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RETENTION VALUES OF SOME STANDARD SOLUTES ON NON-POLAR STATIONARY PHASES

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SUMMARY

Three selectivity parameters (relative retention, molar heat of solution and entropy factor, F^0) were compared for three alkane stationary phases (squalane, polyisobutylene and the non-polar stationary phase C_{87}). These selectivity parameters depend on molecular weight of the stationary phase for non-polar or low-polarity solutes; the interphase adsorption depends on the molecular weight of the stationary phase for polar solutes.

INTRODUCTION

Non-polar and low-polarity stationary phases have certain advantages in gas-liquid chromatography (GLC). A high column performance is easily obtained, and there are simple rules correlating the retention values of solutes with their boiling points, making such stationary phases attractive, especially for identification purposes. Different alkanes have been used as solutes, the best known example of a non-polar stationary phase with zero polarity being squalane, a C_{30} branched alkane. Some technical greases, polyethylene and polypropylene have been applied in high-temperature separations. Unfortunately, the polymers are polydisperse mixtures and the greases are mixtures of different hydrocarbons. The retention values depend on the molecular weight of the alkane stationary phase¹⁻³, which prevents the use of hydrocarbon mixtures as a standard, reproducible stationary phase.

The synthesis of the liquid branched alkane C_{87} in the laboratory of Kováts⁴ provides a possible solution to this non-polar standard stationary phase problem when the stationary phase has temperature limits of use from 35 to 260°C. The properties of C_{87} have been described in several papers⁴⁻⁶, but only few thermodynamic selectivity data have been published and little attention has been paid to the comparison of thermodynamic data on C_{87} with those for widely used alkane stationary phases.

The determination of thermodynamic selectivity parameters for some standard solutes and a comparison of these values with those for widely used alkane stationary phases are described in this paper. These data may be useful for the re-calculation of the retention data from one alkane stationary phase to another and for a comparison of different alkane stationary phases.

EXPERIMENTAL

Materials

Three alkane stationary phases were used: squalane, C_{87} and polyisobutylene; the last compound has an average molecular weight of about 2000. Because of the presence of impurities consisting of different types of hydrocarbons, which can change the retention data markedly^{7,8}, squalane and polyisobutylene were purified by passage through a silica gel column. Polyisobutylene becomes a colourless liquid after purification and the average molecular weight decreased slightly. C_{87} consists of a single hydrocarbon with 0.2–0.3% of volatile impurities. The sample used was purer than that reported in ref. 4.

The packings were prepared by coating Chromaton N AW HMDS (Lachema, Brno, Czechoslovakia) (0.16–0.20 mm) with 5% of the stationary phase. Such relatively lightly loaded columns are suitable for a comparison of the different stationary phases when the support remains the same. Indeed, interphase adsorption of the polar solutes in the non-polar stationary phases is observed even with 20–25% of the stationary phase on the support; therefore, highly loaded columns have no advantages over lightly loaded columns for the comparison.

All packings were pre-conditioned; the squalane packing was conditioned at 100°C for 30 h and the other two packings were conditioned at 250°C for 30 h.

Two groups of the solutes were used: (a) low-boiling solutes, viz., *n*-nonane, benzene, toluene, chloroform, ethyl acetate, methyl ethyl ketone, 1-pentanal and 1-propanol, with *n*-heptane as the standard and a standard temperature of 50°C; (b) high-boiling solutes, viz., naphthalene, pyridine, benzaldehyde, nitrobenzene and 1-decanol, with *n*-undecane as the standard and a standard temperature of 150°C.

Apparatus and calculations

Retention times were measured using a Varian 1860 gas chromatograph with a flame-ionization detector, in the temperature range 50–70°C for low-boiling solutes and 110–130°C for high-boiling solutes. Glass columns of length 1 m and I.D. 3 mm were used. Low-boiling solutes were injected as vapours and high-boiling solutes as liquids. Retention times were measured with an electronic timer with a mean standard deviation of 0.1 sec. The relative mean standard deviation for the relative retentions (*r*) was 0.2%, and that for the relative molar heats of solution (ΔH_s^0) was 5%.

ΔH values were calculated graphically with the aid of 3–5 points using the equation

$$\Delta H_s^0 = \frac{4.58(\log r_1 - \log r_2)}{1/T_1 - 1/T_2} \quad (1)$$

where the subscripts 1 and 2 refer to different column temperatures, $T^\circ\text{K}$. Using the relationship between $\log r$ and $1/T$, the relative retentions were calculated at the chosen standard temperatures.

Relative retention is related to the general selectivity of the stationary phase, involving the thermodynamic selectivity parameters ΔH_s^0 , which characterizes the enthalpic selectivity, and F^0 (ref. 9), which arises due entropy effects:

$$F^0 = \Delta S_s^0 - \Delta H_s^0 \cdot \frac{0.435}{T} \quad (2)$$

where ΔS_s^0 is the difference between the entropies of solution of the solute and the standard and is given by

$$\Delta S_s^0 = \Delta H_s^0/T + R \ln r \quad (3)$$

Combination of eqns. 2 and 3 gives

$$F^0 = 4.58 \log r + 0.565 \Delta H_s^0/T \quad (4)$$

where ΔH_s^0 is measured in calories and temperature in $^{\circ}\text{K}$, giving F^0 in entropy units (e.u.) ($\text{cal} \cdot \text{mole}^{-1} \cdot ^{\circ}\text{K}^{-1}$).

If the net retention time, t_N , did depend on peak height, h , because of the inter-phase adsorption, the procedure described in ref. 10 was used. If B and A_1 are constants, the following linear relationship is valid:

$$t_N = B + A_1/\log h \quad (5)$$

By interpolation, t_N for any chosen h can be calculated in accordance with eqn. 5. Because the retention time of a polar solute in a non-polar stationary phases depends on h , we calculated t_N corresponding to $1/\log h = 0.3$ [h (mm) was re-calculated to full-scale deflection on the recorder of 10^{-11} A and a chart width 250 mm]. Using eqn. 5, the degree of non-linearity of the sorption isotherm was calculated and this value is denoted as A (ref. 10). This procedure permits the determination of comparable reproducible data for the same support, the same loading, the same column length and roughly the same carrier gas flow-rate. At these conditions all differences in retention data relate only to the stationary phases.

Some comments must be made about the physico-chemical nature of the thermodynamic functions (heats and entropies of solution) which are calculated from the retention data. In fact, these functions relate to the distribution between the gas and the packing, involving transfer of the solute from the gas to the solution and interphase adsorption. Therefore, these thermodynamic functions are the result of the complex distribution process in chromatographic columns; these restrictions should be taken into account when interpreting the results.

It should be noted that determination of retention data for polar solutes on non-polar stationary phases must be carried out very carefully because of considerable tailing of the peaks. This tail is eluted from the column over a long period and modifies the solid-liquid interphase. Such a modification changes markedly the retention data of the sample that follows. For example, when a methyl ethyl ketone sample is injected before the previous polar sample has been completely eluted the r and ΔH_s^0 values are changed by 1.6-fold and 1 kcal/mole, respectively, in comparison with those obtained on full elution. Taking into account this fact, all measurements of retention data for polar solutes were carried out only with pure solutes, never with mixtures.

RESULTS AND DISCUSSION

Comparison of inter-laboratory retention data on C_{87}

Table I allows a comparison of our experimental retention data on C_{87} with those reported in ref. 4. The data for *n*-nonane were calculated from ref. 4 with the

TABLE I

RETENTION DATA ON DIFFERENT ALKANE STATIONARY PHASES

n-Heptane is the standard for solutes 1-8 and *n*-undecane for solutes 9-13. The data for solutes 1-8 were measured at 50°C and for the remaining solutes at 150°C.

No. Solute	r				ΔH_s^0 (kcal/mole)			F^0 (e.u.)			A		
	Sq	C ₈₇	C ₈₇ *	PIB	Sq	C ₈₇	PIB	Sq	C ₈₇	PIB	Sq	C ₈₇	PIB
1 <i>n</i> -Nonane	6.95	7.06	6.84	7.35	-2.10	-2.40	-2.60	1.61	1.32	1.18	-	-	-
2 Benzene	0.505	0.635	0.595	0.640	1.40	1.30	1.40	0.14	0.48	0.61	-	-	-
3 Toluene	1.58	1.91	1.94	1.93	-0.20	-0.40	-0.30	0.69	0.86	0.99	-	-	-
4 Chloroform	0.295	0.335	-	0.380	1.75	2.10	1.85	-0.56	0.08	0.06	-	-	-
5 Ethyl acetate	0.285	0.58	-	0.81	1.30	0.55	-0.2	-1.11	-0.49	-0.63	0.3	0.7	0.7
6 Methyl ethyl ketone	0.275	0.615	-	0.89	1.50	2.55	-	-0.96	2.47	-	0.4	0.9	1.3
7 <i>n</i> -Pentanal	0.60	0.70	-	1.26	-0.15	-0.40	-1.40	-2.66	-1.13	-1.04	0.1	0.15	0.3
8 1-Propanol	0.265	0.39	-	0.90	1.40	1.20	-0.30	-1.14	-1.18	-0.55	0.8	0.6	0.6
9 Naphthalene	-	2.11	2.11	2.14	-	0.65	0.75	-	1.59	1.64	-	-	-
10 Pyridine	-	0.12	-	0.12	-	7.20	9.55	-	-3.00	-2.74	-	0.3	0.5
11 Benzaldehyde	-	0.435	-	0.665	-	2.00	2.35	-	-1.31	-0.41	-	0.03	0.15
12 Nitrobenzene	-	0.833	-	1.04	-	0.05	0.15	-	-0.35	0.20	-	0.03	0.10
13 1-Decanol	-	1.91	-	2.03	-	-0.6	-0.3	-	1.19	1.35	-	0.05	0.10

* Values for r on C₈₇ taken from the literature⁴.

aid of regression coefficients and some differences can be seen between our data and those from ref. 4. Our ΔH_s^0 value for *n*-nonane is 0.4 kcal/mole lower than that from ref. 4. These differences seem to be related to the different amounts of the stationary phase on the supports which were used in the different laboratories and, partially, to some errors in the regression calculations.

Other relative retention data were calculated using retention indices from ref. 4 and compared with our experimental data. The differences in r are 7 and 1.5% for benzene and toluene, respectively, while for naphthalene the inter-laboratory retention data agree well. It seems that the agreement between inter-laboratory retention data improves as the boiling point of the solute increases; this effect may be explained by decreasing interphase adsorption at higher column temperatures.

Relative molar heats of solution

The ΔH values for *n*-nonane decrease as the molecular weight of the stationary phases increases (Table I); this effect corresponds to increasing the intermolecular forces in the solution. No dependence of ΔH_s^0 for aromatic hydrocarbons on the molecular weight of the stationary phases is observed; the small deviations have a random nature. The same effect occurs with chloroform. A decrease in the ΔH_s^0 values with increasing molecular weight of the stationary phases is observed for many polar solutes, especially ethyl acetate and *n*-propanol, for which differences of about 1.5 kcal/mole are observed. The dependence of ΔH_s^0 on the molecular weight of the stationary phase is much greater for polar than for non-polar solutes.

Only two stationary phases are available for high-boiling solutes (C₈₇ and polyisobutylene), and therefore the information on the influence of the molecular weight of the stationary phases on retention data for high-boiling solutes is less valid

than that for low-boiling solutes. The experimental data (Table I) show that only a small increase in the ΔH_2^0 values is observed on passing from C₈₇ to polyisobutylene (pyridine is the only exception). It seems that increasing the column temperature decreases the dependence of ΔH_2^0 on the molecular weight of the stationary phases.

The observed increase in the intermolecular forces for *n*-nonane may be explained as follows. It has been proposed¹¹ that for condensed systems (liquids, solids) the dispersion forces between a particle and the surrounding environment increase when the dielectric constant of the environment increase. This effect is applicable to the solute molecule and the surrounding stationary phase. Because some proportionality is observed between the molecular weight of alkanes and their dielectric constant, the decrease in the ΔH_2^0 value on passing from squalane to polyisobutylene may be related to the change in dielectric constant.

Although the increase in the dispersion forces with the molecular weight of the stationary phase influences the ΔH_2^0 values of polar solutes, the larger changes observed need some other explanation. The experimental data for the polar solutes were determined under conditions where the interphase adsorption influences the retention data. Therefore, it is reasonable to relate the observed changes in ΔH_2^0 for the polar solutes to some changes in the interphase adsorption (the solid-liquid interphase). Although we used a silanized support, some adsorption activity towards the polar solutes on the solid-liquid interphase is observed due to non-silanized active centres. Some shielding of the active centres by the adsorbed layer of stationary phase is possible and, therefore, the observed differences in ΔH_2^0 for polar solutes relate to different degrees of shielding the support surface.

*F*⁰ values

The experimental data (Table I) show that the *F*⁰ values for *n*-nonane decrease with increasing molecular weight of the stationary phase. This result indicates the greater hindrance of free rotation of the solute molecule in the denser stationary phase (in passing from squalane to polyisobutylene). However, the *F*⁰ values of many other solutes increase with increasing molecular weight of the stationary phase. Considering the group of solutes with small interphase adsorption (the *A* value is negligibly small), one should take into account that the dependence of *F*⁰ on the molecular weight of the stationary phase has a different slope, which is related to shape of the solute molecule, viz., long-chain (*n*-nonane) or spherical (aromatic hydrocarbons, chloroform). The main difference between these groups lies in the hindrance of internal (*n*-nonane) or external (spherical molecule) rotation.

Ethyl acetate, methyl ethyl ketone, *n*-pentanal and 1-propanol are closer to *n*-nonane than to aromatic hydrocarbons when one considers their molecular shape. Therefore, the differences in *F*⁰ for these solutes can be explained mainly by interphase adsorption.

On increasing the column temperature, the *F*⁰ value becomes smaller by passing from C₈₇ to polyisobutylene e.g., this change is about 0.6 e.u. for 1-propanol (low column temperature) and 0.16 e.u. for 1-decanol (high column temperature). In general, the differences in *F*⁰ decrease as the column temperature increases because of freer rotation of the solute molecules in the stationary phases.

Non-linearity of the adsorption isotherm

This parameter is evaluated from the A value, which depends on the particular conditions. The experimental values for polar solutes are listed in Table I. Some increase in the A values is observed on passing from squalane to polyisobutylene. This difference is especially great for high-boiling polar solutes. The possible reason for this difference is the different degree of surface shielding by the stationary phase, because the low-molecular-weight stationary phase has a greater mobility of molecules and forms a more uniform adsorbed layer on the support surface.

The A value for n -propanol does not depend on the molecular weight of the stationary phase, which is related to the absence of free hydroxyl groups on the support surface.

Relative retentions

The experimental r values are listed in Table I; they are influenced by both the ΔH_s^0 and the F^0 values (eqn. 4). It can be seen from eqn. 4 that the same increase in r is achieved by changing F^0 by 1 e.u. or by changing ΔH_s^0 by 0.5714 kcal/mole at a column temperature of 323.2°K. Taking into account these values, we can evaluate the influences of F^0 and ΔH_s^0 on the r values when comparing the alkane stationary phases.

On passing from squalane to polyisobutylene, the ΔH_s^0 of n -nonane decreases by 0.5 kcal/mole and F^0 decreases by 0.43 e.u. Comparison of these values shows that the main factor in the difference in the r value of n -nonane is ΔH_s^0 .

Only small differences in ΔH_s^0 values for aromatic hydrocarbons were observed between the different stationary phases; hence, the main influence in increasing the retention of aromatic hydrocarbons is the entropy factor. The more complex influence of the thermodynamic functions on the relative retention is seen for chloroform: on comparing squalane and polyisobutylene, the main factor is entropic whereas on passing from C_{87} to polyisobutylene, the enthalpy term becomes the main factor.

Comparing ΔH_s^0 and F^0 for the polar solutes we can distinguish two groups of the solutes: the enthalpy factor is more important for n -pentanal, 1-propanol, pyridine and 1-decanol and the entropy factor is more important for the remaining polar solutes.

Knowledge of the thermodynamic factors that cause selectivity changes is of importance for the temperature dependence of the selectivity: when the enthalpy factor is more important, the changes in the column temperature alter the selectivity markedly. The experimental data show that the different factors change the relative retentions on non-polar stationary phases; it is difficult to accept that the empirical "polarity" of the alkane stationary phases increases with the molecular weight of the stationary phase as suggested by Huber and Kováts¹.

The data on the selectivity of the alkane stationary phases permits us to draw some conclusions about the requirements for a standard non-polar stationary phase. It has been shown that the r , ΔH_s^0 and F^0 values depend on the molecular weight of the stationary phase for all solutes. Hence the standard non-polar stationary phase must be a substance of the highest purity; this requirement applies not only to the different classes of hydrocarbons but also to the homologous alkanes. This point agrees with the work of Sojak and Rijks¹², who found that the selectivity for aromatic hydrocarbons is affected by the alkane impurities in squalane. Although squalane can be

purified by column chromatography, it has a low temperature limit: some decomposition of squalane during a long column life (several years) was observed when the column was used at temperatures between 80 and 140°C¹². Also, mixtures such as polyisobutylene cannot be considered as a standard stationary phase. Hence the C₂₇ stationary phase is now the only available standard for precise and reproducible GLC.

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