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Separation of Selected Derivatives of Hoszczawa-Silanates, Taking Advantage of π – π Interactions

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Abstract: In this paper, are considered optimum conditions of separation and determination of two newly synthesized heptacoordinated benzyl derivatives from the group of ES-silanates: Homo{O,O',O'',O'''-oxalic acid's Si[N-benzylaminomethyl]dihydroxysilanate} and Homo{O,O',O'',O'''-oxalic acid's Si[N-benzylaminomethyl]diethoxysilanate}. In the investigation an advantage of interactions of π – π type between analyzed compounds and stationary phases were studied. Three stationary phases (phenylbutyl, naphthylpropyl, and Hypercarb, with porous graphitized carbon) and two mobile phases (acetonitrile and dichloromethane) in various intensities of flow were considered. The best selectivity and the highest separation factor ($\alpha=9.69$) was obtained using, as the mobile phase acetonitrile (100%) and the Hypercarb column. The phenylbutyl column was characterized by a slightly lower separation factor. Obtained results show that dominating interactions in the chromatographic process are interactions of π – π type. Unfortunately, so far information concerning the chromatography of Hoszczawa-silanates have been not published in the chemical literature.

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INTRODUCTION

Silica is a basic and necessary constituent for growth and extension of living organisms. However, mechanisms of silicon transport are not entirely understandable. Biogenic silica has various functions.^[1]

Numerous organosilicon compounds also show biological activity. Some of them are very toxic (usually selective in action) and they are used for the fight against rodents.^[2]

Some are used in medicine (antitumor drugs, antibiotics).^[3] Organosilicon compounds are also used in the preservation of antiques. Rarely are they used as heat carriers, for warming or cooling of heating installations, nuclear energetic devices, etc.^[2]

An application of organosilicon hypercoordinated compounds is similar to the application of other organosilicon derivatives.

Presently, a synthesis of new compounds based on the structure of natural systems is undertaken from the point of view of their potential biological activity and possibilities of further use. As an example, they can serve in the preparation of different hypercoordinated derivatives belonging to the ES-silanate group.^[4-7]

Recently, some organosilicon compounds were found to be useful as effective bioregulators of plant organisms.^[4]

In the last several years, syntheses and structures of a number of zwitterionic λ^5 Si-silanates and λ^5 Si, λ^5 Si-disilanates, containing structures SiO_4C , were reported. Systematic research is carried out concerning the chemistry of molecular λ^5 Si-silanates and their practical application.^[5,68-10] Due to x-ray spectroscopy investigations, shapes and lengths of bonds between atoms in ES-silanates were able to be determined. Electronic spectra made in visible and ultraviolet range gave important information about orbital energy and shapes of molecules.

Taking into account various possibilities of an application of hypercoordinated compounds, determination of newly obtained Hoszczawa-silanates seems to be advisable. The aim of this work was to elaborate optimum conditions of chromatographic separation and determination of two newly obtained derivatives: Homo{O,O',O'',O'''-oxalic acid's Si[N-benzylaminomethyl]dihydroxysilanate} and Homo{O,O',O'',O'''-oxalic acid's Si[N-benzylaminomethyl]diethoxysilanate}. This work is a continuation of the research concerning new ES-silanates.^[11-13] Unfortunately, so far information concerning the chromatography of Hoszczawa-silanates have been not published in the chemical literature.

EXPERIMENTAL

HPLC Analysis of Hyper Coordinated Compounds

Samples of Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl]dihydroxysilanate (ES.1) and Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl]diethoxysilanate (ES.2) (Figure 1) were dissolved in DMSO (HPLC purity, Fluka AG, Buchs, Switzerland), to obtain a concentration at about $20 \mu\text{g cm}^{-3}$. Analyses were performed at 326 nm and at temperature of 20°C . In the investigation, three stationary phases were used: commercial Hypercarb with porous graphitized coal (PGC, Figure 2a, Thermo Electron Corporation, UK), naphthylpropyl (RP Si-NAF, Figure 2b,^[14]), and phenylbutyl (RP Si-PB, Figure 2c, Table 1).^[14] The main properties of steel columns are shown in Table 1. Their dimensions are: PGC- 100×4.6 mm, RP Si-NAF- 125×4.6 mm, and RP PB- 125×4.6 mm. Two anhydrous systems of mobile phase were applied: acetonitrile and dichloromethane.

The hypercoordinated compounds were prepared by the method described in the literature.^[12,13]

Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl] dihydroxysilanate: ^{13}C NMR (DMSO- d_6) δ (ppm) = 52.5 (SiCH₂), 63.3 (ArCH₂), 129.4, 129.8, 130.3, 131.3 (C_{arom.}), 160.0 (C=O). ^1H NMR, (DMSO- d_6).^[8] UV (DMSO): λ_{max} = 324.5, 325–327, 340, 358, 373.5 nm. ^{29}Si NMR (DMSO- d_6) δ (ppm) = -174.2.

Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl] diethoxysilanate: ^{13}C NMR (DMSO- d_6) δ (ppm) = 19.1 (CH₃), 52.0 (SiCH₂), 56.6 (OCH₂), 67.6 (ArCH₂), 129.3, 129.6, 130.3, 132.5 (C_{arom.}),

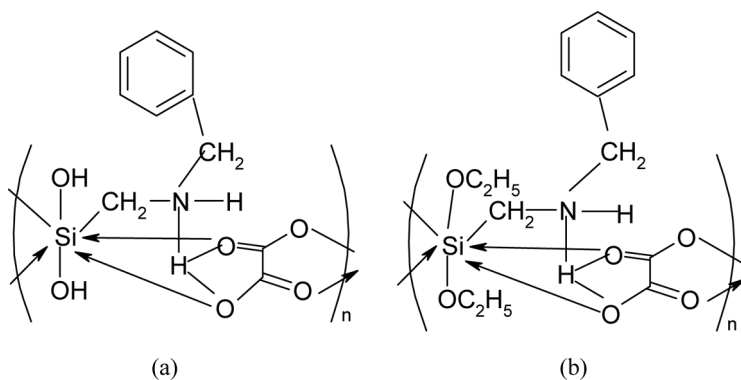


Figure 1. Structures of: (a) Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl]dihydroxysilanate}, and (b) Homo{O,O',O'',O'''-oxalic acid's Si-[N-benzylaminiomethyl]diethoxysilanate}.

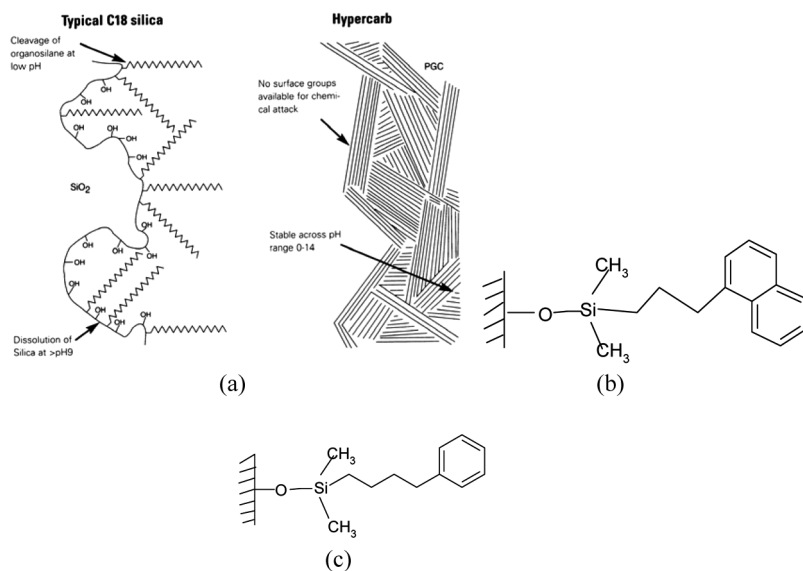


Figure 2. Scheme of chemically bonded stationary phases: (a) typical C₁₈ silica and Hypercarb (b) naphthylpropyl, (c) phenylbutyl.

160.2 (C=O). ¹H NMR, (DMSO-d₆).^[9] UV (DMSO): λ_{max} = 325.5, 326, 327, 374, 457.5 nm. ²⁹Si NMR (DMSO-d₆) δ (ppm) = -174.0.

Apparatus

¹H, ¹³C, ²⁹Si NMR spectra were recorded on a Varian Mercury 400 MHz in DMSO-d₆, with TMS as internal standard. The UV/Vis spectra were recorded on a spectrophotometer DU-68 (Beckman, USA).

Chromatographic measurements were performed on a liquid chromatograph SPD-6A (Shimadzu, Kyoto, Japan) equipped with a gradient pump LC-6A, UV detector, a sampling valve Rheodyne (Berkeley, CA,

Table 1. Characteristics of stationary bonded phase

Column name	Carbon (%)	Column dimensions (mm)	Manufacturer of column
Hypercarb	100	100 × 4.6	Thermo Electron Corporation
Naphthylpropyl	16.1	125 × 4.6	Home made
Phenylbutyl	14.9	125 × 4.6	Home made

USA), model 7125, with a 20 μL sample loop, and a Shimadzu C-R6 A data recorder. The obtained chromatogram was recorded by the use of OriginPro 7.5 program (OriginLab Corporation, Northampton, USA).

RESULTS AND DISCUSSION

In the case of this paper and the results of investigation presented here, we can use a word precursor, because the chemical literature did not report the chromatography of heptacoordinated ES-silanates, so-called Hoszczawa-silanates. Moreover, because of various possibilities of the application of hypercoordinated compounds, attempts were made to elaborate optimum conditions of chromatographic separation and determination of two newly obtained Hoszczawa-silanates. Investigations concern: Homo{O,O',O'',O'''-oxalic acid's Si[N- benzylaminiomethyl]dihydroxysilane} and Homo{O,O',O'',O'''-oxalic acid's Si[N- benzylaminiomethyl] diethoxysilane}.

The obtained data are collected in Table 2. The work is a continuation of earlier researches concerning optimization of the process of separation and determination of numerous new Hoszczawa-silanates.^[12,13]

Two mobile phases (acetonitrile and dichloromethane) in different flow intensity and three stationary phases (naphthylpropyl, phenylbutyl

Table 2. Chosen dependence k' for ES.1 and ES.2 from on type of stationary and mobile phase. Chromatographic conditions: flow -1.0 or 0.5 Ml min^{-1} , wavelength -326 nm , temperature -20°C

Type of stationary phase	^a Mobile phase/	k'_1	k'_2	$\alpha = k'_2/k'_1$
PGC	Acetonitrile/1.0	0.26	2.52	9.69
	Acetonitrile/0.5	0.83	5.61	6.76
	Dichlormethane/1.0	0.27	2.47	9.15
	Dichlormethane/0.5	0.85	5.56	6.54
RP Si-NAF	Acetonitrile/1.0	0.47	0.58	1.23
	Acetonitrile/0.5	2.15	2.18	1.01
	Dichlormethane/1.0	0.49	0.57	1.16
	Dichlormethane/0.5	2.16	2.20	1.02
RP Si-FB	Acetonitrile/1.0	0.37	3.40	9.19
	Acetonitrile/0.5	2.11	8.14	3.86
	Dichlormethane/1.0	0.47	3.47	7.38
	Dichlormethane/0.5	2.18	8.34	3.83

^aIn the Table are presented only optimum data of separation of the analyzed derivatives.

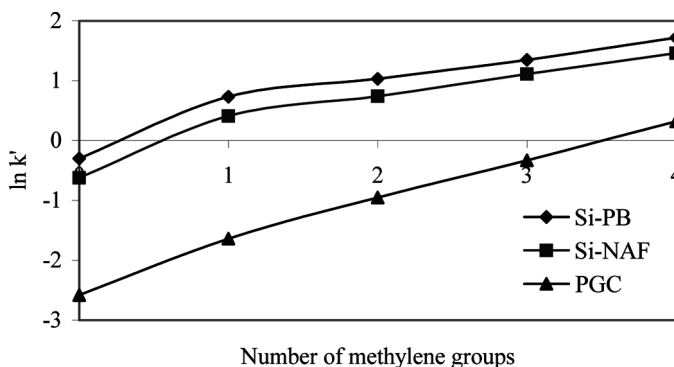


Figure 3. Dependence $\ln k'$ on the number of carbon atoms in alkyl chain of alkyl-benzenes for phenylbutyl, naphthylpropyl and Hypercarb packing. Chromatographic conditions: mobile phase 75/25 vol.% acetonitrile/water, flow – 0.5 mL min^{-1} , wavelength – 254 nm, temperature – 20°C.

and commercial, Hypercarb) were tested during the research. Good selectivity and high separation factor for the mobile phases: acetonitrile (100%) and dichloromethane (100%) were achieved.

The investigated stationary phases have different structures and strengths of interaction with the analyzed compounds. Phenylbutyl and naphthylpropyl phases are characterized by the presence of an aromatic ring. On the other hand, Hypercarb consists of porous graphitized coal. Phases of this type are destined, first of all, to π electrons containing compounds.^[15–17] Then, in the chromatographic process interactions of π – π type are dominating (Figure 3). Owing to these interactions, very high selectivity, a high separation factor, and significantly shorten retention times of analyzed compounds were achieved in numerous determinations.

The use of stationary phases: phenylbutyl and Hypercarb and the mobile phase's acetonitrile (100%) and dichloromethane (100%) enabled achievement of good separation already at flow 1 mL \cdot min $^{-1}$. Retention times were 4.84 and 7.94, respectively. However, the naphthylpropyl phase yielded poorer results. Neither acetonitrile nor dichloromethane allowed obtaining proper separation at flow 1 mL \cdot min $^{-1}$ or 0.5 mL \cdot min $^{-1}$. Only at flow 0.3 mL \cdot min $^{-1}$ of acetonitrile (100%) was the separation satisfactory. Retention times of analyzed derivatives were 11.92 and 13.85, respectively (Figs. 4–6, Table 2).

The best effects of separation of analyzed compounds are shown in Figures 4–6, whereas optimum conditions of separation of Homo{O,O',O'',O'''-oxalic acid's Si[N- benzylaminomethyl]dihydroxysilanate} and Homo{O,O',O'',O'''-oxalic acid's Si[N- benzylaminomethyl]diethoxysilanate} are reported in Table 2.

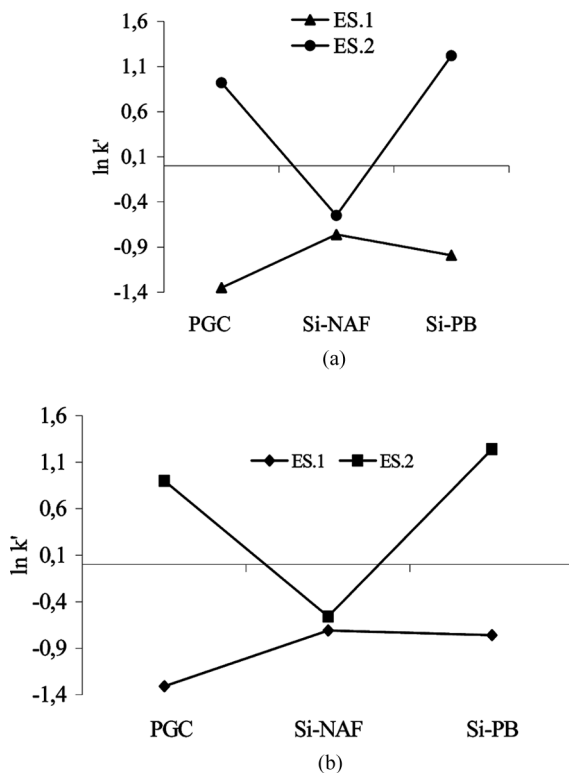


Figure 4. Effect of the separation of ES.1 and ES.2 with the use of stationary phases PGC, RP Si-NAF and RP Si-PB. Mobile phase: (a) acetonitrile (vol.100%), flow rate: 1.0 ml min^{-1} , (b) dichloromethane (vol.100%), flow rate: $1.0 \text{ mL} \cdot \text{min}^{-1}$, detection – 326 nm (see Table 2).

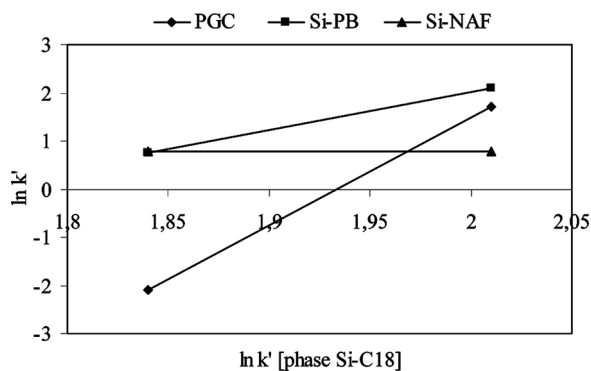


Figure 5. Dependence of $\ln k'$ of the RP Si-C₈ and RP Si-PB phases on $\ln k'$ obtained for the octadecyl phase for ES.1 and ES.2.

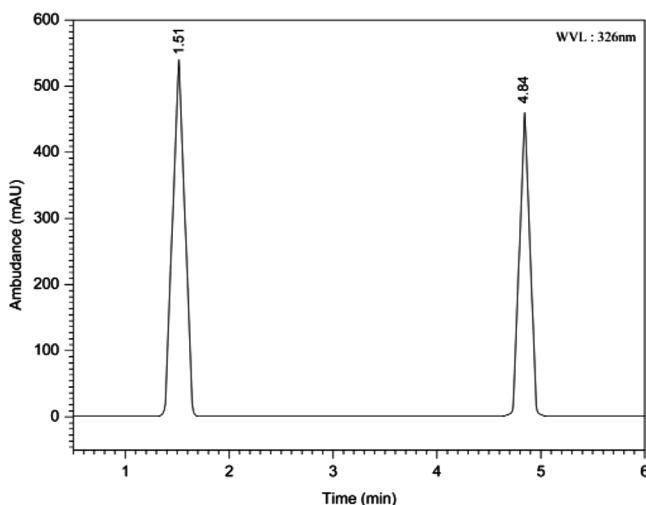


Figure 6. A chromatogram of separation of the Homo{O,O',O'',O'''}-oxalic acid's Si-[N-benzylaminomethyl]dihydroxysilanate (1.51 min) and Homo{O,O',O'',O'''}-oxalic acid's Si-[N-benzylaminomethyl]diethoxysilanate (4.84 min) on the stationary RP Si-PB phase. Mobile phase: acetonitrile (100 vol. %), flow – 1 mL min⁻¹, wavelength – 326 nm, temperature – 20°C.

To recapitulate, the highest selectivity in case of analyzed derivatives: Homo{O,O',O'',O'''}-oxalic acid's Si[N- benzylaminomethyl] dihydroxysilanate} and Homo{O,O',O'',O'''}-oxalic acid's Si[N-benzylaminomethyl]diethoxysilanate}, was shown by the commercial stationary phase – Hypercarb. However, shorter retention times (less than 5 min), a good separation factor, and proper selectivity was achieved by means of the phenylbutyl column. Therefore, the chromatography performed using the phenylbutyl column is reported here as a proper final effect of separation (Figure 6). The structures of analytes after analysis were examined again. They answered the initial structures of analyzed relationships.

CONCLUSIONS

Analyzed Hoszczawa-silanates: Homo{O,O',O'',O'''}-oxalic acid's Si[N-benzylaminomethyl]dihydroxysilanate} and Homo{O,O',O'',O'''}-oxalic acid's Si[N- benzylaminomethyl]diethoxysilanate} can be determined using as stationary phase: commercial phase Hypercarb, phenylbutyl phase, and naphthylpropyl phase. As the mobile phase, acetonitrile as

well as dichloromethane can be used. The highest separation factor (α) was obtained using the mobile phase acetonitrile.

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