TECHNICAL PROGRESS REPORT
ON
FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

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ABSTRACT

We have been highly successful in applying the high-precision gas chromatograph to obtain: (a) differential measurements of heats and entropies of solution, (b) adsorption isotherms from tailed chromatographic peaks, (c) improved sensitivity in trace analyses through ensemble averaging, (d) further indications of the effects of adsorbent porosity on peak shape, and (e) useful analytical data from overlapped chromatographic runs. Other gas-chromatographic studies have shown that greatly improved separations of enantiomeric amines could be obtained if pentafluoropropionyl derivatives were used instead of trifluoroacetyl and if the optically active ureide, used as the stationary phase, was solid instead of liquid.

Two other highlights deserve mention. First, our preliminary data on the methyl orange system have revealed very unusual polymerization behavior. Second, in the area of gel chromatography, our preliminary evidence appears to indicate that the use of a wide column, instead of a narrow column, may sometimes be advantageous because of the ease of working at very low linear flow rates while maintaining a reasonable rate of throughput.

Finally, we have enjoyed excellent cooperation with chemists at Lawrence Radiation Laboratory (Livermore) and at Oak Ridge National Laboratory.

INTRODUCTION

Excellent progress has been made in a number of areas. We have tried to take advantage of our unique capabilities for high-precision gas chromatography and for order-of-magnitude higher pressures in liquid chromatography. Our accomplishments would have been even greater had we not suffered the early loss of two students - one teaching assistant who withdrew from graduate work and one fellowship holder who is suffering from a prolonged illness - plus the virtual loss of a third student who agreed to take on a full-time teaching assignment.

Like the report of last year, the major topics will be discussed in the same order in which they appeared in the proposal.

HIGH-PRECISION GAS CHROMATOGRAPHY

The high-precision system permitted us to show for the first time in gas chromatography that restricted diffusion in an adsorbent would produce changes in retention time and in peak shape (COO-1222-29). During the past year, this phenomenon has been examined in much more detail using adsorbates of different sizes and zeolites of different pore sizes (COO-1222-37). In brief, if an adsorbate could enter the pore easily or if it was totally excluded, conventional behavior was found with changes in flowrate and temperature. However,

for molecules which were not much smaller than the pores, larger-than-expected changes in efficiency and peak distortion occurred. In addition to the implications these findings have for those interested in using chromatography to obtain physical chemical data, the results should serve as a warning to those who now make quantitative deconvolutions of overlapping peaks based upon the assumption of constant peak shape.

Our chromatographic system, which can routinely measure retention time to better than 5 parts in ten thousand, has been tested in a differential mode. As we had hoped, when one peak was measured relative to another, the small differences in retention times could be determined with essentially the same relative precision as an individual retention time (COO-1222-36). As a result, differences in heats and entropies of solution can be measured with standard deviations of the means of about 0.02 calorie and 0.002 entropy unit, respectively. Hence, very subtle structural effects can now be studied quantitatively - when the chemistry of the system will permit. As a matter of fact, we are now starting to examine an unfavorable system to see if our precision will permit us more nearly quantitatively to characterize independently the contributions of dissolution in the liquid and of adsorption on its surface (1-3). The fact that our chromatographic system permits us easily to determine adsorption isotherms from the tails of badly distorted peaks (COO-1222-36) will give us a substantial "jump" on the problem.

Two other studies, have been undertaken to exploit the run-to-run reproducibility of our chromatograph. The first has demonstrated that ensemble averaging is feasible, and it should prove to be advantageous for continuous monitoring at the ppb level (COO-1222-39). The expected improvement in signal-to-noise was attained over a wide range of concentrations, and, as a by-product, we received a liberal education in the measurement of areas of noisy peaks. The study was greatly expedited by a newly designed exponential dilution flask which is not only relatively cheap to build but also easy to take apart and reassemble for cleaning (COO-1222-34).

In the second study, the feasibility of using our high-precision system to make quantitative measurements on two or more chromatograms overlapped in a single column has been started (4,5). An interesting special case has been found. If the injection interval is short compared to the width of the peak(s), a relatively flat plateau will be formed, the height of which is a function of the concentration(s) of the species and the injection interval. Any peaks which are about one-fourth, or less, of that width will appear as sharp spikes on the plateau. We hope to complete this study, which will include the effects of tailing, by the end of the summer.

HIGH-PRESSURE CHROMATOGRAPHY

Our first efforts in liquid-solid chromatography at pressures up to 60,000 psi were made using aqueous solutions of methyl orange and ethyl orange with silica as an adsorbent. That chemical combination was selected because we had a backlog of experience with it and because our stabilized photometer operated in the visible range. However, we had expected to use the combination only to test the system - until we encountered the interesting differences in pressure dependence of the distribution ratios (COO-1222-31). Now, over a year later, we find ourselves still working on that system - and the results are continuing to be highly unusual. If our most recent results stand up under detailed scrutiny, they will represent new concepts in the area of micelle formation.

Thanks to Dr. William Marshall of Oak Ridge National Laboratory, who permitted Mr. Bidlingmeyer to work in his laboratory, conductivity measurements of solutions of methyl orange were made over a wide range of concentrations and pressures. Graphs of specific conductivity vs concentration showed the hoped-for change in slope, but the change went in the wrong direction. That is, above an intermediate concentration, the specific conductivity increased. Just recently, preliminary studies of molecular weights using steric exclusion chromatography (using controlled-porosity silica) indicate that, at low ionic strengths, the methyl orange is largely in the form of a

polymer. At higher ionic strengths, it is largely monomer. .
So, we are working with ever-increasing interest on a system
which we had expected to abandon after making a few test runs
on the apparatus.

Unfortunately, the area of super-critical gas chromatography
was a victim of the manpower problem mentioned in the introduction.
Hopefully, the next year will see action in that area.

ENANTIOMERS AND ISOTOPICALLY-SUBSTITUTED COMPOUNDS

During the past year, our study of gas chromatographic
separations of enantiomers of amine derivatives has been very
rewarding. As pointed out in an accompanying preprint (C00-1222-35),
we have extended the work of Feibush and Gil-Av (6) by showing
that gas-solid adsorption, just below the melting point of the
ureide (stationary phase), gives much faster separations than
gas-liquid partition. Furthermore, the advantage can be
increased by using pentafluoropropionyl derivatives of the
amines rather than trifluoroacetyl.

More recently, two other optically active phases, which,
as liquids, can separate enantiomeric amine derivatives, have
been found to be incapable of making those separations
after solidification of the stationary phase. Hence, the
ureide appears to represent an exception rather than the rule.

At the present time, we are extending the study in a different direction. In order to explore more thoroughly how such separations come about, we have changed to dipeptide stationary phases (7,8). We are synthesizing dipeptides using different amino acids so as to be able to evaluate the structural contribution of each moiety to the overall separation. From such a study, selection of optimal combinations should be possible.

In contrast to the progress made with enantiomeric systems, separation studies of isotopically-substituted compounds have progressed little since last year's proposal was written. A low-temperature gas chromatograph was constructed which could operate down to -100°C . Then, a separation of the cyclohexanes, C_6H_{12} and C_6D_{12} , was successfully completed. At that point, the student decided to drop out of graduate school.

To end on a brighter note, another student has been starting up and testing a recycling system which will be used in our studies of isotopically-substituted compounds. In that connection, we are indebted to J. W. Frazer of Lawrence Radiation Laboratory for arranging to lend us temporarily two switching valves when ours turned out to be defective and required a long time to be reconditioned.

GEL CHROMATOGRAPHY

Isolation of pure polymeric species of polyethyleneglycol by gel chromatography for later characterization by gas chromatography

proved to be impossible in our equipment. Extremely long columns or the equivalent of a recycling system proved to be necessary. As a result, rather than trying to isolate pure species from high-molecular-weight commercial preparations, we decided to start at the low-molecular-weight end where pure species are easy to obtain. We have successfully synthesized (9) very pure species up to (monomer)₈ as shown by gas chromatographic analysis of the trimethylsilyl derivatives (10). We are just about to start characterizing the stationary phases using a variety of volatile solutes.

Other work in gel chromatography has gone very slowly because the student has been a full-time teacher. After a brief investigation of the behavior of Sephadex in alcohol-water mixtures, attention was turned to comparisons of efficiencies in columns of different diameters. We soon discovered that wider columns permitted smaller linear flow rates than narrow columns while still maintaining a useful rate of throughput. As a result, wide columns sometimes proved to be more efficient. Rather than going to narrower columns, the analytical, as well as the preparative, chemist may find the use of wider columns advantageous.

SPECTROSCOPY

One year ago, our NMR studies of adsorbed species had nearly been completed, so no mention of that work was made in the proposal. However, it should be noted that we were successful

in defining the conditions under which high-resolution spectra of adsorbates on silica could be obtained (C00-1222-32). In addition, we demonstrated that measurements of chemical shifts and integrated intensities could be used to characterize the surfaces and their interactions with adsorbates (C00-1222-33). Finally, we pointed out discrepancies between interpretations based upon infrared, NMR, and gas chromatography which emphasize that these techniques are not always "seeing" the same aspect(s) of an overall interaction.

MISCELLANEOUS

The original high-precision chromatographic system was designed for read-out on punched paper tape. During the last month, an interface has been designed that will permit the operator to decide whether to send the data to the tape punch or directly into a small "roll-around" computer. Hence, when the computer is free, results will be available at once and will permit the experiments that follow to be modified, if necessary, thereby saving considerable time.

At the same time, interfacing of a second high-precision chromatograph has been completed. This new version incorporates computer control of oven temperature and carrier-gas flowrate as well as data acquisition. In addition, software has nearly been completed, so we expect to be operating the complete system in the very near future.

Thanks to the help of Mr. Stanley Deming, a student doing his thesis work with Professor H. L. Pardue, a highly sensitive and stable circuit was designed and built for the Spectronic 20. As a result, it has been possible to study the chromatographic behavior of 1.0×10^{-6} M samples of methyl orange.

Finally, it is appropriate to point out that the Chemistry Department has contributed over \$1400 to supplement the amount budgeted for supplies. In addition, when the small departmental computers have broken down, the Dean of Science has permitted us to use over \$300 worth of time at the Computer Center.

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(Accepted, Anal. Chem.)
2. COO-1222-35 J. A. Corbin and L. B. Rogers, "Improved Gas
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