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SELECTIVITY RELATED TO CARBON LOADING AND END-CAPPING OF OCTADECYL-BONDED SILICA GELS IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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SUMMARY

Four types of octadecyl-bonded silica gel were synthesized from the same silica gel and their chromatographic properties were examined by studying the retention behaviour of *n*-alkanes, alkylbenzenes, alkyl alcohols, halogenated benzenes and polyaromatic hydrocarbons. The packings were high-carbon (HIC)-loaded packings with and without end-capping (HIC-ODS-E and HIC-ODS-NE) and low-carbon (LOC)-loaded packings with and without end-capping (LOC-ODS-E and LOC-ODS-NE). Although the capacity ratios measured on the two LOC-ODS were smaller than those obtained on the two HIC-ODS, the retention behaviour of compounds on LOC-ODS-E was similar to that on HIC-ODS, including two other ODS packings (Hypersil ODS and Develosil ODS).

The π -energy effect, defined as the influence of double bonds of solutes on the retention, calculated for polyaromatic hydrocarbons and alkylbenzenes was almost the same on all these packings. The energy effect of these hydrophobic compounds measured on LOC-ODS-NE was slightly different from that on the two HIC-ODS. LOC-ODS-E showed a small selectivity difference in the retention of aromatic and aliphatic compounds. LOC-ODS-NE showed a greater selectivity difference than others, but its lack of stability made it unsuitable for chromatographic purposes.

INTRODUCTION

As alkyl-bonded silica gels are widely used in reversed-phase liquid chromatography (RPLC), their structure and properties and the retention mechanism of the alkyl groups have attracted considerable attention. The solvophobic interaction model proposed by Horváth *et al.*¹ indicates that a solute with more or less hydrophobicity is excluded from an aqueous eluent and is adsorbed on a non-polar alkyl-bonded stationary phase. However, this theory is still inadequate to explain the selectivity differences of stationary phases with hydrocarbon ligands having different chain lengths^{2,3} and the differences in chromatographic behaviour between octadecyl- and phenyl-bonded silica gels⁴.

TABLE I
 PHYSICAL PARAMETERS AND LOGARITHM OF CAPACITY RATIOS OF STANDARD COMPOUNDS ON LOC-ODS-E

No.	Compound	VWV* (cm ³ /mol)	DLE**	log k'	Concentration of acetonitrile in water (%)			ΔE***	ΔE [§]	ΔE ^{§§}
					90	80	70			
1	Benzene	48.36	2.000	-0.5489	-0.2268	0.0313	0.2665	1.902	1.856	1.948
2	Naphthalene	73.96	3.683	-0.3885	-0.0618	0.2341	0.5049	3.776	3.893	3.874
3	Biphenyl	90.08	4.383	-0.3265	0.0244	0.3466	0.6530	5.235	5.693	5.625
4	Fluorene	93.22	4.750	-0.2723	0.0700	0.3908	0.6962	5.141	5.375	5.285
5	Phenanthrene	99.56	5.448	-0.2255	0.1144	0.4780	0.7484	5.588	5.789	5.708
6	Anthracene	99.56	5.314	-0.2025	0.1394	0.4631	0.7825	5.248	5.387	4.513
7	Pyrene	109.04	6.506	-0.0917	0.2416	0.5672	0.8892	5.451	5.351	5.414
8	Chrysene	125.16	7.190	-0.0424	0.3169	0.6801	1.0162	7.057	7.289	7.413
9	Tetraphene	125.16	-	-0.0305	0.3274	0.6941	1.0319	6.891	-	-
10	3,4-Benzopyrene	134.64	-	0.1094	0.4673	0.8368	1.1861	6.617	6.488	6.226
11	Toluene	59.51	2.150	-0.4546	-0.1256	0.1489	0.3978	2.364	2.303	2.322
12	Ethylbenzene	69.74	-	-0.3637	-0.0376	0.2579	0.5271	2.758	2.752	2.755
13	Isopropylbenzene	77.02	-	-0.2994	0.0415	0.3623	0.6395	2.875	2.878	2.879
14	Propylbenzene	79.97	-	-0.2685	0.0718	0.3940	0.6672	2.965	2.927	2.900
15	Butylbenzene	90.20	-	-0.1724	0.1792	0.5254	0.8280	3.134	3.092	3.061
16	Hexylbenzene	110.66	-	0.0188	0.4065	0.7986	1.1335	3.448	3.336	3.312
17	Heptylbenzene	120.89	-	0.1210	0.5234	0.9560	1.3279	3.429	3.385	3.365
18	Octylbenzene	131.12	-	0.2193	0.6461	1.0862	-	3.583	3.478	3.489
19	Nonylbenzene	141.35	-	0.3178	0.7668	1.2334	-	3.655	3.453	-
20	Decylbenzene	151.58	-	0.4174	0.8941	-	-	3.702	3.655	-
21	Chlorobenzene	57.84	2.050	-0.4468	-0.1297	0.1574	0.3996	2.034	2.194	2.153
22	1,2-Dichlorobenzene	67.32	-	-0.3582	-0.0338	0.2466	0.5187	2.368	2.343	2.378

23	1,3-Dichlorobenzene	67.32	-	-0.3197	0.0034	0.3074	0.5678	1.785	1.608	1.678
24	1,4-Dichlorobenzene	67.32	-	-0.3538	-0.0229	0.2861	0.5471	2.135	2.100	2.043
25	1,2,4-Trichlorobenzene	76.80	-	-0.2201	0.1044	0.4239	0.6999	1.946	1.763	1.747
26	1,3,5-Trichlorobenzene	76.80	-	-0.1821	0.1579	0.4803	0.7599	1.298	0.834	0.763
27	1,2,3,4-Tetrachlorobenzene	86.28	-	-0.1325	0.2063	0.5359	0.8243	2.187	1.924	1.897
28	1,2,3,5-Tetrachlorobenzene	86.28	-	-0.1068	0.2391	0.5746	0.8669	1.756	1.217	1.248
29	1,2,4,5-Tetrachlorobenzene	86.28	-	-0.1203	0.2259	0.5612	0.8531	1.931	1.451	1.259
30	Pentachlorobenzene	95.76	-	-0.0729	0.3367	0.6874	0.9966	2.014	1.212	1.230
31	Hexachlorobenzene	105.24	-	-0.0278	0.4446	0.8134	1.1381	2.122	1.157	1.084
32	Bromobenzene	60.96	-	-0.4262	-0.0968	0.1896	0.4373	2.175	2.205	2.161
33	Iodobenzene	65.48	-	-0.3798	-0.0459	0.2489	0.5044	2.228	2.241	2.180
34	Butyl alcohol	52.40	-	-0.8125	-0.5606	-0.3950	-0.2336	7.262	7.493	7.359
35	Pentyl alcohol	62.63	-	-0.7092	-0.4602	-0.2787	-0.0967	7.522	7.861	7.569
36	Hexyl alcohol	72.86	-	-0.6060	-0.3674	-0.1535	0.0431	7.780	8.174	7.758
37	Heptyl alcohol	83.09	-	-0.5032	-0.2521	-0.0246	0.1850	7.942	8.211	7.884
38	Octyl alcohol	93.32	-	-0.3986	-0.1425	0.1027	0.3327	8.110	8.407	7.990
39	Decyl alcohol	113.78	-	-0.1938	0.0838	0.3609	0.6386	8.405	8.609	8.093
40	Dodecyl alcohol	134.24	-	0.0108	0.3192	0.6414	0.9595	8.574	8.855	8.086
41	Pentane	58.03	-	-0.1784	0.1356	0.4249	0.7105	-	-	-
42	Hexane	68.26	-	-0.0746	0.2536	0.5684	0.8740	-	-	-
43	Heptane	78.49	-	0.0316	0.3756	0.7163	1.0428	-	-	-
44	Octane	88.72	-	0.1436	0.5003	0.8682	1.2147	-	-	-
45	Decane	109.18	-	0.3545	0.7536	1.1733	-	-	-	-
46	Dodecane	129.64	-	0.5539	1.0123	-	-	-	-	-

* Van der Waal's volume, calculated by Bondi's method¹².

** Delocalization energy, from ref. 11.

*** Energy effect (ΔE) was measured on LOC-ODS-E (15 cm \times 4.6 mm I.D.) at 30°C.

§ Energy effect obtained on Hypersil ODS, from ref. 9.

§§ Energy effect obtained on Develosil ODS, from ref. 9.

The prediction of the retention times of solutes is very important. Experimental data have been correlated with topological and physico-chemical parameters of solutes in order to predict their chromatographic behaviour, such as molecular connectivity⁵, Hansch's π constant⁶, Hammett's σ constant⁷ and Rekker's hydrophobic fragmental constant ($\log P$)⁸. However, the energy and enthalpy effects and the Van der Waal's volumes of solutes were found to play an important role in the retention of solutes with different polarity^{9,10}. In this work, we investigated the retention behaviour of hydrophobic compounds, including *n*-alkanes, alkylbenzenes, alkyl alcohols, halogenated benzenes and polyaromatic hydrocarbons, on different types of octadecyl-bonded silica gels and considered the influence of carbon content and the presence or absence of end capping of the gels on retention.

The capacity ratios of these compounds were first measured in mixtures of acetonitrile and water to calculate the energy effect. The energy effect on a compound is defined as the difference in retention between *n*-alkanes and the compound. This difference, $\Delta \log k'$, is related to the delocalization energy of polyaromatic hydrocarbons¹¹. The energy effects obtained on different ODS packings were compared in order to explain the selectivity differences between these packings in RPLC. The capacity ratios of these compounds were also measured at different temperatures to study the effect of enthalpy on their retention.

EXPERIMENTAL

The instruments included a Model 576 HPLC pump from Gasukuro Kogyo (Tokyo, Japan), an SIC Chromatocorder recorder from Gasukuro Kogyo, a 502T spectral detector (operated at 220 nm) from Gasukuro Kogyo and a column (150 mm \times 4.6 mm I.D.) packed with different carbon-loaded 5- μ m octadecyl-bonded silica gels from Gasukuro Kogyo. The column was thermostated at 20–50°C, the temperature being controlled by a circulator and water-bath. An ERC Model 7510 refractive index detector from ERMA Inc. (Tokyo, Japan) was used for non-UV absorbing solutes. The degasser was an ERC Model 3310 from ERMA Inc. The eluent consisted of acetonitrile in water ranging in concentration from 60 to 90%. The test compounds and their physical parameters are given in Table I. The column void volume, V_0 , was determined from the elution volume of fructose for each eluent and at each temperature. All measurements were made in duplicate. The Van der Waal's volume of the solutes was calculated by Bondi's method¹².

RESULTS AND DISCUSSION

The capacity ratios of solutes measured on an end-capped LOC-ODS-E (8.9 wt.-% C) for mixtures of acetonitrile and water and their physical parameters are listed in Table I. The capacity ratios measured on a non-end-capped LOC-ODS-NE (8.9 wt.-% C), HIC-ODS-E (16 wt.-% C) and HIC-ODS-NE (16 wt.-% C) are given in Tables II–IV, respectively.

The capacity ratios of these compounds on HIC-ODS-E were about 40% larger than those obtained on LOC-ODS-E. The difference was not simply related to the carbon content of these packings, although the surface area of their silica gel was the same, *i.e.*, about 300 m²/g. The correlation coefficient (r) of the $\log k'$ values

TABLE II
 PHYSICAL PARAMETERS AND LOGARITHM OF CAPACITY RATIOS OF STANDARD COMPOUNDS
 ON LOC-ODS-NE

No.	Compound	VWV* (cm ³ /mol)	DLE**	log k'			ΔE ***
				Concentration of acetonitrile in water (%)			
				80	70	60	
1	Benzene	48.36	2.000	-0.6343	-0.3699	-0.1266	1.907
2	Naphthalene	73.96	3.683	-0.4569	-0.2036	0.0660	3.767
3	Biphenyl	90.08	4.383	-0.4311	-0.1309	0.1495	6.233
4	Fluorene	93.22	4.750	-0.3746	-0.0835	0.1933	5.816
5	Phenanthrene	99.56	5.448	-0.3161	-0.0180	0.2619	5.853
6	Anthracene	99.56	5.314	-0.2931	0.0033	0.2769	5.394
7	Pyrene	109.04	6.506	-0.1530	0.1070	0.3875	4.829
8	Chrysene	125.16	7.190	-0.0938	0.1874	0.4914	6.795
9	Tetraphene	125.16	—	-0.0906	0.1916	0.5035	6.671
10	3,4-Benzopyrene	134.64	—	0.0452	0.3410	0.6490	5.658
11	Toluene	59.51	2.150	-0.5516	-0.2844	-0.0260	2.485
12	Ethylbenzene	69.74	—	-0.4793	-0.2103	0.0578	3.128
13	Isopropylbenzene	77.02	—	-0.4384	-0.1489	0.1308	3.565
14	Propylbenzene	79.97	—	-0.4085	-0.1240	0.1597	3.607
15	Butylbenzene	90.20	—	-0.3216	-0.0347	0.2666	3.877
16	Hexylbenzene	110.66	—	-0.1450	0.1535	0.4847	4.298
17	Heptylbenzene	120.89	—	-0.0548	0.2529	0.6029	4.405
18	Octylbenzene	131.12	—	0.0180	0.3555	0.7267	4.643
19	Nonylbenzene	141.35	—	0.1290	0.4513	0.8395	4.589
20	Decylbenzene	151.58	—	0.2025	0.5516	0.9741	4.779
21	Chlorobenzene	57.84	2.050	-0.5578	-0.3033	-0.0130	2.234
22	1,2-Dichlorobenzene	67.32	—	-0.4522	-0.2081	0.0815	2.165
23	1,3-Dichlorobenzene	67.32	—	-0.4286	-0.1833	0.1069	1.622
24	1,4-Dichlorobenzene	67.32	—	-0.4607	-0.2140	0.0894	2.252
25	1,2,4-Trichlorobenzene	76.80	—	-0.3366	-0.0962	0.2082	1.711
26	1,3,5-Trichlorobenzene	76.80	—	-0.2945	-0.0556	0.2498	0.787
27	1,2,3,4-Tetrachlorobenzene	86.28	—	-0.2548	0.0003	0.3112	1.833
28	1,2,3,5-Tetrachlorobenzene	86.28	—	-0.2359	0.0223	0.3373	1.354
29	1,2,4,5-Tetrachlorobenzene	86.28	—	-0.2519	0.0080	0.3258	1.676
30	Pentachlorobenzene	95.76	—	-0.1533	0.1055	0.4305	1.610
31	Hexachlorobenzene	105.24	—	-0.0455	0.1828	0.5366	1.580
32	Bromobenzene	60.96	—	-0.5481	-0.3037	0.0143	2.705
33	Iodobenzene	65.48	—	-0.4408	-0.2517	0.0652	2.012
34	Butyl alcohol	52.40	—	-0.8199	-0.6033	-0.4185	7.825
35	Pentyl alcohol	62.63	—	-0.7550	-0.5124	-0.3094	8.297
36	Hexyl alcohol	72.86	—	-0.6767	-0.4201	-0.1960	8.601
37	Heptyl alcohol	83.09	—	-0.5837	-0.3310	-0.0821	8.772
38	Octyl alcohol	93.32	—	-0.4847	-0.2320	0.0384	8.782
39	Decyl alcohol	113.78	—	-0.2866	-0.0236	0.2772	8.737
40	Dodecyl alcohol	134.24	—	-0.0731	0.1945	0.5348	8.372
41	Pentane	58.03	—	-0.3922	-0.1280	0.1822	—
42	Hexane	68.26	—	-0.3031	-0.0282	0.2906	—
43	Heptane	78.49	—	-0.2318	0.0759	0.4130	—
44	Octane	88.72	—	-0.1378	0.1794	0.5367	—
45	Decane	109.18	—	0.0543	0.4012	0.8008	—
46	Dodecane	129.64	—	0.2456	0.6242	1.0648	—

* Van der Waal's volume, calculated by Bondi's method¹².

** Delocalization energy, from ref. 11.

*** Energy effect (ΔE) was measured on LOC-ODS-NE (15 cm × 4.6 mm I.D.) at 30°C.

TABLE III
 PHYSICAL PARAMETERS AND LOGARITHM OF CAPACITY RATIOS OF STANDARD COMPOUNDS ON HIC-ODS-E

No.	Compound	VWV* (cm ³ /mol)	DLE**	log k'	Concentration of acetonitrile in water (%)			ΔE^{***}
					90	80	70	
					60	70	80	
1	Benzene	48.36	2.000	-0.2638	-0.0181	0.2123	0.4237	1.857
2	Naphthalene	73.96	3.683	-0.0726	0.2047	0.4532	0.7136	3.919
3	Biphenyl	90.08	4.383	0.0033	0.3004	0.5856	0.8794	5.594
4	Fluorene	93.22	4.750	0.0701	0.3714	0.6507	0.9454	5.396
5	Phenanthrene	99.56	5.448	0.1240	0.4271	0.7096	1.0099	5.906
6	Anthracene	99.56	5.314	0.1540	0.4532	0.7513	1.0521	5.501
7	Pyrene	109.04	6.506	0.2832	0.5865	0.8808	1.1912	5.726
8	Chrysene	125.16	7.190	0.3498	0.6827	1.0017	1.3425	7.503
9	Tetraphene	125.16	-	0.3589	0.6909	1.0173	1.3633	7.348
10	3,4-Benzopyrene	134.64	-	0.5374	0.8810	1.2014	-	6.416
11	Toluene	59.51	2.150	-0.1397	0.1109	0.3567	0.5890	2.310
12	Ethylbenzene	69.74	-	-0.0441	0.2272	0.4886	0.7479	2.775
13	Isopropylbenzene	77.02	-	0.0398	0.3330	0.6058	0.8867	2.852
14	Propylbenzene	79.97	-	0.0777	0.3711	0.6477	0.9330	2.926
15	Butylbenzene	90.20	-	0.1942	0.4957	0.8112	1.1185	3.138
16	Hexylbenzene	110.66	-	0.4265	0.7816	1.1417	-	3.392
17	Heptylbenzene	120.89	-	0.5508	0.9400	1.3099	-	3.435
18	Octylbenzene	131.12	-	0.6743	1.0915	-	-	3.531
19	Nonylbenzene	141.35	-	0.8030	1.2446	-	-	3.555
20	Decylbenzene	151.58	-	0.9322	-	-	-	3.631
21	Chlorobenzene	57.84	2.050	-0.1622	0.0988	0.3528	0.5893	2.118

22	1,2-Dichlorobenzene	67.32	-	-0.0515	0.2314	0.4790	0.7383	2.386
23	1,3-Dichlorobenzene	67.32	-	-0.0032	0.2894	0.5415	0.8073	1.696
24	1,4-Dichlorobenzene	67.32	-	-0.0369	0.2526	0.5093	0.7715	2.103
25	1,2,4-Trichlorobenzene	76.80	-	0.1176	0.4210	0.6884	0.9733	1.832
26	1,3,5-Trichlorobenzene	76.80	-	0.1983	0.4911	0.7743	1.0645	0.872
27	1,2,3,4-Tetrachlorobenzene	86.28	-	0.2429	0.5494	0.8263	1.1261	2.022
28	1,2,3,5-Tetrachlorobenzene	86.28	-	0.2910	0.5986	0.8883	1.1932	1.365
29	1,2,4,5-Tetrachlorobenzene	86.28	-	0.2697	0.5818	0.8692	1.1706	1.600
30	Pentachlorobenzene	95.76	-	0.3983	0.7210	1.0325	1.3507	1.605
31	Hexachlorobenzene	105.24	-	0.5197	0.8580	1.1869	-	1.603
32	Bromobenzene	60.96	-	-0.1092	0.1429	0.3906	0.6340	2.169
33	Iodobenzene	65.48	-	-0.0431	0.2201	0.4695	0.7220	2.115
34	Butyl alcohol	52.40	-	-0.5681	-0.4552	-0.3084	-0.1846	7.996
35	Pentyl alcohol	62.63	-	-0.4600	-0.3298	-0.1718	-0.0236	8.374
36	Hexyl alcohol	72.86	-	-0.3496	-0.2037	-0.0281	0.1471	8.696
37	Heptyl alcohol	83.09	-	-0.2334	-0.0642	0.1270	0.3228	8.917
38	Octyl alcohol	93.32	-	-0.1166	0.0727	0.2826	0.5029	9.128
39	Decyl alcohol	113.78	-	0.1238	0.3578	0.6079	0.8761	9.423
40	Dodecyl alcohol	134.24	-	0.3711	0.6530	0.9456	1.2624	9.596
41	Pentane	58.03	-	0.1760	0.4659	0.7210	0.9972	-
42	Hexane	68.26	-	0.2981	0.6088	0.8955	1.1937	-
43	Heptane	78.49	-	0.4287	0.7652	1.0705	1.3986	-
44	Octane	88.72	-	0.5574	0.9189	1.2537	-	-
45	Decane	109.18	-	0.8204	1.2335	-	-	-
46	Dodecane	129.64	-	1.0913	-	-	-	-

* Van der Waal's volume, calculated by Bondi's method^{1,2}.

** Delocalization energy, from ref. 11.

*** Energy effect (ΔE) was measured on HIC-ODS-E (15 cm x 4.6 mm I.D.) at 30°C.

TABLE IV

PHYSICAL PARAMETERS AND LOGARITHM OF CAPACITY RATIOS OF STANDARD COMPOUNDS ON HIC-ODS-NE

No.	Compound	VWV* (cm ³ /mol)	DLE**	log k'			ΔE***
				Concentration of acetonitrile in water (%)			
				80	70	60	
1	Benzene	48.36	2.000	-0.0906	0.0970	0.3227	1.856
2	Naphthalene	73.96	3.683	0.1078	0.3180	0.5862	3.834
3	Biphenyl	90.08	4.383	0.1943	0.4276	0.7281	5.468
4	Fluorene	93.22	4.750	0.2588	0.4894	0.7897	5.273
5	Phenanthrene	99.56	5.448	0.3217	0.5534	0.8590	5.646
6	Anthracene	99.56	5.314	0.3511	0.5863	0.8970	5.233
7	Pyrene	109.04	6.506	0.4824	0.7160	1.0306	5.368
8	Chrysene	125.16	7.190	0.5705	0.8283	1.1718	6.985
9	Tetraphene	125.16	—	0.5767	0.8385	1.1873	6.857
10	3,4-Benzopyrene	134.64	—	0.7633	1.0239	1.3780	6.295
11	Toluene	59.51	2.150	0.0216	0.2217	0.4686	2.366
12	Ethylbenzene	69.74	—	0.1195	0.3324	0.6027	2.870
13	Isopropylbenzene	77.02	—	0.1995	0.4264	0.7177	3.046
14	Propylbenzene	79.97	—	0.2363	0.4637	0.7591	3.120
15	Butylbenzene	90.20	—	0.3543	0.5968	0.9173	3.350
16	Hexylbenzene	110.66	—	0.6014	0.8763	1.2447	3.664
17	Heptylbenzene	120.89	—	0.7315	1.0235	—	3.875
18	Octylbenzene	131.12	—	0.8635	1.1719	—	3.941
19	Nonylbenzene	141.35	—	0.9967	1.3225	—	3.985
20	Decylbenzene	151.58	—	1.1321	—	—	4.077
21	Chlorobenzene	57.84	2.050	0.0253	0.2258	0.4748	1.996
22	1,2-Dichlorobenzene	67.32	—	0.1411	0.3472	0.6114	2.225
23	1,3-Dichlorobenzene	67.32	—	0.1847	0.3943	0.6646	1.632
24	1,4-Dichlorobenzene	67.32	—	0.1498	0.3626	0.6353	2.032
25	1,2,4-Trichlorobenzene	76.80	—	0.3016	0.5211	0.8093	1.803
26	1,3,5-Trichlorobenzene	76.80	—	0.3689	0.5897	0.8827	0.936
27	1,2,3,4-Tetrachlorobenzene	86.28	—	0.4202	0.6461	0.9491	1.992
28	1,2,3,5-Tetrachlorobenzene	86.28	—	0.4615	0.6910	0.9987	1.432
29	1,2,4,5-Tetrachlorobenzene	86.28	—	0.4432	0.6739	0.9824	1.648
30	Pentachlorobenzene	95.76	—	0.5717	0.8122	1.1367	1.682
31	Hexachlorobenzene	105.24	—	0.6929	0.9458	1.2900	1.774
32	Bromobenzene	60.96	—	0.0649	0.2657	0.5193	2.067
33	Iodobenzene	65.48	—	0.1273	0.3337	0.5972	2.053
34	Butyl alcohol	52.40	—	-0.3712	-0.2762	-0.1376	7.157
35	Pentyl alcohol	62.63	—	-0.2627	-0.1495	0.0129	7.485
36	Hexyl alcohol	72.86	—	-0.1470	-0.0200	0.1682	7.752
37	Heptyl alcohol	83.09	—	-0.0194	0.1198	0.3295	7.899
38	Octyl alcohol	93.32	—	0.1075	0.2617	0.4942	8.027
39	Decyl alcohol	113.78	—	0.3735	0.5580	0.8361	8.131
40	Dodecyl alcohol	134.24	—	0.6502	0.8664	1.1914	8.084
41	Pentane	58.03	—	0.3033	0.5121	0.7971	—
42	Hexane	68.26	—	0.4328	0.6552	0.9637	—
43	Heptane	78.49	—	0.5683	0.8064	1.1383	—
44	Octane	88.72	—	0.7048	0.9586	1.3180	—
45	Decane	109.18	—	0.9779	1.2752	—	—
46	Dodecane	129.64	—	1.2615	—	—	—

* Van der Waal's volume, calculated by Bondi's method¹².

** Delocalization energy, from ref. 11.

*** Energy effect (ΔE) was measured on HIC-ODS-NE (15 cm × 4.6 mm I.D.) at 30°C.

of the above compounds, measured on LOC-ODS-E and HIC-ODS-E, was 0.9992 ($n = 41$).

The energy effect of the various compounds was obtained from the difference between the $\log k'$ values of n -alkanes and the compounds in relation to the delocalization energy of polyaromatic hydrocarbons. The calculated values of the energy effect are given in Tables I–IV. The r values of the energy effect (ΔE values), measured on LOC-ODS-E and HIC-ODS-E in 70 and 90% aqueous acetonitrile, were 0.9977 ($n = 37$) and 0.9961 ($n = 40$), respectively. This means that the retention mechanisms of these compounds on both LOC-ODS-E and HIC-ODS-E are similar, and the selectivity differences between these packings seems to be negligible.

However, the correlation of $\log k'$ values and ΔE values obtained on LOC-ODS-E and LOC-ODS-NE is poor. The correlation of $\log k'$ measured with 70% aqueous acetonitrile is 0.9778 ($n = 44$) and the correlation of ΔE measured with 70 and 80% aqueous acetonitrile is 0.9771 ($n = 39$) and 0.9329 ($n = 40$), respectively. The plot of ΔE values obtained on LOC-ODS-E against LOC-ODS-NE with 80% aqueous acetonitrile is shown in Fig. 1 and the plot of HIC-ODS-E against HIC-ODS-NE with 80% aqueous acetonitrile in Fig. 2.

The correlation of ΔE between LOC-ODS-E and HIC-ODS-NE is 0.9881 ($n = 40$) for 80% aqueous acetonitrile and 0.9924 ($n = 39$) for 70% aqueous acetonitrile and that between HIC-ODS-E and HIC-ODS-NE is 0.9864 ($n = 39$) and 0.9949 ($n = 37$) for 80 and 70% aqueous acetonitrile, respectively. This means that ODS-NE packings have some kinds of selectivity. It seems, moreover, that compounds with longer alkyl chains have a maximum energy effect, as shown in Fig. 1, especially for highly concentrated acetonitrile solution.

In general, the energy effect of biphenyl increased and those of pyrene and benzopyrene decreased with highly concentrated acetonitrile–water solutions; that of highly chlorinated benzenes followed the tendency with pyrene. In addition, increasing the alkyl chain length increased the value of the energy effect. However, a steric influence on the energy effect was found for LOC-ODS-NE. This phenomenon cannot be explained from known theory, and it may occur on other ODS packings with over 90% aqueous acetonitrile. The turning point of the energy effect may be related to a change in the retention mechanism from partition to adsorption. If this assumption is correct, the enthalpy must increase dramatically at this point. The work on enthalpy will be discussed further below.

Further, $\log k'$ values and the energy effect of these compounds, measured on two commercial ODS packings (Hypersil ODS and Develosil ODS), were obtained from ref. 9. Good correlations can be found between the $\log k'$ values obtained on LOC-ODS-E and these packings. The correlation coefficient of $\log k'$ was 0.9986 ($n = 41$) and 0.9977 ($n = 42$) for Hypersil ODS and Develosil ODS, respectively. The carbon content of LOC-ODS-E is about 8.9 wt.-% whereas Hypersil ODS contains about 14 wt.-% carbon. However, the difference in capacity ratios is about 25% compared with a 35% difference in carbon content, which indicates that there is no specific selectivity effect due to carbon loading. The correlation of the energy effect of these hydrophobic compounds between LOC-ODS-E and Hypersil ODS is 0.9954 ($n = 39$) and 0.9930 ($n = 37$) between LOC-ODS-E and Develosil ODS.

From the regression analysis of the energy effect, it seems that no obvious selectivity difference occurred due to the carbon loading of octadecyl-bonded silica

TABLE V
ENTHALPIES ($-\Delta H$) OBTAINED ON SEVERAL ODS-SILICA GELS

No.	Compound	VWV* (cm^3/mol)	$-\Delta H$ (kcal/mol)			
			LOC-ODS-E**	HIC-ODS-E**	HIC-ODS-NE**	Hypersil ODS***
1	Benzene	48.36	1.807	1.589	2.435	1.423
2	Naphthalene	73.96	1.996	2.110	2.651	1.882
3	Biphenyl	90.08	2.040	2.199	2.871	2.013
4	Fluorene	93.22	2.148	2.378	2.953	2.206
5	Phenanthrene	99.56	2.291	2.608	3.174	2.424
6	Anthracene	99.56	2.374	2.721	3.301	2.532
7	Pyrene	109.04	2.584	3.045	3.654	2.862
8	Chrysene	125.16	2.789	3.380	3.919	3.190
9	Tetraphene	125.16	2.815	3.398	3.923	—
10	3,4-Benzopyrene	134.64	3.231	3.987	4.588	3.742
11	Toluene	59.51	1.880	1.783	2.331	1.667
12	Ethylbenzene	69.74	1.911	1.916	2.426	1.801
13	Isopropylbenzene	77.02	1.985	2.055	2.539	1.919
14	Propylbenzene	79.97	2.048	2.172	2.642	2.044
15	Butylbenzene	90.20	2.203	2.383	2.871	2.348
16	Hexylbenzene	110.66	2.950	2.984	3.436	2.950
17	Heptylbenzene	120.89	2.835	3.400	3.766	3.302
18	Octylbenzene	131.12	3.110	3.719	4.052	3.673
19	Nonylbenzene	141.35	3.388	4.143	4.441	—
20	Decylbenzene	151.58	3.694	4.821	4.790	—
21	Chlorobenzene	57.84	1.884	1.798	2.349	1.656
22	1,2-Dichlorobenzene	67.32	1.965	2.013	2.546	1.868

23	1,3-Dichlorobenzene	67.32	1.990	2.078	2.554	1.937
24	1,4-Dichlorobenzene	67.32	1.895	2.094	2.573	1.930
25	1,2,4-Trichlorobenzene	76.80	2.097	2.282	2.757	2.166
26	1,3,5-Trichlorobenzene	76.80	2.094	2.282	2.798	2.192
27	1,2,3,4-Tetrachlorobenzene	86.28	2.260	2.513	3.021	2.330
28	1,2,3,5-Tetrachlorobenzene	86.28	2.207	2.471	2.966	2.358
29	1,2,4,5-Tetrachlorobenzene	86.28	2.201	2.492	2.965	2.371
30	Pentachlorobenzene	95.76	2.327	2.658	3.162	2.562
31	Hexachlorobenzene	105.24	2.443	2.841	3.303	2.780
32	Bromobenzene	60.96	1.914	1.896	2.304	1.687
33	Iodobenzene	65.48	1.993	1.979	2.566	1.848
34	Butyl alcohol	52.40	1.440	1.133	1.888	1.109
35	Pentyl alcohol	62.63	1.378	1.233	2.018	1.061
36	Hexyl alcohol	72.86	1.349	1.388	2.214	1.304
37	Heptyl alcohol	83.09	1.582	1.618	2.434	1.743
38	Octyl alcohol	93.32	1.616	1.818	2.718	2.026
39	Decyl alcohol	113.78	2.065	2.421	3.388	2.628
40	Dodecyl alcohol	134.24	2.544	3.129	4.184	3.388
41	Pentane	58.03	2.057	2.510	2.731	2.387
42	Hexane	68.26	2.250	2.776	3.021	2.716
43	Heptane	78.49	2.493	3.112	3.389	2.963
44	Octane	88.72	2.759	3.478	3.722	3.500
45	Decane	109.18	3.352	4.382	4.483	—
46	Dodecane	129.64	3.999	5.499	5.268	—

* Van der Waal's volume, calculated by Bondi's method¹².

** Enthalpy was measured with 80% aqueous acetonitrile at 20–50°C.

*** Enthalpy obtained with 80% aqueous acetonitrile as eluent, from ref. 13.

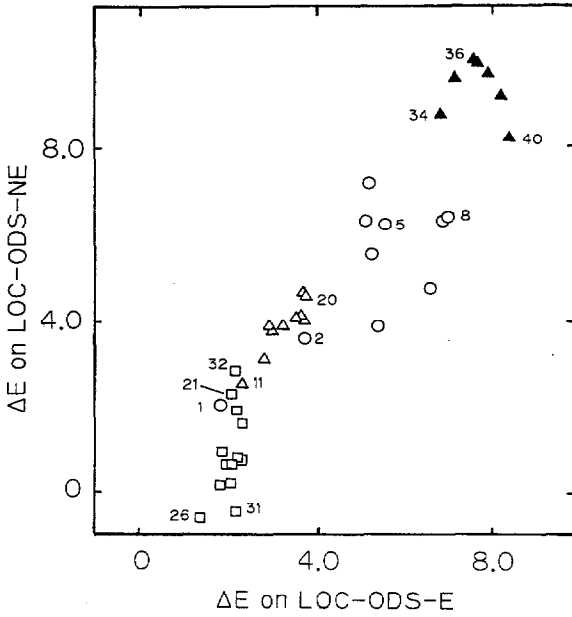


Fig. 1. Relationship between the energy effect (ΔE) of hydrophobic compounds on LOC-ODS-E and LOC-ODS-NE with 80% aqueous acetonitrile as eluent. Column temperature, 30°C. Each symbol indicates a group of compounds; the numbers beside the symbols are the same as in the tables. ○, Polyaromatic hydrocarbons; △, alkylbenzenes; □, halogenated benzenes; ▲, alkyl alcohols.

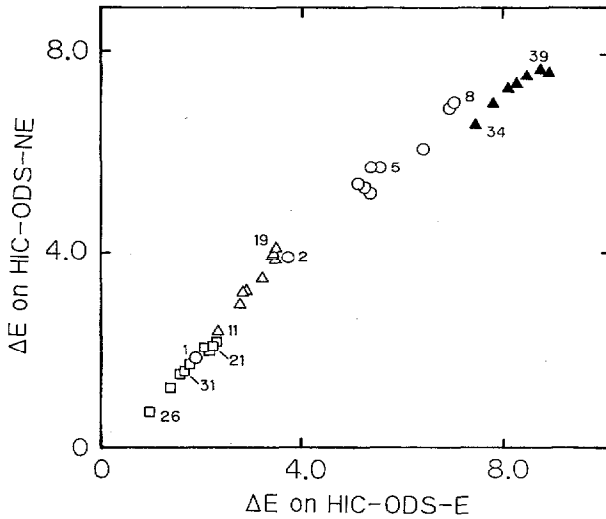


Fig. 2. Relationship between the energy effect (ΔE) of hydrophobic compounds on HIC-ODS-E and HIC-ODS-NE. Experimental conditions, symbols and numbers as in Fig. 1.

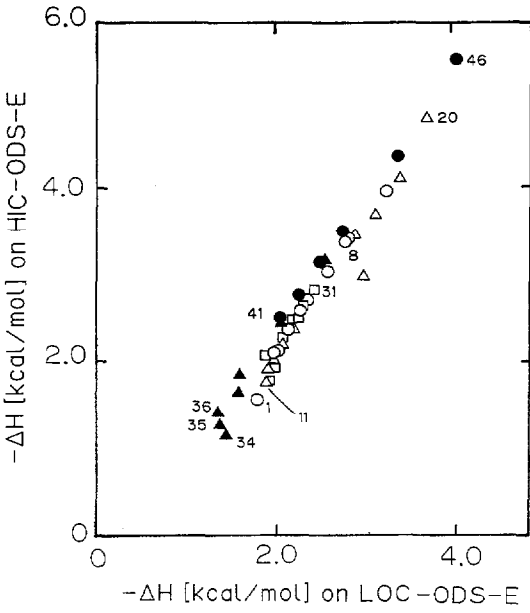


Fig. 3. Relationship between enthalpies ($-\Delta H$) of hydrophobic compounds on LOC-ODS-E and HIC-ODS-E with 80% aqueous acetonitrile as eluent. The column temperature ranged from 20 to 50°C. The numbers beside the symbols are as in the tables. O, Polyaromatic hydrocarbons; Δ , alkylbenzenes; \square , halogenated benzenes; \blacktriangle , alkyl alcohols; \bullet , alkanes.

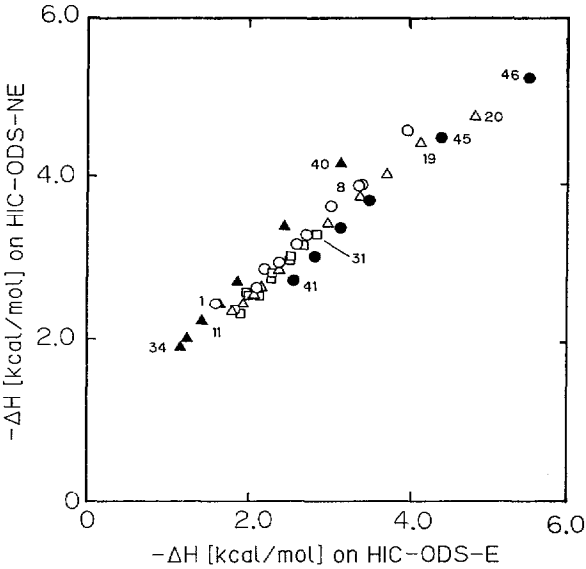


Fig. 4. Relationship between enthalpies ($-\Delta H$) of hydrophobic compounds on HIC-ODS-E and HIC-ODS-NE. Experimental conditions, symbols and numbers as in Fig. 3.

gels if the packings were well end-capped. However, there is selectivity in the retention of chlorobenzenes on these packings. The correlation of ΔE values of halogenated benzenes obtained between LOC-ODS-E and Hypersil ODS is 0.7614 ($n = 11$) and 0.7143 ($n = 11$) between LOC-ODS-E and Develosil ODS.

The enthalpies of the compounds tested on LOC-ODS-E, HIC-ODS-E, HIC-ODS-NE and Hypersil ODS were compared, and these values are given in Table V. The enthalpy of a homologous series of compounds showed a linear relationship with their Van der Waal's volumes, and this linear relationship was independent in each homologous series of compounds.

Alkanes and aromatic compounds have a greater enthalpy than alkyl alcohols on ODS-silica gels. The enthalpies are slightly higher on HIC-ODS-E than on LOC-ODS-E, as shown in Fig. 3. Non-end-capped ODS silica gels exhibit a greater selectivity difference between aromatic compounds and alkyl alcohols, as shown in Fig. 4, where alkyl alcohols have lower enthalpy on HIC-ODS-E. This means that hydrophobic compounds may be adsorbed more directly than alkyl alcohols on these end-capped-ODS silica gels. Increasing their Van der Waal's volumes increased their enthalpy, on both HIC-ODS-E and HIC-ODS-NE, and the relationships between their Van der Waal's volumes and enthalpies are similar.

From these comparisons, it can be concluded that the retention mechanism of hydrophobic compounds on octadecyl-bonded silica gels with different carbon loadings is similar. However, there is a selectivity difference in retention between alkyl alcohols and other compounds, depending on the end-capping treatment applied. This may be due to the existence of untreated silanol groups. The capacity ratios of the above compounds are not simply related to their Van der Waal's volumes. Each group of compounds has its own linear relationship between $\log k'$ values and Van der Waal's volumes. The difference cannot simply be related to the energy effect or enthalpy measured on one octadecyl-bonded silica gel. In particular, the end-capping process may dominate the selectivity of octadecyl-bonded silica gels, and the density of the alkyl chains bonded on their surface may not be directly related to selectivity. Further experiments are required to elucidate the retention mechanism on octadecyl-bonded silica gels in RPLC.

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