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SPECIFICATION OF GAS CHROMATOGRAPHIC BEHAVIOR USING KOVATS INDICES AND ROHRSCHNEIDER CONSTANTS

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DISCLAIMER

ABSTRACT

The effects of sample size, nature of the liquid phase, and the existence of mixed separation mechanisms upon Kovats indices have been examined. Evaluation of retention profiles for several systems allowed for determination of the sample concentration at which sorption mechanisms made major contributions to the overall retention. That point was dependent upon the polarity difference between the solute and solvent and upon the nature of the inert support. For small samples, sorption mechanisms caused large changes in Kovats indices. Thus, care must be used in applying Kovats indices in analyses of trace components.

The use of pure, discrete polymeric entities as stationary liquids has been examined as a better means of specifying stationary liquids. Such a method should improve interlaboratory comparison of relative retention data. With that point in mind, a set of low molecular weight polyethylene glycol species have been characterized as stationary liquids using the Rohrschneider system.

One of the major problems facing the gas chromatographer is interlaboratory reproducibility of results. The nature of these problems can be divided into two categories. First, insturmental factors, such as the proper determination of dead volumes, are generally well recognized and have been discussed in a recent paper [1]. Second, combinations of chemical and/or physical phenomena can lead to complex situations. For example, a combination of solution and sorption effects can drastically affect the retention volume for a solute as a function of sample size because the net retention of a solute in gas-liquid chromatography is the sum of the solubility effect and adsorption at the gas-liquid interface, at the gas-solid interface, and at the liquid-solid interface. Recent discussions by Conder [2] and by Conder, Locke, and Purnell [3] have developed this topic in detail. It is, therefore, apparent that mixed separation mechanisms can lead to errors in qualitative analysis, especially in instances where comparisons are made between laboratories where sample sizes or column loadings might differ.

The Kovats retention index [4] has been advocated [5-8] as a means for standardization of retention data. Retention indices offer a means for reporting retention data on a relative basis. Normal alkanes are used as reference standards and are selected to bracket the retention time for the compound that is being characterized. Such data are

useful for qualitative identification. Even though the Kovats system was designed to minimize errors in the reporting of retention data from different columns, large ranges of values have sometimes been reported for solutes on supposedly similar columns operated under identical conditions [7]. Sample-size effects, the presence of contaminants or varied polymeric distribution in supposedly identical stationary phases, and temperature effects appear to be likely reasons for the reported range of retention-index values.

The problem of sample-size effects has often been overlooked despite the occasional warnings that have been published. Those warnings have dealt with sample sizes that overload the column [9] and samples that give badly tailed peaks [7]. To avoid overloading, the common suggestion has been to use small sample sizes. However, in heeding that suggestion, one can experience severe problems from the effects of mixed separation mechanisms which may also lead to tailed peaks. Therefore, portions of this study have been devoted to the examination of Kovats retention indices as a function of sample size. Particular emphasis was placed on the behavior of the Kovats indices under conditions where mixed separation mechanisms might exist.

The second source of error in Kovats indices centers about the composition of the stationary phase.

Often, contaminants in the stationary phase or oxidation of the phase on the column have been thought to be the cause for unexpected deviations of the indices [7]. Another problem is derived from the polymeric distribution in the stationary phase. Evans and Smith [10] have shown that there were significant differences in the indices when Carbowax of the same average molecular weight was obtained from several different suppliers. Work in our own laboratory [11] has shown that the actual polymeric distribution can vary considerably while the mean average molecular weight of the samples remains about the same. Those studies emphasized the need for better specifications of stationary phases. Others have also recently recognized this problem. Janak [12] and Kaiser [7, 8] have commented on the need for better stationary phases and a better means of specification and control of the distribution actually present. Preston [13] and McReynolds [14] have proposed that a general set of standard stationary phases be selected and be well characterized. In addition, they proposed that, where many nearly similar phases exist, only one be selected for general use and the others be abandoned.

In order to determine the difference in retention behavior that arises on going from one oligomer to another we have investigated the use of pure oligomers as stationary liquids. At the same time, the use of a single pure oligomer would give a very meaningful, concrete means of

specifying the stationary phase. In the present examination, a series of low molecular weight polyethylene glycols have been studied since they could be obtained in a pure state and also analyzed for purity with relative ease. The results clearly justify the extension of such studies to less volatile phases even though such phases will be more difficult to purify and to analyze.

The last problem concerning Kovats indices centers around their variations with temperature. Some workers [15-20] have previously examined this aspect of the problem, but no attempt has been made in the present study to isolate temperature-related effects.

Experimental

Apparatus. The gas chromatograph was essentially that described earlier by Oberholtzer and Rogers [21]. Modifications in the system included a new digital programmer, whcih has been described by Culp, et. al [22], and a 5.5 dm^3 plexiglass housing for the detector system to buffer the detector from short-term pressure spikes and local temperature changes from drafts.

The sampling system consisted of a Seiscor Model VIII gas sampling valve (Seismograph Service Corp., Tulsa, Okla.) having a 25 µl sample loop. Liquid samples of 1 to 5 µl were injected into an exponential dilution flask [21] with diluent flow rates ranging from 5 to 30 ml per minute,

depending upon the retention volume of the solute, so as to have only one sample on the column at any given time. For larger sample sizes, solutes were injected into the flask but it was not operated in an exponential dilution mode. The sampling valve was then used to inject a known volume of sample from the effluent stream of the exponential dilution flask onto the chromatographic column. In order to lessen the problem of adsorption in the flask and in the valve, this apparatus was placed in a thermostated box held at 85 $\pm$ 1°C.

Chemicals. The hydrocarbon solutes used in this study were obtained from Phillips Petrolium Company or from J. T. Baker Chemical Company and were 99^{+} mole percent purity. The ethanol used in this study was 100% bonded Gold Seal alcohol (Chemical Solvents Corporation). The remaining chemicals used as solutes were J. T. Baker spectrograde chemicals, when available, or Baker reagent grade chemicals.

The squalane used in this study was obtained from Eastman Organic Chemicals and was used as received. Chromatographic analysis of the squalane showed only one peak and, therefore, the material was assumed to be pure.

The tri-, tetra-, and penta-ethylene glycols were obtained from Aldrich Chemical Co. Chromatographic analysis of the bistrimethylsilyl derivatives by the method of Calzolari, et. a. [24] showed only one peak for each of these

species. Therefore, these materials were used as received.

The hexa-and octa-ethylene glycols used in this study were prepared by the method of Fordyce, et. al. [25] using the appropriate glycols and ethers to obtain the desired oligomer. After completion of the reaction, ether was used in a continuous liquid-liquid extractor to remove the glycol from the salt and other organic contaminates. Fractional distillation under vacuum was carried out on the extract, and several distillation cuts with purities of 90 to 95% were obtained. The best cuts of each of the oligomers were then further purified by gel chromatography. A 118 cm x 1 cm column was filled with Sephadex LH20 (Pharmacia Fine Chemicals Inc.) in a methanol medium. After one pass through the column a cut of hexaethylene glycol with a purity of 98.1% with about 1.9% heptaethylene glycol was obtained. Similar results for the octaethylene glycol showed a purity of 98.3% with about 1.7% of the nonaethylene glycol as the principle contaminate.

The carrier gas was high purity Airco helium (Air Reduction Company) which was passed through 4A molecular sieve traps. The traps were frequently conditioned overnight at 350°C while backflushing with helium at a flow rate of 1 to 2 ml/min. Hydrogen (Air Reduction Co.) and Linde compressed air (Union Carbide Corp.) were also passed through similar traps and used as the fuel supply for the flame ionization detector.

Column Preparation. Packing materials were prepared by coating 20% by weight of liquid on Teflon 6 (Varian) and on Chromosorb P (Johns-Manville), which had been silanized by the method of Purnell et. al. [26]. Teflon was used for all of the studies involving polyethylene glycols in an attempt to avoid decomposition of the glycol on the basic Chromosorb surfaces as pointed out by Akizoshi et. al. [27]. Squalane packings of 10 to 30 percent by weight were prepared on both Chromosorb P and Teflon supports. All column packing materials were analyzed by extraction to constant weight in a soxhlet apparatus. In all cases, packings were within $\pm$ 0.2% of the absolute value as determined in the preparation of the materials.

Columns were prepared by packing 50 cm x 0.28 cm stainless steel tubing with the coated support materials. Critical values for the weights of liquids in the columns and the operating parameters are given in Table I.

Data Handling. The points corresponding to the beginning and end of the peak as well as the sections of data desired for establishment of base line were selected by visual examination of the printed digital data. The data were then smoothed using a quadratic eleven-point smooth after the method of Savisky and Golay [28]. Peak areas, and net retention volumes based on the peak mean and the peak maximum were calculated. A peak maximum was obtained by fitting a second-order equation over the top using the

Crout technique [29] and setting the first derivative equal to zero.

The retention data as a function of peak area were used to determine retention profiles for each of the solutes run on a given column. Procedures utilizing power-series type fits [30] were applied to overlapping regions of the peak profiles. A set of standardized detector responses were then used to calculate the retention volume for the desired sample size using the appropriate equation over the desired sector of the peak profile. The calculated retention volumes were then used to determine Kovats indexes from a series of samples and hydrocarbon reference standards, where the value of the ratio of the number of moles of solute to the number of moles of solvent on a column was selected. Comparisons of Kovats indices between columns were also made on the basis of a given mole ratio of solute to total solvent in the column. Values for several sets of mole ratios were determined.

Rohrschneider constants [31] were determined for each of the glycols as a means of characterizing them as stationary phases. The Rohrschneider values were determined using the normal set of solutes: benzene, ethanol, 2-butanone, nitromethane, and pyridine.

Results

Retention Volumes. In order to determine where sorption mechanisms might become a dominant means of separation, investigations similar to those of Purnell et. al. [33] were carried out on the squalane-2-butanol system. However, our studies extended the retention profiles to much smaller samples than have previously been examined. Figure 1-3 show the retention profiles at 50.0°C for three different loadings of stationary phases on Chromosorb P. In these figures, one can compare the behavior of the peak mean, shown by the solid lines, and the peak maximum, shown by the broken lines. Values of log area in the region 3.5 to 5 correspond to the range studied by Purnell et. al. [33] and are in agreement with their work.

In these figures, as the sample size decreases, the retention volume begins to increase rapidly for areas on the order of 1×10^3 picocoulombs, which corresponds to a sample size of about 1×10^{-7} grams. Note also that, as the amount of stationary liquid increases, the onset of curvature starts at smaller sample sizes. Hence, the large change in retention volume appears to be due to adsorption on the support. In addition, a comparison of Figures 2 and 3 shows that the change in the index for the maximum over the range of area from log 2 to log 4 was smaller for the column with the lower liquid loading. That result points somewhat to adsorption at the gas-liquid interface for the more heavily loaded column.

In Figure 1, where retention volumes appear to decrease for very small samples, the signal-to-noise ratio was very low and led to difficulties in peak detection. Therefore, the observed decrease in retention volume at very small sample size is highly suspect, and additional data are required to conclusively support or refute that behavior.

Figures 4 and 5 are typical of the retention profiles obtained for the squalane, 2-butanol system when Teflon 6 was used as the inert support. Examination of these curves shows that the break in the retention profile occurs at smaller areas and, therefore, sorption mechanisms do not assume a dominant role in this system as early as in the Chromosorb system. However, evaluation of this set of retention profiles at 50°C on Teflon 6 as a function of loading of the stationary phase showed that the breaks in the retention profiles occurred at larger peak areas as the amount of the stationary phase increased. That behavior points to a significant contribution from adsorption at the gas-liquid interface assuming that the surface area of the liquid increased with liquid loading. In that connection, it is important to note that, even for samples larger than 1×10^3 picocoulombs, all of these figures showed a significant change in retention volume with sample size. Hence, in the 10^3 - 10^5 picocoulomb range, which was also studied by Conder, Locke and Purnell [33], the observed adsorption appears to have been occurring primarily on the surface of

the liquid for those cases where Teflon was used as the inert support.

It should be noted that the breaks in the curves for the retention volume generally occurred at larger areas for the peak mean than for the peak maximum. Hence, the maxima are much less sensitive to peak tailing that results from the adsorption processes. Also, considerable divergence between values from the peak means and the peak maxima is observed in certain portions of these curves. That divergence can be qualitatively related to the greater peak asymmetry. Finally, as indicated earlier, the larger amount of scatter in the data for the peak means reflects the problem of detecting the end of the peak and the fact that the tail has a large influence upon the peak mean.

Profiles similar to those in Figures 1-5 were also obtained at different temperatures. In all cases, going to a higher temperature shifted the onset of a large increase in retention volume to a smaller sample size. For example, at 70°C, the column having 17% squalane on Chromosorb P showed a break for the peak maximum at an area of 1×10^2 picocoulombs instead of at an area of $1 \times 10^{2.8}$ picocoulombs as it did at 50°C. The same trend was found for the columns in which Teflon was used as the support.

Kovats Indices. The behavior of the Kovats indices was examined over a large range of sample sizes.

Particular emphasis was placed on the behavior of the retention index where two or more separation mechanisms contributed significantly to the overall separation. Table II shows a series of Kovats indices for benzene and ethanol on squalane, triethylene glycol, and hexaethylene glycol columns. In this table, comparisons between columns are made for a series of samples where the ratio of the number of moles of solute to the number of moles of solvent in the column was constant. In all cases the general trends in the data depend upon the difference in polarity of the solute-solvent combination. The index values seem to show smaller changes for polar compounds on polar compounds, such as ethanol on triethylene glycol, than for polars on nonpolars, such as ethanol on squalane. For nonpolar hydrocarbons, such as benzene on triethylene glycol and benzene on squalane, the behavior of the indices showed much larger deviations for differences in separation mechanism with respect to sample size.

A detailed examination of Table II shows several interesting trends. First, the Kovats indices based on peak maxima may be smaller than or larger than those indices based on peak means. Except for the case of ethanol on squalane, the polarity differences of the solute-solvent combination was such that one would expect the extent of the peak tailing of the reference alkanes to be greater than, or equal to, the peak tailing for the sample.

As the normal alkanes increase in chain length, the amount of tailing in the corresponding peak increases. With these points in mind, examination of the peak elution characteristics along with the equation for Kovats index offers an explanation for the differences between the peak means and peak maxima. The Kovats equation is

$$\underline{I} = 100\underline{N} + 100\left[\frac{\log R_x - \log R_N}{\log R_{N+1} - \log R_N}\right]$$

where $\underline{N}$ is the carbon number for the normal alkane whose retention volume is less than that of the sample and $\underline{R_{N+1}}$ is the normal alkane whose retention volume is larger than that of the sample. In cases where the peak tailing of the reference compounds is greater than, or equal to, that of the reference compound, the differences in indices based on peak maxima and peak means can be explained using Figure 6. As peak tailing of the reference increases, the difference in using $\underline{B}$-$\underline{A}$ will become larger. This will, in turn, cause the denominator in the Kovats equation to become larger when data for the peak mean are used rather than data for the peak maxima. Likewise, in instances where the peak tailing of the sample is more severe than that of the references, one would expect the numerator of the Kovats equation to become larger. This would cause the indices for the peak means to be larger as was the case in the ethanol-squalane system.

Examination of Table II with respect to sample size shows considerable variance in behavior of Kovats indices with the polarity differences between the solute and solvent. In the benzene-squalane system, the Kovats indices are almost constant with a difference of only 0.4 unit in the means and 0.7 unit in the maxima. Although this solute-solvent combination is probably one of the most nearly ideal cases, the results are rather good considering that these differences are for sample sizes which ranged over 5 orders of magnitude. In similar squalane-hydrocarbon systems, van Kemenade and Groenendijk [32] have reported internal consistency of 0.06 unit and interlaboratory consistency on the order of 0.5 unit. For benzene-glycol systems, the Kovats indices show a general decrease in value with a range of about 30 index units for the triethylene glycol and about 10 to 12 for the hexaethyelene glycol system. The minimum value in the pattern for retention indices on the benzene-triethylene glycol system is the result of peak tailing and to differences in the location where sorption mechanisms become dominant for the benzene and corresponding bracketing hydrocarbons. In cases where ethanol was used as the solute, the behavior is somewhat more complex. For the ethanol-squalane system, the Kovats indices increase by 50 to 100 units over a 5-fold concentration range. The reason for this type of behavior has been discussed above in comparing differences between the

Kovats indices based on mean and maximum peak retention data. In cases where ethanol was used as a solute with glycol columns, the retention indices first increased, went through a maximum value, and then decreased. The initial increase in retention indices with sample size might be the result of column overloading although it would seem that such behavior should also be evident for the ethanol-squalane system. Therefore, the actual cause for the initial increase in retention index values for these sample size profiles is unclear.

The prime cause for much of the variation of Kovats indices at low sample concentrations is evident from Figure 7 where retention profiles of a hydrocarbon reference solute and a polar solute are given for a hexaethylene glycol column. These retention profiles show that the onset of a dominant sorption mechanism comes at much larger sample concentrations for the hydrocarbon than for the polar solute. As a result, the Kovats index for the polar compound is decreased. Likewise, the combination of polar solutes on nonpolar solvents such as squalane show just the opposite behavior with the polar solutes now changing more than the reference. Therefore, it is obvious that retention profiles of a system would be quite useful for determination of the sample size range over which the Kovats indices give valid data for a given solute solvent system.

Using an exponential dilution apparatus, the determination of retention profiles is simplified.

In the course of obtaining these data, several important practical problems arose. One problem involved the temperature of the column. As one went to higher temperatures in a given system, the dominance of sorption mechanisms decreased and was only apparent for smaller samples. However, the practical limitation became the volatility of the stationary phase. Since squalane began to show a considerable bleed rate between 65 and 70°C, as did the tri- and tetra-ethylene glycol, the upper temperature had to be limited to about 60°C in these studies. A second problem involved column conditioning with respect to particular solutes. This phenomenon was found to be quite important for solutes such as nitromethane and pyridine in the glycol systems. In those instances, the peak retention volume decreased and the peak area increased as successive equivalent-size samples were injected onto the column. At least five to ten samples were required before consistent results were obtained. Therefore, when a sample conditions a column, care must be used in the application of Kovats indices, and the column should be thoroughly conditioned to that species before use of the column for evaluation of retention data as well as for quantitative determinations.

In the glycol systems, negative dips in the baseline were often observed before and after the elution of the

solute peak. This phenomenon was observed only on the most sensitive scales. This behavior might involve interaction of the surface of the stationary liquid with very small amounts of solute to lower the vapor pressure of the solvent. This, in turn, lowered the bleed rate of the solvent from the column over the zone in which the solute resided. The prime practical problem in those cases, then, became one of determining not only the beginning and end of the peak but also the establishment of a valid baseline for the peak.

Rohrschneider Constants. One goal of this study was to evaluate and characterize several pure polyethylene glycol species for use as stationary phases. In these studies, retention profiles similar to those in Figure 7 were obtained for the set of solutes needed to determine the five standard Rohrschneider constants for the different glycol species. These profiles were then used to determine Kovats indices at various solute-to-solvent mole ratios. The Kovats indices of the solutes on the various glycols were used in conjunction with similar Kovats indices at the equivalent mole ratios on squalane columns to obtain the standard set of Rohrschneider values. In obtaining Rohrschneider constants, one must bear in mind that the problems and pheomena which caused difficulties in the Kovats system are not only present but compounded in the Rohrschneider calculations.

Rohrschneider constants for a series of low molecular weight polyethylene glycols are given in Table III.

This table gives a compilation of the Rohrschneider constants based on peak means and peak maxima for a range of sample sizes. Examination of any glycol species in Table III shows that, as sample size decrease, the Rohrschneider constants increase, go through a maximum, and then decrease. The range of this variation goes from a value of 0.06 in the octaethylene glycol to about 2.0 units in the triethylene glycol systems. The data in Table III, therefore, indicate that the polarity of a column decreases with decreasing sample concentration. Thus, caution must be used in trace analysis by gas chromatography since the apparent polarity of the column for small sample concentrations may be quite different from that determined for more nearly normal chromatographic concentrations.

Figure 8 shows the behavior of the Rohrschneider constants based on peak maxima as the length of the polymer is increased. A break in the curves between the pentaethylene glycol and the hexaethylene glycol species is evident. A possible explanation for such a discontinuity might involve a structural change in the stationary phase. Added evidence for this comes from the work of Persinger [34, 35] and Koenig [36] who have shown that the polyethylene glycol species begin to exhibit a spiralled structure for the penta- or hexa- ethylene glycol structure. The observed breaks in our data indicate that this spiralling becomes important for the hexaethylene glycol. Thus it appears that the tri- tetra- and penta-ethylene glycols are similar and probably

straight chains while the hexa- and octa- ethylene glycols structures are similar and probably spiralled.

Further examination of Figure 8 shows that the behaviors of the solutes on the glycol, with the possible exception of nitromethane, are parallel. Examination of data at other sample sizes shows similar characteristics. In the case of nitromethane, it should be pointed out again that this solute strongly conditioned the column, so the actual characteristics of its separation behavior are somewhat in doubt.

Discussion

The present study has served to emphasize the importance of sorption mechanisms in gas-liquid chromatography. By extending the retention data to very small sample sizes, adsorption on the surface of the support has been shown to lead to very large errors, even when reference compounds were used, especially if the polarities of the solute and solvent were different. By using reference compounds having more nearly the same polarity as the samples, such differences have been minimized in determinations of steriods and biologically oriented samples [37]. However, the use of different types of references would still leave the problem of relating the behaviors of compounds of different polarities to one another on a given column.

The present study has also shown that adsorption at the gas-liquid interface can be quite significant. It can be distinguished from adsorption at the gas-solid interface by working at higher percentages of liquid loading.

Probable sources for errors and deviations of results for many thermodynamic examinations of solution processes by chromatographic techniques have been elucidated by this study. In many instances, data for thermodynamic determinations have been obtained at very small sample concentrations on the assumption that the separation system was based only on solution mechanisms throughout the entire

sample range. However, our work clearly refutes such contentions and shows that data may often have been acquired in regions where sorption may have been a very significant contributor to the overall separation. Thus, to obtain valid thermodynamic data for a system, determination of the retention profile for that system is a necessary step so as to be able to select the best range of sample sizes. In any case, one should select sample sizes in a region where the principle separation mechanism is the one of interest. Because detectable sorption of some kind will be present in most systems, caution must be exercised. Therefore, methods such as those outlined by Conder and Purnell [2, 3, 33] appear necessary in order to determine valid thermodynamic values. The above procedures could also be applied in determinations of adsorption parameters, provided adequate determinations of the effective surface areas for each of the interfaces could be obtained.

Both peak means and peak maxima have been used throughout this study. The peak means are important since they are often easier to obtain by computer techniques involving moment analysis. Kucera [38] and Grubner [39] have also shown that the peak means are more meaningful from a thermodynamic viewpoint. However, the true value of the peak mean is very difficult to obtain if there is bad peak tailing. As a result the value of the peak mean often varies considerably, depending upon values chosen for the

beginning and end of the peak. Furthermore, peak means start to change rapidly at noticeably larger sample sizes than the peak maxima. In contrast retention volumes based on peak maxima are much less influenced by peak shape so they show less scatter in the data. Therefore, even though retention volumes based on peak means may have more theoretical meaning, retention volumes based on peak maxima may be more useful in practice when used for qualitative identifications.

In characterizing stationary liquids, Rohrschneider constants are often applied. Since Rohrschneider constants are comparisons between Kovats indices, they share the same problems as the Kovats indices. Again, the difficulties are particularly acute for small samples where the differences in polarities between the solute and solvent is large. However, as shown in Figure 8, reliable comparisons can be made between similar liquid phases with few exceptions provided sample sizes and conditioning are controlled.

The use of pure stationary phases showed several very useful qualities. Such specification of stationary phases gives a concrete means of identification. This should, in turn, help interlaboratory comparisons of data since it ought to be possible to prepare much more nearly identical columns. The use of single polymeric entities could also be extremely useful in another approach for

standardization in specifying stationary liquids. Instead of using mean average molecular weight as a specification, the separations obtained from a polymeric mixture could be expressed in terms relative to the separation qualities of a specific polymeric entity of that same series or a closely related series. However, even that approach will not be free from problems. The smaller polymeric entities of any series are usually the easiest to obtain in pure form and analyze for purity. However, they are relatively less useful because of greater volatility as was discovered for the polyethylene glycols and small species in a series may posess different structural features than those of larger species. Therefore, there may be a minimum size polymer which is of useful importance. Further studies with other stationary liquids are underway in which larger polymers and different types of polymers are being examined in order to determine the full capabilities and limitations of this approach. Finally, the present approach to characterization should be very useful if the recommendations of Preston [13] and McReynolds [14] concerning a set of standard stationary liquids are adopted in actual practice.

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TABLE I

CRITICAL COLUMN PARAMETERS

Stationary Liquid	Support	% Loading	Weight of Liquid in Column	Operating Temperature °C
Triethylene Glycol	Teflon	20.0	0.1741	60.0
Tetraethylene Glycol	Teflon	20.0	0.1706	60.0
Pentaethylene Glycol	Teflon	20.0	0.1717	60.0
Hexaethylene Glycol	Teflon	20.0	0.1709	60.0
Octaethylene Glycol	Teflon	20.0	0.1414	60.0
Squalane	Teflon	20.0	0.1735	60.0
Squalane	Teflon	9.9	0.1532	50.0, 60.0, 70.0
Squalane	Teflon	19.9	0.1806	50.0, 60.0, 70.0
Squalane	Teflon	22.0	0.1913	50.0, 60.0, 70.0
Squalane	Chrom P	10.1	0.0699	50.0, 60.0, 70.0
Squalane	Chrom P	15.3	0.1069	50.0, 60.0, 70.0
Squalane	Chrom P	22.3	0.1742	50.0, 60.0, 70.0
Squalane	Chrom P	29.5	0.2492	50.0, 60.0, 70.0

TABLE II

Kovats Indices for Mean and Maximum Peak Retention Volumes as a Function of Sample Size.

All data were determined at 60.0°C on columns containing 20% by weight liquid on Teflon.

Mole Ratio[a]	Peak Mean			Peak Maximum		
	SQUAL[b]	TRI[b]	HEXA[b]	SQUAL[b]	TRI[b]	HEXA[b]
Benzene						
$1x10^{-3}$	640.03	-	902.01	640.43	925.32	907.37
$5x10^{-4}$	640.01	931.43	900.01	640.43	934.06	907.35
$1x10^{-4}$	639.98	907.76	895.76	640.43	927.49	904.23
$5x10^{-5}$	639.80	900.70	897.63	640.43	922.59	903.60
$1x10^{-5}$	639.68	891.55	893.28	640.36	917.06	902.01
$5x10^{-6}$	639.66	892.52	892.53	640.68	916.18	901.44
$1x10^{-6}$	639.65	896.47	890.15	641.02	909.48	902.13
$5x10^{-7}$	639.65	896.91	889.23	641.07	908.74	901.07
$1x10^{-7}$	639.65	897.27	888.72	641.11	908.24	901.03
$5x10^{-8}$	639.65	897.31	888.63	641.11	908.20	901.03
Ethanol						
$1x10^{-3}$	394.22	-	983.36	392.87	1016.98	977.69
$5x10^{-4}$	394.34	1051.98	983.32	392.97	1041.98	988.99
$1x10^{-4}$	394.44	1066.65	977.12	393.05	1091.39	988.40
$5x10^{-5}$	394.45	1061.72	975.94	393.06	1083.37	986.19
$1x10^{-5}$	394.45	1051.02	979.54	393.07	1075.14	985.54
$5x10^{-6}$	457.48	1049.29	978.19	426.67	1070.71	986.03
$1x10^{-6}$	492.80	1047.85	976.02	450.87	1045.35	987.11
$5x10^{-7}$	497.35	1047.71	975.71	454.14	1036.78	987.27
$1x10^{-7}$	500.91	1047.56	975.46	456.79	1028.52	987.41
$5x10^{-8}$	501.32	1047.55	975.42	457.12	1027.39	987.42

[a]Ratio of number of moles of sample to number of moles of solvent.

[b]Abbreviations are SQUAL = Squalane, TRI = Triethylene glycol, HEXA = Hexaethylene glycol.

Table III

Rohrschneider Constants for Five Polyethylene Glycol Oligomers as a Function of Sample Size.

All values were determined at 60.0°C from columns containing 20% by weight liquid on Teflon.

Mole Ratio[a]	Peak Mean					Peak Maxima				
	BZb	ETOHb	MEKb	NMb	PYb	BZb	ETOHb	MEKb	NMb	PYb
					Triethylene Glycol					
$5x10^{-3}$	1.72	4.88	2.87	---	---	1.71	4.96	2.89	4.53	---
$5x10^{-4}$	---	6.58	4.86	6.04	2.85	2.94	6.49	4.28	6.06	3.44
$5x10^{-5}$	2.61	6.67	3.97	6.50	4.40	2.82	6.90	4.24	6.73	4.55
$5x10^{-6}$	2.53	5.92	3.79	6.32	4.28	2.75	6.44	4.18	6.53	4.28
$5x10^{-7}$	2.57	5.50	3.77	6.29	4.26	2.67	5.83	3.90	6.45	4.29
$5x10^{-8}$	2.57	5.46	3.77	6.31	4.26	2.67	5.70	3.87	6.44	---
					Tetraethylene Glycol					
$5x10^{-3}$	2.66	5.38	3.68	4.89	---	2.75	5.74	3.82	5.38	---
$5x10^{-4}$	2.98	6.66	4.41	6.47	4.41	2.91	6.60	4.10	6.64	4.69
$5x10^{-5}$	2.64	6.35	3.82	6.39	3.94	2.81	6.48	3.99	6.49	4.13
$5x10^{-6}$	2.59	5.69	3.69	6.37	3.82	2.79	6.16	3.96	6.51	3.95
$5x10^{-7}$	2.48	5.29	3.58	6.37	3.80	2.78	5.85	3.95	6.39	3.98
$5x10^{-8}$	2.47	5.25	3.57	6.39	3.80	2.78	5.82	3.95	6.38	---

Table III cont.

Mole Ratio[a]	Peak Mean					Peak Maxima				
	BZ[b]	ETOH[b]	MEK[b]	NM[b]	PY[b]	BZ[b]	ETOH[b]	MEK[b]	NM[b]	PY[b]
					Pentaethylene Glycol					
$5x10^{-3}$	---	5.12	---	4.61	---	2.34	5.21	3.41	4.79	---
$5x10^{-4}$	2.82	---	3.93	6.55	---	2.94	---	4.07	6.69	4.53
$5x10^{-5}$	2.74	6.26	3.86	6.48	4.02	2.85	6.36	3.97	6.63	4.14
$5x10^{-6}$	2.69	5.41	3.72	6.48	3.99	2.83	6.01	3.94	6.62	4.14
$5x10^{-7}$	2.69	5.23	3.76	6.48	3.98	2.82	5.78	3.91	6.62	---
$5x10^{-8}$	2.69	5.19	3.83	6.51	---	2.70	5.77	3.93	6.62	---
					Hexaethylene Glycol					
$5x10^{-3}$	2.11	5.21	3.11	5.56	---	2.12	5.13	3.14	4.90	---
$5x10^{-4}$	2.60	5.89	3.62	6.04	3.21	2.67	5.96	3.66	6.08	3.74
$5x10^{-5}$	2.58	5.81	3.56	6.24	3.76	2.63	5.93	3.65	6.36	3.86
$5x10^{-6}$	2.53	5.21	3.46	6.16	3.62	2.61	5.59	3.61	6.31	3.80
$5x10^{-7}$	2.50	4.78	3.44	6.13	3.61	2.60	5.33	3.59	6.29	3.79
$5x10^{-8}$	2.49	4.74	3.44	6.15	3.60	2.60	5.30	3.59	6.29	---
					Octaethylene Glycol					
$5x10^{-3}$	---	---	3.58	6.23	---	2.70	5.75	3.63	6.22	---
$5x10^{-4}$	2.62	5.73	3.54	6.68	4.12	2.71	5.81	3.62	6.72	4.32
$5x10^{-5}$	2.59	5.66	3.51	6.60	3.78	2.68	5.78	3.61	6.68	3.73
$5x10^{-6}$	2.62	5.67	3.47	6.58	3.73	2.66	5.45	3.58	6.65	3.67
$5x10^{-7}$	2.63	4.73	3.46	6.58	3.73	2.66	5.18	3.56	6.65	3.65
$5x10^{-8}$	2.63	4.70	3.46	6.59	---	2.66	5.15	3.56	6.64	---

Table III cont.

[a]Moles of solute per moles of solvent

[b]Abbreviations. BZ = Benzene, ETOH = Ethanol, MEK = Methyl ethyl ketone
NM = Nitromethane, Py = Pyridine.

List of Figure Captions

Figure 1. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on a 10.1% by weight squalane on Chromosorb P at 50.0 °C.

Figure 2. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on a 15.3% by weight squalane on Chromosorb P at 50.0 °C.

Figure 3. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on 22.3% by weight squalane on Chromosorb P at 50.0 °C.

Figure 4. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on 9.9% by weight squalane on Teflon at 50.0 °C.

Figure 5. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on 19.9% by weight squalane on Teflon at 50.0 °C.

Figure 6. The spreading of retention volumes for peak means and peak maxima. As peak tailing increases the distance between the peak means (B) becomes larger than the distance between the peak maxima (A).

Figure 7. Peak profiles based on peak maxima for 2-butanane (solid line) and nonane (broken line) on 20% Hexaethylene glycol at 60.0 °C.

Figure 8. The effect of polymer length upon the Rohrschneider constants.

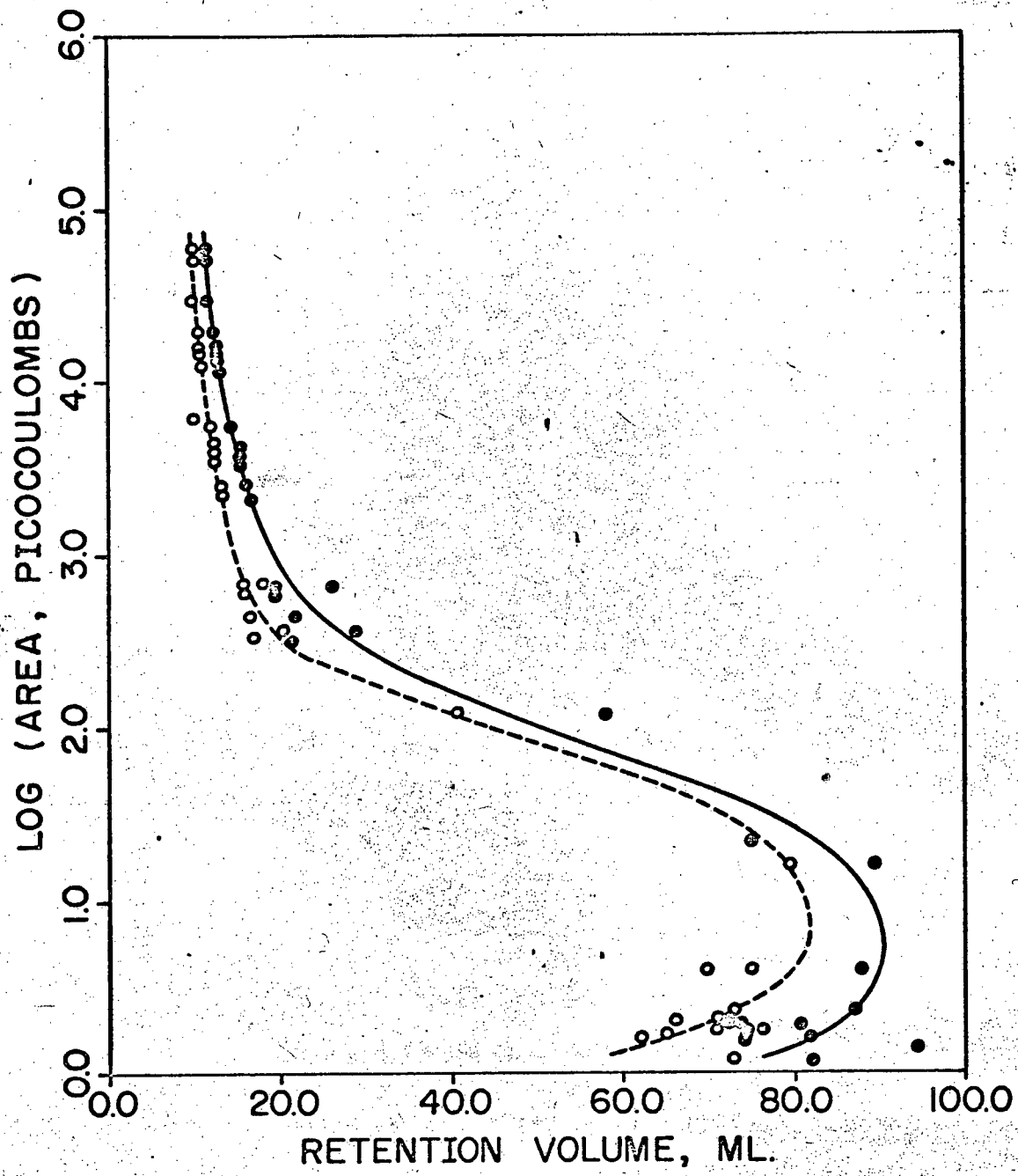


Figure 1. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on a 10.1% by weight squalane on Chromosorb P at 50.0°C.

FIG 2

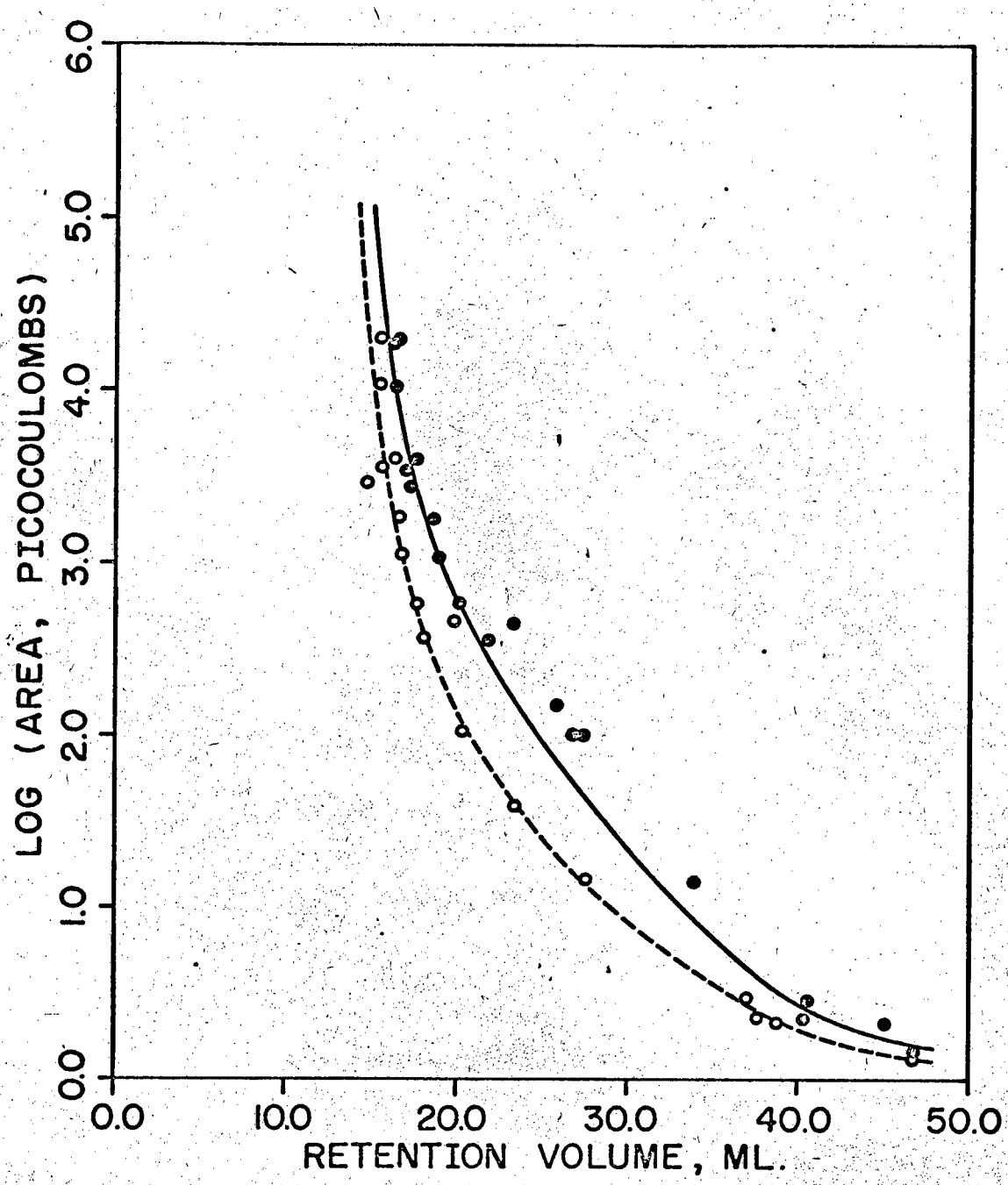


Figure 2. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on a 15.3% by weight squalane on chromosorb P at 50.0°C.

FIG 3

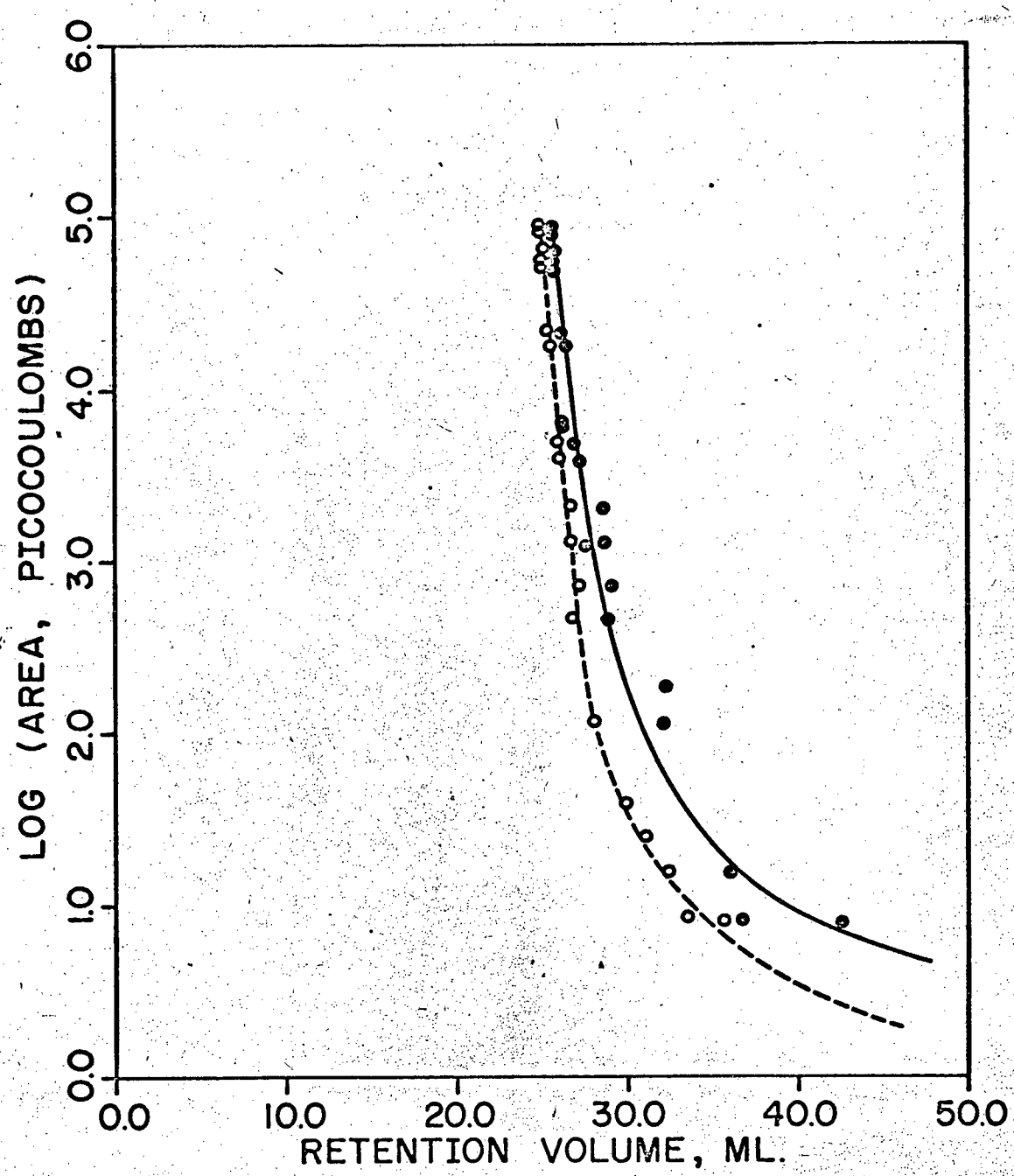


Figure 3. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on 22.3% by weight squalane on Chromosorb P at 50.0°C.

FIG 4

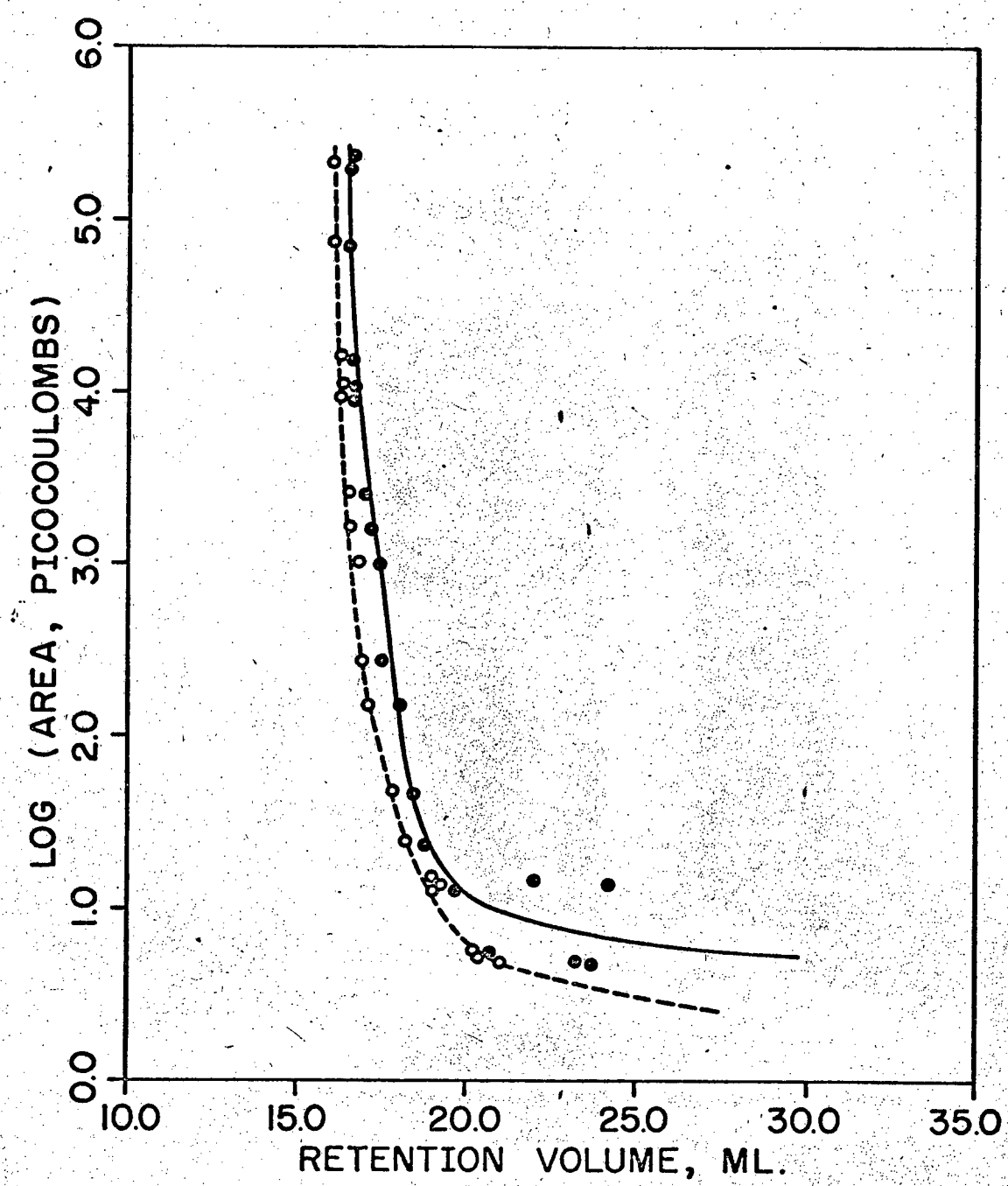


Figure 4. Retention profiles based on peak means (solid line) and peak maxima (broken line) for 2-butanol on 9.9% by weight squalane on Teflon at 50.0°C.

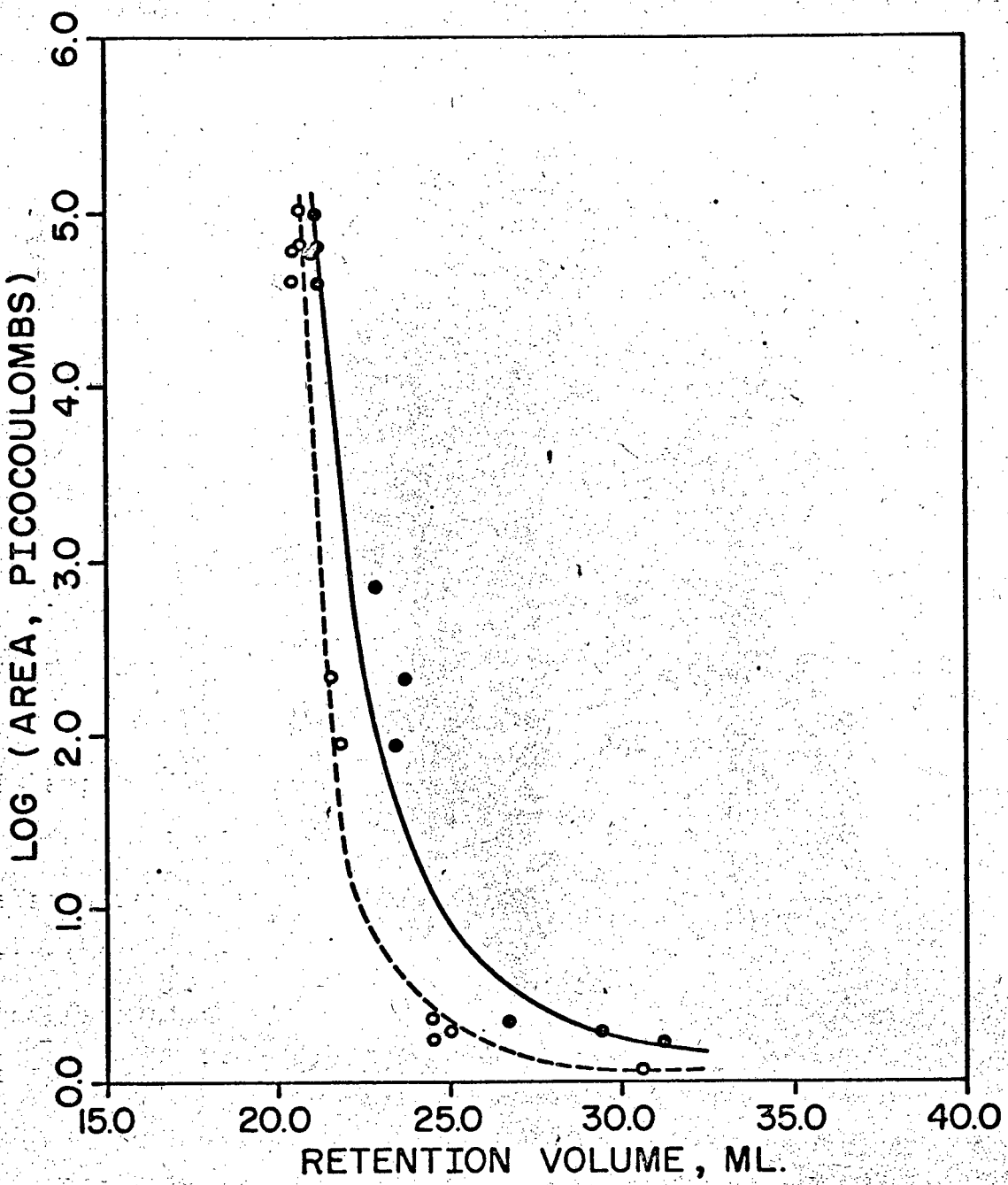
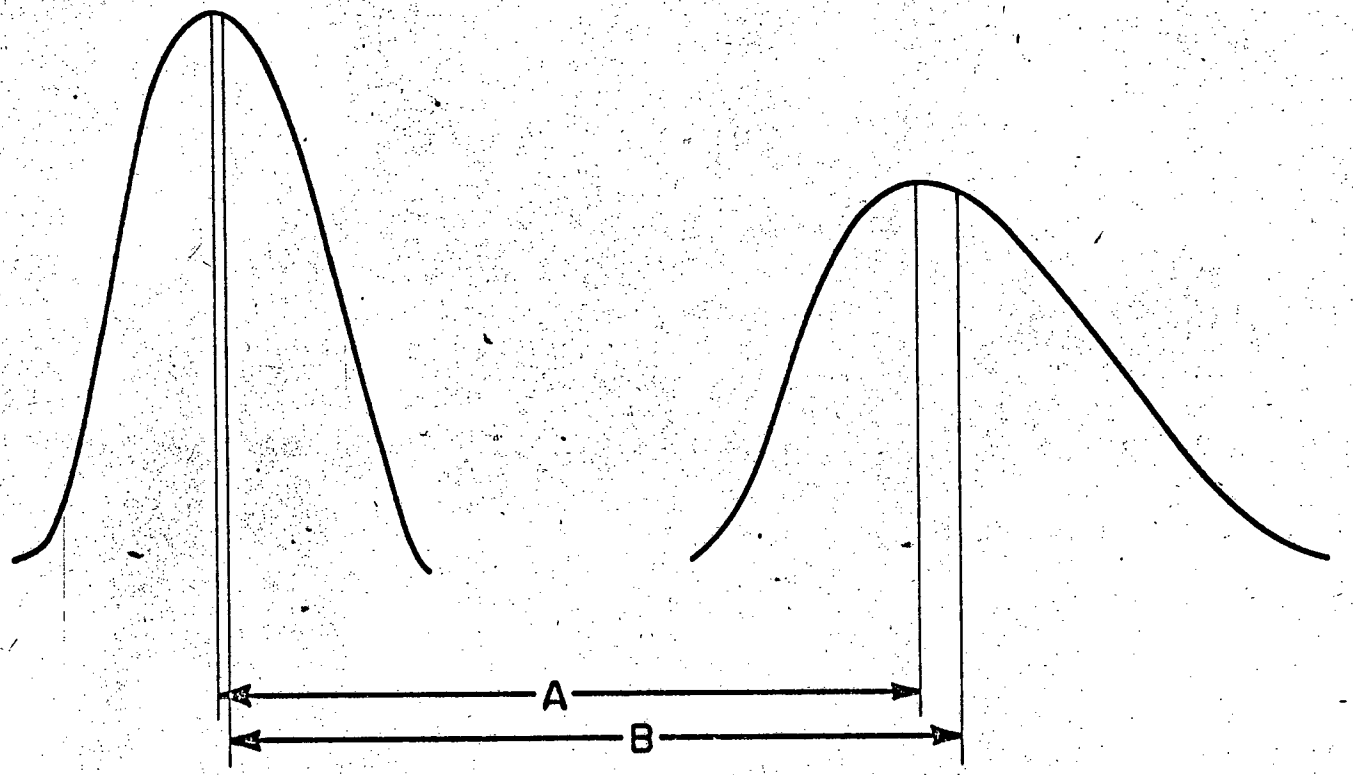


Figure 5. Retention profiles based on peak means (solid line) and peak maxima (broken line for 2-butanol on 19.9% by weight squalane on Teflon at 50°C.



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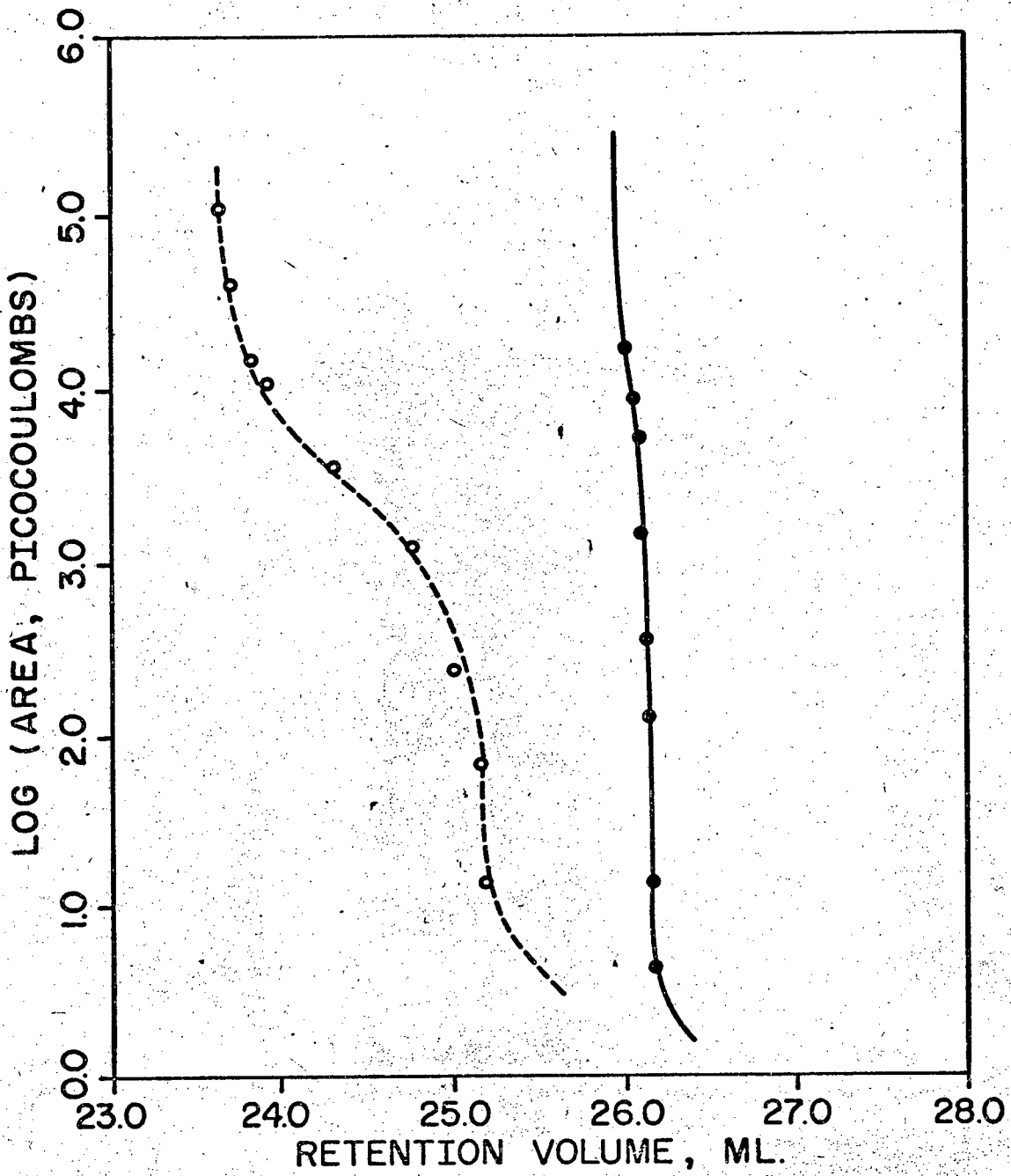
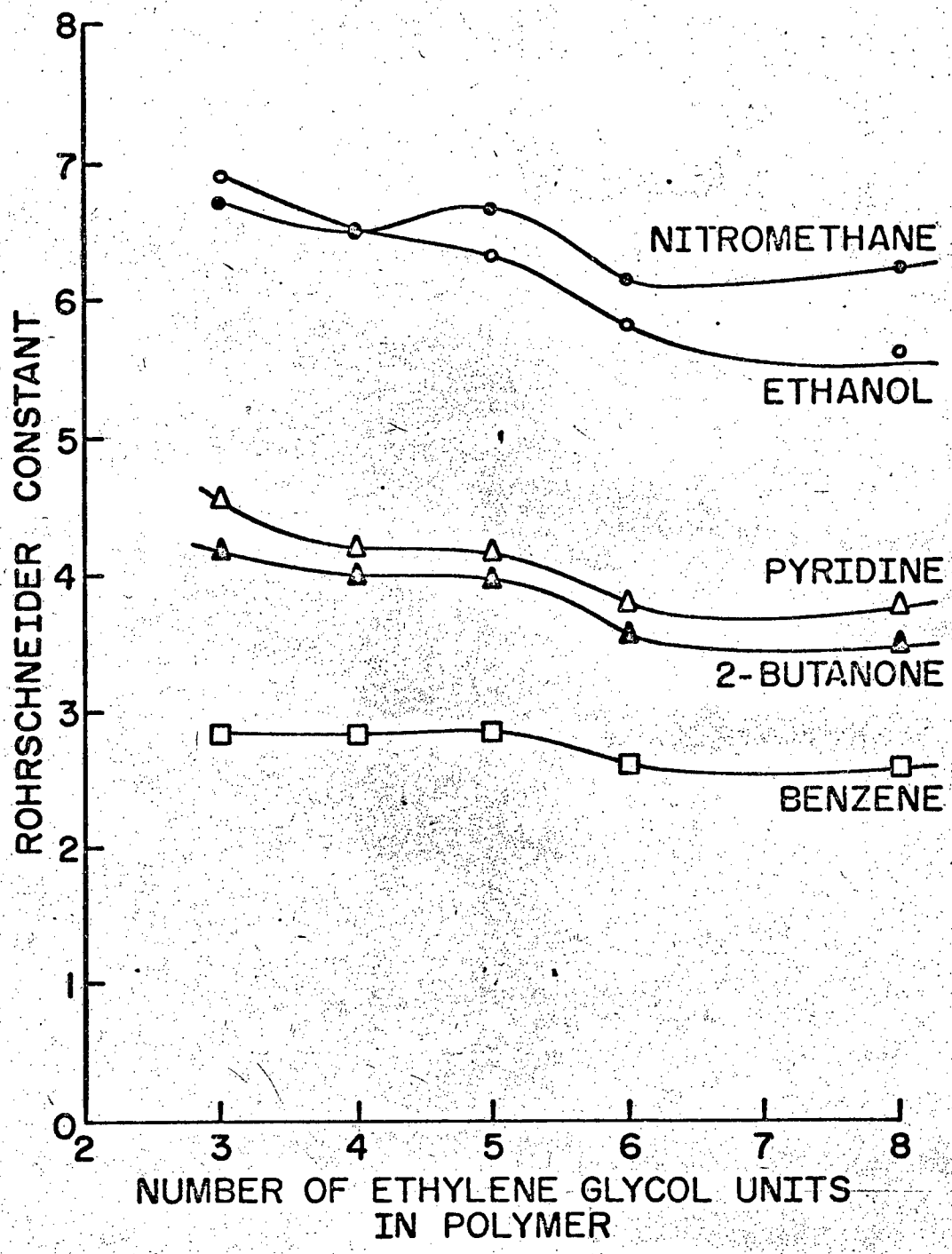


Figure 7. Peak profiles based on peak maxima for 2-butanone (solid line) and nonane (broken line) on 20% Hepaethylene glycol at 60.0°C.



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