Calix[4]arene Derivatives as Stationary Phases for Capillary Gas Chromatography

L. Lin / C. Y. Wu* / Z. Q. Yan / X. Q. Yan / X. L. Su / H. M. Han
Department of Chemistry, Wuhan University, Wuhan 430072, Hubei Province, China

Key Words
Gas chromatography
Stationary phases
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Summary

Introduction
Calixarenes, cyclic phenol-formaldehyde polycondensates, have been regarded as the third generation of host compounds after cyclodextrins and crown ethers since they can complex with ionic and neutral molecules and are easily modified to the more functionalized host calixarenes which may have great potential in analytical chemistry. A few articles reported their use as stationary phases in gas chromatographic separation [1-3]. The first experiments in gas chromatography were in 1983 at Parma University, Italy [3]. Homologues of alcohols, chlorinated hydrocarbons and aromatic compounds were separated on a column packed with calix[8]arene supported on silanized Chromosorb W. Little progress has been reported since then due to poor solubility and coating difficulties of the parent ligands. Recently, Feltl et al. [4, 5] further studied the inclusion properties of the basic, unsubstituted calixarenes in gas chromatography but, as the result of low column efficiency, the utility of calixarenes in separations and the precision of the results were greatly limited. We have synthesized new calix[4]arene derivatives C[4]A and C[4]B (Figure 1) for use as selective components of stationary phases in OV1701. The lipophilicity of the derivatives was greatly improved when undecenyl groups were introduced on the basic calix[4]arene and coating difficulties were alleviated by mixing with OV1701. These phases were tested for efficiency, polarity, thermal stability, selectivity and inclusion properties.

Experimental
Synthesis
5,11,17,23-Tetra-tert-butyl-25,27-bis(isopropyl carbamoyl-methoxy)-26,28-diundecenyoxy calix[4]arene (C[4]A) was synthesized according to references [6, 7]. The 1H NMR spectrum showed it existed in a conical conformation.


Column Preparation
Fused-silica capillary columns (Yorignian Optical Fibre Factory, Hubei Province, P.R. of China) were rinsed with 10 mL methanol and purged with nitrogen at 250 °C for 2 h to remove acidic impurities. Columns were then statically coated with a solution of 0.5 % (w/v) C[4]A-OV1701, C[4]B-OV1701 (1:1) and reference OV1701 in dichloromethane at 33 °C. Following the coating procedure and flushing with nitrogen for 3 h, the columns were conditioned at 280 °C for 6 h under a slow stream of nitrogen before use.

Column Evaluation
A GC-7A gas chromatograph (Shimadzu, Japan) equipped with capillary split injection system and flame ionization detector was used throughout. Nitrogen was the carrier gas at a linear velocity of 12-15 cm s⁻¹. The...
Injection split ratio was (50:1) and the injector and detector temperatures were maintained at 250 °C and 280 °C, respectively. The efficiency of columns was determined as the number of plates per metre for naphthalene at 120 °C. The polarity of the stationary phases was characterized by McReynolds constants which include dispersion forces, dipole-dipole forces, hydrogen-bonding forces, etc. The glass transition temperature was determined by the change in slope of the plot of the logarithm of the capacity factor (k) versus reciprocal absolute temperature for naphthalene. Aromatic positional isomers were used to demonstrate the unique selectivity of these stationary phases.

Results and Discussion

New compounds C[4]A and C[4]B were both disubstituted by undecenyl groups in the lower rim of calix[4]arene which greatly improved the lipophilicity of the compounds. The other two phenolic groups of calix[4]arene were modified by different substituents which may exhibit different properties in some aspects. After mixing with OV1701, we predicted that they would have good film-forming ability, high thermal stability and unique selectivity.

Chromatographic Properties


Figure 2 gives chromatograms for the Grob test mixture obtained on C[4]A-OV1701 and C[4]B-OV1701 columns. They show that the mixtures were well separated (except for decane and 1,3-butanediol on a C[4]B-OV1701 column) and each peak is symmetrical. It is notable that naphthalenes all eluted at the end of the chromatogram which is different from pure OV1701. This can be explained by strong π-π interaction between solute and calixarenes which implies special retention behavior of calixarenes toward aromatics. The average polarities of the two combined columns, represented by McReynolds constants, are shown in Table II. It can be seen that C[4]B is weakly polar due to the four phenolic hydroxyl groups in the lower rim of calix[4]arene, all substituted by weak polar residues. As regards C[4]A, it exhibits stronger polarity than OV1701 as the result of the imide substituent.

The operating temperature range is determined by the glass transition temperature and column bleeding. Figure 3 shows the plot of log k for naphthalene on the two columns. The changes in slope at 86.7 °C for C[4]A-OV1701 and 80 °C for C[4]B-OV1701 correspond to glass transition points. This indicates that calix[4]arene derivative, adduct stationary phases have lower minimum operating temperatures than dibenzo crown.

<table>
<thead>
<tr>
<th>Stationary phase</th>
<th>Column dimensions, length x I.D. (m x mm)</th>
<th>Peak asymmetry</th>
<th>Column efficiency (plates m⁻¹)</th>
<th>Naphthalene capacity factor (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C[4]A-OV1701</td>
<td>13.5 x 0.25</td>
<td>1.14</td>
<td>3138</td>
<td>4.31</td>
</tr>
<tr>
<td>C[4]B-OV1701</td>
<td>12 x 0.25</td>
<td>1.05</td>
<td>4602</td>
<td>5.17</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Column</th>
<th>Benzene</th>
<th>Butanol</th>
<th>2-Pentanone</th>
<th>Nitropropane</th>
<th>Pyridine</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>C[4]B-OV1701</td>
<td>41</td>
<td>104</td>
<td>106</td>
<td>180</td>
<td>139</td>
<td>104</td>
</tr>
<tr>
<td>OV1701</td>
<td>67</td>
<td>170</td>
<td>153</td>
<td>228</td>
<td>171</td>
<td>158</td>
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