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EFFECTS OF TEST SOLUTES ON THE CHARACTERIZATION OF STATIONARY PHASES IN GAS CHROMATOGRAPHY USING A SNYDER TRIANGLE

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SUMMARY

The effect of the choice of test solutes on the location of a stationary phase in the Snyder selectivity triangle was examined. The properties of proton-donating ability, proton-accepting ability and polarity were estimated using ethanol, dioxane and nitromethane, respectively. Significant changes in the selectivity, *e.g.*, the locations of stationary phases in the triangle, were observed when the solute probes were changed by substituting homologues of ethanol for ethanol. However, modifying the calculation of selectivity so as to obtain a normalized value served to restore a phase to its original position in the selectivity triangle. This resulted in two corners of the triangle not having a representative phase.

This study also confirmed the earlier report that additional liquid phases are needed because of the absence of phases in two of the three corners of the selectivity triangle.

INTRODUCTION

Classification of gas chromatographic (GC) stationary phases involves two properties, selectivity and strength of the stationary phase. Classically Rohrschneider[1] classified stationary liquid phases used in GC by their abilities to retard probe solutes. This system was further developed by McReynolds[2]. In their classification, Rohrschneider and McReynolds compared the retention indices on a particular stationary phase with those on squalane and reported the differences. In all cases, squalane was used as the reference. Rohrschneider–McReynolds constants are often stated to be based upon the "polarity" of the stationary phase, and, as the overall interaction of the solute with the stationary phase increases, the Rohrschneider–McReynolds constants also increase.

Based on Rohrschneider–McReynolds indices, another approach to the selectivity was reported by Semenchenko and Vigdergauz[3]. They classified the phases into

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seven different types based on five different polarity factors. Yet another method has been based upon a thermodynamic parameter for characterization of stationary phases as given by Novák *et al.*[4] and Risby *et al.*[5].

Snyder[6] proposed that liquid chromatographic (LC) solvent phases be classified by the relative strength of the hydrogen bonding interaction and of dipole interactions. Klee *et al.*[7] proposed a method to classify GC phases along the same line using three test solutes representing proton donor, proton acceptor and polarity. Those solutes were ethanol, dioxane and nitromethane, the same ones used by Snyder in his classification of LC solvents[8]. The work of Klee *et al.*[7], although based upon an approach used for liquid chromatography turned out to be quite similar to a much earlier study by Brown[9] in which he used retention ratios for various combinations of three solutes that were selected primarily to represent electron donor, electron acceptor and ion polar hydrocarbon types. Note that Snyder's proton acceptor, proton donor, and "polarity" are closely related.

The present study, which was carried out without knowledge of Brown's work, confirmed his finding that the location of a stationary phase in a Snyder-type triangle depended on the choice of the test solutes. In addition, the present study shows how the resulting differences can be corrected for when the different solutes used for one corner of the triangle fall into a homologous series.

The primary goal of the present study was to examine the dependence on the choice of solute of the calculated selectivity parameters for the stationary phase, *i.e.*, the effect of the test probes on the location of the stationary phase in the selectivity triangle. For example, does one find that the proton-donating property of the stationary phases is stronger if pyridine is used instead of dioxane? What happens if another alkanol is used in place of ethanol, or nitropropane (or acetonitrile) instead of nitromethane?

After differences were indeed found, an attempt was then made to understand better the effect of different test probes on the location of the stationary phases in the selectivity triangle. As a result, the calculations used by Klee *et al.*[7] were modified so as to minimize the changes that resulted from substituting a homologous probe having the same type of dominant interaction.

EXPERIMENTAL

Chemicals

Ethanol, dioxane, nitromethane, *n*-butanol, 1-propanol, methanol, and nitropropane were laboratory grade reagents (J. T. Baker, Phillipsburg, NJ, U.S.A.).

The support was 100–120 mesh Supelcoport (Supelco, Bellefonte, PA, U.S.A.). Stationary phases used in this study were SE-30, OV-17, 1-hexadecanol (C_{16}-OH), QF-1 (trifluoropropylsilicone), Carbowax 20M (CW-20M), and Silar-10CP, all from Alltech Assoc. (Deerfield, IL, U.S.A.).

Procedures and calculations

All of the packings were prepared by dissolving a liquid phase in an appropriate solvent and adding 10% (w/w) Supelcoport, 100–120 mesh. The solvent was removed by rotoevaporating under vacuum. The packings were further dried in a vacuum oven. All of the columns were stainless-steel tubes, 1.8 m × 2.1 mm I.D.

(Supelco). Before packing, the tubing was washed with methanol, chloroform, and acetone before being dried by passing nitrogen through it.

Packed columns were conditioned by slowly increasing the column temperature to 150°C and holding it overnight. Helium carrier gas at a flow-rate of 30 ml/min was used.

In the cases of non-polar or slightly polar stationary phases, additional precautions were taken. In the case of squalane, the column was silanized before and after packing. On-column silanization was done using 50 μl of Silyl-8 (Pierce, Rockford, IL, U.S.A.) in five portions of 10 μl, each one injected after a 25–30-min interval. The column temperature was held at 120°C and, after 2–3 h, the column was connected to the detector and retention indices were determined. Periodic silylation was also carried out in order to see the effect on the values of the retention indices of the alcohols. A test mixture consisting of acetonitrile, 2-propanol, 1,2-dichloroethane, triethylamine and octane was used to check the efficiency of each column packed.

A Hewlett-Packard (Avondale, PA, U.S.A.) Model 5880A chromatograph, equipped with a thermal conductivity detector, was used in this study. A 20-μl gas sample and an oven temperature of 120°C was used throughout all of the experiments.

Calculations of retention indices and selectivity parameters

A Kováts retention index[10], I, was calculated from the corrected retention time for each solute on each stationary phase. At least five measurements were made per probe on each phase. The index values for the solutes on the deactivated squalane column were substracted from the values for the same solute on each stationary phase so as to obtain the ΔI values. The three selectivity parameters (X_i) were calculated by following the procedure of Klee *et al.*[7]. In this procedure the ΔI values for the three test solutes representing the three selectivity parameters for the proton-accepting (dioxane), proton-donating (ethanol) and polarity (nitromethane) properties were added together to get the $\Sigma\Delta I$ values. Each selectivity parameter was calculated using the following equation:

$$X_i = \frac{\Delta I_i}{\Delta I_e + \Delta I_d + \Delta I_n} \tag{1}$$

where ΔI_e, ΔI_d and ΔI_n values are the ΔI values for ethanol, dioxane and nitromethane, respectively. The three selectivity parameters were then plotted on the selectivity triangle.

RESULTS

Preliminary studies

Silylation. The corrected retention indices for the three test probes on squalane were determined from a series of experiments. Assuming that the support was completely silanized. The values for ethanol, dioxane, and nitromethane were 480, 681 and 533 whereas those reported by Klee *et al.*[7] were 280, 645 and 415, respectively. These large differences, especially that for ethanol, indicated that there were some free silanol groups on the support. To minimize that problem, on-column, *in situ*

deactivation was done, including wall deactivation, in addition to silylation before packing the squalane column. The corrected retention indices for the three test solutes on the squalane column after these silylation steps were I_e = 350, I_d = 661, and I_n = 467. Because these values were not yet as low as those of Klee *et al.*, some studies of repeated *in situ* silylations were performed. After a second silylation, there were significant changes in the retention indices values only for ethanol and nitromethane, the retention indices being I_e = 304, I_d = 662 and I_n = 424. A third silylation after a period of fifteen days produced the same values. Note that only the ethanol value was larger than its counterpart by Klee *et al.* However, further periodic silylations showed no improvements in the index values.

Table I shows the stationary phases used along with their Kováts retention indices and selectivity parameters. The important point to note is that, as the polarity of the stationary phase increased, the $\Sigma\Delta I$ values increased as well. It is also clear from this table that the retention indices found on SE-30 were higher than those reported by Klee *et al.* whereas, for the more polar phases, the retention index we found was less than that reported by Klee *et al.* Hence, the relative contribution of the free Si–OH groups on the support was higher in the cases of less polar phases than in those of the more polar phases. For that reason, percentage loading of the stationary phase was increased so as to reduce the effect of the free silanols.

Effect of liquid loading. Table I shows the selectivity parameters for the 20% SE-30 and 20% Silar-10CP columns. When the loading increased, the $\Sigma\Delta I$ value decreased from 447 to 357 units for SE-30, a value much closer to that of Klee *et al.* In the case of the polar Silar-10CP, the higher loading increased the $\Sigma\Delta I$ value from 2021 to 2243.

Comparison with earlier data

Positions of six GC stationary phases on the selectivity triangle are shown in Fig. 1. In this triangle, methyl silicone fell into Group II in Snyder's selectivity triangle and 1-hexadecanol fell near Group I. However, most of the phases fell into the

TABLE I

EFFECT OF SILYLATION AND PERCENT LIQUID LOADING ON STATIONARY PHASE SELECTIVITY

Squalane: I_e = 302, I_d = 662, I_n = 424; ref. 7: I_e = 280, I_d = 645, I_n = 415.

Phase	*Kováts indices**		X_e**			X_n**			X_d**		
	a	*b*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
SE-30	477	310	0.533	0.449	0.518	0.346	0.413	0.347	0.119	0.133	0.135
1-Hexadecanol	603	629	0.461			0.335			0.204		
OV-17	721	977	0.373			0.400			0.229		
QF-1	995	1065	0.271			0.490			0.243		
Carbowax 20M	1502	1759	0.350			0.414			0.234		
Silar-10CP	2021	2421	0.319		0.344	0.428		0.387	0.260		0.268

* a = Our studies, average of five measurements; b = reported by Klee *et al.*[7].

** A = Selectivity values obtained from our studies; B = effect of silylation on selectivity; C = effect of liquid loading on selectivity.

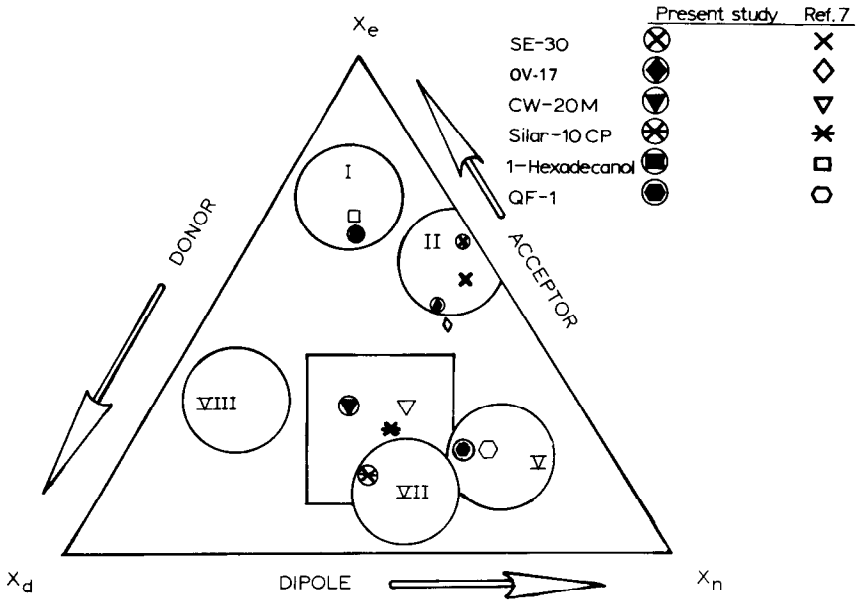

Fig. 1. Selectivity triangle comparing locations of six stationary phases reported by Klee *et al.*[7] with those from the present study.

bottom center of the triangle. QF-1 was the nearest to the dipolar corner and, thus, the most polar phase.

Fig. 1 also compares the selectivities of the six GC stationary phases. Our results correlated well with those reported by Klee *et al.*[7]. It is also evident from this figure that there was no stationary phase which showed good proton-donating character. Klee *et al.* reached the same conclusion.

Effects of test probes on the calculated selectivity

Table II shows the effect on the apparent selectivities of the stationary phases of changing the probe from ethanol to butanol. Note that there were relatively large changes in the selectivity values of the non-polar phases, particularly those for SE-30 and OV-17, which moved towards the polarity corner of the triangle. There was

TABLE II

EFFECT OF TEST PROBE AND EFFECT OF COLUMN TEMPERATURE ON SELECTIVITY

Test probes: *n*-butanol, dioxane, nitromethane.

Phases	*120°C*				*80°C*			
	$\Sigma\Delta I$	X_e	X_d	X_n	$\Sigma\Delta I$	X_e	X_d	X_n
SE-30	142	0.246	0.225	0.528	188	0.234	0.245	0.521
OV-17	522	0.252	0.291	0.456	570	0.228	0.291	0.480
QF-1	786	0.208	0.264	0.522	830	0.233	0.264	0.504
CW-20M	1450	0.310	0.252	0.421	1498	0.316	0.252	0.431

TABLE III

EFFECT OF TEST SOLUTES ON QF-1 AND SILAR-10CP

Stationary phase	*Solute*	X_e	X_d	X_n
QF-1	Nitropropane, dioxane, ethanol	0.248	0.275	0.476
	Acetonitrile, dioxane, ethanol	0.233	0.258	0.509
	Nitromethane, dioxane, ethanol	0.232	0.257	0.511
Silar-10CP	Nitropropane, dioxane, ethanol	0.389	0.264	0.347
	Acetonitrile, dioxane, ethanol	0.363	0.245	0.393
	Nitromethane, dioxane, ethanol	0.343	0.232	0.424
1-Hexadecanol	Ethanol, dioxane, nitromethane	0.493	0.205	0.302
	Propanol, dioxane, nitromethane	0.504	0.200	0.294
	n-Butanol, dioxane, nitromethane	0.410	0.238	0.351
SE-30	Ethanol, dioxane, nitromethane	0.534	0.119	0.346
	Propanol, dioxane, nitromethane	0.403	0.310	0.287
	n-Butanol, dioxane, nitromethane	0.246	0.225	0.528

also a large decrease in the $\Sigma\Delta I$ value of all phases as a result of using butanol instead of ethanol. Furthermore, the proton-accepting property (X_e) of SE-30 was very low using butanol as test probe whereas there was a dramastic increase in dipole contribution (X_n value).

As a result of this change in the position of the SE-30 when butanol was used as test probe, other homologous alcohols were examined for their effects on the apparent selectivity of the SE-30. It is evident from Table III that, as the number of

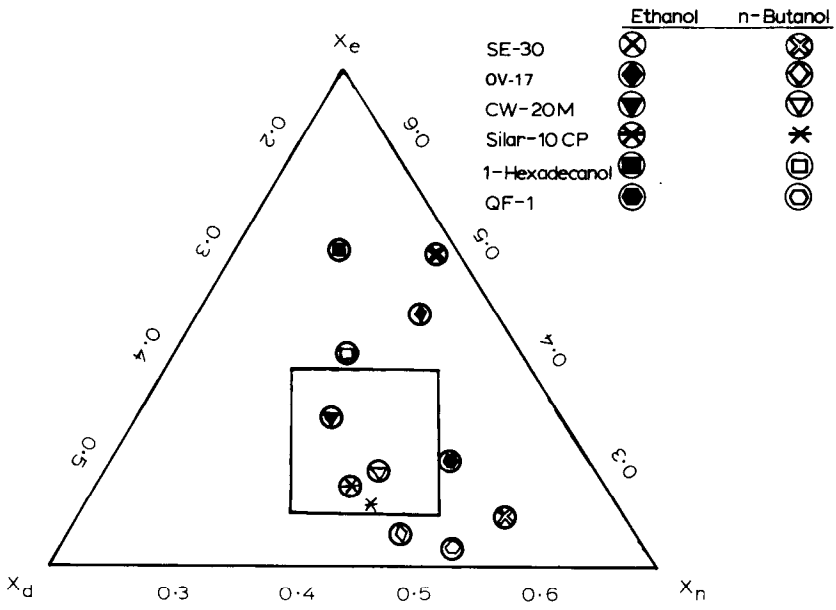

Fig. 2. Effect on apparent selectivity of changing the test probe from ethanol to *n*-butanol.

carbon atoms increased, the dipole contribution increased, *i.e.*, SE-30 shifted toward the X_n corner compared to its location in Fig. 2.

The locations in the triangle of the more polar phases (higher $\Sigma\Delta I$ values) were comparatively less affected by the changes in the test probes as illustrated by the displacements of QF-1 and CW-20M. Table III shows the effects on QF-1, Silar-10CP, SE-30 and 1-hexadecanol. The polarity contributions for acetonitrile and nitromethane were the same, while that for nitropropane was less for QF-1. The same type of behavior was observed with CW-20M. The polarity contribution increased on going from nitropropane to acetonitrile to nitromethane.

In order to see how the $-CH_2$ interactions were affecting the "specific" interaction, 1-hexadecanol, which falls near the upper proton-accepting corner, was examined. When the solute probe was changed from ethanol to propanol to butanol, the location on the triangle changed for 1-hexadecanol. Table III shows that there was positive interaction between the proton-donating solute and the proton-accepting stationary phase. Thus, C_{16}–OH, which is usually viewed as a proton donor, was classified as an proton acceptor. If that is the case, alcohols should be strongly retained on this column. Actually, that is not the case with 1-hexadecanol; dioxane is strongly retained compared to ethanol and propanol, but less strongly retained than butanol. This emphasized the need to apply a "correction" factor.

In order to minimize the solute dependence for homologues, a simple normalization was performed. In this normalization method, the corrected retention time of the alcohol homologue was divided by that of its corresponding *n*-alkane. This normalized value was then used to calculate the Kováts indices. The relative fractions of the three selectivity parameters were then calculated by following the procedure of Klee *et al.*[7].

Fig. 3 shows that there was then little effect of the test probe on the location

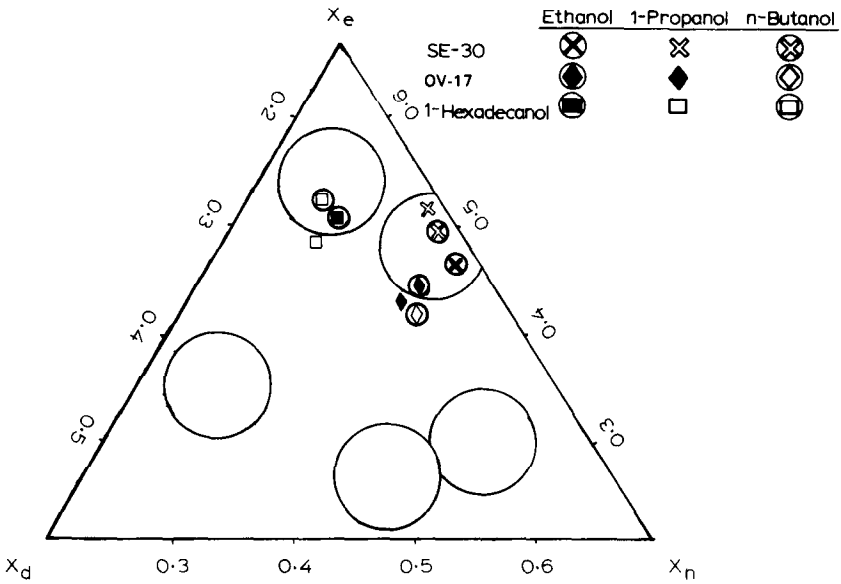

Fig. 3. Effect of changing test probe on apparent selectivity after normalization.

of the stationary phase. In contrast, the non-normalized locations shown in Fig. 2 for SE-30, OV-17 and 1-hexadecanol changed considerably when different alcohols were used. Furthermore, after the values had been normalized, the positions calculated for SE-30 when using the three alcohols were in the same area of Group II.

Effect of column temperature on calculated selectivity

When the column temperature was lowered from 120 to 80°C, there was a considerable increase in $\Sigma\Delta I$ values but the change in the three selectivity terms was relatively small (Table II). This result was not unexpected because the changes in Kováts indices with temperature are usually small.

CONCLUSION

This study suggests that the classification of GC phases is solute dependent, possibly more so than that of LC solvents. As shown in the present study, the selection of the solute probe can greatly affect the location of the stationary phase in the selectivity triangle. If, as in the case of acetonitrile, there is no way to correct the data, as was done for homologous test probes, a significant change in location may result. The normalization also indicated that, in this type classification, the effect of the dispersive $-CH_2$ interactions is important and must be taken into account along with the "specific" interaction.

Finally, our study confirmed the conclusion of Klee *et al.*[7] that there are no good commercial polymeric liquid phases in the proton-donor corner of the triangle. This means that one would have to test more acidic stationary phases (or use more basic test solutes).

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