Deuterium Isotope Effect on the Refractive Index of Liquids and its Application to Permeation Chromatography

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Synopsis

Differences in refractive index between deuterated and normal solvents have been determined using a conventional gel permeation chromatograph equipped with a differential refractometer detector. Three molecular systems have been studied, namely, water–deuterium oxide, acetone–acetone (d_6), and tetrahydrofuran–tetrahydrofuran (d_8). A plot of the signal intensity versus the concentration of the deuterated solvent in the normal solvent gave a linear relationship for all three systems studied. The effect of deuteration is found to result in a lowering of the refractive index which is at least three orders of magnitude larger than the sensitivity of the differential refractometer. Consequently, for permeation chromatographic studies, the addition of 1% or less of the deuterated solvent in the injection sample would be more than sufficient to produce a peak characteristic of the mobile phase.

INTRODUCTION

In permeation chromatography, the flow characteristics within the packed columns will evidently be of paramount importance among the various factors affecting the elution volume and the peak shape obtained with a given solute. Since the solvent is the vehicle for the solute, the flow behavior of the latter will be dictated in large part by the flow behavior of the solvent itself. Of constant concern to the experimentalist is the reproducibility of the flow characteristics from run to run. An ideal situation would be one which would permit obtaining a record, in a single operation, of the elution volume and peak shape of both the solute and the solvent in the injected sample. With the differential refractometer, the most commonly used detector in permeation chromatography, it would seem that this goal could be achieved by preparing the sample for study with a certain amount of deuterated solvent, providing deuteration produces enough difference in refractive index with the normal solvent. To test the practicality of this idea, differences in refractive index between the deuterated and normal solvent have been measured in a permeation chromatograph under static conditions.

RESULTS AND DISCUSSION

For the three systems studied, water–deuterium oxide, acetone–acetone(d$_6$), and tetrahydrofuran–tetrahydrofuran(d$_8$), solutions of the deuterated solvent in the normal solvent were prepared on a vol-% basis, and the difference in refractive index between each solution and the corresponding normal solvent was recorded using the optics of a conventional gel permeation chromatograph. Plots of the intensity of the signal at the lowest sensitivity of the instrument (1X) versus solution compositions are given in Figures 1 through 4. (The curves in Figures 1 through 4 should meet at the origin. In Figures 3 and 4, this expectation is not realized, the curves intercept the ordinate at some positive value, probably as a result of having set the instrument at zero before thermal equilibrium was actually reached on both sides of the refractometer cell.)

All measurements were conducted at 30°C. With the normal solvent placed in the reference side of the refractometer, the signal was negative,
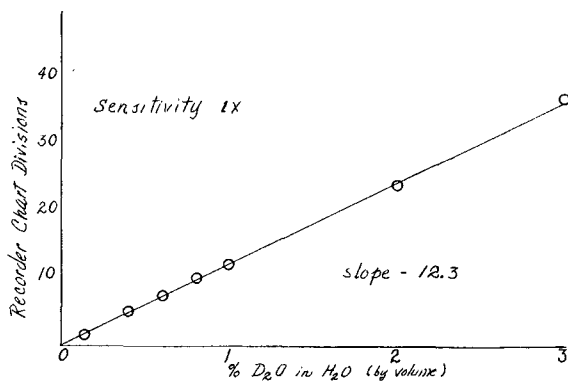

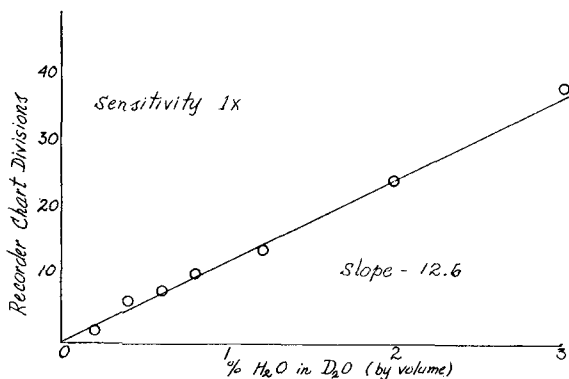Fig. 1. Effect of deuterium oxide concentration in water on the differential refractometer signal.

Fig. 2. Effect of water concentration in deuterium oxide on the differential refractometer signal.
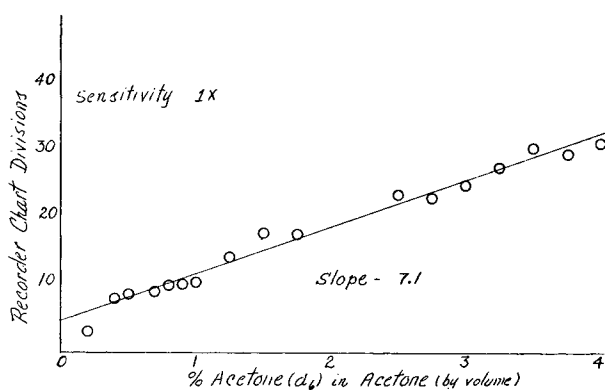
Fig. 3. Effect of acetone(d_6) concentration in normal acetone on the differential refractometer signal.

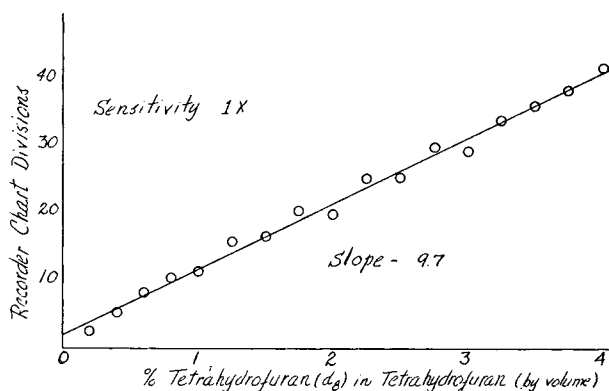Fig. 4. Effect of tetrahydrofuran(d_8) in normal tetrahydrofuran on the differential refractometer signal.

i.e., all solutions containing the deuterated solvent had a lower refractive index than the normal solvent. As can be observed from the figures, the experimental points fall closely on the straight line obtained by applying a least-squares treatment on the data.

The System H_2O-D_2O

The vapor phase chromatograms for both water and deuterium oxide, previously degassed by boiling for $^1/_2$ hr, revealed the presence of a single peak. The purity of the two solvents is estimated to be better than 99.99%.

Solutions of D_2O in H_2O were prepared over a concentration range of 0–3% D_2O, and each solution was placed in the permeation chromatograph with H_2O in the reference side of the differential refractometer. Also, in order to test if the slope of the experimental curve remains constant over the

entire D_2O–H_2O composition range, solutions of H_2O in D_2O (0–3% H_2O) were prepared and measured under the same conditions.

It is observed that the slope is 12.3 for the solutions of D_2O in H_2O and 12.6 for the solutions of H_2O in D_2O. This discrepancy in the value of the slopes is not unexpected and can be accounted for principally from the scattering of the experimental data. The difference in molar volume between H_2O (18.0 cc) and D_2O (18.1 cc) could itself account for only part of the observed deviation in the slope values. Taking the average value of the experimental slopes, i.e., 12.45, this gives 1245 as the number of chart divisions equivalent to the difference of 0.00456 in refractive index between pure H_2O and pure D_2O.[1] Each division on the recorder chart at the sensitivity (1×) used is then equivalent to 3.7×10^{-6} refractive index unit. This value will be used later as a basis for determining the refractive index of the other two deuterated molecules considered in this study.

It is evident on the basis of these results that the flow characteristics for an aqueous system could be easily monitored by the addition of very small amounts of D_2O in the injection sample. For example, a peak maximum of 20 chart divisions could be obtained by injecting a sample containing less than 2% D_2O. In fact, as little as 0.2% D_2O would be required at the highest sensitivity (16×) of the instrument.

The System Acetone–Acetone(d_6)

Vapor phase chromatograms indicated that acetone and acetone(d_6) contained water as the only impurity, but to a different extent. Since the presence of water in acetone produces a significant nonlinear change in refractive index even at very low concentrations, it seemed questionable to simply apply a correction from a preestablished calibration curve. Consequently, it was judged that the most reliable and practical approach would be to raise the water content of one sample to match that of the other and to compare the water contents by means of vapor phase chromatography. In this fashion, the water content in both samples could be made to agree to better than 1%.

Solutions of acetone(d_6) in normal acetone over the range 0–4% in concentration measured against normal acetone gave the results shown in Figure 3. Extrapolation of the experimental curve to 100% acetone(d_6) gives 710 chart divisions. Based on the value of 3.7×10^{-6} refractive index unit per chart division, the difference in refractive index between acetone and acetone(d_6) is calculated to be 0.002627, which yields a value of 1.3564_7 for the refractive index of acetone(d_6).

Considering permeation-chromatographic experiments conducted with acetone as solvent, the results obtained above demonstrate that the flow characteristics could be easily determined and analyzed by adding 2% acetone(d_6) in the injection sample at a sensitivity setting of 1×, or 0.1% at a sensitivity of 16×.

The System Tetrahydrofuran–Tetrahydrofuran(d_8)

The vapor phase chromatograms revealed two small peaks in THF(d_8) which are absent in the chromatogram of normal THF. Although the origin of these peaks was not established, the concentration of these unknowns as estimated from peak areas appears to be less than 0.05%.

Solutions of THF(d_8) in THF over the concentration range 0–4% when measured against THF gave the results shown in Figure 4. Extrapolation to 100% THF(d_8) gives 970 chart divisions which calculate to a refractive index difference of 0.00359 between THF(d_8) and THF. Based on the handbook value of 1.4076 for THF, the refractive index for THF(d_8) is calculated to be 1.4040.

THF has been one of the most used solvents in gel permeation-chromatographic work. Hence it is especially interesting to note that in this system it is also possible to follow the flow characteristics by adding as little as 1.5% THF(d_8) in the injection sample at a working sensitivity of $1\times$, or 0.1% at a sensitivity of $16\times$.

CONCLUSIONS

For the three solvents examined in this study, deuteration produces a lowering in refractive index quite large relative to the sensitivity of conventional instruments. Consequently, the addition of relatively small amounts of deuterium-labelled solvent in the injection sample is sufficient to give a peak characteristic of the solvent flow in the system. This simple technique could then prove to be an economical and extremely convenient approach for obtaining on a routine basis a permanent record of the performance of the instrument. Furthermore, there are good reasons to believe that the substitution of deuterium in a molecule will generally result in a detectable lowering of the refractive index. Therefore, this technique could prove to be quite general in scope.

References

1. N. Bauer, K. Fajans, and S. Z. Lewin, Chap. XVIII in *Techniques of Organic Chemistry*, Vol. I, Physical Methods, Part II, A. Weissberger, Ed., Interscience, New York, 1960. p. 1161.