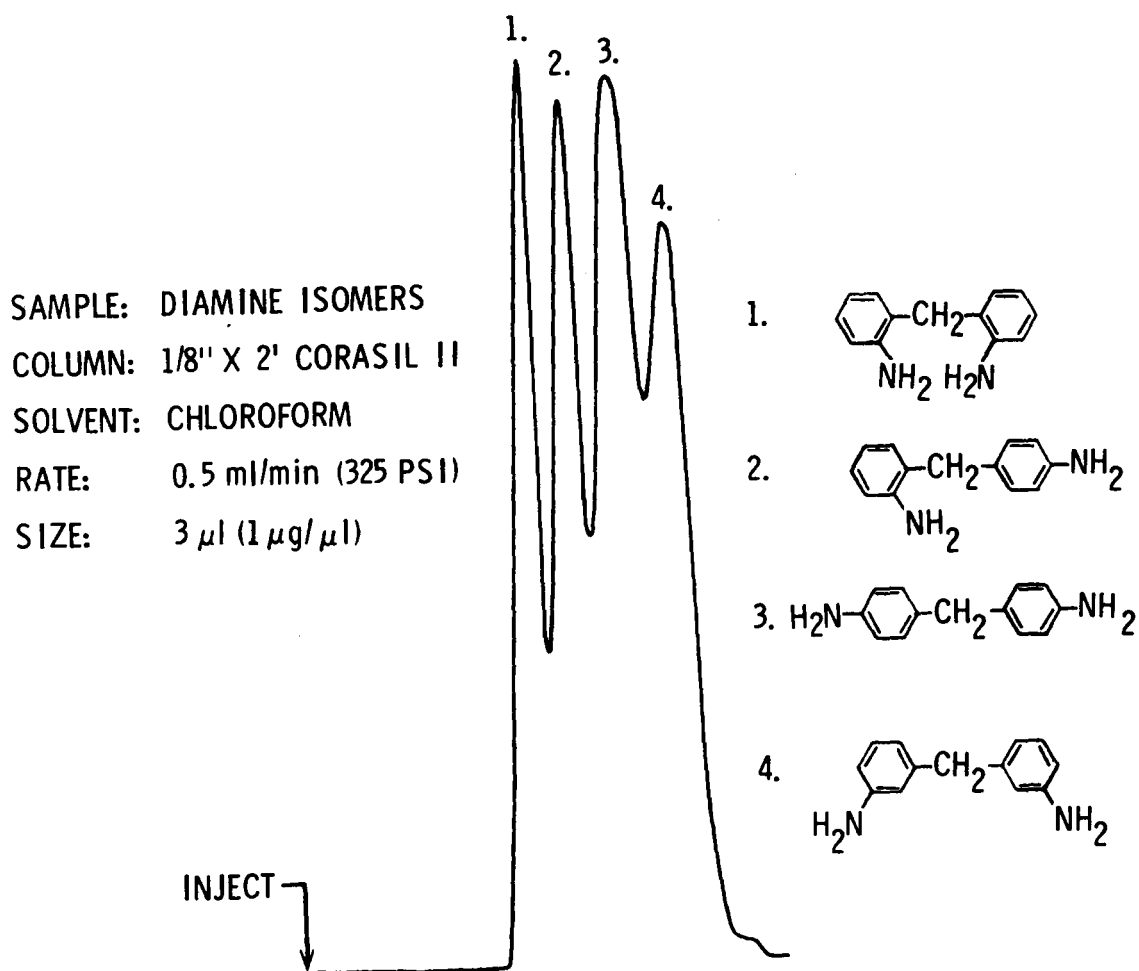


Figure 3. - Analytical chromatogram of methylenedianiline isomer mixture.

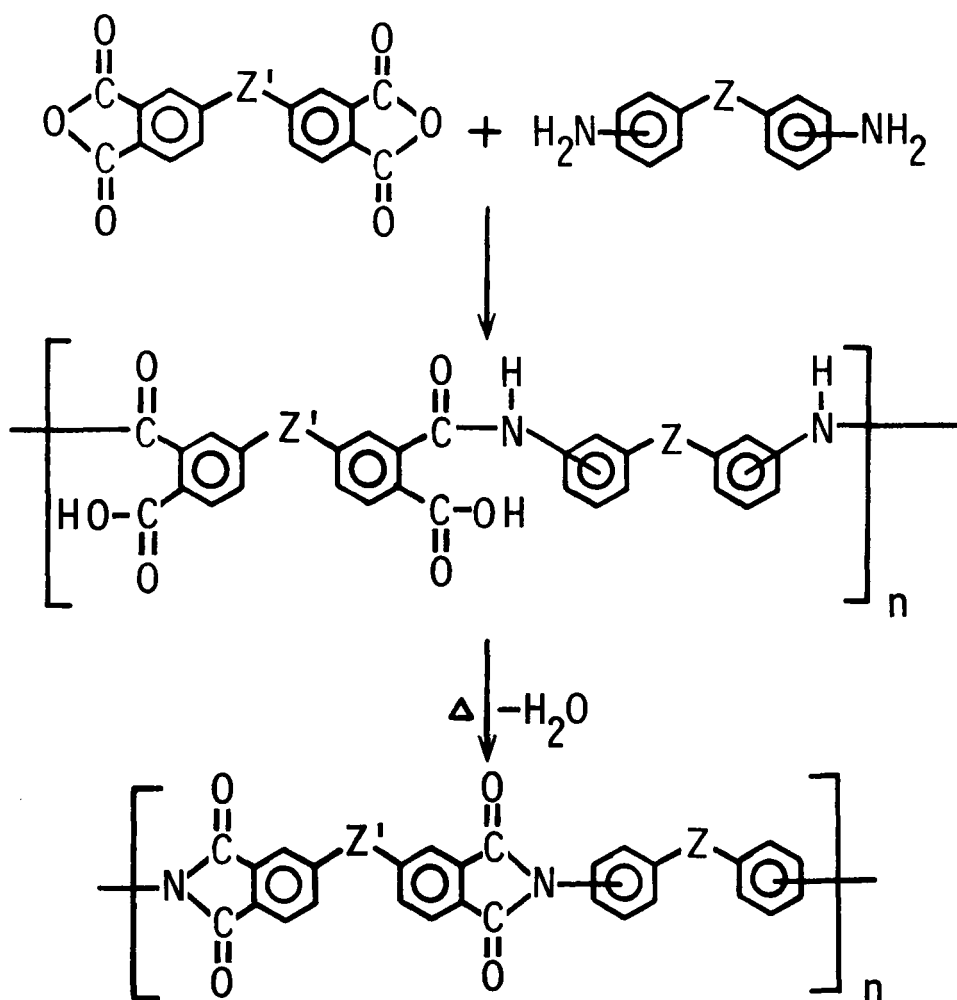


Figure 4. - General polyimide chemistry.



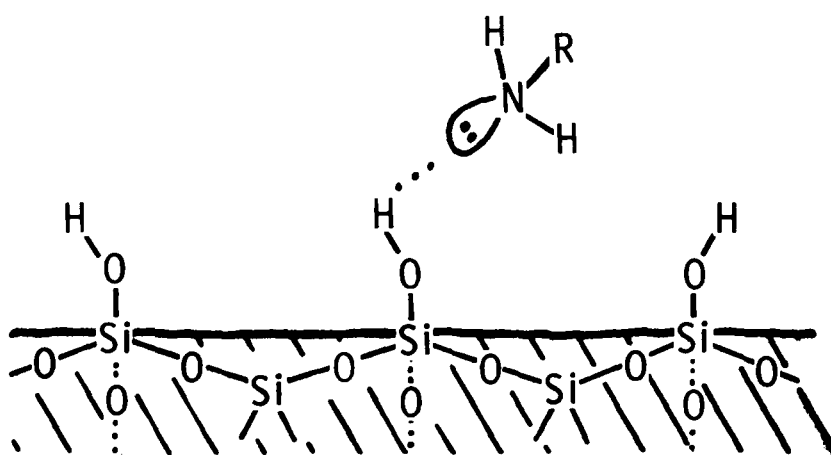


Figure 5. - Liquid-solid separation mechanism.

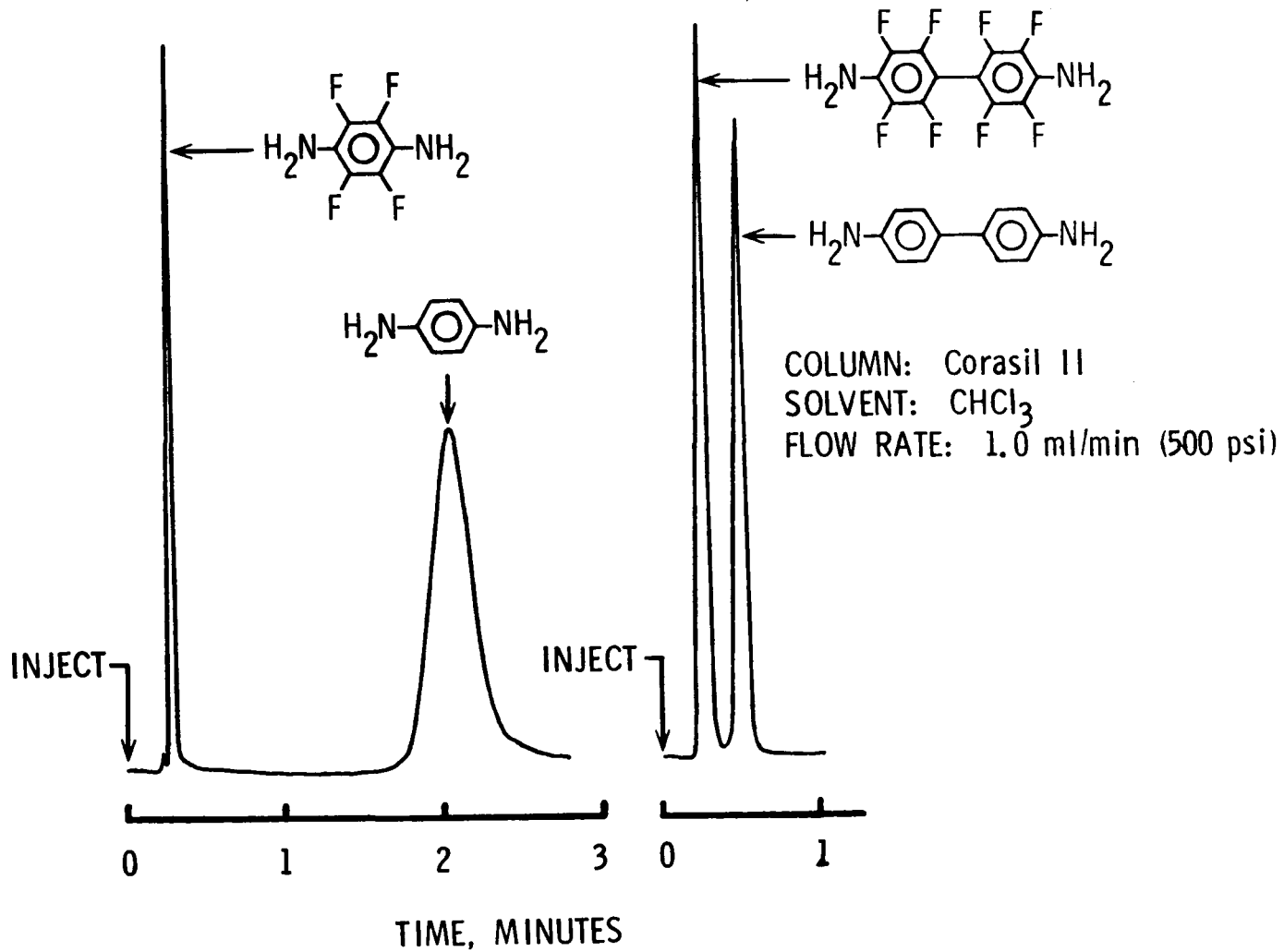


Figure 6. - Separation of diamine isomers.

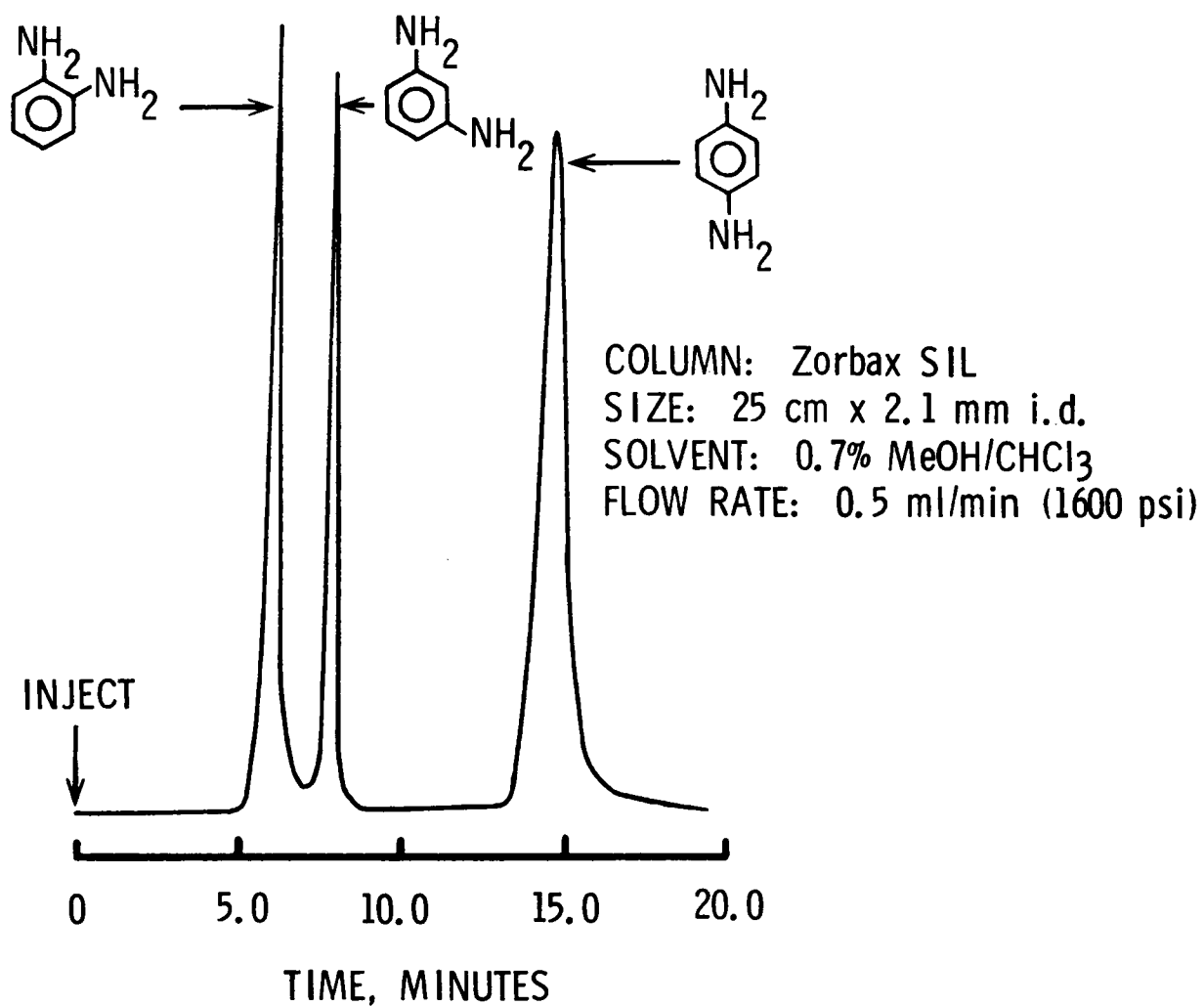


Figure 7. - Separation of phenylenediamine isomers.

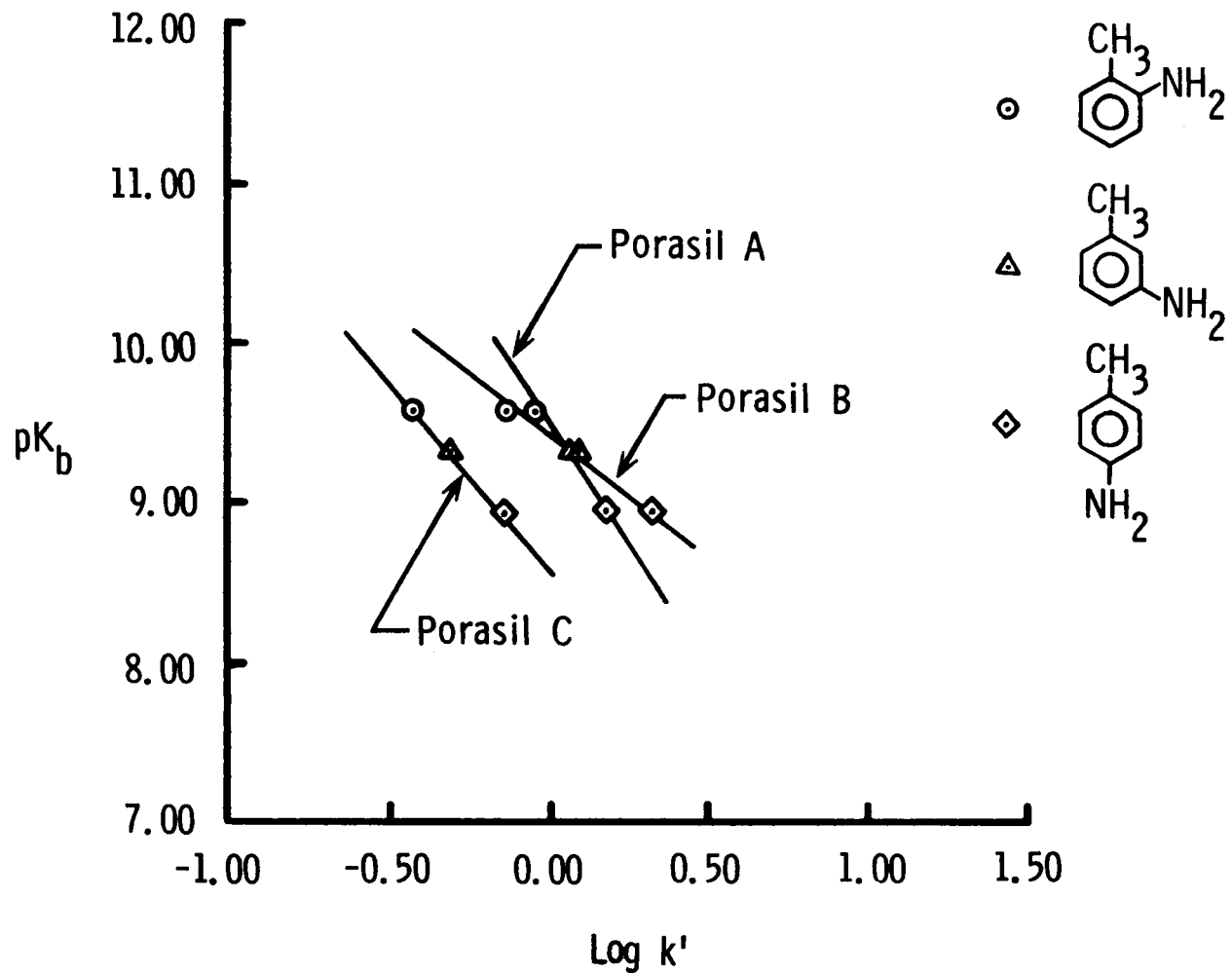


Figure 8.- Plot of  $pK_b$  versus log of capacity factor for toluidine isomers. Conditions: Porasils A, B, and C mobile phase- 75/25 (v/v) chloroform/cyclohexane, flow- 0.5 ml/min, pressure- A 400 psi, B and C 350 psi.

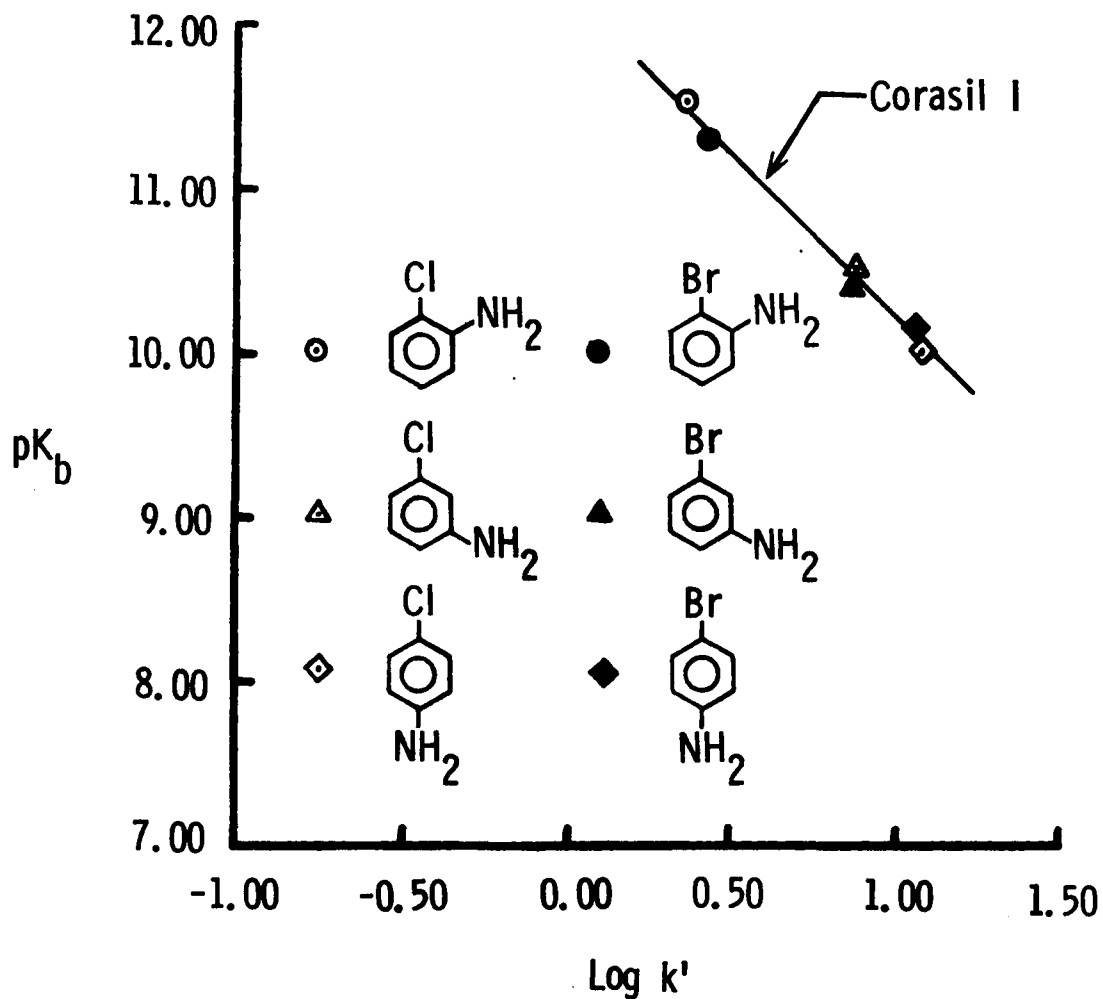


Figure 9. - Plot of  $\text{pK}_b$  versus log of capacity factor for aniline isomers. Conditions: Corasil I mobile phase-cyclohexane, flow-2.0 ml/min, pressure-1400 psi.

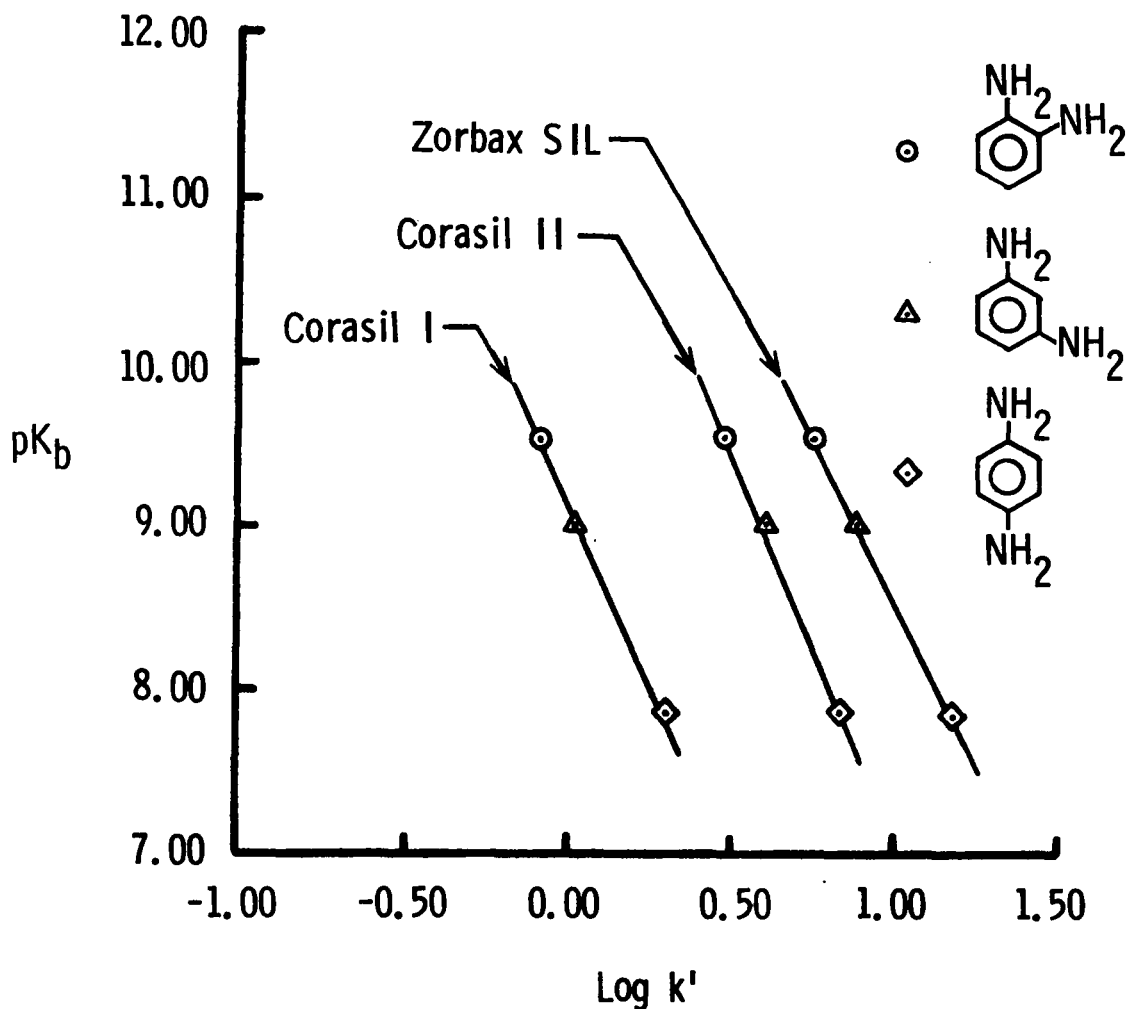


Figure 10. - Plot of  $\text{pK}_b$  versus log of capacity factor for phenylenediamine isomers. Conditions: Corasil I mobile phase-chloroform, flow-2.0 ml/min, pressure-1000 psi; Corasil II mobile phase-chloroform, flow-2.0 ml/min, pressure-1000 psi; Zorbax-SIL mobile phase-0.7% (v/v) methanol in chloroform, flow-0.5 ml/min, pressure-1600 psi.

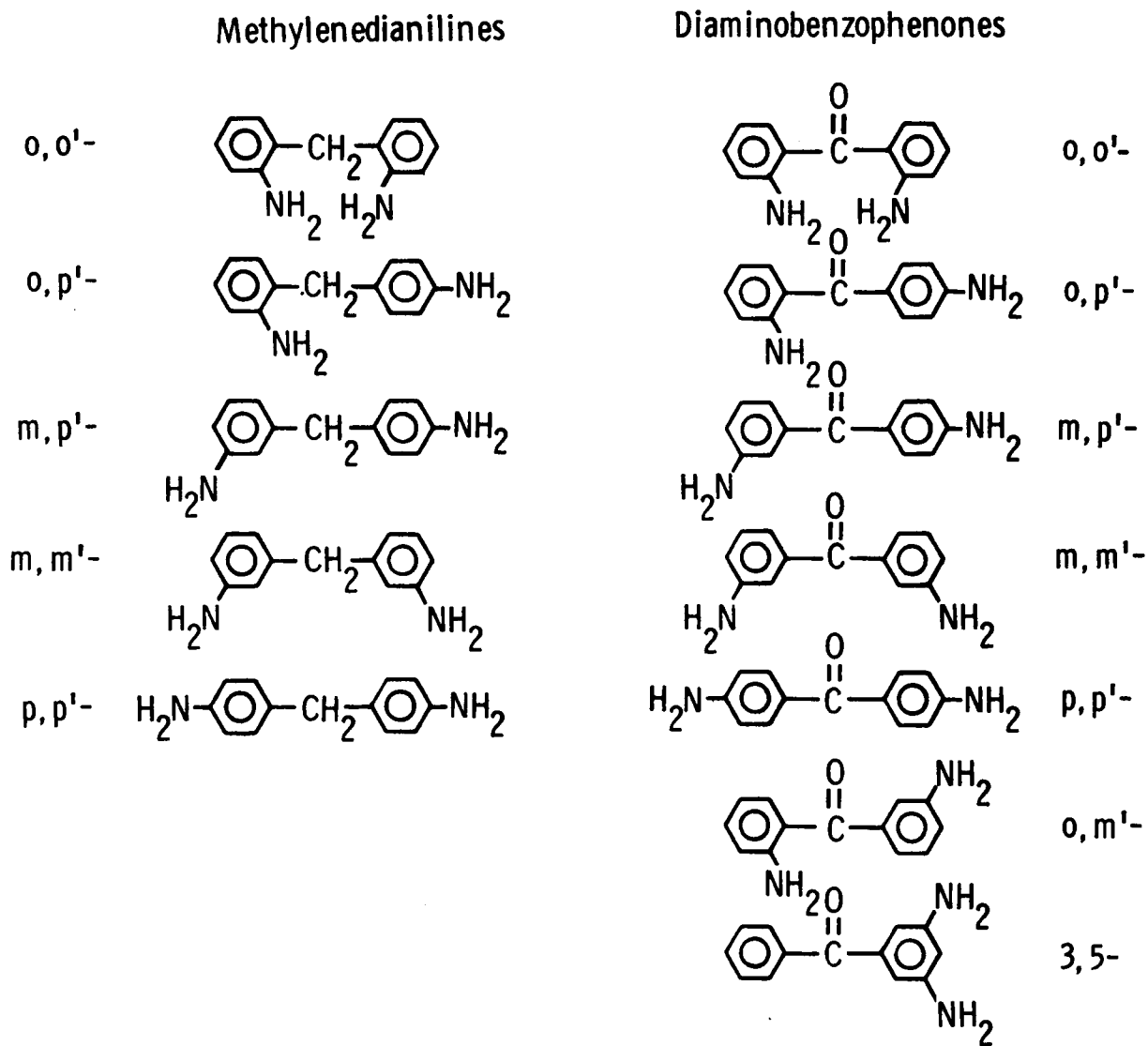


Figure 11. - Two series of isomeric aromatic diamines studied by high pressure liquid chromatography.

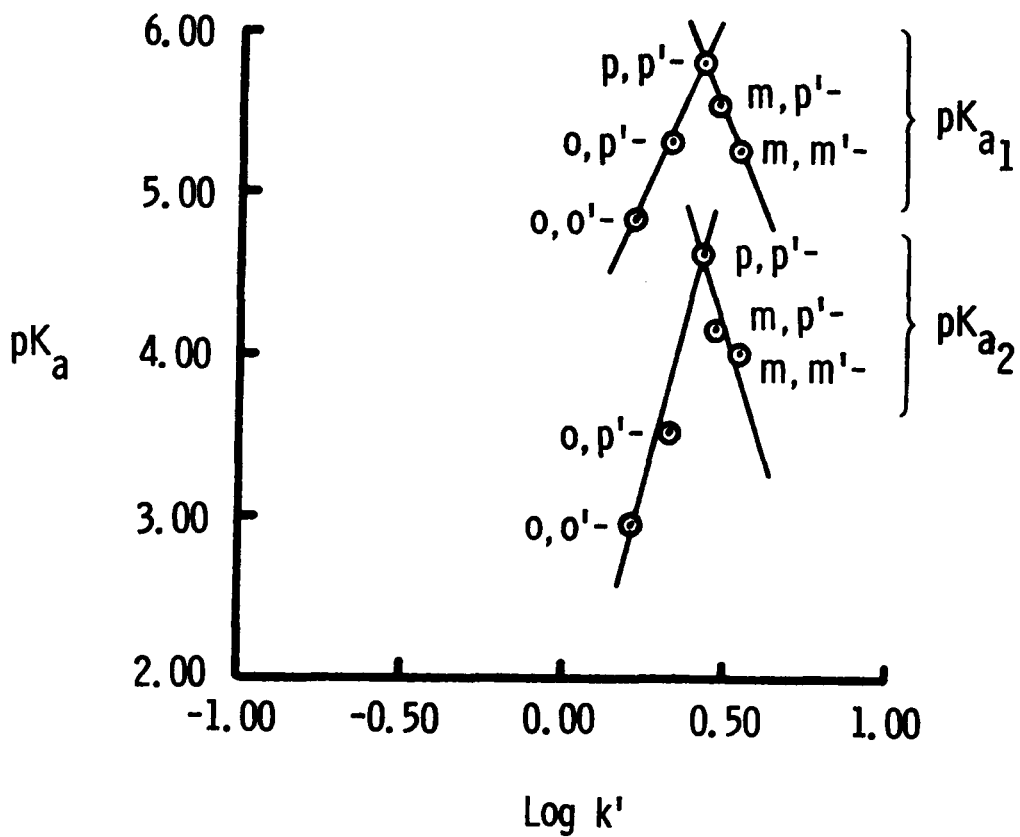


Figure 12. - Plot of  $pK_a$  versus log of capacity factor for methylenedianiline isomers. Conditions: adsorbent-Corasil II, mobile phase-chloroform, flow-0.5 ml/min, pressure-325 psi.



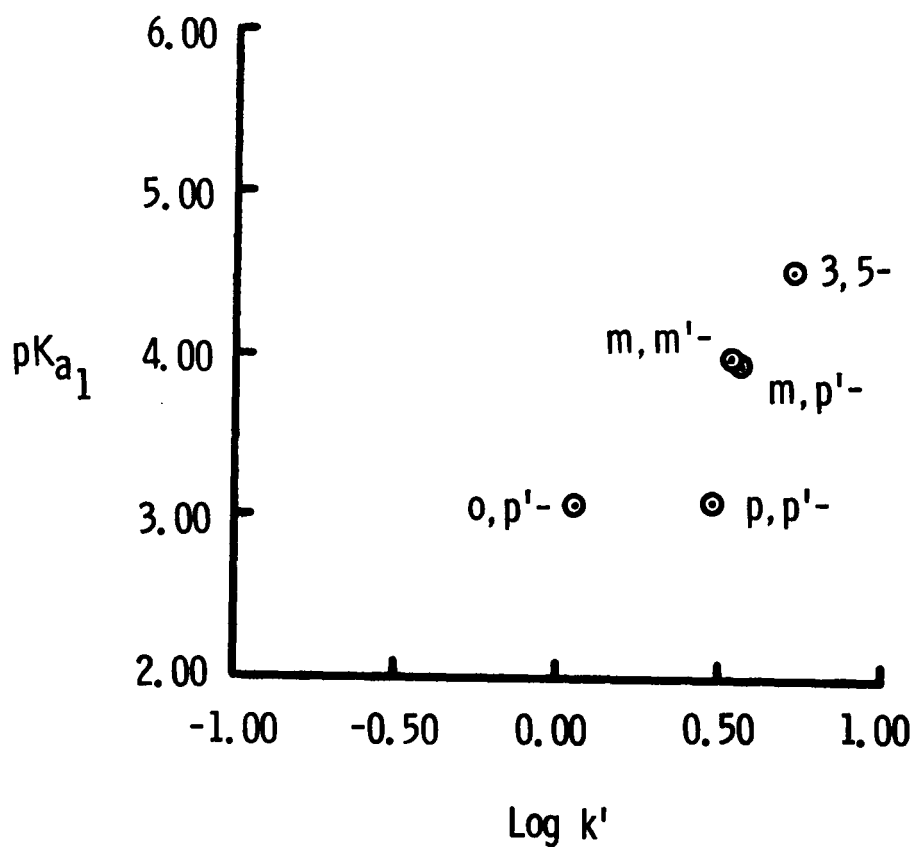


Figure 13. - Plot of  $pK_a$  versus log of capacity factor for diamino-benzophenone isomers. Conditions: adsorbent-Corasil II, mobile phase-chloroform, flow-1.0 ml/min, pressure-475 psi.

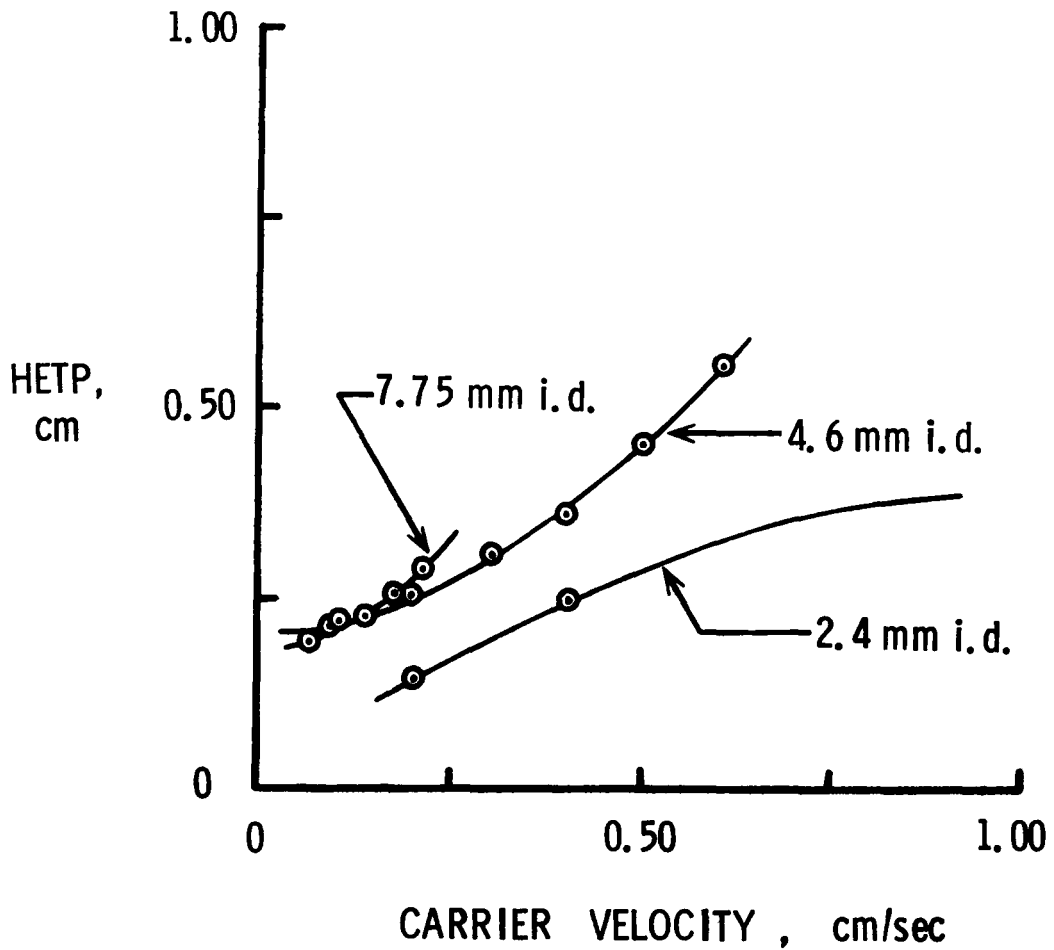


Figure 14. - Plate height versus carrier velocity for 2.4, 4.6, and 7.75 mm i.d. columns. Conditions: adsorbent-Porasil C, column length-2 ft., mobile phase-chloroform.

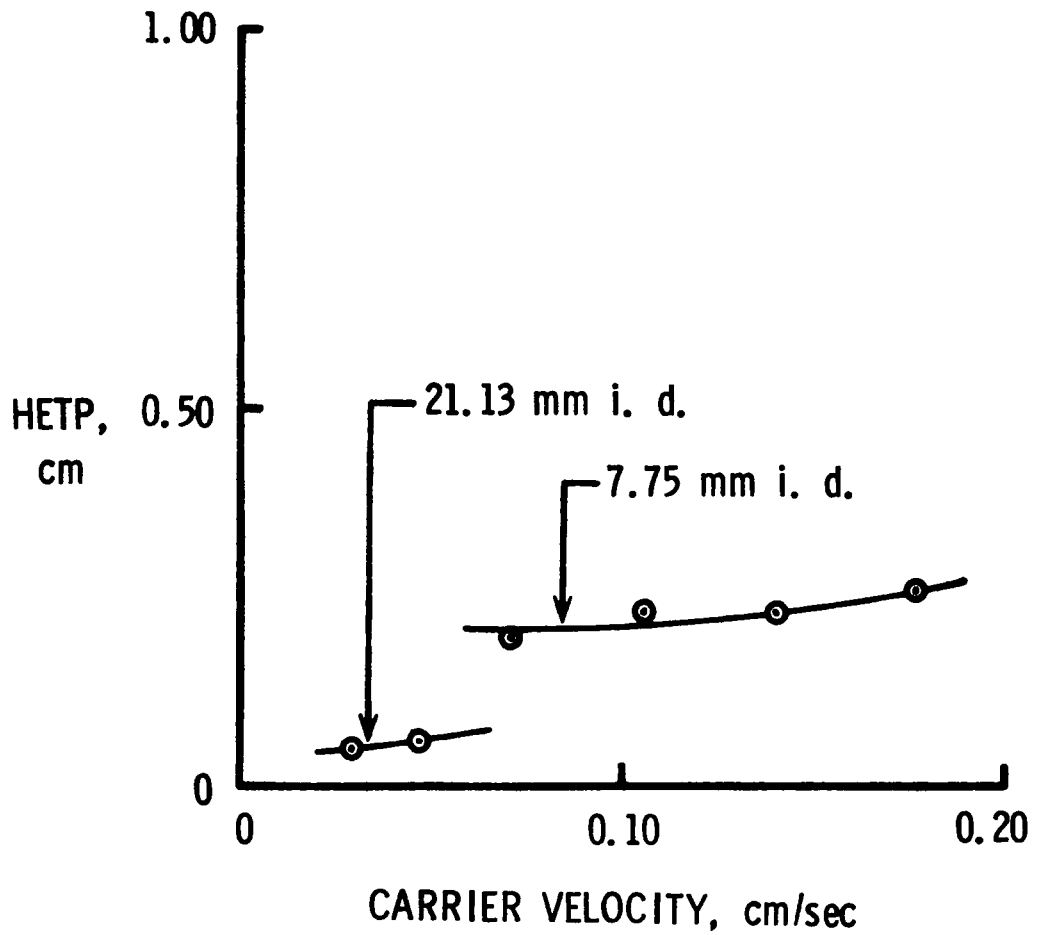


Figure 15. - Plate height versus carrier velocity for 7.75 and 21.13 mm i.d. columns. Conditions: adsorbent-Porasil C, column length-2 ft., mobile phase-chloroform.

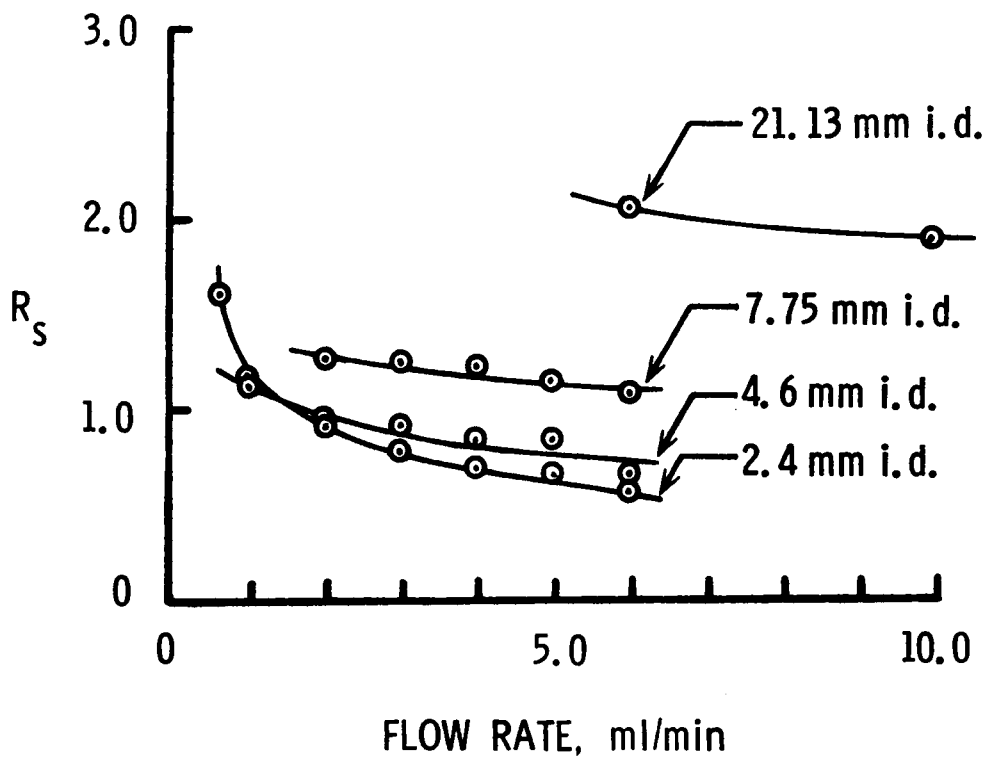


Figure 16. - Effect of flow rate on resolution. Conditions: adsorbent-Porasil C, column length-2 ft., mobile phase-chloroform.

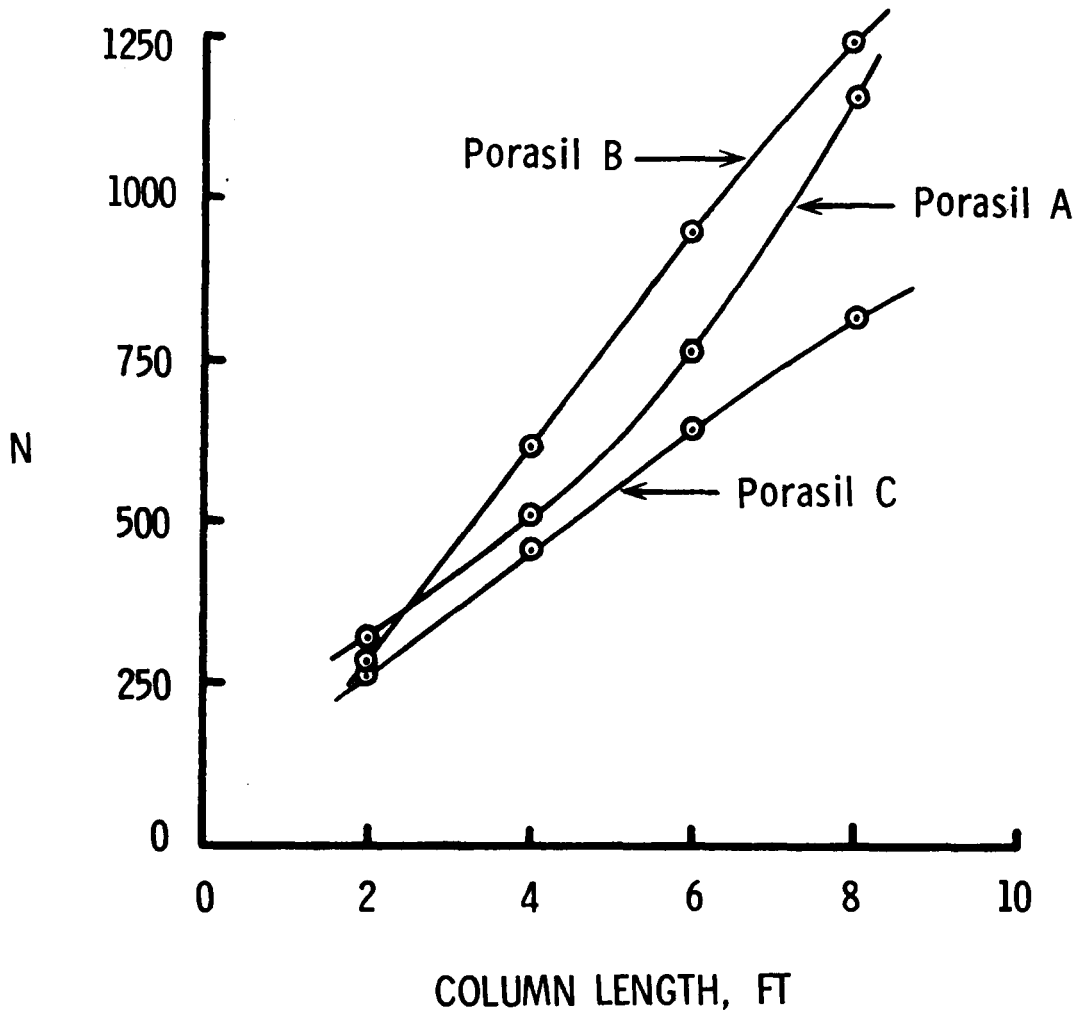


Figure 17. - Theoretical plates versus column length for three adsorbents. Conditions: column diameter-3/8 in., mobile phase-chloroform, flow rate-6.0 ml/min.

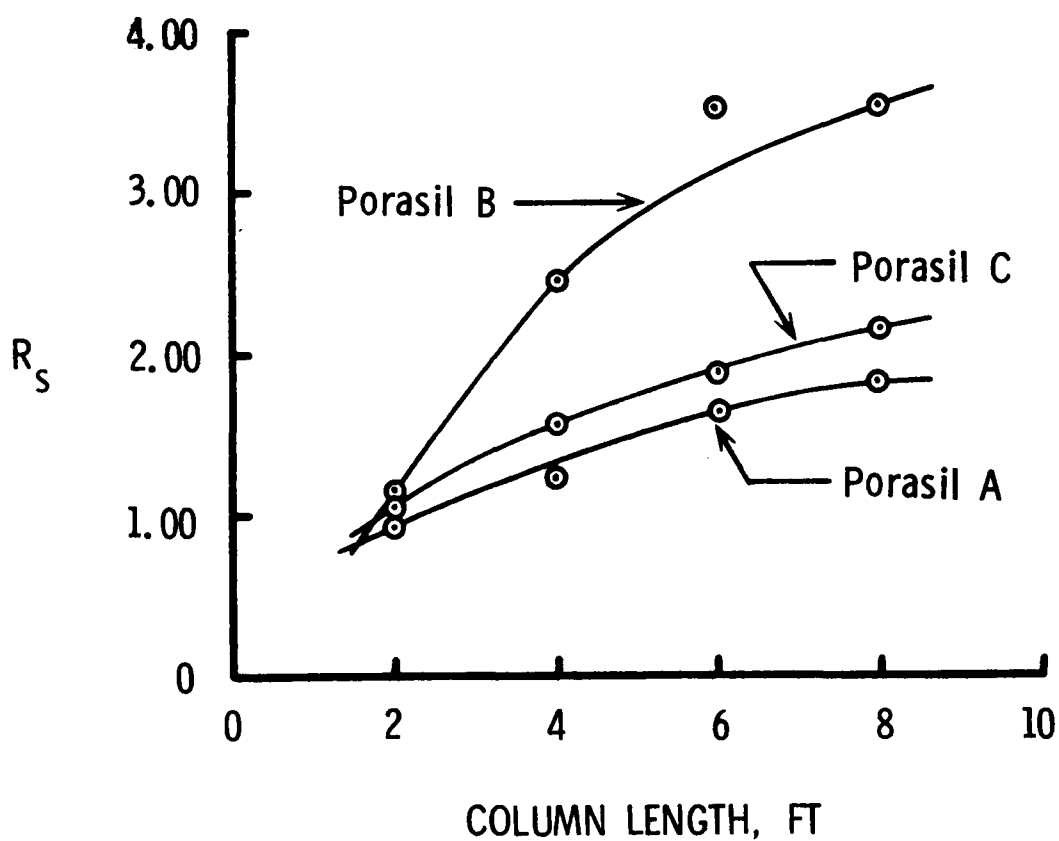


Figure 18. - Resolution versus column length for three adsorbents.  
Conditions: column diameter-3/8 in., mobile phase-chloroform, flow rate-6.0 ml/min.

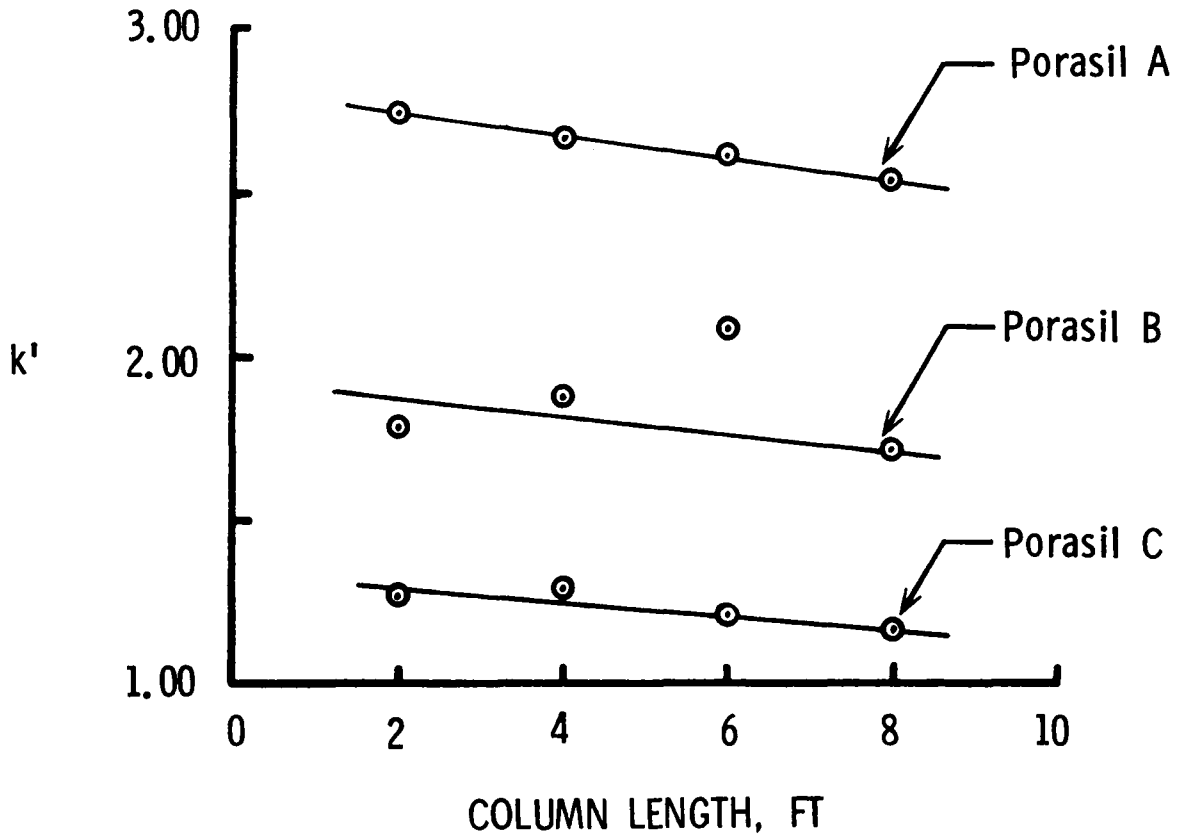


Figure 19. - Capacity factor versus column length for three adsorbents.  
Conditions: column diameter-3/8 in., mobile phase-  
chloroform, flow rate 6.0 ml/min.

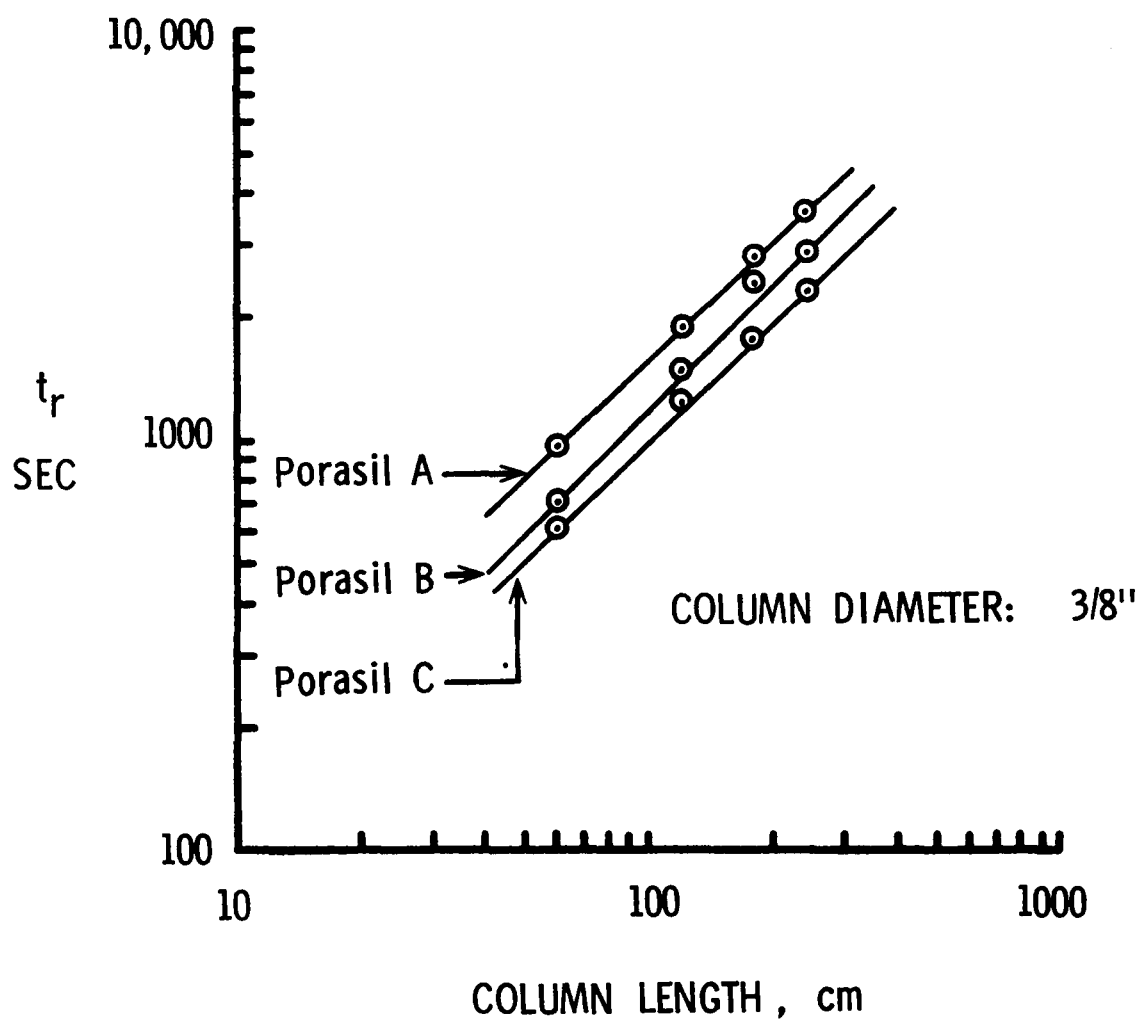


Figure 20. - Effect of column length on retention time. Conditions: column diameter-3/8 in., mobile phase-chloroform, flow rate-6.0 ml/min.



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THE LIQUID CHROMATOGRAPHY OF AROMATIC  
DIAMINES: ANALYTICAL AND PREPARATIVE

Philip R. Young

ABSTRACT

Liquid chromatographic methods were developed for determining the purity, reactivity, and preparative separation of aromatic diamine isomers used in the synthesis of aromatic polyimides. Approximately 50 diamine isomers were separated on various silica gels using chloroform and/or cyclohexane mobile phases. A linear relationship between  $pK_b$  and log of the capacity factor was discovered for four series of simple aromatic amines. This suggested that the relative basicities of more complex diamine isomers might be established from chromatographic retention data. A chromatographic basicity index for two series of isomers was then proposed and correlated with polymer viscosity measurements.

Several parameters which can effect the efficiency of preparative separations of diamine monomers were also evaluated. These parameters included the effect of the column packing technique, flow rate, column diameter and length, adsorbent surface area and particle size, and column capacity. The results of this evaluation indicate that preparative liquid chromatography can be used to prepare highly purified milligram quantities of monomers for polymer synthesis.