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Correlations between HPLC and NMR Properties of Some Selected Alkyl Bonded Phases

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Reversed-phase HPLC
Solid state NMR
Surface characterization

1 Introduction
The silica alkyl bonded phases (SAP's) popular in HPLC encounter a number of problems in practice. The surface properties of SAP's are determined by source of the silica, the modifying reagent, the reaction conditions, etc., and are at least partly responsible for instances of non-reproducible capacity ratios \((k')\), selectivity \((r)\), and efficiency \((N)\) found with several SAP's. Differences in behavior are observed between products from several sources, as well as batch to batch from one manufacturer. Packing, aging processes, and stability of columns cause problems in practice. Pertinent investigations are published regularly [1-4]. This state of affairs motivated our group to start an investigation into the subject in 1976 [5]; surface studies were done by the mull IR technique. The availability of CP-MAS-NMR prompted us to undertake further studies.

Recently, information has been published regarding the characterization of silica-attached system by \(^{29}\)Si-and \(^{13}\)CP-MAS-NMR [6-11]. It was shown that a number of structural features of SAP-binding can be deduced from \(^{29}\)Si and \(^{13}\)C chemical shifts [7,8,10]. Although quantitative interpretation of CP-MAS-NMR spectra is notoriously difficult [6], it was shown that some of the problems can be overcome [9]. Here, preliminary solid-state NMR results of eight SAP's are correlated with HPLC properties (Table 1).

Table 1
Survey of packing materials (SAP's) under investigation

<table>
<thead>
<tr>
<th>SAP number</th>
<th>Name</th>
<th>Batch</th>
<th>Mean particle size</th>
<th>Specific area m²/g</th>
<th>% Carbon load</th>
<th>Endcapping</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Nucleosil C-8</td>
<td>2111</td>
<td>10</td>
<td>300</td>
<td>11</td>
<td>no</td>
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<tr>
<td>2</td>
<td>Polygosil C-8</td>
<td>9091</td>
<td>10</td>
<td>500</td>
<td>8.5</td>
<td>no</td>
</tr>
<tr>
<td>3</td>
<td>CP-Spher C-8</td>
<td>E-68</td>
<td>7.5</td>
<td>325</td>
<td>11</td>
<td>yes</td>
</tr>
<tr>
<td>4</td>
<td>LiChrosorb RP-8</td>
<td>1417</td>
<td>10</td>
<td>250</td>
<td>12</td>
<td>no</td>
</tr>
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<td>LiChrosorb RP-8</td>
<td>1459</td>
<td>10</td>
<td>250</td>
<td>12</td>
<td>no</td>
</tr>
<tr>
<td>6</td>
<td>LiChrosorb RP-18</td>
<td>2406</td>
<td>10</td>
<td>250</td>
<td>19.5</td>
<td>no</td>
</tr>
<tr>
<td>7</td>
<td>CP-Spher C-18</td>
<td>077</td>
<td>7.5</td>
<td>325</td>
<td>16</td>
<td>no</td>
</tr>
<tr>
<td>8</td>
<td>Hypersil ODS</td>
<td>9/1042</td>
<td>5</td>
<td>170</td>
<td>9.5</td>
<td>yes</td>
</tr>
</tbody>
</table>

2 Experimental
Chromatographic test conditions: columns 25 cm × 0.46 cm internal diameter; flow rate 1 ml/min; injections 1 µl; detection 254 nm, 0.04 aufs.

Each column was tested three times:
Exp. 1: eluent MeOH/H₂O = 60 : 40 v/v; test mixture (a) consisting of phenol, p-cresol, anisol, 2,5-dimethylaniline, ethyl benzoate, and toluene in MeOH.
Exp. 2: eluent, anhydrous n-hexane; test mixture (b) consisting of 1-octene (dead time) and nitrobenzene in n-hexane.
Exp. 3: same as exp. 1. The \(k'\) values and selectivities were calculated from the chromatograms.

Between experiment 1 and 2, the columns were flushed with 100 ml anhydrous MeOH, 100 ml anhydrous 2-propanol, and 200 ml anhydrous hexane. Between experiment 2 and 3 the same program was used in reversed mode.

CP-MAS-NMR spectra were run on a Bruker CXP-300 spectrometer at 75.48 MHz for \(^{13}\)C and 58.63 MHz for \(^{29}\)Si. Proton \(\pi/2\) pulses of 3 µs were used throughout. Contact times were 5 ms.
Short Communications

(13C) and 4 ms (29Si), decoupling times were 50 ms (13C) and 10 ms (29Si), while 1 s repetition times were used in both cases. Computer resolution was 4.9 Hz, chemical shifts were referred to TMS. Samples were spun in Andrew-type Delrin rotors at 4 kHz.

3 Results and Discussion

At constant eluent composition, k' values will contain information about solute-surface interaction of the SAP's. The k' values of test mixture (a) were corrected for differences in specific area, % carbon load of the SAP's. The result is a consequent sequence of k' values for the C-8 SAP's (Table 2a). To get information about the residual silanol groups, k' values of nitrobenzene were determined in experiment 2 (Table 2b).

Table 2

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
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<tr>
<td>2</td>
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<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
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</tr>
</tbody>
</table>

(detailed assignments have to await the availability of appropriate model compounds [8]. The presence of -OCH3 groups was detected with 13C NMR. Distinction of type 1 from end-capping (with HMDS) is possible by 29Si NMR chemical shifts. From the ratios of integrated intensities of the signals in the 29Si NMR spectra, sequences of coverage (29Si signal from silane divided by the total 29Si signal) and residual silanol groups (29Si signal near -102 ppm divided by the total 29Si signal) were deduced. Typical test chromatograms of SAP's 1 and 5 are shown in Figure 2.

According to reversed-phase retention theory, k' values depend on ligand mass and silanols exposed to solutes. The k' values of nitrobenzene are assumed to provide information about the residual silanols, as do the k' values of apolar toluene about the ligand mass. The k' values of both nitrobenzene and toluene for each SAP were normalized to SAP no. 3. These two values correspond to the relative amount of residual silanols and the ligand mass of the SAP's, respectively. From these values the amount of ligand was calculated according to eq. (1).

Ligand coverage = \[ \frac{L}{S + L} \]  

where:

S = relative residual silanols calculated from k' nitrobenzene for SAP i
L = relative ligand mass calculated from k' toluene for SAP i

A number of interesting correlations were observed. The sequence of concentrations of residual silanol groups correspond well (one to one) with the order of k' values of nitrobenzene in hexane (Table 2b, c). Moreover, there is approximate agreement between the ligand coverage (determined by NMR and HPLC independently, vide supra) and the k' values of the test compounds in methanol/water (Table 2a, d, e). The same is true.
to be correlated with a low residual silanol coverage, for C8 as well as for C18. Finally, the nature of silane surface bonding seems to play only a minor role in connection with the present results. Possible effects could, however, very well be masked by a dominating influence of either residual silanol or silane coverage.

In experiment 3, behavior of the column differing from experiment 1 was observed with respect to $k'$ values, plate height, and peak symmetry. A lack of any systematic trend in these deviations merits further investigation.

Future research in these laboratories will include, inter alia:

- Influence of organic modifiers on surface properties.
- Improvement of qualitative and quantitative CP-MAS-NMR aspects.
- Study of aging and packing processes.
- Relation between surface morphology and retention; selectivity behavior.

Figures 2

Typical test chromatograms; see Experimental for conditions.

1 = phenol; 2 = p-cresol; 3 = anisole; 4 = 2,5-dimethylaniline; 5 = ethyl benzoate; 6 = toluene.

for relative selectivities taking CP-Spher C8 as a standard. When comparing C8 and C18 on the same silica base (i.e., LiChrosorb and CP-Spher) the latter contains more residual silanol groups and less silanes. Asymmetric LC peaks for 2,5-dimethylaniline appear

References


MS received: May 5, 1983