GAS CHROMATOGRAPHIC SEPARATION OF cis-trans ISOMERS OF NORMAL ALKENES USING AgNO₃ SOLUTIONS AS STATIONARY PHASES

AgNO₃ solutions in ethylene glycol, diethylene glycol a. o. have been successfully used as highly selective stationary phases for the analytical and preparative separation of the cis-trans isomers of normal alkenes, mainly in the C₄—C₆ region [1—3].

The separation of n-decenes and n-undecenes is described in [4, 5].

No references concerning gas chromatographic separation of cis-trans isomers of the higher boiling normal alkenes using AgNO₃ solutions as stationary phases could be found.

In the present work, the investigation of the relationship between the structure and gas chromatographic data on AgNO₃ columns has been extended to the cis-trans isomers of internal normal alkenes up to C₁₃ (of a single carbon number). Some solvents not examined so far (butane-1,4-diol, butane-1,3-diol, butane-2,3-diol, hexane-1,6-diol a. o.) were included.

In order to improve separation, the effect of working parameters (temperature, AgNO₃ content, carrier gas flow rate) on the resolution of cis-trans isomers was investigated.

The UH-1 gas chromatograph with a thermal conductivity detector was used. The inlet system was modified so that the inlet pressure was read on the mercury manometer. The desired amount of silver nitrate was dissolved in liquid stationary phase or in liquid stationary phase solution in 50 ml ethanol at 40—50°C. The solution was filtered, when necessary, before adding a known amount of Chromosorb P (30—60 mesh). The ethanol was then removed by warming under reduced pressure, protecting the column packing from light. The columns used were 1 m tubes made from 6 mm internal diameter stainless steel tubing. The weight of the stationary phase in column was determined. The columns were operated at 40—100°C with helium flow of about 60—100 ml/min. Liquid sample sizes were 1—5 μl.
The \( n \)-alkenes were prepared by selective hydrogenation of alkynes either with metallic sodium in liquid ammonia to \textit{trans}-alkenes or in the presence of the Lindlar catalyst at a room temperature predominantly to \textit{cis}-alkenes.

### Resolutions of \textit{cis-trans} isomers of \( n \)-alkenes

<table>
<thead>
<tr>
<th>Stationary liquid phase (Solvent for ( \text{AgNO}_3 ))</th>
<th>Temperature, °C</th>
<th>( \text{AgNO}_3 ) content in the solvent, %</th>
<th>The content of the ( \text{AgNO}_3 ) solution in column packing, %</th>
<th>Resolution**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>60 sat.*</td>
<td>40.0</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>60 sat.</td>
<td>42.5</td>
<td>2.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Butane-1,3-diol</td>
<td>60 sat.</td>
<td>40.0</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Butane-2,3-diol</td>
<td>60 sat.</td>
<td>33.2</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>60</td>
<td>24.5</td>
<td>3.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Hexane-1,6-diol</td>
<td>60</td>
<td>29.4</td>
<td>3.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

* Saturated \( \text{AgNO}_3 \) solution.

** Resolution \( R_s = \frac{\text{lI}}{\text{b}_{0.5} - \text{b}_{0.5}^\text{I}} \), where \( d_{R}^{\text{lI}} \) and \( d_{R}^{\text{I}} \) are the true retention distances of \textit{cis} and \textit{trans}-isomers and \( b_{0.5}^\text{I}, b_{0.5}^{\text{lI}} \) the peak widths at half height.

The diols used were commercial products.

In Table, the resolutions for pairs of \textit{cis-trans} isomers investigated are reported. For comparison, the data for ethylene glycol—\( \text{AgNO}_3 \) stationary phase are included.

The use of butane-1,4-diol as a solvent for \( \text{AgNO}_3 \) considerably increased the column performance as compared to ethylene glycol, and the resolutions of about 3.8 and 3.4 at 80° for \textit{cis-trans} isomers of 2-decene and 2-dodecene were obtained (Fig.). With ethylene glycol the respective values were 2.7 and 1.3.

At lower temperatures, butane-1,4-diol—\( \text{AgNO}_3 \) stationary phases compared favourably to those of butane-2,3-diol—\( \text{AgNO}_3 \). The selectivity of the latter diminishes appreciably at higher temperatures and \textit{cis-trans} isomers of dodec-2-ene could not be separated with this column.

At 100°, the separation of \textit{cis-} and \textit{trans}-5-tridecenes with the butane-1,4-diol column was possible (Fig.). The latter columns are not stable at temperatures of about 100°, at which they can be used only for a few hours without essential loss of selectivity.

Separation of \textit{cis-trans} isomers was poor on butane-1,3-diol as compared to that on ethylene glycol.
Hexane-1,6-diol was not such a good solvent as butane-1,4-diol, but its lower volatility enables higher working temperatures to be used, which is especially needed when separating higher boiling isomers.

According to the decrease of column selectivity at higher temperatures (60—80°), the solvents used can be given in the following order: butane-1,4-diol > hexane-1,6-diol > ethylene glycol > diethylene glycol > butane-1,3-diol.

Thus, solvent effect could not be neglected, although the selectivity of stationary phases containing AgNO₃ is attributable to the Ag-ion and no resolution of cis-trans pairs of normal alkenes occurs when using short columns with these solvents alone as stationary phases.

**REFERENCES**


*Academy of Sciences of the Estonian SSR, Institute of Chemistry*

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