

# Temperature Dependence Study of Several Polarity Scales Used in Gas–Liquid Chromatography Stationary Phase Characterization

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## Abstract

Substance-specific factors (SPF<sub>i</sub>), average polarity factors (APF), retention polarities (RP), McReynolds polarities (MP), and effective polarities (P) for 26 stationary phases spanning the entire range of polarity were recently determined at 120°C. Here, their temperature dependence for 8 stationary phases and the first 5 McReynolds probes at the 60–150°C temperature range is studied. A very good correlation between ln SPF versus temperature is found for most cases. Decreasing straight lines are obtained for benzene, pentan-2-one, and pyridine, and increasing straight lines are obtained for *n*-butanol and 1-nitropropane. Regarding ln APF versus temperature dependence, a linear correlation is merely adequate for Squalane (coefficient of regression  $r^2 = 0.9999$ ) and XF-1150 ( $r^2 = 0.9944$ ) and somewhat worse for TFPS35 ( $r^2 = 0.9249$ ) and OV-101 ( $r^2 = 0.9023$ ); the variation for the rest of the trifluoropropyl siloxanes is negligible, and straight lines quasi-parallel to the temperature axis are obtained. The correlation with temperature is very good for the Kováts coefficient but rather unequal for RP, MP, and P.

## Introduction

The evaluation of different polarity scales was carried out at 120°C for some stationary phases in a recent work (1). It is convenient to establish the relationship of temperature and these polarity scales with which stationary phases are characterized in gas–liquid chromatography (GLC), so that the behavior of a given stationary phase may be predicted at any temperature without having to proceed with its characterization. Szentirmai et al. (2) used retention index ratios of the first 5 McReynolds probes of the investigated stationary phase to those of Squalane at 120°C to calculate its retention polarity as:

$$RP^{\text{st.ph.}}(T) = 20 \sum_{k=1}^5 \left[ \frac{I^{\text{st.ph.}}(T)}{I^{\text{SQ}}(T)} \right]_k - 100 \quad \text{Eq 1}$$

where SQ stands for Squalane and “st.ph.” stands for the other stationary phase. Retention indices were calculated with the

Kováts equation as usual (3). Squalane, in spite of its widespread use in GLC stationary phase characterization by Rohrschneider (4) and McReynolds (5), has been questioned as a standard stationary phase because of its low operation temperature limit and other reasons involving its tendency to oxidize with oxygen eventually contained in the carrier gas, its poor support deactivation, and the possibility of it containing Squalane’s impurities (6,7). Because of these reasons, it has been suggested several times that Squalane be replaced by Apolane-87 (6–8). Takács et al. (9) proposed another stationary phase (hypothetically) that they called “Zerolane” because of its zero polarity, defined by the following characteristics: molecular mass, 1360.0 g; stationary phase amount in the capillary column WCOT, 0.0136 g; mole fraction,  $1 \times 10^{-5}$ ; density at 120°C, 0.8106 g/mL; *b*-value, 0.3038 at 120°C;  $V_{\text{gn-C8}}$  (the *n*-octane specific retention volume), 155.7 mL/g;  $\Delta G(\text{CH}_2)$ , 2170.2 J/mol; retention polarity, –20.83 (retention polarity for Squalane was 0.00); McReynolds polarity (MP), 0.00 ( $\text{MPSQ} = 0.9405$  at 120°C).

On the other hand, the molecular structural coefficient  $S_{\text{ci}}$  (10,11,14) of a solute on a given stationary phase at a given temperature has been defined as the difference between its retention index and the column’s Kováts coefficient at the given temperature

$$S_{\text{ck}}(T) = I_{\text{k}}(T) - K_{\text{c}}(T) = 100 \frac{\ln V_{\text{gk}}(T)}{\ln Q(T)} \quad \text{Eq 2}$$

where

$$I_{\text{k}}(T) = 100 \left( Z + \frac{\ln V_{\text{gk}}(T) - \ln V_{\text{g,Z}}(T)}{\ln V_{\text{g,Z+1}}(T) - \ln V_{\text{g,Z}}(T)} \right) \quad \text{Eq 3}$$

$V_{\text{gk}}$ ,  $V_{\text{g,Z}}$ , and  $V_{\text{g,Z+1}}$  are the specific retention volumes of the probe and the *n*-alkanes of *Z* and *Z* + 1 carbon atoms, respectively;  $I_{\text{k}}$  stand for the retention (or Kováts) indices; and *T* is the column temperature. The denominator is as follows:

$$\ln \left[ \frac{V_{\text{g,Z+1}}(T)}{V_{\text{g,Z}}(T)} \right] = \ln Q(T) \quad \text{Eq 4}$$

Therefore, the value *Q* is the adjusted retention times ratio of two adjacent reference *n*-alkanes:

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$$Q(T) = \frac{V_{g,Z+1}(T)}{V_{g,Z}(T)} = \frac{V_{N,Z+1}(T)}{V_{N,Z}(T)} = \frac{t_{R,Z+1}(T) - t_M(T)}{t_{R,Z}(T) - t_M(T)} \quad \text{Eq 5}$$

where  $t_M(T)$  is the holdup retention time of the unretained methane, and  $V_g$  and  $V_N$  are specific and net retention volumes, respectively. On the other hand, from the Kováts coefficient's definition,

$$K_c(T) = 100 \left[ Z - \frac{\ln(V_{g,Z}(T))}{\ln Q(T)} \right] \quad \text{Eq 6}$$

The substance-specific factors  $SPF_k$  (1) of the first 5 McReynolds solutes on a given stationary phase are defined as a function of temperature as the ratio of their molecular structural coefficients on the examined stationary phase to those on Zerolane:

$$SPF_k(T) = \frac{S_{ck}^{\text{st.ph.}}(T)}{S_{ck}^{\text{Zerolane}}(T)} \quad \text{Eq 7}$$

Then, the average polarity factors (1)  $APF^{\text{st.ph.}}(T)$  are defined as the arithmetic means of the corresponding  $SPF_k(T)$  values.

$$APF^{\text{st.ph.}}(T) = \sum_{k=1}^5 \left[ \frac{SPF_k(T)}{5} \right] \quad \text{Eq 8}$$

Then, the McReynolds polarity  $MP^{\text{st.ph.}}(T)$  (1) as a function of the temperature was evaluated using the following equation:

$$MP^{\text{st.ph.}}(T) = 2 \left[ \frac{K_c^{\text{st.ph.}}(T)}{K_c^{\text{AP-87}}(T)} \right] - 1 \quad \text{Eq 9}$$

where AP-87 stands for the Apolane C-87 stationary phase. Finally, the effective polarity  $P^{\text{st.ph.}}(T)$  (1) at various temperatures was calculated as:

$$P^{\text{st.ph.}}(T) = 10MP(T)^{\text{st.ph.}} [APF^{\text{st.ph.}}(T) - APF^{\text{Zerolane}}(T)] \quad \text{Eq 10}$$

Because, by definition, the average polarity factor of Zerolane is the unit, Equation 10 will take the following shape:

$$P^{\text{st.ph.}}(T) = 10MP^{\text{st.ph.}}(T) [APF^{\text{st.ph.}}(T) - 1] \quad \text{Eq 11}$$

Calculations of the polarity scales for Zerolane, Squalane, and OV-101 were carried out by Takács (9) at the 60–130°C temperature interval by means of his retention data precalculation program recently reported (15), and using Equations 1–11, the calculations for the other 6 stationary phases were performed: the packed XF-1150 column, characterized by Santiuste (16–19) at the 90–150°C range, and the another 5 trifluoropropyl siloxanes of low percentage of trifluoropropyl substitution (from 0 to 35%) at the 60–140°C range, characterized by Dai (20–22).

Therefore, the goal of this work was to investigate the correlations of the solute–solvent interactions evaluated as  $SPF_k$  (and also as  $\ln SPF$ ) versus temperature. Along with the relationships of  $K_c$ ,  $MP$ , average polarity factors ( $APF$ ), retention polarities ( $RP$ ), and effective polarities ( $P$ ) with temperature for all of these stationary phases, the effect of the heating of the column on the

solute–solvent retention interactions to which these substance-specific factors  $SPF_k(T)$  are assigned was investigated, so that the possibility of predicting the retention behavior of these solutes on these stationary phases can be firmly established over the temperature ranges explored.

## Experimental

### Stationary phases

The poly(methyl 3,3,3-trifluoropropyl)siloxanes TFPS00, TFPS09, TFPS15, TFPS26, and TFPS35 (20–22) with trifluoropropyl group percentages of substitution (0, 9, 15, 26, and 35%)

**Table I. Molecular Structural Coefficients of the First 5 McReynolds Probes at 60–130°C on the Stationary Phase Zerolane.**

Temperature (°C)	Probe*				
	1	2	3	4	5
60	502.0	449.2	459.7	468.4	457.5
70	500.8	433.5	457.8	455.2	457.1
80	499.4	417.8	456.3	441.6	456.6
90	497.6	401.9	455.1	427.6	456.0
100	495.6	385.9	454.2	413.1	455.1
110	493.2	369.7	453.6	398.1	453.7
120	493.3	353.2	453.2	382.4	451.4
130	487.4	336.3	453.0	366.2	446.8

\* Probes: 1, benzene; 2, *n*-butanol; 3, pentan-2-one; 4, 1-nitropropane; and 5, pyridine.

**Table II.  $SPF_k$  Values of the First 5 McReynolds Probes for Squalane and OV-101 Calculated Using Equation 7**

Temperature (°C)	Solute*				
	1	2	3	4	5
<b>Squalane</b>					
60	1.06490	1.18834	1.13235	1.17705	1.19388
70	1.05411	1.19061	1.11811	1.19148	1.19362
80	1.04337	1.19325	1.10269	1.20722	1.19306
90	1.03247	1.19624	1.08612	1.22439	1.19214
100	1.02122	1.19957	1.06841	1.24314	1.19080
110	1.00954	1.20326	1.04957	1.26369	1.18897
120	0.99717	1.20731	1.02958	1.28628	1.18657
130	0.98409	1.21174	1.00843	1.31125	1.18353

### OV-101

60	1.09432	1.26413	1.18588	1.24797	1.26968
70	1.08271	1.26950	1.16982	1.26920	1.27234
80	1.07123	1.27561	1.15525	1.29320	1.27352
90	1.05958	1.28250	1.13323	1.31745	1.27418
100	1.04762	1.29033	1.11280	1.34491	1.27460
110	1.03520	1.29887	1.09097	1.37500	1.27490
120	1.02217	1.30853	1.06779	1.40811	1.27512
130	1.00838	1.31934	1.04321	1.44477	1.27529

\* Solutes: 1, benzene; 2, *n*-butanol; 3, pentan-2-one; 4, 1-nitropropane; and 5, pyridine.

were prepared from borosilicate glass capillary tubing (20–31 m × 0.25-mm i.d.) drawn on a Shimadzu (Kyoto, Japan) GDM-1B machine. The tubes were leached, washed, and dehydrated according to Grob's method (23), and the tube walls were silyanized according to Blomberg's procedure (24) using 3,3,3-trifluoropropyl cyclosiloxanes. Coating was performed using the static method with a solution of the stationary phase on dichloromethane; film thicknesses were between 0.26 and 0.32 μm. The commercial stationary phase TFPS00, a polydimethylsiloxane containing 1–2% vinyls, was purchased from Petrarch (Hüls America, Bristol, PA) (PS-255). Cyanoethylpolysiloxane with 50% cyanoethyl (XF-1150) was built as a packed column

(4 m × 0.25-inch i.d., 19.2% loading, Chromosorb W AW, 80/100 mesh). OV-101 (9) was a WCOT column (50.0 m × 0.25-mm i.d. glass capillary, mass of stationary phase  $m_s = 0.0325$  g).

The gas chromatographs used for TFPS phases characterization were two Hewlett-Packard HP 5890 A for the WCOT columns and a Varian 3300 for the packed column. An HP 5880-II (Hewlett-Packard) was used for OV-101.

Nitrogen was used as the carrier gas. *n*-Alkanes with 6–16 carbon atoms and the first 5 McReynolds probes were used as solutes.

The temperatures over which the stationary phase's characterization was carried out were 60, 80, 100, 120, and 140°C for TFPS00, TFPS09, and TFPS15; 80, 100, 120, and 140°C for TFPS26 and TFPS35; 90, 105, 120, 135, and 150°C for XF-1150; and 60, 70, 80, 90, 100, 110, 120, and 130°C for Zerolane, Squalane, and OV-101.

**Table III. SPF<sub>k</sub> Values of the First 5 McReynolds Probes for Poly(methyl 3,3,3-trifluoropropyl)siloxanes and XF-1150 Calculated Using Equation 7**

Temperature (°C)	Solute*				
	1	2	3	4	5
<b>TFPS00</b>					
60	1.15333	1.26975	1.28664	1.34579	1.41223
80	1.12346	1.30578	1.24820	1.38101	1.37321
100	1.09775	1.35591	1.20861	1.43148	1.34479
120	1.07194	1.41049	1.16193	1.49133	1.31696
140	1.04349	1.48028	1.10847	1.55098	1.29159
<b>TFPS09</b>					
60	1.16412	1.30029	1.39480	1.48674	1.49145
80	1.13599	1.35020	1.35637	1.52743	1.45254
100	1.11004	1.39838	1.31359	1.58275	1.41929
120	1.07285	1.44856	1.25824	1.65045	1.38117
140	1.05106	1.54654	1.21275	1.73222	1.35215
<b>TFPS15</b>					
60	1.16438	1.31305	1.44481	1.55535	1.52105
80	1.13453	1.35418	1.40736	1.60682	1.48211
100	1.09504	1.39304	1.35618	1.72662	1.44648
120	1.06748	1.45451	1.30601	1.74603	1.41125
140	1.04289	1.52626	1.25131	1.82497	1.38122
<b>TFPS26</b>					
80	1.13183	1.40433	1.50740	1.73487	1.62228
100	1.09575	1.44760	1.45801	1.80879	1.56369
120	1.05270	1.48863	1.39668	1.89133	1.50851
140	1.02085	1.55670	1.34105	1.99491	1.47920
<b>TFPS35</b>					
80	1.12411	1.39294	1.55592	1.82690	1.61253
100	1.08214	1.43089	1.50282	1.90162	1.56139
120	1.03413	1.46850	1.43970	1.98486	1.51070
140	0.97478	1.49371	1.35421	2.06421	1.45963
<b>XF-1150</b>					
90	1.30888	2.04329	1.77126	2.37208	2.02192
105	1.30598	2.17930	1.75132	2.56850	2.08095
120	1.30357	2.27718	1.78751	2.68855	2.05945
135	1.29821	2.42459	1.71353	2.91708	2.10795
150	1.23872	2.56487	1.71042	3.14728	2.14292

\* Solute: 1, benzene; 2, *n*-butanol; 3, pentan-2-one; 4, 1-nitropropane; and 5, pyridine.

## Results and Discussion

Table I contains the molecular structural coefficients (10–14) of the solutes on Zerolane (hypothetical zero polarity stationary phase) over the aforementioned temperature interval found by fitting with computer (9). Correlations of  $S_{ck}^{\text{Zerolane}}$  with temperature (°C) were used to obtain the values needed for calculations at any temperature:  $S_{c1}^{\text{Zerolane}} = -0.2075T + 515.5$  (coefficient of regression  $r^2 = 0.977$ );  $S_{c2}^{\text{Zerolane}} = -1.6096T + 546.3$  ( $r^2 = 0.9998$ );  $S_{c4}^{\text{Zerolane}} = -1.4576T + 557.5$  ( $r^2 = 0.9988$ ), where  $k = 1, 2,$  and  $4$  stand for benzene, *n*-butanol, and 1-Nitropropane, respectively, and  $S_{c3}^{\text{Zerolane}} = 0.001417T^2 - 0.3620T + 476.3$  and  $S_{c5}^{\text{Zerolane}} = -0.002467T^2 + 0.3362T + 445.8$  represent pentan-2-one and pyridine, respectively.

Table II contains the substance-specific factors  $SPF_k(T)$  defined by means of Equation 7, calculated for the aforementioned solutes on Squalane and OV-101. Table III shows the corresponding  $SPF_k(T)$  values for the other 6 stationary phases. A common feature of these results is that the gradients of *n*-butanol and 1-nitropropane are positives (i.e.,  $\Delta SPF/\Delta T > 0$ ), showing an increase with increasing temperature, but an opposite trend was found for the other 3 solutes. Pentan-2-one and 1-nitropropane are the solutes with the biggest temperature gradients variation relative to benzene [ $(\Delta SPF/\Delta T)_k / (\Delta SPF/\Delta T)_{\text{benzene}} = 1.5\text{--}2$ ] on the apolar Squalane and on the slightly polar OV-101. Relative gradients vary very little: 0.1–0.3 and 0–0.6 for *n*-butanol and pyridine, respectively, on the same columns by the same order. The variation of the relative gradient  $\Delta SPF_k/\Delta T$  (referring to benzene) shows the same trend in the trifluoropropyl siloxanes, decreasing with increasing temperature for *n*-butanol and 1-nitropropane, ( $\Delta SPF_k/\Delta T > 0$ ), but increasing for the other McReynolds solutes. The lowest relative gradients were for pyridine (1–1.2) and pentan-2-one (1–1.4), with values of 1.5 and 2 for *n*-butanol and 1-nitropropane, respectively.

Examining the most polar stationary phase, XF-1150, the most significant temperature variation was observed for *n*-butanol and 1-nitropropane with relative gradient values of –7.5 and –11.0, respectively, while the variation for pentan-2-one and pyridine was much smaller ( $\Delta SPF_k/\Delta T = 1$  and 2, respectively).

Table IV shows the results obtained for various polarity scales:

Kováts coefficients (8,10,13,25), RP (2), APF (1,11), MP (1,11), and P (1–11), calculated by means of Equations 1, 6, 8, 9, and 11.  $K_c(T)$  clearly increases with increasing temperature, and good straight lines were obtained; the best correlation coefficient ( $r^2 = 0.9995$ ) was for TFPS26, and the worst ( $r^2 = 0.9932$ ) was for XF-1150. Retention polarity decreased with increasing polarity, except for TFPS35, XF-1150, and OV-101, for which slopes were positive. Correlation coefficients for RP versus temperature were worse than those of  $K_c$  versus  $T$ : 0.944, 0.834, 0.869, and 0.911 for TFPS00, TFPS09, TFPS15, and TFPS26, respectively, and 0.998, 0.837, and 0.803 for XF-1150, OV-101, and Zerolane, respectively. Correlations of RP with  $[1/(T + 273.15)]$  did not improve the results in general. Except for Squalane and OV-101, other types of correlations can be thought of as adequate to explain the temperature dependence of MP and P for the stationary phases in this work.

Table V shows the  $\ln \text{SPF}_k$  values of the first 5 McReynolds probes on the 8 stationary phases at the 60–150°C temperature range. Decreasing values with increasing temperature were obtained for benzene, pentan-2-one, and pyridine, whereas increasing values with increasing temperature were obtained for the more polar solutes *n*-butanol and 1-nitropropane.

**Table IV. Variation of Several Polarity Scales with Temperature on 9 Stationary Phases**

Temperature (°C)	$K_c$	RP	APF	MP	P
<b>TFPS00</b>					
60	75.30	7.543	1.2935	0.814	2.3865
80	96.49	6.898	1.2863	0.940	2.7083
100	117.95	6.426	1.2877	1.068	3.0613
120	141.41	6.110	1.2905	1.200	3.4686
140	166.73	5.979	1.2950	1.336	3.9564
<b>TFPS09</b>					
60	83.81	13.347	1.3675	0.910	3.3426
80	105.39	13.717	1.3645	1.028	3.7433
100	127.67	13.157	1.3648	1.157	4.2056
120	155.89	12.889	1.3622	1.298	4.7604
140	178.76	13.009	1.3812	1.451	5.4604
<b>TFPS15</b>					
60	98.69	19.069	1.3997	1.065	4.2541
80	121.78	18.572	1.3970	1.194	4.7336
100	147.65	17.922	1.4035	1.329	5.2594
120	172.57	17.662	1.3971	1.467	5.8378
140	200.97	17.777	1.4053	1.611	6.5125
<b>TFPS26</b>					
80	149.73	28.773	1.4801	1.508	7.2569
100	177.00	28.194	1.4748	1.475	6.9772
120	207.62	27.551	1.4676	1.459	6.8515
140	235.37	27.514	1.4785	1.451	6.7800
<b>TFPS35</b>					
80	180.28	35.146	1.5025	2.021	10.1393
100	211.85	35.019	1.4958	1.963	9.7607
120	248.23	35.084	1.4876	1.938	9.4327
140	288.72	36.068	1.4693	1.924	9.0322

Figure 1 shows the plot of  $\ln \text{SPF}_{\text{benzene}}$  versus temperature of the 8 stationary phases: XF-1150, the 5 trifluoropropyl siloxanes, Squalane, and OV-101. Decreasing straight lines were obtained in all cases, with more abrupt slopes for the more polar stationary phases, ranking from the lowest  $\ln \text{SPF}$  values, Squalane and OV-101 (1 and 2, respectively) to trifluoropropyl siloxanes with percentages of TFP group 0, 9, 15, 26, and 35 (numbers 3–7). XF-1150 (number 8) corresponds to a soft curve with a quite smooth  $\ln \text{SPF}$  increase with a very flat maximum.

Figure 2 shows the plots of  $\ln \text{SPF}_k$  versus temperature for *n*-butanol and for pyridine on Squalane and OV-101. In the first case Figure 2A), increasing straight lines  $\ln \text{SPF}_{n\text{-butanol}}$  versus temperature were obtained, showing an increase in the variation of  $\ln \text{SPF}$  versus temperature. For pyridine (Figure 2B), things appear less clear, and there is hardly variation because of the observed plateau in the curves obtained.

Figure 3 shows the plot of  $\ln \text{SPF}$  as a function of temperature of the first 5 solutes of McReynolds on TFPS35 (80, 100, 120, and 140°C). Good descending straight lines were obtained for pyridine, pentan-2-one, and benzene (the solute with the lowest  $\ln \text{SPF}$  values). Good increasing straight lines for *n*-butanol and

**Table IV. (cont.)**

<b>XF-1150</b>					
90	319.37	82.163	1.9062	3.945	35.8753
105	342.95	86.146	1.9819	3.597	34.5069
120	386.34	90.579	2.0232	3.522	35.8413
135	416.51	93.940	2.0898	3.490	37.0250
150	456.67	98.094	2.1533	3.471	40.3389
<b>Squalane</b>					
60	93.43	0.000	1.1513	0.922	1.3951
70	104.25	0.000	1.1496	0.9260	1.3852
80	115.32	0.000	1.1479	0.9295	1.3748
90	126.70	0.000	1.1463	0.9326	1.3641
100	138.48	0.000	1.1446	0.9354	1.3529
110	150.72	0.000	1.1430	0.9380	1.3414
120	163.52	0.000	1.1414	0.9405	1.3297
130	176.94	0.000	1.1398	0.9428	1.3180
<b>OV-101</b>					
60	105.55	6.403	1.2125	1.1713	2.4894
70	117.06	6.542	1.2126	1.1625	2.4718
80	128.78	6.678	1.2129	1.1547	2.4587
90	140.81	6.808	1.2134	1.1478	2.4494
100	153.22	6.935	1.2141	1.1415	2.4436
110	166.09	7.059	1.2150	1.1357	2.4417
120	179.51	7.719	1.2162	1.1302	2.4439
130	193.55	7.298	1.2179	1.1251	2.4512
<b>Zerolane</b>					
60	48.61	-18.172	1.000	0.000	0.000
70	54.13	-18.617	1.000	0.000	0.000
80	59.77	-19.068	1.000	0.000	0.000
90	65.56	-19.524	1.000	0.000	0.000
100	71.55	-19.986	1.000	0.000	0.000
110	77.77	-20.456	1.000	0.000	0.000
120	84.27	-20.934	1.000	0.000	0.000
130	91.07	-24.422	1.000	0.000	0.000



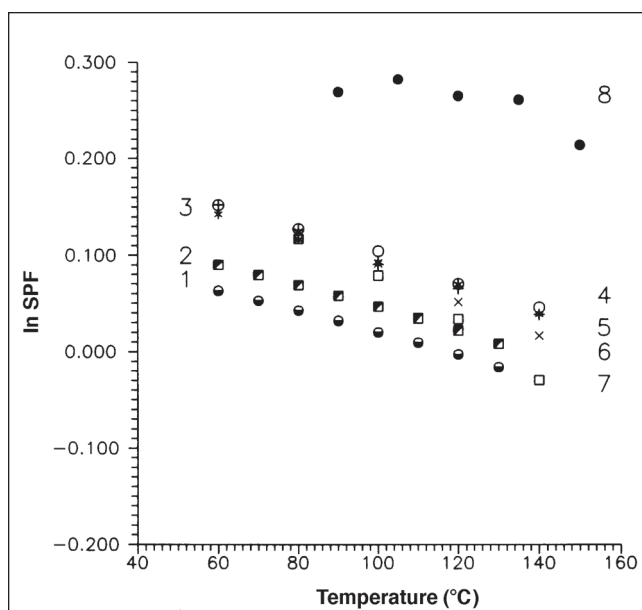


Figure 1. Plot of  $\ln \text{SPF}_1$  versus temperature ( $^{\circ}\text{C}$ ) of benzene for 8 stationary phases at the 60–150 $^{\circ}\text{C}$  temperature range. 1, Squalane; 2, OV-101; 3, TFPS00; 4, TFPS09; 5, TFPS15; 6, TFPS26; 7, TFPS35; and 8, XF-1150.

Table V. The  $\ln \text{SPF}$  Temperature Dependence (60–150 $^{\circ}\text{C}$  range) of the First 5 McReynolds Probes for 8 Stationary Phases

Temperature ( $^{\circ}\text{C}$ )	Solute*				
	1	2	3	4	5
<b>TFPS00</b>					
60	0.14265	0.23882	0.25204	0.29698	0.34517
80	0.11641	0.26680	0.22170	0.32282	0.31715
100	0.09326	0.30447	0.18952	0.35871	0.29624
120	0.06947	0.34394	0.12392	0.39967	0.27532
140	0.04257	0.39223	0.10298	0.43889	0.25587
<b>TFPS09</b>					
60	0.15197	0.26259	0.33275	0.39659	0.39975
80	0.12750	0.30025	0.30481	0.42358	0.37332
100	0.10439	0.33531	0.27277	0.45916	0.35015
120	0.07032	0.37057	0.22971	0.50105	0.32293
140	0.04980	0.43602	0.19289	0.54946	0.30170
<b>TFPS15</b>					
60	0.15219	0.27235	0.36798	0.44170	0.41940
80	0.12622	0.30230	0.34171	0.47426	0.39436
100	0.09079	0.33149	0.30467	0.54616	0.36913
120	0.06530	0.37467	0.26698	0.55734	0.34447
140	0.04199	0.42282	0.22419	0.60156	0.32297
<b>TFPS26</b>					
80	0.12383	0.33956	0.41038	0.55093	0.48383
100	0.09144	0.3699	0.37707	0.59266	0.44705
120	0.05136	0.39786	0.33410	0.63728	0.41112
140	0.02063	0.44263	0.29345	0.69064	0.39150

1-nitropropane (the solute with biggest  $\ln \text{SPF}$  values) were obtained. The same was observed in all stationary phases. Table VI shows the goodness of the  $\ln \text{SPF}$  versus temperature dependence for all stationary phases. Correlations were very good, except for benzene and pentan-2-one on XF-1150 and pyridine on OV-101. An increase in absolute value can be seen on the straight lines slopes as the polarity of the trifluoropropyl siloxanes increases for the solutes benzene, pyridine, and 1-nitropropane, but it is not as clear for *n*-butanol and pentan-2-one. Finally, the APF relationships with temperature were not linear for the trifluoropropyl siloxane polymers (Table IV), but all right straight lines were obtained for XF-1150 ( $r^2 = 0.994$ ), Squalane ( $r^2 = 0.9999$ ), and somewhat worse for TFPS35 ( $r^2 = 0.966$ ) and OV-101 ( $r^2 = 0.9029$ ). So, the dependence of  $\ln \text{APF}$  on temperature showed acceptable correlations for XF-1150, Squalane, TFPS35, and OV-101 (Figure 4). Very little change in  $\ln \text{APF}$  was observed for the other trifluoropropyl siloxanes; quasi-parallel straight lines were obtained. The slopes of the least mean squares regression straight lines obtained were positive for OV-101 and XF-1150, negative for TFPS35 and Squalane, and almost negligible for the other stationary phases, which shows that the  $\ln \text{APF}$ -versus-temperature dependence of these polymers was very scarce. Other types of mathematical expressions might be investigated for improving the correlation on the fluorinated stationary phases.

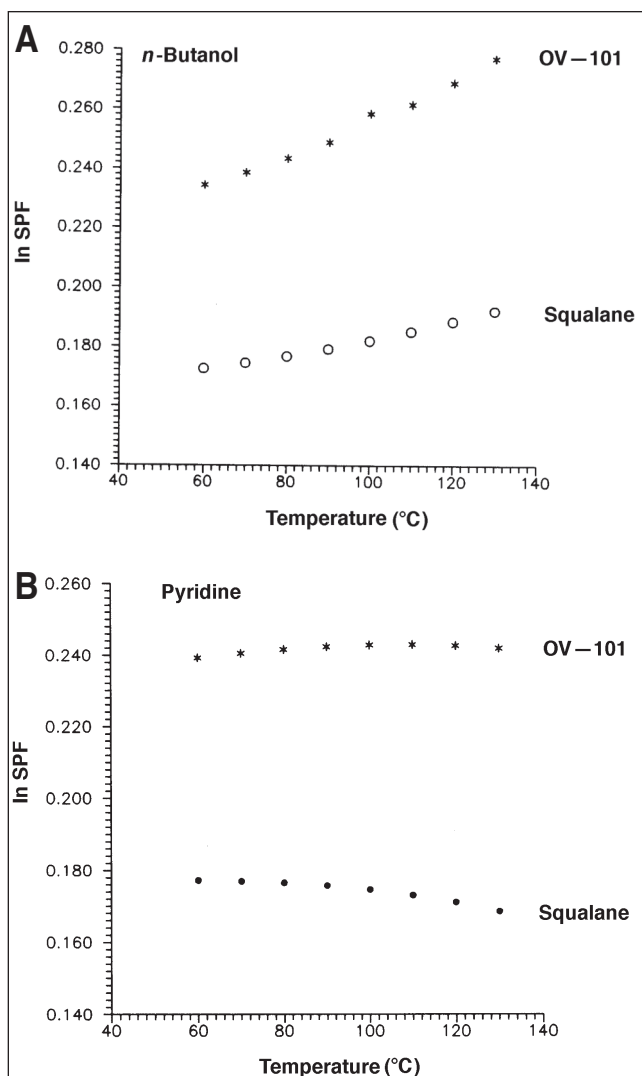
Table V. (cont.)

<b>TFPS35</b>					
80	0.11699	0.33142	0.44027	0.60262	0.47780
100	0.07894	0.35830	0.40739	0.64271	0.44557
120	0.03356	0.38424	0.36443	0.68555	0.41257
140	-0.02554	0.40126	0.30322	0.72472	0.37818
<b>XF-1150</b>					
90	0.26917	0.71456	0.57169	0.86377	0.70405
105	0.28215	0.77900	0.56307	0.94332	0.73282
120	0.26510	0.82294	0.58087	0.98900	0.72244
135	0.26099	0.88566	0.53856	1.07058	0.74571
150	0.21409	0.94191	0.53674	1.14654	0.76217
<b>Squalane</b>					
60	0.06288	0.17256	0.12429	0.16301	0.17721
70	0.05270	0.17446	0.11164	0.17520	0.17699
80	0.04246	0.17669	0.09775	0.18832	0.17652
90	0.03195	0.17918	0.08261	0.20244	0.17575
100	0.02010	0.18196	0.06617	0.21764	0.17462
110	0.00949	0.18503	0.04838	0.23404	0.17309
120	-0.00283	0.18839	0.02915	0.25175	0.17107
130	-0.01604	0.19206	0.00839	0.27098	0.16850
<b>OV-101</b>					
60	0.09013	0.23438	0.17048	0.22152	0.23928
70	0.07947	0.23862	0.15685	0.23839	0.24053
80	0.06881	0.24342	0.14172	0.25642	0.24159
90	0.05787	0.24881	0.12507	0.27570	0.24233
100	0.04652	0.25482	0.10688	0.29633	0.24280
110	0.03459	0.26149	0.08707	0.31845	0.24290
120	0.02193	0.26890	0.06559	0.33798	0.24259
130	0.00834	0.27713	0.04230	0.36789	0.24182

\* Solutes: 1, benzene; 2, *n*-butanol; 3, pentan-2-one; 4, 1-nitropropane; and 5, pyridine.

## Conclusion

The existence of a temperature dependence of various polarity scales (Kováts coefficient, RP, APF, MP, and P) used at 120°C to characterize 26 stationary phases (1) has become apparent. A mostly linear dependence between  $\ln \text{SPF}_k$  on temperature of the first 5 McReynolds probes for the 8 stationary phases studied in this work has been shown. This is important, because the polarity scales mentioned previously and the substance-specific factors  $\text{SPF}_k$  or  $\ln \text{SPF}_k$  (which are associated with the solute-stationary phase retention interactions) had been studied only at 120°C, the temperature chosen by McReynolds (5), because he used Squalane (which could not be heated over this temperature) as a reference stationary phase. The main contribution of this paper and its novelty is the study of all of the aforementioned scales and interaction forces at several temperatures; this may permit the establishment of the necessary relationships to study every temperature of the interval, which has never been

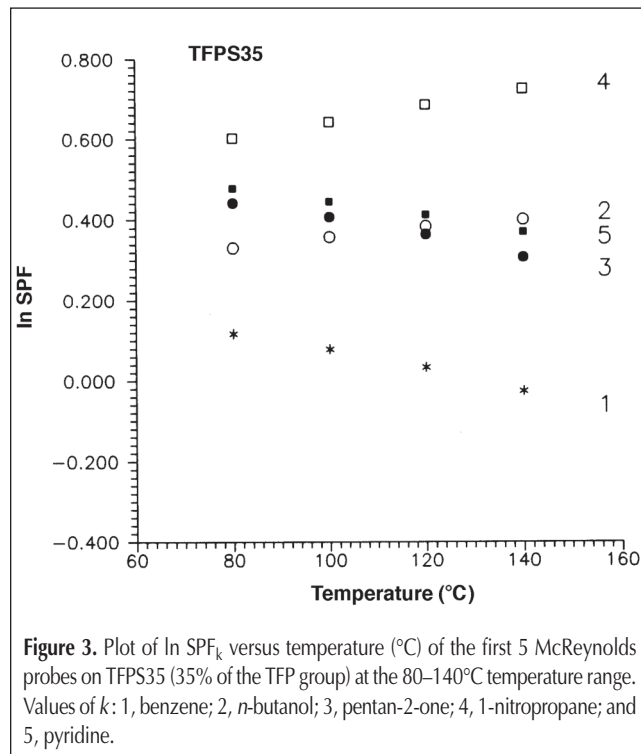


**Figure 2.** Plot (A) of  $\ln \text{SPF}_2$  versus temperature (°C) of *n*-butanol on Squalane and OV-101 at the 60–130°C temperature range. Plot (B) of  $\ln \text{SPF}_5$  versus temperature (°C) of pyridine on Squalane and OV-101 at the 60–130°C temperature range.

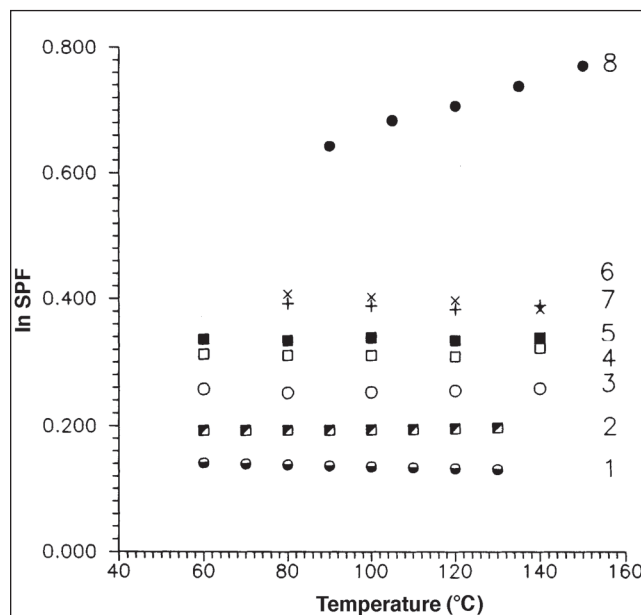
done before. Therefore, it will undoubtedly be important, promising, and useful in predicting retention data at every temperature.

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**Figure 3.** Plot of  $\ln \text{SPF}_k$  versus temperature (°C) of the first 5 McReynolds probes on TFPS35 (35% of the TFP group) at the 80–140°C temperature range. Values of  $k$ : 1, benzene; 2, *n*-butanol; 3, pentan-2-one; 4, 1-nitropropane; and 5, pyridine.



**Figure 4.** Plot of  $\ln \text{APF}$  versus temperature (°C) of the first 5 McReynolds solutes on 8 stationary phases. 1, Squalane; 2, OV-101; 3, TFPS00; 4, TFPS09; 5, TFPS15; 6, TFPS26; 7, TFPS35; and 8, XF-1150.

**Table VI. The In SPF-versus-T Least Mean Squares Regression Straight Lines of the First 5 McReynolds Solutes on 8 Stationary Phases**

Solute	Slope	Intercept	$r^2$	Covariance
<b>TFPS00</b>				
Benzene	-1.2355E-03	0.21642	0.9993	-1.2355
<i>n</i> -Butanol	1.9197E-03	0.11728	0.9911	1.9197
Pentan-2-one	-1.9795E-03	0.37598	0.9749	-1.9795
1-Nitropropane	1.8038E-03	0.18304	0.9934	1.8038
Pyridine	-1.0210E-03	0.40816	0.9948	-1.1021
<b>TFPS09</b>				
Benzene	-1.3076E-03	0.21356	0.9949	-1.3076
<i>n</i> -Butanol	2.0586E-03	0.13237	0.9808	2.0858
Pentan-2-one	-1.7741E-03	0.44400	0.9938	-1.7741
1-Nitropropane	1.9160E-03	0.27436	0.9884	1.9160
Pyridine	-1.2320E-03	0.47282	0.9987	-1.2324
<b>TFPS15</b>				
Benzene	-1.4066E-03	0.23596	0.9949	-1.4066
<i>n</i> -butanol	1.8670E-03	0.15470	0.9863	1.8665
Pentan-2-one	-1.8115E-03	0.48262	0.9922	-1.8115
1-Nitropropane	2.0138E-03	0.32281	0.9620	2.0140
Pyridine	-1.2137E-03	0.49144	0.9991	-1.2137
<b>TFPS26</b>				
Benzene	-1.7484E-03	0.26414	0.9975	-1.1656
<i>n</i> -Butanol	1.6860E-03	0.20204	0.9876	1.1239
Pentan-2-one	-1.9688E-03	0.57032	0.9973	-1.3125
1-Nitropropane	2.3187E-03	0.36282	0.9962	-1.1271
Pyridine	-1.6329E-03	0.61413	0.9773	-1.0886
<b>TFPS35</b>				
Benzene	-2.3648E-03	0.31112	0.9900	-1.5766
<i>n</i> -Butanol	1.1773E-03	0.23930	0.9902	0.7849
Pentan-2-one	-2.2705E-03	0.62859	0.9806	-1.5137
1-Nitropropane	2.0457E-03	0.43887	0.9997	1.3638
Pyridine	-1.6593E-03	0.61105	0.9998	-1.1062
<b>XF-1150</b>				
Benzene	-0.0875E-03	0.36336	0.6399	-0.4924
<i>n</i> -Butanol	3.7424E-03	0.37973	0.9975	2.1051
Pentan-2-one	-0.6294E-03	0.63371	0.5692	-0.3570
1-Nitropropane	4.6187E-03	0.44840	0.9935	2.5980
Pyridine	0.8609E-03	0.63013	0.8503	0.4842
<b>Squalane</b>				
Benzene	-1.1200E-03	0.13149	0.9982	-0.6720
<i>n</i> -Butanol	0.2787E-03	0.15484	0.9893	0.1671
Pentan-2-one	-1.6530E-03	0.22806	0.9934	-0.9916
1-Nitropropane	1.5368E-03	0.06693	0.9943	0.9228
Pyridine*	-0.1214E-03	0.18575	0.9062	-0.0728
<b>OV-101</b>				
Benzene	-1.1598E-03	0.16114	0.9981	-0.6959
<i>n</i> -Butanol	0.6125E-03	0.19571	0.9884	0.3649
Pentan-2-one	-1.8280E-03	0.28567	0.9924	-1.0969
1-Nitropropane	2.0590E-03	0.09347	0.9946	0.2352
Pyridine*	0.0387E-03	0.23806	0.5665	0.0271

\* Parabolic fittings:  $a = -1.94345E-06$ ,  $b = 0.0002478$ ,  $c = 0.16923$ , and  $r^2 = 1.00$  for Squalane and  $a = -1.68452E-06$ ,  $b = 0.00035873$ ,  $c = 0.223768$ , and  $r^2 = 1.00$  for OV-101.

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