Journal of Chromatography A, 659 (1994) 143–150
Elsevier Science B.V., Amsterdam

CHROM. 25 569

Effect of adsorption on the retention values in capillary columns coated with OV-225 and PEG 20M

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(First received July 7th, 1993; revised manuscript received September 16th, 1993)

ABSTRACT

The effect of adsorption of compounds of different homologous series (*n*-alkanes, *n*-alkenes, *n*-alkynes, *n*-alkylcyclohexenes, arenes, alkanones) on capillary columns with different contents of polycyanopropylphenylmethylsiloxane (OV-225) and polyethylene glycol (PEG 20M) on retention indices, relative retention and capacity factors was quantitatively studied. The relationships between the retention characteristics and the stationary phase film thickness or capacity factor of a standard solute were established. These correlations permit the prediction of retention data depending on film thickness. It has been shown that among the compounds studied, the adsorption of *n*-alkanes and *n*-alkenes is maximum and comprises up to one third of the relative retention on columns with a thin film of PEG 20M.

INTRODUCTION

Problems connected with the reproducibility of retention values in capillary gas chromatography (GC) are of great importance. The most important factor affecting the reproducibility of retention values is the adsorption phenomena on the gas–liquid and liquid–solid interfaces. A more polar stationary phase (SP) leads to more variation in the retention data caused by variations in the coating thickness of the SP. The influence of the thickness of the SP film on retention due to adsorption has been studied by several investigators [1–11]. In recent studies [12,13] we examined the effect of adsorption on retention indices and their temperature coefficients for *n*-tetradecenes in capillary columns coated with PEG 20M.

This work was aimed at elucidating the influence of the thickness of polycyanopropylphenylmethylsiloxane (OV-225) and polyethylene glycol (PEG 20M) films coated on stainless-steel surfaces on the retention indices, relative retentions and capacity factors of compounds of different homologous series (*n*-alkanes, *n*-alkenes, *n*-alkynes, *n*-alkylcyciohexenes, arenes and alkanones). On this basis, adsorption parameters were evaluated for these solutes.

EXPERIMENTAL

An unmodified stainless-steel tube (50 m × 0.25 mm I.D.) was used for preparation of capillary columns. The columns were cleaned by rinsing with 20 ml of different solvents (chloroform, methanol, 2-propanol, 10% nitric acid, water, methanol, chloroform). Coating with the liquid phases (OV-225 and PEG 20M) was carried out by the dynamic method using chloroform solutions of different concentrations. The film thickness (d_f) of the SP was calculated by using the amount of the liquid phase present in the column. The precision of d_f values was about 0.01 μm.

Experiments were performed on Chrom-4 and Chrom-5 chromatographs (Laboratórní Přístro-

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0021-9673/94/$07.00
SSDI 0021-9673(93)E0993-5

je, Prague, Czech Republic) equipped with a flame ionization detector. The splitting ratio was about 1:150 and helium was used as the carrier gas. The oven temperature was 70–100°C at 10°C intervals calibrated with an accuracy of 0.2°C. The injector temperature was 200–250°C. Retention times were measured with an accuracy of 0.1 s. The column hold-up time was determined by extrapolation from the retention times of *n*-alkanes. *m*-Xylene was used as a reference standard owing to its weak adsorption in the chromatographed system used, controlled as in ref. 5.

The reproducibility of the retention indices, *I*,

TABLE I

CHARACTERIZATION AND WORKING CONDITIONS OF CAPILLARY COLUMNS AT 80°C

Parameter	Stationary phase					
	OV-225			PEG 20M		
Column No.	1	2	3	4	5	6
Stationary phase film thickness, d_f (μm)	0.30	0.58	0.65	0.13	0.19	0.22
No. of theoretical plates for *n*-dodecane	79 000	70 000	64 000	86 000	72 000	70 000
Capacity factor *k* for *m*-xylene	1.37 ± 0.02	2.60 ± 0.03	3.09 ± 0.01	0.869 ± 0.003	0.899 ± 0.002	1.40 ± 0.02
Helium flow-rate (ml/min)	0.46	0.40	0.57	0.51	0.51	0.67
Hold-up time (min)	5.34 ± 0.06	6.07 ± 0.13	4.31 ± 0.46	4.95 ± 0.03	4.96 ± 0.02	3.81 ± 0.01

TABLE II

RETENTION INDICES *I* AT 80°C AND TEMPERATURE INCREMENTS $10(\delta I/\delta T)$ OF SELECTED COMPOUNDS ON OV-225

Peak No.	Compound	Column 1		Column 2		Column 3	
		I	$10(\delta I/\delta T)$	*I*	$10(\delta I/\delta T)$	*I*	$10(\delta I/\delta T)$
1	*trans*-2-Decene	1036.8	0.5	1037.7	−0.1	1037.8	0.1
2	*cis*-2-Decene	1053.1	0.9	1054.2	0.8	1054.3	1.0
3	*trans*-5-Decene	1020.9	0.2	1021.4	0.2	1021.5	0.2
4	*cis*-5-Decene	1028.7	0.9	1029.3	0.8	1029.5	1.0
5	*trans*-2-Dodecene	1237.1	0.0	1238.3	−0.6	1237.7	0.0
6	*cis*-2-Dodecene	1252.4	0.8	1253.6	0.8	1253.3	0.8
7	*trans*-5-Dodecene	1217.8	0.3	1217.3	0.6	1217.8	0.4
8	*cis*-5-Dodecene	1222.4	0.9	1222.2	1.2	1222.9	1.0
9	1-Decyne	1139.3	0.6	1140.0	0.6	1140.6	0.5
10	3-Decyne	1147.7	−0.1	1149.0	0.2	1149.4	−0.1
11	1-Ethyl-1-cyclohexene	954.3	4.2	955.4	4.3	956.8	4.6
12	1-Butyl-1-cyclohexene	1135.1	4.9	1136.1	4.6	1137.9	4.7
13	3-Butyl-1-cyclohexene	1130.2	4.8	1131.4	5.0	1133.2	5.1
14	Benzene	853.1	5.3	854.1	5.0	856.1	5.5
15	Toluene	956.6	5.5	957.9	5.2	959.8	5.6
16	*m*-Xylene	1056.4	5.5	1057.8	5.4	1059.4	5.6
17	*o*-Xylene	1095.7	6.5	1097.5	6.3	1099.5	6.6
18	2-Pentanone	–	–	944.0	4.0	945.1	4.4
19	3-Hexanone	1029.3	4.0	1030.5	3.9	1030.9	4.1
20	4-Heptanone	1109.4	4.1	1111.3	3.9	1111.5	4.0

TABLE III

RETENTION INDICES I AT 80°C AND TEMPERATURE INCREMENTS $10(\delta I/\delta T)$ OF SELECTED COMPOUNDS ON PEG 20M

Peak No.	Compound	Column 4		Column 5		Column 6	
		I	$10(\delta I/\delta T)$	I	$10(\delta I/\delta T)$	I	$10(\delta I/\delta T)$
1	1-Dodecene	1238.4	1.7	1240.6	1.5	1241.9	1.4
2	*trans*-2-Dodecene	1251.8	1.6	1254.4	1.4	1255.7	1.3
3	*cis*-2-Dodecene	1262.3	2.5	1265.7	2.3	1267.2	2.3
4	1-Tridecene	1337.2	1.8	1339.4	1.7	1340.9	1.7
5	*trans*-2-Tridecene	1350.4	1.8	1353.1	1.5	1354.9	1.4
6	*cis*-2-Tridecene	1360.5	2.7	1363.7	2.5	1365.6	2.5
7	1-Decyne	1215.6	1.4	1221.9	1.3	1226.3	1.0
8	2-Decyne	1240.7	2.9	1248.0	2.8	1251.7	2.4
9	3-Decyne	1190.3	1.7	1196.2	1.7	1199.2	1.0
10	1-Dodecyne	1410.3	2.4	1416.4	2.2	1421.8	2.2
11	2-Dodecyne	1434.0	3.9	1441.2	3.6	1445.9	3.6
12	3-Dodecyne	1382.5	2.9	1388.6	2.4	1392.5	2.4
13	1-Butyl-1-cyclohexene	1156.1	7.3	1163.5	7.2	1166.9	6.6
14	3-Butyl-1-cyclohexene	1151.5	7.3	1158.8	7.2	1161.8	7.2
15	1-Hexyl-1-cyclohexene	1342.4	8.1	1350.0	7.7	1354.6	7.3
16	3-Hexyl-1-cyclohexene	1344.3	8.3	1352.0	7.8	1355.7	7.8
17	Benzene	945.2	6.3	958.2	6.2	959.5	6.0
18	Toluene	1039.5	7.2	1052.3	6.9	1054.2	6.8
19	*m*-Xylene	1134.6	7.7	1147.3	7.7	1149.9	7.4
20	*o*-Xylene	1174.6	8.6	1188.7	8.6	1191.4	8.3
21	2-Pentanone	979.4	4.6	992.6	–	994.6	4.0
22	3-Hexanone	1050.0	4.7	–	–	1065.0	4.4
23	4-Heptanone	1120.8	5.2	1131.9	5.2	1135.5	4.9
24	5-Nonanone	1309.9	6.1	1321.0	6.0	1325.6	6.0
25	2-Nonanone	1367.9	6.6	1380.0	6.5	1385.7	6.5

expressed in terms of the standard deviation (S.D.) was 0.1–0.2 index unit (i.u.). The accuracy of the capacity factors k and relative retentions r in terms of the relative standard deviation (R.S.D.) was below 2%.

The characterization and working conditions of capillary columns 1–6 are given in Table I and the retention indices I and their temperature increments, $10(\delta I/\delta T)$, for the compounds studied on OV-225 and PEG 20M columns are given in Tables II and III.

The contribution of adsorption and dissolution to retention was investigated using known linear equations [5,9,10,12]:

$$I = I_0 + a/k_{st} \quad (1)$$

$$I = I_0 + b/d_f \quad (2)$$

$$k = A + r_0 k_{st} \quad (3)$$

$$r = r_0 + r_0(\Delta f/d_f) \quad (4)$$

where I_0 and r_0 are an invariant retention index and an invariant relative retention, respectively, d_f is the film thickness of the stationary phase, a, b, A and Δf are adsorption coefficients and the subscript st represents the reference standard (*m*-xylene).

RESULTS AND DISCUSSION

It can be seen from the experimental data (Tables II and III) that the I values increase differently with increasing film thickness d_f for different homologous series (ΔI, i.u.), as shown in Table IV.

TABLE IV

DIFFERENCE IN I VALUES (ΔI, i.u.) FOR THE DIFFERENT HOMOLOGOUS SERIES

Homologous series	OV-225 (0.30–0.65 μm)	PEG 20M (0.13–0.22 μm)
n-Alkenes	<1.2	4–5
n-Alkynes	1–2	9–12
n-Alkylcyclohexenes	2.5–3.0	10–12
Arenes	3–4	14–17
Alkanones	1.5–2.0	15–18

The lower I values on the column with a thin film of PEG 20M are connected with the higher adsorption of *n*-alkanes in comparison with the other solutes studied. On the column with silicone OV-225 the dependence of I on d_f is less significant. At a sufficiently large film thickness the values of I do not depend markedly on d_f. As found previously [13], the temperature increments of I for *n*-alkenes on PEG 20M decrease with increasing d_f. A similar decrease in $10(\delta I/\delta T)$ values is observed for the other homologous series (*n*-alkynes, *n*-alkylcyclohexenes, arenes, alkanones) on PEG 20M, but not on OV-225. In order to minimize ΔI and $10(\delta I/\delta I)$, one should use a column of large d_f at high temperature [7].

The retention index I, relative retention r (standard compound *m*-xylene) and capacity factor k calculated from the experimental data for the solutes studied are described satisfactorily by the linear eqns. 1–4. By means of the least-squares linear regression, the slope and intercept for each linear plot were calculated (Tables V and VI). From the intercept of eqns. 1 and 2 we can calculate the values of invariant retention indices I_0 which are determined only by dissolution of a solute in the stationary phase, but not by secondary retention forces [5,6,12,13]. The invariant retention indices for the solutes studied on OV-225 determined by eqns. 1 and 2 were in good agreement, the differences not exceeding 0.1 i.u. The intercept of eqn. 3, A, characterizes the contribution of the adsorption of the solutes to the capacity factor k. The A values are negative when the adsorption of the carrier gas–SP interface for the solutes studied (arenes, alkanones) is less significant than for the standard solute (*m*-xylene) [11]. The A values for more polar solutes (arenes, alkanones) are markedly lower than those for less polar (alkenes, alkynes, *n*-alkylcyclohexenes) or non-polar (alkanes) solutes on both liquid phases. It has been found that a linear relationship can be observed between log A and carbon atom number n in a homologous series (Fig. 1). This linear relation-

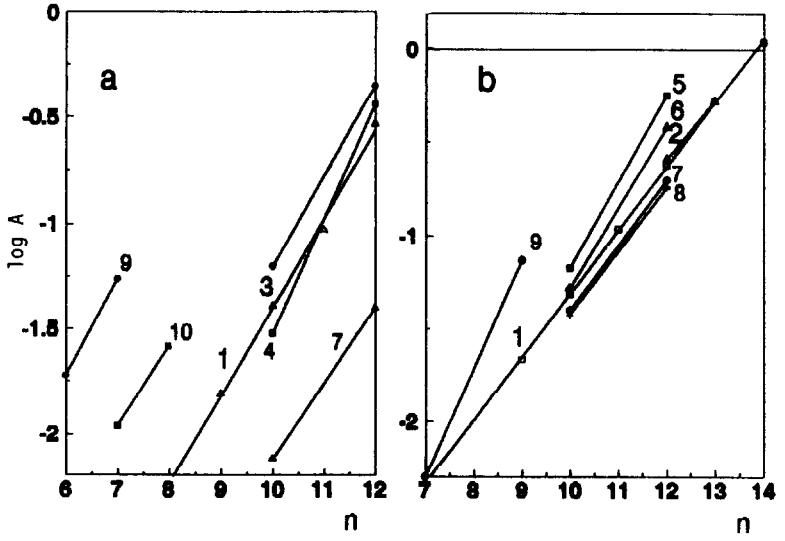

Fig. 1. Dependence of log A on the number of carbon atoms, n, in the solute molecule on (a) OV-225 and (b) PEG 20M at 80°C. 1 = *n*-Alkanes; 2 = 1-alkenes; 3 = *trans*-2-alkenes; 4 = *cis*-2-alkenes; 5 = 1-alkynes; 6 = 3-alkynes; 7 = 1-alkyl-1-cyclohexenes; 8 = 3-alkyl-1-cyclohexenes; 9 = alkanones; 10 = arenes.

TABLE V

PARAMETERS OF EQNS. 1–4 AND S.D. VALUES FOR SELECTED COMPOUNDS ON OV-225 AT 80°C

Compound	Eqn. 1			Eqn. 2			Eqn. 3			Eqn. 4			
	I_0	a	S.D.	I_0	b	S.D.	A	r_0	S.D. $\cdot 10^{-2}$	r_0	$(r_0\Delta f)_x 10^{-2}$	$\Delta f \cdot 10^{-2}$	S.D. $\cdot 10^{-3}$
n-Octane	–	–	–	–	–	–	−0.001	0.18	0.1	0.18	0.10	0.56	2.2
n-Nonane	–	–	–	–	–	–	0.015	0.35	0.5	0.35	0.27	0.78	1.9
n-Decane	–	–	–	–	–	–	0.041	0.66	1.9	0.67	0.59	0.89	0.2
n-Undecane	–	–	–	–	–	–	0.093	1.3	4.5	1.3	1.4	1.1	5.6
n-Dodecane	–	–	–	–	–	–	0.29	2.4	10	2.5	4.0	1.6	17
trans-2-Decene	1038.7	−2.5	0.01	1038.7	−0.56	0.0	0.030	0.87	3.3	0.86	0.69	0.80	2.6
cis-2-Decene	1055.3	−3.0	0.0	1055.4	−0.67	0.01	0.063	0.95	5.0	0.96	0.57	0.59	1.4
trans-5-Decene	1022.0	−1.5	0.2	1022.0	−0.33	0.02	0.026	0.78	2.8	0.77	0.58	0.75	1.3
cis-5-Decene	1030.1	−1.9	0.0	1030.1	−0.42	0.1	0.055	0.81	4.2	0.82	0.54	0.66	0.8
trans-2-Dodecene	1238.8	−2.1	0.4	1238.8	−0.50	0.2	0.36	3.1	14	3.1	5.6	1.8	8.1
cis-2-Dodecene	1254.4	−2.6	0.2	1254.4	−0.60	0.2	0.45	3.4	17	3.5	6.2	1.8	6.2
trans-5-Dodecene	1217.4	0.49	0.1	1217.4	0.12	0.3	0.34	2.7	10	2.7	5.6	2.1	1.3
cis-5-Dodecane	1222.8	−0.61	0.3	1222.8	−0.12	0.2	0.33	2.8	9.9	2.8	5.5	1.3	0.6
1-Decyne	1141.3	−2.8	0.1	1141.3	−0.61	0.2	0.068	1.7	7.8	1.7	0.88	0.52	4.3
3-Decyne	1150.7	−4.0	0.2	1150.7	−0.89	0.1	0.084	1.8	7.5	1.8	1.7	0.93	6.4
1-Ethyl-1-cyclohexene	958.0	−5.1	0.5	958.0	−1.1	0.5	−0.008	0.52	1.1	0.51	0.005	0.01	1.9
1-Butyl-1-cyclohexene	1139.0	−5.5	0.7	1139.0	−1.2	0.7	0.040	1.7	6.9	1.7	0.17	0.10	1.2
3-Butyl-1-cyclohexene	1134.5	−6.0	0.6	1134.5	−1.3	0.4	0.048	1.6	5.7	1.6	0.94	0.59	0.8
Benzene	857.2	−5.8	0.7	857.2	−1.3	0.7	−0.010	0.27	0.2	0.26	−0.16	−0.61	2.7
Toluene	961.2	−6.4	0.7	961.2	−1.4	0.7	0.011	0.51	1.6	0.52	−0.08	−0.15	3.1
m-Xylene	1060.9	−6.2	0.6	1060.9	−1.4	0.5	–	–	–	–	–	–	–
o-Xylene	1101.4	−9.7	0.6	1101.4	−1.7	0.7	0.026	1.3	14	1.3	0.43	0.33	0.0
3-Hexanone	1032.1	−3.7	0.2	1032.1	−0.83	0.1	0.019	0.83	0.3	0.83	0.22	0.27	0.0
4-Heptanone	1113.3	−5.2	0.0	1113.2	−1.2	0.1	0.055	1.4	5.7	1.4	0.79	0.56	5.9

TABLE VI

PARAMETERS OF EQNS. 2–4 AND S.D. VALUES FOR SELECTED COMPOUNDS ON PEG 20M AT 80°C; $n = 3$

Compound	Eqn. 2			Eqn. 3			Eqn. 4			
	I_0	b	S.D.	A	r_0	S.D. $\cdot 10^{-2}$	r_0	$(r_0\Delta f)\cdot 10^{-2}$	$\Delta f \cdot 10^{-2}$	S.D. $\cdot 10^{-3}$
n-Octane	–	–	–	0.005	0.10	0.4	0.09	0.29	3.3	1.7
n-Nonane	–	–	–	0.022	0.18	0.6	0.17	0.59	3.5	1.0
n-Decane	–	–	–	0.049	0.34	1.1	0.32	1.2	3.6	2.2
n-Undecane	–	–	–	0.11	0.64	2.1	0.62	2.4	3.9	1.7
n-Dodecane	–	–	–	0.24	1.2	4.4	1.2	5.0	4.3	3.8
*n*Tridecane	–	–	–	0.52	2.3	9.4	2.2	10.7	4.9	4.9
n-Tetradecane	–	–	–	1.09	4.3	18	4.1	22.2	5.4	0.6
1-Dodecene	1246.5	−1.1	0.1	0.26	1.6	4.7	1.6	5.6	3.6	7.1
trans-2-Dodecene	1260.9	−1.2	0.0	0.31	1.8	5.2	1.7	6.2	3.6	4.4
cis-2-Dodecene	1273.9	−1.5	0.2	0.40	1.8	5.1	1.9	6.1	3.3	7.5
1-Tridecene	1345.6	−1.1	0.3	0.52	3.1	9.8	2.9	12.0	4.1	10
trans-2-Tridecene	1360.7	−1.4	0.3	0.41	3.5	11	3.3	12.0	3.6	17
cis-2-Tridecene	1372.3	−1.5	0.4	0.57	3.7	11	3.6	11.6	3.2	5.1
1-Decyne	1239.9	−3.2	0.8	0.068	1.6	2.7	1.5	2.4	1.6	13
2-Decyne	1266.5	−3.4	0.6	0.039	1.9	2.9	1.8	2.5	1.4	9.2
3-Decyne	1211.1	−2.7	0.5	0.053	1.4	2.1	1.3	2.1	1.7	6.8
1-Dodecyne	1435.9	−3.4	1.2	0.56	5.4	11	5.3	12.0	2.3	33
2-Dodecyne	1461.2	−3.6	1.0	0.70	6.4	11	6.3	13.3	2.1	20
3-Dodecyne	1405.4	−3.0	0.8	0.38	4.6	9.6	4.4	10.7	2.5	21
1-Butyl-1-cyclohexene	1181.6	−3.3	0.4	0.040	1.1	1.7	1.1	1.3	1.2	5.5
3-Butyl-1-cyclohexene	1176.1	−3.2	0.3	0.038	1.1	2.0	1.0	1.4	1.3	4.9
1-Hexyl-1-cyclohexene	1370.5	−3.7	0.8	0.20	3.7	6.6	3.5	6.5	1.9	7.8
3-Hexyl-1-cyclohexene	1371.1	−3.5	0.4	0.18	3.8	6.3	3.6	6.2	1.7	16
Benzene	982.0	−4.8	0.9	−0.002	0.29	0.06	0.29	−0.08	−0.28	0.6
Toluene	1076.8	−4.8	0.6	−0.001	0.53	0.12	0.54	−0.13	−0.23	0.08
m-Xylene	1172.8	−5.0	0.4	–	–	–	–	–	–	–
o-Xylene	1216.7	−5.5	0.4	−0.001	1.3	2.3	1.3	−0.21	−0.16	0.7
2-Pentanone	1017.9	−5.0	0.7	−0.011	0.37	0.04	0.36	−0.06	−0.16	0.3
3-Hexanone	1086.7	−4.8	0.9	−0.010	0.59	0.01	0.58	−0.09	−0.16	53
4-Heptanone	1156.5	−4.7	0.04	0.005	0.90	0.37	0.90	0.14	0.16	2.1
5-Nonanone	1347.3	−4.9	0.5	0.074	3.1	2.5	3.1	2.0	0.66	11
2-Nonanone	1409.9	−5.5	0.7	0.077	4.6	4.2	4.6	2.0	0.44	20

ship can be used to predict the A values for the higher members of the homologous series studied. The values of the invariant relative retention r calculated by eqns. 3 and 4 are in good agreement (<0.02), but the mean values of the errors are lower for eqn. 4.

The values of the adsorption coefficient, Δf, increase with increasing carbon number n in the solute molecule for the homologous series of *n*-alkanes, *n*-alkenes, *n*-alkynes and *n*-alkylcyclohexenes. For arenes and alkanones this relationship between Δf and n is less pronounced (Fig. 2). The Δf values are the highest for *n*-alkanes and *n*-alkenes on PEG 20M and the lowest for arenes and alkanones on both phases. The value of Δf may be used to express the percentage adsorption contribution to the relative retention, Δr (Table VII):

$$\Delta r\ (\%) = \frac{\Delta f}{d_f} \cdot 100$$

The maximum contribution of adsorption to the relative retention of the compounds studied was 33% for *n*-dodecane on PEG 20M and 6% for *trans*-2-dodecene on OV-225 (Fig. 3). On columns with a thin film of PEG 20M the adsorption represents a significant contribution to the retention data for *n*-alkanes and *n*-alkenes.

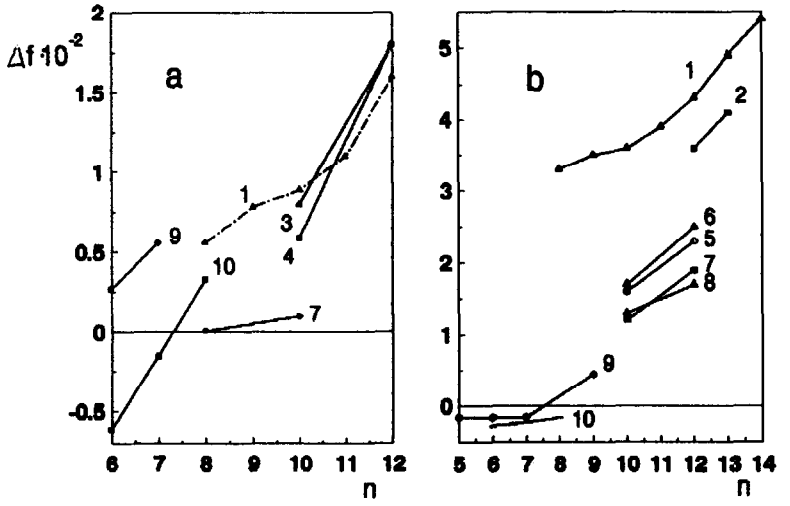

Fig. 2. Dependence of Δf on the number of carbon atoms, n, in the solute molecule on (a) OV-225 and (b) PEG 20M at 80°C. Symbols as in Fig. 1.

The effect of adsorption is lower for *n*-alkynes or *n*-alkylcyclohexenes, and lowest for arenes and alkanones. On OV-225 the Δr values differ from those obtained on the more polar PEG 20M. On OV-225 the adsorption of *n*-alkanes and 2-alkenes with the same carbon number is similar, being more pronounced than that for the other compounds studied.

TABLE VII

CONTRIBUTION OF ADSORPTION TO THE RELATIVE RETENTION (Δr, %) OF SELECTED COMPOUNDS ON OV-225 AND PEG 20M COLUMNS 1–6 AT 80°C

Compound	OV-225			PEG 20M		
	1	2	3	4	5	6
n-Nonane	2.6	1.4	1.2	27	19	16
n-Decane	3.0	1.5	1.4	28	19	16
n-Undecane	3.5	1.8	1.6	30	21	18
n-Dodecane	5.4	2.8	2.5	33	23	20
trans-2-Dodecene	6.0	3.1	2.8	28	19	16
cis-2-Dodecene	5.9	3.1	2.7	25	17	15
1-Decyne	1.7	0.9	0.8	12	8.2	7.0
3-Decyne	3.1	1.6	1.4	13	8.7	7.5
1-Butyl-1-cyclohexene	0.3	0.2	0.2	9.2	6.3	5.5
3-Butyl-1-cyclohexene	2.0	1.0	0.9	10	7.0	6.0
Benzene	2.0	1.1	0.9	2.2	1.5	1.3
Toluene	0.5	0.3	0.2	1.8	1.2	1.1
o-Xylene	1.1	0.6	0.5	1.2	0.8	0.7
2-Pentanone	–	–	–	1.2	0.8	0.7
3-Hexanone	0.9	0.5	0.4	1.3	0.9	0.8
4-Heptanone	1.9	1.0	0.9	1.2	0.8	0.7

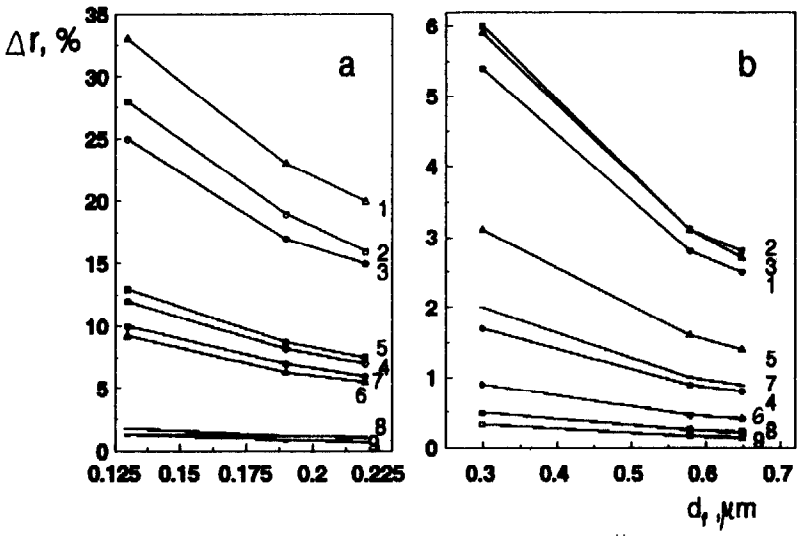

Fig. 3. Dependence of Δr on the film thickness of the SP, d_f, on (a) PEG 20M and (b) OV-225 at 80°C. 1 = *n*-Dodecane; 2 = *trans*-2-dodecene; 3 = *cis*-2-dodecene; 4 = 1-decyne; 5 = 3-decyne; 6 = 1-butyl-1-cyclohexene; 7 = 3-butyl-1-cyclohexene; 8 = toluene; 9 = 3-hexanone.

CONCLUSIONS

The experimental data for some *n*-alkanes, *n*-alkenes, *n*-alkynes, *n*-alkyl-1-cyclohexenes, arenes and alkanones (38 compounds) on OV-225 and PEG 20M capillary columns with different thicknesses of the SP film appear to be in agreement with the linear relationships of I *versus* $1/k_{st}$ or $1/d_f$, k *vs.* k_{st} and r *vs.* $1/d_f$. These equations were used to demonstrate the adsorption effects of compounds of different homologous series when using a polar column. Among the compounds studied, *n*-alkanes make the maximum contribution of adsorption to the relative retention (up to 30%) on PEG 20M with a thin SP film. On the less polar silicone phase (OV-225) the effect of adsorption of *n*-alkanes and alkenes is lower than on PEG 20M.

The results obtained can be used to predict the variation of retention data (I, k, r) with film thickness and also for the identification of and physico-chemical calculations on the compounds studied.

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