CHROMSYMP. 445

DEPENDENCE OF THE RETENTION OF PHENOLS UPON VAN DER WAALS VOLUME, π-ENERGY AND HYDROGEN-BONDING EFFECTS

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SUMMARY

The retention of polyaromatic hydrocarbons (PAHs) and alkylbenzenes (Ph–R) can be predicted from their Van der Waals volume and π-energy effect, and that of alkyl alcohols (R–OH) from their Van der Waals volume and hydrogen-bonding effect. The maximum retention is related to the Van der Waals volume, log k' (VWV). Retention is reduced by the π-energy effect, log k' (π), or the hydrogen-bonding effect, log k' (HB). Therefore, the retention time is given by

$$\log k' \text{ (PAH and Ph–R)} = \log k' \text{ (VWV)} - \log k' (\pi)$$

or

$$\log k' \text{ (R–OH)} = \log k' \text{ (VWV)} - \log k' \text{ (HB)}$$

Furthermore, the retention of phenols (Ph–OH) is given by

$$\log k' \text{ (Ph–OH)} = \log k' \text{ (VWV)} - \log k' (\pi) - \log k' \text{ (HB)}$$

in acidic acetonitrile–water mixtures on octadecyl-bonded silica gels.

INTRODUCTION

Among several parameters used for the prediction of retention time in liquid chromatography, solubility parameters are promising because with these there is the possibility of characterizing the nature of the molecules. The maximum retention time of a molecule can be predicted from its Van der Waals volume in simple reversed-phase liquid chromatography when octadecyl-bonded silica gels are used as the packing and acetonitrile–water mixtures as the eluent.

The retention of polyaromatic hydrocarbons, alkylbenzenes and halogenated benzenes is reduced by their π-energy effect[1,2], and that of alkyl alcohols by their hydrogen-bonding effect[3].

The retention of phenols can be predicted from their log P values (partition coefficient between octanol and water) in acidic acetonitrile–water mixtures on octadecyl-bonded silica gels[4]. However, the equation used cannot be applied to other

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TABLE I

COMPOUNDS AND THEIR PHYSICAL PARAMETERS

Experimental conditions: column, ERC-1000 (ODS), 15 cm × 6.0 mm I.D.; eluent, 0.01M phosphoric acid in acetonitrile–water mixtures; column temperature, 30°C.

	Compound	VWV*	log k' (% acetonitrile)					π**	H***	Eδ
			90	80	70	60	50			
1	Benzene	48.36	-0.170	0.051	0.270	0.482	0.717	1.861	—	—
2	Naphthalene	73.96	0.015	0.274	0.528	0.784	1.090	3.871	—	—
3	Phenanthrene	99.56	0.215	0.506	0.791	1.089	—	5.762	—	—
4	Chrysene	125.16	0.444	0.770	1.090	—	—	7.281	—	—
5	Tetrasene	125.16	0.502	0.841	1.172	—	—	6.475	—	—
6	Toluene	59.51	-0.051	0.191	0.424	0.658	0.926	2.262	—	—
7	Ethylbenzene	69.74	0.047	0.306	0.563	0.825	1.125	2.735	—	—
8	Propylbenzene	79.97	0.169	0.453	0.729	1.015	1.354	2.891	—	—
9	Butylbenzene	90.20	0.280	0.593	0.896	1.206	—	3.119	—	—
10	Hexylbenzene	110.66	0.527	0.889	1.236	—	—	3.386	—	—
11	Heptylbenzene	120.89	0.654	1.043	—	—	—	3.467	—	—
12	Octylbenzene	131.12	0.783	1.198	—	—	—	3.516	—	—
13	Nonylbenzene	141.35	0.914	—	—	—	—	3.678	—	—
14	Decylbenzene	151.58	1.043	—	—	—	—	3.751	—	—
15	Chlorobenzene	57.84	-0.059	0.180	0.417	0.652	0.925	2.068	—	—
16	1,2-Dichlorobenzene	67.32	0.053	0.306	0.553	0.806	1.105	2.307	—	—
17	1,3-Dichlorobenzene	67.32	0.107	0.365	0.619	0.880	1.185	1.617	—	—
18	1,4-Dichlorobenzene	67.32	0.073	0.326	0.585	0.846	1.151	2.037	—	—
19	1,2,4-Trichlorobenzene	76.80	0.223	0.501	0.773	1.052	—	1.750	—	—
20	1,3,5-Trichlorobenzene	76.80	0.303	0.588	0.864	1.150	—	0.745	—	—
21	1,2,3,4-Tetrachlorobenzene	86.28	0.341	0.632	0.915	1.208	—	1.928	—	—
22	1,2,3,5-Tetrachlorobenzene	86.28	0.394	0.691	0.982	1.281	—	1.240	—	—
23	1,2,4,5-Tetrachlorobenzene	86.28	0.374	0.671	0.962	1.262	—	1.475	—	—
24	Pentachlorobenzene	95.76	0.503	0.822	1.126	—	—	1.454	—	—
25	Hexachlorobenzene	105.24	0.630	0.970	1.292	—	—	1.447	—	—
26	Bromobenzene	60.96	-0.015	0.223	0.463	0.704	0.980	2.099	1	—
27	Iodobenzene	65.48	0.048	0.295	0.545	0.797	1.087	2.070	—	—
28	Butanol	52.40	-0.465	-0.372	-0.274	-0.165	-0.046	—	7.335	—
29	Pentanol	62.63	-0.362	-0.246	-0.119	0.017	0.168	—	7.696	—

30	Hexanol	72.86	-0.231	-0.114	0.039	0.206	0.401	—	7.892	7.883
31	Heptanol	83.09	-0.111	0.040	0.210	0.399	0.626	—	8.012	8.259
32	Octanol	93.32	0.014	0.182	0.379	0.596	0.857	—	8.165	8.704
33	Decanol	113.78	0.270	0.489	0.729	0.993	1.321	—	8.310	9.116
34	Dodecanol	134.24	0.532	0.801	1.086	—	—	—	8.387	9.013
35	Tetradecanol	154.70	0.800	1.118	—	—	—	—	8.121	8.524
36	Pentane	58.03	0.291	0.565	0.834	1.139	—	—	—	9.762
37	Hexane	68.26	0.422	0.717	1.015	1.311	—	—	—	9.489
38	Heptane	78.49	0.550	0.875	1.205	—	—	—	—	9.851
39	Octane	88.72	0.689	1.039	1.384	—	—	—	—	9.360
40	Decane	109.18	0.960	—	—	—	—	—	—	9.175
41	Phenol	53.88	-0.558	-0.397	-0.198	-0.020	0.154	—	—	7.883
42	2-Methylphenol	65.03	-0.441	-0.251	-0.042	0.151	0.360	—	—	8.259
43	4-Methylphenol	65.03	-0.469	-0.292	-0.090	0.104	0.306	—	—	8.704
44	2,3-Dimethylphenol	76.18	-0.346	-0.159	0.062	0.274	0.509	—	—	9.116
45	2,5-Dimethylphenol	76.18	-0.340	-0.146	0.070	0.288	0.523	—	—	9.013
46	2,6-Dimethylphenol	76.18	-0.298	-0.106	0.113	0.326	0.558	—	—	8.524
47	3,4-Dimethylphenol	76.18	-0.399	-0.208	-0.002	0.208	0.433	—	—	9.762
48	3,5-Dimethylphenol	76.18	-0.379	-0.185	0.025	0.239	0.470	—	—	9.489
49	2,3,5-Trimethylphenol	87.33	-0.255	-0.045	0.184	0.415	0.674	—	—	9.851
50	2,3,6-Trimethylphenol	87.33	-0.214	-0.005	0.228	0.456	0.716	—	—	9.360
51	2,4,6-Trimethylphenol	87.33	-0.198	0.013	0.242	0.473	0.730	—	—	9.175
52	2,3,5,6-Tetramethylphenol	98.48	-0.124	0.104	0.348	0.590	0.870	—	—	10.126
53	2-Ethylphenol	75.26	-0.365	-0.176	0.036	0.253	0.492	—	—	9.192
54	4-Ethylphenol	75.26	-0.369	-0.183	0.040	0.254	0.491	—	—	9.122
55	2-Chlorophenol	63.03	-0.447	-0.264	-0.052	0.152	0.370	—	—	8.017
56	3-Chlorophenol	63.03	-0.418	-0.233	-0.017	0.199	0.437	—	—	7.647
57	4-Chlorophenol	63.03	-0.444	-0.246	-0.037	0.177	0.405	—	—	7.884
58	2,3-Dichlorophenol	72.51	-0.334	-0.138	0.093	0.319	0.580	—	—	8.225
59	2,4-Dichlorophenol	72.51	-0.295	-0.085	0.144	0.377	0.643	—	—	7.673
60	2,5-Dichlorophenol	72.51	-0.314	-0.105	0.131	0.372	0.640	—	—	8.004
61	2,6-Dichlorophenol	72.51	-0.310	-0.107	0.118	0.345	0.595	—	—	7.829
62	3,4-Dichlorophenol	72.51	-0.307	-0.099	0.138	0.370	0.641	—	—	7.830
63	3,5-Dichlorophenol	72.51	-0.233	-0.015	0.228	0.477	0.761	—	—	7.204
64	2,3,4-Trichlorophenol	81.99	-0.194	0.024	0.264	0.517	0.815	—	—	7.943
65	2,3,5-Trichlorophenol	81.99	-0.258	-0.047	0.184	0.415	0.676	—	—	8.226
66	2,3,6-Trichlorophenol	81.99	-0.183	0.036	0.279	0.531	0.818	—	—	7.989

TABLE I (continued)

Compound	VWV*	log k' (% acetonitrile)					π**	H***	E§
		90	80	70	60	50			
67 2,4,5-Trichlorophenol	81.99	-0.168	0.061	0.317	0.577	0.884	—	—	8.083
68 2,4,6-Trichlorophenol	81.99	-0.124	0.102	0.347	0.602	0.892	—	—	7.415
69 3,4,5-Trichlorophenol	81.99	-0.138	0.088	0.342	0.606	0.916	—	—	7.411
70 2,3,4,5-Tetrachlorophenol	91.47	-0.034	0.214	0.478	0.760	1.095	—	—	7.489
71 2,3,5,6-Tetrachlorophenol	91.47	-0.013	0.232	0.496	0.771	1.099	—	—	7.335
72 Pentachlorophenol	100.95	0.116	0.376	0.654	0.948	1.304	—	—	7.434
73 2-Chloro-5-methylphenol	74.51	-0.359	-0.148	0.073	0.299	0.544	—	—	8.420
74 4-Chloro-2-methylphenol	74.51	-0.304	-0.097	0.128	0.362	0.622	—	—	8.011
75 4-Chloro-3-methylphenol	74.51	-0.327	-0.130	0.087	0.311	0.563	—	—	8.587
76 3-Bromophenol	66.48	-0.389	-0.192	0.023	0.243	0.486	—	—	7.966
77 4-Bromophenol	66.48	-0.393	-0.213	0.010	0.227	0.401	—	—	8.199
78 2,4-Dibromophenol	79.08	-0.219	-0.008	0.230	0.472	0.754	—	—	7.854
79 2,6-Dibromophenol	79.08	-0.223	-0.014	0.219	0.453	0.718	—	—	7.942
80 2-Nitrophenol	67.11	-0.346	-0.142	0.075	0.280	0.504	—	—	7.585
81 3-Nitrophenol	68.16	-0.594	-0.386	-0.159	0.049	0.267	—	—	9.836
82 4-Nitrophenol	68.16	-0.594	-0.404	-0.201	0.006	0.221	—	—	9.678
83 2,4-Dinitrophenol	81.39	-0.513	-0.295	-0.052	0.172	0.420	—	—	11.291
84 2,5-Dinitrophenol	81.39	-0.517	-0.287	-0.035	0.200	0.456	—	—	11.413
85 2,6-Dinitrophenol	81.39	-0.522	-0.283	-0.044	0.188	0.431	—	—	11.707
86 3,4-Dinitrophenol	82.44	-0.666	-0.415	-0.152	0.094	0.361	—	—	12.959

* Van der Waals volume calculated by Bondi's method[5].

** π-Energy effect (kcal/mol); for calculations see refs. 1, 2.

*** Hydrogen-bonding energy effect (kcal/mol); for calculations see ref. 1.

§ Energy effect for phenols related to π-energy and hydrogen-bonding energy (kcal/mol).

compounds, due to the lack of solvent effects in the calculation of log P values. Therefore, the basic parameters, Van der Waals volume, π-energy and hydrogen-bonding effects, have been examined experimentally from the difference in log k' values of phenols.

EXPERIMENTAL

The instrumental details have been described previously[4] and the chemicals used are listed in Table I. The octadecyl-bonded silica gel column ERC-1000 (ODS) was obtained from ERMA Optical Works (Tokyo, Japan); the column temperature was 30°C.

The Van der Waals volumes were calculated by Bondi's method[5], and the hydrogen-bonding and π-energy effects were determined experimentally.

RESULTS AND DISCUSSION

The log k' values measured are listed in Table I together with the π-energies. The hydrogen-bonding energy of alcohols is 8.10 kcal/mol in this acidic eluent, and it is 8.13 kcal/mol in acetonitrile–water mixtures[3]. The energy effect on the retention of phenols is 7.88 kcal/mol, which value is close to the hydrogen-bonding energy of an alcohol with a Van der Waals volume similar to that of phenol. If the value of the delocalization energy of phenol is 2.20 kcal/mol[6], the hydrogen-bonding effect of phenol must be 5.68 kcal/mol. Furthermore, the delocalization energy of monochlorobenzene is 2.24 kcal/mol and that of mononitrophenols and monohydroxyphenols is 2.59 and 2.39 kcal/mol, respectively[6]. This means that the hydrogen-bonding energy of a hydroxy group, conjugated to a benzene ring, is about 5.7 kcal/mol. This value is very different from the ref. 7 value, 20 kcal/mol. The difference in energy levels among isomers of phenols may be due to the inductive effect of substituentes to π- and hydrogen-bonding energy effects.

The inductive effect of the π-energy can be obtained from the results for the benzene derivatives, except phenols. The difference between the π-energy effect of alkylbenzenes and that of benzene is 2.3–3.7 kcal/mol, and the solvent effect is less than 0.2 kcal/mol. The total energy effect of alkylphenols is 8.3–10.1 kcal/mol, and the solvent effect is less than 0.4 kcal/mol. This means that the energy effect of the alkyl group can be considered as being constant and the small difference as due to the size of the alkyl group.

The inductive effect of halogen is not negligible. The π-energy effect is 0.7–2.3 kcal/mol for benzene derivatives, and the values are changed by up to 0.7 kcal/mol by the solvent effect. The effect of the total energy change for halogenated phenols is 7.2–8.2 kcal/mol and the maximum solvent effect is 1.5 kcal/mol in the above system. The inductive effect is not linearly related with Hammett's σ constant or Taft's σ^* constant. The prediction of retention time for di-, tri- and tetrasubstituted compounds is, therefore, very difficult at present.

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