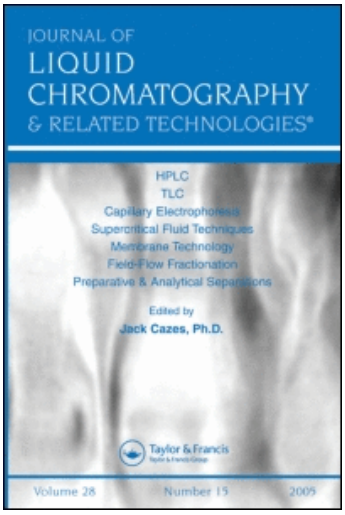

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Thermodynamic Approaches to Intermolecular Interaction and Retention Behavior in Liquid Chromatography

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ABSTRACT

In this work, we investigated the intermolecular interaction between the stationary phases and solutes and retention behavior in liquid chromatography by thermodynamic analysis. The intermolecular interactions between four stationary phases chemically bonded with octadecyl (ODS), phenyl (Ph), pyrenyl (PYE), and β-cyclodextin bromide (β-CD), and 53 solutes including 27 compounds of *p*-substituted alkylbenzenes (PSABs), 14 compounds of polyaromatic hydrocarbons (PAHs), and 26 compounds of substituted benzenes were examined by using both methanol–water and acetonitrile–water as mobile phases. It has been observed that there are obvious differences in π–π intermolecular

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interactions among the stationary phases of ODS, Ph, and PYE by plotting $\ln k'$ with enthalpies (ΔH). Based on the thermodynamic analysis on the interaction between β-CD column and solutes, it was known that the solutes having similar molecular lengths with β-CD resulted in large enthalpy changes in the host–guest interaction. Besides, both hydrophobic and host–guest interactions make contributions to the retention of solutes on the β-CD stationary phase; and the structures of solutes have critical influence on the retention. Further, from the thermodynamic point of view, the retention mechanisms such as partitioning or adsorption in liquid chromatography have been discussed.

Key Words: Liquid chromatography; Intermolecular interaction; Thermodynamics; Retention behavior; Enthalpy; Entropy.

INTRODUCTION

Since invented by Tswett in the early 1900s, chromatographic science has had about one century's history. The separation modes were notably developed from classical column chromatography in about 1930s, to paper chromatography in 1940s, gas chromatography (GC), and thin layer chromatography (TLC) in 1950s, high performance liquid chromatography (HPLC) in 1960s, supercritical fluid chromatography (SFC) in 1980s, capillary electrophoresis (CE), and electrochromatography (CEC) in 1990s.[1] In recent decades, chromatographic scientists paid attention to the miniaturization of chromatographic techniques. For examples, CE, CEC, and capillary- or chip-based micro- or nano-LC have become the most fascinating research fields in the chromatographic sciences. Despite their promise of better resolving power and more sensitive detection for some samples, the future impact of CE and CEC is as yet uncertain.[1] Because of its advantages such as excellent reproducibility and convenient separation and analysis of almost any samples, HPLC is a key technology widely used for separating and analyzing complex mixtures now.

On the other hand, in addition to being useful for analytical separation, chromatography can be used as a tool to study itself, for example, the retention mechanism. It is on the basis of the intermolecular interaction among the solutes, stationary phases, and mobile phases that the solute mixtures can be separated. Quantitative and qualitative analysis can be achieved by the chromatograms obtained. Meanwhile, as the chromatograms contain a significant amount of quantitative and qualitative information of intermolecular interaction, HPLC has also used as a measurement tool of physicochemical interactions. In the nearly five decades since the advent of LC, a broad

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scope of physicochemical measurements has been realized, including the determination of binding constants, partition coefficient, and diffusional parameters, as well as interaction and reaction kinetics.[2] In fact, not only LC but also other separation techniques like CE, CEC can be used as measurement tools.

van't Hoff analysis has been used to probe the thermodynamics of the partitioning process and to investigate possible phase transitions of the bonded, aligned alkyl chains. Cole et al.[3,4] reported that van't Hoff analysis was used to show that hydrophobicity is not the driving force for retention with most mixed aqueous-organic mobile phase. They also showed that the change in entropy during the transfer process increases with increasing chain density of the bonded alkyl groups. Wheeler et al.[5] reviewed that van't Hoff plots have been used to investigate the possibility of phase transition in the aligned alkyl chain stationary phases, including pertinent theory relating to these phenomena. Yamamoto et al.[6] studied the thermodynamic retention behavior on various C_{18} columns different in their hydrophobicity. Jackson et al.[7] studied the intermolecular interactions involved in solute retention on carbon media in reversed-phase HPLC.

In recent years, in addition to studying new systems of molecular recognition and monolithic column technology for CEC[8] and micro-LC,[9] one of our studies was to study the new measurement methods of physicochemical constants by separation techniques like CE and LC. Recently, we reported the estimations of the critical micelle concentration (CMC) of anionic surfactants[10] and the formation constant of Cu(II) complexes with mixed amino acid enantiomers by ligand exchange CE.[11] We studied the interaction between 18-crown-6-tetracarboxylic acid and the positional enantiomers by CE.[12] In the present work, our goals were focused on investigating the intermolecular interaction and obtaining some thermodynamic information of retention mechanism by using HPLC as a tool of thermodynamic measurement. Another purpose of this work was to provide a database (Tables 1–4) of thermodynamic data in LC for chromatographic researchers to do other thermodynamic analysis and chromatographic study. The intermolecular interactions between four stationary phases chemically bonded with octadecyl (ODS), phenyl (Ph), pyrenyl (PYE), and β-cyclodextin bromide (β-CD), and 53 solutes including 27 compounds of *p*-substituted alkylbenzenes (PSABs), 14 compounds of polyaromatic hydrocarbons (PAHs), and 26 compounds of substituted benzenes were examined by using both methanol–water and acetonitrile–water as mobile phases. The chemical structures of stationary phases and solutes are shown in Figs. 1 and 2. Based on a large number of thermodynamic data measured, the intermolecular interaction between stationary phases and solutes and retention mechanism were discussed.

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Table 1. Enthalpies (ΔH°) and entropies (ΔS°) of PSABs, PAHs, and other solutes on ODS column.

	Mightysil RP-18 (ODS)					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzene	−6.470	−2.752	0.9996	−6.720	−2.975	0.9940
Toluene	−8.328	−3.040	0.9994	−8.046	−3.174	0.9991
Ethylbenzene	−10.04	−3.363	0.9997	−8.809	−3.189	0.9984
n-Butylbenzene	−13.47	−3.913	0.9997	−11.62	−3.621	0.9992
n-Hexylbenzene	−17.34	−4.634	0.9997	−14.92	−4.229	0.9994
n-Octylbenzene	−21.49	−5.457	0.9998	−18.46	−4.909	0.9996
Phenol	−7.701	−4.527	0.9976	−6.646	−4.048	0.9850
p-Cresol	−7.852	−4.232	0.9974	−7.670	−4.200	0.9964
p-*n*-Propylphenol	−10.54	−4.462	0.9987	−8.323	−3.883	0.9990
p-*n*-Butylphenol	−12.21	−4.701	0.9996	−9.684	−4.091	0.9982
p-*n*-Pentylphenol	−13.90	−4.953	0.9996	−10.80	−4.200	0.9972
p-*n*-Hexylphenol	−15.59	−5.208	0.9995	−12.35	−4.464	−0.9993
Iodobenzene	—	—	—	−9.110	−3.332	0.9992
p-Methyliodobenzene	−11.46	−3.572	0.9999	—	—	—
p-Ethyliodobenzene	−12.73	−3.714	0.9998	−11.07	−3.459	0.9980
p-*n*-Propyliodobenzene	−14.58	−4.045	0.9998	−12.57	−3.706	0.9987
p-*n*-Butyliodobenzene	−16.55	−4.408	0.9998	−14.11	−3.966	0.9992
p-*n*-Pentyliodobenzene	−18.64	−4.827	0.9998	−15.83	−4.298	0.9993

Acetophenone	−4.881	−2.973	0.9987	−5.408	−3.039	0.9801
p-Methylacetophenone	−6.441	−3.196	0.9971	−7.113	−3.428	0.9983
p-Ethylacetophenone	−7.533	−3.249	0.9992	−8.410	−3.650	0.9994
p-*n*-Propylacetophenone	−9.128	−3.468	0.9987	−8.934	−3.535	0.9976
p-*n*-Butylacetophenone	−10.90	−3.753	0.9993	−10.72	−3.888	0.9991
p-*n*-Pentylacetophenone	−12.81	−4.095	0.9991	−12.26	−4.161	0.9979
Aniline	−5.431	−3.789	0.9702	−7.019	−4.050	0.9903
p-*n*-Butylaniline	−9.162	−3.665	0.9980	−9.369	−3.827	0.9973
p-*n*-Hexylaniline	−12.69	−4.233	0.9987	−12.13	−4.238	0.9987
p-*n*-Octylaniline	−16.46	−4.893	0.9992	−15.30	−4.781	0.9986
Benzene	−6.470	−2.752	0.9996	−6.720	−2.975	0.9940
Naphthalene	−10.42	−3.575	0.9997	−9.113	−3.412	0.9989
Fluorene	−14.05	−4.323	0.9997	−11.00	−3.741	0.9993
Biphenyl	−12.01	−3.819	0.9994	−9.977	−3.510	0.9988
Anthracene	−15.03	−4.533	0.9998	−12.46	−4.106	0.9995
Phenanthrene	−14.18	−4.305	0.9996	−11.69	−3.893	0.9973
Fluoranthene	−16.14	−4.719	0.9998	−13.29	−4.251	0.9978
Pyrene	−16.69	−4.810	0.9998	−13.98	−4.384	0.9993
Chrysene	−18.63	−5.231	0.9987	−15.70	−4.852	0.9992
Triphenylene	−17.81	−5.012	0.9998	−14.64	−4.521	0.9993
Perylene	—	—	—	−17.62	−5.240	0.9995
o-Terphenyl	−15.02	−4.288	0.9992	−12.50	−3.908	0.9989
m-Terphenyl	−17.24	−4.767	0.9993	−13.30	−4.072	0.9992
p-Terphenyl	−18.85	−5.303	0.9998	−14.44	−4.443	0.9995

(*continued*)

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Table 1. Continued.

	Mightysil RP-18 (ODS)					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzylalcohol	—	—	—	−5.293	−3.547	0.9817
Benzamide	—	—	—	−7.513	−4.908	0.9792
Benzylamine	−7.823	−2.895	0.9963	—	—	—
Benzonitrile	—	—	—	−7.590	−3.906	0.9979
Nitrobenzene	−6.730	−3.428	0.9997	−6.946	−3.491	0.9979
Nitrosobenzene	—	—	—	−6.875	−3.261	0.9924
Fluorobenzene	−6.397	−2.833	0.9989	−6.798	−3.093	0.9965
Chlorobenzene	—	—	—	−8.067	−3.209	0.9971
Bromobenzene	−8.706	−3.144	0.9991	−8.343	−3.208	0.9996
Benzophenone	−8.560	−3.454	0.9991	−8.716	−3.596	0.9983
Thioanisole	−9.080	−3.459	0.9995	−7.614	−3.148	0.9985

o-tert-Butylphenol	−12.91	−4.934	0.9998	−9.557	−3.962	0.9991
p-tert-Butylphenol	−11.54	−4.678	0.9994	−8.919	−3.985	0.9988
p-Phenylphenol	−11.74	−4.921	0.9998	−8.667	−4.141	0.9981
Dibenzyl	−14.60	−4.355	0.9994	−10.91	−3.553	0.9988
N,N-Diethylaniline	−10.52	−3.414	0.9992	−9.770	−3.398	0.9993
Dibenzoyl	—	—	—	−9.188	−3.815	0.9971
o-Xylene	—	—	—	−9.239	−3.372	0.9974
m-Xylene	—	—	—	−9.141	−3.264	0.9982
p-Xylene	—	—	—	−9.614	−3.433	0.9975
α-Naphthol	—	—	—	−8.413	−4.164	0.9944
β-Naphthol	—	—	—	−8.007	−4.130	0.9930
α-Naphthylamine	—	—	—	−7.825	−3.878	0.9890
Dimethylnaphthalene	−11.98	−3.810	0.9993	−10.05	−3.534	0.9993
1-Bromonaphthalene	−12.95	−3.922	0.9994	−11.37	−3.711	0.9993
9-Anthracenemethanol	−11.94	−4.762	0.9998	−8.605	−3.877	0.9969

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Table 2. Enthalpies (ΔH°) and entropies (ΔS°) of PSABs, PAHs, and other solutes on Phe column.

	Develosil PheA					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln\phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln\phi$	R
Benzene	−2.511	−0.6819	0.9895	−8.734	−4.356	0.9974
Toluene	−3.691	−1.001	0.9965	−8.782	−4.229	0.9969
Ethylbenzene	−4.208	−1.077	0.9964	−9.074	−4.190	0.9983
n-Butylbenzene	−6.349	−1.607	0.9975	−10.03	−4.262	0.9997
n-Hexylbenzene	−8.718	−2.191	0.9983	−10.69	−4.231	0.9990
n-Octylbenzene	−11.31	−2.833	0.9982	−11.19	−4.144	0.9992
Phenol	−1.095	−0.4246	0.9534	−9.185	−5.119	0.9940
p-Cresol	−1.520	−0.5110	0.9590	−9.414	−5.102	0.9955
p-*n*-Propylphenol	−3.356	−1.012	0.9869	−9.162	−4.713	0.9946
p-*n*-Butylphenol	−4.081	−1.168	0.9958	−9.233	−4.588	0.9981
p-*n*-Pentylphenol	−5.135	−1.440	0.9971	−9.633	−4.612	0.9975
p-*n*-Hexylphenol	−6.326	−1.758	0.9968	−10.31	−4.736	0.9979
Iodobenzene	—	—	—	−9.154	−4.167	0.9986
p-Methyliodobenzene	−5.284	−1.293	0.9956	−9.254	−4.061	0.9990
p-Ethyliodobenzene	−6.315	−1.533	0.9969	−9.640	−4.053	0.9997
p-*n*-Propyliodobenzene	−7.576	−1.857	0.9967	−10.62	−4.290	0.9986
p-*n*-Butyliodobenzene	−8.791	−2.145	0.9972	−10.69	−4.162	0.9997
p-*n*-Pentyliodobenzene	−10.08	−2.466	0.9974	−10.90	−4.106	0.9987

Acetophenone	−2.639	−0.7829	0.9908	−8.329	−4.418	0.9985
p-Methylacetophenone	−3.355	−0.9552	0.9910	−8.309	−4.302	0.9992
p-Ethylacetophenone	−4.266	−1.177	0.9938	−8.421	−4.188	0.9951
p-*n*-Propylacetophenone	−5.358	−1.458	0.9968	−8.584	−4.101	0.9967
p-*n*-Butylacetophenone	−6.550	−1.767	0.9980	−9.413	−4.275	0.9974
p-*n*-Pentylacetophenone	−7.775	−2.081	0.9984	−9.727	−4.249	0.9978
Aniline	−1.954	−0.6641	0.9952	—	—	—
p-*n*-Butylaniline	−6.833	−2.012	0.9988	—	—	—
p-*n*-Hexylaniline	−8.877	−2.527	0.9990	—	—	—
p-*n*-Octylaniline	−11.31	−3.154	0.9990	—	—	—
Benzene	−2.511	−0.6819	0.9895	−8.734	−4.356	0.9974
Naphthalene	−4.788	−1.228	0.9993	−8.982	−4.131	0.9974
Fluorene	−7.131	−1.812	0.9985	−9.079	−3.942	0.9994
Biphenyl	−6.479	−1.674	0.9988	−9.468	−4.156	0.9997
Anthracene	−7.103	−1.747	0.9992	−9.625	−4.051	0.9992
Phenanthrene	−6.717	−1.639	0.9991	−9.521	−4.047	0.9992
Fluoranthene	—	—	—	−9.411	−3.884	0.9998
Pyrene	−7.584	−1.796	0.9995	−9.274	−3.787	0.9998
Chrysene	−8.995	−2.134	0.9994	−10.09	−3.970	0.9994
Triphenylene	−8.943	−2.113	0.9994	−10.06	−3.959	0.9990
Perylene	—	—	—	−9.998	−3.747	0.9993
o-Terphenyl	−9.974	−2.544	0.9983	−10.26	−4.055	0.9992
m-Terphenyl	−11.21	−2.865	0.9980	−10.49	−4.107	0.9991
p-Terphenyl	−11.17	−2.866	0.9975	−10.74	−4.203	0.9998

(*continued*)

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Table 2. Continued.

	Develosil PheA					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzylalcohol	—	—	—	−7.510	−4.724	0.9971
Benzamide	—	—	—	−9.423	−5.576	0.9942
Benzylamine	−3.404	−1.043	0.9985	—	—	—
Benzonitrile	—	—	—	−9.163	−4.724	0.9971
Nitrobenzene	−3.647	−1.051	0.9988	−8.609	−4.410	0.9991
Nitrosobenzene	—	—	—	−9.249	−4.609	0.9979
Fluorobenzene	−2.734	−0.7480	0.9995	−9.074	−4.510	0.9995
Chlorobenzene	—	—	—	−8.681	−4.173	0.9988
Bromobenzene	−4.242	−1.109	0.9987	−9.250	−4.314	0.9996
Benzophenone	−5.881	−1.608	0.9989	−8.978	−4.202	0.9979
Thioanisole	−4.872	−1.318	0.9985	−9.012	−4.255	0.9986

o-tert-Butylphenol	−4.680	−1.345	0.9965	−9.165	−4.455	0.9988
p-tert-Butylphenol	−4.461	−1.341	0.9958	−9.006	−4.599	0.9983
p-Phenylphenol	−4.555	−1.345	0.9988	−9.308	−4.735	0.9977
Dibenzyl	−8.431	−2.192	0.9984	−9.724	−4.082	0.9992
N,*N*-Diethylaniline	−19.20	−6.107	0.9993	—	—	—
Dibenzoyl	−6.545	−1.821	0.9981	−9.753	−4.466	0.9989
o-Xylene	—	—	—	−8.435	−3.969	0.9993
m-Xylene	—	—	—	−9.222	−4.246	0.9957
p-Xylene	—	—	—	−9.392	−4.326	0.9993
α-Naphthol	—	—	—	−8.819	−4.619	0.9952
β-Naphthol	—	—	—	−8.050	−4.403	0.9976
α-Naphthylamine	—	—	—	−9.372	−4.536	0.9989
Dimethylnaphthalene	−6.408	−1.647	0.9988	−8.898	−3.918	0.9997
1-Bromonaphthalene	−6.479	−1.606	0.9988	−9.592	−4.086	0.9990
9-Anthracenemethanol	−5.772	−1.581	0.9982	−7.671	−3.914	0.9955

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Table 3. Enthalpies (ΔH°) and entropies (ΔS°) of PSABs, PAHs, and other solutes on PYE column.

	COSMOSIL 5PYE (PYE)					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzene	−2.675	−0.4545	0.9961	−9.176	−4.268	0.9996
Toluene	−3.816	−0.6972	0.9966	−9.092	−4.034	0.9989
Ethylbenzene	−5.552	−1.176	0.9992	−9.762	−4.089	0.9997
n-Butylbenzene	−9.148	−2.107	0.9997	−11.03	−4.174	0.9998
n-Hexylbenzene	−13.35	−3.211	0.9992	−12.74	−4.421	0.9997
n-Octylbenzene	−17.40	−4.241	0.9996	−14.56	−4.726	0.9998
Phenol	−1.025	−0.1402	0.9676	−8.932	−4.843	0.9937
p-Cresol	−1.883	−0.3502	0.9866	−8.873	−4.662	0.9943
p-*n*-Propylphenol	−4.237	−0.9560	0.9965	−9.301	−4.427	0.9991
p-*n*-Butylphenol	−5.942	−1.413	0.9980	−9.395	−4.264	0.9984
p-*n*-Pentylphenol	−7.832	−1.927	0.9983	−10.14	−4.340	0.9992
p-*n*-Hexylphenol	−9.722	−2.427	0.9989	−10.93	−4.444	0.9994
Iodobenzene	—	—	—	−9.542	−3.829	0.9997
p-Methyliodobenzene	−7.919	−1.578	0.9986	−10.12	−3.793	0.9998
p-Ethyliodobenzene	−9.691	−2.024	0.9991	−10.69	−3.800	0.9991
p-*n*-Propyliodobenzene	−11.41	−2.433	0.9991	−11.56	−3.924	0.9991
p-*n*-Butyliodobenzene	−13.44	−2.928	0.9992	−12.62	−4.121	0.9992
p-*n*-Pentyliodobenzene	−15.27	−3.373	0.9994	−13.51	−4.266	0.9994

Acetophenone	−4.998	−1.141	0.9994	−8.397	−4.043	0.9978
p-Methylacetophenone	−7.582	−1.839	0.9996	−8.819	−3.973	0.9977
p-Ethylacetophenone	−9.256	−2.275	0.9997	−9.647	−4.081	0.9997
p-*n*-Propylacetophenone	−11.00	−2.725	0.9997	−10.04	−4.027	0.9994
p-*n*-Butylacetophenone	−13.18	−3.301	0.9997	−11.03	−4.197	0.9997
p-*n*-Pentylacetophenone	−15.17	−3.816	0.9998	−12.11	−4.406	0.9998
Aniline	−2.030	−0.4123	0.9715	—	—	—
p-*n*-Butylaniline	−8.781	−2.267	0.9974	—	—	—
p-*n*-Hexylaniline	−12.63	−3.300	0.9989	—	—	—
p-*n*-Octylaniline	−16.31	−4.235	0.9995	—	—	—
Benzene	−1.304	0.05870	0.9828	−9.003	−4.200	0.9985
Naphthalene	−4.504	−0.5881	0.9975	−9.207	−3.742	0.9997
Fluorene	−9.089	−1.635	0.9973	−10.24	−3.688	0.9997
Biphenyl	−7.365	−1.313	0.9978	−10.72	−4.024	0.9995
Anthracene	−9.404	−1.544	0.9991	−10.56	−3.592	0.9998
Phenanthrene	−8.983	−1.447	0.9988	−10.41	−3.578	0.9996
Fluoranthene	−10.64	−1.668	0.9987	−10.76	−3.449	0.9997
Pyrene	−10.33	−1.502	0.9990	−10.40	−3.250	0.9990
Chrysene	−13.66	−2.210	0.9988	−12.02	−3.516	0.9997
Triphenylene	−14.48	−2.418	0.9991	−13.02	−3.804	0.9997
Perylene	—	—	—	−13.63	−3.571	0.9999
o-Terphenyl	−11.12	−2.111	0.9989	−12.05	−4.015	0.9996
m-Terphenyl	−13.66	−2.628	0.9990	−12.41	−3.965	0.9996
p-Terphenyl	−14.75	−2.902	0.9990	−13.50	−4.221	0.9996

(*continued*)

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Table 3. Continued.

	COSMOSIL 5PYE (PYE)					
	$CH_3OH : H_2O = 80 : 20$			$ACN : H_2O = 80 : 20$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzylalcohol	—	—	—	−7.344	−4.201	0.9921
Benzamide	—	—	—	−7.832	−4.726	0.9946
Benzylamine	—	—	—	—	—	—
Benzonitrile	—	—	—	−9.276	−4.420	0.9990
Nitrobenzene	−4.783	−0.8800	0.9945	−8.947	−4.069	0.9997
Nitrosobenzene	—	—	—	−8.853	−4.032	0.9981
Fluorobenzene	−1.320	0.04690	0.9687	−9.248	−4.343	0.9994
Chlorobenzene	—	—	—	−9.049	−3.969	0.9986
Bromobenzene	−3.377	−0.3725	0.9943	−9.141	−3.878	0.9996
Benzophenone	−7.144	−1.382	0.9967	−9.290	−3.778	0.9988
Thioanisole	−4.816	−0.8295	0.9953	−9.529	−4.028	0.9996

o-tert-Butylphenol	−3.320	−0.5340	0.9933	−9.429	−4.275	0.9987
p-tert-Butylphenol	−3.375	−0.5942	0.9940	−9.094	−4.308	0.9988
p-Phenylphenol	−5.007	−0.9647	0.9955	−9.365	−4.246	0.9993
Dibenzyl1	−9.264	−1.801	0.9976	−10.86	−3.929	0.9988
Dibenzyl2	−9.530	−1.598	0.9976	−10.44	−3.544	0.9989
Dibenzoyl	−8.649	−1.802	0.9974	−9.699	−3.868	0.9991
o-Xylene	—	—	—	−9.385	−3.957	0.9984
m-Xylene	—	—	—	−9.556	−3.992	0.9991
p-Xylene	—	—	—	−9.260	−3.906	0.9986
α-Naphthol	—	—	—	−8.647	−4.189	0.9981
β-Naphthol	—	—	—	−8.680	−4.269	0.9974
α-Naphthylamine	—	—	—	−10.56	−4.259	0.9996
Dimethylnaphthalene	−7.390	−1.324	0.9974	−10.55	−3.963	0.9996
1-Bromonaphthalene	−7.693	−1.219	0.9975	−10.09	−3.567	0.9990
9-Anthracenemethanol	−8.312	−1.564	0.9987	−7.731	−3.161	0.9997

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Table 4. Enthalpies (ΔH°) and entropies (ΔS°) of PAHs and other solutes on YMC CHIRAL β-CD BR (β-CD) column.

	$CH_3OH : H_2O = 40 : 60$		
Solutes	ΔH° (kJ/mol)	$\Delta S^\circ/R + \ln \phi$	R
Benzene	−33.03	−12.30	0.9984
Naphthalene	−38.19	−14.04	0.9987
Fluorene	−41.22	−14.96	0.9993
Biphenyl	−44.45	−15.48	0.9994
Anthracene	−46.26	−15.99	0.9993
Phenanthrene	−41.04	−14.99	0.9999
Fluoranthene	−38.51	−14.32	0.9996
Pyrene	−40.30	−15.04	0.9996
Chrysene	−48.85	−16.97	0.9995
Triphenylene	−39.46	−14.33	0.9997
p-Phenylphenol	−46.78	−16.30	0.9998
Nitrobenzene	−32.59	−12.86	0.9991
Dimethylnaphthalene	−44.80	−15.61	0.9997
1-Bromonaphthalene	−42.92	−16.04	0.9999
Bromobenzene	−36.09	−13.23	0.9991
Fluorobenzene	−33.11	−12.64	0.9991
Benzophenone	−43.63	−15.95	0.9994
Dibenzyl1	−45.72	−15.82	0.9988
Dibenzyl2	−51.66	−17.76	0.9988
Thioanisole	−38.29	−14.13	0.9988
9-Anthracenemethanol	−34.05	−13.31	0.9998
o-Cresol	−31.62	−13.12	0.9981
m-Cresol	−34.37	−13.86	0.9985
p-Cresol	−34.70	−13.40	0.9984
o-Nitroaniline	−31.09	−12.71	0.9983
m-Nitroaniline	−30.47	−12.45	0.9985
p-Nitroaniline	−39.27	−14.63	0.9991

EXPERIMENTAL

Chemicals

p-Substituted benzenes, PAHs, and substituted benzenes were purchased from Kanto Chemicals and Tokyo Kasei Chemicals, Japan. HPLC-grade methanol and acetonitrile obtained from Nacalai tesque (Kyoto, Japan) were used. Purified water (18.2 MΩ) was used.

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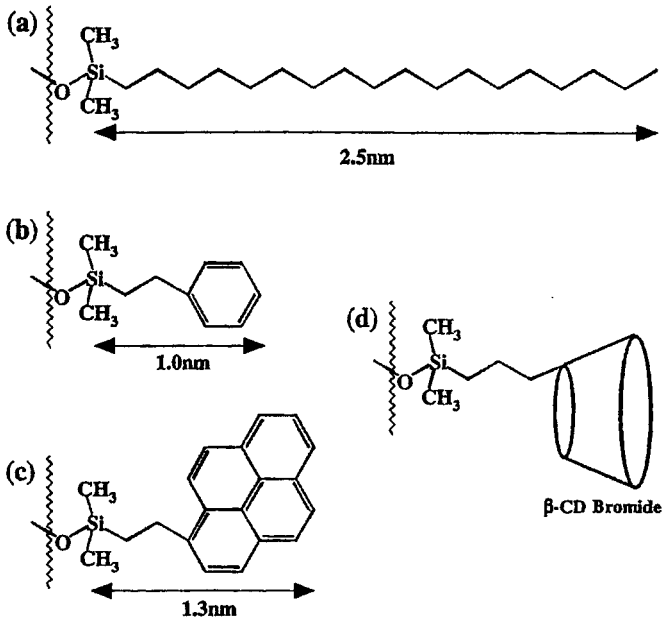

Figure 1. Structure and ligand length of stationary phases (a) ODS, (b) Ph, (c) PYE, and (d) β-CD. Ligand densities of all stationary phases are ca. 1.5 groups/nm^2.

Apparatus

An HPLC instrument was set up equipped with the following (Shimadzu, Japan): pump (LC-10AD), UV-VIS detector (SPD-6AV), auto-sampler (SIL-10A), system controller (SPD-10A), and a chromatopac (CR-4A). Column temperatures were controlled by a column oven (CTO-6A) or gas chromatographic oven (GC-9A). The controlled temperature precision was $\pm 0.1^{\circ}$C.

Chromatography

Commercially available columns, Mightysil RP-18 (ODS, 150×2.1 mm I.D.), Develosil PheA (Ph, 150×2.1 mm I.D.), COSMOSIL 5PYE (PYE, 150×4.6 mm I.D.), and YMC CHIRAL β-CD BR (β-CD, 150×4.6 mm I.D.) were employed in this work. All these columns had densities of stationary phases 1.5 groups/nm^2. Methanol–water or acetonitrile–water (80/20) was used as mobile phases, but methanol/water (40 : 60) for the β-CD column. To obtain a similar linear velocity, 0.2 and 0.8 mL/min of flow rates were used for 2.1 and

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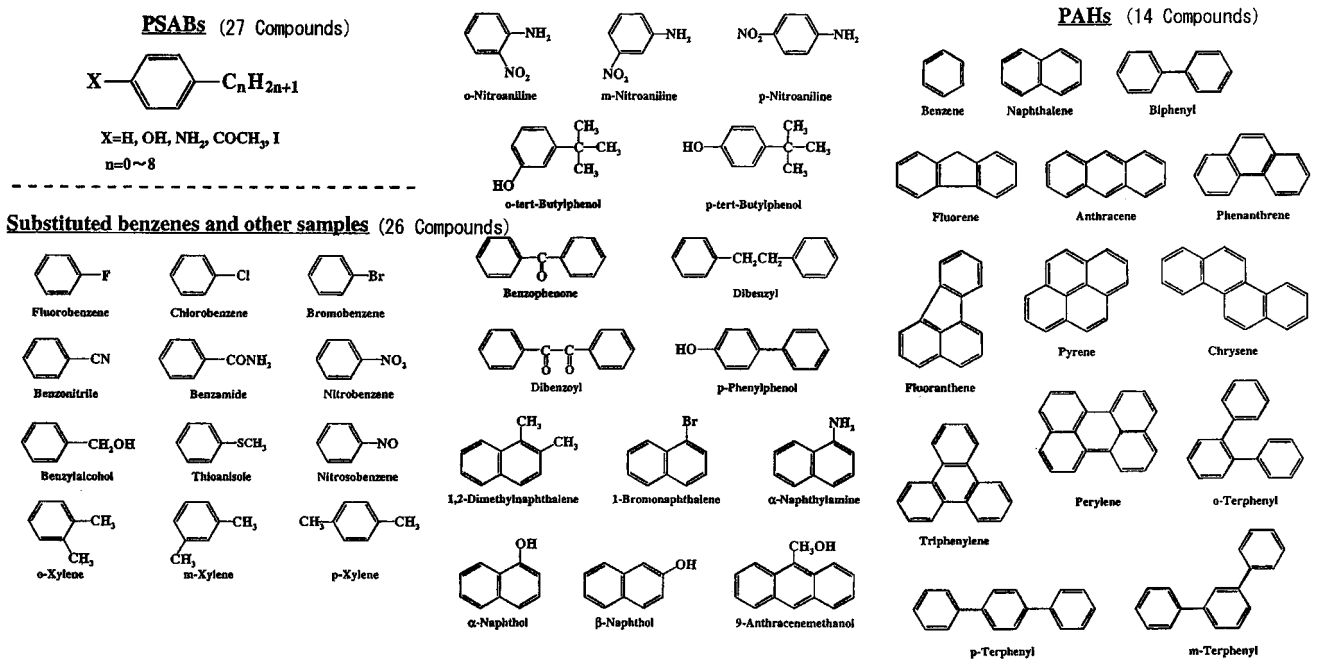

Figure 2. Structures of PSABs, PAHs, and substituted benzenes.

4.6 mm I.D. columns, respectively. Detection wavelength was 254 nm. The retention factors were determined at five to seven different temperatures in the range of 25–70°C. The retention time of organic solvent in mobile phase or 2,4-dichlorobenzoic acid was determined as t_0. The retention factor used was the average values determined for three to seven times.

RESULTS AND DISCUSSION

Thermodynamic Measurements in Liquid Chromatography

van't Hoff analysis has been used to probe the thermodynamics of chromatographic processes. The van't Hoff expression for chromatography is

$$\ln k' = \left(\frac{-\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) + \ln \phi \tag{1}$$

where k' is the capacity factor, ΔH° and ΔS° represent the enthalpy and entropy of transfer of the solute from the mobile phase to the stationary phase; R and T are the gas constant and absolute temperature, respectively; and ϕ is the volume phase ratio (stationary/mobile). Plotting $\ln k'$ vs. $1/T$ will give a slope of $-\Delta H^\circ/R$, and the entropy and phase ratio are combined in the intercept. Thus, the ΔH° can be calculated from the slope of a van't Hoff plot. It has been pointed out that the linearity in van't Hoff plots can easy be found in the temperature range of 30–50°C or 60°C, but there are significant deviations from linearity if the temperature range is widened.[3,4,13] Besides, the high content of water in the mobile phase and the binding density of stationary phases have influence on the linearity of van't Hoff plot. Thus, to obtain excellent linearity, the content of organic solvent higher than 60% and the binding density of stationary phase of about 3.0 μmol/m^2 (1.8 groups/nm^2) were used in this work.

After measuring the capacity factors at five to seven different temperatures with an increment of 5°C in the temperature range of 25–75°C, the thermodynamic data in LC retention process were calculated and listed in Tables 1–4 according to van't Hoff analysis. It was shown that excellent linearity with correlation factors (R) higher than 0.992 were obtained for almost all measurements with some exceptions. As an example, the van't Hoff plot of PAHs on the ODS column in methanol–water mobile phase is shown in Fig. 3. As shown in Tables 1–4, all the changes of enthalpy (ΔH°) show negative values, it suggests that energy is released when solutes transfer from mobile phase to stationary phase. In other words, it is more stable for solutes to be retained on the stationary phases than in mobile phase. Besides, it was

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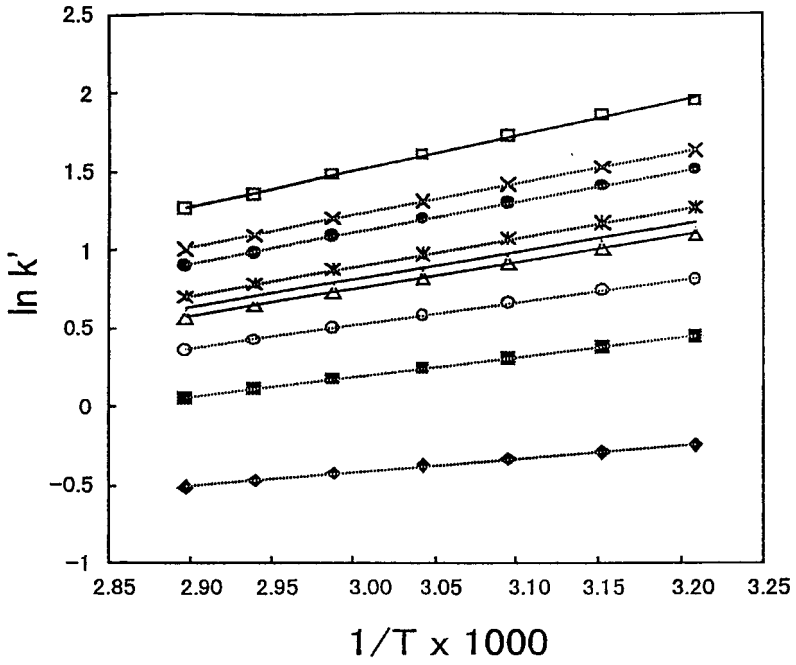

Figure 3. Plots of logarithm of capacity factor, $\ln k'$, and reciprocal of column temperature, $1/T$, for polyaromatic hydrocarbons on Mightysil RP-18 (ODS) in methanol–water (80/20) mixture as a mobile phase. Solutes: (◆) benzene; (■) naphthalene; (○) biphenyl; (△) fluorine; (—) phenanthrene; (×) anthracene; (●) fluoranthene; (×) pyrene; and (□) chrysene.

noticed that the differences in ΔH° among all solutes in methanol–water mobile phases were significant; but insignificant in acetonitrile–water mobile phases with the exception of ODS stationary phase. The differences in ΔS° among the solutes had a similar tendency to ΔH°. The absolute values of ΔH° and ΔS° in acetonitrile–water system were higher than that in methanol–water system. It suggests that there are differences in the retention mechanism between methanol–water and acetonitrile–water mobile phases.

Thermodynamic Analysis for the Differences in π–π Intermolecular Interaction

Based on the thermodynamic data shown in Tables 1–3, the differences in the π–π intermolecular interaction between stationary phases and solutes can

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be observed. The logarithm of capacity factors of solutes on ODS, Ph, and PYE columns at 35°C were plotted with the enthalpy of solute transfer (ΔH°) in methanol–water (80 : 20) mixture and shown in Fig. 4. For ODS column shown in Fig. 4(a), the plot of PAHs located within the area of PSABs. It suggested that the PAHs showed similar retention behavior to PSABs due to the absence of functional groups providing π–π interaction on the ODS column. For the PYE column shown in Fig. 4(c), the plot of PAHs obviously located above and far from all PSABs. It indicated that the π–π intermolecular interaction between the PYE stationary phase and the solutes made a dominate contribution for the chromatographic retention. For the Ph column shown in Fig. 4(b), the plot of PAHs is also located above the plots of PSABs, but is unlike the PYE column having very obvious differences between PAHs and PSABs. The reasons could be regarded as the size of Ph being smaller than the size of PYE groups and the π–π interaction between Ph stationary phase and analytes being weaker than that between PYE stationary phase and analytes. On the other hand, the differences in $\ln k' \sim \Delta H^\circ$ plots among stationary phases are affected by the differences in the binding density of stationary phases and the stereo-selectivity of stationary phase for solutes.

Thermodynamic Analysis for the Differences in Host–Guest Interaction

Based on the thermodynamic data on the β-CD column in Table 4, the logarithm of the capacity factors at 35°C ($\ln k'$) was plotted with the molar enthalpy (ΔH°) in Fig. 5. The mobile phase was methanol–water (40 : 60), and the solutes were PAHs and substituted benzene derivatives. As shown in Table 4, the change of enthalpies (ΔH°) and entropies (ΔS°) on the β-CD column for the solutes examined were relatively larger than that on other columns, probably due to the presences of not only the hydrophobic but also the host–guest interactions. Further, as shown in Fig. 5(a), an increasing tendency of the change of enthalpy (ΔH°) was observed with the strong formation of the host–guest interaction. It was interestingly found that there were significant changes of enthalpy (ΔH°) and exceptional retention for the solutes having similar sizes of β-CD (ca. 0.78 nm), as shown in the cyclic area of Fig. 5(a). In chromatography, the logarithm of the partition coefficients in 1-octanol-water ($\log P$) was usually considered as the parameter of evaluating the hydrophobicity of solutes. The $\log P$ values of solutes examined were calculated by a method.[14] The logarithm of the capacity factors at 35°C ($\ln k'$) was plotted with the $\log P$ in Fig. 5(b). It has been shown that the retention of solutes on the β-CD column depends on the hydrophobicity of solutes. On the basis of Fig. 5(a) and (b), we can draw a conclusion that the retention of

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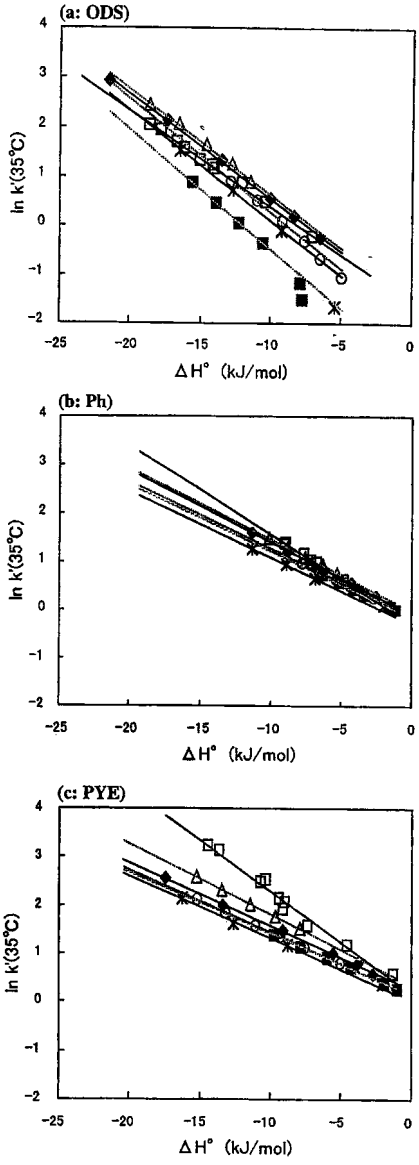

Figure 4. Plots of the logarithm of capacity factor at 35°C [$\ln k'(35°C)$] and the enthalpy of solute transfer ($\Delta H°$), in methanol–water (80 : 20) mixture on (a) ODS, (b) Ph, and (c) PYE columns. Solutes: (◆) *p-n*-alkylbenzenes; (■) *p-n*-alkylphenols; (△) *p-n*-alkyliodobenzenes; (○) *p-n*-alkylacetophenones; (×) *p-n*-alkylanilines; and (□) PAHs.

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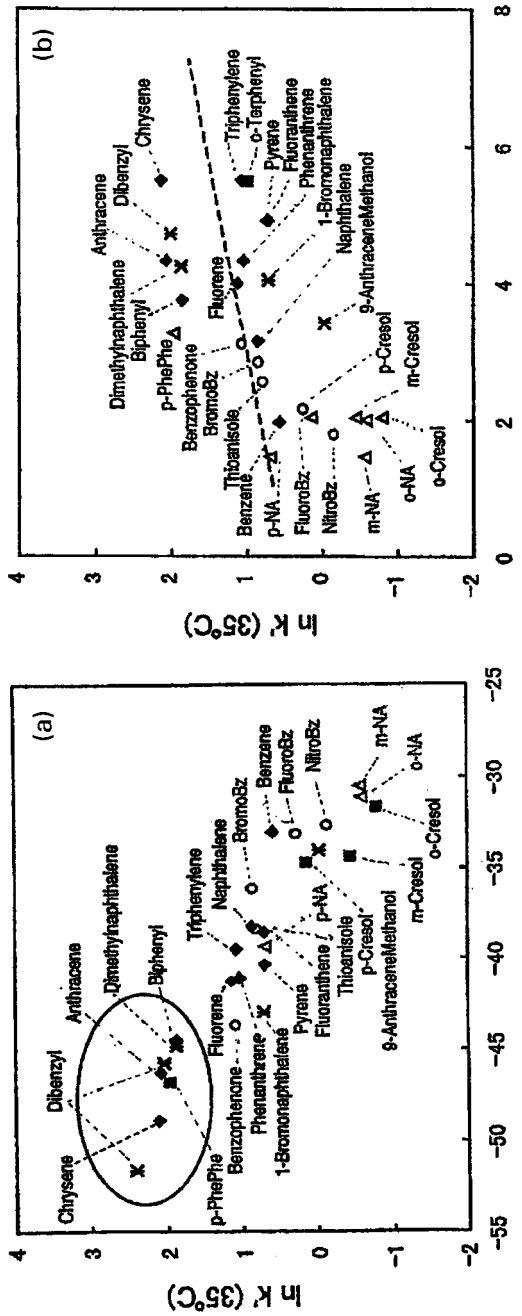

Figure 5. Plots of logarithm of the capacity factor at 35°C [$\ln k'(35°C)$] vs. molar enthalpy ($\Delta H°$) (a) and logarithm of partition coefficient in 1-octanol-water ($\log P$) (b) on β-CD column in methanol–water (40 : 60) mixture. Solutes: (♦) PAHs; (○) mono-substituted benzene; (×) mono-substituted PAHs; (■) phenols (a); (■) terphenyl (b); (△) nitroanlines (a); and (△) phenol (b).

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solutes on the β-CD column contributes not only to the hydrophobic interaction, but also mainly to the host–guest interaction dependent on the stereochemical structures of solutes.

Retention Mechanism in LC: Adsorption or Partitioning?

There are two main theories, namely solvophobic theory and the partition model describing the retention mechanism in RRLC.[15] Solvophobic theory, first applied to RPLC by Horvath and co-workers in 1976, proposes that retention is primarily related to hydrophobic interactions between the mobile phase and solutes.[16,17] The role of the stationary phase is minimized by solvophobic theory, and retention is thought to occur through an adsorption rather than partitioning process. The partitioning model of retention considers, more explicitly, the role of the stationary phase in the retention process. In 1983, Martire and Boehm published the first retention model to consider the effects of stationary phase chain organization.[18] Later, Dill proposed a partitioning model of retention based upon mean-field statistical thermodynamic theory, which describes a three-step molecular process by which the solute transfers from the mobile phase to the stationary phase.[15,19] On the basis of thermodynamic data, the retention mechanisms are discussed as follows.

As shown in Fig. 6, the plot of molar enthalpy (ΔH°) vs. the alkyl chain length of PSABs indicates the change of enthalpy with an increment of one methyl group. For the ODS column shown in Fig. 6(A-a) and (B-a) the ΔH° showed a linear relationship with the length of alkyl chain, and slopes were almost independent on the length of alkyl chain. As well known in the field of liquid–liquid equilibrium, this linear relationship shows a typical partitioning behavior. For example, the plots in Fig. 6 is very similar to the plots of the free energy change of solutes transferring from the water phase to heptane or octanol phases, vs. the length of carbon chain of the solutes, as shown in Fig. 7.[20] However, the enthalpy changes resulting from the increase of one carbon chain length of the solutes (the slopes of lines) in Fig. 6 are quite smaller than those in Fig. 7. The reason is that the methanol–water (80 : 20) was used as a phase in Fig. 6, but 100% water in Fig. 7. Based on above facts, we can deduce that the retention of solutes on the ODS stationary phase results from the partitioning mechanism. Although the ODS groups were chemically bonded on the surface of silica gel, they work as if they are a highly hydrophobic organic phase in liquid–liquid equilibrium. Solutes are partitioned between the stationary phase and mobile phase.

Like the ODS stationary phase, the Ph stationary phase also showed an excellent linear relationship of ΔH° vs. alkyl chain length of solutes in the

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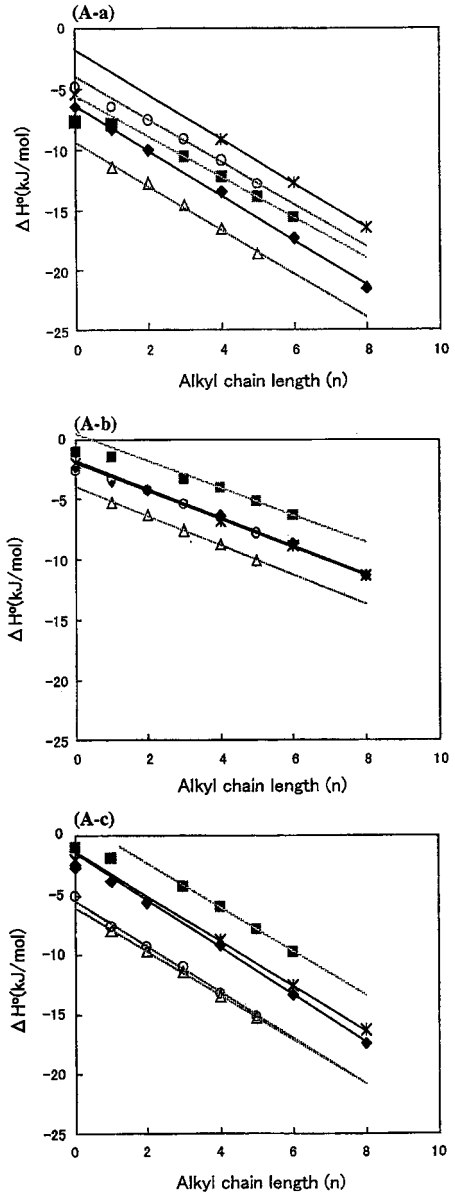

Figure 6. Plots of alkyl chain length of PSABs (n) and molar enthalpy (ΔH°). Mobile phase: (A) methanol–water (80 : 20), (B) acetonitrile–water (80 : 20). Columns: (a) ODS; (b) Ph; and (c) PYE. Solutes: (◆) *p-n*-alkylbenzenes; (□) *p-n*-alkylphenols; (△) *p-n*-alkyliodobenzenes; (○) *p-n*-alkylacetophenones; and (×) *p-n*-alkylanilines.

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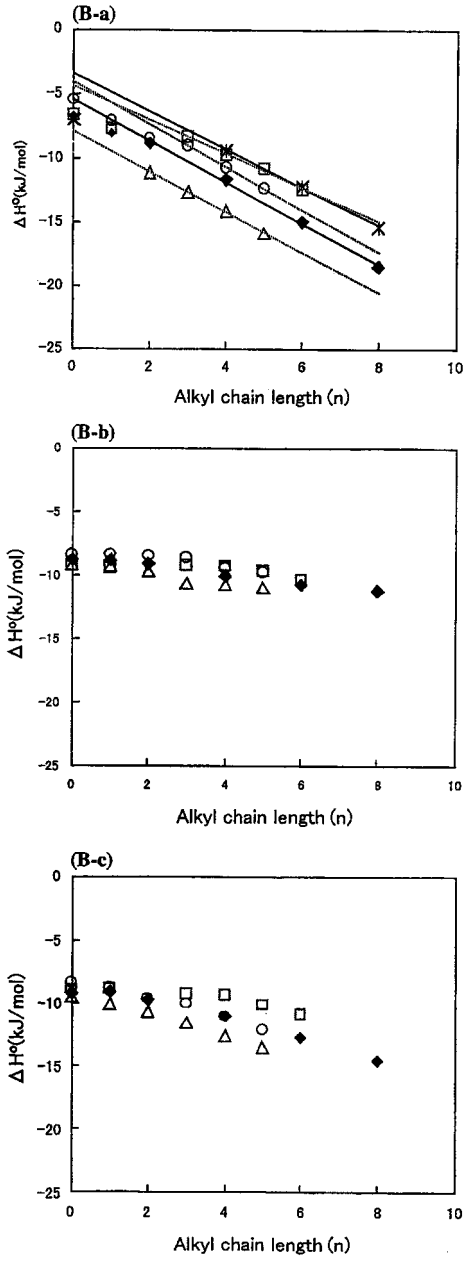

Figure 6. Continued.

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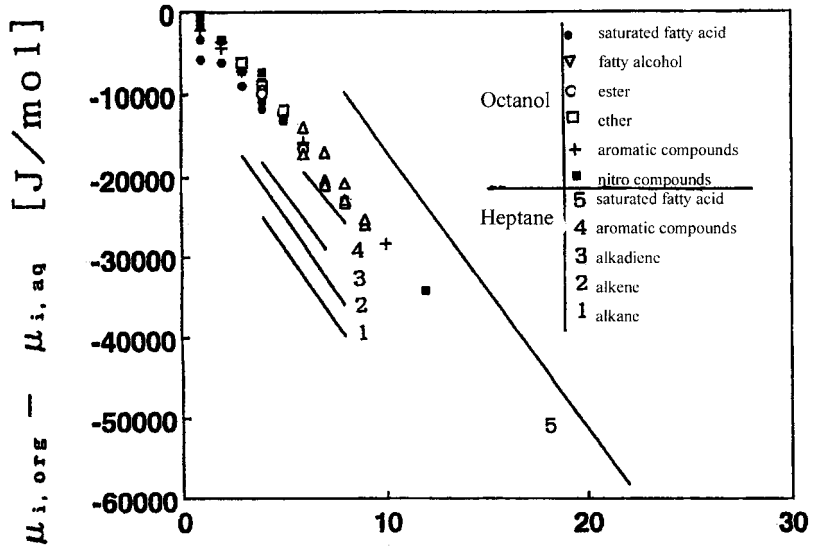

Figure 7. Plots of free energy of solutes transferring between water and organic phases (heptane and octanol) with the carbon chain length of solutes, from Ref.[20].

methanol–water mobile phase, as shown in Fig. 6(A-b). However, the ΔH° almost did not change with the alkyl chain length in the acetonitrile–water mobile phase, as shown in Fig. 6(B-b). As shown in Tables 1–4, the ΔH° in the acetonitrile–water system was larger than in the methanol–water system. The increase of enthalpy means the molecular ordering is based on the thermodynamic viewpoint. Thus, it is more stable for solutes to situate in the mobile phase than to embed in stationary phase when the acetonitrile–water mixture is used as the mobile phase. Based on these thermodynamic results, we could deduce that adsorption mechanism also plays an important role in the retention of solutes on the Ph column when an acetonitrile–water system was used as the mobile phase. As shown in Fig. 6(A-c) and (B-c), the PYE stationary phase showed a similar tendency with the Ph stationary phase in both methanol–water and acetonitrile–water systems. In other words, the retention is mainly based on the partitioning in a methanol–water mobile phase, but also on the adsorption in the acetonitrile–water mobile phase. Further, it was noticed that the plot in Fig. 6(B-c) was also similar with Fig. 6(A-c). Therefore, a reasonable explanation for the retention of solutes on the PYE stationary phase in the acetonitrile–water mobile phase should be the concomitance of partitioning and adsorption.

Effect of the Characteristic of Stationary Phase on Thermodynamic Values

As described above, the retention mechanism in LC is affected by the type of mobile phases. The effect of the characteristics of stationary phase, like the binding density and the log *P* of monomeric molecule of stationary phase, will be discussed as follows. As shown in Table 5, the enthalpy change with the increase of one carbon number of methylene ($\Delta\Delta H^\circ$) almost correlates with the binding carbon density of stationary phase, and the enthalpy changes of all solutes depends on the log *P*. The enthalpy change for solutes to transfer from the mobile phase to the stationary phase was increased with the increase of log *P*. This suggests that it is more stable for solutes to embed in the high hydrophobic stationary phase with higher log *P*. Thus, based on the partitioning, the retention on the stationary phase with higher log *P* is stronger and the enthalpy change is more significant.

CONCLUSIONS

The thermodynamic data (ΔH and ΔS°) of chromatographic interactions, including four stationary phases and 53 solutes and two mobile phase systems (methanol–water and acetonitrile–water), were measured by van't Hoff analysis. It has been found that there are obvious differences in π–π intermolecular interactions among the stationary phases of ODS, Ph, and PYE by comparing the plots of $\ln k' \sim \Delta H$. Based on thermodynamic analysis, both hydrophobic

Table 5. Comparison of thermodynamic values, carbon density, and log *P* of monomeric selector of ODS, Phe, and PYE.

Column	ODS	Ph	PYE
$\Delta\Delta H^\circ$/methylene (kJ/mol)[a]	−1.79	−1.17	−1.89
Carbon density (Cn/nm^2)[b]	30	15	30
p-*n*-Butylbenzene [ΔH° (kJ/mol)][c]	−13.5	−6.35	−9.15
p-*n*-Butylphenol (ΔH°)[c]	−12.2	−4.08	−5.94
p-*n*-Butyliodobenzene (ΔH°)[c]	−16.6	−8.79	−13.4
log *P* (monomeric selector)[d]	9.18	3.03	6.07

Note: Mobile phase: methanol–water (80 : 20).
[a]The enthalpy change with the increase of one carbon in the length of methylene chain.
[b]Carbon density means the carbon number per one unit area.
[c]The enthalpy change of solutes.
[d]log *P* of monomeric molecule of stationary phase.

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and host–guest interactions make contributions to the retention of solutes on the β-CD stationary phase, and the structures of solutes having similar molecular size with the cavity of β-CD, show exceptional retention and resulted in large enthalpy changes. Further, the type of mobile phases and the characteristics of stationary phase have critical influence on the retention mechanisms in liquid chromatography.

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