Substance-Specific and Average Polarity Factors for Characterization of Stationary Phases Used in Gas–Liquid Chromatography

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Abstract

Kováts coefficients (K^p_c) and molecular structural coefficients (SP_{ci}), as well as their dependences on column temperature, stationary phase polarity, and solute chemical nature, have been dealt with in some earlier papers. Three new polarity values based on the above parameters are presented to characterize gas–liquid chromatographic stationary phases: the substance-specific polarity factor, the average polarity factor, and its derived polarity. The new scales describe the interaction capacity of 26 stationary phases from squalane (retention polarity, 0) to bis(cyanoethoxy)formamide (retention polarity, 144.6) with the first five McReynolds solutes. Their physicochemical meanings are also shown.

Introduction

Polarity in gas chromatography (GC) is controversial and must be managed carefully. It is relatively simple to assign polarity to a solute because it suffices to look at its chemical constitution for associating its dipolar moment or its capacity to give or take protons or electrons (etc.) to its polarity. n-Alkanes are nonpolar (zero dipolar moment), whereas n-alcohols, ketones, esters, and amines are polar because these chemical functions have a finite dipolar moment. However, the polarity of a stationary phase (SP) toward a solute depends on the reciprocal interaction forces between them: dispersion, induction, orientation, and donor–acceptor (e.g., hydrogen bond).

Rohrschneider [1] and McReynolds [2] pioneered the work on characterization of organic liquids used as GC SPs based on these solute–SP interactions. The latter method is still widely used; McReynolds polarity is one of the most characteristic SP data appearing in commercial catalogs, although it has been claimed that n-alkanes are unadvisable as standard probes for very polar SPs [3]. Other methods of characterization are the solvent selectivity triangles of Snyder and others [4–8], the Hildebrand solubility parameter approach [9–12], spectroscopic methods [13–15], and thermodynamic approaches [16–17].

These procedures have yielded a series of standardized polarity scales for SPs. The Rohrschneider polarity ($P = \log r_p - \log r_a$) is the difference between the logarithms of the relative retentions (r) of butadiene and butane on a polar (p) and a nonpolar (a) SP [18], ranging from squalane ($P = 0$) to β,β'-oxydipropionitrile ($P = 100$). Kováts [19] introduced a retention index (RI) scale to characterize SPs using the equation $\Delta I = I^p_x - I^{SQ}$. Schomburg [20] defined polarity as the RI differences for benzene and cyclohexane on the polar SP with respect to squalane: $P = \Delta I^{benzene} - \Delta I^{cyclohexane}$. McReynolds [2] characterized an SP by its "McReynolds polarity" ($\Sigma[\Delta I]$), calculated as the sum of the differences $X, Y, Z, U,$ and S of the retention indices for the solutes benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine, respectively, on the given SP and on squalane, taken as the apolar reference SP. Lee et al. [21] proposed the RI of the polarizable biphenyl to determine the SP polarity. Snyder [4] used the solvent polarity parameter (P'), determined as $P' = 1.2 + \Sigma \Delta I_i b/100$, where b is the slope of the straight line $\log V_{g,Z}$ versus Z (the carbon atom number of the n-alkanes), and $\Sigma \Delta I_i = \Delta I_i/x_i$, where x_i is the selectivity parameter for the three interactions of the SP and the solutes ethanol, dioxane, and nitromethane (proton acceptor, proton donor, and orientation, respectively). Novák [22] equated the SP polarity to its resistance to retain a nonpolar hydrocarbon, expressed as $\Delta G^0_{k(-CH2-)}(T)$, the partial molar Gibbs energy of the solution of a methylene group. Tarján et al. [23] used the coefficients of Kováts [24–26], defined as: $K^p_c = 100 (Z - \log V_{g,Z}/b)$, depending on the column temperature and carrier gas but not on the chosen n-alkane, provided that Z is greater than 7. Szentirmai et al. [27] coined the retention polarity (RP) (see Equation 13), based on the idea that the chromatographic interaction between a substance and an SP can be characterized by the RI ratios. The scale, a refinement of the Snyder's scale, is due to Kersten et al. [7]: $[\Sigma \delta \Delta G^0_K(i)]^p_{SQ} = \delta(\Delta G^0_{kethanol})^p_{SQ} + \delta(\Delta G^0_{knitromethane})^p_{SQ} + \delta(\Delta G^0_{kdioxane})^p_{SQ}$. Finally, Poole et al. [28] devised the scale of the solvent strength parameter (SSP): $\Delta G^0_{k(-CH2-)}(T)/\rho$, where ρ is the density of the SP.

Here average polarity factor (APF^p) and polarity (P^p) for 26 SPs are proposed. Also, a new concept of substance-specific polarity factor (SPF^p_k) for some solutes is proposed, and a relationship between them and their respective molecular structural coefficients is also suggested.

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Table I. Four Polarity Scales: Retention Polarity, Average Polarity Factor, McReynolds Polarity, and Polarity of 26 Stationary Phases at 120°C

Stationary phase	Retention polarity	McReynolds polarity	Average polarity factor	Polarity
Zerolane	−20.83	0.0000	1.0000	0.0000
Squalane	0.00	0.8968	1.1659	1.4879
SPB-OCTYL	1.65	0.9709	1.1783	1.7312
Apolane-87	2.30	1.0000	1.1831	1.8314
Apiezon-L	6.38	1.1855	1.2131	2.5263
OV-101	7.17	1.2217	1.2188	2.6734
SE-54	10.51	1.3760	1.2427	3.3402
OV-7	18.39	1.7480	1.2973	5.1969
OV-1701	24.58	2.0481	1.3383	6.9296
SP-392	29.60	2.2969	1.3704	8.5082
OV-25	35.86	2.6140	1.4089	10.6895
SAIB	44.34	3.0563	1.4584	14.0109
OV-215	47.95	3.2492	1.4786	15.5492
Pluronic F-68	58.70	3.8407	1.5351	20.5524
NPGS	65.23	4.2131	1.5670	23.8872
PEG-20M	71.91	4.6047	1.5976	27.5170
EGA	82.61	5.2558	1.6423	33.7601
SP-2380	86.79	5.5184	1.6584	36.3320
SP-2310	99.31	6.3349	1.7014	44.4311
DEGS	102.55	6.5538	1.7112	46.6134
Silar 10-CP	114.51	7.3905	1.7431	54.9181
EGS	116.77	7.5539	1.7482	56.5241
SP-222-PS	122.51	7.9769	1.7602	60.6422
OV-275	131.38	8.6538	1.7752	67.0810
CES*	136.31	9.0428	1.7816	70.6754
BCEF	144.60	9.7188	1.7891	76.6959

* Cyanoethyl sucrose.

Theory

The molecular structural coefficient for a solute at a temperature T was defined by Takács (29) as:

$$S^p_{cx}(T) = I^p_x(T) - K^p_c(T) = 100 \frac{\ln [V^p_{gx}(T)]}{\ln [Q^p(T)]} \qquad \text{Eq 1}$$

where S^p_{cx} is the molecular structural coefficient of a solute x in a given polar SP (ln [cm³/g]); T is the column temperature (°C), fixed in this case at 120°C; I^p_x is the isothermal retention index of a solute x in SP p (according to Kováts [30]); K^p_c is the Kováts coefficient of SP p (−ln [cm³/g]) (23–25,31,32); ln is a natural logarithm; V^p_{gx} is the specific retention volume of a solute x (cm³/g) in the SP p; and $Q^p(T)$ is the relative volatility of two adjacent n-alkanes in the SP p:

$$Q^p(T) = \frac{t'_{R,Z+1}}{t'_{R,Z}} \qquad \text{Eq 2}$$

where t'_R is the adjusted retention time (min)

$$t'_R = t_R - t_M \qquad \text{Eq 3}$$

where t_M is the dead (holdup) time (min), which is a transit ("retention time") of the inert substance used (hydrogen, neon, and in practice, methane). With the following equation in mind,

$$b = \log \frac{t'_{R,Z+1}}{t'_{R,Z}} = \log \frac{V_{g,Z+1}}{V_{g,Z}} \qquad \text{Eq 4}$$

Equation 1 can be rewritten as:

$$S^p_{cx}(T) = 100 \log \frac{V^p_{gx}(T)}{b} \qquad \text{Eq 5}$$

The molecular structural coefficient has the following physico-chemical meaning (E.B. Lorenz and J.M. Takács. Twenty-fifth anniversary of the gas chromatographic research group for study of the retention index systems, private communication, Budapest, Hungary, 1996). Bearing in mind the following equations,

$$S^p_{cx}(T) = \frac{100 [RT \log (V^p_{gx}(T))]}{\log (Q^p(T)/RT)} \qquad \text{Eq 6}$$

$$[\Delta G^0_x(T)]^p = -2.3RT \log [V^p_{gx}(T)] \qquad \text{Eq 7}$$
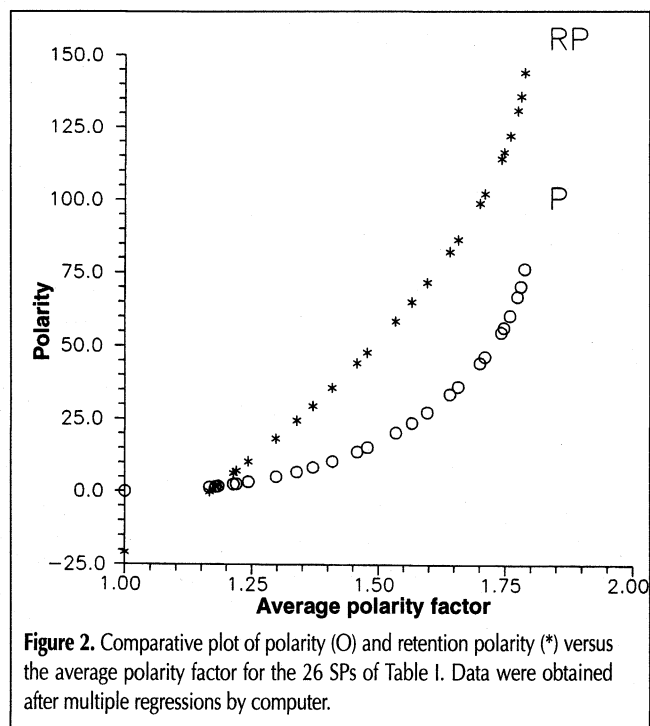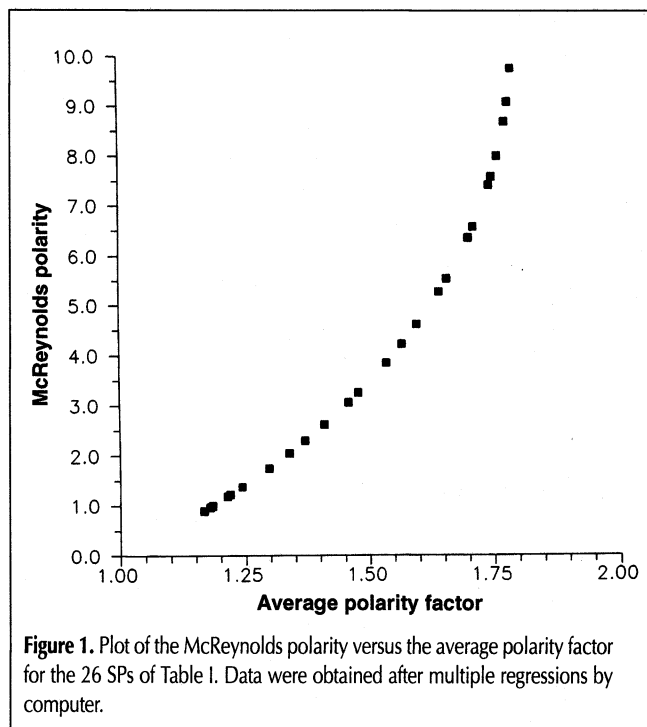
$$[\Delta G^0_{k(-CH2-)}(T)]^p = -2.3RTb \qquad \text{Eq 8}$$

it can be written:

$$S^p_{cx}(T) = 100 \frac{[\Delta G^0_x(T)]^p}{[\Delta G^0_{k(-CH2-)}(T)]^p} \qquad \text{Eq 9}$$

where $[\Delta G^0_x(T)]^p$ is the partial molar Gibbs energy necessary to take 1 mole of solute x from the gas phase to the SP p at a temperature of T; $[\Delta G^0_{k(-CH2-)}(T)]^p$ is the partial molar Gibbs energy for the -CH₂- group, whose physicochemical meaning is the energy to be spent for creating a cavity in the SP p to house the methylene group (i.e., it would account for the reluctance of the SP to do so). The partial molar Gibbs energy for the methylene group is equal to the product of −2.3RT and the slope (b) (Equation 4); expressing R in cal/mol K, its units are calories per mole.

According to the above (31), the molecular structural coefficient of a given solute on a given SP equals the ratio between the partial molar Gibbs energy of a solute x at a temperature T and a hundredth of the value of the partial molar Gibbs energy for a methylene group:

$$S^p_{cx}(T) = \frac{[\Delta G^0_x(T)]^p}{([\Delta G^0_{k(-CH2-)}(T)]^p/100)} \qquad \text{Eq 10}$$

Figure 1. Plot of the McReynolds polarity versus the average polarity factor for the 26 SPs of Table I. Data were obtained after multiple regressions by computer.

Figure 2. Comparative plot of polarity (O) and retention polarity (*) versus the average polarity factor for the 26 SPs of Table I. Data were obtained after multiple regressions by computer.

In recent papers (31,32), the effect of column temperature, SP retention polarity, and chemical nature of the solute have been studied. Here the substance-specific polarity factor term is defined as:

$$SPF^p_k\ (T) = \frac{S^p_{ck}\ (T)}{S^{zerolane}_{ck}\ (T)} \qquad \text{Eq 11}$$

In other words, the substance-specific polarity factor of a solute k (benzene [$k = 1$], n-butanol [$k = 2$], pentan-2-one [$k = 3$], 1-nitropropane [$k = 4$], and pyridine [$k = 5$]) is equal to the ratio of the molecular structural coefficient of the given McReynolds solutes k on the given SP and that on zerolane, a hypothetical apolar SP. Searching for the physicochemical meaning of the above parameter, Equation 11 can be transformed into the following, where the magnitudes can be easily calculated:

$$SPF^p_k\ (T) = \frac{[\Delta G^0_{k\,(-CH2-)}\ (T)]^{zerolane}}{[\Delta G^0_{k\,(-CH2-)}\ (T)]^p} \times \frac{[\Delta G^0_k\ (T)]^p}{[\Delta G^0_k\ (T)]^{zerolane}} \qquad \text{Eq 12}$$

The first term of the product is simply ($b^{zerolane}/b^p$), and the second is the ratio of the partial molar Gibbs solution energy of the solute k in the given SP and on zerolane, which are also simple calculations (16).

The retention polarity, $RP^p(T)$, at a temperature T is defined as (27):

$$RP^P\ (T) = 20 \sum_{i=1}^{5} \left[\frac{I^P\ (T)}{I^{SQ}\ (T)} \right]_i - 100 \qquad \text{Eq 13}$$

Next, a McReynolds polarity (MP) is defined by Takács (29) with the following expression:

$$MP^P\ (T) = 20 \sum_{i=1}^{5} \left[\frac{2K^P_c\ (T)}{K^{AP-87}_c\ (T)} \right] - 1 \qquad \text{Eq 14}$$

where AP-87 is the apolane 87 SP made by Kováts (34) to replace squalane, K^P_c represents the Kováts coefficient for the SP p, and K^{AP-87}_c is the Kováts coefficient for apolane-87.

Also, the average polarity factor of an SP p is defined as the averaged substance-specific polarity factor from benzene to pyridine for a given SP:

$$APF^P\ (T) = \left[\sum_{i=1}^{5} (SPF_K^P\ (T)) \right] / 5 \qquad \text{Eq 15}$$

It is a dimensionless magnitude, as are SPF_k, S^p_c, I, K_c, etc. Finally, another new polarity term simply called polarity (P^p) is defined by Takács (29):
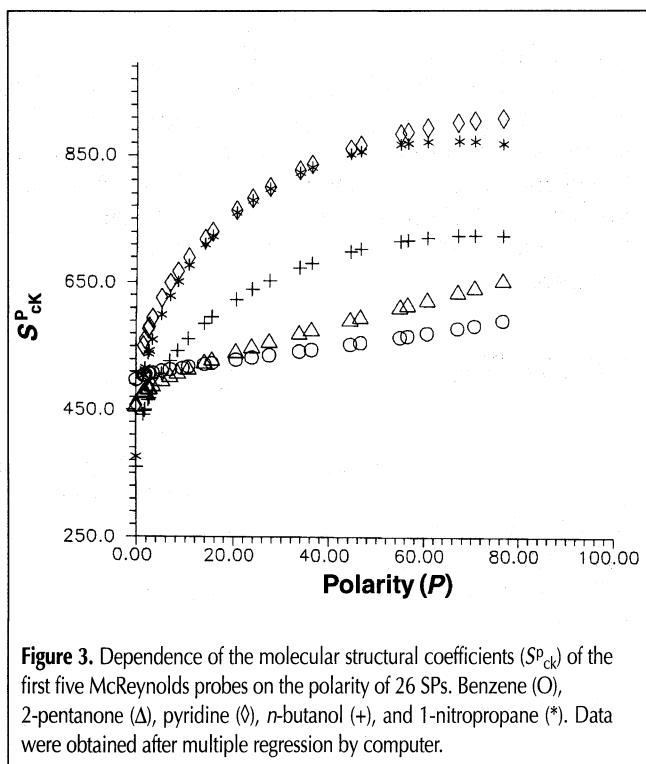
$$P^P\ (T) = 10 \cdot MP^P\ (T)\ [\ APF^P\ (T) - APF^{ZEROLANE}\ (T)] \qquad \text{Eq 16}$$

By definition, $MP^{zerolane} = 0$, so from Equation 14, $K_c^{zerolane} = 78.3$, and from Equation 15, $APF^{zerolane} = 1$. Therefore:

$$P^p\ (T) = 10 MP^p\ (T) \times [APF^p\ (T) - 1] \qquad \text{Eq 17}$$

Finally, the molecular structural coefficients of n-decane were computed from the following equation:

$$S_{c,n-C10}\ (T) = 100 \times Z - K^p_c\ (T) = 1000 - K^p_c\ (T) \qquad \text{Eq 18}$$

Figure 3. Dependence of the molecular structural coefficients (S^P_{ck}) of the first five McReynolds probes on the polarity of 26 SPs. Benzene (O), 2-pentanone (Δ), pyridine (◊), n-butanol (+), and 1-nitropropane (*). Data were obtained after multiple regression by computer.
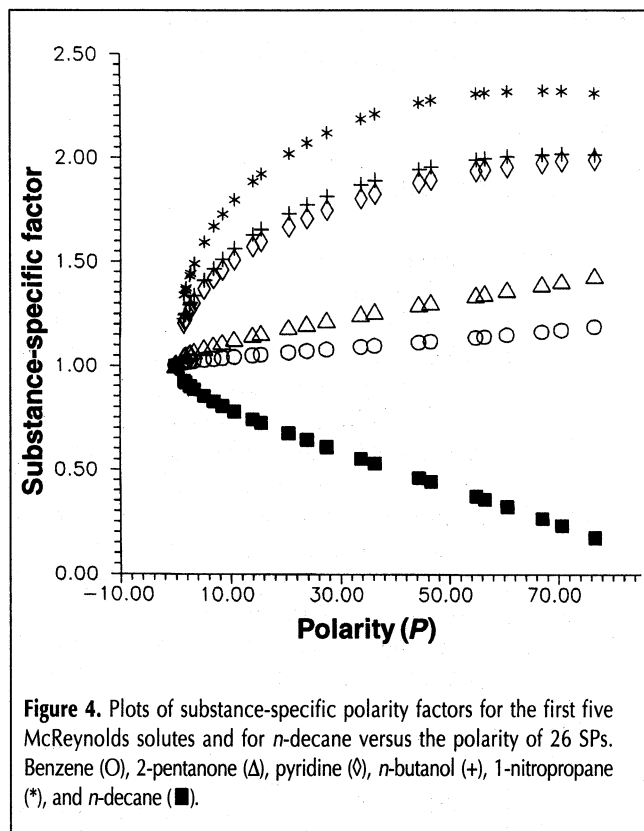
Experimental

Different types of packed (on various supports obtained from Johns-Manville [Denver, CO] and Supelco [Bellefonte, PA]) and capillary (WCOT) columns from Hewlett-Packard (Palo Alto, CA) and Chrompack (Middburg, The Netherlands) were used; polarity ranged between squalane and bis(cyanoethoxy)formamide (BCEF). Two apolar SPs were used as standards: zerolane and apolane 87. The first five McReynolds probes were benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine; the n-alkanes were used as markers.

Results and Discussion

Results were obtained at 120°C throughout. Table I shows the list of the 26 SPs used in this work together with the values of the four following polarity scales: retention polarity (RP), McReynolds polarity (MP), average polarity factor (APF), and polarity (P), calculated according to Equations 13, 14, 15, and 17, respectively. The range of the different polarity scales was between –21 and about 145 for RP, between 0 and about 10 for MP, between 1 and about 2 for APF, and between 0 and about 77 for P. Therefore, the two new polarity terms, APF and P, are polarity scales as correct as the RP and the MP and can be used as a tool for characterizing SPs, but without using squalane as a standard SP. Because the first five McReynolds probes were involved in the equations leading to the calculation of these magnitudes, the values of the different columns in Table I quantify the global solute–solvent interactions of the 26 SPs listed with the mentioned McReynolds solutes. For characterizing each individual interaction, other parameters such as molecular structural coefficients and substance-specific polarity factors are much more useful, as can be seen below.

Figure 1 shows the plot of McReynolds polarity obtained using Equation 14 versus the average polarity factors obtained using Equation 15 for 26 SPs. Figure 2 shows the plot of retention polarity and polarity calculated by Equations 13 and 17, respectively, versus the average polarity factors for the same SPs (Equation 15). Data were optimized by multiple regression carried out by computer. Monotonically increasing curves were obtained in all cases. Quadratic least-mean squares fits yielded the following results. For Figure 1, the coefficients for the grade-2 polynomial fitting in decreasing order ($y = ax^2 + bx + c$) were as follows: $a = 6.8672$, $b = -7.77348$, and $c = 0.16967$; the correlation coefficient was 0.97. For the RP–APF curve in Figure 2, $a = 180.686$, $b = -320.535$, and $c = 127.095$; the correlation coefficient was 0.99. For the P–APF curve in Figure 2, $a = 184.171$, $b = -437.911$, and $c = 260.753$; the correlation coefficient was 0.97.

Table II. Molecular Structural Coefficients (S^P_{ck}) for the First Five McReynolds Probes on 26 Stationary Phases at 120°C

Stationary phase	Benzene	n-Butanol	Pentan-2-one	1-Nitropropane	Pyridine
Zerolane	497.5	359.6	457.6	376.3	457.3
Squalane	504.4	441.7	478.6	503.5	550.5
SPB-octyl	505.0	447.9	480.3	512.7	557.5
Apolane-87	505.2	450.3	480.9	516.3	560.2
Apiezon-L	506.7	465.1	485.2	538.5	577.2
OV-101	507.0	468.0	486.0	542.7	580.5
SE-54	508.2	479.8	489.5	560.3	594.1
OV-7	511.2	506.9	497.9	599.7	625.4
OV-1701	513.7	527.2	504.6	628.8	649.0
SP-392	515.8	543.1	510.2	651.2	667.5
OV-25	518.6	562.1	517.1	677.6	689.8
SAIB	522.4	586.4	526.8	710.8	718.6
OV-215	524.2	596.2	530.9	724.0	730.3
Pluronic F68	529.5	623.6	543.5	760.1	763.5
NPGS	533.0	638.9	551.3	779.7	782.2
PEG-20M	536.7	653.3	559.4	797.8	800.2
EGA	543.0	674.0	572.7	823.0	826.5
SP-2380	545.6	681.3	577.9	831.5	836.0
SP-2310	553.9	699.9	594.1	852.6	861.3
DEGS	556.1	704.0	598.3	857.0	867.1
Silar 10CP	565.0	716.1	614.3	869.0	885.6
EGS	566.8	717.9	617.3	870.6	888.6
SP-222-PS	571.4	721.7	625.2	873.5	895.4
OV-275	579.0	725.3	637.5	875.1	903.8
CES*	583.5	726.1	644.5	874.4	907.2
BCEF	591.4	725.4	656.3	870.6	910.9

* Cyanoethyl sucrose.

Figure 4. Plots of substance-specific polarity factors for the first five McReynolds solutes and for n-decane versus the polarity of 26 SPs. Benzene (O), 2-pentanone (△), pyridine (◊), n-butanol (+), 1-nitropropane (*), and n-decane (■).

Table III. Kováts Coefficients (K^p_c), Molecular Structural Coefficients (S^p_{cn-C10}), and Substance-Specific Factors (SPF_{n-C10}) for n-Decane on 26 Stationary Phases at 120°C

Stationary phase	K^p_c	S^p_{cn-C10}	SPF_{n-C10}
Zerolane	78.3	921.7	1.0000
Squalane	148.5	851.5	0.9237
SPB-octyl	154.3	845.7	0.9174
Apolane-87	156.6	843.4	0.9149
Apiezon L	171.1	828.9	0.8991
OV-101	173.9	826.1	0.8961
SE-54	186.0	814.0	0.8830
OV-7	215.2	784.8	0.8513
OV-1701	238.7	761.3	0.8258
SP-392	258.1	741.9	0.8048
OV-25	283.0	717.0	0.7778
SAIB	317.6	682.4	0.7402
OV-215	332.7	667.3	0.7238
Pluronic F68	379.0	621.0	0.6736
NPGS	408.2	591.8	0.6419
PEG-20M	438.8	561.2	0.6087
EGA	489.8	510.1	0.5533
SP-2380	510.4	489.6	0.5311
SP-2310	574.3	425.7	0.4618
DEGS	591.5	408.5	0.4431
Silar 10CP	657.0	343.0	0.3721
EGS	669.8	330.2	0.3582
SP-222-PS	702.9	297.1	0.3223
OV-275	755.9	244.1	0.2648
Cyanoethyl sucrose	786.3	213.7	0.2318
BCEF	839.3	160.7	0.1743

Table II lists the molecular structural coefficients (S^p_{cx}) at 120°C of the first five McReynolds probes (i.e., benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine) calculated using Equation 5. Molecular structural coefficients of n-decane (S^p_{cn-C10}) for the 26 proposed SPs, calculated using Equation 18, can be seen in Table III.

Taking the differences $\Delta S_{ck} = S_{ck}^{BCEF} - S_{ck}^{zerolane}$ for each solute k and $\Delta P = P^{BCEF} - P^{zerolane} = 76.7$ (for all k solutes), the molecular structural coefficient increment gradients relative to the polarity increment from zerolane to BCEF ($\Delta S_{ck}/\Delta P$) for benzene, n-butanol, pentan-2-one, 1-nitropropane, pyridine, and n-decane were 1.224, 4.769, 2.591, 6.445, 5.914, and -9.922, respectively. To compare with benzene, the parameter $q_{Sck} = \Delta S_{ck}/\Delta S_{c1}$ was used. Table IV shows that 1-nitropropane and pyridine had a gradient q_{Sck} four times that of benzene, pentan-2-one had a gradient twice that of benzene, n-butanol's gradient was three times benzene's, and n-decane had a gradient eight times that of benzene, but with the opposite sign.

Figure 3 is a plot of S^p_{cx} versus P calculated using Equation 17. Optimized data were obtained by multiple regressions carried out by computer. Benzene and pentan-2-one yielded straight lines with the lowest gradients of S^p_{cx} versus P when P was greater than 10. The n-butanol curve lies in the middle, and both 1-nitropropane and pyridine curves lie in the upper part of the plot with the highest molecular structural coefficient values (i.e., showing the strongest solute–solvent interaction). The fitted parameters can be seen in Table IV.

Table V lists the substance-specific polarity factor values (SPF^p_k) for the same solutes on the same 26 SPs, calculated using Equation 11. The molecular structural coefficients ($S_{ck}^{zerolane}$) for the zerolane standard apolar SP were: 497.5, 359.6, 457.6, 376.3, and 457.3 for benzene, n-butanol, pentan-2-one, 1-nitropropane, and pyridine, respectively (Table II).

Next, the differences $\Delta SPF_k = SPF_k^{BCEF} - SPF_k^{zerolane}$ for the first five McReynolds probes and n-decane could be calculated (Tables III and V) as 0.1889, 1.0173, 0.4342, 1.3213, 0.9916, and -0.8257 for solutes 1–5 and n-decane, respectively. In reference to benzene, $q_{SPFk} = \Delta SPF_k/\Delta SPF_1$ and $\Delta SPF_{n-C10}/\Delta SPF_1$; q_{SPFk} values were 5.38, 2.30, 6.99, 5.25, and -4.37 for n-butanol, pentan-2-one, 1-nitropropane, pyridine, and n-decane, respectively (substance-specific polarity factor for benzene, $SPF_1 = 0.1889$) (Table IV). It can be inferred that 1-nitropropane had a q_{SPFk} gradient seven times that of benzene, pyridine and n-butanol had one an average of five times as high, pentan-2-one about twice as high, and n-decane had one four times that of benzene. Again, the negative sign of the n-alkane might mean a difference with respect to the polar solutes.

Table III lists the values of the Kováts coefficients (K_c^p) calculated from the relevant MP values in Table I, according to Equation 14; the molecular structural coefficient ($S^p_{c,n-C10}$) of n-decane, calculated (32) from Equation 18; and the substance-specific polarity factor of n-decane from Equation 11, bearing in mind that $K_c^{zerolane} = 78.3$ and $S_{c,n-C10}^{zerolane} = 100 \times 10 - 78.3 = 921.7$. It is shown that both S^p_{cn-C10} and SPF_{n-C10} increased for increasingly apolar SPs; correspondingly, they reached their minimum value for the most polar SP, BCEF.

The SPF_k values of the first five McReynolds probes (see Table V) and the substance-specific polarity factor for n-decane (see

Table IV. Correlation Data of SPF^p_k and SP_{ck} Versus P^p

| | SP_{ck} versus P^p correlation data | | | | |
| | Polynomial coefficients | | | Correlation coefficient | |
Solute	a	b	c	r^2	q_{Sck}*
n-Decane	0	–9.108	838.64	0.99	–8.1
Benzene	0	1.1238	504.41	1.00	1.0
n-Butanol	–0.0878	10.1395	439.18	0.96	3.0
Pentan-2-one	0	2.3762	484.17	0.98	2.1
1-Nitropropane	0.1294	14.2288	501.84	0.95	3.8
Pyridine	–0.0966	11.7857	547.12	0.97	3.9

| | SPF^p_k versus P^p correlation data | | | | |
| | Polynomial coefficients | | | Correlation coefficient | |
Solute	a	b	c	r^2	q_{Sck}†
n-Decane	0	–0.0099	0.9097	0.99	–4.37
Benzene	0	0.0023	1.0139	1.00	1.00
n-Butanol	–0.00024	0.02820	1.2213	0.96	5.38
Pentan-2-one	0	0.00519	1.05795	0.98	2.30
1-Nitropropane	–0.00034	0.03781	1.33372	0.95	6.99
Pyridine	–0.00021	0.02577	1.19627	0.97	5.25

* S_c increment gradient relative to benzene from zerolane to BCEF.
† SPF increment gradient relative to benzene from zerolane to BCEF.

Table III) have been plotted against the polarity values calculated using Equation 17 for the 26 (see Table I) studied SPs (Figure 4). Optimized values were obtained as those of the precedent figures. Like the previous S_{ck} versus P plots, identical curves were obtained for the latter solutes. Benzene and pentan-2-one made good straight lines showing the lowest SPF_k values; the highest SPF_k values corresponded to 1-nitropropane, and pyridine and n-butanol laid in the middle of the plot. On the contrary, n-decane points fell in a descending straight line with a slope of –0.0098802 (0.909723 intercept and 0.99 correlation coefficient). Then, whereas SPF_k of solutes 1–5 increased from unity (zerolane) to about 2.5 (BCEF), the SPF_{n-C10} diminished from 1 (zerolane) to about 0.17 for BCEF, the most polar SP. The strong SPF increase for the more polar solutes (i.e., 1-nitropropane, pyridine, and n-butanol), is in contrast with the strong decrease observed in the n-alkane. The data were fitted to grade 1 and 2 polynomials, and the parameters obtained are given in Table IV. As a hydrocarbon, benzene behaved somewhat similarly to n-decane because its SPF value did not increase much with P. Once again, as when the molecular structural coefficients (32) and their SP polarity dependence were examined, it is deduced from the opposite behavior of the n-alkane and the polar solutes that only dispersion interaction forces may act between the SP and n-decane, whereas, between the SPs and the McReynolds solutes, other interaction forces might intervene; the more polar the solute, the more intense the individual SPF_k is. Summing up, at least qualitatively, the SPF plots allow one to distinguish fairly well between n-alkanes and other polar solutes. In light of these results, it appears that the polarity APF and P scales data and the substance-specific polarity

factors proposed in this work open up a new possibility for characterization of GC SPs.

Conclusion

Two new polarity scales, APF and P, are proposed and calculated for 26 SPs spanning the entire polarity range. As with other scales (i.e., McReynolds polarity, retention polarity, Kováts coefficients, solvent strength polarity, etc.), they faithfully indicate the chromatographic behavior of the organic liquids used as SPs in GC. The use of zerolane, a hypothetical apolar SP, instead of squalane minimizes the criticism of the use of both this SP and the n-alkanes as markers for very polar SPs. A new field of SP characterization has been opened.

The molecular structural coefficients (SP_c) and substance-specific polarity factors (SPF_k^p) are a useful approach for determining the solute–solvent interactions. Both increased with SP polarity in polar solutes (McReynolds probes in this work), but they decreased for the apolar n-decane. This indicates that in the two cases, the SP–solute interaction is different in the sense that a polar solute may present not only dispersion interaction but also interaction by orientation, hydrogen bond (proton donor and proton acceptor), etc. Evidence of this difference is given by the SP_c and SPF_k^p versus P plots reported in this work.

Finally, the thermodynamic link between the molecular structural coefficients and the substance-specific polarity factors of a solute in a given SP at 120°C is established.

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Table V. Substance-Specific Polarity Factors (SPF_k) for the First Five McReynolds Probes on 26 Stationary Phases at 120°C

Stationary phase	Benzene	n-Butanol	Pentan-2-one	1-Nitropropane	Pyridine
Zerolane	1	1	1	1	1
Squalane	1.0139	1.2284	1.0457	1.3380	1.2036
SPB-octyl	1.0151	1.2455	1.0494	1.3626	1.2189
Apolane-87	1.0155	1.2521	1.0509	1.3722	1.2249
Apiezon-L	1.0185	1.2935	1.0602	1.4312	1.2621
OV-101	1.0191	1.3014	1.0620	1.4424	1.2692
SE-54	1.0216	1.3344	1.0697	1.4890	1.2991
OV-7	1.0277	1.4097	1.0880	1.5938	1.3673
OV-1701	1.0327	1.4662	1.1027	1.6711	1.4190
SP-392	1.0369	1.5103	1.1148	1.7306	1.4595
OV-25	1.0424	1.5631	1.1300	1.8008	1.5082
SAIB	1.0502	1.6307	1.1510	1.8890	1.5712
OV-215	1.0536	1.6581	1.1601	1.9241	1.5969
Pluronic F68	1.0644	1.7343	1.1876	2.0200	1.6693
NPGS	1.0714	1.7767	1.2046	2.0720	1.7102
PEG-20M	1.0788	1.8169	1.2223	2.1203	1.7496
EGA	1.0915	1.8744	1.2513	2.1872	1.8072
SP-2380	1.0967	1.8945	1.2629	2.2099	1.8279
SP-2310	1.1134	1.9463	1.2981	2.2659	1.8832
DEGS	1.1179	1.9576	1.3074	2.2774	1.8959
Silar 10CP	1.1358	1.9915	1.3422	2.3095	1.9364
EGS	1.1393	1.9965	1.3489	2.3137	1.9429
SP-222-PS	1.1487	2.0070	1.3661	2.3215	1.9578
OV-275	1.1640	2.0170	1.3930	2.3257	1.9760
CES*	1.1730	2.0193	1.4082	2.3238	1.9835
BCEF	1.1889	2.0173	1.4342	2.3214	1.9916

* Cyanoethyl sucrose.

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