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GAS CHROMATOGRAPHIC RETENTION BEHAVIOR OF POLYCYCLIC AROMATIC COMPOUNDS ON SMECTIC LIQUID-CRYSTALLINE POLYSILOXANE STATIONARY PHASES

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SUMMARY

Factors affecting gas chromatographic retention on smectic liquid-crystalline phenyl and biphenyl carboxylate ester polysiloxane stationary phases were studied for neutral polycyclic aromatic hydrocarbons (PAHs) and slightly polar sulfur heterocycles. Retention was greatly affected by the molecular geometry of the solutes in addition to other contributions such as solute vapor pressure and polarity. The major geometrical factor was the length-to-breadth (L/B) ratio of the solutes, while of less importance, but still significant, was the solute molecular shape. The effect of solute L/B on selectivity was larger in the smectic region than in the nematic region. Furthermore, the selectivity of the smectic phase was generally better than that of the nematic phase. Compounds with at least four aromatic rings annelated in a straight line were retained much longer, and compounds with aromatic rings annelated in a curved or arc-like arrangement were retained much less, than predicted by the L/B ratios for these compounds. Arc-like molecules with groups attached to the outer curved side were, however, retained longer than predicted. Lower chromatographic efficiencies were measured for the arc-like molecules as compared to the latter type of molecules. The latter appear to penetrate the laminar arrangement of the polymer liquid-crystalline side groups more easily, thus leading to better solute diffusion and improved mass transfer.

INTRODUCTION

Liquid crystals are unique stationary phases in gas chromatography (GC) because of their temperature dependent ordered structures. The rod-like liquid-crystalline molecules retain their orientation with respect to each other with their long axes parallel. Solutes which are also rigid rod-like molecules interact with the ordered structure of the stationary phase[1]. While compounds usually elute in order of their increasing boiling points on conventional, non-polar stationary phases, retention is additionally affected by solute geometry when using liquid-crystalline stationary phases[1].

Polycyclic aromatic compounds (PACs) generally are rigid planar molecules

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