GENERAL CONTRIBUTION TO THE THEORY OF RETENTION INDEX SYSTEMS IN GAS–LIQUID CHROMATOGRAPHY

III. CONTRIBUTION TO THE POLARITY OF GAS CHROMATOGRAPHIC STATIONARY PHASES EXPRESSED BY RETENTION INDICES

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SUMMARY

The importance of the polarity of gas chromatographic stationary phases is well known and many workers have studied the classification of stationary phases according to polarity and selectivity. In this paper, the results of our studies on a polarity scale obtained with the help of retention indices are described. These results were obtained by applying Rohrschneider's and McReynolds' concepts.

INTRODUCTION

The importance of the effect of the polarity of the stationary phases on retention data is well known, and the classification of stationary phases according to polarity has been considered by many workers, such as Chovin[1], Rohrschneider[2], McReynolds[3], Ettre[4], Parr and Howard[5], Bruening and Bruening[6], Fritz and Kováts[7], Hubert and Kováts[8], Wold and Andersson[9], Hartkopf[10], Hartkopf *et al.*[11], Lowry *et al.*[12], Kruppa and Henly[13], Snyder[14], Dimov and Muchtarova[15], Chastrette and Tagand[16], Supina[17] and Novák *et al.*[18].

The absolute determination of the polarity of stationary phases is impossible because the standard substances used for polarity measurements have different effects on the values obtained, and therefore only relative data are obtained. Although the theoretical value of these data is open to question, they are important for practical purposes[19–23].

In this paper, the results of our studies on a polarity scale, obtained with the help of retention indices, are described. These results were attained by applying Rohrschneider's concept[2] and on McReynolds's system[3].

Rohrschneider recognized the importance of polarity and suggested five standard substances, benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine[2], for the classification of stationary phases and for predicting retention data. The thermodynamic basis of his concept depends on the additivity of interaction forces and their effect on retention indices.

Based on Rohrschneider's concept, McReynolds used 10 standard substances[3]. According to McReynolds's basic concept, the 10 standard substances yield better results on average as the individual effects become indistinct. This basic concept gave very favourable results, which were discussed earlier[21]. In this paper, an account is given of the further development and the practical applicability of our method.

THEORETICAL

Retention indices for five standard substances are used to describe the polarity of stationary phases. This can be effected with Rohrschneider's standards (Rohrschneider's polarity values), but the calculations can also be made by using the first five of McReynolds ten standards (McReynolds's polarity values). At present, the column temperature determines which of the standards should be used; the standards used by Rohrschneider refer to 100.0° and McReynolds's standards to 120.0°. It would, of course, be expedient to use identical substances with known retention index *versus* column temperature dependences, but this has not yet been carried out.

As referred to in Part II, the difference in the retention indices of a substance yields the individual interaction contributions:

$$\Delta I = I^p - I^{sq} = I_{ii}^p \tag{1}$$

where

I = retention index, in index units (i.u.);
p = polar stationary phase;
sq = squalane stationary phase;
I_{ii} = individual interaction index contribution (i.u.).

The polarity is defined by designating the ability of a stationary phase to govern the individual interactions as polarity, provided that the polarity of squalane is zero:

$$I_{ii}^{sq} = 0.00 \tag{2}$$

Further, by definition:

$$I_{ig}^{sq} = I_{ig}^p \tag{3}$$

where I_{ig} = general interaction index contribution (i.u.).

Introducing the idea of relative polarity, we obtain

$$P_r = \frac{I^p - I^{sq}}{I^{sq}} = \frac{\Delta I}{I^{sq}} \tag{4}$$

where P_r = relative polarity, in polarity units (p.u.). Taking the average of the P_r values for the five standard substances, the average relative polarity value is obtained, from which the retention polarity is defined as follows:

$$\bar{P}_R = 100 \cdot \frac{\sum_{i=1}^{5} \left(\frac{I^p - I^{sq}}{I^{sq}}\right)_i}{5} = 20 \sum_{i=1}^{5} \left(\frac{\Delta I}{I^{sq}}\right)_i \tag{5}$$

where

$\bar{P}_R$ = retention polarity (p.u.);
i = serial number of standard substance.

The retention polarity also has a physical meaning: it indicates the average interac-

tion factor (π_{ti}^p) formed on a polar stationary phase (p) as percentage of the general interaction factor formed on squalane (π^{sq}). Since

$$I = \pi I_m \tag{6}$$

where

I_m = molecular index contribution (i.u.);
π = interaction factor;

then

$$\frac{\Delta I}{I^{sq}} = \frac{\pi_{ti}^p}{\pi^{sq}} \tag{7}$$

where π_{ti} = individual interaction factor.

The retention polarities for the stationary phases that are most frequently used in gas chromatography are given in Table I, based on McReynolds's polarity values at 120.0°.

TABLE I

RETENTION POLARITIES OF STATIONARY PHASES BASED ON McREYNOLDS' POLARITY VALUES[3] AT 120.0°

McReynolds code	Stationary phase	Retention polarity (p.u.)	McReynolds code	Stationary phase	Retention polarity (p.u.)
2000	Squalane	0.00	2169	Ditridecyl phthalate	21.46
2226	Hexatriacontane	0.69	2149	Bis(2-ethylhexyl)tetra-	21.47
2063	Nujol	1.01		chlorophthalate	
2298	Mineral oil	1.16	2310	DEG stearate	21.74
2270	Liquid paraffin	1.19	2250	Dilauryl phthalate	22.01
2128	Apiezon M	4.24	2313	Octyl decyl adipate	22.04
2127	Apiezon L	4.39	2170	Diisooctyl adipate	22.20
2013	Apiezon L (treated)	4.49	2024	TMP tripelargonate	22.77
2082	Polybutene-32	4.82	2057	Diisooctyl adipate	23.01
2081	Polybutene-128	4.90	2187	Diisodecyl phthalate	23.93
2012	Apiezon L	5.11	2124	OV-11	24.37
2318	DC-330	6.37	2070	Dinonyl phthalate	25.07
2195	Apiezon J	6.38	2229	DC-710	25.64
2066	SF-96	6.43	2060	Dioctyl phthalate	25.93
2077	SE-30	6.80	2276	Flexol GPE	25.94
2039	OV-101	7.17	2103	Hallcomid M-18	26.64
2316	DC-510	9.24	2116	Diisooctyl phthalate	26.77
2078	SE-52	10.42	2038	OV-17	27.40
2314	DC-556	12.18	2114	Hallcomid M-18 OL	28.83
2204	OV-3	13.17	2205	SP-392	29.60
2100	Beeswax	13.18	2022	Flexol 8N8	29.88
2144	Fluorolube HG-1200	15.30	2291	Span-60	30.17
2080	Halocarbon wax	15.70	2247	Hercoflex-600	30.28
2171	Butoxyethyl stearate	15.89	2162	Versamid-930	30.46
2123	OV-7	18.39	2059	UCON LB-550-X	31.19
2120	DC-550	19.25	2069	Span-80	31.70
2323	Apiezon W	19.41	2049	UCON 50-HB-1800-X	31.93
2179	Dinonyl sebacate	19.90	2096	Castorwax	31.94
2061	DC-703	20.32	2254	Flexol B-400	32.88
2052	Dioctyl sebacate	20.39	2175	Estynox	33.29
2056	Diisodecyl adipate	20.91			

TABLE I (continued)

McReynolds code	Stationary phase	Retention polarity (p.u.)	McReynolds code	Stationary phase	Retention polarity (p.u.)
2266	Atpet-200	33.92	2138	NPGA	56 63
2264	Pluracol P-2010	33.97	2300	UCON 75-H-90000	57.57
2113	UCON LB-1715	34.16	2004	Pluronic F-88	58.70
2182	Dibutoxyethyl adipate	34.28	2037	HI-EFF 8BP	60.22
2253	Thanol PPG-1000	35.01	2142	CW-4000 monostearate	62.40
2044	OV-25	35.86	2152	Zonyl E-7	63.97
2007	Pluronic L-81	36.01	2094	CW-4000 monostearate	64.79
2177	Didecyl phthalate	36.14	2215	NPGS	65.23
2068	OS-124	36.37	2098	IGEPAL CO-990	65.84
2111	Tributyl citrate	37.01	2042	EGSP-Z	67.51
2319	GE SR-119	37.71	2028	Carbowax 20M	70.75
2017	OS-138	38.06	2084	Epon-1001	71.91
2147	Diethoxyethyl sebacate	38.39	2029	Carbowax-6000	71.95
2048	Dibutoxyethyl phthalate	38.73	2079	Ethylene glycol isophthalate	72.29
2174	Dibutoxyethyl phthalate	39.38			
2108	NPG sebacate	39.43	2153	XF-1150	75.43
2132	Squalene	40.60	2133	Sorbitol hexaacetate	77.68
2046	UCON 50-HB-280-X	43.41	2135	FFAP	78.86
2131	Polytergent J-300	43.74	2089	STAP	79.14
2164	Paraplex G-25	44.27	2026	Carbowax-1000	79.84
2047	Tricresyl phosphate	44.34	2196	Sucrose octaacetate	80.59
2085	SAIB	44.34	2334	MER-2	81.43
2302	Ethomeen 18/25	44.50	2119	PEG-600	81.90
2180	Polytergent J-400	44.75	2208	Butanediol succinate	82.46
2025	Oronite MIW	45.75	2212	EGA	82.61
2086	QF-1	45.99	2139	Butanediol succinate	83.11
2252	UCON 50-HB-660	46.56	2219	PDEAS	84.19
2093	PPG sebacate	46.63	2151	Reoplex-400	85.08
2126	OV-210	46.78	2157	LAC IR-296	85.50
2021	Ethofat 60/25	47.18	2209	DEG adipate	85.61
2251	UCON 50-HB-3520	47.20	2027	Carbowax-1540	86.24
2062	Ethomeen S-125	47.53	2304	Resoflex R-296	86.63
2261	Igepal CO-630	47.77	2225	LAC-2-R-446	87.67
2092	LSX-3-0295	47.86	2041	EGSS-Y	88.11
2005	Pluronic P-65	48.32	2339	Hyprose SP-80	91.54
2008	Pluronic P-85	48.43	2040	ECNSS-M	100.39
2067	Tergitol NPX	48.74	2338	Diglycerol	102.40
2176	Emulphor ON-870	49.32	2107	DEGS Supelco-1045	102.55
2183	Cresyl diphenyl phosphate	49.36	2036	EGSS-X	105.30
			2325	DEGS	106.63
2003	Pluronic L-35	49.37	2327	Ethylene glycol phthalate	106.69
2184	Polytergent G-300	50.46			
2228	Polyglycol 15-200	50.83	2210	DEGS Supelco-1303	108.87
2129	Stepan DS-60	51.02	2303	DEGS	110.03
2055	UCON 50-HB-5100	53.09	2329	Glycol succinate	115.21
2146	Diethoxyethyl phthalate	53.15	2110	THEED	116.20
2091	Siponate DS-10	53.24	2097	Tetracyanoethoxy PE	116.38
2075	XE-60	53.83	2213	EGS	116.77
2102	Renex-678	54.18	2035	TCEP	128.91
2045	OV-225	55.63	2099	Cyanoethyl sucrose	136.31
2185	Bis(ethoxyethoxyethyl) phthalate	56.41	2117	BCEF	144.60

TABLE II

RELATIONSHIP BETWEEN THE PHENYL CONTENTS OF SILICONE STATIONARY PHASES WITH DIFFERENT PHENYL CONTENTS AND THEIR RETENTION POLARITIES

Stationary phase	Phenyl content (mole%)	Retention polarity (p.u.)
SE-52	5	10.4
OV-3	10	13.2
OV-7	20	18.4
OV-11	35	24.4
OV-17	50	27.4
SP-392	55	29.6
OV-22	65	33.1
OV-25	75	35.9

TABLE III

RETENTION POLARITIES OF DEGS STATIONARY PHASES OF VARIOUS ORIGINS

Stationary phase origin	Retention polarity (p.u.)
Supelco-1045	102.5
Chemical Research Services	106.6
Supelco-1303	108.8
PolyScience	110.0

The retention polarity scale can be used for solving practical problems, and two examples are shown here. In the first example, the phenyl content of silicone stationary phases with different phenyl contents was determined by means of their polarity. In the second example, the polarities of chemically identical stationary phases of various origins (DEGS) were compared. Some of the results obtained are given in Tables II and III. Very good results were obtained in both instances. Similar good results were obtained when the polarities of mixed stationary phases were studied.

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