

System constants of synthesized poly(methyl-3,3,3-trifluoropropyl) siloxanes

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Abstract

The method of solvation model has been applied to five poly (methyl-trifluoropropyl) siloxanes (TFPSXX) prepared in our laboratories, at five trifluoropropyl (TFP) group contents, XX = 0, 11.5, 26.3, 35.5 and 50.0%, at 80, 100, 120 and 140 °C. Previously, specific retention volumes of 60-odd solutes of varied polarities were measured upon each of these stationary phases within the above temperature range. Constant *s* prevails over all other constants, TFPSXX stationary phases showing strong dipole/induced dipole forces with the solutes, moderate acidity and no basicity at all. Constant *e* is zero in the stationary phase without TFP groups, but has negative low-medium values for the other fluorine contents, XX from 11.5 to 50.0%, hinting at repulsive forces, as expected. Normal values for constant *l*, decreasing from the less cohesive TFPS00 to the more cohesive TFPS50, were found. For each TFP content constants *s*, *a* and *l* show a negative temperature dependence, while constant *e* increases as temperature increases. Constant *c* also decreases with increasing temperature. At each temperature, constants *s* and *a* increase with increasing %TFP (or increasing stationary phase polarity), whereas constants *e* and *l* show the opposite trend, diminishing with increasing polarity of the stationary phase. Principal component analysis shows that the five stationary phases presented in this work conform a group with other earlier synthesized trifluoropropyl siloxanes and other fluorinated stationary phases taken from literature: VB-210, QF-1, DB-200, DB-210 and PFS6, showing the same selectivity which only the fluorine atom confers. A dendrogram of 38 stationary phases supports these results.

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1. Introduction

The solvation parameter model based on the studies of Kamlet and coworkers [1,2] was promoted in 1980s by Abraham et al. [3,4], Carr and coworkers [5,6], and Poole and coworkers [7,8]. It describes with effectiveness and solvency the interactions between solutes and stationary phases, assuming that only retention plays a role in the chromatographic phenomenon at a given temperature, in which adsorption has been minimized as much as possible. Earlier, most columns used were packed or glassy columns [9], but, at present, fused-silica capillary columns are preferred owing to their many advantages [10]. Recently, already

in this century, an appreciable number of studies by Poole and coworkers [11–22] have fructified in the building of a very consistent database of system constants.

Trifluoropropyl siloxanes (TFPSXX) are very interesting stationary phases of moderate polarity [23], especially suitable for the chromatography of alcohols and ketones. The stationary phase with 50% trifluoropropyl group has been the preferred among trifluoropropyl siloxanes by scientists [24] and column manufacturers, but other TFPSXX of low polarity or with XX < 50% were never considered. Dai [25] synthesized trifluoropropyl siloxanes with 0–26% trifluoropropyl group (TFP) in 1995. The constants of these polymers were determined and published in 1998 [26]. In this paper we describe the application of the solvation parameter model to the synthesized trifluoropropyl siloxanes with 0, 11.5, 26.3, 35.5 and 50.0%, and some remarkable improvements in the determination of the experi-

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mental retention magnitude (a new equation for evaluating the specific retention volumes and a new, more accurate hold-up time determination).

The aim of this paper is the characterization of the above trifluoropropyl siloxanes of compositions $0 < \% \text{TFFP} < 50$ over the 80–140 °C temperature range by applying the solvation model. The variations of the properties of these polymers with column temperature and %TFFP content are investigated. To do this, multivariate procedures as multiple linear regression analysis (MLRA), principal component analysis (PCA) and cluster analysis (CA) are used. The more recent way to present the solvation model is as follows [27]:

$$\log \text{SP} = c + lL + eE + sS + aA + bB \quad (1)$$

where L , E , S , A and B are the descriptors of the solutes with the stationary phase, and the same low case letter symbols, l , e , s , a and b , stand for the mutual specific constants that describe the interactions of the stationary phase with the solutes. c is the regression constant, arising from the application MLRA to the measured retention data (SP, the retention magnitude, can be specific retention volume, V_g ; retention time, t_R ; retention factor, k ; distribution coefficient, K_L , etc.). The c -value depends on the retention magnitude chosen. Related with the stationary phase ratio β , it is considered unimportant but necessary for retention magnitude prediction.

l represents the cavity formation and dispersion contributions taking part between the stationary phase and the solutes; e the ability of the stationary phase to interact with n or π electron pairs; s the capacity of the stationary phase to interact with solute dipoles; a , the ability of the stationary phase to behave as a base in the donor–acceptor interaction through hydrogen bonds with acid solutes; b , the tendency of the stationary phase to interact as an acid with basic solutes through acceptor/donor hydrogen bonds.

In addition, the solute descriptors compiled mostly by Abraham [28], which are complementary to the stationary phase constants, have the following meanings: L , earlier denoted as $\log L^{16}$, is the distribution coefficient of n -hexadecane at 298 K; E , earlier denoted as R_2 , is the excess molar refraction of the solute; S , earlier denoted as π_2^H , is the effective dipolarity/dipolarizability of the solutes; A , earlier denoted as $\sum \alpha_2^H$, is

the effective hydrogen bond acidity of the solute, and B , earlier referred to as $\sum \beta_2^H$, the effective hydrogen bond basicity of the solute.

The different product terms lL , eE , sS , aA and bB quantify the different stationary phase–solute interactions operating in the retention, if adsorption is disregarded. The four last binomials are polar interactions, while the first one represents non-polar interactions, dispersive forces and the cavity formation. So, the sum ($c + lL$) adequately describes the interactions of non-polar solutes as n -alkanes on non-polar stationary phases.

2. Experimental

2.1. Instrumentation

Gas chromatographs HP5890 A (Hewlett-Packard) equipped with a flame ionization detector (FID), injection system split/splitless and “back pressure” regulator, and Varian 3300 with split/splitless injection system, FID and conventional pressure regulator were used.

Electronic integrators SP-4270 (Spectraphysics) were used for data acquisition.

Microsyringes of 1 μl from Hamilton (serie 7001) were used for sampling.

Nitrogen used as carrier gas (99.999% pure) was produced by a NITROX (Domnick Hunter) gas generator. Hydrogen of 99.995% purity (Air Liquid) and air produced by a conventional compressor were used for the FID.

2.2. Probes

Hydrocarbons: methane (from natural gas), n -alkanes (from C5 to C17), aromatics (benzene, toluene, ethylbenzene, n -propylbenzene and n -butylbenzene), cyclohexane and *cis*-hydrindane; ketones (2-ketones from propanone to 2-undecanone) and cyclohexanone; alcohols (n -alkanols from n -propanol to n -decanol and cyclohexanol); esters (methyl, ethyl, n -propyl and n -butyl acetates); amines (n -propylamine, n -butylamine, n -pentylamine, n -hexylamine, n -heptylamine, and aniline); nitriles (n -butanenitrile, n -

Table 1
Characteristics of the chromatographic columns used in this work

Parameter	TFPS00	TFPS12	TFPS26	TFPS35	TFPS50
L (m)	30.1	24.7	25.3	25.3	25.7
d_c (mm)	0.225	0.211	0.214	0.214	0.216
d_f (μm)	0.300	0.300	0.300	0.300	0.300
c_s (g cm^{-3})	0.00520	0.00607	0.00661	0.00692	0.00732
%TFFP group	0	11.5	26.3	35.5	50.0
R_p^a , retention polarity	6.39	15.22	26.77	35.1	49.13
$\Delta G_s^\circ(\text{CH}_2)^b$ (kJ mol^{-1})	−1.884	−1.830	−1.737	−1.667	−1.552

^a $R_p = 20 \sum_{i=1}^5 (I(\text{TFPSXX})/I(\text{squalane}) - 100)$ [32]. I are the retention Kovats indices [33] of the first five McReynold's probes (benzene, n -butanol, 2-pentanone, 1-nitropropane and pyridine) on the trifluoropropyl siloxanes and squalane.

^b $\Delta G_s^\circ(\text{CH}_2) = -2.303RT \times \text{slope}$. $R = 8.313 \text{ J mol}^{-1} \text{ K}^{-1}$; T , column temperature = 393 K; slope is the slope of the $\log(V_{g,z})$ of then-alkanes vs. their carbon number Z plot [42].

pentanenitrile, *n*-hexanenitrile and benzonitrile); nitrocompounds (1-nitropropane and nitrobenzene), halogenated compounds (*n*-butyl iodide, *n*-propyl chloride, *n*-butyl chloride, *n*-pentyl chloride, *n*-hexyl chloride and chlorobenzene), heterocyclic compounds (1,4-dioxane, tetrahydrofuran and pyridine), *N,N*-dimethylformamide and 2-octyne. The solutes were purchased from Fluka, Merck, Riedel de Haën, Carlo Erba, Probus, Scharlau, Sigma and Aldrich. Purity, from 98 to 99.5%, sufficed for gas chromatographic use.

2.3. Chromatographic columns

Several glass WCOT columns (Table 1) were prepared with the five TFPSXX synthesized (TFP group percentages were 0, 11.5, 26.3, 35.5 and 50.0) [29–31]. To check the absence of adsorption, three capillary columns of different film thicknesses ($d_f = 0.1, 0.2$ and $0.3 \mu\text{m}$) per polymer were prepared, and the specific retention volumes of the solutes used (see Table 2) were calculated. The V_g 's of the three film thicknesses were identical. Columns of $d_f = 0.3 \mu\text{m}$ were selected in the present work for determining the V_g of the solutes in Table 2. Geometric characteristics, TFP percentage and polarity, expressed as retention polarity [32,33], are also given in Table 1.

Specific retention volumes were determined with the expression:

$$V_g = \frac{k}{c_s} \left(1 - \frac{c_s}{2\rho_s} \right)^2 \frac{273.15}{T_c} \quad (2)$$

where k is the retention factor $[(t_R - t_M)/t_M]$; t_M , the hold-up time; c_s , the concentration of the stationary phase solution used to prepare the capillary column; T_c the column temperature, and ρ_s , the stationary phase density [34,35]. The concentration, c_s , of the solution used depends on the film thickness desired, on the column diameter and on the stationary phase density, according to the expression:

$$d_f = \frac{d_c c_s}{4\rho_s} \quad (3)$$

The hold-up time was determined with the expression:

$$t_R = \exp(A + Bz + Cz^D) \quad (4)$$

where A, B, C and D are constants, and z is the carbon atom number of the *n*-alkanes [36,37].

Other chromatographic columns used for this work are (i) the earlier synthesized TFPSXX coated on glassy capillary columns of compositions from 0 to 26% TFP: TFPS001, TFPS09, TFPS15, TFPS26(1) [25], and (ii) the capillary columns: DB-200 and DB-VRX [11]; DB-1701, DB-210 and SP-2340 [12]; DB-1 and DB-5 [14]; HP-5(1) [16]; Rtx-20, DB-35, Rtx-65 and DB-23 [19]; DB-1301 and DB-225 [20]; DB-608 and DB-624 [21]; HP-88 and Rtx-440 [22], BP-10, BPX70, VB-210 [38], QF-1(2), OV-105 and PSF6 [9].

2.4. Mathematical treatment

Microcal Origin 6.0 was used for MLRA fits and for the construction of the plots. The Unscrambler 6.11 program was used for principal components analysis and the Statgraphics Plus 5.1 for the dendrogram. The Microsoft Excel utility was also used.

3. Results and discussion

Table 2 lists the descriptors L, E, S, A and B , and the specific retention volumes, V_g , of the 60-odd solutes chromatographed on the synthesized TFPS26 at 80–140 °C in this work. Descriptor limits are $2.03 < L < 8.2$ from *n*-propanol to *n*-heptadecane; $0 < E < 0.955$ *n*-alkanes to aniline; $0 < S < 1.31$ from *n*-alkanes to *N,N*-dimethyl formamide; $0 < A < 0.37$ from *n*-alkanes to *n*-alkanols, and $0 < B < 0.74$ from *n*-alkanes to *N,N*-dimethyl formamide. Histograms give shapes of distribution close to the normal one, which do not differ much from the ones found in the literature [39]. For the sake of brevity, Table 2 lists only a part of the specific retention volumes, V_g ($\text{cm}^3 \text{g}^{-1}$) of the probes measured in this work. It is seen that *n*-alkanes and aromatics have small V_g , while polar compounds as alcohols, 2-ketones, amines, nitriles, etc. have much more higher V_g values. In principle, the former solutes may be little retained because of their scant interaction with TFPS26, whereas the latter, whose retention times on the column are much longer, may show a strong interaction with TFPS26. The solvation model establishes easily the retention of these solutes on the TFPSXX polymers by calculating the different non-polar and polar contributions depending on the system constant values that will be presented below.

Considering the measurements carried out at the four temperatures and five TFP percentages, a large matrix of 60×20 retention data is obtained. MLR analysis was applied to obtain the system constants of each of the five polymers in all cases.

Table 3 lists the values of the characteristic constants e, s, a, l, c and the errors expressed as standard deviations of the 20 [column temperature–%TFP polymer composition] possible combinations. The low constant errors obtained support the trustworthiness of Eq. (2) for calculating V_g values.

Statistical multiple correlation coefficients (R), Fischer's factors (F), standard errors of fitting (s_y) [see Eq. (1)] and number of solutes used in the regression (n) are also given.

According to Table 3, if the values of constants for TFPS12 at 140 °C and for TFPS50 at 80 °C are compared, it is found that e -values range between -0.082 and -0.457 , s -values between 0.427 and 1.385 , a -values between 0.141 and 0.400 , and l -values between 0.442 and 0.510 . Then, the more significant change is that of s -constant (difference = 0.958), followed by the variations of e -constant (difference = 0.375) and a -constant (difference = 0.259), the l -constant variation being the less important (difference = 0.068).

Constant b is zero, indicating that these stationary phases are not acidic at all. Although c constant is not properly a constant but a regression factor, it is pertinent to establish its decrease both

Table 2
Solute descriptors and specific retention volume, V_g ($\text{cm}^3 \text{g}^{-1}$) on TFPS26

#	Solute	Solute descriptors					V_g			
		<i>L</i>	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	80 °C	100 °C	120 °C	140 °C
1	Benzene	2.786	0.61	0.52	0	0.14	38.45	22.24	13.97	9.19
2	Toluene	3.325	0.601	0.52	0	0.14	78.53	42.37	24.82	15.44
3	Ethylbenzene	3.778	0.613	0.51	0	0.15	142.48	72.39	40.17	23.88
4	<i>n</i> -Propylbenzene	4.23	0.604	0.5	0	0.15	257.78	123.23	64.75	36.78
5	<i>n</i> -Butylbenzene	4.73	0.6	0.51	0	0.15	497.28	221.80	109.60	58.96
6	Propanone	1.696	0.179	0.7	0.04	0.49	23.57	14.21	9.12	6.12
7	2-Butanone	2.287	0.166	0.7	0	0.51	45.13	25.48	15.46	9.90
8	2-Pentanone	2.755	0.143	0.68	0	0.51	83.51	44.33	25.46	15.62
9	2-Hexanone	3.262	0.136	0.68	0	0.51	168.15	82.92	44.74	25.97
10	2-Heptanone	3.76	0.123	0.68	0	0.51	329.28	151.35	76.71	42.22
11	2-Octanone	4.257	0.108	0.68	0	0.51	642.01	274.83	130.94	68.35
12	2-Nonanone	4.735	0.119	0.68	0	0.51		497.18	222.61	110.06
13	2-Decanone	5.245	0.108	0.68	0	0.51			375.98	176.12
14	2-Undecanone	5.732	0.101	0.68	0	0.51				280.95
15	Cyclohexanone	3.792	0.403	0.86	0	0.56	387.99	183.61	95.55	53.65
16	<i>n</i> -Propanol	2.031	0.236	0.42	0.37	0.48	19.83	11.93	7.68	5.25
17	<i>n</i> -Butanol	2.601	0.224	0.42	0.37	0.48	41.33	23.15	14.03	9.06
18	<i>n</i> -Pentanol	3.106	0.219	0.42	0.37	0.48	84.17	43.99	25.02	15.30
19	<i>n</i> -Hexanol	3.61	0.21	0.42	0.37	0.48	167.60	81.60	43.62	25.25
20	<i>n</i> -Heptanol	4.115	0.211	0.42	0.37	0.48	330.25	149.76	75.24	41.19
21	<i>n</i> -Octanol	5.124	0.193	0.42	0.37	0.48	645.46	272.58	128.63	66.76
22	<i>n</i> -Nonanol	5.628	0.191	0.42	0.37	0.48		492.91	218.64	107.52
23	<i>n</i> -Decanol	3.758	0.46	0.54	0.32	0.57			369.84	172.18
24	Cyclohexanol	3.081	0.169	0.3	0.31	0.6	202.36	99.92	54.07	31.52
25	Methyl acetate	1.911	0.142	0.64	0	0.45	71.55	38.03	22.03	13.61
26	Ethyl acetate	2.314	0.106	0.62	0	0.45	38.87	21.67	13.08	8.36
27	<i>n</i> -Propyl acetate	2.819	0.092	0.6	0	0.45	77.46	40.34	22.92	13.92
28	<i>n</i> -Butyl acetate	3.353	0.071	0.6	0	0.45	152.52	74.16	39.61	22.85
29	<i>n</i> -Propylamine	2.141	0.225	0.35	0.16	0.61	18.13	11.03	6.88	4.62
30	<i>n</i> -Butylamine	2.618	0.224	0.35	0.16	0.61	37.13	20.74	12.26	7.88
31	<i>n</i> -Pentylamine	3.139	0.211	0.35	0.16	0.61	74.93	38.42	21.67	13.15
32	<i>n</i> -Hexylamine	3.655	0.197	0.35	0.16	0.61	147.79	70.40	37.49	21.67
33	<i>n</i> -Heptylamine	4.703	0.193	0.35	0.16	0.61	289.97	128.43	64.22	35.34
34	Aniline	3.934	0.955	0.96	0.26	0.41	423.94	194.52	98.36	54.06
35	<i>n</i> -Butanenitrile	2.548	0.188	0.9	0	0.36	95.74	51.04	29.54	18.23
36	<i>n</i> -Pentanenitrile	3.108	0.177	0.9	0	0.36	195.06	96.90	52.68	30.81
37	<i>n</i> -Hexanenitrile	3.608	0.166	0.9	0	0.36	389.38	180.01	91.85	50.84
38	Benzonitrile	4.039	0.742	1.11	0	0.33	711.76	319.03	158.17	85.27
39	1-Nitropropane	2.894	0.242	0.95	0	0.31	145.27	74.52	41.69	24.95
40	Nitrobenzene	4.557	0.871	1.11	0	0.28	38.42	564.74	267.23	138.11
41	Butyl iodide	3.628	0.628	0.4	0	0.15	108.71	57.71	33.29	20.41
42	<i>n</i> -Propyl chloride	1.202	0.216	0.4	0	0.1	18.66	11.54	7.66	5.21
43	<i>n</i> -Butyl chloride	2.722	0.21	0.4	0	0.1	37.94	21.95	13.64	8.89
44	<i>n</i> -Pentyl chloride	3.223	0.208	0.4	0	0.1	76.35	41.15	24.03	14.88
45	<i>n</i> -Hexyl chloride	3.777	0.201	0.4	0	0.1	150.85	75.58	41.57	24.46
46	Chloro benzene	3.657	0.718	0.65	0	0.07	143.38	74.30	41.90	25.20
47	1,4-Dioxane	2.892	0.329	0.75	0	0.64	71.53	38.45	22.50	14.03
48	Tetrahydrofuran	3.022	0.631	0.84	0	0.52	38.42	22.05	13.66	8.99
49	Pyridine	2.636	0.289	0.52	0	0.48	103.03	53.99	30.76	18.86
50	<i>N,N</i> -Dimethylformamide	3.173	0.367	1.31	0	0.74	299.79	141.09	73.57	41.52
51	2-Octyne	3.85	0.225	0.3	0	0.1	116.45	57.71	31.40	18.37
52	<i>n</i> -Pentane	2.162	0	0	0	0	8.85	5.77	3.99	
53	<i>n</i> -Hexane	2.668	0	0	0	0	17.74	10.83	7.06	4.85
54	<i>n</i> -Heptane	3.173	0	0	0	0	35.02	19.98	12.27	7.97
55	<i>n</i> -Octane	3.677	0	0	0	0	68.60	36.50	21.07	13.02
56	<i>n</i> -Nonane	4.182	0	0	0	0	133.59	66.27	35.96	21.02
57	<i>n</i> -Decane	4.686	0	0	0	0	258.79	119.60	61.01	33.81
58	<i>n</i> -Undecane	5.191	0	0	0	0	499.43	215.04	103.09	54.11
59	<i>n</i> -Dodecane	5.696	0	0	0	0	960.94	385.31	173.59	86.30
60	<i>n</i> -Tridecane	6.2	0	0	0	0		688.06	291.43	137.26
61	<i>n</i> -Tetradecane	6.7	0	0	0	0			487.94	217.76
62	<i>n</i> -Pentadecane	7.2	0	0	0	0				344.67
63	Cyclohexane	2.964	0.305	0.1	0	0	30.06	18.04	11.51	7.79
64	<i>cis</i> -Hydrindane	4.635	0.439	0.25	0	0	264.34	130.23	70.11	40.52

Table 3
Characteristic constants of trifluoropropyl siloxanes

Polymer	T (°C)	e	$\pm s_{n-1}$	s	$\pm s_{n-1}$	a	$\pm s_{n-1}$	l	$\pm s_{n-1}$	c	$\pm s_{n-1}$	n	R	s_y	F
TFPS-00 (%TFP = 0)	80	0.000	0.000	0.198	0.014	0.265	0.034	0.619	0.005	-0.131	0.021	54	0.9981	0.032	4274
	100	0.000	0.000	0.189	0.011	0.221	0.026	0.558	0.004	-0.199	0.015	57	0.9988	0.026	7188
	120	0.000	0.000	0.180	0.010	0.179	0.023	0.504	0.003	-0.252	0.014	57	0.9988	0.022	7618
	140	0.000	0.000	0.176	0.009	0.149	0.021	0.456	0.003	-0.303	0.012	60	0.9989	0.022	8841
TFPS-12 (%TFP = 11.5)	80	-0.214	0.023	0.563	0.017	0.258	0.035	0.604	0.006	-0.189	0.022	53	0.9979	0.032	2889
	100	-0.162	0.020	0.513	0.015	0.205	0.029	0.544	0.004	-0.261	0.017	57	0.9984	0.029	4022
	120	-0.120	0.017	0.467	0.013	0.169	0.025	0.490	0.003	-0.316	0.015	60	0.9987	0.026	5250
	140	-0.082	0.016	0.427	0.012	0.141	0.024	0.442	0.003	-0.363	0.013	62	0.9987	0.025	5644
TFPS-26 (%TFP = 26.3)	80	-0.346	0.029	0.912	0.022	0.304	0.044	0.571	0.007	-0.257	0.027	54	0.9968	0.041	1879
	100	-0.284	0.026	0.839	0.020	0.247	0.039	0.516	0.006	-0.336	0.023	58	0.9972	0.038	2373
	120	-0.233	0.023	0.769	0.018	0.199	0.035	0.464	0.004	-0.389	0.020	61	0.9976	0.036	2861
	140	-0.188	0.023	0.706	0.018	0.169	0.034	0.419	0.004	-0.436	0.020	62	0.9974	0.035	2726
TFPS-35 (%TFP = 35.4)	80	-0.412	0.036	1.110	0.027	0.360	0.053	0.548	0.008	-0.318	0.033	53	0.9951	0.049	1228
	100	-0.337	0.030	1.027	0.023	0.291	0.043	0.494	0.006	-0.398	0.025	60	0.9967	0.044	2062
	120	-0.285	0.028	0.943	0.022	0.242	0.041	0.443	0.005	-0.449	0.024	61	0.9965	0.043	1989
	140	-0.238	0.027	0.870	0.021	0.208	0.040	0.400	0.004	-0.500	0.023	63	0.9965	0.041	2074
TFPS-50 (%TFP = 50.0)	80	-0.457	0.042	1.385	0.032	0.400	0.063	0.510	0.009	-0.428	0.038	54	0.9936	0.058	955
	100	-0.384	0.037	1.282	0.029	0.328	0.053	0.457	0.007	-0.495	0.032	60	0.9947	0.055	1298
	120	-0.334	0.034	1.186	0.027	0.284	0.051	0.410	0.006	-0.549	0.029	62	0.9948	0.053	1353
	140	-0.289	0.034	1.100	0.027	0.246	0.050	0.369	0.005	-0.595	0.029	63	0.9943	0.052	1268

$\pm s_{n-1}$: standard error of the measurement; s_y : standard error of the fit.

with increasing temperature (at each polymer %TFP) and with increasing polymer polarity (at each temperature). The decrease must be understood as the increase of a negative amount.

3.1. The influence of temperature upon the polymer system constants

Regressions of the constants versus column temperature in Table 3 are given in Table 4. Good straight lines with low error $s_y < 0.0046$ were obtained for the l -constant versus T (°C) fit for each one of the five TFPSXX polymers. Slopes decrease with increasing polymer polarity. Also, a linear fit is sufficient to describe the s -constant temperature dependence, with good decreasing straight lines ($0.0019 < s_y < 0.0060$) and slopes that increase strongly with increasing TFP percentage. The opposite trend was found for the e -constant temperature dependence, with standard errors $s_y < 0.0103$, and slopes that equally decrease with increasing polymer polarity. Much better correlations were obtained for square regressions at XX = 26.3, 35.5 and 50.0% contents. Slightly worse linear correlations are obtained for the a -constant temperature dependence, yielding straight lines with standard error $0.0052 < s_y < 0.0125$ and whose slopes increase significantly with increasing polymer polarity. Better correlations are again obtained for square fit for 26.3 and 35.5% TFP.

The variation of the c constant with column temperature is well described by good descending straight lines, with standard errors between 0.0063 and 0.0117, the slopes decreasing with increasing %TFP in the polymer.

Fig. 1 is the plot of the temperature dependence of the above constants for the two TFPSXX polymers: XX = 26.3 and 50.0%. Basically, the two plots have similar straight lines for the constants temperature dependence, in which s , l and a decrease upon

column heating, while e increases with increasing temperature. However, the %TFP difference determine that l and a get closer for TFP = 50.0%. Values of s increase much for the more polar TFPS50, while the other constants vary little with TFP content.

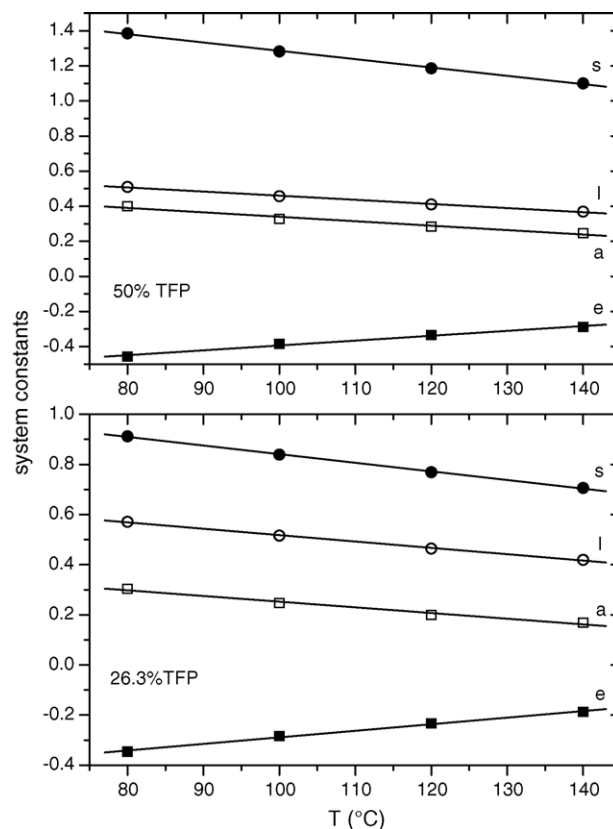


Fig. 1. Plot of the temperature dependence of the system constants e , s , a and l of the TFPSXX polymers (XX = 26.3 and 50%). Temperature range, 80–140 °C.

Table 4
Linear regressions ($y=A+B1x$) for the system constants temperature dependence of trifluoropropyl siloxane stationary phases

Constant	%TFP	A	B1	R	s_y
<i>l</i>	0	0.833 ± 0.012	−0.00272 ± 0.00010	−0.9986	0.0046
	11.5	0.817 ± 0.011	−0.00270 ± 0.00009	−0.9988	0.0042
	26.3	0.772 ± 0.009	−0.00254 ± 0.00008	−0.9990	0.0036
	35.5	0.743 ± 0.010	−0.00248 ± 0.00009	−0.9987	0.0040
	50.0	0.695 ± 0.011	−0.00235 ± 0.00009	−0.9984	0.0042
<i>s</i>	0	0.227 ± 0.005	−0.00038 ± 0.00004	−0.9869	0.0019
	11.5	0.742 ± 0.009	−0.00227 ± 0.00008	−0.9988	0.0036
	26.3	1.185 ± 0.009	−0.00344 ± 0.00008	−0.9995	0.0036
	35.5	1.430 ± 0.010	−0.00402 ± 0.00009	−0.9995	0.0040
	50.0	1.761 ± 0.151	−0.00475 ± 0.00014	−0.9992	0.0060
<i>e</i>	11.5	−0.385 ± 0.013	0.00219 ± 0.00011	0.9974	0.0050
	26.3	−0.551 ± 0.015	0.00262 ± 0.00014	0.9973	0.0061
	35.5	−0.634 ± 0.026	0.00287 ± 0.00023	0.9936	0.0103
	50.0	−0.671 ± 0.026	0.00277 ± 0.00023	0.9932	0.0103
<i>a</i>	0	0.418 ± 0.013	−0.00195 ± 0.00012	−0.9865	0.0052
	11.5	0.406 ± 0.023	−0.00194 ± 0.00020	−0.9895	0.0090
	26.3	0.479 ± 0.024	−0.00226 ± 0.00022	−0.9910	0.0097
	35.5	0.553 ± 0.031	−0.00252 ± 0.00028	−0.9816	0.0124
	50.0	0.593 ± 0.031	−0.00253 ± 0.00003	−0.9880	0.0125
<i>c</i>	0	0.092 ± 0.016	−0.00284 ± 0.00014	−0.9975	0.0063
	11.5	0.035 ± 0.022	−0.00289 ± 0.00020	−0.9952	0.0089
	26.3	−0.030 ± 0.029	−0.00295 ± 0.00026	−0.9922	0.0117
	35.5	−0.088 ± 0.028	−0.00298 ± 0.00025	−0.9930	0.0112
	50.0	−0.211 ± 0.019	−0.00277 ± 0.00017	−0.9964	0.0075

3.2. Polymer constants dependence with the %TFP group at each temperature

Table 5 lists the parameters of the linear and quadratic equations describing the effect of the polarity of the trifluoro-

propyl TFPSXX polymer (or the TFP percentage from XX = 0 to 50.0%) on the system constants (see Table 3).

l-constant versus %TFP group yields good straight lines at each temperature, the slopes decreasing with increasing temperature, but better correlations are obtained for square fit. The

Table 5
Least mean squares regression of the dependence of system constants (y) on the stationary phase TFP trifluoropropyl percentage ($y=A+B1x$ and $y=A+B1x+B2x^2$)

Constant	T_c (°C)	A	B1	B2	R	s_y
<i>l</i>	80	0.625 ± 0.004	−0.0022 ± 0.0004	0	−0.9938	0.0056
	100	0.564 ± 0.005	−0.0020 ± 0.0002	0	−0.9914	0.0061
	120	0.509 ± 0.004	−0.0019 ± 0.0013	0	−0.9932	0.0050
	140	0.460 ± 0.003	−0.0017 ± 0.0001	0	−0.9935	0.0045
<i>s</i>	80	0.253 ± 0.041	0.0235 ± 0.0014	0	0.9950	0.0537
	100	0.233 ± 0.034	0.0217 ± 0.0011	0	0.9960	0.0003
	120	0.214 ± 0.027	0.0200 ± 0.0009	0	0.9971	0.0002
	140	0.200 ± 0.020	0.0185 ± 0.0007	0	0.9982	0.0255
<i>e</i>	80	−0.0099 ± 0.0177	−0.0179 ± 0.0017	18.2E−05 ± 3.2E−05	0.9973	0.0191
	100	−0.0050 ± 0.0087	−0.0143 ± 0.0008	13.6E−05 ± 1.6E−05	0.9990	0.0094
	120	−0.0007 ± 0.0012	−0.0113 ± 0.0002	9.3E−05 ± 0.2E−05	0.9999	0.0013
	140	0.0034 ± 0.0059	−0.0087 ± 0.0006	5.6E−05 ± 1.1E−05	0.9992	0.0069
<i>a</i>	80	0.244 ± 0.016	0.0030 ± 0.0005	0	0.9555	0.0212
	100	0.199 ± 0.016	0.0024 ± 0.0005	0	0.9344	0.0209
	120	0.159 ± 0.015	0.0023 ± 0.0005	0	0.9331	0.0199
	140	0.131 ± 0.013	0.0021 ± 0.0005	0	0.9380	0.0176
<i>c</i>	80	−0.121 ± 0.012	−0.0058 ± 0.0004	0	−0.9931	0.0156
	100	−0.193 ± 0.007	−0.0059 ± 0.0002	0	−0.9977	0.0090
	120	−0.246 ± 0.008	−0.0059 ± 0.0002	0	−0.9973	0.0097
	140	−0.296 ± 0.008	−0.0058 ± 0.0002	0	−0.9972	0.0098

polymers, as already seen, become slightly more cohesive at higher temperatures, i.e., the effect of the TFP percentage is not significant.

e -constant decreases with increasing %TFP content, but linear regression of e -constant versus %TFP is poorer than those of the previous case. Parabolas, with standard errors between 0.0013 and 0.0191, describe better than straight lines the e -constant versus %TFP dependence looked for, especially at the highest temperature. The decrease with %TFP group means that the polymers do not show any tendency to give donor–acceptor interactions with other molecules through n or π electrons, the trend being more marked as the %TFP increases in the polymer. This could be explained because of the strong electronegativity of fluorine atom, making the fluoroalkanes have a lesser tendency than n -alkanes to give unshared electron pairs to molecules with stable empty molecular orbitals. This is the reason for its negative value. In addition, fluorine cannot give these interactions acting as electron acceptors either since the TFP group do not have stable empty molecular orbitals.

s -constant and a -constant versus %TFP dependence follow an opposite trend to that of the constants e and l , both increasing with increasing %TFP at each temperature, especially the first one. s increases considerably with increasing %TFP group, even at low TFP percentages, i.e., the polymer capacity to get involved in dipolar type interactions increases substantially as the %TFP increases in the polymer, showing the tendency of the trifluoropropyl siloxanes to give dipolar interactions with the solutes. This is important since it can help in the separation of determined compounds without significant changes in the stationary phase that could affect their good characteristics of stability and separation of homologues of dimethylsilicones. Acceptable straight lines were obtained for s -constant versus %TFP group dependence, the slopes decreasing with increasing temperature. Better correlations were also obtained with a second order polynomial fit.

The variation of a -constant versus %TFP is very low, so the capacity of the fluorinated stationary phases to participate in hydrogen bond acceptor type (constant a) is similar to the one of the unsubstituted TFPS00 in spite of the presence of electronegative atoms. This behaviour is due to the strong localization of the unshared electron pairs around the fluorine atom nucleus which makes this type of interactions difficult. Therefore, the introduction of 3,3,3-trifluoropropyl groups in the siloxane bone does not suppose a significant variation of the basic properties of the stationary phase.

Finally, decreasing straight lines were obtained for c constant versus %TFP group dependence, with standard errors between 0.0090 and 0.0156. The highest lines are placed at 80 °C. Slopes decrease with increasing %TFP substitution. Fig. 2 is the plot of constant s , l , a and e versus %TFP group variation at 80–140 °C.

3.3. The trifluoropropylsiloxanes– n -alkanes interactions

Constants l and c are involved in the evaluation of these interactions. Constant l is the sum of the dispersive forces, which

make a positive or exoergic contribution to it, and the endoergic cavity term, which makes a negative contribution to it. Its sign is always positive since the former contribution is the dominant in all stationary phases [40]. l is related to the power of separation of homologous compounds of a given stationary phase [4,41]

The high values of l (from 0.504 for TFPS00 to 0.410 for TFPS50) show how little it varies with %TFP, therefore, all synthesized polymers used as stationary phases would permit a good separation of homologous series. It is related to the partial molar Gibbs energy per the methylene group, $\Delta G_s^\circ(\text{CH}_2)$ (see Table 1) because the greater the l -value, the larger the separation between adjacent members within a homologous series [4]. In our case, the $\Delta G_s^\circ(\text{CH}_2)$ versus l gives a good straight line: $\Delta G_s^\circ(\text{CH}_2) = -0.110 \pm 0.018 - (3.51 \pm 0.04)l$, with a correlation coefficient $R^2 = 0.9996$ and standard error of 0.029 [9,42].

Constant c , the less defined in Abraham's equation, probably accounts for the differences in units in the temperature used to determine the solvation parameter [43]; it is a regression constant that “does not stand for any specific stationary phase constant” [12], whose importance for the calculation of retention is widely recognised, and when using retention factors as dependent variable it would incorporate the column phase ratio numerical value [12,15,16]. In principle, both l and c constants decide the importance of the interactions of the apolar n -alkanes

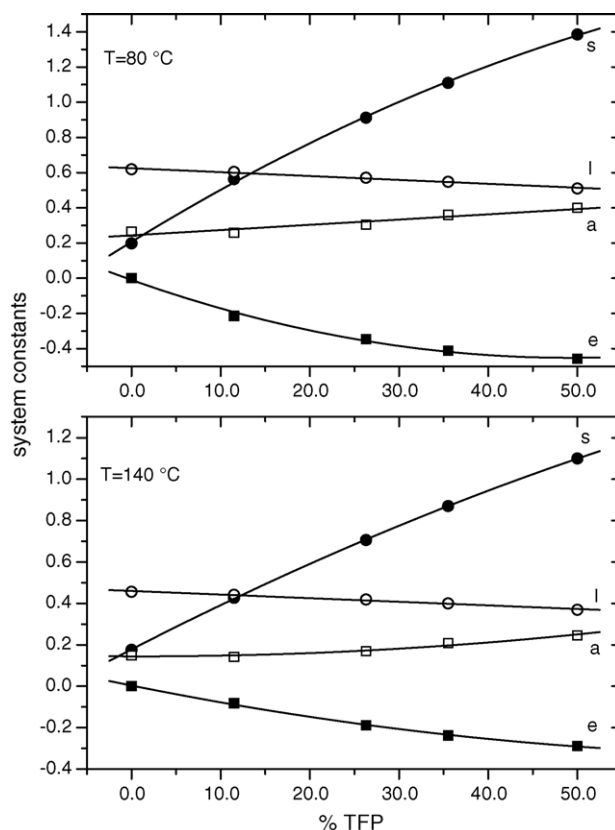


Fig. 2. Plot of the variation of the system constants e , s , a and l with the TFP group percentage XX for trifluoropropyl siloxanes at 80 and 140 °C.

Table 6

Non polar dispersive forces and cavity formation interaction contribution to the solvation of *n*-decane on the TFPSXX stationary phases at 120 °C

Stationary phase	<i>l</i>	<i>c</i>	<i>lL</i>	(<i>c</i> + <i>lL</i>)
TFPS00	0.504	−0.252	2.362	2.110
TFPS12	0.490	−0.316	2.296	1.980
TFPS26	0.464	−0.389	2.174	1.785
TFPS35	0.443	−0.449	2.076	1.627
TFPS50	0.410	−0.549	1.921	1.372

with the trifluoropropyl siloxanes. Such interactions use to be expressed as the sum (*c* + *lL*) for *n*-decane, through which the cavity formation and the dispersion forces are evaluated [40,44]. In a simpler way, the term *lL* could be used with the same intention, which may have the advantage of circumventing the use of *c*.

According to Table 6, the two, *lL* and (*c* + *lL*) decrease with increasing polymer polarity. Obviously, the former does because *l* decreases as much as 20% from 0.504 (0% TFP substitution) to 0.410 (50.0% TFP substitution), the less cohesive polymer. But the decrease of the latter is larger, about a 35%, because of the additional decrease of constant *c* from −0.252 (TFPS00) to −0.549 (TFPS50); then, for the more polar polymers the two *lL* and (*c* + *lL*) have lower values because the energy necessary to generate the cavity for the *n*-alkane increases (remember the negative contribution of this term to *l*) since the cohesion of the polymer increases the more substituted it is. This seems logical given that the presence of the polymer of TFP groups with important dipole moments leads to stronger molecular interactions, with the subsequent greater energy expenses to form the cavity. On the other hand, for the more cohesive stationary phases, *c* is larger (more negative) while *l* is smaller, so the sum (*c* + *lL*) will be smaller than *lL* for the terms with more TFP substitution. Comparison of (*c* + *lL*)(TFPS00) = 2.110 with (*c* + *lL*)(TFPS50) = 1.372 gives a deviation of 0.74, whereas comparison of *lL*(TFPS00) = 2.36 with *lL*(TFPS50) = 1.92 gives a deviation of 0.44. Therefore, *lL* and (*c* + *lL*) variations from the apolar TFPS00 to the polar TFPS50 differ exclusively for constant *c*, which is of not much importance in this case (*c* values do not exceed −0.549). But for capillary columns this model is limited for the considerable higher *c*-values obtained. A serious study of this subject is undertaken in recent work [45].

3.4. Principal component analysis

Principal component analysis (PCA) was applied to the values of the constants *l*, *e*, *s* and *a* of our five polymers and of another 33 stationary phases taken from literature (see Section 2.2).

Fig. 3 is a pictorial description of the scores obtained for the 38 chromatographic columns: PSF6, the 12 TFPS, and another 26 capillary columns recently characterized by Poole and coworkers [11–22] and by us [38] (see figure captions). Three groups appear in the plot. Group I is composed of the

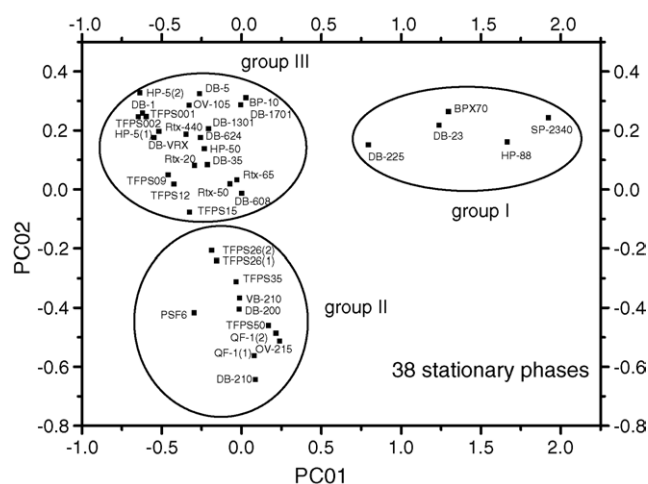


Fig. 3. Principal component analysis of system constants for 38 chromatographic columns: 26 capillary columns taken from literature [11–22] and 12 TFPSXX polymers mostly glassy capillary columns [9,24–26]. Stationary phases: 1, DB-200; 2, DB-VRX; 3, DB-1701; 4, HP-50; 5, DB-210; 6, SP-2340; 7, DB-1; 8, DB-5; 9, HP-5(1); 10, Rtx-20; 11, DB-35; 12, Rtx-50; 13, Rtx-65; 14, DB-23; 15, DB-1301; 16, DB-225; 17, DB-608; 18, DB-624; 19, HP-88; 20, Rtx-440; 21, HP-5(2); 22, BP-10; 23, VB-210; 24, BPX70; 25, OV-105; 26, QF-1(1); 27, PSF6; 28, TFPS002; 29, TFPS12; 30, TFPS26(2); 31, TFPS35; 32, TFPS001; 33, TFPS09; 34, TFPS15; 35, TFPS26(1); 36, OV-215; 37, QF-1(2), and 38, TFPS50.

five very polar cyanopropyl stationary phases DB-225, DB-23, BPX70, HP-88 and SP-2340.

Group III is constituted by the less polar stationary phases distributed in various subgroups: a subgroup of two (DB-1701 and BP-10, cyanopropyl siloxanes of the same cyanopropyl content, 14%), a subgroup of three (Rtx-50, Rtx-65 and DB-608) polymethylphenyl siloxanes, a subgroup of three (TFPS09, TFPS12 and Rtx-20), a subgroup of seven (TFPS001, TFPS002, DB-1, DB-5, HP-5(2), DB-VRX and HP-5(1)), and a subgroup of six (Rtx-20, DB-35, HP-50, Rtx-440, DB-1301 and DB-624). So, four low-polarity TFPS polymers fall inside this group.

Group II is composed mostly of the non-capillary column PSF6 and 11 TFPSXX stationary phases, three of the five contributed in this work, TFPS26(2), TFPS35 and TFPS50, five 50% TFP, DB-200, DB-210, VB-210, QF-1(1), QF-1(2) and OV-215, and the early TFPSXX of Dai [25,26]: TFPS15 and TFPS26(1).

Fig. 4 is the dendrogram of the same 38-stationary phases system constructed with the single linkage clustering method of the nearest neighbour, which corroborates the previous distribution of columns in the plane: VB-210, DB-210, the two QF-1, OV-215, and TFPS50, all of them with 50% TFP, and other trifluoropropyl siloxanes with lower %TFP, viz. TFPS26(1), TFPS26(2), TFPS12, TFPS15, TFPS09, TFPS35, placed between the Poole's columns DB-200 (50% TFP) and DB-VRX. The two TFPS00 fall between the non polar DB-1 and Rtx-20, low polarity 20% phenyl polymethylphenyl siloxane. PSF6, which is not a TFPS, is located between HP-50 and SP-2340 in the dendrogram. BPX70 is placed with the more polar stationary phases of the set, DB-225, HP-88, DB-23, etc., in agreement with the plot of Fig. 3.

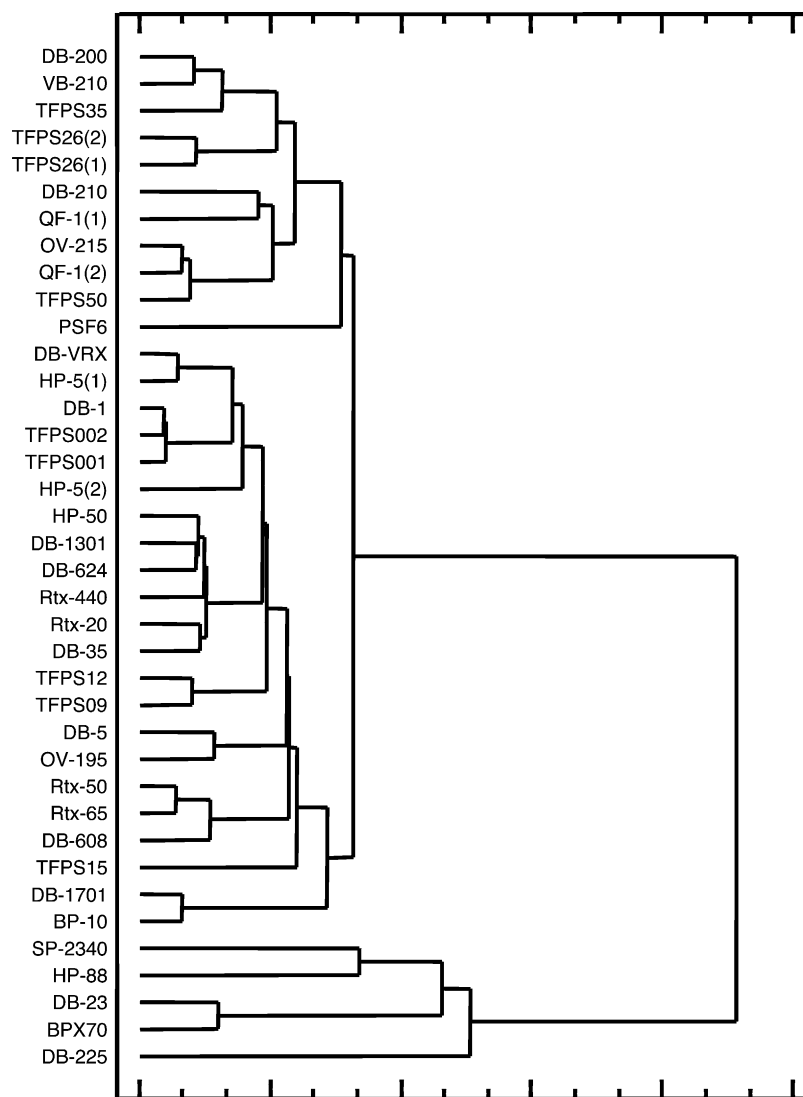


Fig. 4. Dendrogram of this column set by the nearest neighbour method.

4. Conclusions

Synthesized trifluoropropylsiloxanes of five different TFP contents (0, 11.5, 26.3, 35.5 and 50.0%) were characterised by the solvation parameter model at 80–140 °C.

It is shown that s is the more important constant for explaining the retention interactions. Constants a and e are much smaller, the second being negative owing to the repulsion of the fluorine atom, and b is zero. High constant l values agree with the non-polar or moderately polar character of the TFPSXX polymers.

Constants s , l and a decrease with increasing temperature, while e increases slightly.

On increasing polymer polarity, constant s increases, constant e decreases and constants l and a are quite insensitive to the polarity changes in the polymers.

l -values hardly vary with the %TFP of the polymer and they always present high values (0.504–0.410), therefore, the trifluoropropyl siloxanes used as stationary phases would permit obtaining a good separation of the members of a homologue series.

As TFP percentage increases in the synthesized polymers, an important increase in the dipole-type interactions capacity, a decrease in the donor–acceptor interactions with molecules with n or π electrons, and a decrease in the capacity to form cavities are detected.

But, with respect to the tendency to accept hydrogen bonds, insignificant changes on introducing TFP groups into the polymer were observed.

Cluster analysis studies carried out on 38 stationary phases show that (i) non-polar trifluoropropyl siloxanes like TFPS001 and TFPS002 group with DB-1, DB-VRX, DB-5, HP-5(1) and other non polar stationary phases, (ii) low polarity TFPSXX like TFPS09, TFPS12 group with low polarity polymethylphenyl 20 and 35% phenyl stationary phases as Rtx-20 and DB-35, while the other medium polar stationary phases: TFPS26(1), TFPS26(2), TFPS35 group with other fluorinated polymers with 50% trifluoropropyl percentage, viz., TFPS50, OV-215, QF-1(1), QF-1(2), DB-200 and DB-210. The non-capillary column PSF6 forms part of this group, and (iii) BPX70 can replicate the very polar stationary phases HP-88, SP-2340, DB-23, or HP-50.

The dendrogram of the same 38 stationary phases agrees with the clusters formed in Fig. 3.

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