CHROM. 6223

CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

V. CHARACTERIZATION OF POLARITY OF STATIONARY PHASES. McREYNOLDS SYSTEM

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(Received June 8th, 1972)

SUMMARY

In some of our earlier papers it was shown that the gas chromatographic interaction between the substance being investigated and the stationary phase can be characterized not only by the difference between the retention indices, but also by quotients of their indices.

The present paper shows the practical application of Rohrschneider's concept based on quotients with the help of the McREYNOLDS system. Other possible applications of this system are discussed.

INTRODUCTION

In the last few years, the investigation of the polarity of gas chromatographic (GC) stationary phases has been connected with other problems of the retention index system, *e.g.*, the pre-calculation of retention indices. This can be considered to be fortunate because it leads to the determination of retention indices, but on the other hand it was also unfavourable because of various related problems, the solutions of which were more difficult.

In addition to the work of some authors discussed in our earlier papers[1–3], the most significant work in this field is that of McREYNOLDS[4]. One of his earlier publications[5], described an important advance in research on retention indices. Although McREYNOLDS developed his system in order to characterize the polarities of GC stationary phases, the system developed enables Rohrschneider's concept to be applied in the pre-calculation of retention indices at 120.0°, because of its reliability and the large number of stationary phases. McREYNOLDS[4] suggested that ten substances are necessary in order to characterize the polarities of stationary phases, but after our investigations it is our opinion that five are sufficient; the large

amount of data obtained by him made possible some investigations on the quality of standard substances.

THEORETICAL

As we showed earlier[2], the retention index value is composed of additive contributions and can be distributed into three components:

$$I = I_a + I_b + I_i = I_m + I_i \quad (1)$$

where

I is the retention index of the substance on the given stationary phase at constant column temperature (index units, i.u.);
I_a is the atomic index contribution (i.u.);
I_b is the bond index contribution (i.u.);
I_m is the molecular index contribution (i.u.);
I_i is interaction index contribution (i.u.).

In another paper[6], we published further data to show that the I_m value is independent of column temperature and of the stationary phase, and proved that

$$I_m = I \cdot f_i^* \quad (2)$$

where f_i^* is the interaction factor.

Through the interaction between the substance being investigated and the stationary phase used, the f_i^* value from eqn. 2 is suitable for characterizing the polarity of the stationary phase at constant column temperature. The f_i^* value is more suitable for characterizing the stationary phase than is the difference in retention indices. Applying eqn. 2 to the McREYNOLDS system, f_i^* values were calculated on various stationary phases for five standard substances: 2-pentanone, pyridine, 2-methyl-2-pentanol, 1-iodobutane and *cis*-hydrindane. It is not necessary to give all the results, and some typical results are summarized in Table I. With the exception of squalane, the substances show singular individual interactions[6] on all the other stationary phases used in GC, so there was no instance where the f_i^* value,

TABLE I

CHARACTERIZATION OF THE POLARITY OF STATIONARY PHASES WITH THE HELP OF f_1^* VALUES OF FIVE STANDARD SUBSTANCES DETERMINED AT 120.0°

Code number of McReynolds	*Stationary phase*	f_1^*	f_2^*	f_3^*	f_4^*	f_5^*
2099	Cyanoethyl sucrose	0.1095	0.1038	0.1223	0.1494	0.1917
2326	Ethylene glycol adipate	0.1442	0.1305	0.1484	0.1833	0.2118
2338	Diglycerol	0.1314	0.1119	0.1322	0.1914	0.2401
2028	Carbowax 20M	0.1567	0.1438	0.1593	0.1849	0.2168
2040	ECNSS-M	0.1867	0.1775	0.2057	0.1206	0.2236
2092[a]	LSX-3	0.1570	0.1708	0.1910	0.2114	0.2338
2126[a]	OV-210	0.1583	0.1723	0.1915	0.2125	0.2347
2086[a]	QF-1	0.1587	0.1731	0.1921	0.2132	0.2349

[a] The last three stationary phases are practically identical.

TABLE II

POLARITY FACTORS (f_n) OF THE FIVE SELECTED STANDARD SUBSTANCES DETERMINED AT 120.0°

Code number of McReynolds	*Stationary phase*	f_1	f_2	f_3	f_4	f_5
2226	Hexatriacontane	0.995215	1.015740	1.000000	1.012230	1.007950
2063	Nujol	1.003190	1.015740	1.002900	0.998777	1.005960
2298	Mineral oil	1.004780	1.018600	1.004350	1.013450	1.006960
2270	Liquid paraffin	1.003190	1.018600	1.002900	1.014670	1.008950
2277	Convoil 20	1.012760	1.030040	1.014490	1.018340	1.009940
2128	Apiezon M	1.023920	1.057220	1.017390	1.039120	1.028830
2127	Apiezon L	1.023920	1.060090	1.018840	1.042790	1.032800
2013	Apiezon L, treated	1.025520	1.061520	1.018840	1.039120	1.030810
2082	Polybutene 32	1.038280	1.057220	1.026090	1.029340	1.023860
2033	Montan Wax	1.022330	1.067240	1.030430	1.019560	1.009940
2081	Polybutene 128	1.039870	1.060090	1.020290	1.035450	1.032800
2012	Apiezon L	1.030300	1.067240	1.023190	1.044010	1.032800
2318	DC-330	1.066990	0.908441	1.044930	1.000000	0.994036
2066	SF-96	1.066990	0.909871	1.044930	1.000000	0.994036
2195	Apiezon J	1.043060	1.081540	1.033330	1.051340	1.034790
2077	SE-30	1.070180	1.058660	1.044930	1.003670	0.998012
2101	DC-11	1.076560	1.080110	1.052170	1.003670	0.998012
2316	DC-510	1.095690	1.081540	1.060870	1.019560	1.001990
2078	SE-52	1.103670	1.095850	1.063770	1.028120	1.008950
2314	DC-556	1.127590	1.113020	1.076810	1.039120	1.002980
2186	Butyl stearate	1.103670	1.101570	1.123190	1.045230	0.999006
2204	OV-3	1.129190	1.125890	1.079710	1.047680	1.016900
2100	Beeswax	1.097290	1.174540	1.124640	1.050120	1.017890
2144	Fluorolube HG-1200	1.181820	1.168810	1.098550	1.014670	1.002980
2196	Sucrose octaacetate	1.735250	1.814020	1.662320	1.356970	1.151090
2334	MER-2	1.727270	1.879830	1.610140	1.411980	1.195820
2119	PEG-600	1.682620	1.865520	1.684060	1.376530	1.161030
2208	Butanediol succinate	1.714510	1.874110	1.662320	1.396090	1.176940
2212	Ethylene glycol adipate	1.722490	1.882690	1.669570	1.397310	1.175940
2139	Butanediol succinate	1.728870	1.899860	1.689850	1.397310	1.175940
2219	PDEAS	1.752790	1.935620	1.633330	1.442540	1.211730
2151	Reoplex 400	1.716110	1.959940	1.698550	1.387530	1.169980
2157	LAC IR-296	1.730460	1.937050	1.691300	1.400980	1.175940
2027	Carbowax 1540	1.722490	1.917020	1.694200	1.397310	1.170970
2304	Resoflex R-296	1.738440	1.954220	1.700000	1.404650	1.177930
2225	LAC 2-R-446	1.751200	1.954220	1.708700	1.414430	1.184890
2041	EGSS-Y	1.786280	1.945640	1.679710	1.409540	1.188870
2339	Hyprose SP-80	1.784690	2.040060	1.818840	1.378970	1.194830
2040	ECNSS-M	1.926630	2.047210	1.794200	1.468210	1.209740
2338	Diglycerol	1.893140	2.221740	1.881160	1.299510	1.035790
2107	DEGS Supelco 1045	1.889950	2.114450	1.805800	1.480440	1.213720
2036	EGSS-X	1.885170	2.113020	1.820290	1.503670	1.235590
2325	DEGS	1.878790	2.131620	1.839130	1.511000	1.235590
2327	Ethylene glycol phthalate	1.960130	2.247500	1.811590	1.512220	1.258450
2210	DEGS Supelco 1303	1.940990	2.194560	1.860870	1.513450	1.236580
2045	OV-225	1.539070	1.552220	1.408780	1.276280	1.116300
2185	Di(ethoxyethoxyethyl) phthalate	1.505580	1.556510	1.447830	1.253060	1.091450
2138	NPGA	1.496010	1.606580	1.485510	1.254280	1.102390
2300	UCON 75-H-90000	1.476870	1.580830	1.465220	1.268950	1.109340
2004	Pluronic F88	1.488040	1.599430	1.473910	1.277510	1.113320
2037	HI-EFF 8BP	1.526320	1.662370	1.501450	1.308070	1.126240
2142	CW-4000 monostearate	1.518340	1.642350	1.507250	1.298290	1.121270
2152	Zonyl E-7	1.746410	1.665240	1.489860	1.178480	1.061630
2163	Paraplex G-40	1.566190	1.653790	1.527540	1.301960	1.124250

(*continued on p. 14*)

TABLE II (*continued*)

Code number McReynolds	*Stationary phase*	f_1	f_2	f_3	f_4	f_5
2094	CW-4000 monostearate	1.527910	1.668100	1.517390	1.301960	1.044730
2090	Quadrol	1.569380	1.699570	1.624640	1.254280	1.110340
2215	NPGS	1.582140	1.675250	1.537680	1.297070	1.123260
2098	Igepal CO-990	1.550240	1.679540	1.530430	1.319070	1.132210
2042	EGSP-Z	1.636360	1.785410	1.540580	1.341080	1.166000
2028	Carbowax 20M	1.586920	1.729610	1.560870	1.344740	1.147120
2084	Epon 1001	1.647530	1.859800	1.547830	1.355750	1.185880
2029	Carbowax 6000	1.588520	1.732470	1.565220	1.344740	1.146120
2079	Ethylene glycol isophthalate	1.677830	1.802570	1.579710	1.365530	1.167000
2153	XF-1150	1.749600	1.755360	1.581160	1.369190	1.155070
2133	Sorbitol hexaacetate	1.716110	1.776820	1.646380	1.333740	1.130220
2135	FFAP	1.633170	1.897000	1.613040	1.364300	1.160040
2089	STAP	1.637960	1.897000	1.620290	1.367970	1.162030
2026	Carbowax 1000	1.666670	1.842630	1.650720	1.374080	1.160040
2025	Oronite NIW	1.385960	1.467810	1.386960	1.201710	1.074550
2086	QF-1	1.566190	1.436340	1.294200	1.166260	1.058650
2093	PPG sebacate	1.400320	1.469240	1.392750	1.215160	1.082500
2252	UCON 50-HB-660	1.384370	1.459230	1.384060	1.202930	1.074550
2126	OV-210	1.570970	1.443490	1.298550	1.169930	1.059640
2251	UCON 50-HB-3520	1.384370	1.462090	1.382610	1.206600	1.079520
2021	Ethofat 60/25	1.548640	1.476390	1.401450	1.205380	1.072560
2062	Ethomeen S125	1.545450	1.484980	1.413040	1.206600	1.078530
2261	Igepal CO-630	1.563000	1.492130	1.401450	1.210270	1.077530
2092	LSX-3-0295	1.583730	1.456370	1.301450	1.176040	1.063620
2008	Pluronic P85	1.393940	1.479260	1.392750	1.210270	1.081510
2005	Pluronic P65	1.400320	1.486410	1.400000	1.212710	1.082500
2067	Tergitol NPX	1.411480	1.502150	1.407250	1.215160	1.080520
2183	Cresyl diphenyl phosphate	1.454550	1.480690	1.385510	1.232270	1.087480
2003	Pluronic L35	1.409890	1.499280	1.414490	1.216380	1.084490
2184	Polytergent G-300	1.425840	1.515020	1.420290	1.220050	1.082500
2228	Polyglycol 15–200	1.417860	1.506440	1.418840	1.218830	1.085490
2129	Stepan DS-60	1.483250	1.575110	1.637680	1.135700	1.060640
2146	Diethoxyethyl phthalate	1.486440	1.520740	1.420290	1.232270	1.078530
2055	UCON 50-HB-5100	1.443380	1.536480	1.436230	1.226160	1.085490
2091	Siponate DS-10	1.510370	1.555080	1.675360	1.139360	1.062620
2102	Renex 678	1.443380	1.545060	1.436230	1.242050	1.094430
2075	XE-60	1.542260	1.525040	1.418840	1.248170	1.093440
2113	UCON LB-1715	1.295060	1.347640	1.291300	1.133250	1.045730
2182	Dibutoxyethyl adipate	1.322170	1.333330	1.313040	1.144250	1.027830
2253	Thanol PPG 1000	1.339710	1.336190	1.310140	1.134470	1.045730
2044	OV-25	1.331740	1.400570	1.208700	1.206600	1.112330
2007	Pluronic L-81	1.298250	1.356220	1.305800	1.146700	1.054670
2068	OS-124	1.357260	1.404860	1.256520	1.206600	1.102390
2111	Tributyl citrate	1.339710	1.374820	1.327540	1.145480	1.028830
2319	GE SR-119	1.352470	1.427750	1.253620	1.193150	1.099400
2017	OS-138	1.363640	1.419170	1.262320	1.215160	1.111330
2147	Diethoxyethyl sebacate	1.336520	1.391990	1.344930	1.157700	1.035790
2048	Dibutoxyethyl phthalate	1.362040	1.381970	1.314490	1.168700	1.047710
2174	Dibutoxyethyl phthalate	1.371610	1.389130	1.321740	1.174820	1.049700
2188	Tri(butoxyethyl)phosphate	1.333330	1.391990	1.413040	1.154030	1.030810
2053	Zonyl E-91	1.510370	1.419170	1.340580	1.099020	1.009940
2108	NPG sebacate	1.358850	1.466380	1.372460	1.190710	1.072560
2132	Squalene	1.379590	1.492130	1.359420	1.171150	1.063620
2046	UCON 50-HB-280-X	1.362040	1.432050	1.365220	1.184600	1.064610
2131	Polytergent J-300	1.362040	1.440630	1.385510	1.182150	1.060640
2047	Tricresyl phosphate	1.398720	1.427750	1.350720	1.206600	1.075550

TABLE II (*continued*)

Code number of McReynolds	*Stationary phase*	f_1	f_2	f_3	f_4	f_5
2085	SAIB	1.400320	1.422030	1.382610	1.179710	1.053680
2164	Paraplex G-25	1.381180	1.446350	1.372460	1.206600	1.078530
2302	Ethomeen 18/25	1.366830	1.462090	1.398550	1.193150	1.071570
2180	Polytergent J-400	1.373210	1.453500	1.391300	1.194380	1.067590
2060	Dioctyl phthalate	1.239230	1.238910	1.207250	1.112470	1.024850
2103	Hallcomid M-18	1.207340	1.208870	1.292750	1.100240	1.015900
2116	Diisooctyl phthalate	1.245610	1.248930	1.215940	1.112470	1.023860
2038	OV-17	1.258370	1.288980	1.162320	1.145480	1.068590
2114	Hallcomid M-18 OL	1.228070	1.236050	1.305800	1.113690	1.020870
2022	Flexol 8-N-8	1.261560	1.256080	1.285510	1.119800	1.022860
2205	SP-392	1.280700	1.313300	1.178260	1.162590	1.073560
2291	Span 60	1.251990	1.369100	1.291300	1.100240	1.036780
2162	Versamid 930	1.218500	1.296140	1.321740	1.134470	1.076540
2247	Hercoflex 600	1.267940	1.277540	1.271010	1.136920	1.026840
2088	Zinc stearate	1.094100	1.778250	1.142030	1.061120	1.032800
2059	UCON LB-550-X	1.251990	1.294710	1.256520	1.117360	1.039760
2069	Span 80	1.271130	1.383400	1.300000	1.114910	1.040760
2049	UCON 50-HB-1800-X	1.256780	1.303290	1.259420	1.123470	1.044730
2096	Castorwax	1.279110	1.351930	1.292750	1.128360	1.048710
2254	Flexol B-400	1.269540	1.310440	1.276810	1.122250	1.038770
2125	OV-22	1.304620	1.361950	1.192750	1.185820	1.098410
2282	Triton X-200	1.274320	1.339060	1.260870	1.128360	1.047710
2317	PPG-2000	1.275920	1.323320	1.284060	1.129580	1.044730
2175	Estynox	1.290270	1.324750	1.292750	1.158920	1.051690
2190	Trimer acid	1.259970	1.540770	1.339130	1.114910	1.059640
2264	Pluracol P-2010	1.287080	1.336190	1.285510	1.129580	1.045730
2266	Atpet 200	1.315790	1.336190	1.318840	1.129580	1.047710
2194	Apiezon H	1.129190	1.184550	1.066670	1.064790	1.036780
2171	Butoxyethyl stearate	1.132380	1.138770	1.147830	1.059900	1.004970
2080	Halocarbon wax	1.185010	1.175970	1.101450	1.019560	1.003980
2123	OV-7	1.177030	1.183120	1.111590	1.083130	1.034790
2120	DC 550	1.186600	1.193130	1.117390	1.090460	1.035790
2323	Apiezon W	1.157079	1.220310	1.130430	1.113690	1.058650
2179	Dinonyl sebacate	1.170650	1.168810	1.188410	1.075790	1.007950
2061	DC-703	1.200960	1.200290	1.128990	1.096580	1.030810
2056	Diisodecyl adipate	1.180220	1.183120	1.194200	1.081910	1.009940
2169	Ditridecyl phthalate	1.194580	1.200290	1.172460	1.092910	1.024850
2149	Diethylhexyl tetrachloro phthalate	1.180220	1.240340	1.150720	1.091690	1.033800
2310	Diethylene glycol stearate	1.169060	1.273250	1.213040	1.069680	1.019880
2313	Octyl decyl adipate	1.189790	1.191700	1.204350	1.088020	1.009940
2250	Dilauryl phthalate	1.191390	1.226040	1.173910	1.096580	1.019880
2170	Diisooctyl adipate	1.192980	1.191700	1.208700	1.086800	1.008950
2024	TMP Tripelargonate	1.194580	1.204580	1.207250	1.094130	1.017890
2057	Diisooctyl adipate	1.200960	1.200290	1.214490	1.088020	1.007950
2187	Diisodecyl phthalate	1.218500	1.221750	1.192750	1.101470	1.023860
2124	OV-11	1.231260	1.254650	1.144930	1.125920	1.058650
2070	Dinonyl phthalate	1.234450	1.227470	1.204350	1.100240	1.017890
2168	Triethylhexyl phosphate	1.186600	1.188840	1.326090	1.086800	1.006960
2229	DC-710	1.244020	1.271820	1.155070	1.132030	1.059640
2276	Flexol GPE	1.223290	1.231760	1.240580	1.110020	1.019880
2303	DEGS	1.945770	2.230330	1.862320	1.515890	1.238570
2329	Ethylene glycol succinate	2.014350	2.236050	1.911590	1.525670	1.257460
2110	THEED	1.998400	2.277540	2.081160	1.522000	1.252480
2097	Tetracyanoethoxy PE	2.079740	2.197430	1.900000	1.542790	1.235590
2213	EGS	2.025520	2.271820	1.917390	1.552570	1.257460
2035	TCEP	2.199360	2.309010	1.973910	1.614910	1.265410
2099	Cyanoethyl sucrose	2.271130	2.396280	2.033330	1.665040	1.297220
2117	BCEF	2.360450	2.430620	2.120290	1.680930	1.277340

calculated to within 0.0004 units, would have given the same results for several substances on two different stationary phases. It has now to be decided which of the five standard substances from the ten proposed by McREYNOLDS should be selected. This question could be answered by examining the suitability of all possible combinations of substances by computer. From our previous investigations, five standard substances can be proposed from those suggested by McREYNOLDS[4] in order to characterize the polarity of stationary phases at constant temperature through the corresponding f_i^* values. The f_i^* values of these standard substances are given in Table I.

In order to pre-calculate retention indices, the quotient of the corresponding f_i^* values (that of squalane as stationary phase and that of the polar stationary phase) is necessary:

$$f_n = \frac{\frac{I_m}{I^{sq}}}{\frac{I_m}{I^p}} = \frac{I^p}{I^{sq}} \tag{3}$$

where

f is the polarity factor;
n represents the standard substance: $n = 1$, 2-pentanone; $n = 3$, 2-methyl-2-pentanol; $n = 4$, 1-iodobutane; $n = 2$-pyridine; $n = 5$-*cis*-hydrindane;
sq represents the squalane stationary phase;
p represents the polar stationary phase.

These results are summarized for the proposed substances in Table II. In the experimental part, below, an example is shown for pre-calculating the retention indices with the help of data in Table II and with the following equation:

$$I_x^p(T) = I_x^{sq}(T) \cdot \sum_{n=1}^{5} f_n s_n \tag{4}$$

where:

T is the column temperature;
x is the substance being investigated;
s is the substance-specific factor[3].

EXPERIMENTAL

The nature of our present work was such that it required only minimal experimental GC work (some controlling of the basic index values) but very many calculations by computer. The experimental GC data are not given, nor are the known computer calculations described (the solution of equation systems with five unknowns, calculation of errors, etc.).

As an example of pre-calculating retention indices, the pre-calculation of retention indices of *n*-butanol on different stationary phases is demonstrated. The substance-specific factors of *n*-butanol at 120.0° relative to the five selected standard substances are given in Table III.

TABLE III

SUBSTANCE-SPECIFIC FACTORS OF *n*-BUTANOL AT 120.0°.RELATIVE TO THE FIVE SELECTED STANDARD SUBSTANCES ON ALL STATIONARY PHASES

s_1	s_2	s_3	s_4	s_5
−0.31763	0.18757	1.42712	0.66505	−0.93935

TABLE IV

COMPARISON OF THE RETENTION INDICES OF *n*-BUTANOL CALCULATED AND MEASURED AT 120° (ref. 4) ON DIFFERENT STATIONARY PHASES

Code number of McReynolds	*Stationary phase*	*Retention index*		*Difference (i.u.)*
		Measured (i.u.)	*Calculated (i.u.)*	
2205	SP-392	759	758.6	0.4
2081	Polybutene 128	616	615.4	0.6
2047	Tricresyl phosphate	911	910.6	0.4
2110	THEED	1532	1532.9	−0.9
2013	Apiezon L, treated	614	619.6	−5.6
2082	Polybutene 32	619	622.8	−3.8
2012	Apiezon L	618	623.8	−5.8
2077	SE-30	643	637.1	4.1
2316	DC-510	655	652.3	2.7
2314	DC-556	667	670.4	−3.4
2123	OV-7	703	697.8	5.2
2120	DC-550	706	704.3	1.7
2323	Apiezon W	725	720.2	4.8
2061	DC-703	713	717.4	−4.4
2124	OV-11	763	758.2	4.8
2229	DC-710	739	737.1	1.9
2038	OV-17	748	742.7	5.3
2096	Castorwax	855	859.9	−4.9
2068	OS-124	817	821.6	−4.6
2086	QF-1	823	826.1	−3.1
2126	OV-210	828	830.5	−2.5
2092	LSX-3-0295	831	832.2	−1.2
2183	Cresyl diphenyl phosphate	941	938.7	2.3
2091	Siponate DS-10	1159	1157.8	1.2
2185	Di(ethoxyethoxyethyl)	998	996.0	2.0
2042	EGSP-Z	1064	1068.1	−4.1
2084	Epon 1001	1079	1075.1	+3.9
2334	MER-2	1129	1131.4	−2.4
2338	Diglycerol	1416	1421.1	−5.1

Example:

$I^{OV\text{-}210}_{n\text{-butanol}}$ (120.0°) = 590 [(1.57097 × − 0.31763) + (1.44349 × 0.18757) + (1.29855 × 1.42712) + (1.16993 × 0.66505) + (1.05964 × − 0.93935)] = 590 × 1.407647 = 830.5 i.u.

The value as measured by McREYNOLDS[4] was 828.0 i.u.

The calculated data were compared with the data obtained by McREYNOLDS[4] on different stationary phases, and the results are summarized in Table IV.

It can be seen from the results in Table IV that the calculation of these series

gives very useful results to be used in research and practical work, so that it is absolutely necessary to deal with further temperature dependences and other unsolved problems of the system.

ACKNOWLEDGEMENTS

The authors are very grateful to Prof. Dr. E. PUNGOR for providing the research facilities and to Mrs. GABRIELLA MURÁNYI and Mrs. ANIKÓ SZABÓ for their technical aid.

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