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Comparison of the selectivity of di(methacryloyloxymethyl)-naphthalene–divinylbenzene copolymers in reversed-phase high-performance liquid chromatography

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ABSTRACT

The influence of chemical composition of porous copolymers on chromatographic properties of high-performance liquid chromatography columns was studied. Columns were packed with three di(methacryloyloxymethyl)naphthalene–divinylbenzene copolymers of different molar ratio of monomers. The retention behaviour of five homologous series (alkylbenzenes, N-alkylanilines, alkyl aryl ethers, alkyl benzoates and alkyl aryl ketones) was investigated using different eluents. Using the alkyl aryl ketone scale, the retention indices of the homologues and column test compounds were calculated. Their values were used to compare the selectivities of the studied stationary phases.

INTRODUCTION

The retention of a substance in chromatography depends on its interactions with mobile and stationary phases. In reversed-phase high-performance liquid chromatography (HPLC) the major contribution to retention comes from hydrophobic interactions of the sample with the mobile phase, and the stationary phase plays a largely passive role [1]. An accurate definition of the quality of stationary phase used was stressed by Karch *et al.* [2] and Jandera *et al.* [3]. Smith [4] also reported that even non-polar alkyl-bonded silica gels indicate specific chemical effects on the stationary phase due to the presence of the unprotected silanol groups. According to Antle *et al.* [5] column strength and selectivity depend on the polarity of the bonded phase.

Among the techniques used to compare different stationary phases, the retention indices of standards based on an alkyl aryl ketone scale introduced by Smith [4] are the most effective. In order to determine the selectivity of the HPLC column, Smith and co-workers [6–10] selected a set of column test compounds (toluene, nitrobenzene, *p*-cresol, 2-phenylethanol and N-methylaniline) reflecting effects of specific interactions with different stationary phases. Column test compounds are chosen as the aromatic equivalents of the standards used by Rohrschneider [11] and McReynolds [12] in gas chromatography and represent solutes of different polarity.

As polarity is not a single-valued parameter, but rather the sum of contribu-

tions due to dipole interaction, hydrogen donation, hydrogen acceptance and dispersion interaction, no solute is a probe for only one kind of interaction.

Except for toluene and nitrobenzene, each of the compounds tested belongs to different interaction groups as defined by Snyder [13,14].

Retention indices of column test compounds can be used in a similar manner as Rohrschneider or McReynolds constants for quantitative description of selectivity properties. Their values permit a direct comparison of different columns using the same eluent.

Using the alkyl aryl ketone index scale, Smith and Garside [15,16] studied the behaviour of four series of homologues and column test compounds on two commercially available polystyrene–divinylbenzene (PS–DVB) stationary phases. They showed that the selectivities of the two sorbents were similar but both had very different properties to an octadecyl silane (ODS)-silica column. The linearity of the retentions of the standard alkyl aryl ketones on PS–DVB was much poorer than on an ODS-silica column. The retention indices for test compounds were calculated basing on a linear relationship for the alkyl aryl ketones propiophenone to heptanophenone, because acetophenone is eluted much earlier than expected [16]. Similar deviations were noted for other homologous series studied on PS–DVB stationary phases.

In previous work [17], chromatographic properties of a porous copolymer of di(methacryloyloxymethyl)naphthalene (DMN) and DVB were studied under conditions identical to those used by Smith and Garside [16]. The behaviour of DMN–DVB copolymer in all studied mobile phases [methanol–buffer (90:10), acetonitrile–buffer (70:30) and tetrahydrofuran–buffer (40:60)] was similar to that of PS–DVB stationary phases, e.g. the first members of the homologous series indicated some deviations from linear relationship between the logarithm of the capacity factor and the carbon number. On the other hand, the selectivity of the DMN–DVB copolymer was quite different to that of PS–DVB.

In the present work, the influence of the chemical composition of DMN–DVB copolymers on their selectivities is studied. In order to examine the role of the chemical nature of the stationary phase in the reversed-phase HPLC retention mechanism, three DMN–DVB porous copolymers containing different mole fractions of polar monomer (DMN) were used: 0.2, 0.5 and 0.8.

EXPERIMENTAL

Chemicals and eluents

Methanol. acetonitrile and tetrahydrofuran were HPLC grade obtained from Merck (Darmstadt, Germany). The alkyl aryl ketones retention index standards, homologous alkylbenzenes, N-alkylanilines, alkyl aryl ethers, alkyl benzoates and other test compounds (nitrobenzene, p-cresol and 2-phenylethanol) were laboratory-reagent grade from a range of sources.

Preparation of the phosphate buffer solution (pH 7) has been described previously [17]. The buffer was prepared from 0.0029 M disodium hydrogenorthophosphate (0.5 g) and 0.0022 M potassium dihydrogenphosphate (0.301 g).

All eluents were filtered through suitable filters and degassed by agitation in an ultrasonic bath and kept under a weak stream of helium.

TABLE I

PROPERTIES OF THE DMN–DVB COPOLYMERS

Mole fraction of the DMN–DVB monomers	Weight of the copolymer in the column (g)	Specific surface area (BET), S (m^2/g)	Surface area of the copolymer in the column, S_c (m^2)
0.2:0.8	0.336	235	79.0
0.5:0.5	0.321	85.5	27.4
0.8:0.2	0317	84	26.6

HPLC equiment

Separations were carried out using an HPLC system comprising a Techma–Robot 302 syringe pump (Warsaw, Poland) fitted with a Rheodyne 7125 injection valve equipped with a 10-μl sampling loop, and a 100 mm × 4 mm I.D. column packed with the DMN–DVB copolymers. The column was encased in a water jacket through which water at 30°C was passed.

Peaks were detected using a Laboratorni Pristroje UV–visible LCD 2563 detector set at 254 nm and 0.04 a.u.f.s., and were recorded on a Laboratorni Pristroje 4001 recorder (Praque, Czechoslovakia). The measuring cell of the detector was also water-thermostated at 30°C. The flow-rate of the mobile phase was 0.5 ml/min.

Chromatographic measurements

The column void volume was determined by injecting 10 μl of an aqueous solution of sodium nitrate (24.3 g per 100 ml) [16]. The analyte concentrations in the mobile phases were adjusted to give on-scale peaks from a 10-μl injection. The recorded retention distances were the mean of three determinations.

Capacity factors (k') and retention indices (I) derived from the alkyl aryl ketones butyrophenone to heptanophenone were calculated as described previously [16,17].

Preparation of DMN–DVB copolymers

Porous copolymers of DMN and DVB were synthesized by the procedure published previously [17].

Using the mole fractions of DMN–DVB monomers of 0.2:0.8, 0.5:0.5 and 0.8:0.2 sorbents of different chemical nature were obtained [18].

In Table I the properties of the three copolymers used in this work are summarized.

The sieve fraction of the particles of the DMN–DVB copolymers was 5–15 μm. The HPLC columns were packed according to the procedure described previously [17,19].

RESULTS AND DISCUSSION

Following the work of Smith and Garside [16], the retention indices of five sets of homologous compounds and the selectivity test compounds were measured using methanol–buffer (90:10), acetonitrile–buffer (70:30) and tetrahydrofuran–buffer

(40:60) as the mobile phases. Independent of the mobile phase used, peak shapes were symmetrical, but theorctical plate numbers varying from 1500 to 2000 were rather low. Inlet pressure of the columns with increasing content of the DMN monomer (20, 50 and 80%) was 10, 8.2 and 14.2 MPa with methanol–buffer, 8, 7.8 and 10.7 MPa with acetonitrile–buffer and 12.5 and 18 MPa with tetrahydrofuran–buffer eluent, respectively.

In the case of 0.2 DMN–0.8 DVB copolymer, the measurements with tetrahydrofuran–buffer eluent were not possible because of a variable mobile phase flow-rate. With this mobile phase the inlet pressure of the column was increasing continuously.

In order to use the alkyl aryl ketone index scale in selectivity studies, a linear relationship between the logarithm of the capacity factor and the carbon number must be demonstrated. As expected from the previous work [17], the first members of the alkyl aryl ketone homologous series show some deviations from the expected linearity for all copolymers studied. Thus, the retention indices of the homologous and test compounds were calculated using the linear relationship for the alkyl aryl ketones from butyrophenone to heptanophenone.

In Tables II–IV the values of capacity factors (k') for alkyl aryl ketones, alkyl-benzenes and column test compounds are presented. Using the retention times and the column void volumes measured with an aqueous sodium nitrate solution, the capacity factors on three columns were calculated. We observe that, in all eluents

TABLE II

CAPACITY FACTOR (k') AND SPECIFIC CAPACITY FACTORS ($k'_s = k'/S_c$) FOR ALKYL ARYL KETONES, ALKYLBENZENES AND TEST COMPOUNDS WITH METHANOL–BUFFER (90:10) ELUENT

Compound	0.2 DMN–0.8 DVB		0.5 DMN–0.5 DVB		0.8 DMN–0.2 DVB	
	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$
Alkyl aryl ketone series						
Acetophenone	0.76	9.62	1.07	39.05	1.34	50.38
Propiophenone	1.11	14.05	1.59	58.03	1.90	71.43
Butyrophenone	1.34	16.96	1.94	70.80	2.29	86.09
Valerophenone	1.87	23.67	2.65	96.72	3.12	117.29
Hexanophenone	2.63	33.29	3.68	134.30	4.32	162.24
Heptanophenone	3.64	46.08	5.02	183.21	5.95	233.68
Alkylbenzene series						
Benzene	0.77	9.75	1.09	39.78	1.21	45.49
Toluene	1.14	14.43	1.52	55.47	1.77	66.54
Ethylbenzene	1.33	16.84	1.79	65.33	1.92	72.18
n-Propylbenzene	1.71	21.65	2.20	80.29	2.32	87.22
n-Butylbenzene	2.27	28.73	2.96	108.03	2.95	109.02
Test compounds						
Nitrobenzene	1.34	16.96	2.15	78.47	2.60	97.74
p-Cresol	0.41	5.19	0.54	19.70	0.67	25.19
2-Phenylethanol	0.23	2.91	0.37	13.50	0.45	16.92
N-Methylaniline	0.78	9.87	1.32	48.18	1.14	42.85

TABLE III

CAPACITY FACTOR (k') AND SPECIFIC CAPACITY FACTORS ($k'_s = k'/S_c$) FOR ALKYL ARYL KETONES, ALKYLBENZENES AND TEST COMPOUNDS WITH ACETONITRILE–BUFFER (70:30) ELUENT

Compound	0.2 DMN–0.8 DVB		0.5 DMN–0.5 DVB		0.8 DMN–0.2 DVB	
	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$
Alkyl aryl ketone series						
Acetophenone	0.43	5.44	0.59	21.53	0.76	28.57
Propiophenone	0.66	8.35	0.89	32.48	1.11	41.73
Butyrophenone	0.86	10.89	1.15	41.97	1.45	54.51
Valerophenone	1.20	15.19	1.57	57.29	1.97	74.06
Hexanophenone	1.66	21.01	2.15	78.47	2.68	100.75
Heptanophenone	2.30	29.11	2.94	107.30	3.62	136.09
Alkylbenzene series						
Benzene	0.76	9.62	0.93	33.94	1.08	40.60
Toluene	1.07	13.54	1.23	44.89	1.52	57.14
Ethylbenzene	1.35	17.09	1.51	55.11	1.86	69.92
n-Propylbenzene	1.78	22.53	1.96	71.53	2.40	90.22
n-Butylbenzene	2.39	30.25	2.62	95.62	3.15	118.42
Test compounds						
Nitrobenzene	0.68	8.61	0.95	34.67	1.47	55.26
p-Cresol	0.31	3.92	0.39	14.23	0.49	18.42
2-Phenylethanol	0.22	2.78	0.26	9.49	0.32	12.03
N-Methylaniline	0.63	7.97	0.74	27.00	1.12	42.10

TABLE IV

CAPACITY FACTOR (k') AND SPECIFIC CAPACITY FACTORS ($k'_s = k'/S_c$) FOR ALKYL ARYL KETONES, ALKYLBENZENES AND TEST COMPOUNDS WITH TETRAHYDROFURAN–BUFFER (40:60) ELUENT

Compound	0.2 DMN–0.8 DVB		0.5 DMN–0.5 DVB		0.8 DMN–0.2 DVB	
	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$	k'	$k'_s \cdot 10^3$
Alkyl aryl ketone series						
Acetophenone	—	—	1.21	44.16	1.69	63.53
Propiophenone	—	—	2.01	73.36	2.79	104.88
Butyrophenone	—	—	2.70	98.54	3.78	142.11
Valerophenone	—	—	3.85	140.51	5.42	203.76
Hexanophenone	—	—	5.47	199.63	7.68	288.72
Heptanophenone	—	—	7.52	274.45	10.51	395.11
Alkylbenzene series						
Benzene	—	—	2.64	96.35	3.88	145.86
Toluene	—	—	3.97	144.89	5.15	193.61
Ethylbenzene	—	—	5.13	187.23	6.58	247.37
n-Propylbenzene	—	—	6.52	237.96	8.29	311.65
n-Butylbenzene	—	—	8.53	311.31	10.85	407.89
Test compounds						
Nitrobenzene	—	—	2.58	94.16	3.66	137.59
p-Cresol	—	—	1.07	39.05	1.63	61.28
2-Phenylethanol	—	—	0.35	12.77	0.71	26.69
N-Methylaniline	—	—	2.17	79.20	3.23	121.43

TABLE V

RETENTION INDICES OF THE STUDIED COMPOUNDS WITH METHANOL–BUFFER (90:10) ELUENT

Compound	0.2 DMN–0.8 DVB	0.5 DMN–0.5 DVB	0.8 DMN–0.2 DVB
Alkyl aryl ketone series			
Benzaldehyde	838	835	854
Acetophenone	832	814	834
Propiophenone	943	938	944
Butyrophenone	999	1001	1001
Valerophenone	1100	1098	1098
Hexanophenone	1202	1202	1200
Heptanophenone	1299	1299	1300
Alkylbenzene series			
Benzene	836	819	803
Toluene	952	923	920
Ethylbenzene	998	975	946
n-Propylbenzene	1071	1040	1006
n-Butylbenzene	1158	1133	1081
N-Alkylaniline series			
Aniline	593	655	681
N-Methylaniline	838	877	784
N-Ethylaniline	876	952	894
N-Propylaniline	976	1040	989
N-Butylaniline	1077	1135	1092
Alkyl aryl ether series			
Methyl phenyl ether	934	959	941
Ethyl phenyl ether	980	979	965
n-Propyl phenyl ether	1076	1066	1038
n-Butyl phenyl ether	1172	1163	1131
Alkyl benzoate series			
Methyl benzoate	910	934	884
Ethyl benzoate	939	958	936
n-Propyl benzoate	1040	1045	1026
n-Butyl benzoate	1142	1142	1123
n-Pentyl benzoate	1241	1234	1216
Test compounds			
p-Cresol	650	595	617
Nitrobenzene	999	1032	1041
2-Phenylethanol	479	478	490
Void volume for sodium nitrate (ml)	1.01	0.96	0.93
Correlation coefficients for alkyl aryl ketone series			
Acetophenone–heptanophenone	0.9975	0.9978	0.9974
Butyrophenone–heptanophenone	0.9999	0.9999	0.9999

used, the values of k' increase with the increase of the polar monomer (DMN) content in the copolymers. For example, heptanophenone eluted with methanol–buffer has the capacity factors of 3.64, 5.02 and 5.95 on the studied columns. The corresponding values for *n*-butylbenzene are 2.27, 2.96 and 2.95. In order to make a direct compari-

TABLE VI

RETENTION INDICES OF THE STUDIED COMPOUNDS WITH ACETONITRILE–BUFFER (70:30) ELUENT

Compound	0.2 DMN–0.8 DVB	0.5 DMN–0.5 DVB	0.8 DMN–0.2 DVB
Alkyl aryl ketone series			
Benzaldehyde	809	785	828
Acetophenone	787	785	787
Propiophenone	916	917	913
Butyrophenone	1000	1001	999
Valerophenone	1101	1099	1100
Hexanophenone	1199	1200	1201
Heptanophenone	1300	1300	1299
Alkylbenzene series			
Benzene	960	931	904
Toluene	1066	1021	1017
Ethylbenzene	1137	1087	1082
n-Propylbenzene	1220	1170	1165
n-Butylbenzene	1311	1263	1254
N-Alkylaniline series			
Aniline	706	689	715
N-Methylaniline	902	857	916
N-Ethylaniline	951	931	984
N-Propylaniline	1055	1062	1067
N-Butylaniline	1160	1168	1175
Alkyl aryl ether series			
Methyl phenyl ether	918	968	924
Ethyl phenyl ether	1050	1031	1006
n-Propyl phenyl ether	1147	1125	1096
n-Butyl phenyl ether	1242	1222	1197
Alkyl benzoate series			
Methyl benzoate	882	874	841
Ethyl benzoate	937	937	916
n-Propyl benzoate	1054	1035	1035
n-Butyl benzoate	1160	1142	1137
n-Pentyl benzoate	1262	1235	1236
Test compounds			
p-Cresol	687	653	642
Nitrobenzene	927	938	1004
2-Phenylethanol	580	531	502
Void volume for sodium nitrate (ml)	0.97	0.94	0.89
Correlation coefficients for alkyl aryl ketone series			
Acetophenone–heptanophenone	0.9989	0.9985	0.9991
Butyrophenone–heptanophenone	0.9999	1.0000	0.9999

son of the columns, the values of capacity factors in reference to surface area of the copolymer in the column (k'_s) were calculated. Taking into account values of specific surface areas and the weights of the copolymers in the columns (Table I), the increase of the k' values means that the strength of sample–sorbent interactions also increases.

TABLE VII

RETENTION INDICES OF THE STUDIED COMPOUNDS WITH TETRAHYDROFURAN–BUFFER (40:60) ELUENT

Compound	0.2 DMN–0.8 DVB	0.5 DMN–0.5 DVB	0.8 DMN–0.2 DVB
Alkyl aryl ketone series			
Benzaldehyde	–	773	797
Acetophenone	–	764	762
Propiophenone	–	911	908
Butyrophenone	–	998	997
Valerophenone	–	1101	1102
Hexanophenone	–	1204	1204
Heptanophenone	–	1297	1296
Alkylbenzene series			
Benzene	–	991	1004
Toluene	–	1110	1087
Ethylbenzene	–	1185	1159
n-Propylbenzene	–	1255	1227
n-Butylbenzene	–	1334	1306
N-Alkylaniline series			
Aniline	–	646	733
N-Methylaniline	–	934	951
N-Ethylaniline	–	1019	1046
N-Propylaniline	–	1124	1143
N-Butylaniline	–	1229	1246
Alkyl aryl ether series			
Methyl phenyl ether	–	1000	983
Ethyl phenyl ether	–	1067	1051
n-Propyl phenyl ether	–	1160	1144
n-Butyl phenyl ether	–	1256	1240
Alkyl benzoate series			
Methyl benzoate	–	896	880
Ethyl benzoate	–	950	935
n-Propyl benzoate	–	1039	1029
n-Butyl benzoate	–	1141	1133
n-Pentyl benzoate	–	1238	1233
Test compounds			
p-Cresol	–	728	751
Nitrobenzene	–	985	988
2-Phenylethanol	–	399	506
Void volume for sodium nitrate (ml)	–	0.94	0.86
Correlation coefficients for alkyl aryl ketone series			
Acetophenone–heptanophenone	–	0.9972	0.9974
Butyrophenone–heptanophenone	–	0.9997	0.9995

However, in the methanol–buffer eluent, interactions between alkylbenzenes and copolymers containing 0.5 and 0.8 mole fractions of polar monomer are very similar.

In Tables V–VII, the retention indices of the studied substances are summarized. In all eluents, the retention indices of alkylbenzenes decrease with an increase of

TABLE VIII

RETENTION INDICES OF TEST COMPOUNDS ON DMN–DVB COLUMNS

Copolymer	Retention index				
	Toluene	Nitrobenzene	p-Cresol	2-Phenylethanol	N-Methylaniline
Methanol–buffer (90:10)					
0.2 DMN–0.8 DVB	952	999	650	479	838
0.5 DMN–0.5 DVB	923	1032	595	478	877
0.8 DMN–0.2 DVB	920	1041	617	490	784
Acetonitrile–buffer (70:30)					
0.2 DMN–0.8 DVB	1066	927	687	580	902
0.5 DMN–0.5 DVB	1021	938	653	531	857
0.8 DMN–0.2 DVB	1017	1004	642	502	916
Tetrahydrofuran–buffer (40:60)					
0.2 DMN–0.8 DVB	–	–	–	–	–
0.5 DMN–0.5 DVB	1110	985	728	399	934
0.8 DMN–0.2 DVB	1087	988	751	506	951

the DMN content in the copolymer. It is not clearly noticeable for the first members of the series, but is easily visible for the last members (Fig. 1). This means that interactions between alkylbenzenes and copolymers with an increasing content of DMN monomer are weaker in comparison with those for alkyl aryl ketones.

A similar phenomenon is observed for alkyl aryl ethers, but in this case the decrease in the retention index values is smaller than for alkylbenzenes. As expected, the smallest differences in retention index values are observed for alkyl benzoates, the compounds having the same functional groups as standards and the studied copolymers.

In the case of N-alkylanilines, irregular changes in retention indices occur. Generally, an increase in the polar monomer mole fraction in copolymers causes an increase in the retention indices for N-alkylanilines. However, in the methanol–buffer mobile phase, the greatest values of indices are on the copolymer 0.5 DMN–0.5 DVB (Fig. 2a). Additionally, N-alkylanilines do not exhibit deviations from a linear relationship between the retention index and the carbon number on the copolymer 0.8 DMN–0.2 DVB. With acetonitrile–buffer, the retention indices on all the studied copolymers are very similar, but the slopes of the relationships are different (Fig. 2b). With tetrahydrofuran–buffer, the differences between N-alkylaniline retention index values on both studied copolymers are rather constant (Fig. 2c).

In Table VIII, the retention indices of the column test compounds are presented. Because the results were calculated using the set of alkyl aryl ketones butyrophenone to heptanophenone, for all test compounds, considerable extrapolation is required. Despite this, a comparison of different columns is possible, assuming that each mobile phase is studied separately to remove the effects of sample–solvent interactions [4].

For all studied copolymers, toluene and nitrobenzene are retained most compared with other compounds. With an increase of the DMN mole fraction in
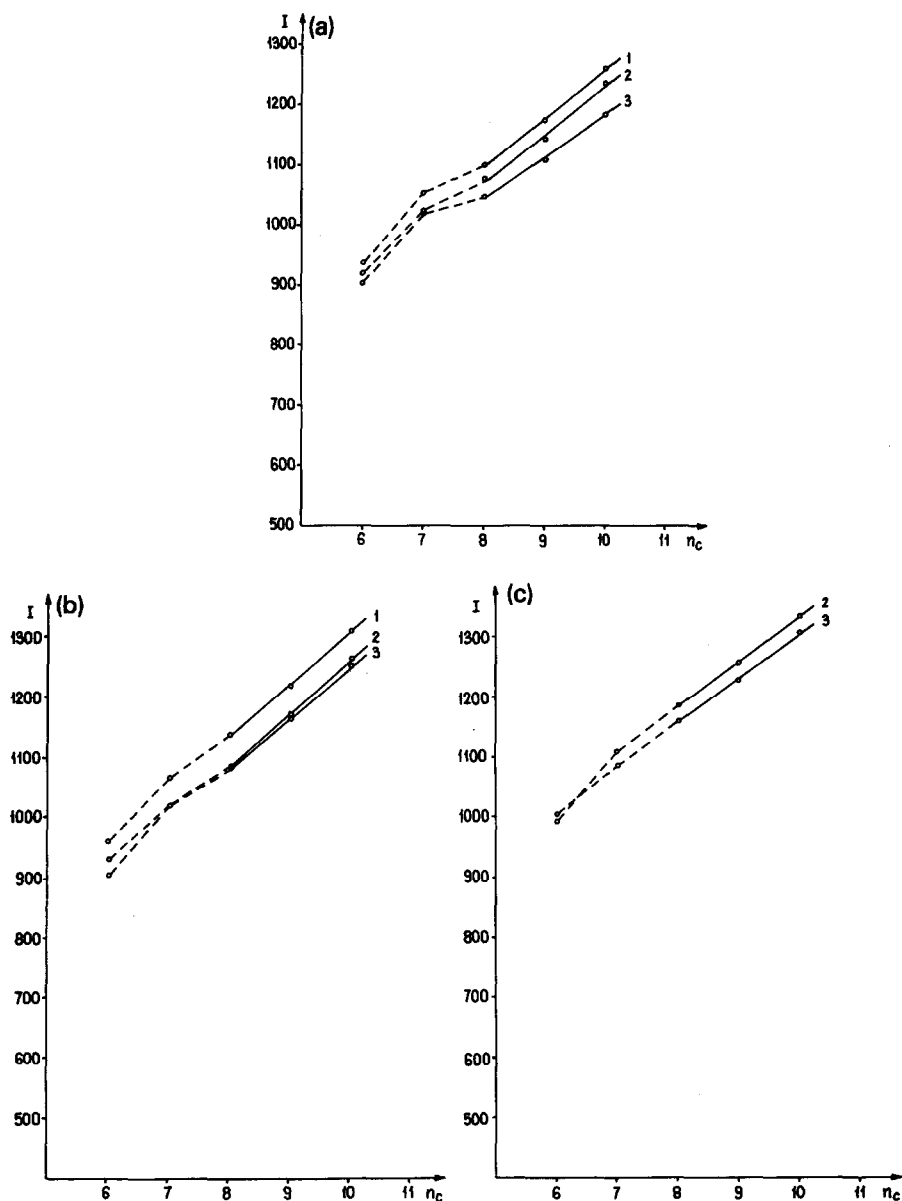
Fig. 1. Relationship between retention indices (I) and the carbon number (n_c) for homologous alkylbenzenes on the copolymers: 1 = 0.2 DMN–0.8 DVB; 2 = 0.5 DMN–0.5 DVB; 3 = 0.8 DMN–0.2 DVB. (a) Methanol–buffer (90:10); (b) acetonitrile–buffer (70:30); (c) tetrahydrofuran–buffer (40:60).

copolymers, the retention indices of toluene decrease and those of nitrobenzene increase.

The least retained compounds are the most polar: *p*-cresol and 2-phenylethanol. In the methanol–buffer mobile phase, changes in the chemical structure of DMN–
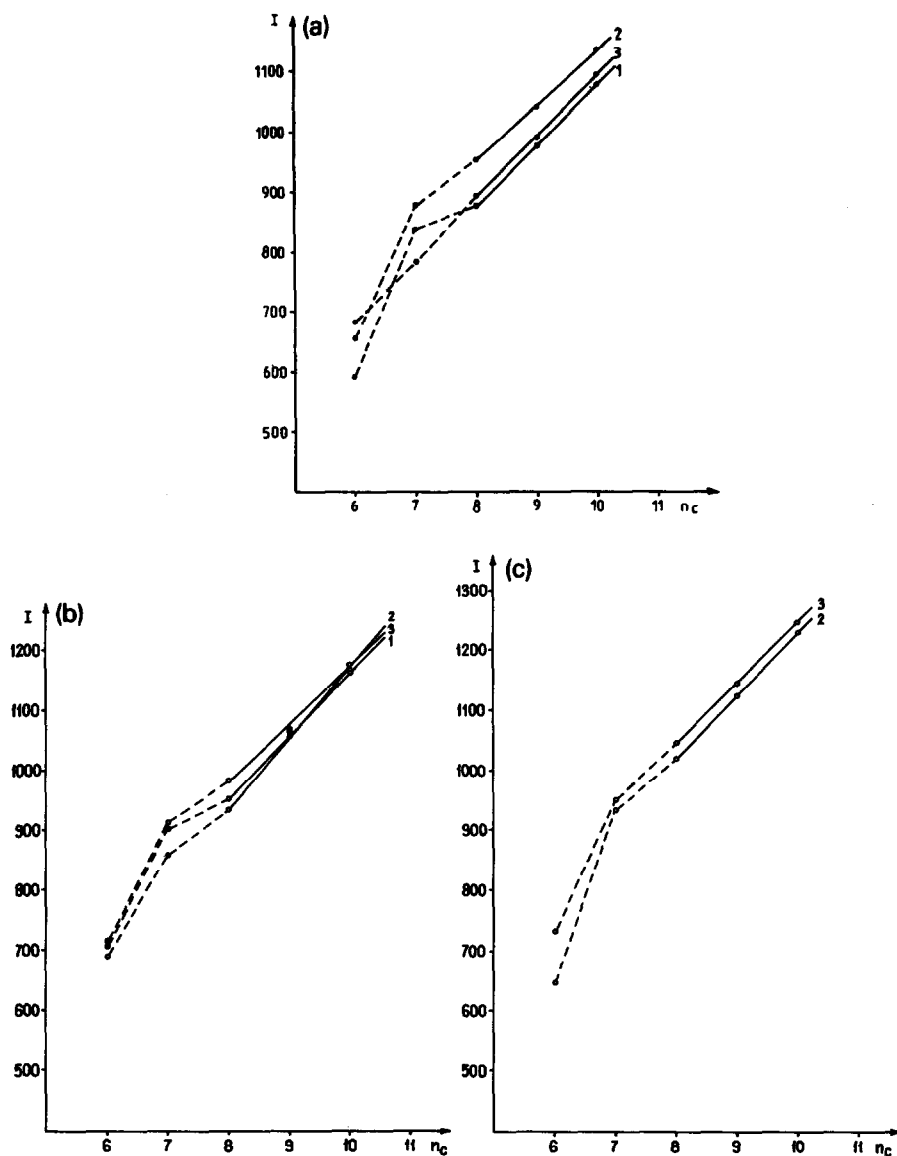
Fig. 2. Relationship between retention index (I) and the carbon number (n_c) for homologous N-alkylani-lines on the copolymers: 1 = 0.2 DMN–0.8 DVB; 2 = 0.5 DMN–0.5 DVB; 3 = 0.8 DMN–0.2 DVB. (a) Methanol–buffer (90:10); (b) acetonitrile–buffer (70:30); (c) tetrahydrofuran–buffer (40:60).

DVB copolymers do not influence the relative retention of 2-phenylethanol. In the two other mobile phases its retention index values are significantly different. In partic-ular, with the tetrahydrofuran–buffer eluent, the retention indices of 2-phenylethanol differ by over 100 units for 0.5 DMN–0.5 DVB and 0.8 DMN–0.2 DVB columns.

p-Cresol is relatively more retained, especially in the tetrahydrofuran–buffer eluent, and its retention indices have similar values.

Particularly noticeable is the variation in the retention index values of N-methylaniline, which range from $I = 877$ on the copolymer 0.5 DMN–0.5 DVB to $I = 784$ on the copolymer 0.8 DMN–0.2 DVB with methanol–buffer. In contrast, in acetonitrile–buffer and tetrahydrofuran–buffer, N-methylaniline is most highly retained on the copolymer 0.8 DMN–0.2 DVB. The behaviour of the copolymer 0.8 DMN–0.2 DVB in methanol–buffer is caused either by inaccessibility of the micropores presented in this copolymer for N-methylaniline [20,21], or by a difference in the nature of the interaction between N-methylaniline and the sorbent with the highest number of ester groups. Probably, these two effects overlap.

The results for column test compounds indicate that the DMN–DVB copolymers have a specifically much weaker retention for analytes containing hydroxyl groups (*p*-cresol and 2-phenylethanol). An increase in the DMN monomer content of the copolymers increases the retention of nitrobenzene and N-methylaniline. This means that the dipolar interactions and proton donation effects of the copolymers become stronger.

The behaviour of the studied compounds suggests that, in the case of polymeric stationary phases formed from monomers of different polarity, the molar ratio is responsible for the character of specific interactions. By changing the molar ratio of the monomers, copolymers of different selectivity can be obtained.

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