GAS–LIQUID CHROMATOGRAPHIC STUDIES OF ELECTRON-DONOR-ACCEPTOR SYSTEMS

IV. DI-*n*-NONYL TETRACHLOROPHTHALATE AS AN ELECTRON-ACCEPTOR STATIONARY PHASE

A. R. COOPER AND C. W. P. CROWNE
Department of Chemistry, Sir John Cass College, London, E.C.3 (Great Britain)
AND
P. G. FARRELL
Department of Chemistry, Queen Elizabeth College, London, W.8 (Great Britain)
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INTRODUCTION

LANGER *et al.*[1] have described the use of tetrachlorophthalate esters as stationnary phases in gas–liquid chromatography (GLC), for the separation of aromatic compounds. They attribute the selectivity of these esters in the retention of such compounds in part to the formation of charge transfer (CT) complexes, following earlier work in which complexes of hexamethylbenzene with these esters were isolated and coloured solutions formed on adding electron donors[2], among them N,N-dimethylaniline[3]. The chromatographic experiments[4] showed the emergence of *p*-xylene after *m*-xylene, in the reverse order of volatility but also in the reverse order of donor strength.

Investigations of other CT acceptors as stationary phases have been reported[5,6] correlating retention data with CT association constants determined spectrophotometrically. This correlation was examined for substituted anilines, aromatic hydrocarbons and heterocyclic compounds which are stronger donors than those employed by LANGER *et al.*[1] in the chromatographic studies of the tetrahalophthalate esters.

Retention data have now been obtained for these stronger donors chromatographed on di-*n*-nonyl tetrachlorophthalate (NTCP). Di-*n*-nonyl phthalate has been used extensively as a stationary phase in GLC[7] and it was found that the tetrachloro-compound also has the low volatility required for use at these temperatures. The esters used by LANGER *et al.*[1] are too volatile to be used as stationary phases at temperatures in the region of $\sim 200°$, these temperatures being desirable for the study of methylated naphthalenes and quinolines. The results are compared with the corresponding values for elution from 2,4,7-trinitrofluorenone (TNF)[5], a stronger acceptor than the ester, and with retention data[8,9] for non-complexing polar stationary phases. Such a comparison supports the contention that CT association contributes to the retention of the donors chromatographed on NTCP columns, but implies that NTCP is a very weak electron acceptor.

TABLE I

RETENTION DATA AND EXCESS THERMODYNAMIC FUNCTIONS OF SOLUTION FOR SUBSTITUTED ANILINES

No.	Compound	$V_{g(SO)}$ (ml) 180°	$V_{g(NTCP)}$ (ml) 180°	γ_{NTCP} 180°	R_{NTCP} 180°	$V_{g(NTCP)}$ (ml) 195°	$\Delta\bar{G}_e^\circ$ (cal) 180°	$\Delta\bar{H}_e^\circ$ (cal)	$\Delta\bar{S}_e^\circ$ (cal deg.$^{-1}$)	R_{TNF}/R_{NTCP}
1	Aniline	24.6	71.5	1.11	2.91	51.6	99.5	182	3.81	2.34
2	*o*-Toluidine	37.7	117.7	1.02	3.12	86.1	21.6	252	5.51	2.32
3	*m*-Toluidine	38.7	121.6	1.08	3.14	88.9	71.7	281	6.05	2.45
4	*p*-Toluidine	35.3	117.9	1.04	3.34	86.8	37.9	283	6.16	2.48
5	*p*-Ethylaniline	57.1	182.1	0.75	3.20	127.5	−256.7	117	3.14	1.78
6	2,4-Xylidine	57.1	193.8	0.90	3.39	131.7	93.9	176	4.08	2.46
7	N-Methylaniline	36.6	106.5	1.02	2.91	77.0	19.7	188	4.11	1.88
8	N,N-Dimethylaniline	41.3	106.8	0.95	2.59	77.6	−46.2	234	5.28	1.32
9	N,N-Diethylaniline	72.3	170.1	1.10	2.32	119.4	85.2	235	5.00	0.64
10	N,N-Dimethyl-*o*-toluidine	37.9	74.8	1.08	1.97	57.5	69.2	343	7.43	0.39
11	N,N-Dimethyl-*p*-toluidine	62.0	164.1	0.96	2.65	118.1	−32.1	234	5.24	1.47
12	N,N-Dimethyl-*p*-*tert*.-butyl-aniline	155.9	416.3	1.17	2.67	281.1	141.4	199	4.09	0.57
13	N,N-Dimethyl-2,4-xylidine	57.4	115.3	1.05	2.01	84.1	40.6	245	5.31	0.36
14	N,N-Dimethyl-2,6-xylidine	50.7	96.0	1.10	1.89	72.6	85.2	324	7.00	0.30
15	2,6-Xylidine	57.4	186.1		3.24					2.25
16	2-Ethylaniline	54.5	168.8		3.10					1.51
17	2,6-Diethylaniline	173.2	350.5		2.02					0.94

EXPERIMENTAL

The apparatus and technique for measuring specific retention data have been described elsewhere[5]. Two-metre glass columns of 4 mm I.D. were packed with hexamethyldisilazane-treated Celite (44–52 mesh) coated with 10–15 % w/w di-*n*-nonyl tetrachlorophthalate.

Retention measurements were made relative to 1,2,3,5-tetramethylbenzene or naphthalene. The fall in retention time for these reference compounds was used to monitor the loss of stationary phase and a column rejected if this loss exceeded 10 % of the weight of stationary phases.

Materials

Di-n-nonyl tetrachlorophthalate. This compound was prepared by the method used by NORLANDER AND CASS[10] for the corresponding octyl and decyl compounds. After distilling excess alcohol from the reaction mixture the product was fractionally distilled at reduced pressure. Di-*n*-nonyl tetrachlorophthalate had a b.p. of 260–270° at 1–2 mm; $n_D^{20} = 1.5155$. (Found: C, 55.2; H, 6.6. Calc. for $C_{26}H_{38}O_4Cl_4$: C, 56.1; H, 6.9 %.)

The presence of anhydride in the stationary phase markedly increases the retention of these donors. Extreme care was taken to exclude it from the ester in these experiments.

In addition to the diester a decarboxylation product, *n-nonyl tetrachlorobenzoate*, was produced. This had a b.p. of 210–215° at 2 mm; m.p. 33–35°. (Found: C, 50.8; H, 5.5. Calc. for $C_{16}H_{20}O_2Cl_4$: C, 49.8; H, 5.2 %.)

Anilines. All samples used were purified in accordance with the literature, redistilled and collected at their recorded boiling points.

Hydrocarbons and heterocycles. Chromatographically pure commercial samples were used.

RESULTS AND DISCUSSION

Anilines

In contrast to the elution of aromatic amines from TNF, where there is a major change in the elution order from that found with silicone oil, the selectivity of NTCP is far weaker with only one instance of a change in elution order, N,N-dimethylaniline emerging after N,N-dimethyl-2,6-xylidine. In spite of the absence of large changes in retention order, the influence of CT interactions can be seen in the data of Table I.

In Table I are shown values for the specific retention volumes V_g at 180 and 195° and the calculated[5] activity coefficients γ, at infinite dilution and 180°, in NTCP for a series of aromatic amines. Also included are the specific retention volumes in silicone oil $V_{g(SO)}$ and $R_{NTCP} = V_{g(NTCP)}/V_{g(SO)}$, at 180°. We have calculated the excess partial molar free energy of solution $\Delta\bar{G}_e°$ at 180° together with the corresponding excess enthalpy $\Delta\bar{H}_e°$ and entropy $\Delta\bar{S}_e°$ as in previous work[5]. The solution process is endothermic and the excess entropy of solution positive; therefore any contribution from CT complexing must be very weak. The values of $\Delta\bar{H}_e°$ are similar to those found for the weaker complexes between TNF and N,N-dimethyl-*o*-toluidine or N,N-dimethyl-2,6-xylidine.

TABLE II

RETENTION DATA FOR HYDROCARBONS AND HETEROCYCLES

Compound	$V_{g(NTCP)}$ (ml) 180°	R_{NTCP} 180°	R_{TNF}[a] 180°	Compound	$V_{g(NTCP)}$ (ml) 180°	R_{NTCP} 180°	R_{TNF}[a] 180°
Decalin (*cis*)	91.3	1.78	(0.21)[b]	2-Methylnaphthalene	380.3	3.32	6.83
Decalin (*trans*)	72.8	1.72	(0.25)[b]	1,6-Dimethylnaphthalene	709.8	4.19	10.21
Tetralin	152.9	2.45	1.39	2,6-Dimethylnaphthalene	634.6	3.91	9.58
Indan	75.5	2.10	1.19	2,3-Dimethylnaphthalene	709.8	4.23	11.63
Indene	91.3	2.54	2.84	1-Allylnaphthalene	837.5	4.12	5.08
1,2,3,4-Tetramethylbenzene	146.4	2.57	2.15	1-Bromonaphthalene	1018.3	4.41	8.48
1,2,4,5-Tetramethylbenzene	1111.1	2.29	1.65	2-Bromonaphthalene	1035.4	4.54	8.08
1,2,3,5-Tetramethylbenzene	114.8	2.28	1.56	Quinoline	310.2	3.74	7.71
Pentamethylbenzene	273.5	2.79	2.66	2-Methylquinoline	405.4	3.72	5.86
Hexamethylbenzene	676.8	3.34	3.73	4-Methylquinoline	634.6	4.33	10.13
Diphenyl	504.3	3.54	4.00	6-Methylquinoline	546.5	4.21	9.41
Benzo[*b*]thiophene	225.5	3.24	5.70	7-Methylquinoline	555.3	4.21	9.50
Indole	482.6	5.10	24.49	8-Methylquinoline	413.7	3.62	5.41
Benzofuran	72.4	2.44	3.36	Isoquinoline	370.3	4.04	8.73
Dibenzofuran	1172.8	4.77	13.92	3-Methylisoquinoline	471.8	4.00	7.24
Naphthalene	222.9	3.30	5.84	2,4-Dimethylquinoline	771.1	4.50	—
1-Methylnaphthalene	417.5	3.45	6.92	2,6-Dimethylquinoline	695.1	4.40	—

[a] Values taken from ref. 6.

[b] Values less accurate than other R values because of the low retention volumes on TNF.

The weaker selectivity of NTCP compared with TNF can be seen in the smaller range of activity coefficients for these solutes in NTCP. Stronger interaction between solute and TNF is reflected by $\gamma < 1$ for compounds 1, 2, 3, 4, 5, 6, 7, 8 and 11 whereas in NTCP $\gamma < 1$ is found only for compounds 5, 6, 8 and 11. The tertiary amines 8 and 11 are the strongest donors of the series as also are 5 and 6 in the primary amine series but in addition the latter are likely to form a hydrogen bond with the acceptor. In view of the paucity of vapour pressure data for many organic donors solute–solvent interaction is discussed in the light of retention parameters alone.

The last column of Table I illustrates the relative selectivity of these stationary phases. Although both solvents are capable of acting as acceptors in hydrogen bonding, the donor hydrogen bonding solutes are held more strongly on TNF. The ratio R_{TNF}/R_{NTCP} for compounds 1, 2, 3, 4 and 6 is roughly constant suggesting that this type of association is a constant factor in each solvent. *p*-Ethylaniline with a larger substituent and N-methylaniline with only one free N-H fall a little way out of this class as they did in the plot of R_{TNF} *vs.* K_x (ref. 5), where K_x is the CT association constant. Compounds 8 and 11, which are the most strongly complexed on TNF, are also the most strongly selected by NTCP relative to other N,N-dimethylated compounds, though the interaction is weaker than on TNF. The more heavily substituted compounds 9, 10, 12, 13 and 14 are favoured by NTCP. It may be that the single aromatic ring and aliphatic side chain are sterically more favourable than TNF.

R_{NTCP} follows the pattern of R_{TNF}, *i.e.* increasing alkyl substitution increases R, the behaviour associated with CT complexing. This is contrary to the effect obtained using the non-complexing stationary phases HCEM and diglycerol[6]. The pattern is repeated exactly for the compounds 1 to 6, the values for the three to luidines being greater than that for *p*-ethylaniline, which is greater than R_{NTCP} for aniline. Ethyl substitution adjacent to the amino group, as in 2-ethylaniline, increases R_{NTCP} whereas the opposite behaviour is observed with TNF. Possibly the steric hindrance is greater in this latter case. This might also explain why 2,6-diethylaniline shows only a small reduction in R_{NTCP} relative to aniline whereas in TNF the effect is considerable.

Aromatic hydrocarbons and heterocyles

The specific retention volumes at 180° and R_{NTCP} values for these compounds are shown, together with previously determined R_{TNF} values[6], in Table II. The range of R_{NTCP} values (1.72–4.77 excluding the H-bonding indole) is much less than that for R_{TNF} (0.21–13.92), showing TNF to be a much more selective solvent. The low values for R_{TNF} for compounds in Table II up to pentamethylbenzene relative to R_{NTCP}, excluding indene, show poor solvent qualities for TNF towards molecules with some aliphatic character. This is most marked with the decalins. The stronger donor hexamethylbenzene would appear to be a clear example of CT interaction exerting considerable influence in spite of aliphatic TNF repulsions. In the series of substituted benzenes the order of R_{NTCP} values is the same as the order of R_{TNF} values. These same substitution effects suggest that CT interactions do contribute to retention on NTCP but to a smaller extent than on TNF.

The compounds following pentamethylbenzene in Table II are all more strongly retained by TNF, the stronger CT acceptor. Dibenzofuran, the most soluble substance

in TNF, is still the most soluble in NTCP, though its "escaping tendency" is much higher than for TNF. The R_{NTCP} and R_{TNF} values both suggest an order of decreasing CT complexing given by indole > benzo[*b*]thiophene > benzofuran, which was the order found spectroscopically with tetracyanoethylene as acceptor[11].

The R_{NTCP} and R_{TNF} figures for the methyl-substituted naphthalenes show the same order of solubility in both solvents, with the stronger complexing dimethyl derivatives showing the greater solubility.

The R_{NTCP} values for the quinoline series parallel the R_{TNF} values with one exception, the R values for quinoline and 3-methylisoquinoline, which lie close together in both solvents, are reversed. 2,4-Dimethylquinoline and 2,6-dimethylquinoline, which we were unable to elute satisfactorily from TNF, have R_{NTCP} values that are slightly larger than the monomethylquinolines (complexing effect). These disubstituted quinolines are both substituted in an unfavourable position (2-) for strong complexing and because of this the R_{NTCP} values are not greatly increased over their corresponding monosubstituted compounds, 4-methylquinoline and 6-methylquinoline, respectively. As expected the effect of the position of methyl groups on R_{NTCP} is in accord with 4-methyl > 6-methyl.

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SUMMARY

Di-*n*-nonyl tetrachlorophthalate has been found to be a good selective stationary phase for the separation of aromatic compounds. It acts as a weak electron acceptor, but comparison of elution data with those obtained for other stationary phases implies that charge-transfer associations do contribute to the retention of the aromatic donors.

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