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Effects of Slow Mass Transfer When Using Microporous Adsorbents in Gas–Solid Chromatography

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Summary

The elution behaviors of CH_4, C_2H_6, n-C_3H_8, iso-C_4H_{10}, Ar, O_2, N_2, and SF_6 were studied in A-type zeolites containing K^+, Na^+, Li^+, Sr^{2+}, Ca^{2+}, and Mg^{2+} and on a 10X zeolite. Temperature- and flow-dependent tailing of peaks and changes in retention volume with flow rate were found for those adsorbates able only to partially penetrate the pores. When diffusivities were large enough to allow total access to the pores, molecular size and the degree of adsorption for the adsorbate had significant effects on HETP values.

INTRODUCTION

The synthetic zeolites have been used as adsorbents in gas–solid chromatography to effect a wide variety of analytical separations. Due to their well-defined pore size and structure (*1*), many separations are possible due to the exclusion of larger molecules from the large internal surface area. Thus, straight-chain and branched-chain hydrocarbons are separated (*2*), as also are aromatic and cyclic hydrocarbons from aliphatic species (*3*). In addition to such molecular effects, the activity of the zeolite surface allows separations based on adsorption. Examples are the separations of permanent gases (*4*) and low molecular weight hydrocarbons on the large internal surface,

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and also the separation of heavier, bulkier molecules on the smaller external surface (*5*).

Since the majority of these separations involve adsorbate molecules that can enter the pores of the zeolites to some degree, the possible effects of slow or restricted intraparticle diffusion on peak shape and retention behavior are of interest. In static gas-adsorption measurements, the presence of slow diffusion into and out of small pore openings has been noted. Anomalously low results for surface area were found for coals and other active porous carbons (*6*). In many cases, the adsorption of gases on various natural and synthetic zeolites showed a very slow approach to equilibrium (*7*). The effects of porosity under the dynamic conditions of gas chromatography have been the subject of a limited number of investigations. Kiselev (*8*) has shown that the height equivalent to a theoretical plate (HETP) increased as pore diameter decreased. His studies with bulk- and surface-porous glasses revealed increases in HETP as constant-diameter pores were made deeper. However, in both studies, the pore diameter was at least two to three times the molecular diameter of the adsorbate. Kiebal et al. (*9*) have attributed low heats of adsorption for the larger members of a homologous series of *n*-paraffins on porous silicas to the effects of restricted diffusion. Also using gas chromatography, Habgood (*10*) measured heats of adsorption for methane and ethane on a wide-pore zeolite, and the disparity between those values and the values measured on a narrow-pore zeolite were rationalized as due to restricted diffusion in the latter case (*11*). Unexpected increases in HETP with increasing temperature have been observed by Altenau and Rogers (*12*) in studies of inorganic salts as chromatographic adsorbents. They suggested that, at the higher temperature, an increased rate of diffusion into fine pores, which contained higher energy adsorption sites, could have been responsible, at least in part, for the anomalous behavior. Surface area measurements using various sized adsorbates have demonstrated that there are micropores present in these inorganic salts (*13*). Oberholtzer and Rogers (*14*) attributed anomalous behavior in the variation of HETP with temperature for methane and ethane on two different zeolites to the effects of slow intraparticle diffusion. They also suggested that the changes in retention volume with flow rate observed were due to the same cause.

For the present study, a series of synthetic zeolites were used as adsorbents. They have a uniform, well-characterized pore structure

(*1*), and the nominal pore size can be varied by exchanging the metal cations. Because these cations occupy positions in the pore channels of the zeolite and partially block these channels, the size of the cation influences the pore dimensions. The sodium form of the A-type zeolite, NaA, has a nominal pore opening of 4 Å, but when potassium ions replace the sodium ions, a pore opening of 3 Å results (*15*). Replacement of the sodium ions with calcium gives a nominal pore size of 5 Å (*15*). Here the exchange of one divalent cation for two monovalent sodium ions effectively enlarges the pore opening. Breck et al. (*7*) have shown that replacement of the calcium with magnesium ions results in a still larger pore size. In addition to changes in the pore size, the substitution of various cations influences the adsorptive properties of the zeolites (*10*).

In the present study, the elution behavior of several different adsorbates was determined as a function of temperature and flow rate on seven different synthetic zeolites. The adsorbates, CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, O_2, Ar, N_2, and SF_6, represented a range of molecular-size types, while the zeolites, KA, NaA, LiA, SrA, MgA, and 10X, represented a range of pore sizes and surface activities.

EXPERIMENTAL

Apparatus and Materials

The gas chromatograph has been described previously (*16*). The only significant change was the use of a thermal conductivity detector (Model 100, Carle Instruments, Inc., Fullerton, Calif.) instead of a flame ionization detector. The output from the detector bridge circuit was amplified from 10 mV full scale to 4 V full scale and then fed to the voltage-to-frequency converter.

Samples of KA and 10X zeolite were obtained in a 60–80 mesh cut (Coast Engineering Laboratory, Redondo Beach, Calif.), while the NaA and CaA zeolites were 70–80 mesh (Analabs, Inc., Hamden, Conn.). The LiA zeolite was prepared by slurrying a sample of NaA in a 2-*M* solution of $LiNO_3$ for 72 hr at room temperature. The exchanged zeolite was filtered and washed with fifteen 100-ml portions of distilled water, and then dried at 135°C for 12 hr before being weighed out and packed into a column. The preparation of the SrA and MgA species proceeded in an analogous fashion, except that the CaA species was the precursor. After preliminary drying, the samples were resieved to 70–80 mesh.

Methane, ethane, propane, isobutane, oxygen, argon, and sulfur hexafluoride were research grade (J. T. Baker Specialty Gases, Chicago, Ill.). The nitrogen used was high-purity grade (Matheson Co., Inc., East Rutherford, N. J.).

Procedures

The zeolites were packed in 0.18 cm i.d. × 40 cm stainless steel columns. Column packings ranged from 0.70 g for the 3A (LiA) species to 0.72 for SrA. Immediately prior to use, each column was conditioned for 24 hr at 400°C, with a helium-purge flow of 10 ml/min. The purge gas was first passed through two consecutive traps of 5A molecular sieve immersed in liquid nitrogen.

Calculations

The punched paper-tape output of the digitizer was processed and calculations (e.g., HETP) performed in a manner analogous to that described previously (*16*), except that the programs were modified for use on a small, general-purpose computer (Hewlett-Packard Model 2116A, Palo Alto, Calif.).

All flow rates and retention volumes were adjusted to the column temperature and were corrected for pressure drop. This means that, in the absence of other effects (e.g., adsorption), recorded retention volumes will be different for different column temperatures.

RESULTS

For the several adsorbates run at various flow rates at two different temperatures, two areas of behavior will be stressed. The first is the peak shape as a function of flow rate and temperature. A convenient and widely used parameter related to peak width is the height equivalent to a theoretical plate, HETP. The effects of many diffusional and adsorptive processes on peak broadening, as reflected by the HETP, have been discussed (*17*, *18*).

Peak skewing can be discerned by comparison of the retention volume of the peak maximum, VRMAX, with that of the peak mean, VRMEAN. In theory, VRMEAN is the parameter of true physical significance, but VRMAX is still widely used, and the difference serves here to indicate any skewing. For an undistorted Gaussian profile, these two retention volumes are identical. If the peak is skewed, then a disparity will result, with a tailed peak showing VRMEAN greater than VRMAX, and vice versa for a peak with a diffuse front edge. While more sophisticated and elaborate parameters are available to define peak skewing, the above approach was sufficient for the purpose of this study.

The second area of interest is the behavior of the absolute value of VRMEAN and VRMAX as a function of flow rate and temperature. Changes with temperature can indicate that adsorption is taking place. Differences in VRMEAN and VRMAX for different species under similar conditions may reflect the exclusion of one species from the pore volume, although adsorption can cause ambiguity here. Finally, if equilibrium does not exist in the adsorption and mass-transfer processes; changes in retention volume, measured by VRMEAN and VRMAX, with flow rate can result.

Accurate absolute measurements of flow rate represented a problem that will become evident later. However, the effect of that difficulty was circumvented to some extent by comparing in a relative way the behaviors of several adsorbates run at the same flow rate. Comparisons between different flow rates *do* include those irregularities, as will be seen later.

After this work had been completed, Habgood (*18a*) pointed out that the value of our relative measurements could have been further enhanced if the entire gas volume of the column, including micropores, had been obtained using a small molecule, such as hydrogen, which could enter all pores but would be adsorbed to a negligible extent. Likewise, determination of the micropore volume should have been made in each case by using a large adsorbate like SF_6 and finding the limiting retention volume at a high temperature. We concur with his suggestions and strongly recommend that such measurements be included in future studies.

KA Zeolite

This zeolite had the smallest pore size with a normal diameter of 3 Å (*15*). This means that all of the adsorbates in this study should be excluded from the interior of the zeolite.

Figure 1 shows the van Deemter plots for O_2 and SF_6, the smallest and largest adsorbates, as a function of temperature. These plots show the expected behavior with flow rate and temperature for slightly or nonadsorbed species. At flows less than the minimum in the curve, the

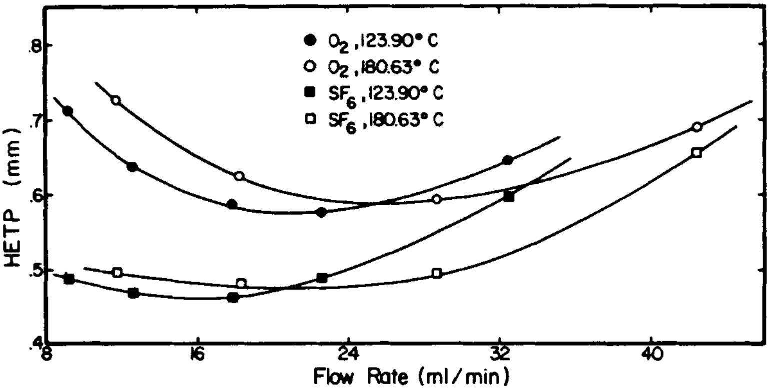

FIG. 1. Van Deemter curves for O_2 and SF_6 on KA zeolite.

HETP is greater at the higher temperature, due to greater longitudinal diffusion at the higher temperature. Past the minimum, the opposite is true since, in this mass-transfer region of flow, HETP is inversely proportional to the diffusion coefficient. The differences between SF_6 and O_2 are most likely due to the differences in their diffusion coefficients, the coefficient for the smaller size and lighter O_2 being greater. The fact that, qualitatively, the behavior for these two species, representing the extremes in size, was the same indicated that the porosity of the adsorbent was of no importance.

Some peak skewing was evident from the fact that ΔVR, (VRMEAN − VRMAX), was always positive and varied with the flow rate. ΔVR ranged from approximately 0.03 to 0.01 ml as the flow rate decreased from approximately 40 to 10 ml/min. Since the same trend was evident for all species, it was attributed to an extra-column effect.

VRMAX values for all species, except isobutane, were the same within 2% at each temperature, thereby indicating little or no adsorption. VRMAX for isobutane was greater, particularly at the lower temperature, as a result of its adsorption on the external surface. VRMAX for all species showed a decrease with decreasing flow rate. The similarity of the trend for all species suggests an instrumental error, most likely in the measurement of flow rate.

NaA Zeolite

The nominal pore size for the NaA zeolite is 4 Å (*15*), and, under static conditions, all the adsorbates except isobutane and sulfur hexafluoride can enter the pores. Under the dynamic conditions of gas chromatography, a range of behavior was observed which indicated that only the smaller adsorbates were able to penetrate the pores to any extent.

In Figs. 2 and 3 the retention behaviors for ethane, methane, argon, nitrogen, and oxygen are shown. Each of the adsorbates was run at a given flow rate in each of the figures. Hence, effects due to errors in flow-rate measurement should not be important in comparisons of different adsorbates at a particular flow rate. Likewise, it is possible to compare the behaviors of different gases with flow rates. However, valid comparisons cannot be made on an absolute basis between the data in Figs. 2 and 3 for two reasons. First, the data were obtained at widely different times with different lengths of connecting tubing (and dead volumes) because the chromatograph was being shared with many others. Second, because retention volumes were calculated for the temperature of the column in question, the retention values at different temperatures cannot be directly compared. Nevertheless, valuable deductions can be made from the relative values for different adsorbates.

The behaviors of methane and ethane were very similar in that VRMAX and VRMEAN were relatively constant with flow rate, as

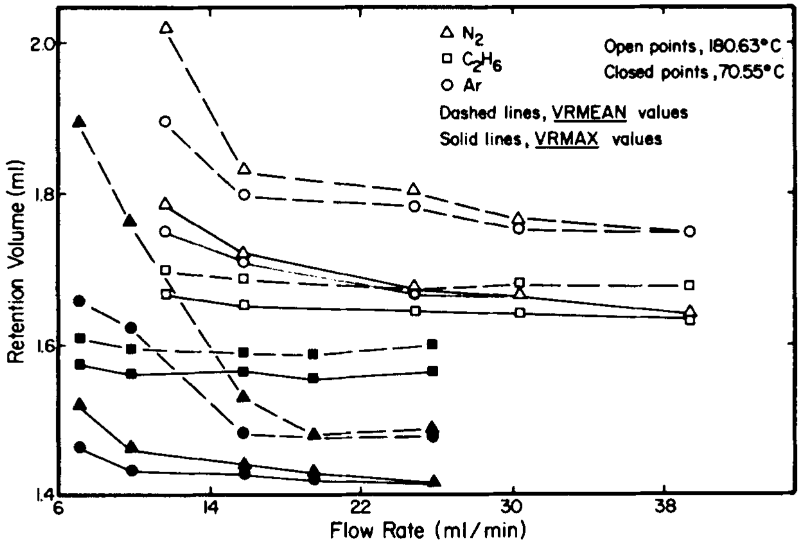

FIG. 2. Retention behavior for Ar, N_2, and C_2H_6 on NaA zeolite.

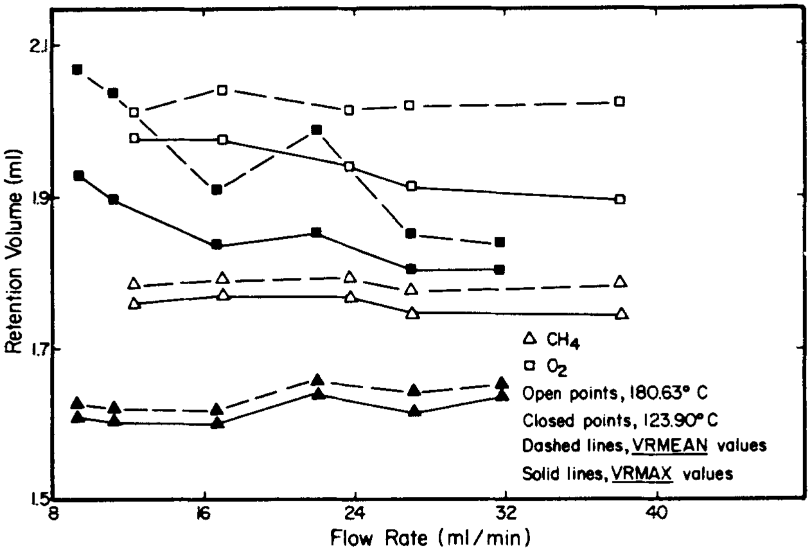

FIG. 3. Retention behavior for CH_4 and O_2 on NaA zeolite.

seen before with the KA zeolite. For nitrogen, argon, and oxygen, however, there were significant increases in VRMAX with decreasing flow rate at both temperatures. VRMEAN values showed similar behavior except for oxygen at the higher temperature. At that temperature, VRMEAN was relatively constant with flow rate, causing ΔVR to decrease with decreasing flow rate. At both temperatures, the retention volumes for oxygen were always greater than those for methane, an effect that cannot be explained by adsorption.

From the work by Oberholtzer and Rogers (*14*) and Habgood and MacDonald (*19*), the progressive changes in the peak profile as penetration into the pores increases (due to higher diffusivity because of higher temperature, slower flow rate, or smaller adsorbate) can be described as follows. For an adsorbate excluded from the pores, peak shape and retention volume are unaffected by flow rate except for the normal symmetrical band broadening. When conditions are such that the adsorbate molecules can just barely enter the pores, the peak will exhibit an extended tail, which is dependent on flow rate. As long as the fraction of the sample that can enter the pores is small, this tail will be a minor part of the peak profile, and VRMAX will remain relatively constant, although VRMEAN will begin to increase, due to the tail. As the degree of penetration increases, the tail will become a larger fraction of the total peak area, causing VRMAX to shift to larger values. If adsorption is neglected, the shift in the peak location will continue until it has gone from the retention volume corresponding to the interstitial volume to that for the interstitial volume *plus* the pore volume. Finally, the retention volume, as measured by VRMAX or VRMEAN, will become constant with flow rate when the accessibility to the pores is great enough. The presence of adsorption will, of course, result in a larger retention volume than that for a nonadsorbed species.

If the retention behavior for the five adsorbates is considered in the light of the preceding discussion, several conclusions can be drawn. It appears that methane and ethane do not penetrate the pores of the NaA zeolite in the range of temperatures and flow rates studied. Nitrogen, argon, and oxygen, on the contrary, all penetrate the pores to varying degrees. At the lower temperature, VRMAX, VRMEAN, and ΔVR all increase for these three adsorbates as the flow rate decreases. However, the change in VRMAX is greatest for oxygen, while ΔVR changes least. This behavior suggests that oxygen penetrates the pores to a greater extent than either argon or nitrogen, since the tailing has become large enough to affect VRMAX to the greatest degree. The fact that changes in VRMAX and VRMEAN for argon and nitrogen commenced at lower flow rates than for oxygen lends additional support to that idea.

At the higher temperature, nitrogen and argon begin to show increases in VRMAX and VRMEAN at higher flow rates than at the lower temperature, as might be expected from their increased diffusivities. This indicates a greater penetration into the pores, but still not free access, even at the lowest flow rates. For oxygen the change in VRMAX is less at the higher temperature than at the lower temperature, and VRMEAN remains fairly constant with flow rate. Also ΔVR at the lowest flow rate is similar in magnitude to that seen for the excluded species, methane and ethane. This suggests that, at this temperature, oxygen, the smallest adsorbate, enjoys almost free and unhindered access to the pores, especially at the lowest flow rate.

One final point concerns the disparity in the retention volumes for nitrogen and argon, and how that difference is affected by the flow rate. Nitrogen, having a quadrupole moment while argon does not, has been shown always to adsorb more strongly on the cationized internal surfaces of zeolites than argon (*20*). On this NaA zeolite, nitrogen and argon do not enter the pores at the fastest flow, and the

VRMAX and VRMEAN values are similar at both temperatures, thereby indicating similar behavior on the external surface. However, as the flow rate decreases, both adsorbates are able to penetrate the pores. Because nitrogen is more strongly adsorbed, both VRMAX and VRMEAN for this adsorbate are larger than for argon.

In Fig. 4, van Deemter curves for four of the five adsorbates discussed above are shown at two temperatures. On this scale, the curves for ethane and methane are not resolved so only the points for methane are shown. The variation in behavior with temperature was also not discernible. However, for methane and ethane the curves and their behaviors with temperature are quite similar to those found with the KA zeolite, indicating again that methane and ethane are excluded from the pores. For both nitrogen and argon, but particularly nitrogen, the curves show a considerable increase in HETP at lower flow rates; much more so than for methane or ethane. This behavior correlates well with the large increases in ΔVR at low flow rates and, thus, an increase in peak width, as discussed above.

The effect of temperature lends further support to those ideas. At the lower temperature, the van Deemter curves for nitrogen and argon above 16 ml/min appear similar to those for methane and ethane, which, again, might have been expected from the behaviors of their

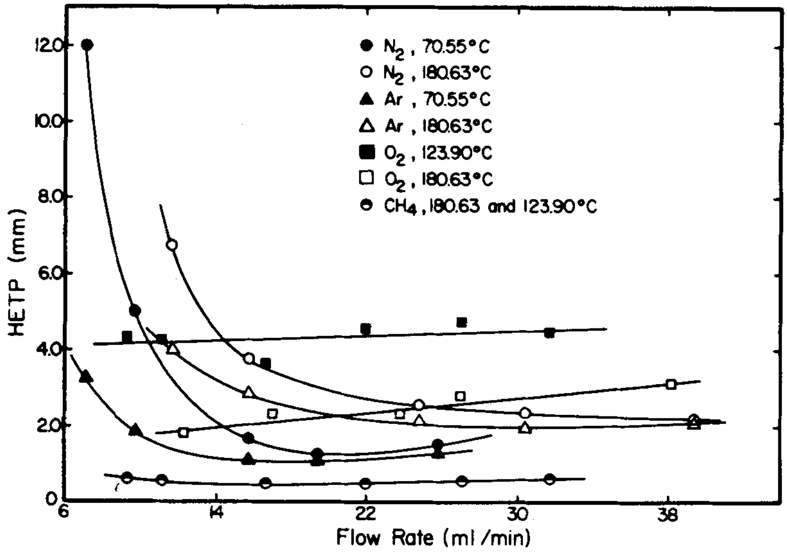

FIG. 4. Van Deemter curves for N_2, Ar, O_2, and CH_4 on NaA zeolite.

retention volumes. At the higher temperature, the distinctive shape of the curves, compared to those for methane and ethane, is evident well past 30 ml/min. Moreover, the van Deemter curves for oxygen at the two temperatures were very different in shape from those for any other adsorbates, reflecting the greater penetration for this molecule. As will be shown below, that same general shape for a van Deemter curve is found for molecules having easy access to the larger pores of the SrA, CaA, and MgA zeolites.

From comparisons of the van Deemter curves for the NaA zeolite, it is obvious that there is a range of behavior for the different sizes of adsorbates. In fact, the NaA zeolite was the one on which the differences in size produced the greatest variety in behavior.

LiA Zeolite

The lithium ion is the smallest of the three monovalent cations and, therefore, should result in a somewhat larger pore size for the LiA zeolite than that for NaA. The retention behaviors for two adsorbates oxygen and nitrogen on this zeolite are shown in Fig. 5. The behavior of nitrogen was representative of that shown by methane, ethane, isobutane, and argon on this zeolite. No increase in VRMAX and

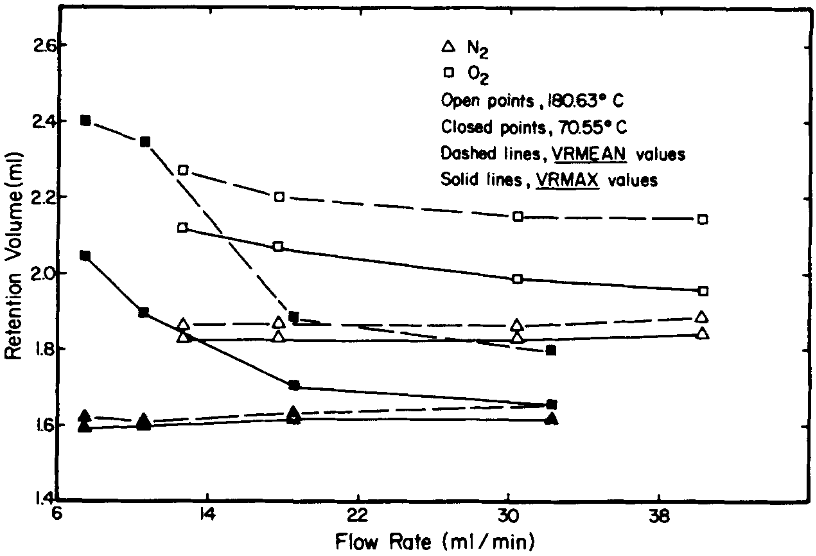

FIG. 5. Retention behavior for N_2 and O_2 on LiA zeolite.

VRMEAN at lower flow rates is evident, nor is Δ*VR* larger, which suggests that nitrogen was excluded from the pores. Oxygen, on the other hand, does appear to have been affected by the porosity of the adsorbent. As for methane and oxygen on NaA, nitrogen and oxygen were run at the same flow rates. The fact that the retention volumes for oxygen are always greater than those for nitrogen is difficult to ascribe to adsorption on the external surface, so it must be adsorption on the internal surface. At the lower temperature, oxygen shows a significant increase in VRMAX at the lower flow rates, along with an increase in Δ*VR*. As discussed earlier, this behavior indicates partial equilibration with the pores. At the higher temperature, VRMAX does not change as much, and Δ*VR* shows a small decrease, although VRMEAN does increase somewhat. This situation is similar to that for oxygen at the higher temperature on the NaA zeolite.

The van Deemter curves for nitrogen and oxygen are shown in Fig. 6. Unexpectedly, the magnitude, shape, and variation with temperature of the curves for nitrogen were similar to those for the other excluded species, and were also similar to those for methane and ethane on the KA and NaA zeolites. At this scale, the variation in the nitrogen curve with temperature is not discernible. Oxygen on this zeolite shows much larger HETP values than the other adsorbates and exhibits a distinctive change with temperature.

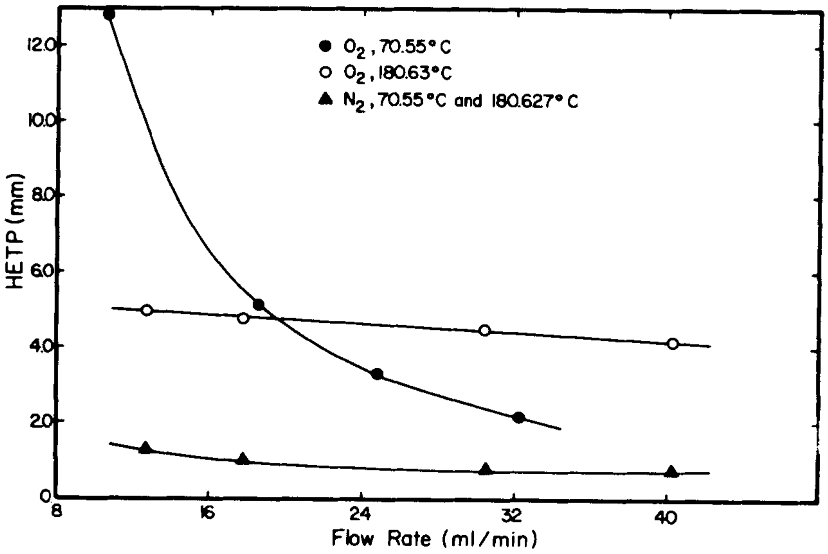

FIG. 6. Van Deemter curves for O_2 and N_2 on LiA zeolite.

As mentioned above, the retention behavior of oxygen at the higher temperature was similar to that found for oxygen at the same temperature on NaA. This similarity extends to the van Deemter curves for these two different situations to some degree, as seen in the flatness of both curves. However, for LiA the minimum in the curve is at higher flow rates. At the lower temperature, where there are large increases in ΔVR for oxygen, the curve resembles the van Deemter curve for nitrogen on NaA. There were also large increases in ΔVR with decreasing flow rate.

The above results suggest that the degree of penetration for oxygen on LiA is less than that for nitrogen or argon on NaA. Also, nitrogen appears to be excluded from the pores on LiA. One must, therefore, conclude that LiA has a somewhat smaller nominal pore size than NaA. A possible explanation may be that the lithium ion is not so easily dehydrated as the sodium ion during the conditioning procedure, so that small amounts of tenaciously retained water effectively decreased the pore size. Habgood (*21*) has observed similar problems with residual water on zeolites.

SrA, CaA, and MgA Zeolites

Results for the several adsorbates on the three zeolites containing the divalent cations can be conveniently discussed together, since all of the adsorbates except isobutane and sulfur hexafluoride could more-or-less freely enter the pores. Therefore, the differences seen for the various adsorbates and zeolites were in degree, not kind, of behavior.

The CaA zeolite has a nominal pore size of 5 Å (*15*). On the basis of ionic radii, the SrA zeolite should be smaller and the MgA larger than 5 Å. All of the adsorbates, other than isobutane and sulfur hexafluoride, could enter the pores, as was evident from comparison of retention volumes for the larger species with those for small ones. For SrA, CaA, and MgA, VRMAX values for ethane were at the least a factor of 2 greater than those for isobutane, while on the SrA zeolite VRMAX values for argon and oxygen were 10–12% greater than those for sulfur hexafluoride. Strong adsorption on the external surface is not a feasible explanation for these results, so they must be attributed to the fact that all of the smaller adsorbates could enter the pores.

In only a few cases did retention volumes show a variation with flow rate. For ethane and methane on SrA, increases in VRMAX with decreasing flow rate were evident, as shown in Fig. 7. Both ethane and

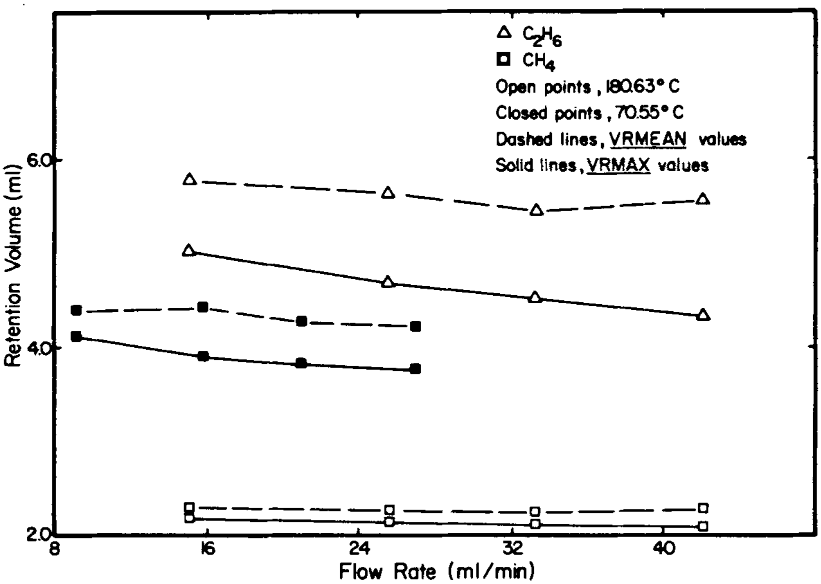

FIG. 7. Retention behavior on SrA.

isobutane had very large retention volumes at the lower temperature, and, hence, it was possible to obtain results only at the fastest flow rate. Ethane showed a larger change in VRMAX than methane. For both ethane and methane, ΔVR decreased as the flow rate decreased, due to the relatively constant VRMEAN values. Similar behavior was seen for oxygen on NaA and, to a lesser degree, on LiA at the higher temperature. This indicates that for both adsorbates the situation was much closer to being one of free diffusion within the pore system than to exclusion from the pores. However, completely free access was not attained. For *n*-propane on MgA a similar situation existed with VRMAX increasing from 21.9 to 23.7 ml as the flow rate decreased from 50.00 to 25.8 ml/min at a column temperature of 180.63°C. At a higher temperature, 226.00°C, VRMAX went from 10.5 to 11.4 ml as the flow rate was decreased from 56.4 to 30.6 ml/min. At both temperatures, VRMEAN was relatively constant, being 26.2 ml at 180.63°C and 12.9 ml at 226.00°C. For the other adsorbates on the SrA, CaA, and MgA zeolites, no trend toward larger VRMAX values at lower flow rates was evident.

Even though all of the adsorbates, except isobutane and sulfur hexafluoride, could enter the pores of the three zeolites, there were large differences in the van Deemter curves for different adsorbates on a given zeolite and for a given adsorbate on different zeolites. The latter effect is shown in Fig. 8 for ethane. As the pore size increases in going from SrA to CaA to MgA, mass transfer in and out of the pores increases and there is a consequent decrease in the flow dependency for HETP. This effect, although greatest for ethane, was seen with all the adsorbates that entered the pores. It must be due to a large extent to the variation in pore size and the corresponding ease of penetration by ethane, since the capacity ratios (based upon the methane time as a measure of total gas volume) were similar, being 2.2, 2.4, and 1.7 for SrA, CaA, and MgA, respectively.

Figures 9–12 show the effect of adsorbate size on the van Deemter curves of each zeolite. The decrease in the HETP values as the adsorbate size decreases can be ascribed to an increase in the ease of mass transfer into and out of the pores. The effect is greatest for the large adsorbates and the smallest pore size, which indicates an extreme sensitivity in the HETP when adsorbate dimensions are close to the pore dimensions. In three instances, "anomalous" behavior with temperature is evident in the van Deemter curves. For ethane on SrA and CaA, and for *n*-propane on MgA, the HETP values at the higher

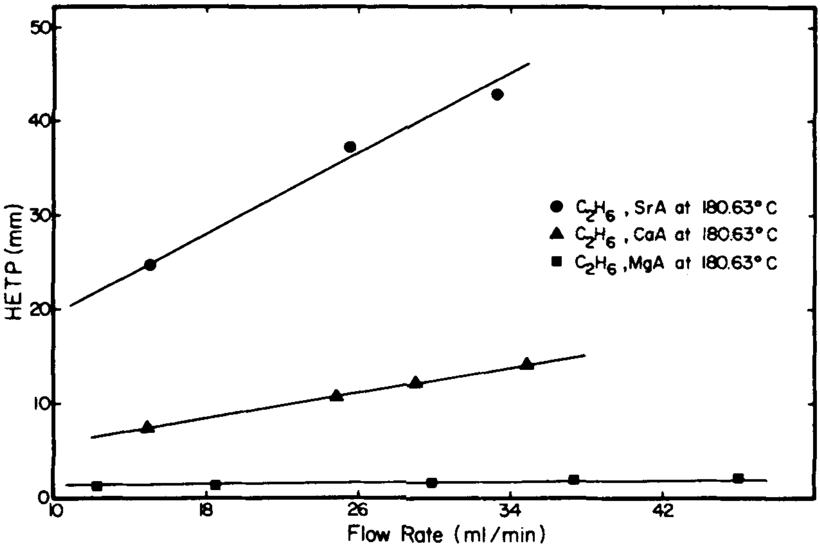

FIG. 8. Van Deemter curves for C_2H_6 on SrA, CaA, and MgA zeolites.

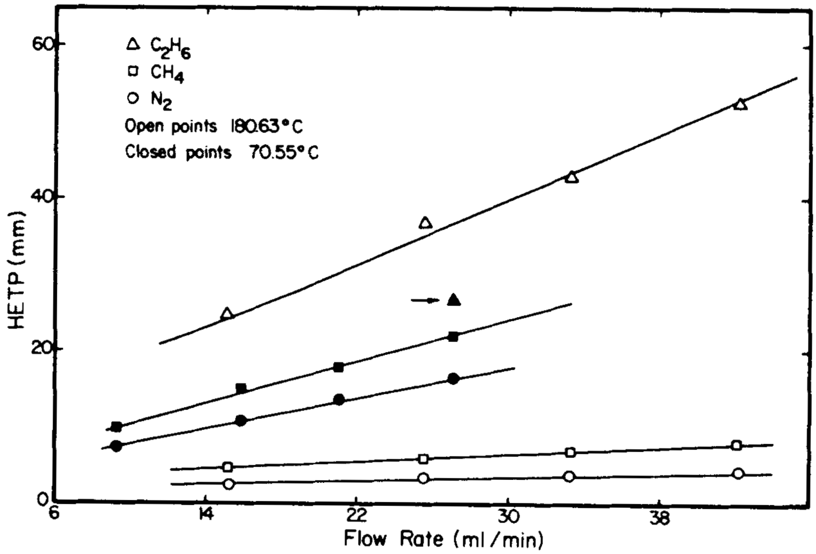

FIG. 9. Van Deemter curves for C_2H_6, CH_4, and N_2 on SrA zeolite.

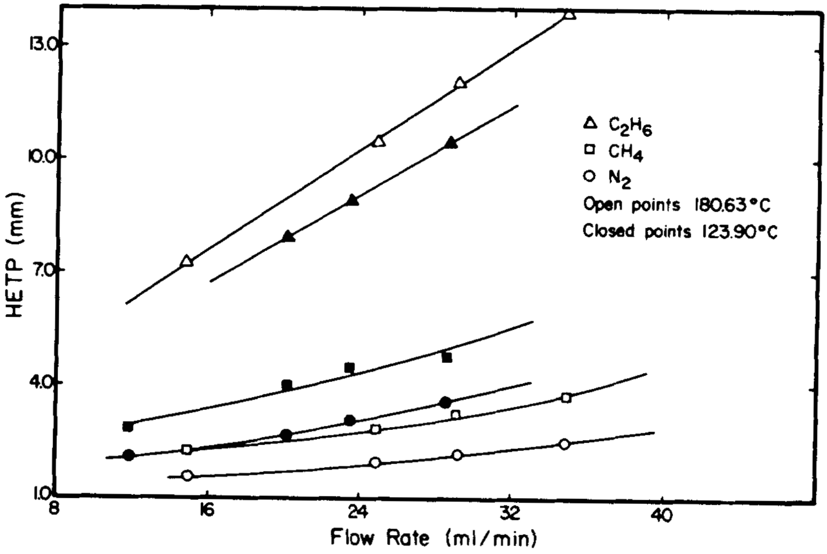

FIG. 10. Van Deemter curves for C_2H_6, CH_4, and N_2 on CaA zeolite.

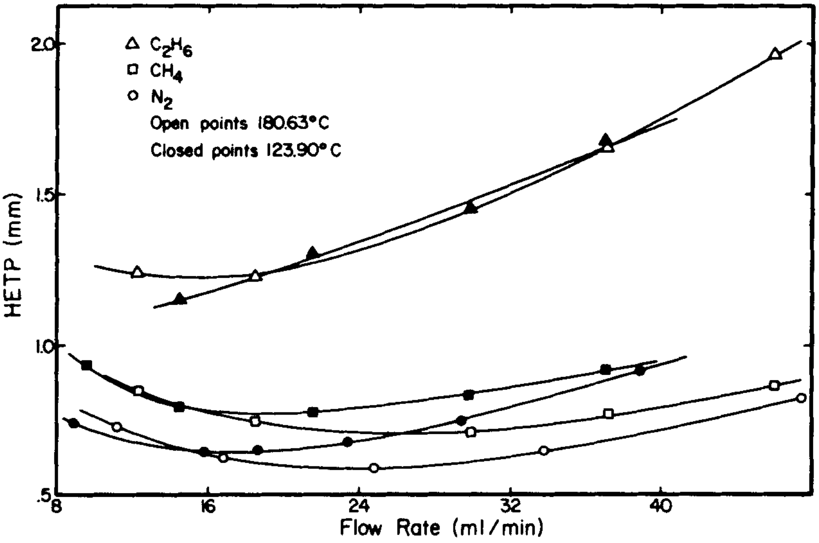

FIG. 11. Van Deemter curves for C_2H_6, CH_4, and N_2 on MgA zeolite.

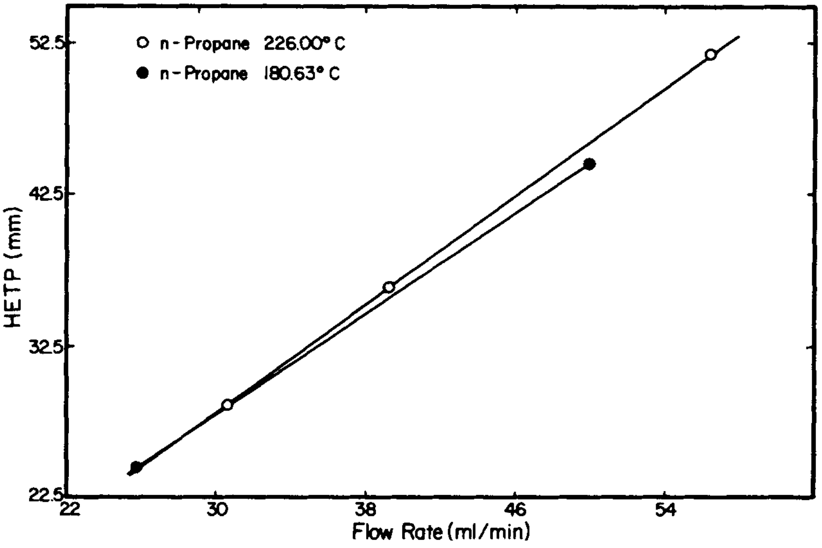

FIG. 12. Van Deemter curves for *n*-propane on MgA zeolite.

temperature are greater than at the lower temperature. For a fourth case, ethane on MgA, there is no reversal, but the curves for the two temperatures are very similar. This behavior does not correlate with the variations in retention value with flow rate discussed above, since ethane on CaA and MgA did not show any discernible change in VRMAX with flow rate. In addition, methane on SrA which *did* show a flow rate dependence in VRMAX, shows no reversal in the van Deemter curves with temperature. This behavior may be a result of restricted diffusion, since it occurs only for the larger adsorbates. However, a completely satisfactory explanation cannot be suggested at this time.

10X Zeolite

Three of the adsorbates, ethane, argon, and sulfur hexafluoride, were studied on the 10X zeolite, which has a nominal pore size of 8 Å (*22*). None of the adsorbates showed any variation in VRMAX or VRMEAN with flow rate. Because this was true even for the large sulfur hexafluoride molecule, which could penetrate the pores, it indicates that restricted diffusion was not an important effect. Further testimony to this is furnished in Fig. 13, which shows the van Deemter plots as a function of temperature for the largest and small-

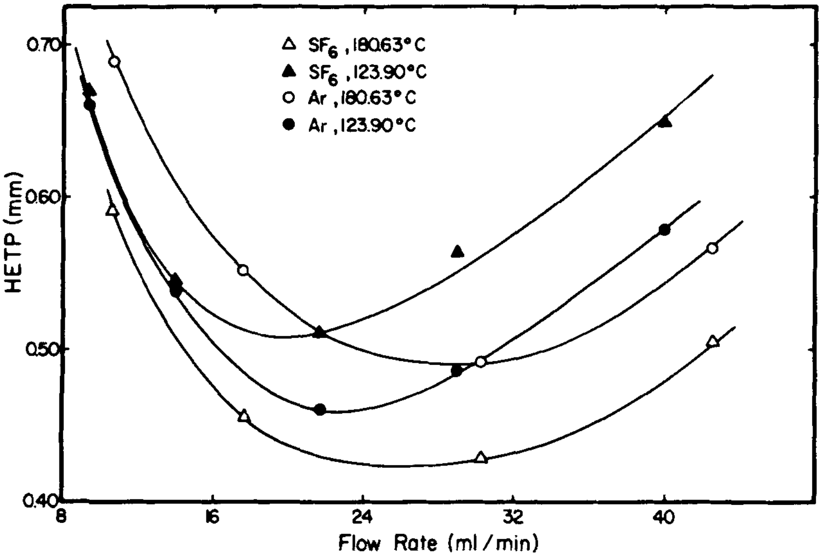

FIG. 13. Van Deemter curves for SF_6 and Ar on 10X zeolite.

est adsorbates. These curves are similar to those found for the adsorbates on the "nonoporous" KA zeolite, Fig. 1, even for sulfur hexafluoride. Again, restricted diffusion did not seem to be an important factor for the adsorbates studied on this zeolite.

DISCUSSION

The present study has shown clearly how VRMAX, VRMEAN, and the difference between them are influenced by the porosity of the adsorbent and the relative size of the adsorbate. When adsorbates have only slight access to the pores, nonequilibrium factors arise, and the retention behavior is influenced by temperature and flow rate. These considerations plus the effect of porosity on HETP values, already shown less completely by others, have important implication for physical chemistry studies and for analytical applications of gas–solid chromatography.

The fact that temperature should have a major effect on the diffusivity is expected since diffusion in zeolites is known to have an energy of activation (*6*). By contrast, gaseous diffusion coefficients have been shown to be much less sensitive to temperature, varying only as the 1.7 power of temperature (*23*). Temperature may also have had an additional minor effect. For example, subtle changes may have occurred due to decreases in the effective pore size when lattice vibrations for the zeolite decreased on going to lower temperatures. An example of this effect is the exclusion of nitrogen and argon from the interior of the NaA zeolite at cryogenic temperatures, even though both adsorbates freely enter the pores at ambient temperatures (*24*). However, over the temperature range in the present study, this is not likely to be important.

Another influence on the diffusivities for molecules on zeolites is the extent of activation of the adsorbent. Habgood (*21*) has found that effective diffusivities for methane and nitrogen changed by a factor of 4 when the activation temperature was raised from 300 to 400°C. Other workers have noted similar effects (*7, 25–27*). It is believed that those variations arose from small amounts of retained moisture which effectively blocked off part of the pore system of the zeolite. Such an explanation can account for the discrepancy between the behavior for methane on the NaA zeolite seen in this study and that found by Oberholtzer and Rogers (*14*). Support for that idea was obtained by preparing another 4A column from the same batch of zeolite and conditioning it in a way as close as possible to that used for the original column. The new column gave trends in the data for CH_4 and O_2 that indicated a degree of penetration intermediate between that reported here and that in Oberholtzer and Rogers (*14*). Similarly, the presence of moisture can explain why results were obtained that indicated a smaller-than-expected pore size for the LiA zeolite. Hence, great care must be exercised in conditioning procedures and drying of gases if reproducible, comparable results are to be obtained, especially between different laboratories.

Grubner (*28*) has developed a theory of chromatography which takes into account quite rigorously the effects of diffusion in porous adsorbents. The theory predicts that a variation in VRMAX, with flow rate, may occur as a result of the intraparticle diffusion, but it concludes that VRMEAN should be independent of flow rate. Such behavior was found for VRMEAN on the SrA, CaA, and MgA zeolites, even though VRMAX did show a flow-rate dependency in several cases. However, for situations where diffusivities and flow rates were such that only partial penetration into the pores occurred, it is also difficult to attach significance to the absolute value of the measured VRMEAN. VRMEAN, under normal circumstances, should be used as the physically significant retention volume, but with porous adsorbents it is subject to influences that can cause it to vary with flow rate. Hence, in practice, it, too, is suspect as a fundamental measure of retention volume. VRMAX is experimentally more convenient to determine, but, in addition to its irrelevancy under normal conditions, its use is further tarnished by the same influences that affect VRMEAN. So, the use of either of these values for measuring the enthalpy of adsorption or other physical properties dependent on retention volume should be undertaken with caution or avoided when dealing with adsorbents that contain micropores.

For the SrA, CaA, MgA, and 10X zeolites, where diffusivities were great enough for all of the smaller adsorbates to have access to the pores, the effect of the porosity was reflected in the HETP values, especially at fast flow rates. The effect of porosity on the HETP values has been treated theoretically by Giddings (*17, 29*), who found that the coefficient of resistance to mass transfer due to the porosity was of the form

$$C = A(k/(k + 1)^2 d^2/D^2 \qquad (1)$$

where A is a constant, k is the capacity ratio, d is the pore depth, and D is the diffusion coefficient, which for zeolites is the effective diffusivity. If we assume, because of the similarity in structure for the zeolites, that d is the same for the various adsorbents, then the HETP behavior reduces to the interaction between k and D. The effects of pore size on HETP values seen in this study appear reasonable, since the diffusivity is sensitive to this parameter. The same argument can be applied to the results for various sizes of adsorbates on a given zeolite. Although there is a paucity of data on diffusivities for the various zeolites, it seems reasonable that the change in the diffusivity in going from one adsorbate to another should be greatest when one of the adsorbates has dimensions very close to those of the pores. This would explain why the difference in HETP values for ethane and methane is greatest for the smallest penetrable pores (SrA), and, for a given zeolite, why the difference in HETP for any two adsorbates decreases as the adsorbates decrease in size. For the MgA and 10X zeolites, this C term becomes much less significant because, as the pore size increases, the diffusivity increases and, for larger pores, should assume more of the characteristics of gaseous diffusion. Since gaseous diffusion coefficients are several orders of magnitude larger than diffusivities on a surface of a narrow-pore zeolite (*23*, *27*), the HETP values are much less. For the NaA and LiA zeolites, where diffusivities and flow rates were such as to allow only partial penetration into the pores, the relationship of the HETP values to those calculated from theoretical considerations is ambiguous. The peak width was not a well-defined parameter, influenced as it was by the flow-dependent tailing, while the retention volume also varied with the flow rate. Therefore, the HETP values must be considered suspect in the same fashion as VRMEAN and VRMAX under those conditions.

The effect of temperature on HETP is complicated by the fact that the several factors which affect HETP change in different manners with temperature (*30*). Generally, it has been found that on going to flow rates higher than the optimum, the rate of increase in HETP with flow rate has been less at higher temperature. For porous adsorbents such as the zeolites, the diffusivity is quite small compared to gaseous diffusion coefficients, so the C term given as Eq. (1) will be a large and dominant factor. Since the diffusivity for adsorbates on zeolites has an activation energy similar to the enthalpy of adsorption (*19*), k and D will change in opposite directions, but by similar amounts, with temperature. However, the dependence of C on k is of the form $k/(1+k)^2$, which varies with k as shown in Fig. 14. So, even if the temperature dependence of k and D were exactly the same, the effect on C would depend on the absolute value of k and the temperature range studied. In the case where k is less than 1, $k/(1+k)^2$ will decrease with an increase in temperature (because k decreases), D will increase, and the net effect will be a decrease in C. For large values of k, $k/(1+k)^2$ is relatively insensitive to changes in k, so C will again decrease because of the increase in D with temperature. For most of the species studied, the former was the case, and HETP values showed the expected change with temperature. The changes with temperature are fairly large here, because of the large change in D with temperature, compared to the case of gaseous diffusion.

In several cases in this study and in the work of Oberholtzer and Rogers (*14*), an increase in HETP with temperature was noted. Rather than ascribe this behaivor to the effects of restricted diffusion, one can note that, for the region of intermediate k values, the quantity $k/(1+k)^2$ can change to a greater degree than k itself. If one assumes that k and D have similar temperature dependencies, then C will increase with temperature, because $k/(1+k)^2$ increases more than D. For microporous adsorbents, where the diffusivities have an activation energy, HETP will definitely decrease with increasing temperature only when the k values are less than 1. For larger k values, the behavior will depend on the temperature dependency of k and D, and on the absolute value of k.

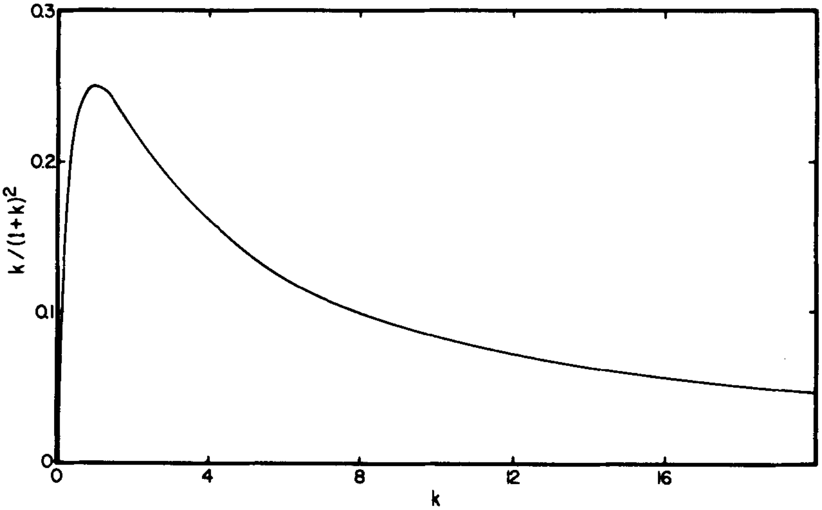

FIG. 14. Plot of k vs. $k(1+k)^2$, the retention factor in C term.

In many analytical applications, these effects of micropores will be important. To minimize the effects of small pores, one should use the lowest temperature and highest flow rate possible in order to minimize the penetration. For larger pores, the large *C* term dictates that the flow rate should be as low as possible in order to preserve column efficiency. This indicates why an adsorbent having a wide range of pore sizes poses a problem. Obviously, compromises must be made and the optimum conditions arrived at empirically.

In some situations, however, the effects of micropores may be useful for increasing selectivity. By the correct choice of pore size, temperature, and flow rate, it should be possible to allow one adsorbate to enter the pores selectively while the other is largely excluded and elutes in the dead volume. The adsorbate entering the pores would have the large internal surface available for adsorption, which could provide even more selectivity if the temperature were low enough for significant adsorption to take place. In gas chromatography, such an approach should be especially promising for columns having a high permeability such as packed capillary columns (*31*), where a wide range of flow rates would be available.

For other forms of chromatography, such as liquid chromatography or gel-permeation chromatography, the results of this study should be applicable. Haller (*32*), using porous glass beads in liquid chromatography, has reported effects similar to those seen here. However, benefits from porosity effects may be more difficult to realize because of the limited range of temperatures and flow rates available under normal circumstances. On the other hand, recent advances in high-pressure liquid chromatographic techniques (*33*) may extend sufficiently the range of flow rates so as to allow more fruitful use of the effects of porosity.

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