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Chemically bonded chelates as selective complexing sorbents for gas chromatography

IV. Silica surfaces modified with Co(II) and Ni(II) complexes

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Abstract

The synthesis of some new packings for complexation gas chromatography (CGC) is proposed in this article. These packings contain acetylacetonates and hexafluoroacetylacetonates of nickel(II) and cobalt(II), which are chemically bonded to a silica gel via β -diketonate groups. The effect of the structure and the configuration of some adsorbates (olefins, cyclic and aromatic hydrocarbons) on the retention of these compounds is determined. Moreover, the usefulness of the packings in the analysis of hydrocarbons is described. The results show the good applicability of the tested packings as well as their high selectivity towards compounds which contain π -electrons.

Keywords: Stationary phases, GC; Silica gel, copper(II) complexes-modified; Silica gel, nickel(II) complexes-modified; Complexing sorbents; Hydrocarbons; Olefins

1. Introduction

Complexation gas chromatography (CGC) is more and more mentioned as a chromatographic technique, in addition to adsorption and partition chromatography. CGC is based on packings which are capable of specific interactions of the π -type with adsorbate molecules characterised by electron-donor properties. A characteristic feature of CGC is a separation mechanism which involves (with a high selectivity) formation of metastable complexes, either organic or with cations of transition metals [1–3].

β -Diketonate complexes are interesting in

CGC for at least four reasons: (i) different metals can be used (ii) different ligands with β -diketonate groups can be employed; (iii) these compounds can be either bonded to a silica surface via appropriate silanes or dissolved in a liquid stationary phase; (iv) a high thermal stability of the obtained packings can be achieved.

Some results of studies on packings with silica-bonded (via the β -diketonate group) acetylacetonates (acac) and hexafluoroacetylacetonates (hfac) of nickel(II) and cobalt(II) are reported in this article. Both compounds are coordinately unsaturated [4–8] and therefore are able to form (through an intermolecular bond) the so-called adducts with Lewis bases. This applies to all

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divalent metals, except palladium and platinum. A gradual substitution of hydrogens from methyl groups in the ligand with fluorine first reduces the σ - and π -donor properties of the acetylacetonate ligands, and then promotes the attachment of additional ligands to the metal. The order of increasing equilibrium constants of this addition is as follows: $(R = R' = CH_3) < (R = CH_3; R' = CF_3) < (R = R' = CF_3)$, where R and R' are substituents in acetylacetonate [7].

The stability of the adducts depends on the nature of the β -diketonate, on the base and on the environment [9]. The studies performed involved packings containing such compounds as $Co(acac)_2$ and $Co(hfac)_2$ as well as $Ni(acac)_2$ and $Ni(hfac)_2$ bonded with a 2,4-pentanedione group via silane. Since some functional groups on the support surface might not be bonded to the metal, chromatographic studies were also performed for a packing with free acetylacetonate groups and for a packing devoid of these functional groups but possessing on its surface chemically bonded C_8 hydrocarbon chains. Taking into account the ability of the metal in the used salts to interact with compounds showing electron-donor properties, chromatographic measurements for such adsorbates as olefins (linear and branched) and cyclic and aromatic hydrocarbons were conducted. The obtained results allowed: (i) for the determination of the effects of the structure and the configuration of adsorbate molecules on their retention, and (ii) for the specification of the applicability of the obtained packings in the analysis of hydrocarbon mixtures.

2. Experimental

2.1. Reagents

Silica (Porasil C, 80–100 mesh, 177–149 μm) was obtained from Waters Associates (Milford, MA, USA) and 3-(3-trimethoxysilylpropyl)-2,4-pentanedione (TMSSP) from the Laboratory of Organometallic Chemistry (UAM, Poznań, Poland). Xylene, hexane, tetrahydrofuran (THF),

which were distilled over metallic sodium prior to use, were obtained from POCh (Gliwice, Poland). This was also the source of methyl alcohol, trichloroethylsilane and hexamethyldisilazane (HMDS). Ni(II) and Co(II) acetylacetonates and hexafluoroacetylacetonates were received from Aldrich (Milwaukee, USA). Chromatographic standards came from different producers, most of them from firms such as Fluka (Buchs, Switzerland) and Aldrich (Milwaukee, USA).

2.2. Apparatus

Chromatographic measurements were performed using the GCHF 18.3 gas chromatograph (Chromatron, Berlin, Germany) equipped with a flame-ionisation detector. The temperature in the thermostat chamber was measured with a DT 200 thermometer (Digital Thermometer, Slandi, Warsaw, Poland).

Stainless-steel columns (2 m \times 3 mm I.D.) were used in the chromatographic studies. Argon was applied as the carrier gas. Argon and other gases (hydrogen, air) were dried by the use of dehydrators equipped with molecular sieves.

The elemental analysis of the packings was performed on an 2400 CHN Elemental Analyser (Perkin-Elmer, Norwalk, CT, USA). The specific surface areas of the packings under study and of the bare silica were measured using a Gravimat apparatus (Sartorius, Gottingen, Germany). The measurements were carried out via the BET method using nitrogen as the adsorbate at a temperature of $-195^\circ C$. The results obtained are presented in Table 1.

2.3. Preparations of packings with β -diketonate-bonded phase

The synthesis of the packings was performed in two stages. The objective of the first stage was to bond silane (TMSSP), ending with a complex-forming functional group, with the surface of silica (Porasil C). This reaction was conducted in

Table 1
Physicochemical parameters of the packings under study

Packing	Elemental analysis (%)			Specific surface area (m ² /g)	[Si] (μmol/m ³)
	C	H	M		
I ^a	2.41	0.43	–	65	4.87
II ^b	2.54	0.61	–	75	3.33
III ^c	2.08	0.44	0.10	71	2.41
IV ^d	2.26	0.43	0.15	79	2.11
V ^e	2.46	0.47	0.11	74	2.88
VI ^f	1.84	0.33	1.73	71	2.33

^a (CH₂)₇CH₃; ^b (CH₂)₃(COCH₃)₂; ^c (CH₂)₃(COCH₃)₂Co(acac); ^d (CH₂)₃(COCH₃)₂Co(hfac); ^e (CH₂)₃(COCH₃)₂Ni(acac); ^f (CH₂)₃(COCH₃)₂Ni(hfac).

anhydrous xylene. This system was heated to boiling under a reflux condenser for 15 h. During this time, the whole system was protected from water. The reaction product (after filtration and extraction with xylene and then with hexane in the Soxhlet apparatus) was dried at 120°C under vacuum.

In the second stage, the silica altered as described above was modified with acetylacetonates and hexafluoroacetylacetonates of Ni(II) and Co(II). In order to attain this, silane-bonded packings (TMSSP) were flooded with a saturated solution of the appropriate salt in tetrahydrofuran. This system of reagents was left at room temperature for seven days. After the first five days the solution was replaced with a fresh solution. Excess of the salt was removed by extraction with THF in the Soxhlet apparatus.

A schematic representation of the reactions taking place during the synthesis is presented in Fig. 1, where MX₂ stands for Co(acac)₂, Co(hfac)₂, Ni(acac)₂ and Ni(hfac)₂.

Synthesis of the packings to be studied was conducted via this method, because, according to the literature [10,11], it reduces the possible formation of a polymer-like layer on the support surface, which takes place when more than one functional group interacts with the metal.

2.4. Preparations of packings with chemically bonded octylsilane

Dried silica was flooded with a solution consisting of 3 ml of trichlorooctylsilane and 80 ml of anhydrous xylene. The system thus obtained was

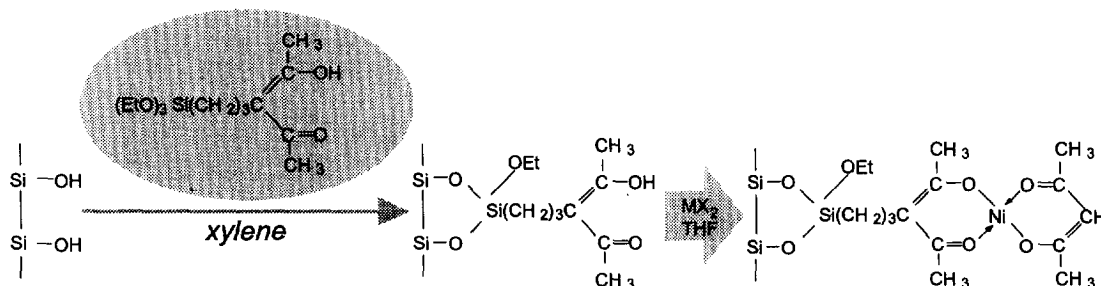


Fig. 1. Schematic representation of packing with chemically bonded metal complexes.

heated to boiling and mixed in an evaporator for 12 h. After washing with xylene, the packing was transferred to the Soxhlet apparatus and extracted with the same solvent for 6 h. The next stage involved the end-capping reaction using HMDS. This reaction was performed also in anhydrous xylene. After this, the packing was extracted and dried.

3. Results and discussion

To characterise the obtained packings, elemental and thermogravimetric analyses were performed. The surface concentration of silane and the percentage surface coverage with silane were calculated. The obtained results are presented in Table 1. Taking into account the fact that the

metal in acetylacetonates and hexafluoroacetylacetonates is able to interact with compounds showing electron-donor properties [12,13], chromatographic studies of such adsorbates as olefines, cyclic hydrocarbons and aromatic hydrocarbons were conducted. The aim of these studies was to assess the influence of the structure and the configuration of the adsorbate molecules on their retention, as well as to define the usefulness of the obtained packings in the analysis of hydrocarbons.

To precisely characterise the interactions for each group of compounds under study, the following retention parameters were determined: capacity factor (k'), retention index (I) and molecular retention index ΔM_e [14]. The latter parameter is calculated from the following formula: $\Delta M_e = M_e - M$, where M indicates the

Table 2
Capacity factors $k' = (t_R - t_M)/t_M$ and retention indices for the studied linear and cyclic hydrocarbons at 130°C

Adsorbate	Packing											
	I ^a		II		III		IV		V		VI	
	k'	I	k'	I	k'	I	k'	I	k'	I	k'	I
Pentane	0.54	500	0.89	500	0.97	500	0.75	500	1.06	500	0.92	500
1-Pentene	0.61	506	0.97	509	1.02	510	0.81	513	1.20	524	1.06	528
Cyclopentane	0.61	517	0.83	520	1.21	520	0.75	512	1.39	518	1.00	508
Cyclopentene	0.55	506	0.84	522	1.34	537	0.82	527	1.57	539	1.05	517
Hexane	1.10	600	1.55	600	1.75	600	1.38	600	1.82	600	1.55	600
1-Hexene	1.02	584	1.61	608	1.87	612	1.55	620	2.05	621	1.67	614
1-Hexyne	1.08	596	2.24	676	2.89	688	2.44	708	3.49	718	2.57	697
<i>cis</i> -2-Hexene	1.12	604	1.76	627	2.00	624	1.61	627	2.26	639	1.73	631
<i>trans</i> -2-Hexene	1.08	597	1.71	621	1.94	618	1.55	621	2.14	629	1.61	617
1,3-Hexadiene	1.12	605	2.05	658	2.55	665	2.05	669	2.84	681	2.22	669
1,4-Hexadiene	1.02	585	1.74	624	2.13	634	1.68	635	2.48	656	1.91	640
1,5-Hexadiene	0.94	567	1.70	620	1.96	620	1.56	622	2.28	641	1.77	626
Cyclohexane	0.97	624	1.36	619	2.24	623	1.35	611	2.52	620	1.70	614
Cyclohexane	0.98	627	1.52	641	2.66	652	1.64	644	3.39	669	2.00	645
1,3-Cyclohexadiene	0.92	613	1.64	658	2.94	669	1.89	668	3.95	694	2.21	663
1,4-Cyclohexadiene	1.05	641	1.83	678	3.41	694	2.19	693	4.66	722	2.55	691
Heptane	0.87	601	2.53	700	3.13	700	2.45	700	3.16	700	2.61	700
1-Heptane	1.83	700	2.59	705	3.37	713	2.84	725	3.59	723	2.86	718
Cycloheptane	1.78	727	2.53	730	4.45	740	2.86	737	5.25	742	3.27	738
Octane	3.03	800	4.12	800	5.61	800	4.44	800	5.49	800	4.46	800

^a Notation as in Table 1.

Table 3
Molecular retention index ΔM_e for the studied linear and cyclic hydrocarbons at 130°C

Adsorbate	Packing					
	I ^a	II	III	IV	V	VI
Pentane	–	–	–	–	–	–
1-Pentene	2.30	3.28	3.39	4.03	5.38	5.94
Cyclopentane	2.72	4.82	4.94	3.79	4.54	3.14
Cyclopentene	4.87	7.12	9.34	7.94	9.50	6.42
Hexane	–	–	–	–	–	–
1-Hexene	–0.23	3.14	3.83	5.01	4.96	3.98
1-Hexyne	3.47	14.69	16.48	19.38	20.58	17.64
<i>cis</i> -2-Hexene	2.58	5.80	5.53	5.95	7.49	6.36
<i>trans</i> -2-Hexene	1.60	4.96	4.75	5.08	6.08	4.40
1,3-Hexadiene	2.72	10.15	13.36	13.87	13.38	11.69
1,4-Hexadiene	0.09	5.38	9.01	9.07	9.87	7.63
1,5-Hexadiene	–2.61	4.82	6.99	7.28	7.77	5.66
Cyclohexane	5.38	4.68	5.42	3.71	4.82	3.98
Cyclohexene	7.82	9.78	11.52	10.30	13.71	10.34
1,3-Cyclohexadiene	7.87	14.18	15.86	15.69	19.23	14.89
1,4-Cyclohexadiene	11.80	16.99	19.35	19.20	23.16	18.81
Heptane	–	–	–	–	–	–
1-Heptene	0.23	2.74	4.00	5.65	5.24	4.54
Cycloheptane	10.01	8.05	7.79	7.45	7.91	7.35
Octane	–	–	–	–	–	–

^a Notation as in Table 1.

true molecular mass, $M_e = 0.14027I + 2.016$ is the effective molecular mass and I is the retention index. The molecular retention index ΔM_e allows us to determine the effect of substituents on the retention of particular adsorbates. According to the definition, this parameter is equal to zero for *n*-alkanes [15,16]. Each additional function introduced to a *n*-alkane molecule (e.g. a substituent, a heteroatom, unsaturated bond) leads to a difference between M and M_e . Consequently, positive values of the molecular retention index indicate positive interactions between a given functional group and a packing, whereas negative values of this parameter testify to repulsion between the adsorbate and the packing.

3.1. Alkenes and cyclic hydrocarbons

Values of capacity factors (k'), retention indices (I), and molecular retention indices (ΔM_e)

for selected olefins and cyclic hydrocarbons are given in Tables 2 and 3. It is possible that on the support surface some of the acetylacetonate groups are not bonded with metal. Thus, retention times for the studied adsorbates were also measured for packings with free diketonate groups, which were treated as a reference with

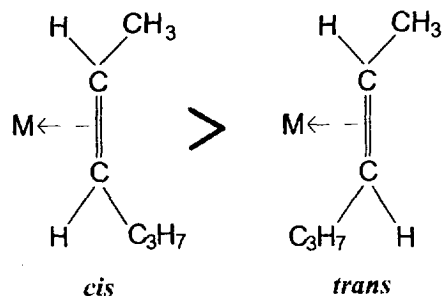


Fig. 2. Structures of the *cis*- and *trans*-isomer of hexene.

respect to packings with bonded cobalt and nickel salts, as well as for packings with bonded C₈ phase. The latter packing was treated as a reference against a packing with β -diketonate groups, which is able to interact specifically with the studied adsorbates.

A characteristic feature of packings with bonded complexes of d-group metals is the order of elution of alkanes and alkenes. This feature was also confirmed in the case of the packings under study. Due to the ability of the metal to coordinately interact with electrons of unsaturated bonds, alkenes are more retained on the column than the corresponding alkanes (e.g. pentane and 1-pentene, hexane and 1-hexene, and heptane and 1-heptene).

As follows from the data compiled in the

tables, specific interactions depend on the type of unsaturated bond (the values of retention parameters for the alkenes are lower than for the corresponding alkanes) and on the number of unsaturated bonds and their positions in the molecule with respect to each other. The values of capacity factors for hexadienes decrease with increasing distance between the unsaturated bonds. The elution in this group of compounds is the following: 1,3-hexadiene > 1,4-hexadiene > 1,5-hexadiene.

The effect of adsorbate molecule structure on the specific interactions of the π -type was observed for geometric isomers. For the columns with bonded Co(II) and Ni(II) acetylacetonates as well as for those with hexafluoroacetylacetonates of these metals, the interactions of the

Table 4
Capacity factors $k' = (t_R - t_M)/t_M$ and retention indices for the studied aromatic hydrocarbons at 130°C

Adsorbate	Packing											
	I ^a		II		III		IV		V		VI	
	k'	I	k'	I	k'	I	k'	I	k'	I	k'	I
Benzene	1.18	613	1.78	680	3.33	698	2.29	694	3.65	721	2.43	698
Toluene	2.09	728	3.20	795	6.77	829	5.20	832	7.63	853	4.38	804
Ethylbenzene	3.32	823	5.15	890	12.11	916	8.32	915	12.95	948	8.02	921
Propylbenzene	5.28	916	8.36	986	20.95	1013	14.43	1008	22.05	1044	13.52	1018
<i>p</i> -Xylene	3.56	836	5.56	905	13.10	940	10.44	953	14.71	971	8.76	937
<i>m</i> -Xylene	–	–	5.60	907	13.35	943	10.49	954	15.24	978	8.91	941
<i>o</i> -Xylene	3.93	857	6.20	927	15.05	963	11.66	972	16.60	993	9.74	957
Styrene	3.75	847	6.45	934	14.78	960	10.30	966	15.36	982	10.25	958
Cumene	4.73	894	7.57	966	17.66	990	14.13	1004	20.30	1032	12.52	994
1,3,5-Trimethylbenzene	5.98	941	9.16	1004	27.01	1058	19.14	1057	28.29	1089	15.98	1048
1,2,4-Trimethylbenzene	6.62	961	10.46	1031	29.19	1071	21.62	1078	30.85	1105	18.36	1074
1,2,3-Trimethylbenzene	7.36	983	11.90	1056	34.12	1098	25.32	1105	34.25	1123	20.90	1097
2-Ethyltoluene	3.80	850	9.61	1013	25.80	1053	19.57	1061	27.81	1086	15.87	1047
2-Methylstyrene	6.28	951	10.70	1035	26.21	1056	20.75	1071	29.09	1097	18.95	1069
3-Methylstyrene	6.49	958	11.46	1049	28.29	1069	22.25	1083	30.35	1105	19.76	1077
3-Phenyl-1-propene	4.97	904	8.62	992	20.46	1015	16.31	1029	23.22	1056	14.40	1019
<i>trans</i> -1-Phenyl-1-propene	0.87	601	13.04	1075	30.53	1082	25.17	1104	35.33	1132	22.16	1097
Butylbenzene	8.76	1018	14.19	1092	39.01	1119	28.44	1126	39.99	1151	24.39	1116
Isobutylbenzene	7.35	983	11.95	1057	31.93	1086	22.90	1088	32.01	1111	20.92	1087
<i>sec.</i> -Butylbenzene	7.12	976	11.43	1048	30.95	1081	27.71	1086	31.37	1108	19.43	1074
<i>tert.</i> -Butylbenzene	6.77	966	11.21	1044	31.10	1082	22.32	1083	32.65	1115	19.83	1077
Fluorobenzene	–	–	2.16	727	6.08	818	4.10	742	4.46	750	2.95	731
Chlorobenzene	–	–	4.79	878	9.72	878	9.43	889	10.43	898	6.78	884
Bromobenzene	–	–	7.29	955	15.80	955	14.90	971	16.09	977	10.47	965

^a Notation as in Table 1.

Table 5
Molecular retention index ΔM_c at 130°C

Adsorbate	Packing					
	I ^a	II	III	IV	V	VI
Benzene	10.16	19.29	21.87	21.41	25.04	21.81
Toluene	11.99	21.39	26.30	26.72	29.53	22.65
Ethylbenzene	11.29	20.69	24.55	24.36	28.82	25.03
Propylbenzene	10.30	20.12	24.15	23.39	28.26	24.61
<i>p</i> -Xylene	13.11	22.79	27.89	29.71	32.05	27.28
<i>m</i> -Xylene	–	23.07	28.30	29.83	33.03	27.84
<i>o</i> -Xylene	16.06	25.88	31.13	32.31	35.13	30.08
Styrene	16.67	28.88	32.71	33.58	35.61	32.24
Cumene	7.22	17.32	20.91	22.88	26.57	21.24
1,3,5-Trimethylbenzene	13.81	22.65	30.37	30.27	34.57	28.82
1,2,4-Trimethylbenzene	16.62	26.43	32.27	33.24	36.81	32.47
1,2,3-Trimethylbenzene	19.70	29.94	36.09	37.07	39.82	35.69
2-Ethyltoluene	1.05	23.91	29.86	30.81	34.15	28.68
2-Methylstyrene	17.23	29.02	32.23	34.25	37.71	33.78
3-Methylstyrene	18.21	30.98	34.02	35.94	41.52	35.01
3-Phenyl-1-propene	10.64	22.98	26.38	28.38	31.96	26.77
<i>trans</i> -1-Phenyl-1-propene	21.58	34.63	35.83	38.93	42.62	37.71
Butylbenzene	10.59	20.97	25.11	25.95	29.53	24.34
Isobutylbenzene	5.68	16.06	20.46	20.64	23.64	20.26
<i>sec.</i> -Butylbenzene	4.70	14.80	19.70	20.44	23.22	18.45
<i>tert.</i> -Butylbenzene	3.30	14.24	19.82	20.02	24.20	18.87

^a Notation as in Table 1.

cis-isomers were found to be stronger than those of the *trans*-isomers (*trans*-2-hexene was eluted before the *cis*-isomer). This is caused by a different accessibility of the unsaturated bond in the isomers (Fig. 2).

3.2. Aromatic hydrocarbons

The main type of interaction in the case of

aromatic hydrocarbons is that between the ring electrons and the cation unoccupied orbitals of the complex bonded metal. Retention parameters for aromatic compounds which were used as adsorbates are given in Tables 4 and 5. The obtained results enabled us to determine the dependence between retention parameters and the type of chain (either linear or branched, or saturated versus unsaturated) as well as the

Table 6

Physicochemical parameters for aromatic hydrocarbons

Adsorbate	bp (°C)	Polarisability (D)	Molar refraction (cm ³ /mol)
Ethylbenzene	135.5	0.59	35.72
Chlorobenzene	131.7	1.69	31.11
Cumene	152.0	0.79	40.34
Bromobenzene	156.0	1.77	34.00

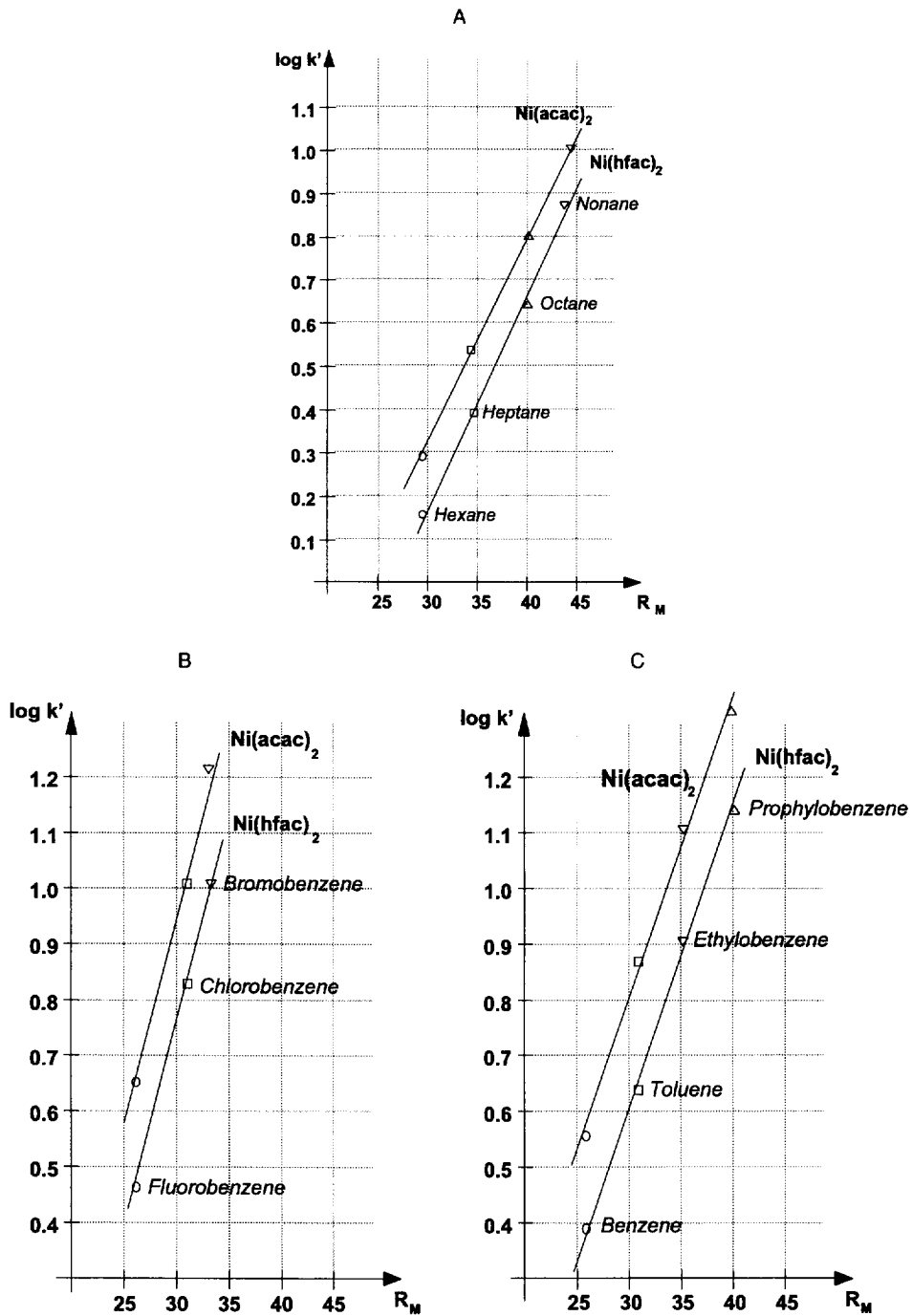


Fig. 3. Dependence between $\log k'$ and the molar refraction R_M for (A) some halogenobenzenes, (B) some aromatic hydrocarbons, (C) some alkanes.

Table 7
Mutual dependencies of the capacity factors k' for aromatic hydrocarbons

	No metal			Co(acac) ₂			Co(hfac) ₂			Ni(acac) ₂			Ni(hfac) ₂		
	130°C	140°C	150°C	130°C	140°C	150°C	130°C	140°C	150°C	130°C	140°C	150°C	130°C	140°C	150°C
Halogenobenzene- alkylbenzene															
Chlorobenzene- ethylbenzene	0.87	0.88	0.89	0.77	0.78	0.76	0.76	0.77	0.78	0.72	0.76	0.77	0.81	0.84	0.85
Bromobenzene- cumene	0.90	0.91	0.93	0.78	0.83	0.89	0.77	0.79	0.80	0.67	0.74	0.76	0.84	0.86	0.87

position of its substitution in a ring. Benzene was selected as the reference compound. On one hand, it is well known that substituents may hinder access to the ring. On the other hand (as a result of induction effects), they may increase the density of the electron cloud in the ring. It was found that substituents with both saturated and unsaturated chains exert a favourable effect on adsorbate interactions with the electron-acceptor centre. In this study, the substituents with saturated chains were mono-, di- and tri-substituted

benzenes. The strongest interactions were noted for the trimethyl-substituted aromatic ring. For all columns, the sequence of isomer elution from these compounds was the following: 1,3,5- < 1,2,4- < 1,2,3-trimethyl benzene.

To compare the effect of a substituent with a saturated chain, styrene and ethylbenzene were taken into consideration. The molecular retention index for styrene for all studied packings was observed to increase by four units with respect to the corresponding values for ethylbenzene.

The position of an unsaturated bond in a substituent also appears to be important. When coupled to an aromatic ring, the influence was greater compared with that found for an isolated

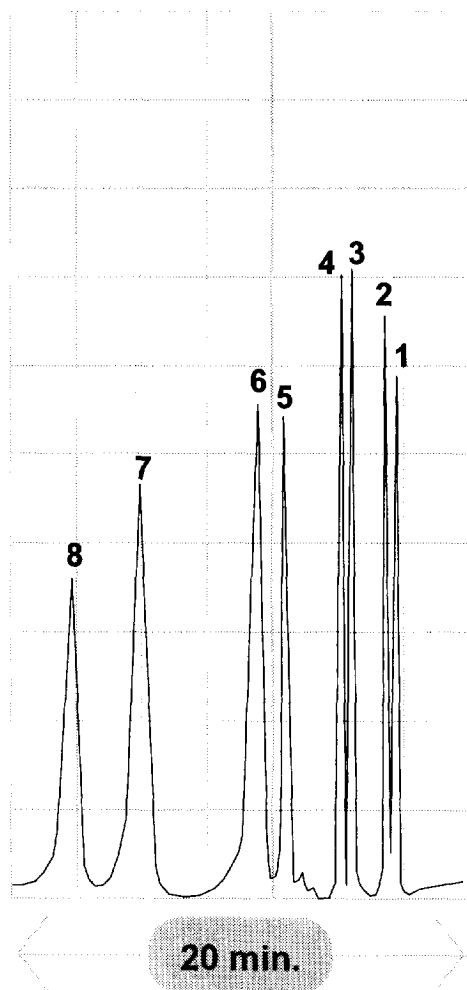


Fig. 4. Separation of a mixture of four alkane-alkene pairs. Packing, Ni(acac)₂; column temperature, 141.4°C; carrier gas flow-rate, 18.5 ml/min. Peaks: 1 = pentane; 2 = 1-pentene; 3 = hexane; 4 = 1-hexene; 5 = heptane; 6 = 1-heptene; 7 = octane; 8 = 1-octene.

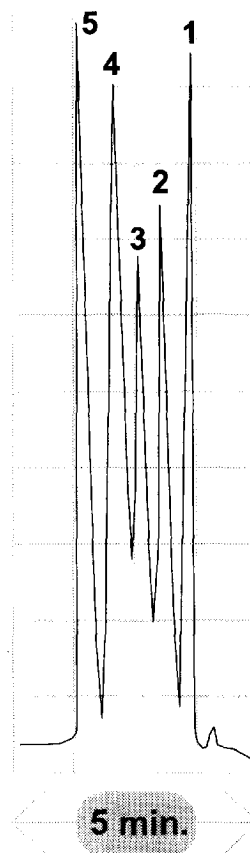


Fig. 5. Separation of a mixture of linear C₆ hydrocarbons. Packing, Ni(acac)₂; column temperature, 111°C; carrier gas flow-rate, 16.6 ml/min. Peaks: 1 = hexane; 2 = 1-hexene; 3 = 1,5-hexadiene; 4 = *cis*-1,4-hexadiene; 5 = 1,3-hexadiene.

unsaturated bond. This can be well observed for 3-phenyl-1-propene and *trans*-1-phenyl-1-propene. The latter was eluted from the column earlier than the former. In this group of compounds, the weakest influence was reported for substituents with branched chains. For these compounds the molecular retention index was lower than for unsubstituted benzene. The closer to the ring the branching of the chain, the

stronger the influence. In this case steric conditions dominated over the induction effect.

To provide a more comprehensive characteristic of the mechanism of adsorbate–adsorbate interactions for aromatic hydrocarbons, the physicochemical and retention parameters for two pairs of compounds with similar boiling temperatures but a different chemical nature are presented (Tables 6 and 7): ethylbenzene and chlorobenzene, cumene and bromobenzene. As

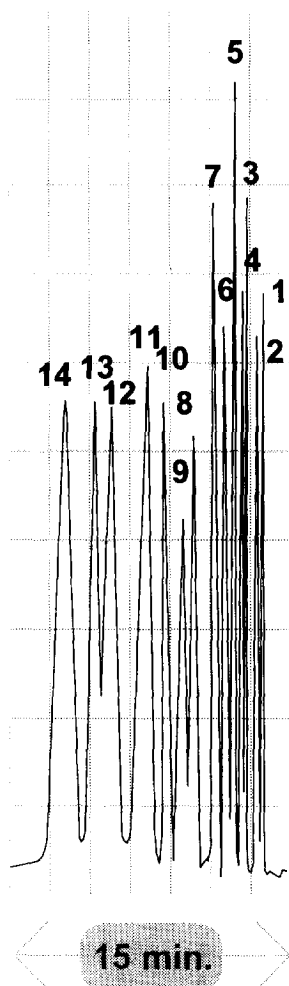


Fig. 6. Separation of a mixture of cyclic hydrocarbons. Packing, Ni(acac)₂; column temperature, 101.0°C; carrier gas flow-rate, 20 ml/min. Peaks: 1 = cyclopentene; 2 = cyclopentane; 3 = methylcyclopentane; 4 = cyclohexane; 5 = 1-methyl-1-cyclopentene; 6 = cyclohexene; 7 = methylcyclohexane; 8 = cycloheptane; 9 = 4-methyl-1-cyclohexene; 10 = cycloheptene; 11 = ethylcyclohexane; 12 = 1,3,5-cycloheptatriene; 13 = cyclooctane; 14 = cyclooctene.

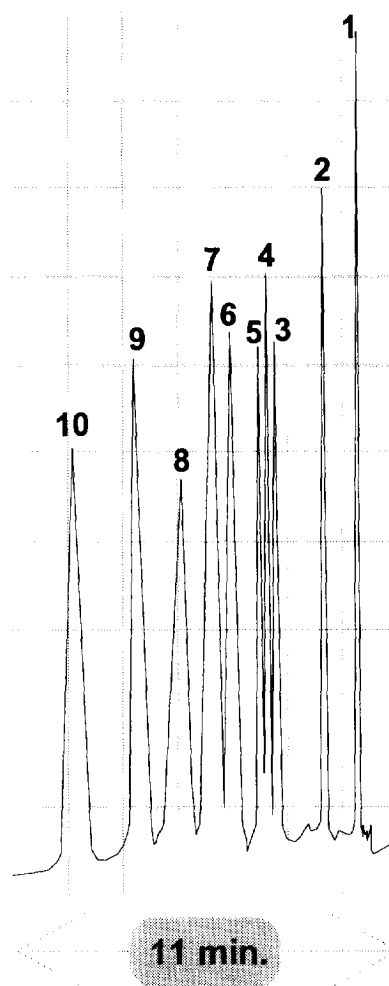


Fig. 7. Separation of a mixture of aromatic hydrocarbons. Packing, Co(acac)₂; column temperature, 139.9°C; carrier gas flow-rate, 14.1 ml/min. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*-xylene; 5 = styrene; 6 = cumene; 7 = propylbenzene; 8 = α -methylstyrene; 9 = *tert*-butylbenzene; 10 = *n*-butylbenzene.

follows from the data, these compounds significantly differ in polarity. Thus, if dipole–dipole-type interactions between the adsorbate and the adsorbent would have been responsible for the retention of polar compounds, then the more polar compound would have eluted after the less polar one. As can be seen in Table 7, the situation in the case of the studied packings is the opposite: ethylbenzene is eluted after chlorobenzene, and cumene after bromobenzene. This is due to the fact that the alkyl substituent, unlike the halogen one, increases the free-electron density in the aromatic ring, and thus promotes the increase of the specific interactions. As an effect of such interactions of the alkyl substituents, bromobenzene, with a boiling point of 156°C, is eluted earlier than cumene, which has a boiling point of 152°C.

Alkyl derivatives of benzene are characterised by a significantly higher polarity than the corresponding halogen derivatives, as reflected in the values of molar refraction. When plotting the dependence between $\log k'$ and the values of molar refraction R_M , it can be seen that adsorption of the studied sorbates is a linear function of polarisability (Fig. 3).

4. Analytical applications

The differences in the specific interactions between the bonded phases and the adsorbates with electron-donor properties were sufficiently large to allow us to separate the mixture of the studied compounds. In the first two chromatograms the analytical application of packings against unsaturated hydrocarbons is shown. A separation of mixtures of four alkane–alkene pairs is shown in Fig. 4. As follows from the chromatogram, the elution order of the alkane–alkene pairs is closely related to the presence of unsaturated bonds in the adsorbate molecule: alkane is always eluted first, despite its higher boiling point, before the corresponding alkene. This is a result of the π -type interactions. Sepa-

ration of linear C_6 hydrocarbons is illustrated in Fig. 5. The packings under study may also be applied in the analysis of cyclic and aromatic hydrocarbons. Separation of these groups of compounds is shown in Figs. 6 and 7. As can be seen in the case of aromatic and cyclic hydrocarbons, two isomers C_8H_{10} (ethylbenzene and *m*-xylene), two isomers C_9H_{12} (propylbenzene and cumene) and a number of other benzene derivatives were separated from one mixture.

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