Structure-Retention Correlation on Methyl Phenyl Polysiloxane Phases in Capillary Gas Chromatography

Yasuhiro YAMANE, Kazuo MIYAJI, Kumi HANAFUSA, Toshihiko HANAI,*,† and Hiroyuki HATANO†
Towa Sci. Tech. Lab., Dejima, Minato-ku, Hiroshima 734
† Int. Inst. Technol. Anal., Health Res. Fond., Inst. Pasteur de Kyoto 5F, Hyakumanben, Sakyo-ku, Kyoto 606
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The selectivity of phenyl methyl polysiloxane phases was examined from the structure-retention correlations of alkanes, alkanols, alkylbenzenes, chlorobenzenes, and polycyclic aromatic hydrocarbons. Selectivity R^* was obtained from plots of van der Waals volume vs. the difference of their logarithm of capacity ratios, and enthalpy of these compounds was calculated from van't Hoff plot. The enthalpy $-\Delta H$ of polycyclic aromatic hydrocarbons was greater on phenyl methyl phases compared to those obtained on 100% methyl polysiloxane phase. The retention time of homologue series of compounds can be predicted from the selectivity or enthalpy, but not for chlorinated benzenes due to the difficulty of the estimation of electron donner effect of chloro group.

The accuracy of gas chromatograph as an instrument has been improved, however the reproducibility of retention times on different columns having the same liquid phase and being supplied from the same manufacturer has not been satisfied. Further, the selectivity of different liquid phases has not been theoretically well examined, and a separation on different phases is not seldom the same. The poor reproducibility of capillary columns may be the difference of molecular weight of polymers used as the liquid phase, the efficiency of surface coverage, the film thickness, the surface treatment method of fused silica tube, etc.

However, if the selectivity of each column could be methematically corrected, the prediction of retention time, that is, determination of physico-chemical constants by gas chromatography becomes practical method, therefore the quantitative structure retention relationship has been studied on different liquid phases to make a standard column test method, furthermore a prediction system of retention times.

Several methods had been published about structure-retention correlations in gas chromatography such as connectivity indices,[1—7] van der Waals volume,[4—6,8—12] and retention indices,[13—22] boiling point,[5,23] free energy,[23] heat formation,[5] molecular surface area,[24] molecular refraction,[5,19] physicochemical parameters.[13,25,26] The most popular retention index, Kováts retention indices,[25] was previously examined on 100% methyl polysiloxane and polyethylene glycol phases. The system using van der Waals volume and delocalization energy as the standard value was however simpler than Kováts retention indices due to not requirement of many alkanes as the standard. In the system, the selectivity of 100% methyl polysiloxane and polyethylene glycol phases was examined from the selectivity index, R^*[11] and enthalpy, $-\Delta H$[12] of alkanes, alkanols, fatty acid methyl esters, olefines, and polycyclic aromatic hydrocarbons. The selectivity index R^* was measured as the difference of capacity ratio ($\log k'$) of alkanes and that of alkanes and that of analytes from Eq. 1.

$$R = R_v + R^* \quad (1)$$

where R is measured $\log k'$, R_v, the molecular size index, is defined as the retention index of a normal alkane having the same van der Waals volume (VWV) as the analyte. The R^* is like I^* proposed by Evans and Haken[27—29] where molecular weight was used as the standard. The R^* was quite constant for homologue series of compounds on these 100% methyl polysiloxane and polyethylene glycol phases. However, the difference in R^* was observed on similar liquid phases.[11] Polar phase demonstrated the strong selectivity based on chemical structure of analytes, and the selectivity difference of columns obtained from different manufactures was also not negligible.[11,12] The R^* is not like Rohrschneider and McReynolds constants which are Kováts retention index differences for selected solutes used as polarity probes.[30]

In this study, the selectivity of weak polar phases, phenyl methyl polysiloxane phases was examined for the physico-chemical explanation of structure-retention correlation from the chromatographic behavior of aromatic compounds following up previous studies which examined on 100% methyl polysiloxane and polyethylene glycol phases. The selected solutes are alkanes, alkanols, alkylbenzenes, chlorobenzenes, and polycyclic aromatic hydrocarbons to examine aliphatic, aromatic, and alcoholic effects.

Experimental

The gas chromatograph and an integrator were a Shimadzu Model 14A and Shimadzu Model 6A from Shimadzu Corp, Kyoto, Japan. Capillary columns, 007—1, 2, and 17 (25 m×0.25 mm i.d., film thickness 0.25 μm) were purchased from Qudrex (New Haven, CT, USA). The liquid phases of 007—1, 2, and 17 are 100% methyl polysiloxane, 5% phenyl 95% methyl polysiloxane and 50% phenyl 50% methyl polysiloxane, respectively. Standard chemicals listed in Table 1 were obtained from several sources, and injected without further purification.

Table 1. Standard Chemicals and Their Physical Values VWV: van der Waals volumes, Bp: boiling point, DLE: delocalization energy from Refs. 31, 32, and 33, R^*: selectivity, $-\Delta H$: enthalpy, Me: 100% methyl polysiloxane phase, 5%Ph: 5% phenyl 95% methyl polysiloxane phase, 50%Ph: 50% phenyl 50% methyl polysiloxane phase,

No.	Chemicals	VWV	Bp	DLE	R^*			$-\Delta H$/cal mol^{-1}		
		cm^3 mol^{-1}	°C		Me	5%Ph	50%Ph	Me	5%Ph	50%Ph
1	Pentane	58.03	36.1	—	—	—	—	—	—	—
2	Hexane	68.26	68.7	—	—	—	—	—	1536	1388
3	Heptane	78.49	98.4	—	—	—	—	1346	1578	1470
4	Octane	88.72	125.7	—	—	—	—	1784	1679	1664
5	Nonane	98.95	150.8	—	—	—	—	2071	1918	1844
6	Decane	109.18	174.1	—	—	—	—	2314	2185	1997
7	Undecane	119.41	196.0	—	—	—	—	2375	2338	2184
8	Dodecane	129.64	216.3	—	—	—	—	2507	2463	2354
9	Tridecane	139.87	235.4	—	—	—	—	2677	2599	2535
10	Tetradecane	150.10	253.7	—	—	—	—	2810	2693	2682
11	Pentadecane	160.33	270.6	—	—	—	—	2900	2873	2846
12	Hexadecane	170.56	287.0	—	—	—	—	3036	3036	2977
13	Heptadecane	180.79	301.8	—	—	—	—	3246	3215	3153
14	Octadecane	191.02	316.1	—	—	—	—	3260	3341	3304
15	Nonadecane	201.25	329.7	—	—	—	—	3365	3467	3438
16	Icosane	211.48	343.0	—	—	—	—	3497	3614	3594
17	1-Butanol	52.40	117.3	—	1.776	1.468	1.645	1681	1282	1600
18	1-Pentanol	62.63	137.5	—	1.770	1.588	1.711	2019	1915	1760
19	1-Hexanol	72.86	158.0	—	1.878	1.790	1.732	2036	1974	1912
20	1-Heptanol	83.09	176.0	—	1.881	1.788	1.738	2174	2093	2081
21	1-Octanol	93.32	194.4	—	1.834	1.799	1.742	2449	2262	2223
22	1-Nonanol	103.53	213.5	—	1.859	1.753	1.753	2545	2344	2402
23	1-Decanol	113.78	229.0	—	1.884	1.746	1.771	2705	2517	2583
24	1-Undecanol	123.99	243.5	—	1.869	1.777	1.780	2805	2588	2716
25	1-Dodecanol	134.24	243.8	—	1.913	1.768	1.790	2869	2763	2887
26	1-Tridecanol	144.49	254.7	—	1.797	1.781	1.787	2968	2925	3042
27	1-Tetradecanol	154.70	263.2	—	1.800	1.783	1.775	3074	3085	3195
28	1-Pentadecanol	164.93	296.8	—	1.805	1.722	1.759	3201	3242	3349
29	1-Hexadecanol	175.16	308.0	—	1.806	1.706	1.758	3331	3372	3516
30	1-Heptadecanol	185.93	320.6	—	1.765	1.652	1.713	3429	3518	3657
31	1-Octadecanol	195.62	356.7	—	1.818	1.665	1.750	3559	3688	3812
32	1-Nonadecanol	205.85	375.0	—	1.841	1.711	1.734	3709	3848	3961
33	1-Icosanol	216.08	382.0	—	1.878	1.703	1.741	3956	4017	4123
34	Toluene	59.51	110.6	—	2.184	2.061	2.029	1598	1560	1682
35	Ethylbenzene	69.74	136.2	—	2.152	2.041	2.028	1773	1754	1820
36	Propylbenzene	79.97	159.2	—	2.093	1.965	1.989	1954	1842	1925
37	Butylbenzene	90.20	183.4	—	1.999	1.960	1.995	2314	1872	2107
38	Hexylbenzene	110.66	—	—	2.062	1.921	2.003	2522	2178	2461
39	Heptylbenzene	120.89	—	—	2.070	1.923	2.002	2597	2465	2637
40	Octylbenzene	131.12	—	—	2.120	1.941	1.995	2733	2717	2810
41	Nonylbenzene	141.35	—	—	2.096	1.978	1.987	2880	2869	2922
42	Decylbenzene	151.58	—	—	2.160	1.955	1.982	2781	3015	3083
43	1,2-Dimethylbenzene	70.66	144.4	—	2.100	2.161	2.166	2182	1995	1897
44	1,3-Dimethylbenzene	70.66	139.1	—	1.952	2.076	1.976	2106	1776	1874
45	1,4-Dimethylbenzene	70.66	138.4	—	1.959	2.076	1.976	2122	1776	1874
46	1,2,3-Trimethylbenzene	81.81	176.1	—	2.304	2.321	2.211	2219	2144	2390
47	1,2,4-Trimethylbenzene	81.81	169.2	—	2.163	2.164	2.187	2119	2005	1872
48	1,3,5-Trimethylbenzene	81.81	—	—	2.060	1.989	1.992	2028	1976	1868
49	1,2,3,4-Tetramethylbenzene	92.96	205.4	—	2.499	2.143	2.440	2343	2346	2287
50	1,2,3,5-Tetramethylbenzene	92.96	198.2	—	2.335	2.148	2.212	2241	2370	2252

Results and Discussion

The capacity ratios of standard compounds were measured at 80—240 °C with increments of 10 °C on 100% methyl polysiloxane, 5% phenyl 95% methyl polysiloxane and 50% phenyl 50% methyl polysiloxane phases, and the retention time of methane was used as void volume of the column. The enthalpy was calculated from retention times measured at least four different temperatures upto twelve different temperatures.

The log k' values of alkanes were used as the standard in this discussion. The difference of the capacity ratios

Table 1. (Continued)

No.	Chemicals	VWV	Bp	DLE	R^*			$-\Delta H$/cal mol^{-1}		
		cm^3 mol^{-1}	°C		Me	5%Ph	50%Ph	Me	5%Ph	50%Ph
51	1,2,4,5-Tetramethylbenzene	92.96	196.8	—	2.285	2.401	2.196	2186	2304	2197
52	Pentamethylbenzene	104.11	231.8	—	2.552	2.485	2.532	2488	2462	2468
53	Hexamethylbenzene	115.26	263.5	—	—	—	—	—	—	—
54	Chlorobenzene	57.84	132.0	—	2.590	2.696	2.487	1758	1740	2204
55	1,2-Dichlorobenzene	67.32	180.5	—	3.336	3.319	3.226	2132	2041	2124
56	1,3-Dichlorobenzene	67.32	173.0	—	3.061	3.144	2.625	2175	1972	2559
57	1,4-Dichlorobenzene	67.32	174.1	—	3.049	3.157	3.117	2146	2023	2033
58	1,2,3-Trichlorobenzene	76.80	218.0	—	3.729	3.707	3.710	2248	2300	2323
59	1,2,4-Trichlorobenzene	76.80	213.0	—	3.606	3.434	3.462	2338	2368	2279
60	1,3,5-Trichlorobenzene	76.80	208.5	—	3.455	3.081	3.053	2167	2440	2320
61	1,2,3,4-Tetrachlorobenzene	86.28	254.0	—	4.140	3.881	3.979	2460	2555	2715
62	1,2,3,5-Tetrachlorobenzene	86.28	246.0	—	3.839	3.991	3.803	2445	2304	2542
63	1,2,4,5-Tetrachlorobenzene	86.28	243.0	—	3.836	3.992	3.816	2437	2307	2569
64	Pentachlorobenzene	95.76	276.0	—	4.348	4.300	4.204	2638	2578	2718
65	Hexachlorobenzene	105.24	—	—	4.779	4.729	4.571	2984	2861	2907
66	Benzene	48.36	80.1	2.000	1.978	1.882	1.979	1414	1572	1533
67	Naphthalene	73.96	219.9	3.683	3.786	3.749	3.741	2315	2211	2287
68	Biphenyl	90.08	245.0	4.383	3.886	3.823	3.870	2550	2590	2506
69	Fluorene	93.22	295.0	4.750	4.772	4.743	4.721	2729	2683	2724
70	Phenanthrene	99.56	340.0	5.448	5.381	5.389	5.389	2869	2870	3076
71	Anthracene	99.56	342.0	5.314	5.432	5.407	5.400	2886	2895	3075
72	Pyrene	109.04	404.0	6.506	6.359	6.440	6.363	3167	3190	3446
73	Chrysene	125.16	448.0	7.190	6.927	7.144	6.978	3443	3532	3892
74	Tetracene	125.16	—	6.932	7.033	7.236	7.085	3468	3573	—
75	Benzopyrene	134.64	—	—	8.011	8.223	—	—	—	—
76	Pentacene	150.76	—	—	—	—	—	—	—	—

($\Delta\log k'$) of an analyte and an alkane having the same van der Waals volumes (VWV) as the analyte should indicate the selectivity of the liquid phase.

$$\Delta \log k' = \Delta \log k' \text{ (alkane having the same VWV)} - \log k' \text{ (measured)} \quad (2)$$

The 5% phenyl 95% methyl polysiloxane phase did not show the great selectivity within alkanols and alkylbenzenes compared to the values obtained on 100% methyl polysiloxane phase as shown in Fig. 1 where the variation of $\Delta\log k'$ values of homologue series of compounds such as alkanols and alkylbenzenes was greater on 100% methyl polysiloxane phase. The $\Delta\log k'$s of alkanols were -0.4545 ± 0.0055 ($n=12$) on 5% phenyl 95% methyl polysiloxane phase, and those increased from -0.275 to -0.428 on 100% methyl polysiloxane phase. The $\Delta\log k'$s of alkylbenzenes were -0.5166 ± 0.0020 ($n=5$) on 5% phenyl 95% methyl polysiloxane phase, and those increased from -0.390 to -0.459 on 100% methyl polysiloxane phase. On the other hand, the variation of $\Delta\log k'$ values of chlorobenzenes was greater on 5% phenyl 95% methyl polysiloxane phase. The correlation coefficient of $\Delta\log k'$s measured on 5% phenyl 95% methyl polysiloxane and 100% methyl polysiloxane phases was 0.713 ($n=8$), and the slope was 0.475. The correlation coefficient of $\Delta\log k'$s of these compounds measured at 200 °C was 0.970 ($n=32$), and the slope was 0.914 on Fig. 1. The similar result was obtained on the 50% phenyl 50% methyl polysiloxane phase where $\Delta\log k'$ values of chlorobenzenes and polycyclic aromatic hydrocarbons were greater than those obtained on the 5% phenyl 95% methyl polysiloxane phase. The correlation coefficient of $\Delta\log k'$s of polycyclic aromatic hydrocarbons was 0.999 ($n=6$), and the slope was 0.823 at 200 °C. The

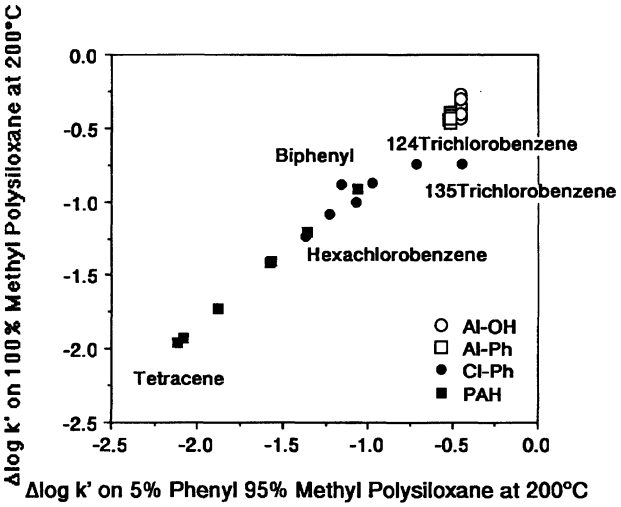

Fig. 1. Difference of $\Delta\log k'$ measured on 100% methyl polysiloxane and 5% phenyl 95% methyl polysiloxane phases at 200 °C. Al-OH: alkanols, Al-Ph: alkylbenzenes, Cl-Ph: perchlorobenzenes, PAH: polycyclic aromatic hydrocarbons.

Table 2. Correlation Coefficient between Boiling Points and Capacity Ratios (log k') measured at 200 °C on 100% Methyl (Me) and 50% Phenyl 50% Methyl (Me 50% Ph) Polysiloxane Phases The detail of the experimental condition: see text.

Chemicals	Me	Me50%Ph
Alkanes	0.955 (n=10)*1	0.998 (n=9)*6
Alkanols	0.958 (n=12)*2	0.962 (n=12)*7
Polymethylbenzenes	0.985 (n=9)*3	0.995 (n=4)*8
Polychlorobenzenes	0.986 (n=11)*4	0.985 (n=6)*9
Polycyclic aromatic hydrocarbons	0.994 (n=7)*5	0.998 (n=5)*10
Total	0.967 (n=49)	0.929 (n=36)

Chemicals used for these calculations, *1: Nos. 7—16, *2: Nos. 22—33, *3: Nos. 43—52except 48, *4: Nos. 54—64, *5: Nos. 67—74, *6: Nos. 8—16, *7: Nos. 21—33, *8: Nos.49—52, *9: Nos.55—64 except 56,57,62,63, *10: Nos. 67—72 except 68.

$\Delta\log k'$ values are dependent on the measured temperature, therefore selectivity R^* was calculated, which is independent from measured temperatures.

The selectivity R^* was obtained from the relation between delocalization energy of polycyclic aromatic hydrocarbons and $\Delta\log k'$ values, and summarized in Table 1. The R^* values of other compounds were further calculated from the same equation obtained for polycyclic aromatic hydrocarbons because of lack of such physico-chemical values of these compounds in litereatures. The R^* values of methylene unit of alkanols and alkylbenzenes measured on 50% phenyl 50% methyl polysiloxane phase was similar to those obtained on 100% methyl polysiloxane phase. No significant difference of R^* values was found on these phases compared to the result obtained on 100% methylpolysiloxane and polyethylene glycol phases.[11] The reason may be that polycyclic aromatic hydrocarbons are used as the standard, therefore the selectivity of phenyl phases was diminished. Further search of physicochemical values is necessary to explain the property of aromatic compounds.

Further, the selectivity was studied from enthalpy of these compounds. If enthalpy indicates the strength of solute–liquid phase interaction in capillary gas chromatography, the enthalpy difference can tell the selectivity of liquid phases. The relation between van der Waals volume and enthalpy measured on 50% phenyl 50% methyl polysiloxane phase indicated that alkyl groups of alkanes, alkanols and alkylbenzenes should have a similar retention mechanism due to the relation between van der Waals volume and enthalpy was very close. The correlation coefficient of enthalpy of alkanes measured on 100% methyl and 50% phenyl 50% methyl polysiloxane phases was 0.986 (n=14) by a quadratic equation and 0.967 by an equation of the first degree. The result is shown in Fig. 2. This phenomenon was also observed on 5% phenyl 95% methyl polysiloxane and 100% methyl polysiloxane phases except small size compounds, and methylated benzenes showed the similar result as alkylbenzenes. The selectivity between different groups was greater on 50% phenyl 50% methyl polysiloxane phase, and that between isomers of polychlorobenzenes was greater too on this phase. 50% phenyl 50% methyl phase demonstrated the aromatic selectivity, where enthalpy measured on 50% phenyl 50% methyl polysiloxane phase of aromatic compounds such as chlorobenzenes and polycyclic aromatic hydrocarbons was greater than that measured on 100% methyl polysiloxane phase. The correlation coefficient of enthalpy of polycyclic aromatic hydrocarbons was 0.993 (n=8) by a quadratic equation and 0.964 by an equation of the first degree.

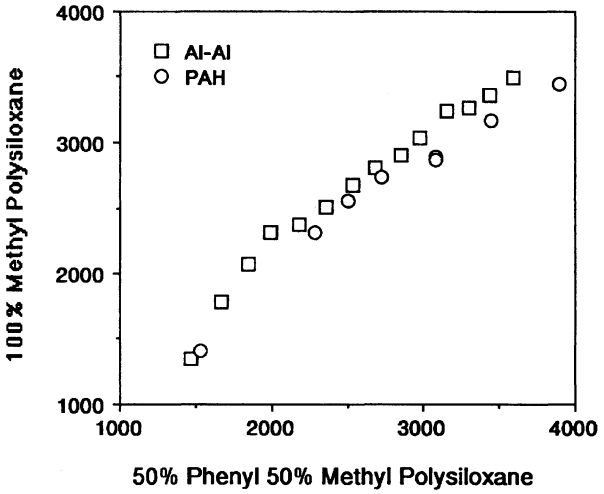

Fig. 2. Enthalpy difference of alkanes (A1-A1) and polycyclic aromatic hydrocarbons (PAH) measured on 100% methyl polysiloxane and 50% phenyl 50% methyl polysiloxane phases. The unit: cal mol^{-1}.

The correlation coefficient of enthalpy of polymethyl and polychlorobenzenes measured on 100% methyl polysiloxane phase and 50% phenyl 50% methyl polysiloxane phase was poor, those values were 0.708 (n=10) and 0.670 (n=12) for polymethyl and polychlorobenzenes, respectively. The enthalpy of larger size molecule was greater on 50% phenyl 50% methyl polysiloxane phase even enthalpy of aliphatic com-

pounds.

The variation of enthalpy of polychlorobenzene isomers was greater on 50% phenyl 50% methyl polysiloxane phase compared to that 100% methyl polysiloxane phase. This means that the separation of isomers of aromatic compounds is much easier on 50% phenyl 50% methyl polysiloxane phase.

However such significant result could not clearly obtained on 5% phenyl 95% methyl polysiloxane phase. The variation of enthalpy of polymethylbenzene isomers was obtained on 100% methyl polysiloxane phase not on 50% phenyl 50% methyl polysiloxane phase. This result indicated that the separation of isomers substituted with electron donor groups could be done on phenyl methyl polysiloxane phases and that with electron acceptor groups could be done on a 100% methyl polysiloxane phase.

There was no great difference for enthalpy of alkanols measured on these phases. This means the prediction of retention time of alkyl group substituted compounds is possible but it is very difficult for compounds substituted with electron donor groups.

Phenyl methyl polysiloxane phase demonstrated the selectivity for polycyclic aromatic hydrocarbons and polychlorobenzenes, and 100% methyl polysiloxane phase demonstrated the selectivity for alkyl groups. However the good correlation between boiling points and log k' was obtained on the 100% methyl polysiloxane phase and not on 50% phenyl 50% methyl polysiloxane phase, and the value of correlation coefficient of homologue series compounds is given in Table 2. A more accurate system is required to measure boiling points under low pressure.

In conclusion, the above analytical method of the selectivity between different homoloque series of compounds on capillary columns having different liquid phases being studied from the difference of van der Waals volume and delocalization energy is simpler than other methods. The prediction of retention time is however still difficult from R^* and enthalpy except a homologue series of compounds. Further precise analysis of the difference within isomers is required to adjust the difference of molecular size and other physico-chemical properties.

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