EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. 19. KÖIDE
KEEMIA * GEOLOOGIA. 1970, Nr. 2

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ 19
ХИМИЯ * ГЕОЛОГИЯ. 1970, № 2

*SILVIA RANG, O. EISEN, K. KUNINGAS*

# GAS CHROMATOGRAPHIC SEPARATION OF UNSATURATED HYDROCARBONS USING $AgNO_3$ SOLUTIONS AS STATIONARY PHASES

## 2. THE EFFECT OF SOLVENT AND OF THE $AgNO_3$ CONCENTRATION ON COLUMN PERFORMANCE

In our previous work, effects of working parameters on column efficiency were discussed [1]. In the present paper, effects of solvent and of $AgNO_3$ concentration on column selectivity are reported.

The reagents, apparatus and procedure are described in [1].

### Gas chromatographic data

The values of relative retentions of normal 2- and 3-alkenes determined on various stationary phases containing $AgNO_3$ at 45, 60, 80 and 100°C are summarized in Table 1. For tridecene-5 *trans*- and *cis*-isomers the relative retentions at 100° and helium flow rate 84 ml/min were 12.9 and 17.0 accordingly on the $AgNO_3$-PG 400 stationary phase. Plots of logarithms of relative retentions of 2-alkenes and 3-alkenes against the number of carbon atoms in molecule are satisfactorily linear, as may be seen from Fig. 1 showing some examples of these plots.

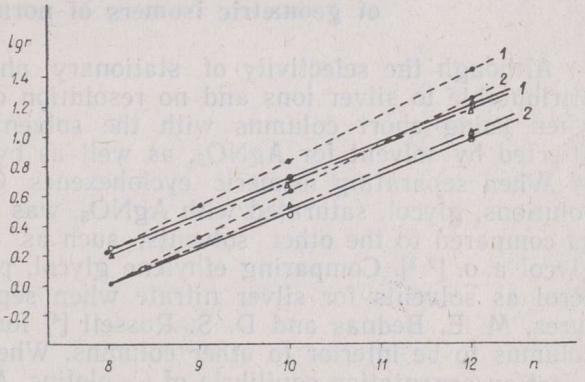


Fig. 1. Lg $r$ (relative retention) as a function of $n$ (number of carbon atoms in the molecule of normal 2-alkenes), at 80°, helium flow rate — 84 ml/min;
———— column No. 33 ($AgNO_3$-B14) (Table 1),
– – – – – „ „ 15 ($AgNO_3$-H16),
——— – ——— „ „ 37 ($AgNO_3$-PG 400);
*1* — *cis*-isomer, *2* — *trans*-isomer.

The straight lines obtained are expressed in the form of the equation $\lg r = a + bn$. In Table 1, the values for constants $a$ and $b$ are given. The relative retentions for the other members of the same series can be calculated from these equations.

The differences in relative retentions of *cis-trans*-isomers of internal alkenes decrease with the shifting of the double bond in the carbon chain towards the centre of the molecule and with the increasing of molecular

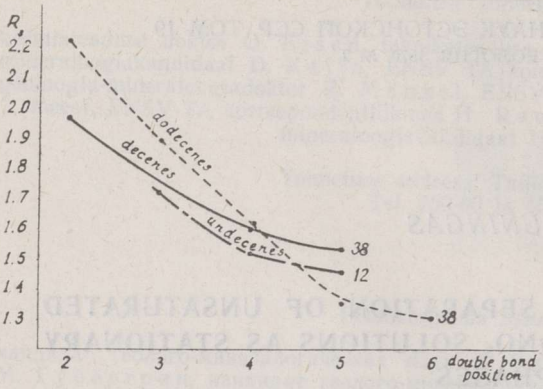


Fig. 2. Variations in $R_s$ values with double bond position and molecular weight.
The numbers refer to the columns listed in Table 1; gas flow rate — 84 ml/min.

weight. The resolutions for pairs of geometric isomers decrease in the same order, as it is seen in Fig. 2. The farther the double bond is located towards the centre, the harder is separation, due to the minimizing of the differences in the physical and chemical properties of the geometric isomers. Therefore, more effective columns for separating 4- and 5-isomers are needed than for those having double bond at the second carbon atom. For instance, *cis-trans*-isomers of dodecene-2 were fully separated by the column No. 38, at 80°, but the isomers of dodecene-5 were separated less successfully. To separate them thoroughly, different operating conditions ought to have been used (a longer column, a more selective stationary phase, etc.).

To guarantee satisfactory resolution of all pairs of geometric isomers (of a single carbon number), the optimum operating conditions are to be created, favourable for separating, first of all, those isomers that have double bond nearest to the centre of the molecule.

## Effects of solvent on column performance with regard to resolution of geometric isomers of normal alkenes

Although the selectivity of stationary phases containing $AgNO_3$ is attributable to silver ions and no resolution of geometric isomers occurs when using short columns with the solvent alone, it is considerably affected by solvent for $AgNO_3$, as well as by $AgNO_3$ concentration.

When separating isomeric cyclohexenes $C_6$—$C_9$ on various $AgNO_3$ solutions, glycol, saturated with $AgNO_3$, was found to give better results as compared to the other solvents, such as benzyl cyanide, triethylene glycol a. o. [2, 3]. Comparing ethylene glycol, polyethylene glycol and glycerol as solvents for silver nitrate when separating alkane-alkene mixtures, M. E. Bednas and D. S. Russell [4] found the polyethylene glycol columns to be inferior to other columns. When investigating the solvent effect on argentation equilibria of $C_5$ olefins, A. Genkin [5] found the equilibrium coefficients to be 2.5 times inferior when ethylene glycol was substituted by diethylene glycol. Thus, the best solvent for $AgNO_3$ was found to be ethylene glycol. D. V. Banthorpe a.o. [6] noticed no essential difference in column performance when working with $TlNO_3$ solutions in polyethylene glycol and ethylene glycol. The activity of the latter decreases rapidly when temperature rises above 65° [4]. High vapour pressure of ethylene glycol leads to variations in retention data due to elution from column when operating at elevated temperatures needed for separating higher molecular weight compounds.

Therefore, for separating higher unsaturated hydrocarbons (above $C_9$), solvents of inferior selectivity with lower vapour pressure, such as di-,

**Relative retentions and values of the constants $a$ and $b$ in the equation $\lg r = a + bn$ for 2- and 3-alkenes**

| Column No. | Solvent for $AgNO_3$ | In text indicated as follows | $AgNO_3$ content in the solvent, % | The content of the $AgNO_3$ solution in column packing, % | Temperature, °C | Relative retentions ** of 2-alkenes | | | | | | | | Relative retentions of 3-alkenes | | | | | | | | $\lg r = a + bn$ for 2-alkenes | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Octene-2 | | Nonene-2 | | Decene-2 | | Dodecene-2 | | Octene-3 | | Nonene-3 | | Decene-3 | | Undecene-3 | | for *trans*-isomer | | for *cis*-isomer | |
| | | | | | | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | $a_t$ *** | $b_t$ | $a_c$ *** | $b_c$ |
| 18 | Ethylene glycol | EG | sat.* | 40.0 | 60 | 1.00 | 3.31 | 2.05 | 4.84 | 3.43 | 8.05 | — | — | — | — | — | — | — | — | 7.05 | 12,9 | —2.110 | 0.268 | —1.168 | 0.208 |
| | | | | | 80 | 1.00 | 2.92 | 1.29 | 3.79 | 2.58 | 5.84 | 7.56 | 13.6 | — | — | — | — | — | — | 5.00 | 8.96 | —1.820 | 0.220 | —0.920 | 0.170 |
| 19 | Diethylene glycol | DEG | sat. | 42.5 | 60 | 1.00 | 2.75 | 1.69 | 4.38 | 3.69 | 7.50 | — | — | — | — | — | — | — | — | 5.20 | 12.25 | —2.148 | 0.270 | —1.296 | 0.218 |
| | | | | | 80 | 1.00 | 2.63 | 1.71 | 4.08 | 3.13 | 6.85 | 8.05 | 14.25 | — | — | — | — | — | — | 5.05 | 9.80 | —1.886 | 0.236 | —1.260 | 0.210 |
| 34 | Triethylene glycol | TEG | 29.4 | 38.8 | 60 | 1.00 | 2.50 | — | — | 3.55 | 7.75 | — | — | 0.98 | 2.26 | 1.77 | 3.84 | 3.71 | 7.10 | 6.85 | 12.50 | —2.188 | 0.274 | —1.546 | 0.246 |
| | | | | | 80 | 1.00 | 2.28 | — | — | 3.14 | 6.56 | 10.7 | 19.0 | 1,14 | 2.23 | 2.00 | 3.57 | 3.14 | 5.72 | 5.37 | 9.44 | —2.018 | 0.252 | —1.466 | 0.230 |
| 37 | Polyethylene glycol 400 | PG 400 | 23.0 | 42.1 | 60 | 1.00 | 1.73 | — | — | 3.98 | 6.51 | — | — | — | — | 1.90 | 2.96 | — | — | 7.45 | 10.83 | —2.416 | 0.302 | —2.024 | 0.284 |
| | | | | | 80 | 1.00 | 1.59 | — | — | 3.14 | 4.80 | 10.15 | 15,3 | — | — | 1.70 | 2.45 | — | — | 5.09 | 7.27 | —2.018 | 0.252 | —1.750 | 0.244 |
| | | | | | 100 | 1.00 | 1.57 | — | — | 2.97 | 4.54 | 9.15 | 13,5 | — | — | 1.55 | 2.28 | — | — | 4.64 | 6.54 | —1.906 | 0.238 | —1.680 | 0.234 |
| 22 | Butane-1,3-diol | B13 | sat. | 40.0 | 60 | 1.00 | 1.69 | — | — | 3.90 | 6.65 | — | — | — | — | — | — | — | — | — | — | —2.378 | 0.298 | —2.142 | 0.296 |
| | | | | | 80 | 1.00 | 1.57 | — | — | 3.33 | 5.35 | — | — | — | — | — | — | — | — | 5.85 | 8.70 | —2.076 | 0.260 | —1.918 | 0.266 |
| 14 | Butane-2,3-diol | B23 | sat. | 33.2 | 60 | 1.00 | 2.48 | 2.00 | 4.72 | — | — | — | — | — | — | — | — | — | — | — | — | —2.416 | 0.300 | —1.838 | 0.278 |
| | | | | | 80 | 1.00 | 2.18 | 1.90 | 4.05 | 3.57 | 7.60 | — | — | — | — | — | — | — | — | 6.63 | 12.54 | —2.218 | 0.276 | —1.816 | 0.270 |
| | | | | | 100 | 1.00 | 1.94 | 1.89 | 3.49 | 3.40 | 6.06 | — | — | — | — | — | — | — | — | 7.95 | 12.93 | —2.118 | 0.264 | —1.696 | 0.250 |
| 33 | Butane-1,4-diol | B14 | 5.3 | 40.0 | 60 | 1.00 | 1.85 | 1.83 | 3.14 | 3.57 | 6.51 | — | — | 1.04 | 1.91 | 2.08 | 3.72 | — | — | — | — | —2.222 | 0.278 | —1.900 | 0.272 |
| | | | | | 80 | 1.00 | 1.70 | 1.61 | 2.62 | 3.12 | 5.21 | 9.71 | 15.5 | 0.97 | 1.58 | 1.61 | 2.62 | 2.91 | 4.65 | 5.24 | 8.20 | —1.974 | 0.250 | —1.726 | 0.246 |
| | | | | | 100 | 1.00 | 1.57 | 1.53 | 2.40 | 2.68 | 4.25 | 7.63 | 11.5 | 1.00 | 1.42 | 1.52 | 2.40 | 2.50 | 3.75 | 4.25 | 6.25 | —1.746 | 0.220 | —1.530 | 0.216 |
| 38 | „ | „ | 5.7 | 40.0 | 80 | 1.00 | 1.74 | 1.80 | 2.80 | 3.16 | 5.25 | 9.80 | 15.8 | 1.05 | 1.64 | 1.80 | 2.80 | 2.96 | 4.75 | 5.25 | 8.25 | —2.010 | 0.250 | —1.712 | 0.244 |
| 26 | „ | „ | 24.5 | 40.0 | 60 | 1.00 | 2.55 | — | — | 3.46 | 8.41 | — | — | 0.98 | 2.35 | 1.76 | 4.18 | 3.46 | 7.65 | 5.90 | 12.70 | —2.180 | 0.270 | —1.650 | 0.256 |
| | | | | | 80 | 1.00 | 2.50 | — | — | 3.07 | 7.19 | — | — | 0.99 | 2.26 | 1.74 | 3.88 | 2.95 | 6.50 | 4.95 | 10.6 | —1.972 | 0.246 | —1.442 | 0.230 |
| | | | | | 100 | 1.00 | 2.60 | — | — | 2.80 | 6.75 | 7.25 | 15.75 | 1.09 | 2.57 | 2.00 | 4.25 | 2.86 | 6.45 | 4.60 | 10.3 | —1.730 | 0.218 | —1.170 | 0.200 |
| 16 | „ | „ | sat. | 40.0 | 60 | 1.00 | 2.54 | 1.90 | 4.54 | 3.42 | 8.13 | — | — | — | — | — | — | — | — | — | — | —2.186 | 0.272 | —1.586 | 0.250 |
| | | | | | 80 | 1.00 | 2.40 | 1.69 | 4.10 | 2.86 | 6.87 | 9.88 | 20.85 | — | — | — | — | — | — | 5.25 | 11.39 | —1.940 | 0.240 | —1.470 | 0.232 |
| | | | | | 100 | 1.00 | 2.48 | 1.62 | 4.00 | 2.55 | 6.25 | 7.47 | 15.55 | — | — | — | — | — | — | 4.50 | 9.50 | —1.720 | 0.214 | —1.204 | 0.200 |
| 35 | Hexane-1,6-diol | H16 | 20.0 | 14.3 | 60 | 1.00 | 1.80 | — | — | 4.06 | 7.12 | — | — | — | — | 1.83 | 3.26 | — | — | 8.90 | 13.9 | —2.462 | 0.308 | —2.140 | 0.300 |
| | | | | | 80 | 1.00 | 1.85 | — | — | 3.85 | 6.55 | 15.95 | 2.62 | 1.13 | 1.77 | 2.04 | 3.25 | 3.87 | 5.89 | 7.14 | 11.3 | —2.390 | 0.298 | —2.040 | 0.290 |
| | | | | | 100 | 1.00 | 1.84 | — | — | 3.23 | 5.46 | 11.6 | 18.5 | 1.03 | 1.61 | 1.87 | 2.87 | 3.39 | 5.04 | 6.13 | 9.07 | —2.130 | 0.266 | —1.720 | 0.248 |
| 15 | „ | „ | 29.4 | 12.3 | 60 | 1.00 | 1.81 | 2.30 | 3.85 | 4.94 | 7.94 | — | — | — | — | — | — | — | — | 12.1 | 18.3 | —2.818 | 0.356 | —2.326 | 0.322 |
| | | | | | 80 | 1.00 | 1.69 | 1.82 | 3.33 | 4.00 | 6.44 | 17.11 | 26.2 | — | — | — | — | — | — | 7.78 | 11.56 | —2.456 | 0.310 | —2.176 | 0.300 |
| | | | | | 100 | 1.00 | 1.67 | 1.93 | 3.04 | 3.56 | 5.59 | 11.85 | 17.8 | — | — | — | — | — | — | 5.89 | 8.85 | —2.176 | 0.272 | —1.876 | 0.260 |
| 27 | Butane-1,4-diol | B14 | 32.8 | 40.0 | 60 | 1.00 | 2.54 | — | — | 3.70 | 8.91 | — | — | 1.08 | 2.52 | 1.93 | 4.55 | 3.69 | 8.00 | 6.85 | 14.5 | —2.266 | 0.286 | —1.782 | 0.274 |
| | | | | | 80 | 1.00 | 2.50 | — | — | 2.74 | 6.29 | 8.60 | 18.4 | 1.03 | 2.28 | 1.70 | 3.72 | 2.83 | 6.22 | 4.87 | 10.6 | —1.838 | 0.230 | —1.346 | 0.216 |
| | | | | | 100 | 1.00 | 2.64 | — | — | 2.40 | 5.96 | 6.80 | 14.7 | 1.00 | 2.34 | 1.63 | 3.43 | 2.96 | 5.66 | 4.03 | 8.66 | —1.620 | 0.204 | —1.050 | 0.184 |
| 23 | 2-Butene-1,4-diol | 2B14 | 35.0 | 40.0 | 60 | 1.00 | 2.22 | — | — | 3.22 | 6.41 | — | — | 0.97 | 1.97 | 1.78 | 3.36 | 3.34 | 5.84 | 6.80 | 10.8 | —2.016 | 0.252 | —1.494 | 0.230 |
| | | | | | 80 | 1.00 | 2.38 | — | — | 3.00 | 6.10 | — | — | 1.28 | 2.22 | 1.72 | 3.34 | 3.34 | 5.55 | 5.55 | 8.95 | —1.892 | 0.236 | —1.270 | 0.206 |
| | | | | | 100 | 1.00 | 2.38 | — | — | 2.31 | 4.15 | 7.23 | 11.5 | — | — | 1.54 | 2.69 | 2.31 | 3.69 | 3.84 | 6.08 | —1.630 | 0.204 | — | — |

* Saturated $AgNO_3$ solution.

** Relative retention $r = \frac{dR_1}{dR_2}$, where $dR_1$ is the actual retention distance for component investigated and $dR_2$ — the same for reference substance (octene-2-*trans*).

*** Indexes $t$ and $c$ refer to *trans* and *cis* respectively.

**Relative retentions and values of the constants $a$ and $b$ in the equation $\lg r = a + bn$ for 2- and 3-alkenes**

*Table 1*

| Relative retentions ** of 2-alkenes | | | | | | | | Relative retentions of 3-alkenes | | | | | | | | $\lg r = a + bn$ for 2-alkenes | | | | $\lg r = a + bn$ for 3-alkenes | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Octene-2 | | Nonene-2 | | Decene-2 | | Dodecene-2 | | Octene-3 | | Nonene-3 | | Decene-3 | | Undecene-3 | | for *trans*-isomer | | for *cis*-isomer | | for *trans*-isomer | | for *cis*-isomer | |
| *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | $a_t$ *** | $b_t$ | $a_c$ *** | $b_c$ | $a_t$ | $b_t$ | $a_c$ | $b_c$ |
| 1.00 | 3.31 | 2.05 | 4.84 | 3.43 | 8.05 | — | — | — | — | | — | — | — | 7.05 | 12,9 | —2.110 | 0.268 | —1.168 | 0.208 | — | — | — | — |
| 1.00 | 2.92 | 1.29 | 3.79 | 2.58 | 5.84 | 7.56 | 13.6 | — | — | — | — | — | — | 5.00 | 8.96 | —1.820 | 0.220 | —0.920 | 0.170 | — | — | — | — |
| 1.00 | 2.75 | 1.69 | 4.38 | 3.69 | 7.50 | — | — | — | — | — | — | — | — | 5.20 | 12.25 | —2.148 | 0.270 | —1.296 | 0.218 | — | — | — | — |
| 1.00 | 2.63 | 1.71 | 4.08 | 3.13 | 6.85 | 8.05 | 14.25 | — | — | — | — | — | — | 5.05 | 9.80 | —1.886 | 0.236 | —1.260 | 0.210 | — | — | — | — |
| 1.00 | 2.50 | — | — | 3.55 | 7.75 | — | — | 0.98 | 2.26 | 1.77 | 3.84 | 3.71 | 7.10 | 6.85 | 12.50 | —2.188 | 0.274 | —1.546 | 0.246 | —2.320 | 0.290 | —1.662 | 0.250 |
| 1.00 | 2.28 | — | — | 3.14 | 6.56 | 10.7 | 19.0 | 1,14 | 2.23 | 2.00 | 3.57 | 3.14 | 5.72 | 5.37 | 9.44 | —2.018 | 0.252 | —1.466 | 0.230 | —1.786 | 0.230 | —1.382 | 0.216 |
| 1.00 | 1.73 | — | — | 3.98 | 6.51 | — | — | — | — | 1.90 | 2.96 | — | — | 7.45 | 10.83 | —2.416 | 0.302 | —2.024 | 0.284 | —2.368 | 0.294 | —2.046 | 0.278 |
| 1.00 | 1.59 | — | — | 3.14 | 4.80 | 10.15 | 15,3 | — | — | 1.70 | 2.45 | — | — | 5.09 | 7.27 | —2.018 | 0.252 | —1.750 | 0.244 | —1.936 | 0.240 | —1.780 | 0.240 |
| 1.00 | 1.57 | — | — | 2.97 | 4.54 | 9.15 | 13,5 | — | — | 1.55 | 2.28 | — | — | 4.64 | 6.54 | —1.906 | 0.238 | —1.680 | 0.234 | —1.962 | 0.240 | —1.690 | 0.226 |
| 1.00 | 1.69 | — | — | 3.90 | 6.65 | — | — | — | — | — | — | — | — | — | — | —2.378 | 0.298 | —2.142 | 0.296 | — | — | — | — |
| 1.00 | 1.57 | — | — | 3.33 | 5.35 | — | — | — | — | — | — | — | — | 5.85 | 8.70 | —2.076 | 0.260 | —1.918 | 0.266 | — | — | — | — |
| 1.00 | 2.48 | 2.00 | 4.72 | — | — | — | — | — | — | — | — | — | — | — | — | —2.416 | 0.300 | —1.838 | 0.278 | — | — | — | — |
| 1.00 | 2.18 | 1.90 | 4.05 | 3.57 | 7.60 | — | — | — | — | — | — | — | — | 6.63 | 12.54 | —2.218 | 0.276 | —1.816 | 0.270 | — | — | — | — |
| 1.00 | 1.94 | 1.89 | 3.49 | 3.40 | 6.06 | — | — | — | — | — | — | — | — | 7.95 | 12.93 | —2.118 | 0.264 | —1.696 | 0.250 | — | — | | — |
| 1.00 | 1.85 | 1.83 | 3.14 | 3.57 | 6.51 | — | — | 1.04 | 1.91 | 2.08 | 3.72 | — | — | — | — | —2.222 | 0.278 | —1.900 | 0.272 | —1.938 | 0.244 | —1.494 | 0.222 |
| 1.00 | 1.70 | 1.61 | 2.62 | 3.12 | 5.21 | 9.71 | 15.5 | 0.97 | 1.58 | 1.61 | 2.62 | 2.91 | 4.65 | 5.24 | 8.20 | —1.974 | 0.250 | —1.726 | 0.246 | —1.920 | 0.238 | —1.706 | 0.238 |
| 1.00 | 1.57 | 1.53 | 2.40 | 2.68 | 4.25 | 7.63 | 11.5 | 1.00 | 1.42 | 1.52 | 2.40 | 2.50 | 3.75 | 4.25 | 6.25 | —1.746 | 0.220 | —1.530 | 0.216 | —1.806 | 0,232 | —1.600 | 0.220 |
| 1.00 | 1.74 | 1.80 | 2.80 | 3.16 | 5.25 | 9.80 | 15.8 | 1.05 | 1.64 | 1.80 | 2.80 | 2.96 | 4.75 | 5.25 | 8.25 | —2.010 | 0.250 | —1.712 | 0.244 | —1.826 | 0.230 | —1.670 | 0.236 |
| 1.00 | 2.55 | — | — | 3.46 | 8.41 | — | — | 0.98 | 2.35 | 1.76 | 4.18 | 3.46 | 7.65 | 5.90 | 12.70 | —2.180 | 0.270 | —1.650 | 0.256 | —2.080 | 0.262 | —1.590 | 0.246 |
| 1.00 | 2.50 | — | — | 3.07 | 7.19 | — | — | 0.99 | 2.26 | 1.74 | 3.88 | 2.95 | 6.50 | 4.95 | 10.6 | —1.972 | 0.246 | —1.442 | 0.230 | —1.886 | 0.236 | —1.486 | 0.230 |
| 1.00 | 2.60 | — | — | 2.80 | 6.75 | 7.25 | 15.75 | 1.09 | 2.57 | 2.00 | 4.25 | 2.86 | 6.45 | 4.60 | 10.3 | —1.730 | 0.218 | —1.170 | 0.200 | — | — | —1.170 | 0.200 |
| 1.00 | 2.54 | 1.90 | 4.54 | 3.42 | 8.13 | — | — | — | — | — | — | — | — | — | — | —2.186 | 0.272 | —1.586 | 0.250 | — | — | — | — |
| 1.00 | 2.40 | 1.69 | 4.10 | 2.86 | 6.87 | 9.88 | 20.85 | — | — | — | — | — | — | 5.25 | 11.39 | —1.940 | 0.240 | —1.470 | 0.232 | — | — | — | — |
| 1.00 | 2.48 | 1.62 | 4.00 | 2.55 | 6.25 | 7.47 | 15.55 | — | — | — | — | — | — | 4.50 | 9.50 | —1.720 | 0.214 | —1.204 | 0.200 | — | — | — | — |
| 1.00 | 1.80 | — | — | 4.06 | 7.12 | — | — | — | — | 1.83 | 3.26 | — | — | 8.90 | 13.9 | —2.462 | 0.308 | —2.140 | 0.300 | —2.828 | 0.342 | —2.320 | 0.314 |
| 1.00 | 1.85 | — | — | 3.85 | 6.55 | 15.95 | 2.62 | 1.13 | 1.77 | 2.04 | 3.25 | 3.87 | 5.89 | 7.14 | 11.3 | —2.390 | 0.298 | —2.040 | 0.290 | —2.064 | 0.264 | —1.876 | 0.266 |
| 1.00 | 1.84 | — | — | 3.23 | 5.46 | 11.6 | 18.5 | 1.03 | 1.61 | 1.87 | 2.87 | 3.39 | 5.04 | 6.13 | 9.07 | —2.130 | 0.266 | —1.720 | 0.248 | —2.048 | 0.258 | —1.806 | 0.252 |
| 1.00 | 1.81 | 2.30 | 3.85 | 4.94 | 7.94 | — | — | — | — | — | — | — | — | 12.1 | 18.3 | —2.818 | 0.356 | —2.326 | 0.322 | — | — | — | — |
| 1.00 | 1.69 | 1.82 | 3.33 | 4.00 | 6.44 | 17.11 | 26.2 | — | — | — | — | — | — | 7.78 | 11.56 | —2.456 | 0.310 | —2.176 | 0.300 | — | — | — | — |
| 1.00 | 1.67 | 1.93 | 3.04 | 3.56 | 5.59 | 11.85 | 17.8 | — | — | — | — | — | — | 5.89 | 8.85 | —2.176 | 0.272 | —1.876 | 0.260 | — | — | — | — |
| 1.00 | 2.54 | — | — | 3.70 | 8.91 | — | — | 1.08 | 2.52 | 1.93 | 4.55 | 3.69 | 8.00 | 6.85 | 14.5 | —2.266 | 0.286 | —1.782 | 0.274 | —2.098 | 0.266 | —1.622 | 0.250 |
| 1.00 | 2.50 | — | — | 2.74 | 6.29 | 8.60 | 18.4 | 1.03 | 2.28 | 1.70 | 3.72 | 2.83 | 6.22 | 4.87 | 10.6 | —1.838 | 0.230 | —1.346 | 0.216 | —1.790 | 0.224 | —1.430 | 0.222 |
| 1.00 | 2.64 | — | — | 2.40 | 5.96 | 6.80 | 14.7 | 1.00 | 2.34 | 1.63 | 3.43 | 2.96 | 5.66 | 4.03 | 8.66 | —1.620 | 0.204 | —1.050 | 0.184 | —1.642 | 0.206 | —1.160 | 0.192 |
| 1.00 | 2.22 | — | — | 3.22 | 6.41 | — | — | 0.97 | 1.97 | 1.78 | 3.36 | 3.34 | 5.84 | 6.80 | 10.8 | —2.016 | 0.252 | —1.494 | 0.230 | —2.142 | 0.268 | —1.680 | 0.246 |
| 1.00 | 2.38 | — | — | 3.00 | 6.10 | — | — | 1.28 | 2.22 | 1.72 | 3.34 | 3.34 | 5.55 | 5.55 | 8.95 | —1.892 | 0.236 | —1.270 | 0.206 | —2.046 | 0.256 | —1.442 | 0.222 |
| 1.00 | 2.38 | — | — | 2.31 | 4.15 | 7.23 | 11.5 | — | — | 1.54 | 2.69 | 2.31 | 3.69 | 3.84 | 6.08 | —1.630 | 0.204 | — | — | —1.620 | 0.200 | —1.148 | 0.174 |

component investigated and $dR_2$ — the same for reference substance (octene-2-*trans*).

tri- and tetraethylene glycols a.o., have been used with success. No systematic data concerning their selectivity could be found in literature.

We have extended the comparative investigation of the solvents for $AgNO_3$ to some other higher boiling homologs of ethylene glycol, such as butanediols, hexane-1,6-diol a.o. For comparison, ethylene glycol, di- and triethylene glycols were included.

Variations in resolution values ($R_s$) for geometric isomers of normal alkenes $C_8-C_{12}$ on various stationary phases are readily seen in Fig. 3.

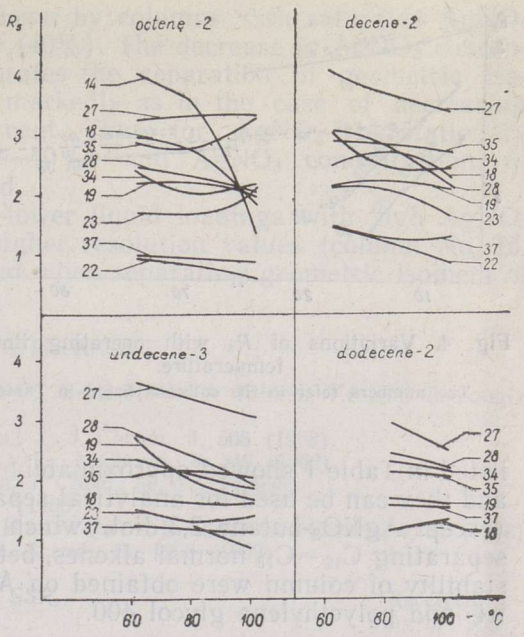


Fig. 3. Variations of $R_s$ with stationary phase composition and temperature.

Chromatograph UH-1 with thermal conductivity detector, 1 m columns with 6 mm diameter, helium flow rate — 84 ml/min. The numbers refer to the columns listed in Tables 1 and 2.

The use of B14 and B23 as solvents for $AgNO_3$ considerably increases the column performance, as compared to the results obtained by using ethylene glycol. So the resolutions of about 3.66 and 3.98 at 60° for *cis-trans*-isomers of nonene-2 have been obtained, the value with $AgNO_3$-EG stationary phase amounting to 2.86. The resolution values at 80—100° are the highest for $AgNO_3$-B14 columns. At 45—60° the $AgNO_3$-B23 stationary phase gives even better resolution for *cis-trans*-isomers of *n*-octene-2 than $AgNO_3$-B14, $R_s$ values being 4 and 3.2 respectively. Thus, the structural peculiarities of the latter two diols obviously provide the most favourable conditions for the separation process.

Unfortunately, the activity of $AgNO_3$-B23 phase diminishes very rapidly at temperatures above 60° and it cannot be used at higher temperatures needed for separating higher isomers (above $C_9$).

The poorest resolution was obtained on $AgNO_3$-B13 stationary phase. As a rule, the $R_s$ values decrease when temperature increases.

As to the decrease of selectivity, the solvents used can be given in the following order:

at 45—60° — B23 > B14 > H16 ≈ EG > TEG > DEG > 2B14 > PG 400 > B13

at 90—100° — B14 > H16 ~ TEG > DEG ~ PG 400.

At 100°, the *cis-trans*-isomers of tridecene-5 with $AgNO_3$-B14 and $AgNO_3$-PG 400 columns were separated. The first column is not stable at temperatures of about 100°, at which it can only be used for a few hours without essential loss of selectivity, as seen in Fig. 4, where variations of resolutions with operating time and temperature are shown.

At 80°, this stationary phase can be used for a little longer time. For instance, on the initial $AgNO_3$-B14 stationary phase, $R_s$ for pairs of decene-2 isomers was 2.1, after operation at 80° for 70 hours, the $R_s$ values diminished up to 1.3.

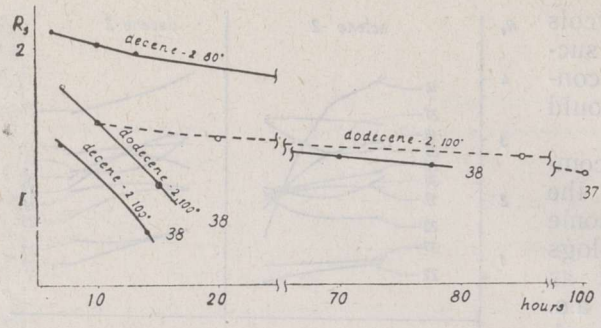


Fig. 4. Variations of $R_s$ with operating time and temperature.
The numbers refer to the columns listed in Table 1.

The most stable stationary phase $AgNO_3$-PG 400 was operating at 100° for 80 hours with a slight decrease of $R_s$ values from 1.5 up to 1.3.

From the above data it may be concluded that the elution of lower boiling $AgNO_3$ solvents from the column during operation at higher temperatures influences, to a certain degree, the activity of the stationary phase.

All stationary phases listed in Table 1 showed approximately the same separation characteristics and they can be used for analytical separation of normal alkenes up to $C_{11}$ (except $AgNO_3$-butane 2,3-diol, which can be used up to $C_9$). When separating $C_{12}-C_{13}$ normal alkenes, better results as to the resolution and stability of column were obtained on $AgNO_3$ solutions in hexane-1,6-diol, tri- and polyethylene glycol 400.

## The effect of $AgNO_3$ concentration

In literature, there are various data concerning the optimum $AgNO_3$ concentration in stationary phase. B. Smith and R. Ohlson [7] found the $AgNO_3$ concentration of 17 per cent to be the best for separating 3- and 4-methylpentenes-1.

In general, when separating lower molecular weight compounds, better results on $AgNO_3$ saturated solutions at highly loaded columns have been obtained. Higher molecular compounds are better separated on lower concentrations of $AgNO_3$ solutions and at lower liquid loadings. According to these data, the optimum compositions of stationary phases for separating $C_{10}-C_{12}$ geometric isomers could not be determined, and it was necessary to determine them experimentally.

From Table 2 it can be concluded that all $AgNO_3$-B14 columns, despite the content of $AgNO_3$, give good separation of $C_{10}-C_{12}$ geometric isomers.

*Table 2*

**Effect of $AgNO_3$ and of liquid loading content on column performance with regard to resolution and efficiency**

| Column No. | Solvent for $AgNO_3$ | $AgNO_3$ concentration in solution, % | Content of the $AgNO_3$ solution in column packing, % | Number of effective plates * $n_{eff}$ at 80° | $R_s$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Decene-2 | | | Dodecene-2 | |
| | | | | | 60° | 80° | 100° | 80° | 100° |
| 28 | Butane-1,4-diol | 8.4 | 40.0 | 342 | 3.0 | 2.7 | 2.1 | 2.4 | 2.2 |
| 25 | „ | 16.1 | 40.0 | 354 | 4.0 | 3.5 | 2.9 | 3.3 | 3.0 |
| 16 | „ | 40.0 | 40.0 | 398 | 3.6 | 3.6 | 3.4 | 3.0 | 2.7 |
| 13 | „ | 22.9 | 11.8 | 307 | 2.0 | 2.7 | — | 1.4 | — |
| 15 | Hexane-1,6-diol | 20.4 | 12.3 | 622 | 2.4 | 2.6 | 2.5 | 1.7 | 1.9 |
| 12 | „ | sat. | 33.9 | 294 | 1.9 | 1.9 | 2.0 | 1.7 | 1.8 |

* $n_{eff}$ — number of effective plates for *trans*-decene-2.

The maximum performance is shown by columns with saturated $AgNO_3$ solution with high liquid loading (40%). The decrease in $AgNO_3$ concentration below 10 per cent deteriorates the separation of geometric isomers to some extent, but not so markedly as in the case of decreasing liquid loading from 40 to 12 per cent. Thus, for $AgNO_3$-B14 stationary phase, high liquid loadings (30—40%) and $AgNO_3$ concentrations of 15—40 per cent are recommended.

For hexane-1,6-diol solutions lower liquid loadings with high $AgNO_3$ concentration (20—30%) gave higher resolution values (column No. 15, Table 2) and can be recommended when separating geometric isomers of normal alkenes $C_{10}$—$C_{12}$.

## REFERENCES

1. Kuningas K., Rang S., Eisen O., Eesti NSV TA Toimet., Keemia. Geoloogia, **19**, 30 (1970).
2. Gil-Av E., Herling J., Shabtai J., J. Chrom., **1**, 508 (1958).
3. Herling J., Shabtai E., Gil-Av E., J. Chrom., **8**, 349 (1962).
4. Bednas M. E., Rusell D. S., Can. J. Chem., **36**, 1272 (1958).
5. Генкин А. Н., Нефтехимия, **5**, 897 (1965).
6. Banthorpe D. V., Gatford C., Hollebone B. R., J. Gas Chrom., **6**, 81 (1968).
7. Smith B., Ohlson R., Acta Chem. Scand., **13**, 1253 (1959).

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

Received
May 5, 1969

*SILVIA RANG, O. EISEN, K. KUNINGAS*

## KÜLLASTUMATA SÜSIVESINIKE GAASIKROMATOGRAAFILINE ERALDAMINE $AgNO_3$ SISALDAVATEL VEDELFAASIDEL

### 2. Lahusti ja $AgNO_3$ kontsentratsiooni mõju kolonni selektiivsusele

Uuriti normaalsete alkeenide $C_8 \ldots C_{13}$ *tsiss-trans*-isomeeride gaasikromatograafilist eraldamist $AgNO_3$ sisaldavatel vedelfaasidel, määrati *n*-alkeenide suhtelised retentsioonid ($r$) ja eralduskoefitsiendid ($R_s$) ning leiti kvantitatiivne seos lg $r$ ja süsiniku aatomite arvu vahel molekulis.

Näidati, et selektiivsuse vähenemise järgi temperatuuridel 80—100°C võib $AgNO_3$ lahustid paigutada järgmisse ritta: B14>H16>TEG>DEG≈PG 400. Kõige selektiivsemateks osutusid $AgNO_3$-lahused B23-s ja B14-s, kuid nende aktiivsused vähenesid kiiresti vastavalt temperatuuridel üle 60 ja 80°.

Leiti $AgNO_3$ ja ta lahuste optimaalsed hulgad, mis tagavad normaalsete alkeenide $C_8 \ldots C_{13}$ geomeetriliste isomeeride parima eraldumise.

*СИЛЬВИЯ РАНГ, О. ЭЙЗЕН, К. КУНИНГАС*

## ГАЗОХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ НЕНАСЫЩЕННЫХ УГЛЕВОДОРОДОВ НА СТАЦИОНАРНЫХ ФАЗАХ, СОДЕРЖАЩИХ $AgNO_3$

### 2. Влияние растворителя и концентрации $AgNO_3$ на селективность колонки

Приведены газохроматографические показатели для нормальных алкенов $C_8$—$C_{13}$ и тридецена-5 на стационарных жидких фазах, содержащих $AgNO_3$ (1), при температурах 60, 80 и 100° С. В качестве внутреннего стандарта использовался *транс*-октен-2. В качестве растворителей для (1) применялись этиленгликоль (*EG*), ди- и триэтиленгликоли (*DEG* и *TEG*), 1,3-, 1,4- и 2,3-бутандиолы (*B*13, *B*14, *B*23), 1,6-гександиол (*H*16) и 2-бутен-1,4-диол (2*B*14). Количественная связь между логарифмом удерживания (lg $r$) и числом атомов углерода в молекуле ($n$) выражена в виде уравнения lg $r = a + bn$.

Даны оптимальные значения концентрации (1) и количества растворов (1) в стационарной фазе, обеспечивающие четкое разделение пар геометрических изомеров одинакового молекулярного веса *н*-алкенов и приведен ряд указанных растворителей по убывающей селективности.