ION PAIR LIQUID CHROMATOGRAPHY OF COAL-DERIVED LIGHT OILS

J. K. Olson and B. W. Farnum

Grand Forks Energy Technology Center, DOE
Box 8213 University Station
Grand Forks, ND 58202

INTRODUCTION

The growing emphasis on coal liquefaction technology has resulted in increased interest in the development of methods to determine the composition of liquids produced by the process. This information can facilitate understanding of the relationship of the occurrence of various chemical species to the structure and reactivity of the parent coal. This report describes an ion pair liquid chromatography study of the light oil fraction from the liquefaction of lignite with CO and H_2 at 460°C and 27.6 MPa.

The light oil is a gas condensate collected in a water-cooled receiver at atmospheric pressure. The sample studied was collected on the 30th recycle pass of a Beulah lignite liquefaction test using anthracene oil as start-up solvent. Based on MAF coal, the light oil represents about 19% of the yield. A detailed description of the GFETC continuous process unit has been published previously (1).

EXPERIMENTAL

Waters* M-6000 pumps, U6K injector, model 440 UV_{254nm} detector, and model 660 solvent programmer were used for the ion pair study. All separations were conducted using Whatman Partisil ODS2, a 10μm octadecyl-silica packing containing about 15% (w/w) carbon. The column was 250 mm long, 6.4 mm O.D. and 4.6 mm I.D. Column temperature was maintained by a Haake FK-2 circulating water bath. Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer.

The mobile phase solvents used were Baker HPLC grade water and Waters HPLC grade methanol and acetonitrile. Buffers were prepared using Baker HPLC grade ammonium acetate, phosphoric and acetic acids, Regis potassium dihydrogen phosphate, potassium monohydrogen phosphate, both 99+% purity, and Waters tetrabutylammonium phosphate (PIC A) and sodium hexanesulfonate (PIC B-6) reagents.

The liquefaction light oil sample was extracted according to a scheme, shown in Figure 1, adapted from Fruchter et al. (2). The resulting four fractions will be designated basic, phenolic, HA(aromatic), and HC(hydrocarbon) throughout this paper.

RESULTS AND DISCUSSION

The light oil is a mixture of relatively low molecular weight, volatile hydrocarbons. The boiling point of 98% of the sample was in the 40-200°C range and the molecular weight range was 60-365 daltons. The nature of each fraction may be described drawing upon information from elemental analysis, shown in Table 1; infrared spectra, shown in Figure 2; and low voltage mass spectra (3).

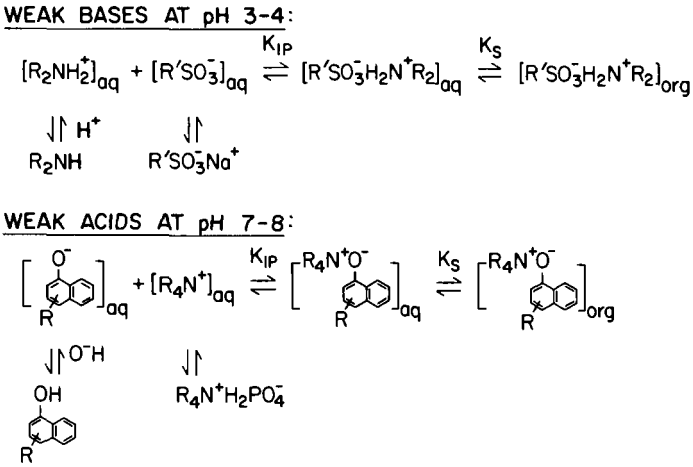
* Reference to specific brand names or models is made to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

The oxygen-containing compounds found in the phenolic and basic fractions appear to be of the same compound class -- substituted phenols. Almost all of the nitrogen-containing compounds, primarily aryl amines, were isolated in the basic fraction. The HA fraction consists primarily of two- and three-ring aromatic compounds. The hydrogen/carbon mole ratio for the HA fraction is 1.0 as compared to 1.6 for the HC fraction. Although the HC fraction contains some of the same aromatic compounds found in the HA fraction, the principal components are saturated hydrocarbons as indicated by the infrared spectrum. To summarize, the phenolic fraction consisted of substituted phenols; the basic fraction contained substituted phenols and aryl amines; the HA fraction contained aromatic compounds; and the HC fraction contained primarily saturated hydrocarbons and some aromatic compounds.

TABLE 1. - Elemental Analysis of Light Oil Fractions

	%C	%H	%O	%N	%S
Basic	79.6	9.2	4.2	6.8	0.0
Phenolic	78.9	8.7	12.8	0.1	0.0
HA	89.4	7.7	1.8	0.6	0.7
HC	88.9	11.6	0.1	0.0	0.0

Favorable separations of ionizeable organic compounds such as those found in the basic and phenolic fractions may be obtained by ion pair liquid chromatography -- a technique originally proposed by Eksborg, Schill, and coworkers (4,5). The method involves adjusting the pH of the mobile phase to assure maximum ionization of the compounds of interest and adding a hydrophobic counter-ion capable of forming ion pairs with the ionized compound. The ion pair behaves as a neutral compound and retention by the nonpolar stationary phase is enhanced. For example,



Criteria for selection of counter-ion, pH, and other considerations in the development of an ion pair separation has been addressed by Gloor and Johnson (6). Briefly, the major considerations are selecting a mobile phase pH that will insure

maximum ionization of the solutes and selecting a counter-ion that will produce the desired effect; for basic solutes, an alkyl sulfonate, and for acidic solutes, a quarternary amine. In general, an increase in the length of the alkyl chain of the counter-ion will result in increased retention of the ion pair.

Liquid chromatographic separations of each of the four light oil fractions were carried out with several ion pair and ion suppression systems, shown in Table 2, at 25°C, 45°C, and 65°C. Because solute-liquid phase solubility and the weak electrostatic ion pair equilibrium are affected by temperature, it was anticipated that an increase in temperature would facilitate the separation. However, all of the separations of the four fractions indicated a decrease in both the resolution and the number of peaks resolved. For example, Figure 3 shows decreased resolution for the phenolic fraction at 65°C as compared to 25°C using an ion suppression system.

TABLE 2. - Ion Pair and Ion Suppression Solvent Systems

ACETATE

0.05M	Ammonium acetate/acetic acid (pH 3.5) → Acetonitrile
0.05M	Ammonium acetate/acetic acid (pH 3.5) → Methanol
0.01M	Ammonium acetate/acetic acid (pH 3.5) → Acetonitrile
1.00M	Ammonium acetate/acetic acid (pH 3.5) → Acetonitrile

PHOSPHATE

0.005M	Potassium dihydrogen phosphate (pH 3.0) → Acetonitrile
0.05M	Potassium dihydrogen phosphate (pH 3.0) → Acetonitrile
0.05M	Potassium monohydrogen phosphate (pH 6.9) → Acetonitrile
0.05M	KH_2PO_4/50% Acetonitrile (pH 3.0) → 0.05M K_2HPO_4/50% Acetonitrile (pH 6.9)

SULFONATE

0.01M	Sodium n-hexane sulfonate (pH 3.5) → Acetonitrile
0.1M	Sodium n-hexane sulfonate (pH 3.5) → Acetonitrile
0.01M	Sodium n-hexane sulfonate (pH 3.5) → Methanol
0.1M	Sodium n-hexane sulfonate (pH 3.5) → Methanol

TETRABUTYLAMMONIUM PHOSPHATE

0.005M	Tetrabutylammonium phosphate (pH 7.5) → Acetonitrile
0.05M	Tetrabutylammonium phosphate (pH 7.5) → Acetonitrile

Since the extent to which the sample is ionized is influenced by the ionic strength of the mobile phase, an increase in buffer concentration should result in an increase in ion pair formation (7). Therefore, if ion pairing is the predominant mechanism in the separation, capacity factors, that is, elution times, of ion-paired components would increase with increasing buffer concentration. Separations of each of the four light oil fractions were carried out at pH 3.5 using two buffer concentrations, 0.01 M and 0.1 M hexane sulfonate. Except for slightly earlier overall elution times at higher concentrations, the phenolic, HA, and HC fractions displayed nearly identical peak pattern and resolution at both concen-

trations. This was expected since there should be no ion pair effect on the components in these fractions. In the separations of the basic fraction, there were distinct shifts in the positions of some of the component peaks at the higher buffer concentration. These peaks were presumed to be due to compounds capable of forming ion pairs at pH 3.5, such as aryl amines.

Three buffer systems were investigated at pH 3-3.5: 0.01 M hexane sulfonate, 0.005 M potassium dihydrogen phosphate, and 0.05 M ammonium acetate. At low pH, two predominant processes affect the separation: ion suppression of weak acids (for example, phenols), and ion pair formation of weak bases (for example, aniline). Compared to reverse phase separations, the buffer separations of the HC and HA fractions indicated no change other than slight overall reduction in retention times. The effect of ion suppression, that is, an increase in elution times of weak acids due to their undissociated state, was not evident in the phenolic fraction separations for any of the three systems. For compounds with small dissociation constants such as phenols and cresols, the distribution coefficients of the undissociated compounds are relatively unaffected by change in pH in the 2-6 pH range (8). Since separation by ion suppression is dependent on liquid/ liquid distribution, the addition of a buffer does not significantly alter the capacity ratios of these compounds. Assuming that the phenolics in the basic fraction are likewise unaffected in these systems, all changes in the separations of the basic fraction were attributed to nitrogen-containing components. All three separations of the basic fraction displayed increased resolution and decreased capacity ratios. The effectiveness of these systems is in the order 0.05 M ammonium acetate > 0.05 M potassium dihydrogen phosphate > 0.01 M hexane sulfonate. Figure 4 compares the separation of the basic fraction with reverse phase and 0.05 M ammonium acetate systems.

At pH 7.5, weak bases are present in the non-ionic form and weak acids in the ionic form. The counter-ion studied at this pH was 0.005 M tetrabutylammonium phosphate. In comparison to reverse phase separations, the phenolic fraction, as well as the basic fraction, displayed increased capacity ratios and improved resolution indicating that both ion suppression and ion pair formation were predominant factors in the separation. Overall, however, the hexane sulfonate separations were superior to the tetrabutylammonium phosphate separations. A comparison of the separations of the phenolic fraction with 0.005 M tetrabutylammonium phosphate and 0.01 M hexane sulfonate systems is shown in Figure 5. Again, the separations of the HC and HA fraction were generally unaffected by the buffer system.

CONCLUSION

It appears that several factors and different mechanisms contribute to the separation of eight oils by ion pair and ion suppression reverse phase liquid chromatography. An increase in column temperature affected the capacity factors reducing elution times, but the viscosity change and disruption of thermal equilibrium adversely affected the resolution.

Due to the variety of species found in the light oil, the separation behavior of certain constituents may be affected by ion pair formation or ion suppression. The relationship depends on the concentration of the counter-ion, its solubility in the bonded phase, and the degree of ionization of the solute which bears a direct relationship to the pH of the mobile phase.

The separation of heteroatom and phenolic compounds are generally enhanced by specific ion pair and ion suppression techniques; however, aromatic and hydrocarbon compounds show separations similar to traditional reverse phase techniques.

In applying these relationships to the separation of light oils, optimization of chromatographic conditions for each class of compounds must be considered. A summary of these parameters and their influence in the separation of light oils is shown in Table 3. Capacity ratios of certain components can be effectively altered by ion pair and ion suppression techniques so as to significantly improve the separation, resolution, and identification of components in the light oil.

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TABLE 3. - Summary of Chromatographic Parameters and Their Influence on Light Oil Separations

PARAMETER	FACTOR(S) AFFECTED	OBSERVATIONS HC HA	Phenolic	Basic	EXPLANATION
Temperature	Liquid phase solubility Ion pair equilibrium	Decrease in resolution and number of peaks with increasing temperature.			Decreased mobile phase viscosity. Disruption of thermal equilibrium of ion pair and increased mobile phase solubility.
Ionic Strength	Ionization of sample ion pair formation	No effect		Some peaks shifted with increasing ionic strength	Should be no ion pair effect in HC, HA, or phenolic. Ion-pair formation occurs with aryl amines in basic fraction
Buffer addition at pH 3-3.5	Ion suppression of weak acids Ion pair formation of weak bases	No effect	No ion suppression effect	Increased resolution and decrease of capacity ratios	Phenols and cresols unaffected in this system.
Buffer addition at pH 7.5	Ion suppression of weak bases. Ion pair formation of weak acids.	No effect	Increased capacity ratios and improved resolution		Both ion suppression and ion pair formation occur
		HC HA	Phenolic	Basic	

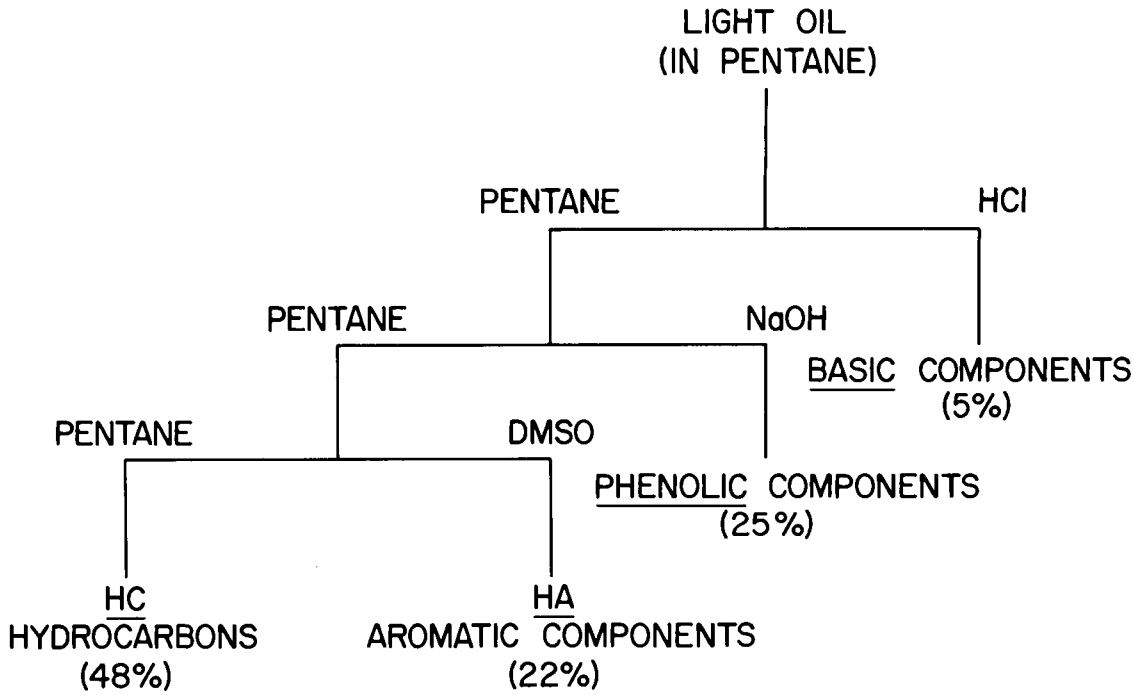


Figure 1. - Flow diagram of light oil separation procedure.

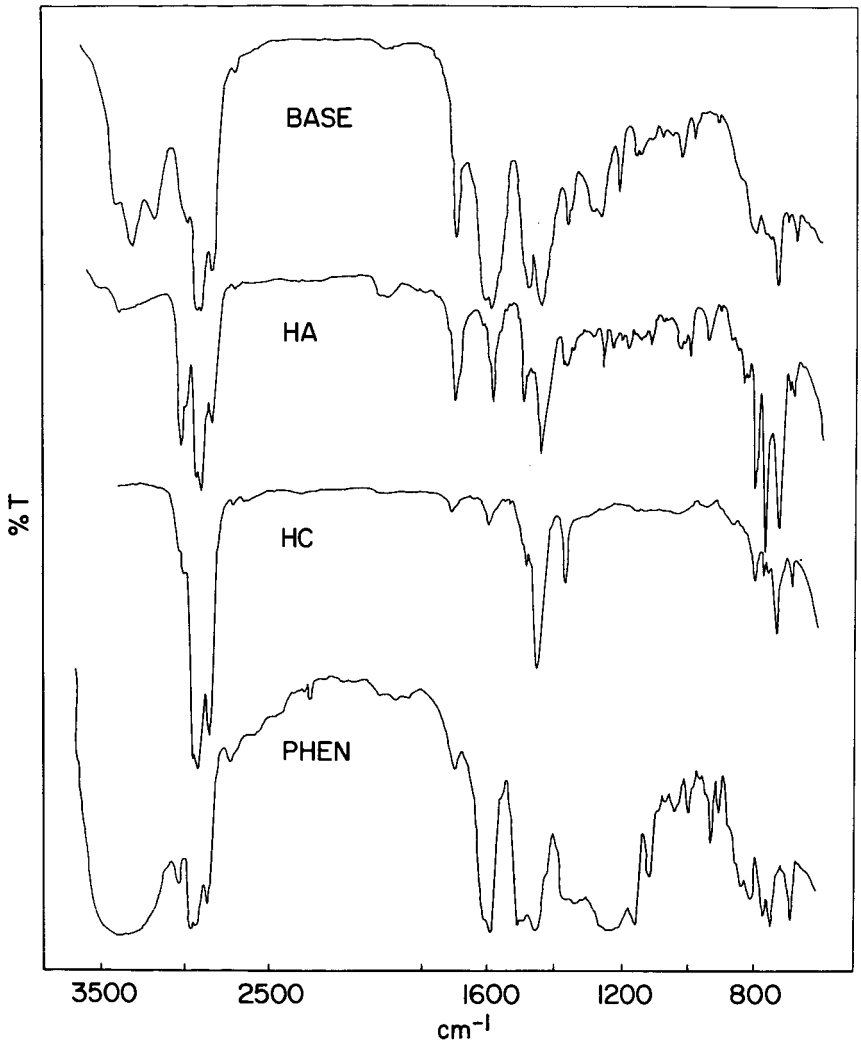


Figure 2. - Infrared spectra of light oil fractions. Capillary films.

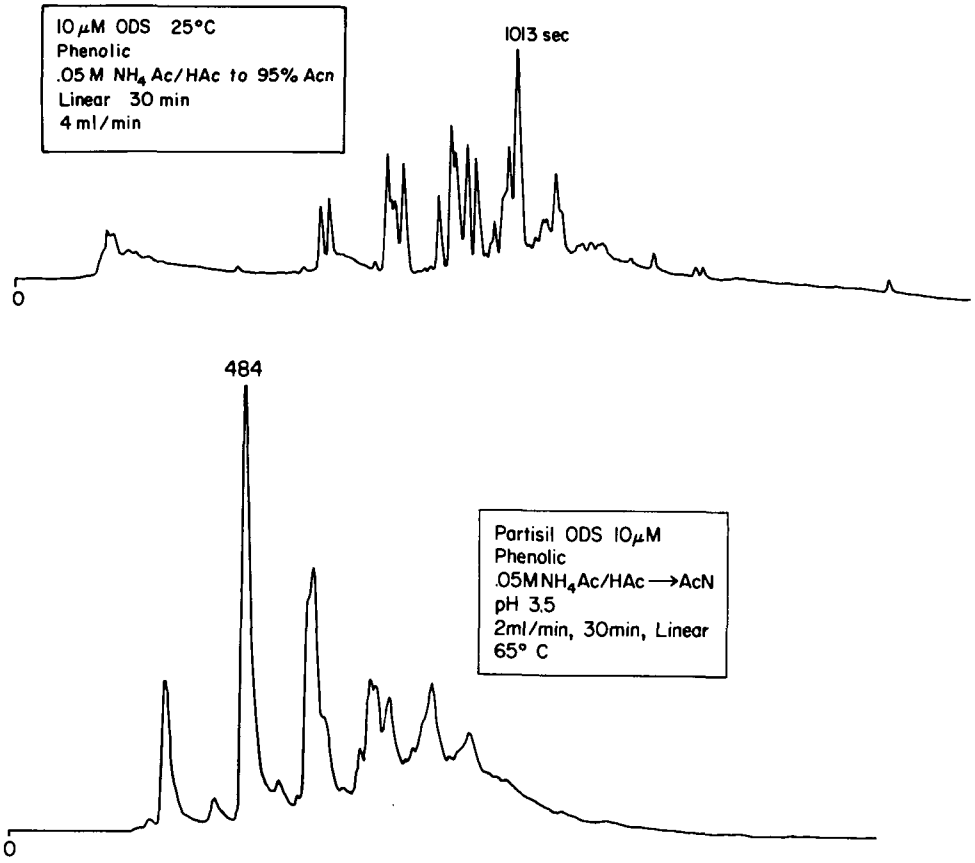


Figure 3. - Comparison of ion suppression LC separations at 25° and 65° of the phenolic fraction of light oil.

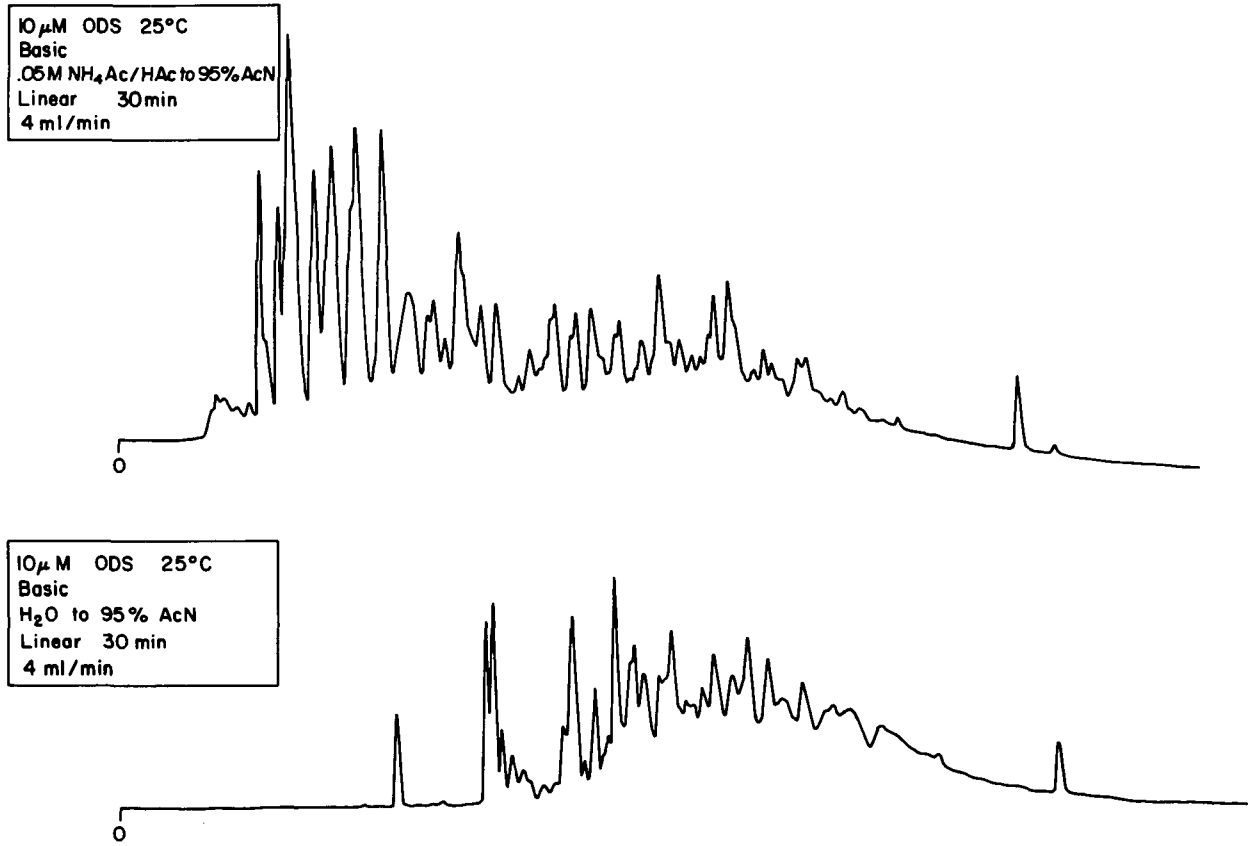
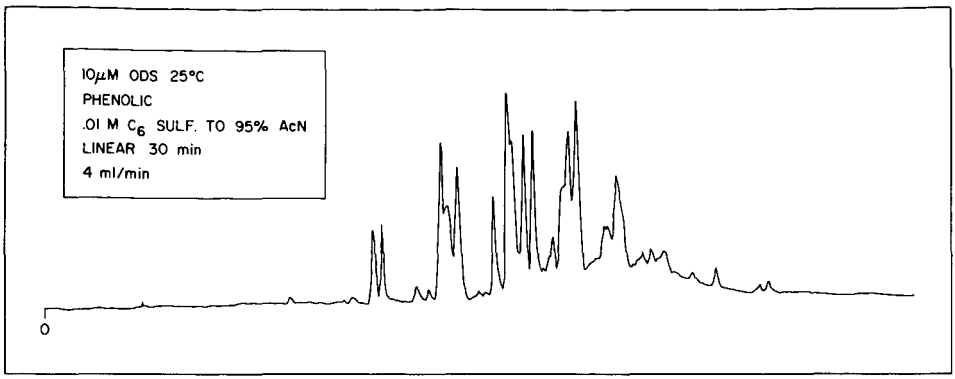


Figure 4. - Comparison of reverse phase and .05M acetate/acetic acid (pH 3.5) LC separations of the basic fraction of light oil.



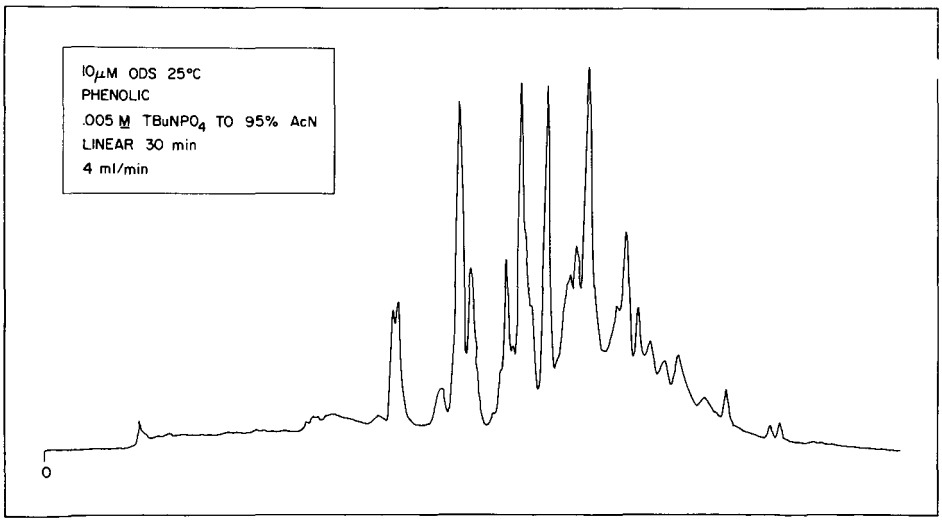


Figure 5. - Comparison of phenolic fraction separations with 0.05 M tetrabutylammonium phosphate (pH 7.5) and 0.01 M n-hexane sulfonate (pH 3.5)