Note

Which determine liquid phase "polarity" in gas chromatography: the standards or the probes?

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The use of I and ΔI values —Kováts indices and their difference when measured on two different liquid phases— has been of great value to gas chromatography. In particular, the characterization of liquid phases by Rohrschneider or McReynolds probes, through their ΔI values relative to squalane, has become very popular (for a comprehensive review of the field, see ref. 1). These values serve, nowadays, two purposes: they provide information on selective interactions, *e.g.* hydrogen bonding as probed by an alcohol, and the general "polarity" of one particular liquid phase compared to another. This note is concerned only with the latter subject.

The five probes chosen by McReynolds, for instance, chromatograph with I values around 600 on a non-polar phase. As phase polarity increases so do the indices —up to around 1600 for the most polar phases in common use. The increasing indices parallel the various increasing polar interactions between solute and solvent.

It is therefore generally accepted that "polar solutes" are stronger retained on polar phases than on non-polar ones. For instance, the attendants of the *31st ACS Annual Analytical Summer Symposium on Chromatography and Ancillary Methods*, held in June, 1978 in Boulder, Colo., U.S.A., were asked by one of us to judge whether the average retention of the five McReynolds probes should increase, stay the same, or decrease, with increasing liquid phase polarity. Shown a blank graph of the type used in Fig. 1, more than 80% of those expressing an opinion believed retention to increase. Similar opinions can be found, in implicit or explicit form, in the chromatographic literature.

Yet, these do not necessarily follow from the obvious fact that Kováts retention indices of polar probes increase drastically with liquid phase polarity. Since the probes' I and ΔI values are measured relative to alkane standards, either the standards or the probes or both can change in their absolute retention on liquid phases of increasing polarity. The question is therefore legitimate whether it is mainly a change in the retention of the probes or mainly a change in the retention of the standards that brings about the increasing I values of the probes on phases of increasing polarity.

The answer to this question has been implicitly given a long time ago (*e.g.* ref. 2) and it is one that must be basically known to any researcher concerned with the determination of ΔI values. However, we would like to restate this answer, and demonstrate it by using the five McReynolds probes.

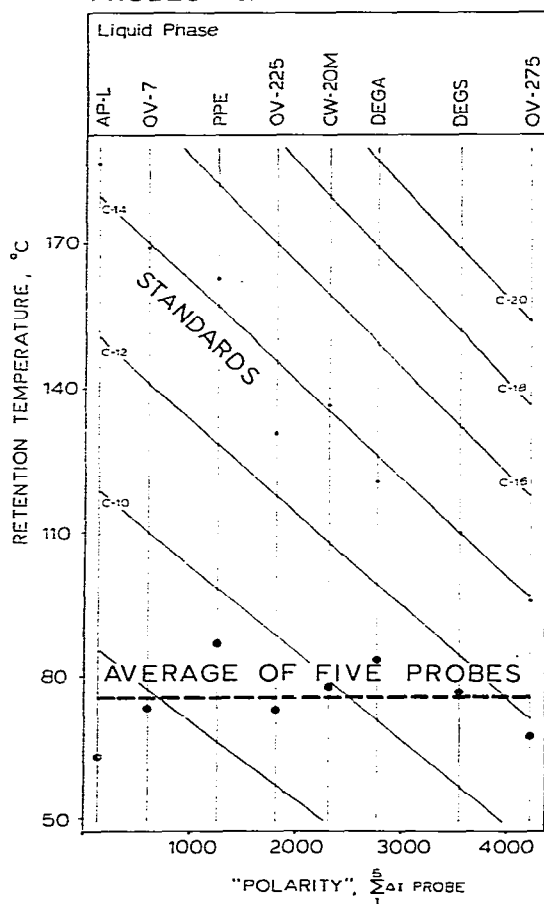MOLAR PLOT,

PROBES VS. STANDARDS

Fig. 1. More or less accurate retention plot of McReynolds probes and *n*-alkanes standards, measured on eight different stationary liquid phases (10% load on Chromosorb W) under otherwise equal conditions. "Polarity" values for liquid phases taken from ref. 5, except that for OV-275, where the value provided by the manufacturer (Ohio Valley Specialty Chemical Co., Marietta, Ohio, U.S.A.; Catalog No. 26 (1977/78) was preferred. Large dots: Average of five probes; small dots: tetradecane standard. The other standards show deviations similar to those of tetradecane. AP-L = Apiezon L; OV-7 = a phenylmethyl-dimethylsilicone (20% phenyl); PPE = polyphenylether (6 rings); OV-225 = a cyanopropylmethyl-phenylmethylsilicone; CW-20M = "Carbowax 20M compound"; DEGA = diethyleneglycoladipate; DEGS = diethyleneglycolsuccinate; OV-275 = "a cyano silicone".

Since the question posed is an approximate and simple one, and since the various selective interactions, even with averaging, could be expected to produce considerable scatter in the data (not to mention the effects of temperature, load, support surface etc.[3,4]), high-precision measurements were clearly not necessary. We chose therefore eight liquid phases that span most of the easily accessible polarity range and coated them at 10% load (rather than the usual 20% which would be

inconvenient to use for most other purposes) on Chromosorb W AW, 45-60 mesh. Equal column lengths, carrier gas flow, etc. were used, and retention temperatures (*cf.* ref. 1, p. 373) in a standard temperature program replaced the more common, much preciser, and less convenient measurement of log V_R' at isothermal conditions.

In Fig. 1, these retention temperatures are plotted for the *n*-alkane standards and an average of the five McReynolds probes (benzene, 1-butanol, 2-pentanone, nitropropane, and pyridine), *vs.* "polarity" as sometimes defined by the sum of the ΔI values of these probes (*e.g.*, ref. 5).

The scatter in the probe data points is, of course, expected. It reflects particular, selective interactions for whose sake, after all, the system of characteristic probes was invented. For this study, we had deliberately chosen different chemical structures for the liquid phases (thereby increasing the scatter) as opposed to, say, covering the polarity range only with silicones. Also, equal volume rather than equal weight load may have been preferable on theoretical grounds.

The answer to our title question, given by Fig. 1 is, however, still quite clear: It is the *alkane standards* whose retention changes drastically with the polarity of the liquid phase; the retention of the probes remains more or less even through the polarity range. It is therefore essentially alkane retention that determines a liquid phase's standing in the polarity scale, in agreement with the early literature on this subject[2].

This answer, while expressing a minority viewpoint, is really not all that surprising. One may consider the problem, along the lines of regular solution theory, as one governed by the difference of energy expanded in forming a cavity for the solute molecule in the liquid phase and the energy gained through interaction of solute and solvent. The probes are relatively small molecules, polarized and easily polarizable. The standards are larger, non-polar and difficult to polarize. Thus, in a first approximation, the larger energy needed for cavity formation in a polar phase *vs.* a non-polar phase is more or less compensated for by increased interactions between probe and phase, leading to approximately the same retention regardless of liquid phase polarity.

For alkane standards, the increased energy required for cavity formation cannot be compensated by solute–solvent interactions. Increasing polarity of the liquid phase thus leads to decreasing retention of alkanes. In a manner of speaking, alkanes are "squeezed out" by highly polar phases —an effect akin to the "hydrophobic effect" sometimes invoked in reversed-phase liquid chromatography[6].

As a matter of speculation, one may even go a step further. In Fig. 1, a straight line was drawn to average the retention of the polar probes, and it turned out to be obligingly horizontal. While that fact underlines the *raison d'être* of this note, it is most likely accidental. First, had liquid phases of still higher polarity been included, the slope may have dipped to negative values. Second, had other probes than those suggested by McReynolds been used, the line may have shown a negative or positive slope, depending on whether these, on the average, would have been less or more polar, respectively. A case in point may be the (less polar) probes suggested by Vernon and Gopal for use at higher temperatures[7].

Furthermore, the use of a *straight* line may be questioned; *i.e.* the problem may be posed, what general shape the retention profile of a typical probe would show in a polarity plot.

If we, for convenience, characterize phases and probes to be of low, medium or high polarity, and consider the case of a low polarity probe in the high polarity phase region, it is likely that the slope should be negative. This can be seen by analogy to alkane behavior, or by consideration of the intermolecular bonds being formed and broken during dissolution of a solute molecule. The weakly polar probe will be "squeezed out" in a similar way, though to a lesser extent, than the alkanes.

When the "polarities" of probes and phases are similar, the strongest interaction, *i.e.* the longest retention, should result (*similia similibus optime solvuntur*). This case, with slope zero, represents the apex in the retention profile.

The case of a highly polar probe on phases of low polarity, on the other hand, should show a positive slope. Therefore, over the total polarity range, single probe retention profiles should have the form of (more or less complete) arches, the position of whose apices would correspond roughly to the "polarity" of the respective probes (molecular weight effects not being considered). Several probes averaged, as in Fig. 1, should therefore produce an extended arch with a relative flat top.

When the experimental probe retentions were plotted singly, one could have indeed imagined a series of arches starting with benzene at the low-polarity side; and the averaged retentions of Fig. 1 do seem to decrease on the low- and high-polarity sides of the graph. This, however, remains unproven. The large effects of selective interactions, and the fact that only eight liquid phases were tested, do not permit any but a purely speculative statement at this point. A much more careful study, involving more probes and many more phases (to average out the various selective interactions) would be needed. Such a study, however, is beyond our present intentions.

It may be noted as an afterthought, that, were the above speculation correct, retention of typical probes would indeed increase with increasing phase polarity as is common belief —but only on low-polarity phases. On high-polarity phases, they would show the opposite behavior. A recent study on phenymethylsilicones does, in fact, show clearly developed "arches", but the authors considered in this case the descending parts anomalous[8].

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