Journal of Chromatography, 209 (1981) 21–28
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,540

SELECTIVITY OF PARAFFINIC STATIONARY PHASES FOR GAS–LIQUID CHROMATOGRAPHY

A. N. KOROL* and T. I. DOVBUSH
Institute of Physical Chemistry, pr. Nauki 31, 252028 Kiev (U.S.S.R.)
(Received November 4th, 1980)

SUMMARY

The selectivities of some paraffinic stationary phases were compared for the non-polar solutes and solutes of low polarity. A linear relationship between the logarithm of relative retention and the reciprocal of the number of methylene groups in the stationary phase molecule was found; this relationship is recommended for use in predicting relative retentions within homologous series of stationary phases. Errors that arise when relative retentions for one paraffinic stationary phase are used to predict those of another are discussed.

INTRODUCTION

The widely used paraffinic stationary phase squalane has zero polarity on the Rohrschneider scale. Other paraffinic stationary phases seem to have the same polarity, but the selectivity of these liquids towards different solutes may differ. Unfortunately, the column temperature that can be used with squalane is restricted, with a maximum of 80–100°C. Many high-molecular-weight liquid paraffins have been proposed for use at higher column temperatures, but they were usually mixtures of polymers with different molecular weights, which precluded the determination of reproducible results. Only one pure paraffinic stationary phase, namely the C_{87} branched-chain paraffin, was found to be a possible standard non-polar stationary phase for gas–liquid chromatography (GLC)[1,2], with an operating range of 40–260°C. The standard non-polar packing was prepared by coating this liquid on a support deactivated by Carbowax 15M[3].

The C_{87} branched-chain paraffin was introduced only recently, so most of the available retention data were determined on different hydrocarbons. It would be useful if these data could be used to predict results with the new standard non-polar stationary phase. No comparisons of the selectivities of paraffinic stationary phases that differ markedly in molecular weight or structure have been reported.

Some papers[4,5] have discussed the influence of molecular weight of paraffinic stationary phases on specific retention volumes (V_g). V_g values, molar heats of solution and activity coefficients for non-polar solutes have been determined in different n-paraffins[6–12], but no conclusions about selectivity were drawn. A considerable in-

0021-9673/81/0000–0000/$02.50

fluence of the purity of squalane on selectivity towards solutes of low polarity has been found[13,14], so that published retention data for these solutes on paraffinic stationary phases may be inaccurate.

Therefore, it seems useful to compare paraffinic stationary phases in two steps: (i) comparison of published retention data for non-polar solutes and (ii) consideration of new retention data for solutes of low polarity on purified stationary phases determined under the same experimental conditions. This paper will discuss these two steps.

THEORETICAL

The total selectivity of the stationary phase, r (relative retention), can be considered much more simply when it is divided into two parts, enthalpic and entropic. Relative retention may be expressed as ratio of two partition coefficients (K_L) or specific retention volumes. When the thermodynamic partition coefficient (K) is used, the following equation for molar heat of solution (ΔH_s) and molar entropy of solution (ΔS_s) may be written:

$$-RT \ln K = \Delta H_s - T\Delta S_s \tag{1}$$

where R is the gas constant and T (°K) is the column temperature.

Now,

$$K = \frac{K_L}{A_L RT} \tag{2}$$

where A_L is the amount of stationary phase (moles) per unit volume[15,16]. Taking into account the relationship between K_L and V_g, we can write

$$-RT \ln \left(\frac{V_g A_L}{273.2\ R}\right) = \Delta H_s - T\Delta S_s \tag{3}$$

Eqn. 3 indicates the relationship between V_g and the energy of the intermolecular forces, ΔH_s.

Let us consider the homologous series of *n*-paraffinic stationary phases. The molecules consist of two different structural groups, methyl and methylene. These groups differ in their energy of dispersion interaction with their environment: the relative values of the dispersion forces[17] of this interaction are 4.65 and 2.05 units when intramolecular shielding is taken into account. Only two methyl groups are present in each *n*-paraffin molecule (one at each end), and therefore the longer the molecule the weaker are the overall dispersion forces because of the increasing number of methylene groups in the molecule.

The solute molecule is much shorter than the stationary phase molecule and interactions take place between part of the stationary phase molecule and the whole solute molecule. When there is no steric hindrance, the solute molecule has to make contact with the part of the stationary phase molecule that contains a methyl group. However, there is some probability in solution for different groups to make contact.

The longer methylene chain, the lower is the probability that a solute molecule will make contact with a methyl group. Then we can write the following relationship:

$$\Delta H_s \approx 1/n_1 \tag{4}$$

where n_1 is the number of methylene groups in the stationary phase molecule.

The validity of eqn. 4 may be proved by plotting experimental ln V_g values *versus* $1/n_1$ (if it is assumed that ln V_g depends mainly on ΔH_s for the case concerned). Fig. 1 shows that eqn. 4 is valid for each series of the experiments; because of poor reproducibility of V_g, the values obtained in different laboratories are not identical. When discussing the data in Fig. 1 one must take into account that the stationary phases relating to lines 1 and 2 relate to branched-chain hydrocarbons.

Relative retention data have much better inter-laboratory reproducibility than V_g, and therefore it would be preferable to consider relative retention as a measure of the selectivity of stationary phases:

$$-RT \ln r = \Delta H_s^\circ - T\Delta S_s^\circ \tag{5}$$

where ΔH_s° and ΔS_s° are relative values of the functions. However, the relative retentions are more difficult to consider because the retentions of two solutes have to be taken into account.

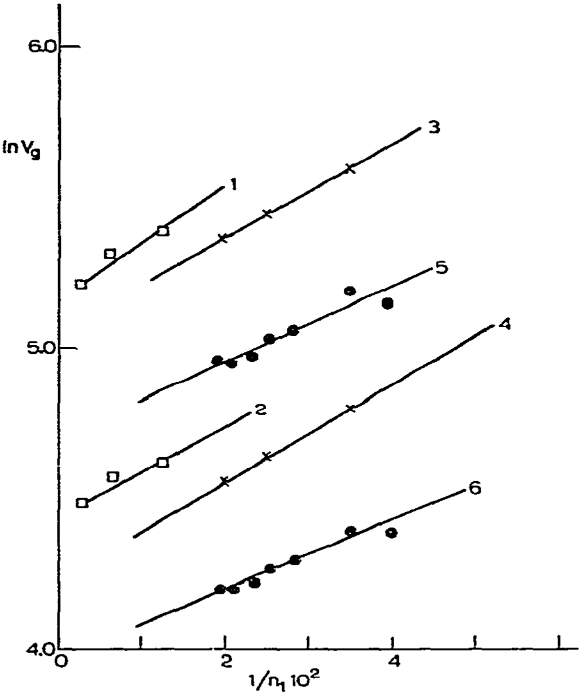

Fig. 1. Relationships between ln V_g and $1/n_1$. Data for lines 1–4 were calculated from ref. 4 and those for lines 5 and 6 from ref. 6. Lines 1 and 3 = *n*-nonane; 2, 4 and 5 = *n*-octane; and 6 = *n*-heptane. Column temperature, 100°C.

Generally, isoparaffins are to be preferred to *n*-paraffins as stationary phases for GLC because they have lower melting points and therefore a wider operating range. For example, the C_{87} branched-chain paraffinic stationary phase has a melting point of about 35°C with a maximum column temperature of 260°C. However, some retention data have been determined employing *n*-paraffin stationary phases, especially for use in theoretical studies.

It is useful also to compare the selectivities of different isomeric stationary phases. Theoretical predictions about the influence of structural changes of the stationary phase molecule on the selectivity are impossible because no information exists about the real conformation of the molecules in solution. Therefore, it is desirable to consider both reported retention data and new data together in order to establish variations for different paraffinic stationary phases.

EXPERIMENTAL

Reagents and apparatus

Retention data were determined by using a Varian Model 1860 gas chromatograph equipped with a flame-ionization detector (FID). The stainless-steel column (1.5 m × 3 mm I.D.) was packed with 10% of the stationary phase on Chromaton N Super (Lachema, Brno, Czechoslovakia), 0.20–0.25 mm. All freshly prepared packings were conditioned for 15 h at the maximum column temperature. Helium was used as the carrier gas.

The solutes were injected by gas or liquid syringes depending on the boiling point. When liquids were injected the injector temperature was maintained 20°C higher than the column temperature. Retention data were determined at column temperatures from 35 to 60°C.

C_{19}, C_{21}, C_{23} and C_{24} *n*-paraffins and squalane were purified by passage through a silica gel column. *n*-Hexane (the standard), *n*-heptane, cyclohexane, 1-heptene, benzene, chloroform and dichloroethane were used as the solutes. Only single solutes were injected.

Calculations

Methane was used for dead time measurements. The ln r values were plotted against $1/T$ for four or five column temperatures and the smoothed r value was calculated for a standard temperature of 50°C. The relative molar heat of solution was calculated graphically by using the equation

$$\Delta H_s^\circ = \frac{R\,(\ln r_1 - \ln r_2)}{1/T_1 - 1/T_2} \tag{6}$$

where the subscripts 1 and 2 refer to different column temperatures.

The mean relative standard deviation of the r value was about 0.1% and that of ΔH_s° was 3%.

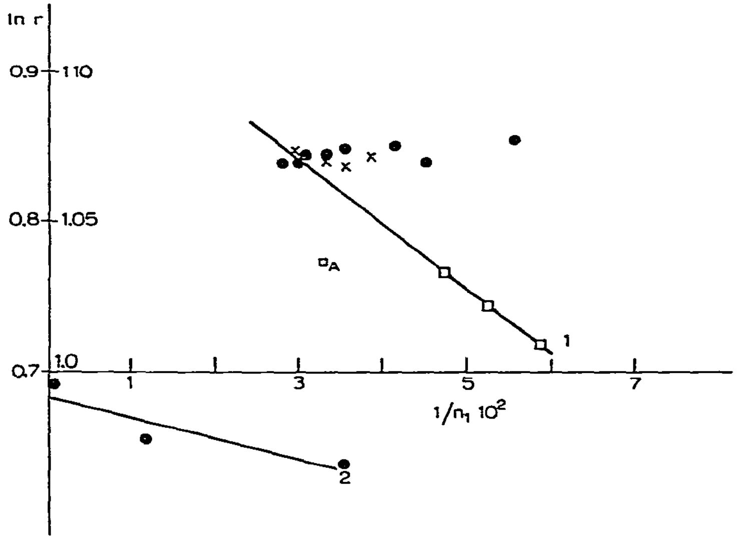

Fig. 2. Relationship between ln r and $1/n_1$ for (with n-hexane as the standard and n-heptane as the solute). Point A refers to squalane. ●, Calculated from ref. 12; ×, calculated from ref. 6 (ln r scale 0.7–0.9). Two lines (1 and 2) were constructed from original data (ln r scale 0.95–1.10). For line 2 three branched-chain paraffin stationary phases were used (see text)[18].

RESULTS AND DISCUSSION

Paraffinic solutes

The relationship between the r value of n-heptane (with n-hexane as standard) and $1/n_1$ is shown in Fig. 2. The n_1 value for squalane (as for other branched-chain paraffins) was calculated by subtracting the contributions due to two carbon atoms in the molecule. The experimental points taken from refs. 6 and 12 show no clear correlation. The original points for C_{19}–C_{23} n-paraffins lie on a common line without marked deviations. Relative retention increases proportionally to $1/n_1$; hence the slopes of ln V_g and ln r *versus* $1/n_1$ are of opposite sign. The increase in the density of the homologous series of n-paraffins seems to be the main reason for the increase in the selectivity of the stationary phases.

The point for squalane (A) is below the line for the n-paraffins, which indicates clearly the influence of molecular structure on selectivity. The three high-molecular-weight stationary phases used (squalane, C_{87} and polyisobutylene, molecular weight 2000; data from ref. 18) have different molecular structures, which explains the deviation of the points from the common line (line 2).

The data in Fig. 2 allow one to predict changes in relative retentions for n-paraffins from one stationary phase to another. For example, the relative retentions on the C_{30} n-paraffin and squalane differ by 2% and those on the C_{30} and C_{40} n-paraffins by 1.2%.

A similar relationship is observed for relative molar heats of solution (Fig. 3). A slight decrease in ΔH°_s is seen for the original data. About the same variations are obtained for the entropic selectivity[19]: the values are −0.95, −1.006, −1.011 and −0.937 for the C_{19}, C_{21} and C_{23} n-paraffins and squalane, respectively. On comparing

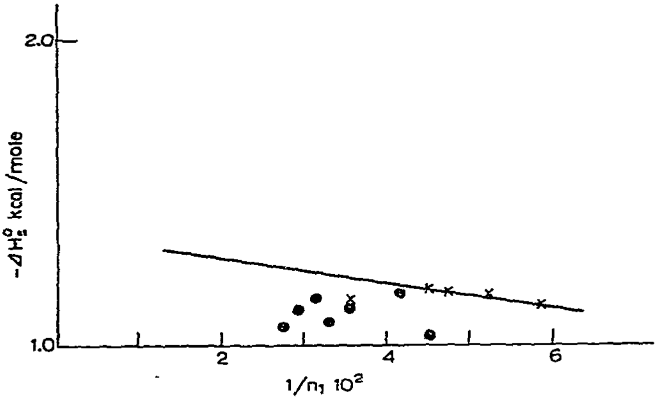

Fig. 3. Relationship between ΔH_s° for *n*-heptane and $1/n_1$ (with *n*-hexane as the standard). ×, New data; ●, data from ref. 12.

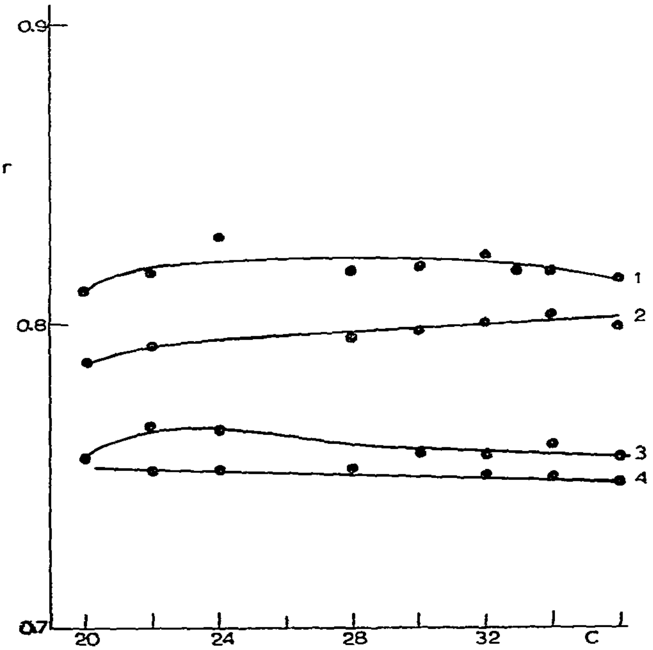

Fig. 4. Relationship between *r* for branched-chain heptanes (with *n*-heptane as the standard) and number of carbon atoms in the *n*-paraffin stationary phase molecule. 1, 3-Methylhexane; 2, 2,3-dimethylpentane; 3, 2,4-dimethylpentane; 4, 2-methylhexane.

the influences of ΔH_s° and the entropic selectivity it can be concluded that ΔH_s° is the dominating factor.

The relative retentions for branched-chain heptanes (with *n*-heptane as the standard) (Fig. 4) were calculated from refs. 6 and 12. No clear relationships were observed for the solutes, the *r* values deviating by 1.5–3%. On comparing these data with the relative retentions for *n*-paraffins it seems that the trends and deviations are similar.

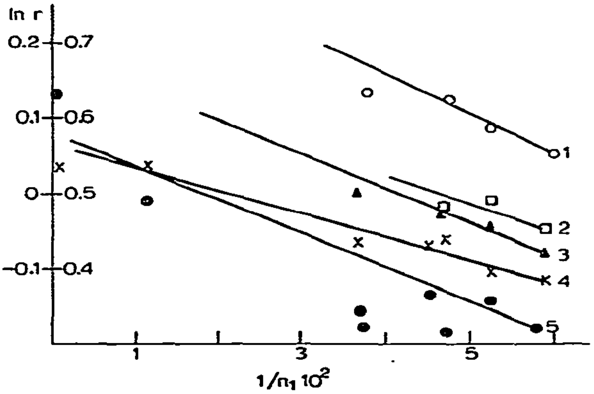

Fig. 5. Relationship between ln r and $1/n_1$ (with n-hexane as the standard) for (1) cyclohexane, (2) heptene-1, (3) dichloroethane, (4) benzene and (5) chloroform. The ln r scale −0.1 to 0.2 relates to lines 3 and 5; scale 0.4–0.7 relates to lines 1 and 4; line 2 lies between ln r values of 0.8 and 0.9.

Solutes of low polarity

Fig. 5 indicates a general tendency for r to increase with decreasing $1/n_1$, corresponding to the relationship for n-paraffins. Thus, this relationship appears to be generally applicable to solutes with different molecular weights and polarities. It should be noted that for solutes of low polarity some deviations from the common line are observed so that the precise slope cannot be evaluated. To a first approximation, the slope depends mainly on the geometrical form of the solute molecules (see the data for benzene and cyclohexane).

Some relative molar heats of solution for the solutes of low polarity are plotted *versus* $1/n_1$ in Fig. 6. A general correlation of ln r and ΔH_s° with $1/n_1$ is observed in Figs. 5 and 6. On increasing the molecular weight of the stationary phase, the relative retentions increase also.

Interesting data were reported recently[20] on a comparison of squalane and C_{87} stationary phases for the separation of pentadecene isomers. It was shown that for many isomers the Kováts retention indices are 0.1–0.7 units lower on C_{87} than on squalane; for only three isomers were the retention indices greater (by 0.1–0.4

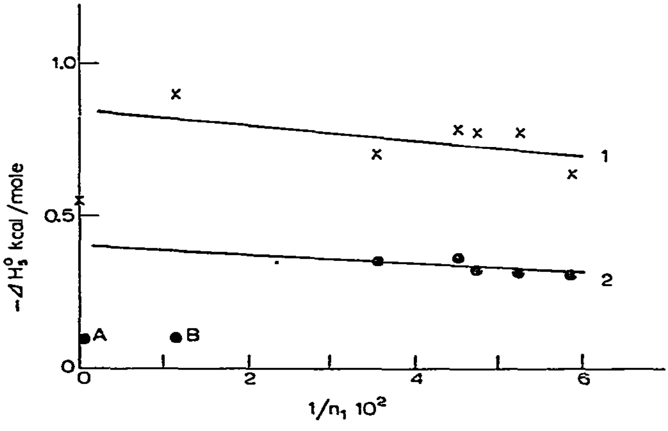

Fig. 6. Relationship between ΔH_s° and $1/n_1$ for (1) chloroform and (2) benzene. Points A and B refer to columns containing 5% of the stationary phases[18].

units) on C_{87}. These data for olefins illustrate the limits of the errors when the retention data for squalane are used to calculate those for C_{87} (about 1.5 units for the case concerned).

CONCLUSIONS

The relationships presented here allow some conclusions to be drawn about the calculation of the retention data for one paraffinic stationary phase from those for another. The most important practical problem is the calculation of hydrocarbon retention data for C_{87} from values for squalane. Data for *n*-paraffins indicate that the relative retentions of paraffinic solutes differ by 1.6% between these two stationary phases, which corresponds to 0.7 Kováts retention index unit. This value is less than the inter-laboratory reproducibility of the determination of paraffin retention data on a non-polar stationary phase. Thus, the retention data for isoparaffins on squalane may be transferred to C_{87} by taking into account the slightly greater retention indices (about 0.5 retention index unit) for C_{87}. This is of great importance because retention data for isoparaffins on squalane are available for isomers up to C_{10}.

Other classes of hydrocarbons show greater changes in relative retention between squalane and C_{87}. For example, the relative retention of benzene is 9.5% higher on the latter. Similar results were obtained for solutes of low polarity. Therefore, preliminary experiments are necessary for each class of solutes in order to establish whether it is possible to predict retention data for C_{87} from those for squalane.

When using relative retentions within homologous series of the paraffinic stationary phases to predict those of other members, it is reasonable to use the relationship between ln r and $1/n_1$ (Figs. 2 and 5). Data for squalane are always below the common line for *n*-paraffinic stationary phases.

The results presented emphasize once again that even paraffinic stationary phases must be very pure products and technical mixtures similar to hydrogenated Apiezons cannot be recommended for use in GLC.

REFERENCES

1 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
2 L. Boksányi and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 87.
3 A. N. Korol, G. M. Belokleytseva and G. V. Filonenko, *J. Chromatogr.*, 194 (1980) 145.
4 G. A. Huber and E. sz. Kováts, *Anal. Chem.*, 45 (1973) 1155.
5 D. F. Fritz and E. sz. Kováts, *Anal. Chem.*, 45 (1973) 1175.
6 E. C. Pease and S. Thorburn, *J. Chromatogr.*, 30 (1967) 344.
7 A. J. B. Cruicshank, B. W. Gainey and C. L. Young, *Trans. Faraday Soc.*, 64 (1968) 337.
8 C. L. Young, *Trans. Faraday Soc.*, 64 (1968) 1537.
9 E. F. Meyer and A. Baiocchi, *J. Chem. Thermodyn.*, 10 (1978) 409.
10 E. F. Meyer and R. H. Weiss, *J. Chem. Thermodyn.*, 9 (1977) 431.
11 P. S. Snyder and J. F. Thomas, *J. Chem. Eng. Data*, 13 (1968) 527.
12 J. F. Parcher, P. H. Weiner, C. L. Hussey and T. N. Westlake, *J. Chem. Eng. Data*, 20 (1975) 145.
13 A. Wičarová, J. Novák and J. Janák, *J. Chromatogr.*, 51 (1970) 3.
14 L. Soják and A. Rijks, *J. Chromatogr.*, 119 (1976) 505.
15 M. R. James, J. C. Giddings and M. Eyring, *J. Phys. Chem.*, 68 (1964) 1725.
16 A. N. Genkin and B. J. Boguslavskaya, *Dokl. Akad. Nauk SSSR*, 164 (1965) 1089.
17 A. N. Korol, *Chromatographia*, 8 (1975) 335.
18 A. N. Korol, *J. Chromatogr.*, 172 (1979) 77.
19 A. N. Korol, *Chromatographia*, 8 (1975) 385.
20 L. Soják, J. Krupčík and J. Janák, *J. Chromatogr.*, 191 (1980) 199.