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RETENTION BEHAVIOUR OF POLYCYCLIC AROMATIC HYDROCARBONS IN SUPERCRITICAL FLUID CHROMATOGRAPHY ON VARIOUS CHEMICALLY BONDED STATIONARY PHASES WITH CARBON DIOXIDE AS A MOBILE PHASE

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SUMMARY

The retention behaviours of polycyclic aromatic hydrocarbons in supercritical fluid chromatography have been studied on various chemically bonded stationary phases with carbon dioxide as the mobile phase. The solute retention is mainly controlled by its molecular size as in liquid chromatography and its dipole moment also determines the elution order on silica and non-endcapped octadecylsilica phases. Phenyl bonded phases such as diphenyl and naphthylethyl show intermediate characters between silica and well covered octadecylsilicas.

INTRODUCTION

In recent years, the dependence of solute retention on column temperature and pressure in supercritical fluid chromatography (SFC) has been investigated by many researchers[1–8]. Schmitz *et al.*[9–11] reported the influence of the physical state of fluids on the retention and resolution of polycyclic aromatic hydrocarbons (PAHs) in SFC. We have also reported the retention characteristics of PAHs in SFC with carbon dioxide as the mobile phase and octadecylsilica as the stationary phase[12,13]. However, it is considered a big advantage of packed column SFC that a number of different types of stationary phases are available for liquid chromatography (LC) and one can use those stationary phases as the column materials.

In this communication, we report the retention behaviours of PAHs in packed column SFC using carbon dioxide as the mobile phase and different types of chemically bonded phases as the stationary phase, at changing mobile phase density and temperature.

EXPERIMENTAL

A Model BIP-I HPLC pump (Jasco, Tokyo, Japan) was used. The pump head was cooled by circulating cold methanol to deliver a fluid as the mobile phase to the analytical column. A Jasco Multi-320 UV photodiode array multichannel detector

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TABLE I
STATIONARY PHASES USED

Index	*Column name*	*Particle diameter (μm)*	*Bonded phase*	*Size (mm)*
Sil	Jasco Finepack Sil	5	Silica	250 × 4.6 I.D.
P-ODS	Brownlee ODS-224	5	Polymeric C_{18}	220 × 4.6 I.D.
M-ODS	Brownlee OD-224	5	Monomeric C_{18}	220 × 4.6 I.D.
C_{18}	Jasco Finepack Sil C_{18}	5	Low polymeric (?)**	250 × 4.6 I.D.
Cap	Shiseido Capcell Pak C_{18}	5	Monomeric C_{18} bonded on silicone polymer	250 × 4.6 I.D.
Diol	Shimadzu Simpak Diol	5	Diol	150 × 4.6 I.D.*
DP	Supelco Sil LC-DP	5	Diphenyl	250 × 4.6 I.D.
NE	Naphthylethyl	5	Naphthylethyl	150 × 4.6 I.D.*

* Laboratory-packed.
** No endcapping.

with a detection cell that can withstand pressures up to 350 kg/cm^2 was used. It was controlled by a NEC PC-9801 VX 16-bit microcomputer (Nippon Electric, Tokyo, Japan). The column temperature was also controlled by the Jasco TU-100 system which was equipped with a manual backpressure regulator to control the column outlet pressure. The chromatographic columns used are summarized in Table I. P-ODS is polymeric ODS (octadecylsilica) and M-ODS is monomeric with endcapping. C_{18} is low polymeric without endcapping, and Cap is an unique ODS which has been bonded on silicone polymer coated on the base silica[14,15]. NE is a naphthylethyl bonded phase donated by N. Tanaka[16], Kyoto Institute of Technology, Kyoto, Japan. DP is a diphenyl bonded phase. Carbon dioxide was used as the mobile phase, at a flow-rate of 1 ml/min. It was pressurized by the pumping system between 100 and 300 kg/cm^2. The PAHs used as the sample probe are

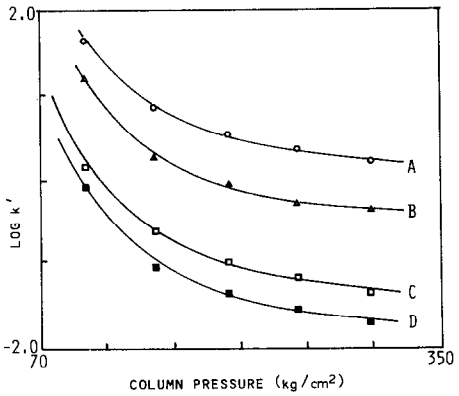

Fig. 1. Relationships between log k' of chrysene and column pressure on various stationary phases at 40°C: (A) P-ODS; (B) M-ODS; (C) Sil; (D) NE.

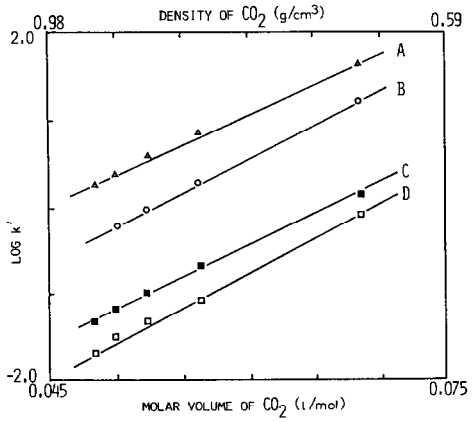

Fig. 2. Relationships between log k' of chrysene and the molar volume of carbon dioxide on various stationary phases at 40°C. Key as in Fig. 1.

commercially available. They were dissolved in dichloromethane which was used as the t_0 probe for capacity factor, k', calculations.

RESULTS AND DISCUSSION

The measured capacity factors of PAHs are summarized in Table II–IX. The retention is strongly dependent on the pressure and temperature of carbon dioxide. Chrysene was selected to demonstrate typical retention behaviours in SFC.

Fig. 1 shows the effect of column pressure on the retention at 40°C. It is apparent that increasing pressure decreases the retention, especially at lower pressures. This trend is the same as in Fig. 2, where the effect of the molar volume of carbon dioxide on the retention with various stationary phases is demonstrated. On increasing the molar

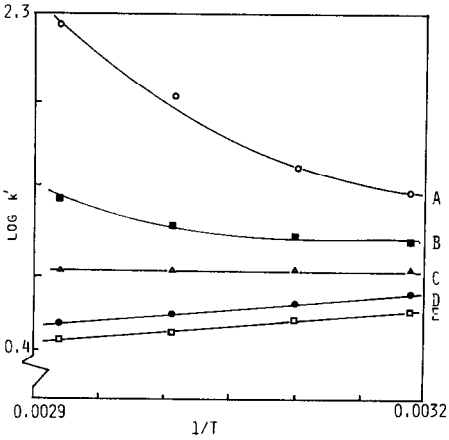

Fig. 3. Relationships between log k' of chrysene and the reciprocal column temperature ($1/T$) on the Cap column. Pressures (kg/cm^2): (A) 100; (B) 150; (C) 200; (D) 250; (E) 300.

TABLE II
RETENTION DATA ON THE Sil COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	1.022	0.512	0.604	0.814	1.176	0.366	0.399	0.464	0.565
Acenaphthylene	2.028	0.992	1.200	1.649	2.419	0.702	0.772	0.901	1.106
Acenaphthene	1.881	0.905	1.099	1.524	2.248	0.625	0.702	0.819	1.012
Fluorene	2.769	1.295	1.604	2.239	3.341	0.888	1.005	1.174	1.449
Phenanthrene	3.405	1.532	1.942	2.789	4.296	1.041	1.176	1.405	1.775
Anthracene	3.167	1.410	1.807	2.623	4.072	0.947	1.089	1.311	1.664
Fluoranthene	5.239	2.245	2.901	4.288	6.800	1.485	1.690	2.064	2.626
Pyrene	5.172	2.205	2.868	4.260	6.781	1.460	1.669	2.049	2.616
Benz[*a*]anthracene	8.750	3.352	4.556	7.188	12.075	2.121	2.493	3.153	4.116
Chrysene	9.294	3.580	4.840	7.613	12.765	2.265	2.648	3.339	4.353

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

TABLE III
RETENTION DATA ON THE P-ODS COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	1.872	0.996	1.150	1.327	1.779	0.775	0.805	0.851	0.898
Acenaphthylene	4.197	2.116	2.419	2.852	3.919	1.597	1.606	1.719	1.812
Acenaphthene	4.450	2.232	2.557	2.992	4.104	1.696	1.700	1.822	1.906
Fluorene	5.330	2.528	2.939	3.475	4.928	1.870	1.882	2.032	2.144
Phenanthrene	10.248	4.622	5.488	6.393	9.360	3.372	3.408	3.629	3.824
Anthracene	10.564	4.622	5.488	6.393	9.360	3.372	3.408	3.629	3.824
Fluoranthene	22.037	9.266	10.764	12.778	18.878	6.577	6.383	6.761	7.129
Pyrene	28.670	12.069	13.992	16.669	24.369	8.549	8.268	8.703	9.144
Benz[*a*]anthracene	53.197	20.189	23.390	29.097	44.239	13.652	12.909	13.546	14.344
Chrysene	60.986	23.210	26.622	33.027	49.919	15.636	14.672	15.278	16.090

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.300	0.301	0.338	0.385	0.260	0.248	0.274	0.303
0.573	0.578	0.657	0.739	0.490	0.477	0.535	0.572
0.506	0.523	0.590	0.668	0.426	0.426	0.469	0.513
0.710	0.744	0.837	0.942	0.588	0.612	0.670	0.714
0.826	0.860	0.987	1.125	0.690	0.691	0.772	0.842
0.753	0.789	0.913	1.054	0.628	0.632	0.716	0.785
1.170	1.215	1.408	1.615	0.976	0.960	1.081	1.182
1.150	1.198	1.392	1.610	0.964	0.946	1.070	1.180
1.616	1.736	2.042	2.390	1.302	1.337	1.525	1.685
1.730	1.843	2.168	2.530	1.402	1.418	1.612	1.783

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.678	0.672	0.654	0.671	0.648	0.591	0.565	0.548
1.288	1.300	1.272	1.293	1.224	1.129	1.065	1.025
1.381	1.382	1.339	1.357	1.324	1.209	1.133	1.082
1.553	1.505	1.464	1.491	1.415	1.291	1.216	1.158
2.825	2.672	2.564	2.572	2.517	2.266	2.095	1.959
2.825	2.672	2.564	2.572	2.517	2.266	2.095	1.959
5.394	4.896	4.629	4.615	4.648	4.074	3.725	3.437
6.994	6.315	5.951	5.933	6.017	5.249	4.793	4.399
10.853	9.517	8.826	8.777	9.098	7.717	6.935	6.244
12.459	10.817	9.927	9.844	10.422	8.757	7.811	6.994

TABLE IV
RETENTION DATA ON THE M-ODS COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	1.647	0.605	0.971	1.249	1.564	0.437	0.701	0.747	0.857
Acenaphthylene	3.480	1.347	1.871	2.466	3.167	0.973	1.292	1.398	1.624
Acenaphthene	3.887	1.510	2.062	2.704	3.449	1.100	1.432	1.536	1.760
Fluorene	4.430	1.675	2.265	3.040	3.978	1.157	1.516	1.650	1.926
Phenanthrene	7.891	2.868	3.787	5.154	6.802	2.046	2.461	2.682	3.132
Anthracene	7.891	2.868	3.787	5.154	6.802	2.046	2.461	2.682	3.132
Fluoranthene	13.765	5.379	6.871	9.490	12.740	3.743	4.279	4.664	5.461
Pyrene	19.330	6.778	8.562	11.794	15.744	4.747	5.325	5.772	6.729
Benz[*a*]anthracene	32.235	10.152	12.996	18.664	26.251	6.816	7.578	8.322	9.892
Chrysene	35.267	11.016	14.081	20.154	28.273	7.391	8.201	8.983	10.612

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

TABLE V
RETENTION DATA ON THE C_{18} COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	2.050	1.088	1.268	1.514	1.983	0.864	0.864	0.924	1.016
Acenaphthylene	4.241	2.105	2.545	3.117	4.220	1.604	1.636	1.777	1.992
Acenaphthene	4.451	2.210	2.661	3.226	4.325	1.690	1.720	1.841	2.047
Fluorene	5.541	2.589	3.208	4.028	5.579	1.949	1.998	2.207	2.479
Phenanthrene	8.493	3.768	4.732	5.983	8.508	2.751	2.861	3.144	3.581
Anthracene	8.241	3.768	4.732	5.983	8.508	2.751	2.861	3.144	3.581
Fluoranthene	15.527	6.555	8.370	10.916	15.958	4.658	4.811	5.434	6.251
Pyrene	17.804	7.669	9.545	12.458	18.220	5.329	5.488	6.215	7.120
Benz[*a*]anthracene	30.611	11.442	15.128	20.735	32.316	7.781	8.134	9.424	11.068
Chrysene	32. 776	12.280	16.201	22.170	34.396	8.302	8.694	10.056	11.770

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.373	0.581	0.600	0.610	0.343	0.506	0.556	0.491
0.803	1.047	1.077	1.123	0.731	0.902	1.041	0.879
0.935	1,171	1.187	1.209	0.820	1.003	1.130	0.952
0.950	1.209	1.239	1.281	0.855	1.027	1.160	0.985
1.634	1.932	1.974	2.041	1.456	1.620	1.748	1.548
1.634	1.932	1.974	2.041	1.456	1.620	1.748	1.548
2.910	3.286	3.323	3.425	2.569	2.719	2.814	2.545
3.677	4.068	4.097	4.202	3.240	3.372	3.438	3.127
5.100	5.587	5.629	5.842	4.406	4.522	4.550	4.203
5.552	6.030	6.074	6.387	4.760	4.869	4.873	4.491

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.714	0.725	0.732	0.759	0.621	0.606	0.595	0.625
1.306	1.346	1.373	1.439	1.105	1.138	1.085	1.152
1.359	1.404	1.428	1.476	1.171	1.194	1.116	1.185
1.551	1.602	1.657	1.784	1.322	1.334	1.278	1.388
2.189	2.224	2.343	2.460	1.812	1.872	1.780	1.906
2.189	2.224	2.343	2.460	1.812	1.872	1.780	1.906
3.636	3.617	3.874	4.149	2.954	3.046	2.853	3.142
4.168	4.135	4.421	4.736	3.383	3.488	3.249	3.577
5.905	5.812	6.362	6.950	4.615	4.828	4.486	5.092
6.277	6.172	6.744	7.262	4.912	5.108	4.764	5.331

TABLE VI
RETENTION DATA ON THE Cap COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	1.233	0.664	0.771	0.968	1.237	0.522	0.548	0.585	0.632
Acenaphthylene	2.476	1.225	1.458	1.881	2.452	0.941	0.991	1.064	1.164
Acenaphthene	2.789	1.396	1.643	2.105	3.724	1.078	1.120	1.195	1.295
Fluorene	3.036	1.433	1.737	2.288	3.039	1.081	1.144	1.243	1.368
Phenanthrene	5.374	2.403	2.946	3.912	5.254	1.775	1.871	2.038	2.237
Anthracene	5.473	2.403	2.946	3.912	5.254	1.775	1.871	2.038	2.237
Fluoranthene	10.273	4.248	5.266	7.021	10.053	3.031	3.192	3.479	3.830
Pyrene	13.258	5.440	6.717	8.842	12.208	3.872	4.039	4.374	4.784
Benz[*a*]anthracene	21.298	7.715	9.848	13.361	19.587	5.250	5.527	6.080	6.751
Chrysene	23.236	8.376	10.657	14.265	21.053	5.678	5.964	6.540	7.234

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

TABLE VII
RETENTION DATA ON THE Diol COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	0.945	0.436	0.532	0.689	1.000	0.325	0.349	0.403	0.473
Acenaphthylene	2.345	1.018	1.266	1.642	2.401	0.755	0.785	0.927	1.075
Acenaphthene	1.885	0.816	1.023	1.344	2.015	0.599	0.632	0.755	0.894
Fluorene	2.415	0.991	1.266	1.708	2.614	0.709	0.762	0.918	1.093
Phenanthrene	4.910	1.908	2.436	3.231	5.020	1.342	1.410	1.670	1.996
Anthracene	4.910	1.908	2.436	3.231	5.020	1.342	1.410	1.670	1.996
Fluoranthene	9.830	3.573	4.587	6.165	9.728	2.409	2.529	2.974	3.580
Pyrene	11.945	4.312	5.500	7.368	11.569	2.899	3.023	3.554	4.248
Benz[*a*]anthracene	19.870	6.330	8.394	11.750	19.510	4.021	4.268	5.137	6.314
Chrysene	22.480	7.151	9.431	13.118	21.644	4.540	4.778	5.721	6.991

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions.

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.453	0.454	0.463	0.488	0.405	0.406	0.393	0.398
0.792	0.795	0.827	0.862	0.701	0.702	0.677	0.691
0.898	0.904	0.934	0.970	0.807	0.800	0.767	0.780
0.909	0.904	0.943	0.994	0.788	0.792	0.767	0.783
1.447	1.448	1.513	1.578	1.261	1.245	1.208	1.226
1.447	1.448	1.513	1.578	1.261	1.245	1.208	1.226
2.436	2.413	2.502	2.596	2.090	2.034	1.975	1.991
3.099	3.038	3.125	3.240	2.655	2.562	2.483	2.481
4.082	3.997	4.140	4.338	3.424	3.301	3.185	3.208
4.412	4.306	4.448	4.644	3.698	3.551	3.421	3.430

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.274	0.282	0.300	0.339	0.235	0.244	0.249	0.264
0.619	0.648	0.680	0.740	0.526	0.544	0.557	0.659
0.488	0.513	0.549	0.607	0.419	0.431	0.443	0.469
0.571	0.612	0.660	0.727	0.484	0.505	0.524	0.527
1.071	1.117	1.186	1.306	0.903	0.915	0.941	0.984
1.071	1.117	1.186	1.306	0.903	0.915	0.941	0.984
1.909	1.941	2.071	2.252	1.568	1.576	1.630	1.663
2.290	2.319	2.466	2.661	1.879	1.876	1.934	1.969
3.083	3.183	3.403	3.719	2.460	2.484	2.637	2.647
3.480	3.575	3.794	4.112	2.768	2.781	2.927	2.919

TABLE VIII
RETENTION DATA ON THE DP COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	0.695	0.354	0.404	0.510	0.738	0.270	0.278	0.314	0.366
Acenaphthylene	1.329	0.625	0.745	0.949	1.415	0.472	0.500	0.551	0.660
Acenaphthene	1.352	0.634	0.752	0.965	1.433	0.482	0.511	0.562	0.670
Fluorene	1.601	0.717	0.866	1.122	1.734	0.533	0.571	0.636	0.767
Phenanthrene	2.456	1.041	1.271	1.676	2.634	0.760	0.818	0.935	1.113
Anthracene	2.456	1.041	1.271	1.676	2.635	0.760	0.818	0.935	1.113
Fluoranthene	4.020	1.578	1.952	2.673	4.277	1.125	1.213	1.418	1.693
Pyrene	4.537	1.767	2.210	2.974	4.762	1.260	1.358	1.579	1.887
Benz[*a*]anthracene	7.570	2.546	3.258	4.593	7.851	1.742	1.909	2.271	2.760
Chrysene	8.003	2.690	3.436	4.836	8.277	1.839	2.008	2.404	2.909

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditions

TABLE IX
RETENTION DATA ON THE NE COLUMN

Compound (PAH)	*P = 100* kg/cm²*	*P = 150 kg/cm²*				*P = 200 kg/cm²*			
	40°C	*40°C*	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
Naphthalene	0.390	0.173	0.228	0.305	0.460	0.128	0.150	0.169	0.197
Acenaphthylene	0.814	0.327	0.435	0.593	0.928	0.249	0.270	0.310	0.373
Acenaphthene	0.915	0.354	0.482	0.661	1.033	0.268	0.301	0.343	0.399
Fluorene	1.113	0.425	0.575	0.785	1.270	0.315	0.350	0.408	0.477
Phenanthrene	1.825	0.655	0.886	1.237	2.040	0.482	0.531	0.610	0.725
Anthracene	1.876	0.655	0.886	1.237	2.105	0.482	0.531	0.610	0.725
Fluoranthene	3.260	1.075	1.456	2.102	3.612	0.763	0.850	0.991	1.186
Pyrene	3.712	1.217	1.653	2.378	4.112	0.856	0.951	1.113	1.337
Benz[*a*]anthracene	6.740	1.951	2.731	4.040	7.408	1.335	1.482	1.746	2.130
Chrysene	7.186	2.071	2.881	4.277	7.816	1.412	1.562	1.840	2.238

* The data for 50, 60 and 70°C at 100 kg/cm² were not measured because of unstable conditons.

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.226	0.230	0.244	0.271	0.206	0.202	0.208	0.216
0.392	0.402	0.416	0.472	0.354	0.347	0.360	0.372
0.401	0.410	0.420	0.475	0.363	0.354	0.365	0.375
0.439	0.449	0.467	0.539	0.390	0.385	0.402	0.414
0.620	0.642	0.658	0.764	0.546	0.542	0.565	0.583
0.620	0.642	0.658	0.764	0.546	0.542	0.565	0.583
0.910	0.943	0.958	1.128	0.785	0.782	0.822	0.847
1.021	1.052	1.066	1.257	0.875	0.874	0.918	0.942
1.377	1.433	1.457	1.755	1.161	1.162	1.232	1.266
1.446	1.509	1.531	1.848	1.222	1.221	1.295	1.335

$P = 250\ kg/cm^2$				$P = 300\ kg/cm^2$			
40°C	*50°C*	*60°C*	*70°C*	*40°C*	*50°C*	*60°C*	*70°C*
0.106	0.118	0.126	0.140	0.097	0.100	0.100	0.104
0.198	0.220	0.230	0.252	0.181	0.178	0.188	0.193
0.223	0.240	0.247	0.270	0.195	0.199	0.200	0.209
0.253	0.276	0.293	0.320	0.225	0.221	0.235	0.241
0.388	0.415	0.431	0.473	0.329	0.331	0.342	0.357
0.388	0.415	0.431	0.473	0.329	0.331	0.342	0.357
0.615	0.646	0.690	0.743	0.513	0.523	0.538	0.554
0.689	0.724	0.778	0.838	0.574	0.580	0.600	0.622
1.040	1.102	1.192	1.270	0.859	0.858	0.892	0.924
1.099	1.154	1.251	1.329	0.903	0.897	0.931	0.964

TABLE X
ELUTION ORDER OF ACENAPHTHENE–FLUORENE AND ACENAPHTHYLENE WITH VARIOUS COLUMNS UNDER VARIOUS SFC CONDITIONS

Column	*Elution order*
Sil	Acenaphthene, acenaphthylene, fluorene
P-ODS	Acenaphthylene, acenaphthene, fluorene
M-ODS	Acenaphthylene, acenaphthene, fluorene
Cap	Acenaphthylene, acenaphthene, fluorene
C_{18}	Acenaphthylene, acenaphthene, fluorene
DP	Acenaphthylene, acenaphthene, fluorene
NE	Acenaphthylene, acenaphthene, fluorene

volume, the retention increases linearly. This means that density is the important factor in the retention, as is generally the case in SFC.

In Fig. 3, Van 't Hoff plots are shown for chrysene. As is typical in SFC, at lower pressures the retention increases with increasing temperature but at higher pressures the opposite occurs.

The retention mechanism for PAHs in SFC is dependent on the following situations:

(1) isothermal situation: the retention is dependent on the change in density of the mobile phase, increasing density leading to decreased retention

(2) isobaric situation: the retention is dependent on the pressure of the mobile phase, at lower pressures, increasing temperature, *viz.*, decreasing density results in increased retention, *ie.*, the retention is controlled by the solute solubility. At higher pressures, increasing temperature results in decreased retention, *i.e.*, the retention is controlled by the volatility of the solute.

The details of the retention behaviours of PAHs were evaluated from the data summarized in Tables II–IX. Roughly, the solute elution is controlled by its size. However, the elution orders sometimes changed depending on the conditions and the separation systems. The typical solute groups which showed changes in the elution order depending on the separation conditions are acenaphthene–acenaphthylene–

TABLE XI
ELUTION ORDER OF THREE PAHs ON THE Diol COLUMN UNDER VARIOUS SFC CONDITIONS
A = Acenaphthene, fluorene, acenaphthylene; C = acenaphtene, acenaphthylene, fluorene; E = acenapthene–fluorene, acenaphthylene.

P (kg/cm²)	*T (°C)*			
	40	*50*	*60*	*70*
100	C	–	–	–
150	A	E	C	C
200	A	A	A	C
250	A	A	A	A
300	A	A	A	A

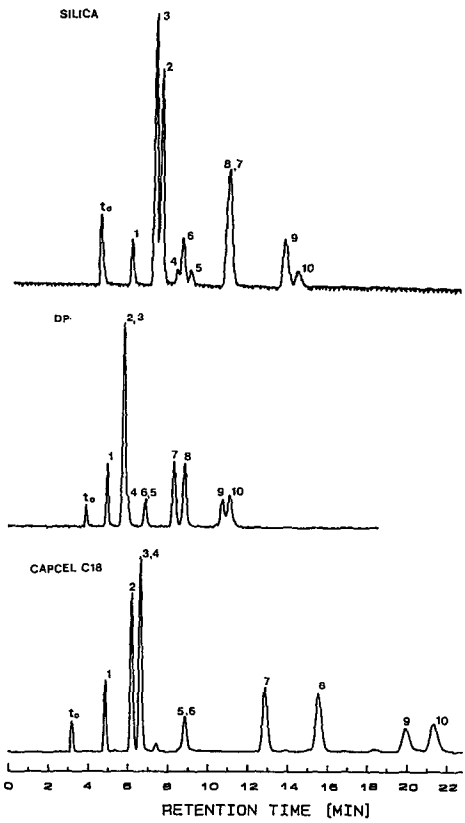

Fig. 4. SFC chromatograms of ten PAHs at 200 kg/cm^2 and 40°C with UV detection at 225 nm. Peak: 1 = naphthalene; 2 = acenaphthylene; 3 = acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = fluoranthene; 8 = pyrene; 9 = benz[*a*]anthracene; 10 = chrysene.

TABLE XII
VALUES OF THE MOLECULAR POLARIZABILITY AND DIPOLE MOMENT OF PAHs

Compound	*Polarizability*	*Dipole moment, D*
Naphthalene	17.48	0.003
Acenaphthylene	22.34*	0.258
Acenaphthene	20.61	0.084
Fluorene	21.69	0.099
Anthracene	25.93	0.005
Phenanthrene	24.70	0.038
Fluoranthene	28.35	0.210
Pyrene	29.34	0.028
Benz[*a*]anthracene	32.86	0.062
Chrysene	33.06	0.004

* Calculated.

TABLE XIII

RELATIONSHIPS BETWEEN k', POLARIZABILITY AND DIPOLE MOMENT ON VARIOUS PHASES

$\log k' = a\,\alpha + b\,\mu^2 + c$ where α is the molecular polarizability and μ is the dipole moment.

Column	*a*	*b*	*c*	*Correlation coefficient (r^2)*
Sil	0.050	12.589	−1.226	0.984
C_{18}	0.061	8.982	−1.125	0.993
NE	0.061	7.738	−1.892	0.994
DP	0.052	6.000	−1.423	0.993
P-ODS	0.073	3.734	−1.450	0.993
M-ODS	0.064	5.051	−1.351	0.990
Cap	0.061	4.912	−1.353	0.987

fluorene, phenanthrene–anthracene and fluoranthene–pyrene. Table X shows those elution orders on various stationary phases except Diol under SFC conditions. On Sil, the elution orders of several PAHs as mentioned above are different from those on other ODS phases. An interesting case is found on the Diol column as shown in Table XI. The elution order of fluorene and acenaphthylene changes between the molar volumes of 0.0607 and 0.665 l/mol. These elution order changes were also found in LC separations[17].

In Fig. 4, typical separations are demonstrated on Sil, DP and Cap columns. The elution order differences are clearly seen for three groups of PAHs. To explain this, the molecular polarizability and dipole moments of particular PAHs should be considered. In Table XII such values are summarized. The dipole moment of the PAHs can explain the elution orders on various stationary phases. On the Sil column, the solutes wich have relatively large dipole moments were eluted later than their counter solutes, *i.e.*, acenaphthylene, phenanthrene and fluoranthene. On C_{18} and DP, similar but weaker trends are seen for those solutes. Therefore, multiregression analysis has been performed for the data sets using molecular polarizability and dipole moments as the parameters[18]. The results are shown in Table XIII. The retention of PAHs with various phases in SFC can be explained by this treatment as shown in the table. On Sil, the contribution of the dipole moment to the retenton is very large, and also on C_{18} which has not been endcapped the contribution of the dipole moment is also larger than on other phases. Therefore, the behaviour can be explained by the interaction of the solute with remaining silanol groups on the stationary phase surface. On NE and DP, resonance structures of the bonded phases influence the dipole–dipole interaction. On Cap, P-ODS and M-ODS, the reason why the contribution of dipole moments to the retention is small can be explained by the small number of residual silanol groups.

In conclusion, the retention of PAHs on various chemically bonded phases in carbon dioxide SFC can be controlled mainly by their sizes and dipole moments under fixed conditions; also their solublity and volatility contribute to the overall retention at various pressures and temperatures.

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