THE SELECTIVE SEPARATION
OF HIGH-BOILING AROMATIC COMPOUNDS

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In connection with a research project involving the pyrolysis of simple model compounds containing some of the groupings thought to occur in coal, separations were required of products boiling at temperatures up to 350°. It proved impossible to separate several of the components with Apiezon L as the stationary phase, and a change was therefore made to a more selective alternative, namely Reoplex 400, which has recently been used by JANÁK AND HŘIVNÁČ[1]. In the course of the work several interesting selectivity relationships were observed due to "π"-electron interactions of the type discussed by the above authors and by LANGER, ZAHN AND PANTAZOPLOS[2], who have recently separated *m*- and *p*-xylene using di-*n*-propyl tetrachlorophthalate as the stationary phase.

EXPERIMENTAL

A modified Pye gas–liquid chromatograph incorporating an argon ionization detector was used for determining the relative retention volumes. The inlet system was modified by introducing a sampling valve based on the design described by TENNEY AND HARRIS[3]. The inlet gas pressure was controlled by means of a Sunvic Nullmatic regulator, and temperature cycling of the column heater was minimized by connecting a variable resistor across the temperature regulator to provide a suitable base load for the heater. The argon flow rate throughout the study was 100 ml/min.

The copper chromatographic columns were 4 ft. long and were packed with 5 % Apiezon L on Embacel and with 5 % Reoplex 400 on Embacel. To ensure accurate comparisons, the same amount of packing was provided on each column.

In one case, retention data for the ω,ω'-diphenylalkanes were determined on a 6 ft. column of 25 % Apiezon L using a Griffin and George Mark II chromatograph with hydrogen as the flow gas (4.0 l/h).

All the quoted relative retention values were means of five injections for each substance on each stationary phase.

DISCUSSION

Table I shows the relative retention volumes of a series of ω,ω'-diphenylalkanes $(C_6H_5[CH_2]_nC_6H_5)$ on Apiezon L (5%) and Reoplex 400 (5%). For comparison, similar retention data for Apiezon L (25%) are included which, although not strictly comparable, indicate that the relationships were unaffected by the amount of stationary phase present.

TABLE I

RETENTION DATA OF ω,ω'-DIPHENYLALKANES

Diphenylalkane	n	B.p. °C	Relative retention volumes		
			Apiezon L (5%) 180°	Reoplex 400 (5%) 180°	Apiezon L (25%) 200°
Diphenyl	0	255	0.881	0.941	0.868
Diphenylmethane	1	265	1.00	1.00	1.00
Dibenzyl	2	284	1.51	1.32	1.47
1,3-Diphenylpropane	3	302	2.55	2.00	2.48
1,4-Diphenylbutane	4	317	3.95	2.77	3.76
1,6-Diphenylhexane	6	348	10.38	5.22	9.06

Plots of the logarithms of these retention data against boiling point for each stationary phase are shown in Figs. 1–3. The curves are essentially linear except for the lower members of the series, namely diphenyl and diphenylmethane. Their
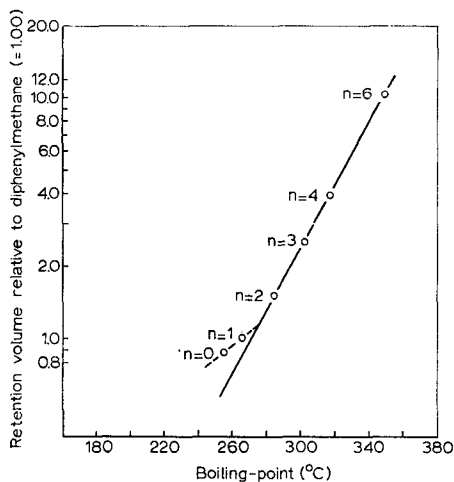

Fig. 1. Log retention volume vs. boiling-point. Sample: ω,ω'-diphenylalkanes $(C_6H_5[CH_2]_n C_6H_5)$; column: 4ft., 5% Apiezon L on Embacel; temperature: 180°; Pye apparatus; flow rate: 100 ml/min; pressure (inlet): 26.5 lb./sq.in.

retention times indicate them to be more strongly retained, relative to their boiling-points, than the other diphenylalkanes. Such behaviour is evidence for polarizability, and the effect is especially pronounced on Reoplex 400, a polar stationary phase (compare the slopes of the relevant portions of each curve).
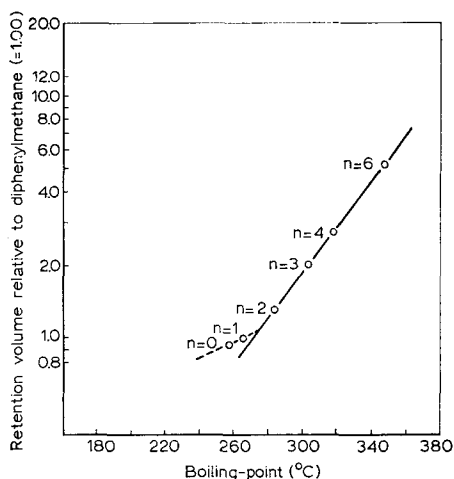
Fig. 2. Log retention volume *vs.* boiling-point. Sample: ω,ω'-diphenylalkanes $(C_6H_5[CH_2]_nC_6H_5)$; column: 4 ft., 5 % Reoplex 400 on Embacel; temperature: 180°; Pye apparatus; flow rate: 100 ml/min; pressure (inlet) 29.5 lb./sq.in.
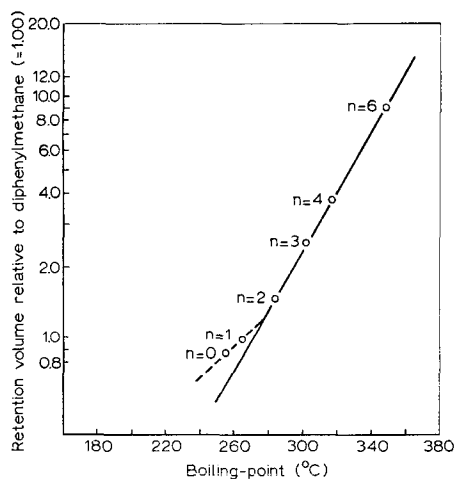

Fig. 3. Log retention volume *vs.* boiling-point. Sample: ω,ω'-diphenylalkanes $(C_6H_5[CH_2]_nC_6H_5)$; column: 6 ft., 25 % Apiezon L on Embacel; temperature: 200°; Griffin and George Mark II apparatus; flow rate: 4.0 l/h.

This revealed polarizability is not surprising because, in both diphenyl and diphenylmethane, the phenyl groups interact electronically, as their ultra-violet spectra[4] show. With diphenyl, the ultra-violet spectrum is unlike that of benzene and is due to the contribution of such dipolar structures as (I).

Similarly, the ultra-violet spectrum of diphenylmethane[4], while not very dissimi-

(I)

lar from that of dibenzyl and the higher, ω,ω'-diphenylalkanes, does show differences which may be attributed to electronic interaction between the benzene rings across the central carbon atom. CRAM AND ANTAR[5] have shown that diphenylmethane can be acylated to give high yields of monosubstituted product, indicating that the substituent is deactivating the other ring, presumably because of electronic interaction between the benzene rings. This contrasts with the behaviour of dibenzyl and the higher ω,ω'-diphenylalkanes which, even when one mole of acylating agent is employed, give mixtures of non-, mono- and bis-substituted material because the rings are electronically independent of one another.

Table II lists the relative retention volumes for a number of representative high-boiling aromatic hydrocarbons (the ω,ω'-diphenylalkanes are included, for comparison). Table III shows some of the separation factors which can be derived from Table II. In brackets are the values found earlier by JANÁK AND HŘIVNÁČ[1].

TABLE II

RELATIVE RETENTION VOLUMES AT 180° FOR HIGH-BOILING AROMATIC
COMPOUNDS

Compound	B.p. °C	Apiezon L (5%)	Reoplex 400 (5%)
Naphthalene	218	0.409	0.436
1-Methylnaphthalene	245	0.732	0.726
Diphenyl	255	0.881	0.941
Diphenylmethane	265	1.00	1.00
Acenaphthene	277	1.58	1.50
Dibenzyl	284	1.51	1.32
3:4-Benzocoumarone	285	2.23	2.90
Diphenylene oxide	287	1.92	1.98
Fluorene	297	2.43	2.66
Diphenylacetylene	297	3.06	2.75
1,3-Diphenylpropane	302	2.55	2.00
trans-Stilbene	307	3.86	4.27
Xanthene	308	3.18	3.10
1,4-Diphenylbutane	317	3.95	2.77
Phenanthrene	338	6.20	7.24
1,6-Diphenylhexane	348	10.38	5.22

Tables II and III reveal the strong "π"-electronic interaction which exists between Reoplex 400 and certain aromatic compounds. Of special interest is the reversal of order shown by the pair phenanthrene/1,6-diphenylhexane on Reoplex 400 compared with their order on Apiezon L. The strong retention of phenanthrene on Reoplex 400 is undoubtedly a consequence of the localization of "π"-electrons at the 9,10-bond, conferring on that bond a marked double-bond character.

Similarly, the pairs fluorene/1,3-diphenylpropane and trans-stilbene/1,4-diphenylbutane are inseparable on Apiezon L, but are readily separated on Reoplex 400. The ω,ω'-diphenylalkanes, where $n \geqslant 2$, suffer no enhanced sorption on Reoplex 400 because the aromatic rings act independently and "π"-electron localization is minimal. Both fluorene and trans-stilbene have structures in which "π"-electron

localization occurs, the former at the methylene bridge and the latter at the central double bond joining the phenyl nuclei. Similarly, the pair acenaphthene/dibenzyl, both of which have ethane bridges, are separated slightly more easily on Reoplex 400. This is not surprising, because the naphthalene nucleus of acenaphthene will confer more polarizability on its molecule than do the two isolated benzene nuclei on dibenzyl.

TABLE III

SEPARATION FACTORS (DERIVED FROM TABLE II) *

| Compound	Apiezon L (5%) 180°	Reoplex 400 (5%) 180°
Diphenylmethane/diphenyl	1.14	1.06
Dibenzyl/diphenylmethane	1.51	1.32
Fluorene/acenaphthene	1.54 (1.51)	1.77 (1.77)
Fluorene/diphenylene oxide	1.27 (1.38)	1.33 (1.23)
Fluorene/1,3-diphenylpropane	0.95	1.33
1-Methylnaphthalene/naphthalene	1.79 (1.78)	1.66 (1.62)
trans-Stilbene/1,4-diphenylbutane	0.98	1.54
Diphenylene oxide/acenaphthene	1.21 (1.09)	1.32 (1.44)
3:4-Benzocoumarone/diphenylene oxide	1.16	1.46
Acenaphthene/dibenzyl	1.05	1.14
Phenanthrene/1,6-diphenylhexane	0.60	1.39
Diphenylacetylene/fluorene	1.26	1.03
Xanthene/fluorene	1.31	1.17
Xanthene/1,4-diphenylbutane	0.80	1.12

* Values in parentheses are those of JANÁK AND HŘIVNÁČ[1].

Our separation factors for the pair diphenylene oxide/acenaphthene differ from those of JANÁK AND HŘIVNÁČ[1]. We were able to separate these substances readily on Apiezon L, and we believe that this separation was due to the use of a more homogeneous support (Embacel) than was employed by JANÁK AND HŘIVNÁČ.

An interesting pair are 3:4-benzocoumarone (II) and diphenylene oxide (III). They are separated fairly readily on Apiezon L but much more easily on Reoplex 400.
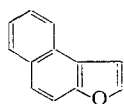
(II)
Boiling-point 285°
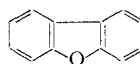
(III)
Boiling-point 287°

The "outside" furan ring of 3:4-benzocoumarone contains a styrene-type double bond where "π"-electrons are localized, and increased sorption on Reoplex 400 results. The polarization accorded to the diphenylene oxide molecule by the oxygen atom is obviously not as strong as that induced by the "π"-electron localization at the 1,2-bond of 3:4-benzocoumarone.

The polarizability of xanthene (IV) is shown by its comparison with 1,4-diphenylbutane, there being a reversal of order on Reoplex 400 compared with the

order on Apiezon L. This polarizability is somewhat less than that of fluorene (V), as a comparison of their separation factors (Table III) reveals. The oxygen bridge in xanthene interrupts conjugation between the aromatic nuclei and lowers the polari-

zability. Table II reveals that, with Apiezon L, 3:4-benzocoumarone, diphenylacetylene and *trans*-stilbene behave anomalously in that they are not eluted linearly with respect to their boiling-points. These anomalies may be due to the high degree of unsaturation present in these compounds. Diphenylacetylene also shows anomalous
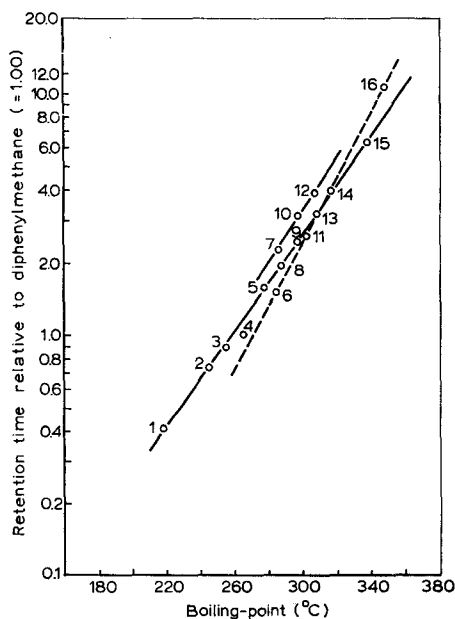

Fig. 4. Log retention volume *vs.* boiling-point. Sample: compounds in Table II; column: 4 ft., 5 % Apiezon L on Embacel; temperature: 180°; Pye apparatus; flow rate: 100 ml/min; pressure (inlet): 26.5 lb./sq.in. 1. Naphthalene; 2. 1-Methylnaphthalene; 3. Diphenyl; 4. Diphenylmethane; 5. Acenaphthene; 6. Dibenzyl; 7. 3:4-Benzocoumarone; 8. Diphenylene oxide; 9. Fluorene; 10. Diphenylacetylene; 11. 1,3-Diphenylpropane; 12. *trans*-Stilbene; 13. Xanthene; 14. 1,4-Diphenyl-butane; 15. Phenanthrene; 16. 1,6-Diphenylhexane.

behaviour on Reoplex 400, for its separation factor with respect to fluorene is not in keeping with the high degree of polarization suggested by its sorption on Apiezon L. This anomalous behaviour on Apiezon L is also readily seen in Fig. 4, in which the logarithms of the relative retention data for the compounds in Table II (5 % Apiezon L at 180°) are plotted against boiling-point. A straight line can be drawn through the points for most of the compounds except 3:4-benzocoumarone, diphenylacetylene and *trans*-stilbene, which are on a different straight line, and the ω,ω'-diphenylalkanes (dotted line).

Comparing the sorption behaviour of those hydrocarbons which are eluted linearly with respect to their boiling-points on 5% Apiezon L (Fig. 4) with their corresponding behaviour on 5% Reoplex 400, and assuming that polarizability is the sole cause of such selective sorption effects, the following empirical series of decreasing polarizability can be suggested: phenanthrene > fluorene > naphthalene = diphenyl > 1-methylnaphthalene > diphenylene oxide > xanthene > acenaphthene.

However, on the basis of molar refraction measurements, SCHUYER, BLOM AND VAN KREVELEN[6] obtained satisfactory agreement between theoretical calculations and experimental results for the following series of decreasing polarizability:

phenanthrene > fluorene > acenaphthene > naphthalene,
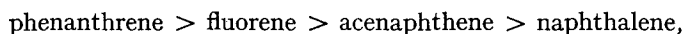
the members acenaphthene and naphthalene being transposed. The position of 1-methylnaphthalene in our series is also noteworthy, as SYRKIN AND DYATKINA[7] indicate 1-methylnaphthalene to be more polarizable than naphthalene while pointing out, however, that molar refraction data are difficult to interpret. It would appear that while selective sorption behaviour is probably mainly a polarizability phenomenon, there may be other factors involved.

Similar differences in selective sorption were observed with several low-boiling aromatic compounds. Their relative retention volumes are listed in Table IV, and some of the derived separation factors are compared in Table V. Since 5% Apiezon L

TABLE IV

RELATIVE RETENTION VOLUMES FOR VARIOUS AROMATIC COMPOUNDS

Compound	B.p. °C	Relative retention volumes	
		5% Apiezon L (110°)	5% Reoplex 400 (80°)
Cumene	152.4	0.460	0.195
n-Propylbenzene	159.5	0.553	0.223
α-Methylstyrene	165.5	0.780	0.426
Coumarone*	171.4	1.00	1.00
Hydrindene	177	1.15	0.509
Indene*	182.8	1.40	0.928
n-Butylbenzene	183	1.09	0.400
Tetralin	207.4	2.66	1.16
Naphthalene	218	3.97	3.22
Thionaphthene*	222	4.91	4.29

* These compounds are in Series 1 (see page 393).

retains a given sample longer than 5% Reoplex 400 for the same length of column, the two phases were investigated at different temperatures, namely, 110° for Apiezon L and 80° for Reoplex 400. Therefore, the separation factors quoted in Table V are for those pairs of compounds where the selective sorption effect is significantly large.

The most interesting comparison here is that of hydrindene (hydro-aromatic) and *n*-butylbenzene (open-chain). These hydrocarbons emerge together on Apiezon L, but are readily separated on Reoplex 400. On the basis of the previous arguments, this selectivity must be due to the fact that hydrindene is more polarizable than *n*-butylbenzene.

TABLE V

COMPARISON OF SEPARATION FACTORS (DERIVED FROM TABLE IV)

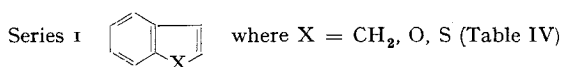| Compounds	Separation factor	
	5% Apiezon L (110°)	5% Reoplex 400 (80°)
Indene/coumarone	1.40	0.93
Hydrindene/indene	1.22	1.80
Hydrindene/*n*-butylbenzene	1.06	1.27
Coumarone/hydrindene	0.87	2.00
Coumarone/*n*-butylbenzene	0.91	2.50
Tetralin/naphthalene	1.49	2.78
Coumarone/thionaphthene	4.91	4.29

This increased polarizability is paralleled by the increased reactivity toward electrophilic substitution of hydrindene in the aluminium chloride-catalysed benzoylation reaction[8]. Although rate figures are not quoted for *n*-butylbenzene, the rate for hydrindene is approximately 28 times that of ethylbenzene[8,9] and presumably greater than that of *n*-butylbenzene to the same degree.
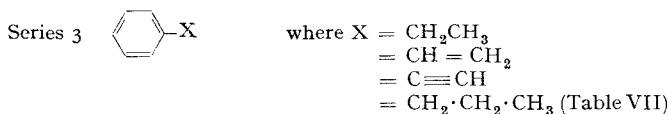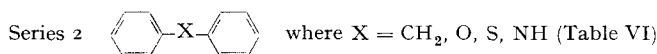
The marked difference in the separation factors of the pair hydrindene/indene is clearly due to the unsaturated linkage in the five-membered ring of indene. This linkage, being a "styrene-type" double bond, interacts strongly with Reoplex 400. Whereas coumarone and indene are easily separated on Apiezon L, no separation was observed on Reoplex 400, indicating that coumarone is retained more strongly on Reoplex 400. Evidently, therefore, coumarone is more polarizable than indene.

In view of these selective sorption effects, it was not surprising that naphthalene and tetralin showed marked differences of behaviour on Reoplex 400, the former being retained more strongly. Naphthalene is more fully aromatic and its "π"-electron cloud is held more strongly than that of the hydroaromatic tetralin.

The order of decreasing polarizability for the compounds in Table IV is: coumarone > naphthalene > indene > hydrindene = tetralin > *n*-butylbenzene. In general, the order of retention is aromatic > hydroaromatic > open-chain for Reoplex 400.

Since there appears to be a qualitative relationship between the degree of polarizability of aromatic compounds. and sorption on a polar phase, the following series were examined on both 5 % Apiezon L and 5 % Reoplex 400:

Series 1   where X = CH_2, O, S (Table IV)

Series 2 ⟨   ⟩-X-⟨   ⟩   where X = CH_2, O, S, NH (Table VI)

Series 3 ⟨   ⟩-X   where X = CH_2CH_3
                              = $CH = CH_2$
                              = $C \equiv CH$
                              = $CH_2 \cdot CH_2 \cdot CH_3$ (Table VII)

Series 1. Examination of the relative retention volumes for indene (X = CH_2), coumarone (X = O), and thionaphthene (X = S) illustrates the effect of the hetero-atom in conferring polarizability on the common nucleus. Oxygen in this series has a noticeably greater influence than sulphur, indicating coumarone to be more polariz-able than thionaphthene, in agreement with the known reactivities of both com-pounds, coumarone being the more reactive[10]. Consistent figures for indole (X = NH) could not be obtained because of its marked asymmetrical peak on both 5 % phases, presumably because of the acidity of the –NH– group.

Series 2. The degree of decreasing polarizability for this series is diphenylamine > diphenyl ether > diphenyl sulphide = diphenylmethane. Diphenylamine is recorded as an asymmetrical peak on both phases, but is much more strongly retained on Reoplex 400—a measure of the polarizability of the molecule.

Diphenyl ether is somewhat more polarizable than either diphenyl sulphide or diphenylmethane, which in this respect are practically equivalent. The oxygen atom confers a slightly greater degree of polarizability on the molecule than does the sulphur atom. However, selective sorption effects are not so pronounced as in Series 1, there being only the conjugation of the two benzene nuclei involved across the central atom.

Series 3. It was expected that an olefinic bond would confer enhanced polariz-ability on a given molecule (compare ethylbenzene and styrene), but the powerful

TABLE VI

RELATIVE RETENTION VOLUMES AT $140°$ FOR COMPOUNDS OF SERIES 2

Compound	B.p. °C	5% Apiezon L	5% Reoplex 400
Diphenyl ether (X = O)	259	0.801	0.925
Diphenylmethane (X = CH_2)	265	1.00	1.00
Diphenyl sulphide (X = S)	296	2.35	2.49
Diphenylamine (X = NH)	302	3.10	12.46

effect of an acetylenic bond (phenylacetylene) was surprising. Phenylacetylene gave a strong asymmetrical peak, presumably because of its acidic hydrogen; and, in addition, its sorption on the non-polar Apiezon L is not in accord with its boiling-point (such behaviour is reminiscent of diphenylacetylene (Table II)). The magnitude of its relative retention volume on 5 % Reoplex 400 is considerably greater than that of styrene, indicating higher polarizability.

There is an interesting selectivity effect in the behaviour of ethylbenzene and *n*-propylbenzene on both phases. The separation factors for these compounds are 2.14 and 1.82 on Apiezon L and Reoplex 400 respectively. Ethylbenzene is therefore more polarizable than *n*-propylbenzene, a result which is in accord with the respective electronegativities of these alkyl substituents.

Often in the pyrolyses of hydroaromatics or alkylaromatics, *o*-xylene is a product. On Apiezon L there is not much separation of *o*-xylene from styrene, a frequent accompanying pyrolysis product, especially if the amount of *o*-xylene is small. From Table VII it can be seen that Reoplex 400 is a selective phase for the easy separation of these two substances.

TABLE VII

RELATIVE RETENTION VOLUMES AT 50° OF VARIOUS LOW-BOILING
AROMATIC COMPOUNDS

Compound	*B.p.* °C	*5% Apiezon L*	*5% Reoplex 400*
Ethylbenzene	136	1.00	1.00
Phenylacetylene	142	1.95	3.67
o-Xylene	144.4	1.48	1.53
Styrene	146	1.70	2.30
n-Propylbenzene	159.5	2.14	1.82

Finally, it should be emphasized that, when the substances under investigation were either fairly acidic or basic, asymmetrical peaks, each with a long trailing edge, were recorded on these columns with 5 % stationary phase. Such departure from ideal conditions was shown by phenol, thiophenol, aniline, diphenylamine, indole, quinoline and carbazole. Since the departure from ideal conditions was less on 25% stationary phase, reaction with the support may be responsible.

SUMMARY

The selective sorption of various aromatic compounds boiling at temperatures up to 350° was studied on a polar phase (Reoplex 400). Comparison of their behaviour on the non-polar Apiezon L indicates that this selectivity may be explained by "π"-electron interaction with the stationary phase (acceptor). While a qualitative estimate of the degree of polarizability of the compounds under investigation could thereby be obtained, sufficient cases of anomalous sorption exist to indicate that factors other than polarizability may be responsible for selective sorption.

From the practical standpoint, Reoplex 400 is a suitable selective stationary phase for the separation of many aromatic hydrocarbons which normally emerge together on non-polar phases. Reoplex 400 retards such hydrocarbons in the order aromatic > hydroaromatic > open-chain.

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