TECHNICAL PROGRESS REPORT
ON
FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

Prepared by
L. B. Rogers
Department of Chemistry
University of Georgia
Athens, Georgia
30602

Submitted to
MASTER
United States Energy Research and Development Administration
for
Contract No. AT(38-1)-854

June 1975

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Studies using high-precision gas chromatography and supercritical fluid chromatography have produced new types of information on liquid crystals and on behavior of substances in the region of the critical temperature, respectively. In addition, the first successful studies of the effects of pressure on cation exchange have been made using aqueous solutions of alkali metal nitrates. In contrast, progress on separations of isotopic species using gas chromatography has been disappointing. In that area, the chief accomplishment has been a determination of the levels of accuracy and precision with which isotopic abundances can be measured using our quadrupole mass spectrometer.

INTRODUCTION

Period of transition

During the past year, a successful transition has been made from Purdue University to the University of Georgia. Much of the last summer at Purdue was spent in dismantling and packing both equipment and special supplies for the move. Three of the four graduate students who transferred to Georgia were studying for their written Ph.D. preliminary examinations scheduled for late August. (Later in the Fall, they returned to Purdue for successful attempts to pass their oral preliminary examinations.)

Two students finished their experimental work late in August and stayed at Purdue to complete the writing of their theses. Their work is reported below. Two others who had just started research, chose to remain at Purdue but changed

both their supervisor and research area. However, four first-year graduate students have recently chosen to do research with the Principal Investigator; three have already started research. Furthermore, Professor Harold McBride of Nebraska Wesleyan is joining our group for what is expected to be a mutually beneficial association. Hence, the rate of progress should soon be much nearer to the levels of former years.

Since arriving on Labor Day weekend in rental trucks, the four students and the PI have not only unpacked and reassembled equipment but have also exerted a major effort to put three chromatographs and a spectrophotometer on-line for data acquisition. Unbelievable delays in delivery of sampling valves (7 months), a pressure transducer (5 months), a shaft encoder, and some special electronic components have prevented us from completing the job. However, the end of the summer is our current target.

Organization of this report

The topics will be discussed in the same order as in the Proposal so as to make it easier for the reader to check our progress against our goals. There have been two major disappointments. First, the isotopic studies have proceeded much slower than expected. In part, this has been due partly to equipment failure and partly to the chemistry. Second, because two Purdue students chose not to move to Georgia, a study of optimization in chromatography has not been started. However, we have definite plans for starting it during the next contract period.

ISOTOPIC SEPARATIONS

CO₂

Although we are using a mass spectrometer as a detector, our goal is to find conditions that will permit $^{13}\text{C}/^{12}\text{C}$ separations to be quantitated using a long capillary column and a micro thermal conductivity detector. For several months, we have worked with a polyethyleneimine which showed great promise. The resolution on short columns was near 0.03, so a very long capillary would have been adequate. However, the columns rapidly lost the ability to separate the isotopes. All types of column pretreatments and careful deoxygenation of the helium carrier gas failed to prevent deterioration.

Recently, diethanolamine has been found to give a similar value for resolution when tested in short columns. However, volatility of diethanolamine may be a problem when we go to capillaries. In any case, we plan to terminate this project by the end of the summer, hopefully in a successful way.

CH₃OH

The relative vapor pressures of the ^{16}O and ^{18}O species have been measured using glycerol as a stationary phase for gas chromatography. The values for CH₃OH are well within the experimental error of those obtained by classical means. We have just started a series of runs using CD₃OH. We hope to have the data for both CH₃OH and CD₃OH written up for publication early in the Fall.

HIGH PRESSURE CHROMATOGRAPHY

Liquid chromatography

Over 10,000 psi. Cation exchange studies using NaNO_3 as an eluent for a sample of KNO_3 from AG 50 X 16 resin, has shown that a significant decrease in retention occurred on going from 25,000 psi to 40,000 psi. Up to 25,000 psi, retention was independent of pressure. Samples of rubidium nitrate showed similar behavior. Although many more runs need to be made, it appears that sodium ions may be losing some water of hydration, thereby becoming better competitors for the sites on the resin.

Unsuccessful attempts were made to do anion exchange studies using pyrophosphate, nitrate, and thiocyanate complexes of some transition metals. An important limitation was the noticeable attack of the pumping system by thiocyanate and by the dilute acid needed to prevent hydrolysis of the nitrate complexes.

Under 10,000 psi. Our conventional high-pressure liquid chromatograph has been pressed into service as a supercritical-fluid chromatograph. Hence the first group of projected ion-exchange studies has not been started. However, the supercritical studies have been quite successful.

The enclosed preprint (SRO-854-1) shows that we were able to fractionate a commercial silicone polymer into approximately 25 species. During that study, we found that small amounts of alcohol greatly affected the resolutions of cyclic and linear species. Hence, a mixed solvent offers an unexpected avenue for facilitating the isolation of pure components for other studies. Finally, from the observed changes in retention with pressure, it appears that the density of the

HIGH PRESSURE CHROMATOGRAPHY

Liquid chromatography

Over 10,000 psi. Cation exchange studies using NaNO_3 as an eluent for a sample of KNO_3 from AG 50 X 16 resin, has shown that a significant decrease in retention occurred on going from 25,000 psi to 40,000 psi. Up to 25,000 psi, retention was independent of pressure. Samples of rubidium nitrate showed similar behavior. Although many more runs need to be made, it appears that potassium and rubidium may be gaining some water of hydration, thereby becoming weaker competitors for the sites on the resin.

Unsuccessful attempts were made to do anion exchange studies using pyrophosphate, nitrate, and thiocyanate complexes of some transition metals. An important limitation was the noticeable attack of the pumping system by thiocyanate and by the dilute acid needed to prevent hydrolysis of the nitrate complexes.

Under 10,000 psi. Our conventional high-pressure liquid chromatograph has been pressed into service as a supercritical-fluid chromatograph. Hence the first group of projected ion-exchange studies has not been started. However, the supercritical studies have been quite successful.

The enclosed preprint (SRO-854-1) shows that we were able to fractionate a commercial silicone polymer into approximately 25 species. During that study, we found that small amounts of alcohol greatly affected the resolutions of cyclic and linear species. Hence, a mixed solvent offers an unexpected avenue for facilitating the isolation of pure components for other studies. Finally, from the observed changes in retention with pressure, it appears that the density of the

fluid does not change linearly with pressure. We hope to explore this matter more deeply in the future.

After completing the supercritical study, we spent some time trying to optimize the resolutions of pairs of linear and cyclic oligomers ($n = 4$ and 5) from the DC-710 (methylphenyl silicone). More recently, fractions have been collected from repeated analytical runs. The goal is to collect approximately 20 mg of each pure oligomer so that two or more capillary columns can be coated. From those columns, differences in Rohrschneider (or McReynolds) Constants will be measured using high-precision gas chromatography. In that way, the effects of structural differences between the two types of oligomers can be evaluated. The cyclic species ($n = 4$ and 5) are now available in sufficient amounts to start characterization studies. Unfortunately, the minor components ($n = 4$ and 5 linear) yield 0.5 mg or less per injection, so many more runs will be required before we have enough material.

One is always concerned about the relative merits of two (or more) methods for performing a particular separation. In 1970, using polystyrene, Jentoft and Gouw (1) found that supercritical fluid chromatography was superior to steric exclusion. Our comparison last Fall of the resolutions of silicone oligomers by supercritical chromatography and by conventional steric-exclusion chromatography confirmed their finding and showed the latter to be far inferior. However, we have just ordered a new packing material, Lichrosphere, which is reported to be capable of much better resolution than conventional packings (2). It will be of great interest to see how much improvement it offers over the conventional column packings.

Unfortunately, time has not permitted an evaluation of the merits of continuous "solvent" gradients in supercritical fluid chromatography. However, we hope to explore it during the next year.

GAS CHROMATOGRAPHY

A study of the effect of an electric field on the diffusion of solutes in liquid crystals (cholesteryl myristate) revealed unusual behavior. First, a "fronting" phenomenon occurred, the formation of a "step" in the front of a chromatographic peak—but only when the electrostatic field was on (SRO-854-2). We have been able to rule out impurities as the cause. A stirring effect is known to occur when some liquid crystals are placed in an electrostatic field, and we have suggested that it may be the cause. However, we plan to check out the generality of our observations on at least one other liquid-crystal system.

Another striking observation was also made on that same liquid-crystal system. Thanks to data acquisition by an on-line digital computer, we were able to demonstrate conclusively that, despite large changes in the peak maximum of solute upon imposition of an electrostatic field, the peak mean remained unchanged. This indicates that a major change in the mass-transfer process occurred when the liquid-crystal stationary phase was placed in the field. At the same time, it demonstrated once again the desirability of using the mean rather than the maximum to characterize a chromatographic peak.

OTHER STUDIES

As indicated earlier, reproducibility studies of the mass spectrometer were very reassuring. Using CO₂, Ar, and Ne, abundances greater than 10% could

be measured with accuracies and precisions close to 0.2%. Although ensemble averaging (256 spectra) was employed so as to minimize noise, the time required for the averaging was much less than that used for another quadrupole spectrometer for which comparable data have recently been published (3).

As a final point, mention should be made once again of the problems we have experienced with slow delivery of a wide variety of components. Despite continual pressure to put all of our equipment on-line, frustrating delays in delivery of key components have slowed us down. Our target date for completion is now early in the Fall. As a result of the interfacing delay and the lack of manpower, optimization studies have been postponed until the next contract period.

REFERENCES

1. Jentoft and Gouw, J. Chromatog. Sci., 8, 138 (1970).
2. Unger et al., J. Chromatog., 99, 435 (1974); see also 83, 5 (73).
3. Caprioli, Fies and Story, Anal. Chem., 46, 453A (1974).

PERSONNEL

September 15, 1974 to June 15, 1974

GRADUATE STUDENTSPurdue

J. A. Nieman (Ph.D. oral in Nov. 1974)

R. B. Westerberg (Ph.D. oral in Nov. 1974)

Georgia

R. E. Pauls

Gabriel Prukop

F. J. Van Lenten

A. T. Shepard (Part-time)

James Conaway (starting July 1, 1975)

Neil Danielson (started April 1, 1975)

J. C. Hodgins (started April 1, 1975)

Bruce Semonian (started April 1, 1975)

UNDERGRADUATE STUDENT

Morris Geffen

POST DOCTORAL ASSOCIATE

Professor Harold D. McBride, Nebraska Wesleyan (June 16-August 16, 1975)

PUBLICATIONS IN PRESS

1. SRO-854-1, J. A. Nieman and L. B. Rogers, "Supercritical Fluid Chromatography Applied to the Characterization of a Siloxane-Based Gas Chromatographic Stationary Phase", (Accepted by Separation Science).
2. SRO-854-2, R. B. Westerberg, F. J. Van Lenten, and L. B. Rogers, "Chromatographic Behavior of a Cholesteryl Myristate Stationary Phase in an Electric Field", (Accepted by Separation Science).