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Chromatographic properties of sorbents based on acetylacetonate metal complexes under steam chromatography conditions

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The chromatographic properties and adsorption heats of aliphatic and aromatic hydrocarbons on stationary phases containing nickel(II), zinc(II), europium(III) and iron(III) acetylacetonates bonded to the silica surface with helium and water vapour as a carrier gas were estimated.

Phifrer and Plummer[1] used a mixture of nitrogen and water vapour as a carrier gas for the chromatographic separation of alcohols. This variant of gas chromatography was investigated in detail.[2] However, this method has some limits, for example, an increase in the background noise and a short column life. The effect of water in the carrier gas on the separation is difficult to predict, but it has an important advantage of the inversion of eluating polar compounds.[3] Salts, inorganic acids, dinonyl phthalate, 1,2,3-tri(cyanoethoxy)propane, propylene glycol and silicone oil were used as stationary phases.[4]

The sorbents containing zinc, iron, europium and nickel acetylacetonates chemically bonded to silica *via* surface hydroxyl groups were investigated under steam chromatography conditions because these complexes are insoluble in water. The ability of the acetylacetonate metal complexes to interact with nucleophilic compounds, aliphatic and aromatic hydrocarbons was studied.

Silipor 075 silica from Lachema (Czech Republic) was used. Chromatographic measurements were performed on a Chrom 5 gas chromatograph (Czech Republic) with a flame-ionization detector. Glass columns (2 m × 3 mm i.d.) were used. Helium dried on molecular sieves 4 Å and water steam were used as carrier gases. A GVP-17 water steam generator (Russian Federation) was used.

To syntesise the phases, a mixture of silica (24 g), a metal chloride (0.01 mol) and chloroform (70 ml) was refluxed under an inert atmosphere for 6 h. A suspension of the obtained silica metal chloride, an excess of acetylacetone and 60 ml of benzene

Table 1 Physico-chemical parameters of the sorbents.

Packing	Concentration (%)		Pore diameter/ nm	Pore volume/ $cm^3\ g^{-1}$	Specific surface area/$m^2\ g^{-1}$
	Metal	C			
Initial Silipore 075	—	—	16.6	1.21	82.3
+$Ni(acac)_2$	0.78	0.81	9.2	0.79	64.2
+$Zn(acac)_2$	0.62	0.60	11.4	0.86	51.6
+$Fe(acac)_3$	0.91	1.94	7.8	0.75	47.7
+$Eu(acac)_3$	0.59	0.47	8.2	0.70	42.3

Table 2 Retention factors (*k*) at 130 °C.

Substances	$Ni(acac)_2$		$Zn(acac)_2$		$Fe(acac)_3$		$Eu(acac)_3$	
	He	H_2O	He	H_2O	He	H_2O	He	H_2O
n-Pentane	0.64	0.61	0.75	0.83	0.79	0.71	0.66	0.82
n-Hexane	1.07	1.08	1.04	0.98	1.16	1.01	1.11	0.99
n-Heptane	1.33	1.43	1.29	1.19	1.44	1.25	1.42	1.22
n-Octane	1.93	2.00	1.71	1.51	2.42	1.57	2.16	1.51
n-Nonane	2.93	2.78	2.24	1.76	3.86	2.02	3.24	1.86
n-Decane	3.89	3.98	2.76	2.14	5.12	2.50	4.83	2.35
Pent-1-ene	0.78	0.71	0.80	0.87	0.82	0.76	0.82	0.84
Hex-1-ene	1.10	1.14	1.08	1.05	1.25	1.07	1.15	1.08
Hept-1-ene	1.52	1.56	1.34	1.24	2.54	1.32	1.46	1.27
Oct-1-ene	2.07	2.12	1.86	1.59	3.96	2.23	2.37	1.63
Pent-1-yne	0.92	0.93	0.96	1.05	1.08	0.99	1.12	1.01
Hex-1-yne	1.26	1.25	1.24	1.22	1.48	1.27	1.38	1.26
Hept-1-yne	1.68	1.76	1.57	1.47	2.89	1.50	1.78	1.48
Benzene	1.52	2.00	1.58	1.51	2.79	1.67	1.44	1.45
Methylbenzene	2.52	2.57	2.16	2.08	3.02	2.08	2.14	2.45
1,3-Dimethylbenzene	3.41	3.29	2.71	2.40	3.48	2.49	2.79	3.07
1,3,5-Trimethylbenzene	3.93	4.31	3.36	3.14	4.72	3.23	3.16	3.70
1,4,5-Trimethylbenzene	4.01	4.42	3.43	3.26	4.93	3.41	3.33	4.01
2-Methylpentane	0.97	0.99	0.87	0.79	1.04	0.86	0.90	0.88
3-Methylpentane	1.07	1.04	1.00	0.95	1.14	1.01	1.03	1.01
4-Methylpent-1-ene	1.08	1.10	0.79	0.73	1.00	0.83	0.87	1.03
2-Methylpent-2-ene	1.12	1.13	1.06	1.04	1.22	1.06	1.12	1.05

Table 3 Retention indexes of compounds for steam chromatography ($\Delta I_X = I_X^{H_2O} - I_X^{He}$), column temperature of 146 °C.

Adsorbate	$Ni(acac)_2$	$Zn(acac)_2$	$Fe(acac)_3$	$Eu(acac)_3$
Benzene	59.2±0.7	91.4±0.5	101.3±0.4	126.3±0.5
Ethanol	138.3±0.8	57.1±0.3	144.0±1.1	139.9±1.6
Butan-2-one	114.3±0.8	137.2±0.7	138.8±0.4	119.6±0.7
Pyridine	151.4±0.3	136.2±0.1	112.6±0.4	152.8±0.9
Nitromethane	117.3±0.4	92.5±0.4	142.1±0.6	129.3±0.3
Hept-1-ene	63.0±0.8	41.2±1.2	42.7±0.3	81.4±0.5
Cyclohexanone	121.6±0.7	91.2±0.5	120.4±0.6	111.4±0.9
Aniline	117.4±0.4	85.4±0.4	124.2±0.7	119.1±0.8
Benzaldehyde	125.3±0.5	67.4±0.2	131.9±0.5	114.5±0.7

Table 4 Values of absorption heat (ΔH_S) and adsorption heat (ΔH) for test compounds (kcal mol^{-1}) on the modified phases under conditions of traditional and steam chromatography at 146 °C.

Adsorbate	Ni(acac)$_2$				Zn(acac)$_2$				Fe(acac)$_3$				Eu(acac)$_3$			
	He		H_2O		He		H_2O		He		H_2O		He		H_2O	
	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH	ΔH_S	ΔH
Decane	0.0	8.1	0.1	7.1	0.0	7.3	0.1	7.1	0.0	7.2	0.1	7.2	0.0	8.2	0.1	7.5
Benzene	0.4	4.0	0.5	4.1	0.3	5.2	0.4	3.9	0.4	4.2	0.5	3.5	0.5	6.4	0.8	5.8
Hept-1-ene	0.2	4.1	0.3	5.6	0.2	4.5	0.2	5.0	0.3	4.2	0.4	4.5	0.3	4.8	0.4	4.7
Ethanol	1.1	7.8	3.2	6.1	1.0	11.5	4.2	9.1	1.2	5.7	3.3	6.5	1.5	6.6	3.6	6.3
Butan-2-one	0.7	6.7	1.6	5.9	0.5	8.7	2.1	7.5	0.6	5.5	2.0	8.1	0.5	7.9	2.0	7.1
Pyridine	1.2	8.4	1.2	9.6	1.8	11.7	1.8	11.6	2.0	6.7	2.3	10.5	1.8	8.5	1.9	7.3
Nitromethane	0.6	8.0	0.7	7.6	1.2	9.3	1.2	9.0	1.4	6.5	1.5	10.1	0.6	7.3	0.8	6.9
Cyclohexanone	0.3	7.2	0.4	5.8	0.1	6.4	0.4	5.0	0.5	5.3	0.8	4.6	0.3	7.6	0.4	6.7
Aniline	0.4	8.0	0.7	7.1	0.2	10.6	3.1	8.1	0.9	4.6	2.4	7.6	0.8	8.8	1.5	8.5
Benzaldehyde	0.3	6.5	0.4	5.9	0.2	7.8	1.0	6.4	0.5	6.4	1.1	6.8	0.4	7.9	0.9	7.4

was stirred at 50 °C for 8 h followed by evaporation of the solvent and an excess of the acetylacetone under reduced pressure and vacuum drying. The packing column was conditioned at a heating rate of 1 K min^{-1} from ambient temperature to 180 °C and maintained at this temperature for 12 h.

The sorbents were evaluated by performing elemental analyses on a MAES-10 Elemental Analyser (Russian Federation). Specific surface areas and pore diameters were measured on a AUS-5 instrument (Russian Federation). The results are presented in Table 1.

The phases were characterised by IR and UV spectroscopy using a Perkin-Elmer 577 (4000–200 cm^{-1}) spectrometer. The formation of metal–oxygen bonds on a silica surface after the first stage of synthesis was cofirmed by an absorption band at 277–283 cm^{-1}. This band remains in the spectra after the formation of acetylacetonate complexes.

A comparison of data obtained for sorbents with acetylacetonate metal complexes reflects changes in the retention for different localisation of unsaturated bonds in an adsorbate molecule. The retention factors $k = (t_x - t_0)/t_0$ and a grow in the retention indexes $I = 100(\lg t'_x - \lg t'_z)/(\lg t'_{z+1} - \lg t'_z) + 100z$ of hydrocarbons under water steam and helium are shown in Tables 2 and 3.

The differences in the values of specific interactions between the acetylacetonate complexes and electron-donor sorbates were sufficient for separation in water steam. The average change of retention indexes is 100–150 units for all of the phases.

In all cases, an alkane is always eluted first in comparison with corresponding alkene and alkyne. The retention increases in the order alkane < linear alkene < branched alkene < alkyne < < aromatic compound. Branched hydrocarbons have the increase in electron density of the unsaturated bond as a result of induction effect. An aromatic system gives more opportunities for donor–acceptor interactions. Thus, despite of the blocking action of water molecules, an increase of specific interactions with π-electrons of the system play the main role. The interactions are stronger in the case of a phase with europium or iron acetylacetonates. The increase in the retention of butan-2-one and nitromethane was related to absorption in the surface layer modified with water molecules.

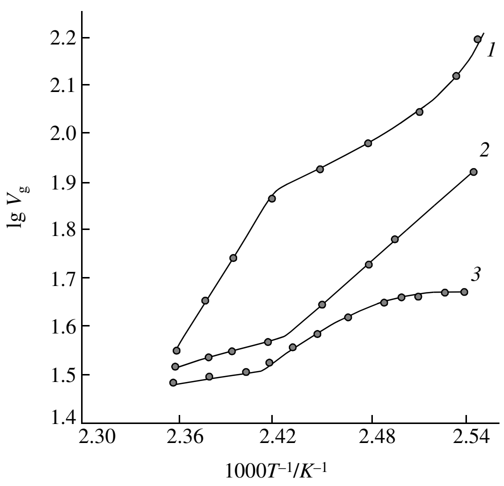

Figure 1 The temperature dependence of the specific retention volume of (*1*) ethanol; (*2*) *n*-decane and (*3*) benzene for a column with Ni(acac)$_2$ under conditions of steam chromatography.

A phase transition can be detected from a plot of $\lg V_g$ *vs.* $1/T$ for ethanol, decane and benzene. The logarithm of the specific retention volume first descreases gradually with increasing column temperature with a sharp slope of around 140 °C and then descreases markedly. Transition temperatures are clearly indicated by the sharp slope of the curves.

Thermodynamic parameters were found at 146 °C. The effective heat of sorption was calculated by the equation $\ln V_g^T = -\Delta H_0/RT + \text{const}$, where V_g^T is the specific retention volume at a certain temperature. The pure heat of sorption is calculated as $\ln K_l = -\Delta H_S/RT + \text{const}$, where K_l is the factor of sorbate distribution in the gas–stationary phase system.[5] The heats of absorption and adsorption are given in Table 4.

The effect of the absorption of organic molecules is caused by the ability of the acetylacetonate complexes to include molecules into the coordination sphere. This follows from the absence of this effect from nonpolar *n*-decane and a large value of the heats of interaction for ethanol and pyridine. The increase of the absorption heat of organic molecules for steam chromatography is a consequence of the influence of a water film on the surface. It depends on shielding the metal ions in complexes by water molecules and additional adsorption on the surface between water and gas phases.

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References

1 L. H. Phifer and H. K. Plummer, *Anal. Chem.*, 1966, **38**, 1652.

2 (*a*) V. G. Berezkin, *American Laboratory*, 1996, **28**, 28C; (*b*) L. G. Berezkina, V. G. Berezkin and E. N. Viktorova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1733 (*Russ. Chem. Bull.*, 1996, **45**, 1642); (*c*) K. Li and R. N. Horne, *SPE Reservoir Evaluation & Engineering*, 2001, **4**, 477; (*d*) V. G. Berezkin, *Adv. Chromatogr.*, 2001, **41**, 337; (*e*) Y.-H. Li, Z.-H. Ren and X.-L. Li, *Biomed. Chromatogr.*, 1995, **9**, 155.

3 M. Koel, M. Kaljurand and E. Kullik, *Anal. Chim. Acta*, 1987, **199**, 197.

4 (*a*) V. G. Berezkin, E. N. Viktorova and V. S. Gavrichev, *J. Chromatogr.*, 1988, **456**, 551; (*b*) A. M. Lafta, *J. Petroleum Research*, 1986, **5**, 89; (*c*) Yu. G. Slizhov and M. A. Gavrilenko, *Zh. Fiz. Khim.*, 2001, **75**, 1864 (*Russ. J. Phys. Chem.*, 2001, **75**, 1709); (*d*) Yu. G. Slizhov and M. A. Gavrilenko, *Koord. Khim.*, 2002, **28**, 783 (*Russ. J. Coord. Chem.*, 2002, **28**, 736); (*e*) Yu. G. Slizhov, M. A. Gavrilenko and T. N. Matveeva, *Neftekhimiya*, 2001, **41**, 149 (*Petroleum Chem.*, 2001, **41**, 131).

5 V. G. Berezkin, *Gas–Liquid–Solid Phase Chromatography*, M. Dekker, New York, 1991.

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