

CHROM. 4369

## THE CHROMATOGRAPHIC PROPERTIES OF POLYETHYLENE AND POLYPROPYLENE

GARY T. BENDER\* AND CLIFTON E. MELOAN

*King Hall, Department of Chemistry, Kansas State University, Manhattan, Kansas (U.S.A.)*

(First received October 28th, 1968; revised manuscript received September 12th, 1969)

---

### SUMMARY

The chromatographic properties of polyolefin molding powders have been determined. Polyethylene molding powders, both high- and low-density, appear to be useless. Uncoated polypropylene on the other hand appears to separate organic compounds from one another by a gas-liquid partition mechanism. The uncoated polypropylene columns are very good for trace water analysis in organic compounds. Coated polypropylene is useful for some separations. Theoretical considerations of the separations are discussed.

---

### INTRODUCTION

In the past few years there has been a great deal of research on nondiatomite solid supports for gas chromatography. The reason for this research is the fact that there has been increasing interest in the analysis of polar compounds as well as compounds which attack siliceous surfaces. OTTENSTEIN has reviewed much of this research up to 1965 (ref. 1).

Of the nondiatomite supports, the most widely used have been the fluorine-containing polymers. These materials have very non-adsorptive surfaces; hence, compounds as polar as water do not interact or tail seriously. These materials do have their disadvantages however. They are costly, some have very bad handling properties and some lack efficiency. Considering the disadvantages of the fluorine-containing supports, the authors became interested in the possible use of the various polyolefin polymers.

A review of the Gas Chromatography Abstracts yielded only two papers on the subject. In 1963 BAUM reported the separation of lacquer thinner on columns containing low-density polyethylene<sup>2</sup>. The next year LECHNER-DECHATEL reported the separation of perchlorocyclopentane from mixtures of chlorinated cyclopentadiene on 0.2-0.3 mm (55-75 mesh) polyethylene powder coated with 1% Apiezon N<sup>3</sup>.

In an effort to understand better the mechanism of separation and extend the

---

\* Present address: Department of Chemistry, Wisconsin State University, La Crosse, Wisc. 54601, U.S.A.

work on polyolefins the authors felt that a critical evaluation of the materials was in order.

#### EXPERIMENTAL

The polyolefins used in this study were solicited from the primary manufacturers of the polymers in the United States. The polymers received were full-range powders and required screening. The 30–60 mesh cuts were used for the study because most of the powders had a good percentage of powder in this range. Surface areas were determined after drying at 60° under reduced pressure (about 20 mm Hg) (see Table I). The surface areas of the various polymers can be easily explained in terms of their history of manufacture. Of the many samples of polymer received, three samples of low-density polyethylene, three samples of high-density polyethylene and two samples of polypropylene were chosen for chromatographic study.

TABLE I  
SAMPLES OF POLYOLEFINS EVALUATED

<i>Manufacturer</i>	<i>Polyolefin</i>	<i>Type</i>	<i>Surface area (m<sup>2</sup>/g)<sup>a</sup></i>
<i>Polyethylene</i>			
DuPont	Alathon 1730	Low-density	0.05
DuPont	Alathon 7050	High-density	0.05
U.S.I.	Microthene 710-20	Low-density	0.03
U.S.I.	Microthene 722	Low-density	0.04
Phillips	Marlex 525	High-density	0.27
Celanese	Fortiflex A60-500	High-density	0.61
<i>Polypropylene</i>			
Phillips	PD 500		0.33
Chevron	9094F		1.82

<sup>a</sup> Determined by a variation of the dynamic BET method. The numbers are based on one BET plot.

The columns evaluated were prepared from the various polymers and stationary phases and were packed in 6-ft. lengths of 1/4-in. copper tubing. The squalene columns were prepared from Eastman practical grade squalene and were deposited from hexane. The Carbowax 600 columns were prepared from Union Carbide Carbowax 600 and were deposited from acetone. The diglycerol columns were prepared from diglycerol obtained from the Applied Science Laboratory and were deposited from methanol. All the coating was done in polypropylene beakers on a steam bath. The polypropylene beakers are necessary because glass competes for the stationary phase at the expense of the polymer packing. The columns were packed vertically with mechanical agitation. The handling properties of the polymers are very good. They are hard particles which handle much like the common supports. They develop static charge only slightly.

A MicroTek Model 2500R with a Sargent Model SR (1 mV) recorder was used in the study. Flow rates were measured with a soap film flow meter. The instrumental conditions were as follows: injection port temp., 130°; detector block temp., 150°;

detector current, 400 mA; the column temperature was variable. Dry helium was used as the carrier gas. Samples were introduced with a 10  $\mu$ l Hamilton syringe.

Several test mixtures were used in the study. Unless otherwise stated, 1- $\mu$ l samples of the test mixtures were used. The test mixtures are listed in Table II.

TABLE II  
COMPOSITION OF TEST MIXTURES

No.	Component	Amount (g)
1	<i>n</i> -Butanol	16.9
	Water	12.0
	Acetone	6.6
	Ethyl acetate	15.4
2	Ethanol	12.7
	Methanol	11.2
	<i>n</i> -Propanol	12.7
3	Water	5.4
	Acetone	13.4
	<i>n</i> -Propanol	15.2
	Ethyl acetate	19.6
4	Water	5.9
	Acetone	17.5
	Ethyl acetate	19.9
5	Water	20.2
	Methanol	23.8

## RESULTS AND DISCUSSION

In this paper, the authors will use three common approaches to the systematic description of a gas chromatographic support. The first approach used will be a description of what the columns will separate. While this approach is probably of the most utility to the practical gas chromatographer, there are also two other quite useful theoretical approaches. The first theoretical approach used will be a study of the variation in efficiency with the variation in other experimental parameters. The second theoretical approach used will be a study of the variation of specific retention volume with increasing loading.

Before a discussion of specific data is presented it should be pointed out that a support to be used in classic gas-liquid chromatography must be very inert with respect to the sample. It is in this respect that the diatomaceous earth support fall short in the analysis of polar compounds. Unfortunately the authors have found that the polyolefins also suffer to varying degrees from a lack of inertness. In direct contrast to BAUM's work, we have found that low-density polyethylene (Mn 710-20, Mn 722 and 1730) is useless as a support. Of the compounds in the test mixtures only water is rapidly eluted, with alcohols eluted as broad bands. Hydrocarbons are not eluted at all or are eluted at concentrations below the limits of detections. The differences between our work and BAUM's may be due to the differences in polymers or additives in his polymer. His polymer was Mipor No. 14PN-G (ESB-Reeves Corporation, Glenside, Pa., U.S.A.) and is said to have a pore size of approximately 10  $\mu$ , while our polymers are of very low surface area.

High-density polyethylene (M525, A60-500 and 7050), while more inert than

low-density polyethylene, is still useless as a support. This is surprising in view of higher surface areas of the two samples. This also makes the significances of the surface area explanation in the preceding paragraph questionable.

On the other hand, the lack of inertness has not been as serious for polypropylene. While few compounds are not retained, those which are retained give good peaks with respect to tailing. Since some important separations can be made on the coated as well as the uncoated polymer, studies on both have been carried out.

#### *Uncoated polypropylene*

While it was found that uncoated polypropylene was not very inert toward most organic compounds, it was found that it does have the ability to separate many compounds. Consider the typical chromatograms in Figs. 1-3.

In an effort to understand better the separations taking place, efficiency studies were carried out. The variations in efficiency with temperature, flow rate, sample

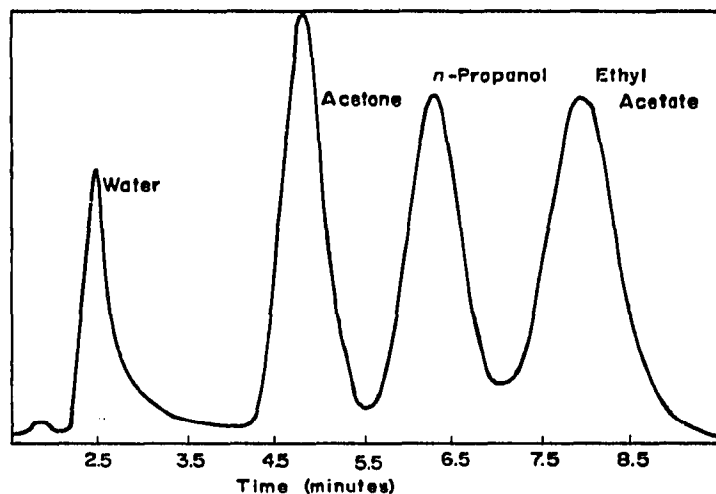


Fig. 1. Separation of Text Mixture 3 on 30-60 mesh Polypropylene PD 500. Column temp., 130°; flow rate, 10 ml/min; sample size, 1  $\mu$ l.

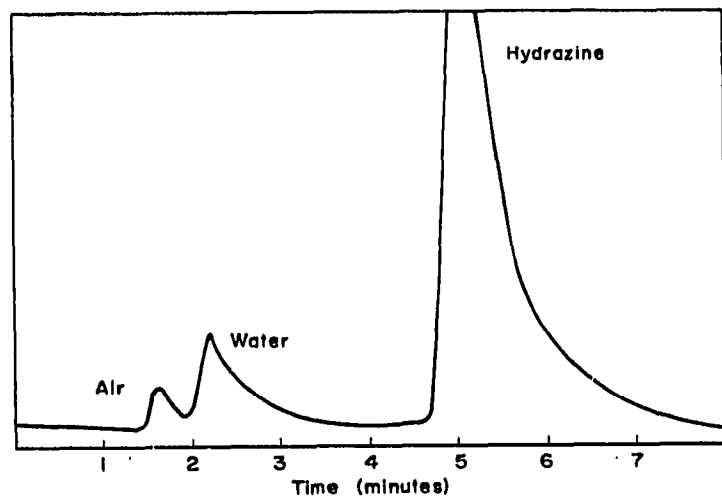


Fig. 2. Separation of water from hydrazine on 60-80 mesh Polypropylene PD 500. Column temp., 105°; flow rate, 25 ml/min; sample size, 1  $\mu$ l.

size and mesh size of the support have all been determined. It must be pointed out, however, that the interpretation of the data may be somewhat artificial. The theory of gas-liquid chromatography is based on columns containing a stationary phase; we speak of diffusion in the liquid phase and liquid film thickness in these theories—hence the discussion of data on polypropylene columns is not realistic in the classical sense.

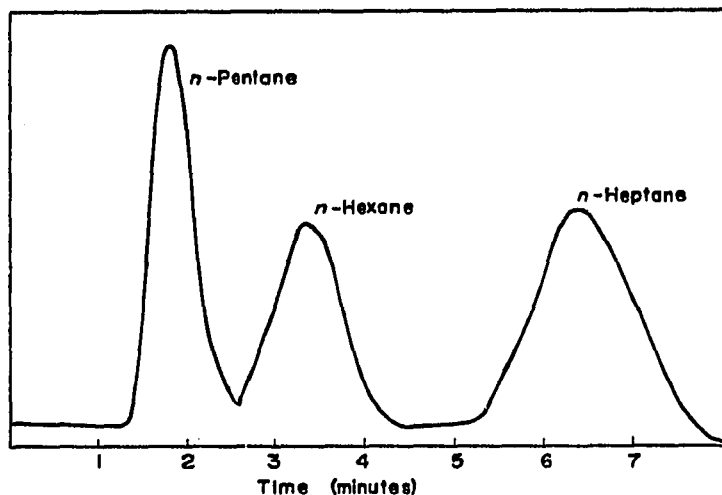


Fig. 3. Separation of *n*-pentane, *n*-hexane and *n*-heptane on 30–60 mesh Polypropylene PD 500. Column temp., 100°; flow rate, 50 ml/min; sample size, 1  $\mu$ l.

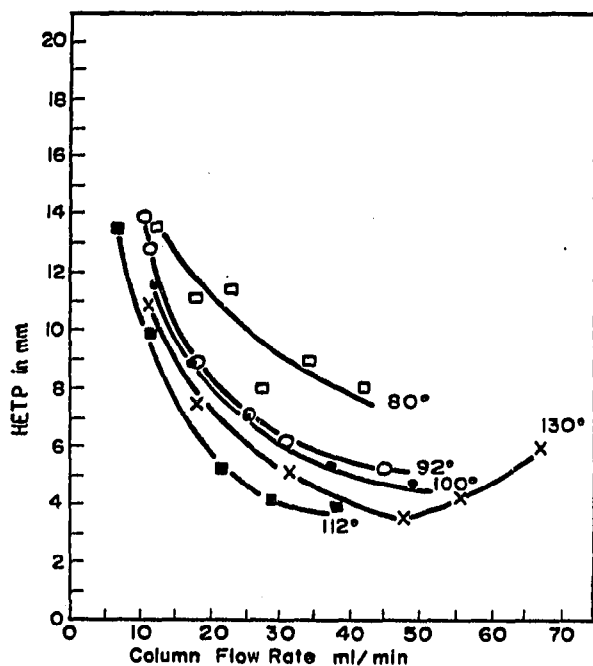


Fig. 4. Van Deemter plot showing the variation of efficiency (HETP) with changes in column flow rate (ml/min) at five temperatures. Column: 30–60 mesh Polypropylene PD 500; sample: water from 1  $\mu$ l of Test Mixture 3.

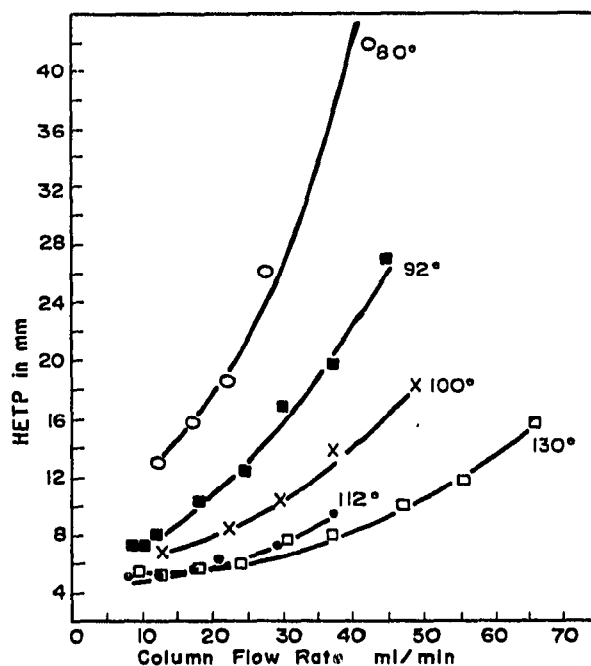


Fig. 5. Van Deemter plot showing the variation of efficiency (HETP) with changes in column flow rate at five temperatures. Column: 30–60 mesh Polypropylene PD 500; sample: ethyl acetate from 1  $\mu$ l of Test Mixture 3.

On the other hand, the column appears to be separating the organic compounds on the basis of a gas-liquid partition mechanism rather than adsorption. The peaks are very symmetrical and in addition many of the trends found in gas-liquid chromatography data also appear in this evaluation. Hence, it appears reasonable to view the separations as gas-liquid in nature.

In the study of the polypropylene columns, Test Mixture 3 containing water, acetone, *n*-propanol and ethyl acetate was injected and the efficiency was calculated from the chromatograms. All of the organic compounds gave much the same shaped curves; hence only one plot for organic compounds is shown. In Figs. 4 and 5 Van Deemter plots for water and ethyl acetate of Test Mixture 3 are shown at five different temperatures. The plots for the organic compounds deviate from the hyperbolic shape predicted by theory. The fact that the polypropylene column is limited as to transfer probably accounts for the atypical shape.

The improvement of efficiency with increasing column temperature is often found for gas-liquid columns and is explained by the decrease in the ratio of  $d_1^2/D_1$ , where  $d_1$  is the liquid film thickness and  $D_1$  is the solute diffusivity in the liquid phase. This same explanation is not too unrealistic for plastic materials if the gas-liquid mode of separation is allowed for such a column.

With respect to the Van Deemter plots for water, the data are much the same as the data found on all columns for a nonpartitioned material. The anomalous curve at 130° can only be explained by increased interaction of water vapor with the polymer at higher temperatures where the polymer is softer.

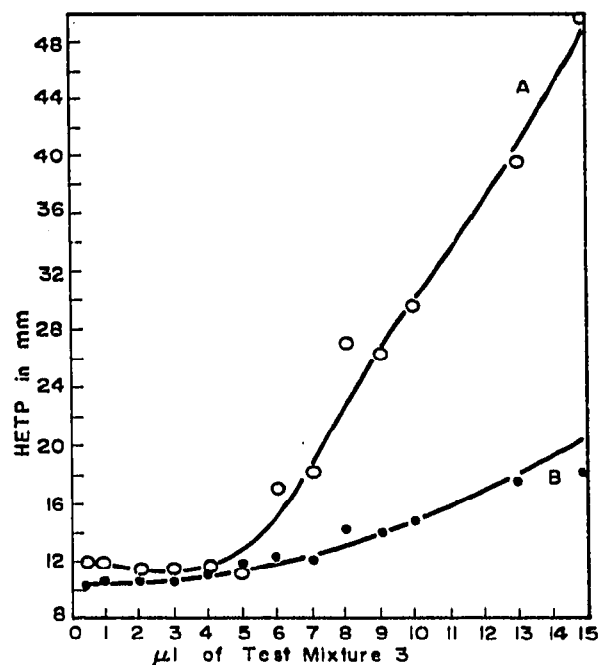
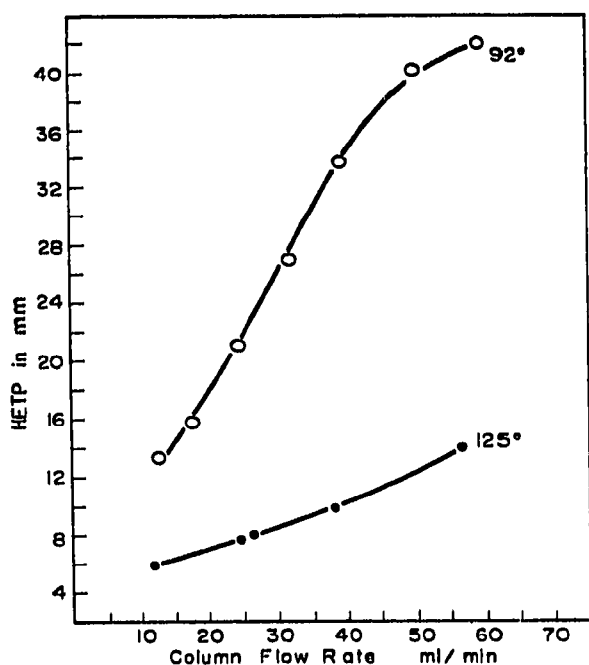


Fig. 6. Van Deemter plot showing the variation of efficiency (HETP) with changes in column flow rate (ml/min) at two temperatures. Column: 30-60 mesh Polypropylene PD 500; sample: 1  $\mu$ l hexane.

Fig. 7. The variation of efficiency with increasing sample size. Column, 30-60 mesh Polypropylene PD 500; column temp., 100°; column flow rate, 13 ml/min; sample, (A) water from Test Mixture 3; (B) *n*-propanol from Test Mixture 3.

To confirm these findings, the author studied the variation in efficiency for a normal hydrocarbon. The data are shown in Fig. 6; they are in complete agreement with the previous data.

In Fig. 7 the variations of efficiency with sample size are reported for water and *n*-propanol of Test Mixture 3. The organic compounds all show much the same dependence. This finding agrees with the gas-liquid partition mechanism proposed. On the other hand, the effect of the sample size on the shape of the water peak is quite different. The shape of the curve could be explained by the limited solubility of water in the polymer or by a nonlinear partition isotherm. Peak shape variations of the type found are often found in gas-solid chromatography.

To prove that the separations were being caused by polypropylene and not by some unknown phenomenon, a second sample of different manufacture was considered. The material was Chevron Polypropylene 9094F with a surface area of 1.8 m<sup>2</sup>/g. (The previous work was on Phillips Polypropylene PD 500 with a surface area of 0.33 m<sup>2</sup>/g.) The results were similar to those found on PD 500. The peaks from organic compounds were still very symmetrical, and the water peak was still a little tailed.

In Fig. 8 the efficiency for 60-80 mesh PD 500 *vs.* flow rate is shown. This is atypical with respect to common coated columns because the efficiency for 60-80 mesh material is no better than for 30-60 mesh material. This indicates that the small particles that make up the larger particles are limiting the efficiency.

Summarizing the data, it has been found that polypropylene can separate mixtures of various compounds. Water for all practical purposes is not retained by the columns but does tail slightly. The origin of the tailing is thought to be either adsorption, or the limited solubility of water in the polymer.

On the other hand, the separation of organic compounds appears to be caused

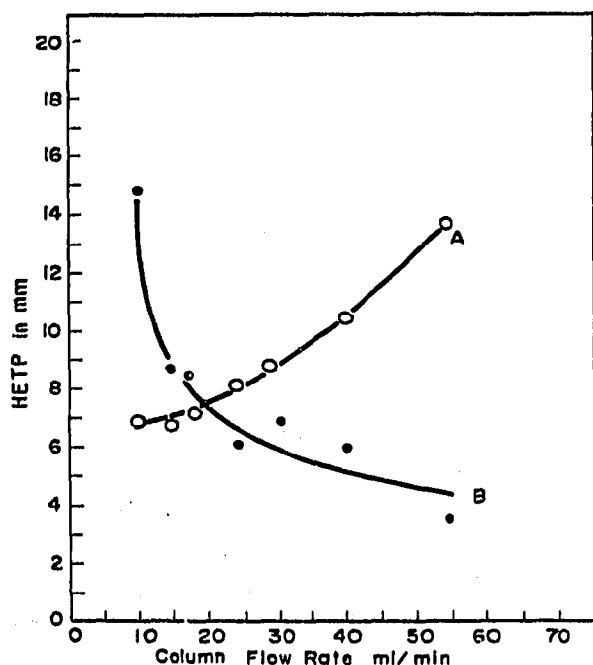


Fig. 8. Van Deemter plot showing the variation of efficiency (HETP) with column flow rate (ml/min). Column, 60-80 mesh Polypropylene PD 500; column temp., 100°; sample, acetone and water from 1  $\mu$ l of Test Mixture 3. A=acetone; B=water.

by a gas-liquid partition mechanism. Their behavior can be successfully explained on the basis of gas-liquid chromatography theory.

While the partition of a gas on a plastic seems a little strange, it has been reported earlier. LYSYJ AND NEWTON<sup>4</sup> prepared a column packing from 50 % Kel-F 300 solid support and 50 % halocarbon oil. The packing was plasticized by refluxing with trichloroethylene. The finished packing was a 50:50 mixture and was a free flowing powder. This monophasic gel, as they called it, had good separating ability for halogenated samples. The author believes that separations on polypropylene are similar in nature to those described by LYSYJ AND NEWTON.

Efficient separations are favored by high column temperature and slow flow rates. The practical temperature limit is above 130°. The softening point of polypropylene is 150°. Although the author never worked above 130°, operation up to 150° appears practical. This might improve efficiency even more if the general trend holds up to 150°.

From the practical point of view, the most significant finding of this study is that polypropylene, in the dry state, can separate most organic compounds from water. Hence, these columns are quite useful for water analysis. Using the 60-80 mesh PD 500 polymer, the author set up a standard curve for water in absolute ethanol.

From the theoretic point of view, the most significant finding of this study is that polypropylene is behaving much like other polymer supports. This means that polypropylene that has been specially prepared for chromatography could be very useful.

#### *Coated polypropylene*

While the use of polypropylene as a generally useful support has been precluded by its lack of inertness, the material is useful as a coated support in several specific cases. As was stated earlier, water and most one-carbon organic compounds are not retained significantly by the polymer. In addition, some inorganics are not retained. A good example of a difficult separation which is possible on a Carbowax polypropylene

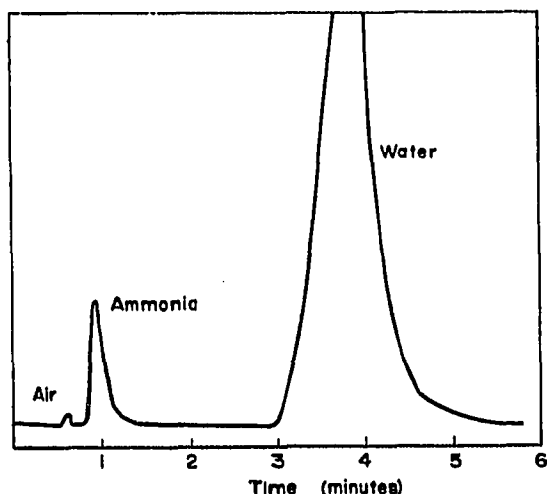


Fig. 9. Representative chromatogram showing the separation of ammonia from dilute ammonium hydroxide. Column, 2.5% Carbowax 600 on 30-60 mesh Polypropylene PD 500; column temperature, 85°; flow rate, 30 ml/min; sample, 1  $\mu$ l dilute ammonium hydroxide.



column is the separation of ammonia from dilute ammonium hydroxide solution, shown in Fig. 9.

The feasibility of useful separations on coated polypropylene columns warranted a study of the columns. The author wished to determine the optimum operating conditions and the effect of the stationary phase surface energy.

In order to determine the optimum flow rate for columns prepared from polypropylene, three columns were prepared which contained 5% loading of squalene, Carbowax, and diglycerol, respectively. The variation in efficiency with changing flow rate was determined using one-microliter samples of Test Mixture 5. The chromatograms and Van Deemter plots show that the columns are all badly limited by mass transfer. Only the plot for the squalene column shows any indication of passing through a minimum. Although an absolute comparison of the HETP data for the three columns is not possible owing to differences in stationary phase viscosity and column temperature, the general trends can be explained in terms of the wetting ability of the stationary phase on the low surface energy support. Diglycerol with its very high surface energy probably cannot wet the polypropylene surface. The fact that the surface is not wetted means that the "film" thickness will be very large, hence the column is badly mass transfer limited. Carbowax and squalene appear to wet the polypropylene surface somewhat better. The Van Deemter plot for the squalene column is typical. Squalene probably wets the support much better than Carbowax.

A second series of polypropylene columns was prepared from squalene and Carbowax 600. Columns containing 2.5%, 5%, 10%, 15% and 20% loadings of the stationary phases were studied to determine the variation of efficiency with loading. Performance of columns with more than 5% diglycerol was too poor to warrant further study. The data indicate that the efficiency decreases with increasing loadings. This fact can be accounted for by the increase of the film thickness of the stationary phase.

To clarify further the behavior of coated polypropylene columns, specific retention volumes for columns of varying loading were obtained. The data indicate that the sample is being adsorbed on or dissolved in the polymer when the columns are lightly loaded.

The work on coated polypropylene columns has shown that polypropylene is useful as a gas chromatography support in some applications. The low surface energy of the polymer causes nonlinear relationships between loading and specific retention volumes. In addition, the resistance to mass transfer severely limits the efficiency. The high mass transfer resistance is ascribed to the low surface area and low surface energy of the polymer. Optimum conditions for separations are generally favored by low flow rates, low loading, and the use of a stationary phase with a low surface energy.

#### GENERAL CONCLUSIONS

In view of the extensive research that has been done on polyolefins, some interesting conclusions can be made. It appears that polyolefins are separating compounds in much the same way as the porous polymer bead supports. The very polar compounds are eluted first with some evidence of adsorption while organic compounds are partitioned by solution in the polymer. This is borne out by the monophasic gel

column of LYSYJ AND NEWTON, the work on various divinylbenzenestyrene polymer beads, our research and the work of BAUM. Judging from BAUM's typical chromatograms the HETP values for his separations are in the same order of magnitude as in our polypropylene work. From the practical standpoint, this makes polypropylene the polyolefin of choice because of its greater temperature limit.

#### DEFINITION OF TERMS

*Column flow rate.* The volume flow rate that has been corrected to the temperature in the column.

*Flow rate.* The volume flow rate measured by a soap bubble flow rate meter at the column exit.

*Efficiency (HETP).* The HETP used in this paper is the normal HETP as opposed to the relative HETP which is measured from the air peak.

*Specific retention volume.* The volume of gas at 0° required to elute one-half of a solute from a column which contains 1 g of liquid phase and has no pressure drop or free gas space.

*Conversion from column flow rate to linear flow rate for 30-60 mesh PD 500 columns.* 1 cm/sec = 7.5 ml/min.

#### REFERENCES

- 1 D. M. OTTENSTEIN, in J. C. GIDDINGS AND R. A. KELLER (Editors), *Advances in Chromatography*, Vol. 3, Marcel Dekker, New York, 1966, p. 137.
- 2 E. H. BAUM, *J. Gas Chromatog.*, 1 (1963) 11.
- 3 A. LECHNER-DECHATEL, *Magy. Kem. Folyoirat*, 76 (1964) 113.
- 4 I. LYSYJ AND P. R. NEWTON, *Anal. Chem.*, 35 (1963) 90.

*J. Chromatog.*, 45 (1969) 220-229