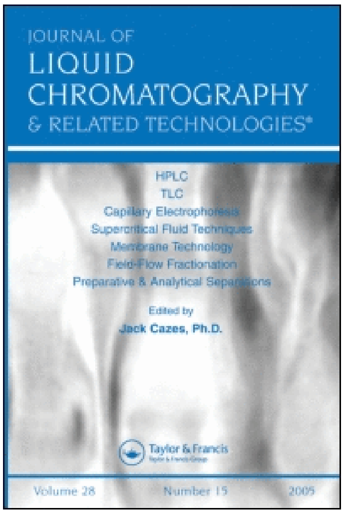

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RETENTION OF PHENOLS ON AN OCTADECYL-BONDED VINYLALCOHOL COPOLYMER GEL

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ABSTRACT

The chromatographic behavior of phenols was studied on an octadecyl-bonded vinylalcohol copolymer gel in acidic acetonitrile/water mixtures. The energy effect of phenols was measured on octadecyl-bonded silica gels where the values of alkylbenzenes were used as the standard instead of polyaromatic hydrocarbons. The selectivity within their isomers was larger on the octadecyl-bonded vinylalcohol copolymer gel than that measured on octadecyl-bonded silica gels. The correlation coefficient between the energy effects of phenols measured on the octadecyl-bonded vinylalcohol copolymer gel and those measured on an octadecyl-bonded silica gel was 0.685 (n=13) for alkylphenols and 0.392 (n=20) for halogenated phenols due to the selectivity of the vinylalcohol copolymer gel. Halogenated phenols were retained more on the organic polymer gel, and the average value of the energy effects was 50% less than the values obtained on the inorganic gel.

INTRODUCTION

Porous organic polymer gels have been used in a variety of research applications. These packing materials are chemically very stable but physically weaker than silica gelbased packings. The recent development of rigid porous organic polymer gels permits high-speed separation of many biologically important compounds. A rigid vinylalcohol copolymer gel, which is very polar and a powerful packing for the analysis of biological substances [1-4], was surface-modified with octadecyl groups, and the selectivity of the new packing was then examined in reversed-phase mode liquid chromatography. Selectivity of retention for polyaromatic hydrocarbons was very weak compared with that of polystyrene gels, but was stronger than that of octadecyl-bonded silica gels [5]. The retention of polyaromatic hydrocarbons and alkylbenzenes can be predicted from their Van der Waals volumes and pi-energy effects, and that of alkylalcohols from their Van der Waals volumes and hydrogen-bonding effects. Similarly,the retention of phenols (ph-OH) was given by the following equation:

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

in acidic acetonitrile/water mixtures on an octadecyl-bonded silica gel. Log k'(VWV) is given as the maximum capacity ratio of a solute, from the Van der Waals volume of the solute, on a calibration curve for alkanes. Log k'(pi) is the pi-energy effect of the phenyl group of phenol, and log k' (HB) is the hydrogen-bonding effect of the hydroxy group of phenol. The chromatographic behavior of 36 phenols was, furthermore, examined on an octadecyl-bonded vinylalcohol copolymer gel. The energy effects obtained on this octadecyl-bonded vinylalcohol copolymer gel are compared with those obtained on an octadecyl-bonded silica gel, and the selectivity of vinylalcohol copolymer gel is discussed.

EXPERIMENTAL

The chromatograph was assembled from several instruments. The degasser used was an ERC Model 3510 from ERMA Optical Works, Tokyo, Japan; the pump was a CCPD from Toyo Soda Inc., Tokyo, Japan; the injector was a Rheodyne Model 7125; the detectors were a Shodex Model SE-11 refractometer from Showa Denko, Inc., Tokyo, Japan, and an ERC Model 8710 ultraviolet detector; the recorder was a Shimadzu Model CR3A from Shimadzu Corp., Kyoto, Japan. An IBM PC5510 computer was used for the calculation. Deionized water was further purified by a Model Pureline from Yamato Sci. Co. Ltd., Tokyo, Japan. Acetonitrile was HPLC grade from Kishida Kagaku Co. Ltd., Tokyo, Japan. Reagents were mainly supplied by Tokyo Chem. Ind. Co. Ltd., and are listed in Table I with their physical parameters.

An octadecyl-modified vinylalcohol copolymer gel, BHST602C18, was obtained from Asahi Chem. Inc., Kawasaki, Japan. Its particle size was 9 µm, and the column was thermostated in a water bath at 30°C. The eluent consisted of acetonitrile/water mixtures containing 0.05M phosphoric acid. The Van der Waals volumes were calculated by Bondi's method [6].

RESULTS AND DISCUSSION

The capacity ratios of standard compounds were measured on an octadecyl-modified vinylalcohol copolymer gel (OD-VAG) in acetonitrile/water mixtures. The values are listed in Table I with their energy effects, together with the results obtained on an octadecyl-bonded silica gel (OD-SG). The energy effect of alkylbenzenes obtained on an OD-SG [1], was used

Table I Phenols and their physical parameters
Experimental conditions: column, 602C18 (10 cm x 6.0 mm I.D.); eluent, acetonitrile/water mixtures containing 0.05M phosphoric acid; flow rate, 1 mL/min; column temperature, 30°C

	Compound	VWV*	log k'(% acetonitrile) 80	 70	 60	 50	E**	E***
1	Toluene	59.51	-0.7084	-0.4484	-0.1903	0.0712	2.527	2.262
2	Ethylbenzene	69.74	-0.6486	-0.3489	-0.0692	0.2354	2.676	2.735
3	Propylbenzene	79.97	-0.4916	-0.1980	0.0919	0.4250	2.823	2.891
4	Butylbenzene	90.20	-0.3461	-0.0509	0.2567	0.6148	2.972	3.119
5	Hexylbenzene	110.66	-0.0832	0.2585	0.5986	1.0001	3.256	3.386
6	Heptylbenzene	120.89	0.0712	0.4150	0.7793	1.2094	3.416	3.467
7	Octylbenzene	131.12	0.2180	0.4230	0.9603	1.4190	3.563	3.516
8	Nonylbenzene	141.35	0.3789	0.7423	1.1323	1.6275	3.712	3.678
9	Decylbenzene	151.55	0.5073	0.7739	1.1927	1.6876	3.860	3.751
10	Phenol	53.88	-0.4835	-0.2931	-1.0544	-0.8133	9.218	7.883
11	2-Methylphenol	65.03	-1.2028	-0.9699	-0.7394	-0.4630	8.127	8.259
12	4-Methylphenol	65.03	-1.2703	-0.9758	-0.8930	-0.6202	9.816	8.704
13	2,3-Dimethylphenol	76.18	-1.0518	-0.9808	-0.5487	-0.2809	8.330	9.116
14	2,4-Dimethylphenol	76.18	-1.1038	-0.8617	-0.5884	-0.3151	8.662	-----
15	2,5-Dimethylphenol	76.18	-1.1179	-0.8572	-0.5839	-0.3251	8.683	9.013
16	2,6-Dimethylphenol	76.18	-1.1122	-0.8497	-0.5620	-0.2958	8.456	8.524
17	3,4-Dimethylphenol	76.18	-1.2467	-1.0036	-0.7280	-0.4586	9.925	9.762
18	3,5-Dimethylphenol	76.18	-1.2623	-1.0047	-0.7259	-0.4390	9.833	9.489
19	2,3,5-Trimethylphenol	87.33	-1.0381	-0.7232	-0.4492	-0.1660	9.247	9.851
20	2,3,6-Trimethylphenol	87.33	-0.9643	-0.6952	-0.4278	-0.1378	9.027	9.360
21	2,4,6-Trimethylphenol	87.33	-0.9744	-0.7122	-0.4313	-0.1514	9.101	9.175
22	2-Ethylphenol	75.26	-1.1080	-0.8452	-0.5728	-0.2766	8.272	9.192
23	3-Ethylphenol	75.26	-1.1858	-0.9460	-0.6852	-0.3820	9.246	-----
24	4-Ethylphenol	75.26	-1.2187	-0.9670	-0.6965	-0.3854	9.314	9.122

25	2-Chlorophenol	63.03	-1.0031	-0.7892	-0.5498	-0.3273	6.661	8.017
26	3-Chlorophenol	63.03	-0.7932	-0.6197	-0.3795	-0.1404	5.261	7.647
27	4-Chlorophenol	63.03	-0.8329	-0.6482	-0.4211	-0.2047	5.700	7.884
28	2,3-Dichlorophenol	72.51	-0.5888	-0.4093	-0.1735	0.0893	4.362	8.225
29	2,4-Dichlorophenol	72.51	-0.5052	-0.3156	-0.0903	0.1736	3.555	7.673
30	2,5-Dichlorophenol	72.51	-0.5393	-0.3313	-0.0988	0.1669	3.511	8.004
31	2,6-Dichlorophenol	72.51	-0.7398	-0.5149	-0.2688	0.0009	5.207	7.829
32	3,4-Dichlorophenol	72.51	-0.4855	-0.2894	-0.0592	0.2024	3.149	7.830
33	3,5-Dichlorophenol	72.51	-0.3317	-0.1603	0.0759	0.3546	2.091	7.204
34	2,3,4-Trichlorophenol	81.99	-0.2875	-0.1018	0.1459	0.4230	3.063	7.943
35	2,3,5-Trichlorophenol	81.99	-0.1741	0.0214	0.2767	0.5531	1.897	8.226
36	2,3,6-Trichlorophenol	81.99	-0.4549	-0.1423	0.0200	0.3015	3.442	7.989
37	2,4,5-Trichlorophenol	81.99	-0.2114	-0.0125	0.2397	0.5230	2.199	8.083
38	3,4,5-Trichlorophenol	81.99	-0.1525	0.0542	0.2961	0.5898	1.651	7.411
39	2,3,4,5-Tetrachlorophenol	91.47	0.0309	0.2386	0.4935	0.7968	1.438	7.489
40	2,3,5,6-Tetrachlorophenol	91.47	-0.1574	0.0694	0.3290	0.6388	2.880	7.335
41	Pentachlorophenol	100.95	0.0313	0.2615	0.5404	0.8704	2.497	7.434
42	3-Bromophenol	66.48	-0.6864	-0.5034	-0.2778	-0.0315	4.374	7.966
43	4-Bromophenol	66.48	-0.6950	-0.5247	-0.3099	-0.0339	4.578	8.199
44	2,4-Dibromophenol	79.08	-0.3153	-0.1342	0.0974	0.3666	3.041	7.854
45	Pentane	58.03	0.0455	0.2739	0.5180	0.8161	---	---
46	Hexane	68.26	0.1656	0.4117	0.6804	1.0091	---	---
47	Heptane	78.49	0.2706	0.5576	0.8581	1.2367	---	---
48	Octane	88.72	0.4104	0.7183	1.0433	1.4383	---	---
49	Decane	109.18	0.6673	1.0312	1.4073	1.8450	---	---
50	Undecane	119.41	0.8165	---	---	---	---	---
51	Dodecane	129.64	0.9516	---	---	---	---	---
Void volume (mL)			2.052	2.120	2.223	2.391		

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* Van der Waals volume calculated by Bondi method, ** energy effect obtained on BHST602C18,
*** energy effect obtained on ODS-silica gel from ref. 7.

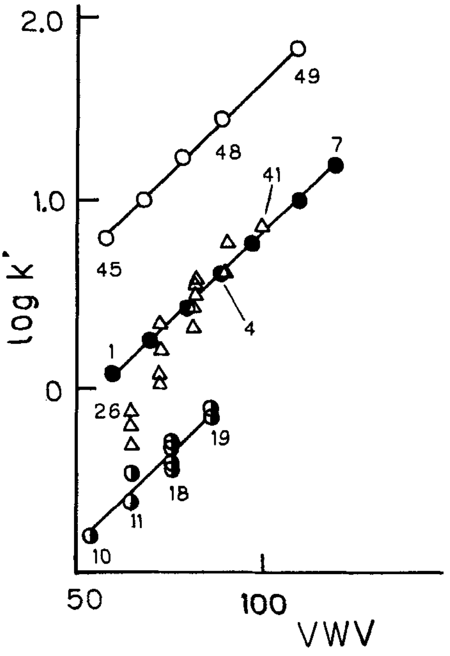

Figure 1 : Relation between Van der Waals volumes and log k' of phenols measured on BHST602C18

column: BHST602C18 packed in 10 cm long,6.0 mm I.D.ss tube, eluent: 50% aqueous acetonitrile containing 0.05M phosphoric acid, column temperature: 30°C, Numbers beside symbols are identical to those in Table I, O:alkanes, ●:alkylbenzenes, ◑:alkylphenols, △:halogenated phenols,

as the standard value, and the energy effect of phenols on an OD-VAG was calculated from their capacity ratios. The log k' values of methylphenols, ethylphenols, chlorophenols and bromophenols were almost linearly related to their Van der Waals volumes as shown in Fig. 1. Chlorophenols and bromophenols were retained more than methylphenols and ethylphenols on the OD-VAG compared with the result on the OD-SG. The difference of retention times among isomers of

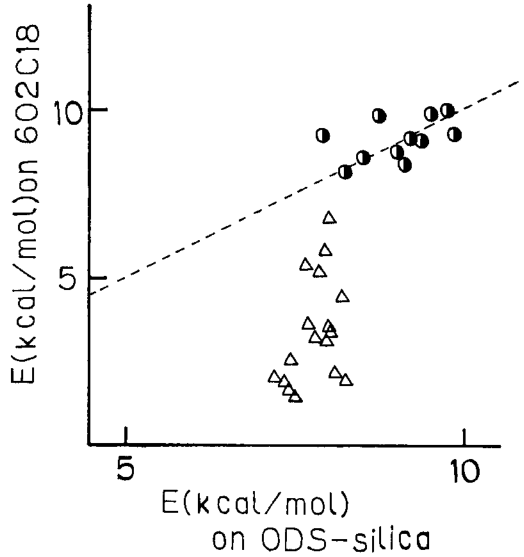

Figure 2 : Comparison of energy effect of phenols measured on an ODS silica gel and BHST602C18

◑:alkylphenols, △:halogenated phenols,

phenols on OD-VAG is larger than that on OD-SG, i.e. the selectivity for isomers on OD-VAG is stronger than that on OD-SG. This behavior is the same as that obtained for aromatic acids [8]. Ortho-substituted compounds were retained less. The correlation coefficient of log k' values of alkylphenols measured on OD-VAG and those measured on OD-SG was 0.941, and that of halogenated phenols was 0.940. In addition,the correlation coefficients of log k' values of ortho-substituted alkylphenols and halogenated phenols between OD-VAG and OD-SG were 0.975 and 0.999, respectively. However,it was not possible to calculate energy effects in 80% acetonitrile/

water mixture using the difference in retention behavior of phenols on OD-VAG compared to OD-SG. The average energy effect of alkylphenols on OD-VAG, except in 80% acetonitrile/water mixture, was the same as that on OD-SG, i.e. about 9.0 kcal/mol. The average energy effect of halogenated phenols on OD-VAG was about 50% less than that on OD-SG, i.e. about 3.5 kcal/mol as shown in Fig. 2. The prediction of retention time of phenols on OD-VAG is however different due to the strong selectivity of the packing. The remaining difficulty in estimating the energy effect is the effect of substituents. The selectivity of OD-VAG may be useful in the analysis of biological samples by separation in columns of unmodified vinylalcohol gels [2-3].

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