

VAPOUR PHASE CHROMATOGRAPHIC SEPARATION OF AROMATICS FROM SATURATED AND OLEFINIC HYDROCARBONS*

By J. R. ANDERSON† and K. H. NAPIER†

Gas-liquid partition chromatography (cf. James and Martin 1952; Ray 1954) has proved to be an attractive technique for the analysis of hydrocarbon mixtures. The use of a non-polar stationary phase such as liquid paraffin or "Apiezon" oil results in the elution of the components in the order of their boiling points and this may cause difficulty in separation when the differences in volatility are small. Thus *cyclohexane* (b.p. 81.4 °C/760 mm) and *benzene* (b.p. 80.1 °C/760 mm) were only partly resolved at 100 °C on a column 4 ft long with "Apiezon" oil as the stationary phase. It has been found that the polyether glycols or their derivatives provide a liquid stationary phase which is selective for the separation of aromatics from saturated and olefinic hydrocarbons of comparable boiling points due to the greater interaction of the aromatic with the polyether.

The equipment used was essentially similar to that described by Ray (1954), except the signal from the thermal conductivity cell which was energized from a D.C. source was amplified by a feedback galvanometer amplifier and recorded on a 1 mA Evershed and Vignols recorder. Later the signal was fed directly to a 5 mV Speedomax recorder. The thermal conductivity cell was operated at room temperature and pressure. The liquid stationary phase (40% w/w) was supported on 44–60 mesh alumina which was obtained by grinding and sieving 16–32 mesh "Type A" alumina from Peter Spence and Sons Ltd., Widnes, England. This support was found to impede the gas flow much less than the keiselguhr packings of James and Martin (1952) and Ray (1954). When carrying the liquid polyether, the alumina was quite inert and formed a highly convenient supporting material. Nitrogen, dried over silica gel, was used as the carrier gas.

Figure 1 (a) shows the chromatogram obtained from a mixture of *cyclohexane*, *benzene*, and *cyclohexene* (b.p. 83 °C/760 mm) with a stationary phase of triethylene glycol (T.G.) at 100 °C, while Figure 1 (b) shows the same mixture over polyethylene glycol cresyl ether (P.G.C.E.) at 131 °C. *Benzen*e, despite its lower boiling point, appears last in both cases and is easily separated from the other two. The presence of one double bond has comparatively little influence on the behaviour of *cyclohexene* compared to *cyclohexane* although these are separated rather better on P.G.C.E. than on T.G. The similar behaviour of the two stationary phases with *benzene* shows that it is the ether link and not the hydroxyl group which is primarily responsible for interaction

* Manuscript received May 10, 1956.

† Department of Physical Chemistry, N.S.W. University of Technology, Broadway, Sydney.

with the aromatic. A comparison of Figures 1 (c) and 1 (d) shows that for equal flow rates the separation of benzene from *cyclohexane* is better at 100 °C than 131 °C.

On P.G.C.E. at 132 °C, *cyclohexane* is not separated from methyl*cyclohexane* (b.p. 100.3 °C/760 mm) although benzene is easily separated from toluene

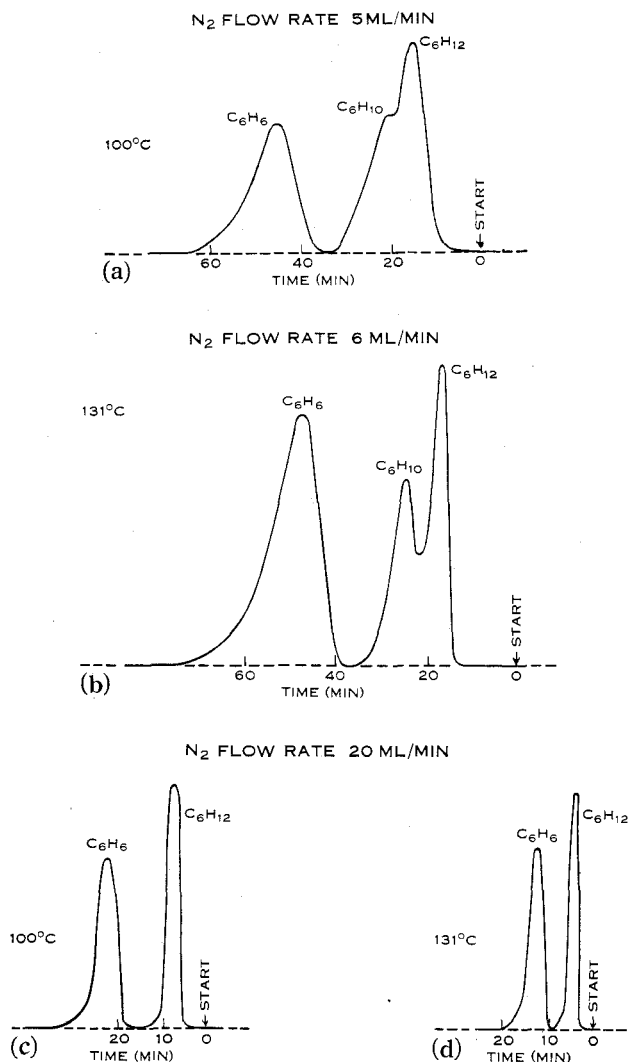


Fig. 1.—Chromatograms on (a) triethylene glycol; (b), (c), (d) polyethylene glycol cresyl ether.

(b.p. 110.8 °C/760 mm). The chromatogram from a four component mixture containing benzene, toluene, *cyclohexane*, and methyl*cyclohexane* is shown in Figure 2. That a saturated hydrocarbon of b.p. 100 °C appears in the eluate well before benzene suggests that this stationary phase may solve the problem of the analysis of the products from a catalytic reforming process for petroleum

(Keulemans, Kwantes, and Zaal 1956), where on a number of stationary phases of various types interference between these components was found.

The enhanced interaction of the polyether with an aromatic molecule is probably due to dipole-induced dipole forces involving the comparatively

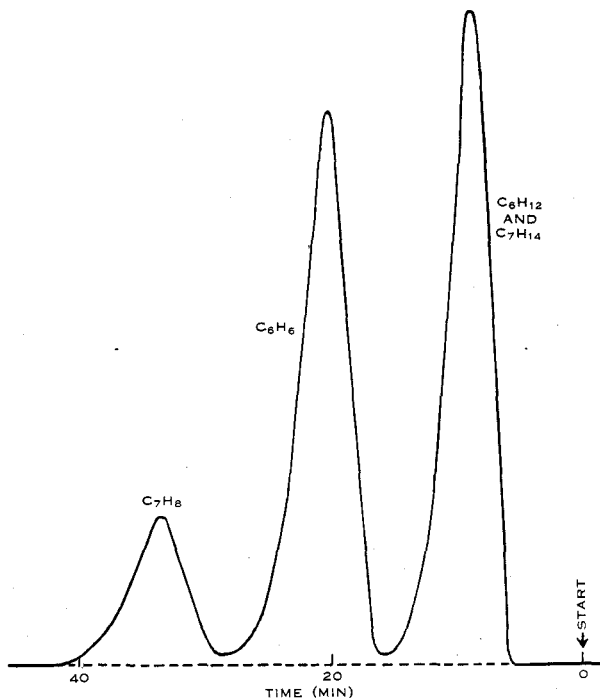


Fig. 2.—Chromatogram on polyethylene glycol cresyl ether.

easily polarizable π -electrons of the benzene molecule. A contribution from charge-transfer forces (Mulliken 1952a) is not likely to be significant since ethers and benzene are both type n donor molecules on the classification of Mulliken (1952b).

References

- JAMES, A. T., and MARTIN, A. J. P. (1952).—*Biochem. J.* **50**: 679.
KEULEMANS, A. I. M., KWANTES, A., and ZAAL, P. (1956).—*Anal. Chim. Acta* **13**: 357.
MULLIKEN, R. S. (1952a).—*J. Amer. Chem. Soc.* **74**: 811.
MULLIKEN, R. S. (1952b).—*J. Phys. Chem.* **56**: 801.
RAY, N. H. (1954).—*J. Appl. Chem.* **4**: 21.