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## Gibbs energy of solution and molecular structural coefficients of 85 solutes on 20 gas chromatographic stationary phases

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### Abstract

Molecular structural coefficients of Takács ( $S_{ci}$ ), relative Gibbs solution energies ( $y_i$ ), and their respective increments,  $[\Delta S_{ci}(\text{RX})]$  and  $[\Delta y_i(\text{RX})]$ , with respect to parent RH  $n$ -alkanes have been determined using specific retention volumes of 85 solutes on 20 stationary phases at two common temperatures. Fair correlations between all these parameters and the cavity/dispersion,  $\Delta G(\text{C/D})$ , and the polar,  $\Delta G(\text{P})$ , Gibbs solution energy contributions, calculated with Abraham's solvation model, were obtained. It is proved that the polar solute–solvent interactions calculated for several RX chemical functions, according to the model proposed in this work, agree satisfactorily with both the polar and the cavity formation and dispersion contributions to the Gibbs solvation energy for the said RX chemical functions, deduced from Abraham's solvation model. The relationship between  $y_i$  and  $S_{ci}$  was also investigated. © 1997 Elsevier Science B.V.

**Keywords:** Thermodynamic parameters; Solute–stationary-phase interactions; Stationary phases, GC; Solvation parameters; Polarity; Molecular structural coefficients; Solution properties

### 1. Introduction

The retention index system devised by Rohrschneider [1] and later refined by McReynolds [2] was the first successful method of characterization and classification of organic solvents in gas–liquid chromatography. The stationary phases (SPs), were characterized by their  $\Delta I$  constants, defined as the retention index differences for benzene,  $n$ -butanol, pentan-2-one, 1-nitropropane and pyridine, respectively, on the given SP and on the reference SP, squalane. Such differences represent the solute–SP interactions, which were related to the dispersion,

orientation, dipoles and proton-donor/proton-acceptor (mostly hydrogen-bond) forces acting in retention [3]. Many papers have been published on this topic, including a recent review [4].

Risby et al. [5] and Golovnya and Misharina [6] used thermodynamic magnitudes derived from the retention index to carry out SP characterization. Golovnya and Misharina [6] deduced an equation relating the partial molar Gibbs energy of solution ( $\Delta G_{ki}^0$ ) of the McReynolds probes to their retention index values. Stationary-phase densities were not taken into account, and therefore the calculated  $\Delta G_{ki}^0$  values were only approximate. As the McReynolds [2] data have been found to be inaccurate [7], these approximations have been questioned [8].

Here a modified Golovnya et al.'s equation, with

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which relative partial molar Gibbs energies of solution,  $y_i = \Delta G_{ki}^0 / \Delta G_{kCH_2}^0$ , have been exactly calculated for about 85 unfunctional solutes with several chemical functions on 20 stationary phases of known density, has been used.  $\Delta G_{kCH_2}^0$  is the partial molar Gibbs energy of solution of the methylene group.

The solvatochromic solvation energy relationships of Taft et al. [9] preceded the modern solvation models of Abraham and co-workers [10,11], Carr [12] and Poole and Poole [13], which will be discussed later on. Although successful, they have to be supplemented by some empirical methods, since the theory of solutions is not yet satisfactorily enough.

The goals of the present work are: (a) on the basis of the calculation of the molecular structural coefficients ( $S_{ci}$ ), according to Takács [14], to study the dependence of  $S_{ci}$  and their  $\Delta S_{ci}(RX)$  unfunctional group increments for 85 solutes on the polarity of 20 SPs in terms of Abraham's solvation model; (b) on the basis of the exact calculation of relative Gibbs solution energies ( $y_i$ ) with a modified Golovnya and Misharina's equation, to study the dependence of  $y_i$  and  $\Delta y_i(RX)$  on the polarity of the above SPs and solutes; (c) finally, to study the relationship between  $y_i$  and  $S_{ci}$  spanning a wide SP's polarity range.

## 2. Experimental

### 2.1. Stationary phases

(a) our own SPs (OV-101, OV-105 [15], OV-225, OV-25 [16]), Carbowax 20M, six methyl(3,3,3-trifluoropropyl)siloxanes (PS-255 (TFPS00), TFPS09, TFPS15, TFPS26 [17,18], OV-215 and QF-1 (TFPS50) [19]); Superox 20M [20]. (b) Eight Tian and Munk' SPs [21]: PEE, poly(ethylene); PP1, polypropylene; PDMS, poly(dimethylsiloxane); PCL, polycaprolactone; PECH, polyepichlorhydrin; PMA, poly(methyl acrylate); PEA, poly(ethyl acrylate); and PBMA, poly(*n*-butyl methacrylate).

### 2.2. Solutes

(a) *n*-Alkanes (from *n*-pentane to *n*-hexadecane, used as standard). (b) The 10 McReynolds probes,

used to characterize the earlier SPs: OV-1, OV-25, OV-225 and CW 20M. (c) Solutes belonging to different chemical families, used to characterize the remaining columns: *n*-alkylbenzenes from benzene to *n*-pentylbenzene; alkanols (from ethanol to *n*-octanol) and cyclohexanol; alkan-2-ones (from propan-2-one to octan-2-one) and cyclohexanone; esters (methyl, ethyl, *n*-propyl and *n*-butyl formates; methyl, ethyl, *n*-propyl and *n*-butyl acetates); aniline and *N,N*-dimethylaniline; nitriles (propionitrile, butyronitrile, valeronitrile, hexanenitrile and benzonitrile); nitrobenzene, chlorobenzene, 1-chlorobutane and 1,1,1-trichloroethane. (d) Other solutes used by Tian and Munk [21] (see Table 4).

Chromatographs and other apparatus have been described elsewhere [15–20]. SPs were built as packed, micropacked and wall-coated open tubular (WCOT) capillary columns. The carrier gas was nitrogen. Temperatures were 383.2 and 393.2 K. Densities of the SPs were determined by picnometric procedures [16–20] or from the equation  $\rho(T) = \rho(T_0) - d\rho/dT(T - T_0)$  [21].

### 2.3. Theory and scope

According to Takács [14], the Kováts coefficient,  $K_c$ , and the molecular structural coefficients of Takács,  $S_{ci}$ , [22,23] are the two parts of the retention index,  $I_i$ , of a solute *i* on a given SP at a given temperature and carrier gas:

$$I_i = K_c + S_{ci} \quad (1)$$

$K_c$  [14,22–26] depends exclusively on column temperature, SP's polarity and carrier gas, and is given by:

$$K_c = 100 \left[ Z - \frac{\log V_{g,Z}}{b} \right] \quad (2)$$

where *Z*, the carbon atom number of the *n*-alkanes used as markers should be at least 7. Some aspects of  $S_{ci}$  have been recently studied [23].  $V_{g,Z}$  is the specific retention volume of the *Z* *n*-alkane and *b*, the slope of the  $\log V_{g,Z}$  vs. *Z* plot. The equation of Golovnya and Misharina [6] gives the partial molar Gibbs solution energy of a solute *i* on a stationary phase as:

$$\Delta G_{ki}^0 = -2.3RT[(0.01I_i - Z)b + \log(V_{r,z}\rho T/273.2)] \quad (3)$$

where  $\rho$  is the density of the SP, in  $\text{g ml}^{-1}$ ;  $T$ , the column temperature, in K; and  $R$ , the gas constant,  $4.576 \text{ cal mol}^{-1} \text{ K}^{-1}$  ( $1 \text{ cal} = 4.184 \text{ J}$ ).

$\Delta G_{k\text{CH}_2}^0$ , the contribution of the methylene group to the partial molar Gibbs solution energy of the solute on the SP at the temperature  $T$  has been calculated as:

$$\Delta G_{k\text{CH}_2}^0 = -2.3RTb \quad (4)$$

its physico-chemical meaning being the reluctance of the solvent to accommodate 1 mol of methylene of the solute. Substituting its value into Eq. (3), and with the help of Eqs. (1) and (2), it can be written:

$$y_i = \frac{\Delta G_{ki}}{\Delta G_{k\text{CH}_2}} = \frac{S_{ci}}{100} + \frac{\log(\rho T/T_0)}{b} \quad (5)$$

$T_0 = 273.2 \text{ K}$  is the reference temperature. Multiplying both sides of Eq. (5) by 100:

$$100y_i = \frac{\Delta G_{ki}^0}{\Delta G_{k\text{CH}_2}^0/100} = S_{ci} + 100 \cdot \frac{\log \rho + 0.15816}{b} \quad (6)$$

where  $0.15816 = \log(393.2/273.2)$ .

Defining:

$$E_R = \frac{100}{b} \cdot (\log \rho + 0.15816) \quad (7)$$

we will have:

$$100y_i = S_{ci} + E_R \quad (8)$$

an expression very similar to the proposed relation [27] between molecular structural coefficients and Gibbs solution energies:

$$S_{ci} = \frac{\Delta G_{ki}^0}{(\Delta G_{k\text{CH}_2}^0/100)} = 100y_i \quad (9)$$

So, according to Eq. (6),  $100y_i$ , the ratio of the partial molar Gibbs energy of the solute  $i$  to one-hundredth of the partial molar Gibbs energy of the methylene group on a given SP at a given temperature  $T$ , is equal to the sum of the molecular structural coefficient,  $S_{ci}$ , of solute  $i$  on the SP plus an  $E_R$  term,

dependent only on the chromatographic column. The solvation models of Poole and Poole [13], Abraham and co-workers [10,11], and its slightly different version by Carr [12], basically explain the retention of a solute on any SP through the transference of 1 mol of solute (as ideal gas) from the carrier gas to the stationary phase (at infinite dilution), this process consisting of the creation of a cavity in the SP of adequate size to lodge the solute, the rearrangement of solvent molecules around the cavity, and, finally, the subsequent solvent–solute molecular interactions. The total Gibbs energy of solution is, as Golovnya and Misharina postulated [6], equal to the sum of the Gibbs energy contributions of these three processes.

According to Poole et al. [8] the above contributions are given by:

$$\Delta G_{Si}(\text{SOLN}) = \Delta G_{Si}(\text{CAV}) + \Delta G_{Si}(\text{NP}) + \Delta G_{Si}(\text{P}) \quad (10)$$

where  $\Delta G_{Si}(\text{SOLN})$  is the partial Gibbs energy of solution for the transference of 1 mol of solute  $i$  from the gas phase to the SP  $S$ ;  $\Delta G_{Si}(\text{CAV})$ , the partial Gibbs energy of cavity formation of solute  $i$  on the SP  $S$ ;  $\Delta G_{Si}(\text{NP})$  and  $\Delta G_{Si}(\text{P})$  are the nonpolar and polar contributions to the Gibbs solution energy of solute  $i$  on the stationary phase  $S$ , respectively.

According to Abraham et al. [11]:

$$\log V_{ri} = a_0 + a_1 R_2 + a_2 \pi_2^H + a_3 \alpha_2^H + a_4 \beta_2^H + a_5 \log L^{16} \quad (11)$$

where  $V_{ri}$  is the specific retention volume of solute  $i$  on a given SP at 393.2 K;  $a_0$  is an independent term; the  $a_1$  to  $a_4$  phase constants describe the ability of the SP to interact with, respectively, solute  $n$ - or  $\pi$ -electrons, dipoles, hydrogen-bond acidity, and hydrogen-bond basicity, and  $a_5$  sums up the contributions from solvent cavity formation and solute–solvent dispersion interaction. These constants were calculated by multiple linear regression analysis using a minimum of 15–30 solutes. The solute descriptors  $R_2$ ,  $\pi_2^H$ ,  $\alpha_2^H$ ,  $\beta_2^H$  and  $\log L^{16}$  are, respectively, the excess molar refraction, accounting for the ability of the solute to interact with a solvent through  $n$ - or  $\pi$ -electron pairs, the dipolarity/polarizability parameter, the solute H-bond donor factor, the solute

H-bond acceptor factor, and the gas–liquid partition coefficient on hexadecane at 298.2 K.

According to Abraham's equation [11], the partial molar Gibbs solution energy of solute  $i$ , would be given by:

$$\Delta G_{S_i}(\text{SOLN}) = -2.3RT \log K_{L_i} \quad (12)$$

where  $K_{L_i}$  is the partition coefficients of solute  $i$  on the stationary phase  $S$ , which in turn can be partitioned into two contributions: nonpolar cavity/dispersion,  $\Delta G(\text{C/D})$ , given by:

$$\Delta G(\text{C/D}) = -2.3RT[a_0 + a_5 \log L^{16}] \quad (13)$$

and the polar contribution,  $\Delta G(\text{P})$ , given by:

$$\Delta G(\text{P}) = -2.3RT[a_1 R_2 + a_2 \pi_2^H + a_3 \alpha_2^H + a_4 \beta_2^H] \quad (14)$$

Kollie et al. [28] compared their separately developed solvation models using  $K_L$  data for a set of 30 solutes and 25 SPs at 120°C. Previously they wrote Eq. (10) as:

$$\Delta G_{S_i}(\text{SOLN}) = \Delta G_{S_i}(\text{CAV} + \text{NP}) + \Delta G_{S_{Q_i}}(\text{P}) + \Delta G_{S_i}(\text{INTE}) \quad (15)$$

where  $\Delta G_{S_i}(\text{INTE})$  is given by:

$$\Delta G_{S_i}(\text{INTE}) = \Delta G_{S_i}(\text{P}) - \Delta G_{S_{Q_i}}(\text{P}) \quad (16)$$

where  $\Delta G_{S_i}(\text{CAV} + \text{NP})$  represents the combined contribution to the Gibbs energy of cavity formation and nonpolar solute–solvent interaction.  $\Delta G_{S_{Q_i}}(\text{P})$  is the solute–solvent interaction term of solute  $i$  on the reference hydrocarbon SP, squalane;  $\Delta G_{S_i}(\text{P})$  is the solute–solvent interaction term of solute  $i$  on  $S$ , and  $\Delta G_{S_i}(\text{INTE})$  is the solvent interaction term for polar interactions.

Excellent correlations for  $[a_0 + a_5 \log L^{16}]$  against  $\log K_{L_i}(\text{CAV} + \text{NP} + \text{P})$  (correlation coefficient  $r^2 = 0.988$ ) and for  $[\Sigma(a_1 R_2 + a_2 \pi_2^H + a_3 \alpha_2^H)]$  versus  $\log K_{L_i}(\text{INTE})$  ( $r^2 = 0.975$ ) were found, showing a very good agreement between the two solvation energy models.

Poole and Poole [13] also characterized two data sets at 120°C by applying principal component analysis, PCA, finding that three factors were enough to describe both systems, these factors being identified as cavity formation and dispersion, solvent

H-bond interactions, and orientation contributions. Factors 1, 2 and 3 were correlated to  $a_2 \pi_2^H$ ,  $a_3 \alpha_2^H$  and  $\Sigma(a_1 R_2 + a_2 \pi_2^H)$ , with correlation coefficients  $r^2 = 0.92, 0.96$  and  $0.95$ , respectively. So, results obtained with PCA agreed well with those obtained with their previous solvation parameter model.

In this work we have compared the different Gibbs solution energies, evaluated by the model presented in this work, with those of the solvation model developed by Abraham et al. [11].

The sequence of operations is as follows: (1)  $S_{ci}$  values of 85 solutes on the 20 given SPs were calculated with Eq. (1); (2) the increments  $\Delta S_{ci}(\text{RX})$  for different unfunctional solutes with respect to the  $n$ -alkane of equal  $Z$ , RH, were calculated with the equation:

$$\Delta S_{ci}(\text{RX}) = S_{ci}(\text{RX}) - S_{ci}(\text{RH}) \quad (17)$$

(3)  $y(\text{RX})$  values were calculated with Eq. (5); (4) the increments  $\Delta y(\text{RX})$ , called 'polar group constant', were calculated with the equation:

$$\Delta y_i(\text{RX}) = y_i(\text{RX}) - y_i(\text{RH}) \quad (18)$$

where RH is the parent  $n$ -alkane molecule; (5)  $\Delta G(\text{C/D})$ , the cavity + dispersion contribution term to the Gibbs solution energy, and  $\Delta G(\text{P})$ , the polar solute–solvent interaction contribution to the Gibbs solution energy, were calculated for several chemical functions with Eqs. (13) and (14), respectively; and (6) Eq. (8) was used to discuss the discrepancy found between  $y_i$  and  $S_{ci}$ .

$V_g$  values, specific retention volumes, were taken as the mean of as many as six chromatograms per each compounds group. Tian and Munk's  $V_g$  values were obtained with an accuracy of 1% [21]. The partial molar Gibbs energy per methylene group,  $\Delta G_{\text{KCH}_2}^0$ , was calculated with Eq. (4) [29], and the coefficients of Kováts,  $K_c$ , calculated with Eq. (2), were used to estimate the polarity of SPs throughout this work. Retention polarities, RP [30], were used in another work [23] as polarity scale.

The retention indices,  $I_i$ , were determined by applying Kováts equation [31] to the specific retention volumes obtained from the experimental chromatograms [15–21]. Tian and Munk's SPs have been corrected for superficial adsorption.

### 3. Results and discussion

#### 3.1. Relationship of Gibbs energy of solution with molecular structural coefficients

Table 1 lists the molecular structural coefficients,  $S_{ci}$  [14], obtained with Eq. (1), of forty-one solutes

on four methyl(3,3,3-trifluoropropyl) siloxane polymers synthesized by Q. Dai [17,18] (PS-255 (TFPS00), TFPS09, TFPS15, TFPS26), with 3,3,3-trifluoropropyl weight percentages of 0, 9, 15 and 26%, and of 16 solutes on OV-215/QF-1 (TFPS50) [19], ordered by increasing  $K_c$  values [22].  $S_{ci}$  has high values for the solutes classified as polar, i.e.,

Table 1  
Molecular structural coefficients,  $S_{ci}$ , of 43 solutes on five methyl(3,3,3-trifluoropropyl) siloxane polymers, at 393.2 K

Solute	TFPS00, $K_c = 144$	TFPS09, $K_c = 156$	TFPS15, $K_c = 173$	TFPS26, $K_c = 208$	TFPS50, $K_c = 270$
<i>n</i> -Hexane	454	444	427	390	330
Benzene	521	526	523	514	532
Methylbenzene	624	630	629	621	644
Ethylbenzene	717	723	719	711	
<i>n</i> -Propylbenzene	808	813	811	802	825
<i>n</i> -Butylbenzene	907	913	910	902	
<i>n</i> -Pentylbenzene	1004	1010	1008	999	1012
Butan-2-one	430	478	499	541	633
Pentan-2-one	522	570	591	631	737
Hexan-2-one	624	673	697	735	
Heptan-2-one	725	774	799	837	
Octan-2-one	825	876	900	939	1040
Cyclohexanone	735	794	826	880	
Butanol-1	494	511	513	523	567
Pentanol-1	598	616	618	628	670
2-Methylpentan-2-ol	572	593	596	601	
Hexanol-1	701	719	722	731	
Heptanol-1	803	822	825	833	
Octanol-1	905	924	928	936	981
Cyclohexanol	729	749	756	772	
<i>n</i> -Propyl formate	456	489	500	523	
<i>n</i> -Butyl formate	559	592	605	626	
Ethyl acetate	445	475	484	512	591
<i>n</i> -Propyl acetate	543	577	587	612	
<i>n</i> -Butyl acetate	645	678	690	711	
Aniline	811	838	853	885	
<i>N,N</i> -Dimethylaniline	932	955	967	987	1075
Benzonitrile	816	880	917	975	
Butyronitrile	496	565	600	660	812
Valeronitrile	599	671	708	766	917
Hexanenitrile	702	773	812	871	
1-Nitropropane	566	631	667	721	
Nitrobenzene	920	981	1018	1006	
Pyridine	589	623	636	678	754
1-Chlorobutane	500	516	515	511	
1,1,1-Trichloroethane	504	514	512	502	
Chlorobenzene	703	716	718	720	
1-Iodobutane	674	684	681	676	
Oct-2-yne	717	709	694	664	
1,4-Dioxane	550	575	586	610	
<i>cis</i> -Hydrindane	858	851	840	817	

$K_c$ , Kováts coefficients.

Table 2

Molecular structural coefficient increments,  $\Delta S_{ci}(\text{RX})$ , and polar contribution,  $\Delta G(\text{P})$  (cal mol<sup>-1</sup>), to the Gibbs solution energy of several chemical functions on five methyl(3,3,3-trifluoropropyl)siloxanes

Solite	TFPS00		TFPS09		TFPS15		TFPS26		TFPS50	
	$\Delta G(\text{P})$	$\Delta S_{ci}$	$\Delta G(\text{P})$	$\Delta S_{ci}$	$\Delta G(\text{P})$	$\Delta S_{ci}$	$\Delta G(\text{P})$	$\Delta S_{ci}$	$\Delta G(\text{P})$	$\Delta S_{ci}$
Benzene	-193	67	-277	82	-342	96	-453	124	-710	202
Hexan-2-one	-232	170	-447	229	-643	270	-938	345	-1361	511
Hexanol-1	-262	247	-391	275	-448	295	-668	341	-953	430
<i>n</i> -Butyl acetate	-203	191	-430	234	-582	263	-853	321	-1235	444
Aniline	-429	357	-627	394	-744	426	-1036	495	-1566	623
Nitrobenzene	-392	466	-675	537	-860	591	-1194	686	-1814	776
Chlorobenzene	-236	249	-359	272	-442	291	-591	330	-926	407
Hexanenitrile	-298	362	-647	329	-860	385	-1248	481	-1833	702
Benzonitrile	-388	362	-698	436	-899	490	-1261	585	-1899	795
Cyclohexanone	-302	281	-562	350	-744	399	-1067	490	-1569	682
Cyclohexanol	-299	275	-414	305	-480	329	-696	382	-1009	482
1-Nitrohexane	-313	312	-681	387	-900	460	-1302	531	-1922	739

hexan-2-one, aniline, nitrobenzene, etc., and low values for benzene, an apolar hydrocarbon.

Table 2 lists the  $\Delta S_{ci}(\text{RX})$  increments, calculated with Eq. (17), and the polar Gibbs solution energy contributions,  $\Delta G(\text{P})$ , calculated with Eq. (14), of 12 polar solutes derived from *n*-hexane, on the five polymers on Table 1. Previously their respective phase constants were determined by multiple linear regression analysis.

It is shown that  $\Delta S_{ci}$  for the above solutes, 1,4-dioxane and 1-nitropropane, increases with increasing polarity ( $K_c$ ) of the five TFP siloxane polymers (Fig. 1a,b). Excellent least-mean-square straight lines were obtained ( $r=0.98$ – $1.00$ ). The plot of  $\Delta S_{ci}(\text{RX})$  of 13 solutes of different chemical functions (ket-2-ones, alkanols, nitriles, esters, etc.) vs. the Gibbs energy of solution polar contribution,  $\Delta G(\text{P})$ , are straight lines with fair correlations:  $r=0.85$ ,  $0.84$ ,  $0.83$ ,  $0.85$  and  $0.96$  for TFPS00, TFPS09, TFPS15, TFPS26 and TFPS50, respectively (see Table 2). Fig. 2 is the plot of  $\Delta S_{ci}$  against  $\Delta G(\text{P})$  for the latter stationary phase.

It is clear that all these RX solutes with  $Z=6$  carbons have a polar part whose polarity is well reflected by their  $\Delta S_{ci}(\text{RX})$  increments; their values increase with increasing sum of their solute–solvent interactions. In other words, the molecular structural coefficients and their  $\Delta S_{ci}(\text{RX})$  increments for the different homologous series are closely related with the polar contribution to the total interaction of each SP with each chemical function, obtained via Ab-

raham's treatment [11]. So, for a given solute, good  $\Delta G(\text{P})$  versus  $\Delta S_{ci}$  correlations are found, and for a given SP, poorer but still good  $\Delta G(\text{P})$  versus  $\Delta S_{ci}$  correlations were obtained.

### 3.2. Relationship of Gibbs solution energy with solute polarity

#### 3.2.1. The dependence of $y_i$ on solute polarity

Table 3 lists retention index,  $I_i$ , calculated with Kováts equation [31], cavity/dispersion,  $\Delta G(\text{C/D})$ , and polar,  $\Delta G(\text{P})$ , Gibbs solution energy contributions, calculated with Eqs. (13) and (14), respectively, and relative partial molar Gibbs solution energies,  $y_i$ , calculated with Eq. (5), for 45 solutes of seven different chemical functions on TFPS15 at 393.2 K. It is shown that: (a) increasing values for  $I_i$  and  $y_i$  are observed for increasing carbon chain length for each homologous series; (b) the  $\Delta G(\text{P})$  term also increases with chain length, which means that more energy is required for lodging the heavier terms within a homologous series; (c) the difference between  $\Delta G(\text{C/D})$  for a term and the next one is exactly  $\Delta G_{k\text{CH}_2}^0$ ,  $-423.1$  cal mol<sup>-1</sup> for this SP; (d) the polar contributive term, i.e., that due to the solute–solvent interactions, is practically constant for each term of a given series:  $\Delta G(\text{P})=0$  for the *n*-alkanes;  $-355$  cal/mol for *n*-alkylbenzenes;  $-647$  cal/mol for alkan-2-ones;  $-444$  cal/mol for *n*-alkanols;  $-589$  cal/mol for esters;  $-856$  cal/mol for

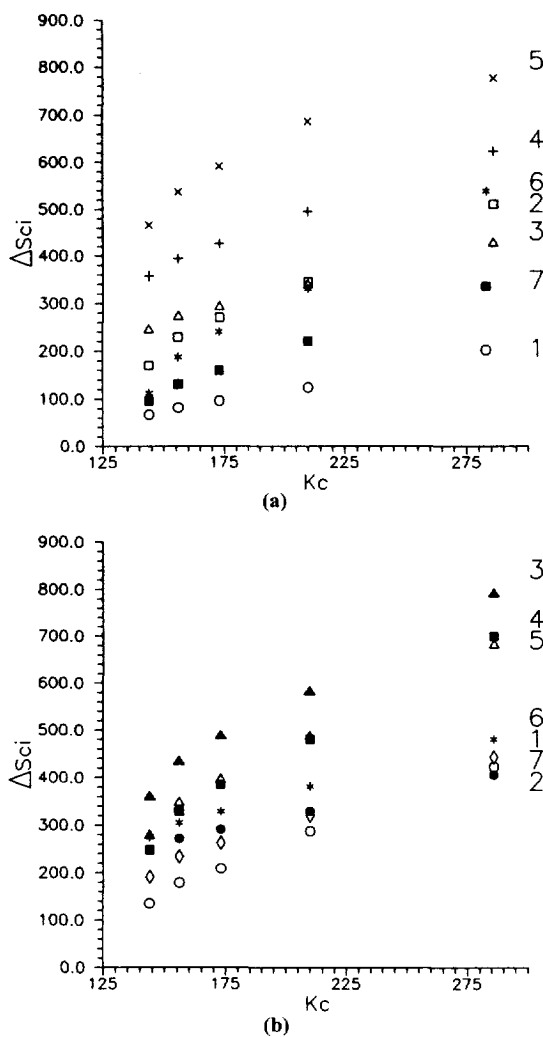


Fig. 1. Plot of  $\Delta S_{ci}$ , molecular structural coefficient increments, of several solutes against the Kováts coefficients,  $K_c$ , of five methyl(3,3,3-trifluoropropyl)siloxane polymers. (a) Solutes: 1, benzene; 2, hexan-2-one; 3, hexanol-1; 4, aniline; 5, nitrobenzene; 6, 1-nitropropane; and 7, 1,4-dioxane. (b) Solutes: 1, *n*-butyl acetate; 2, chlorobenzene; 3, benzonitrile; 4, hexanenitrile; 5, cyclohexanone; 6, cyclohexanol; and 7, pyridine.

linear nitriles; and variable values for the remaining solutes not pertaining to any homologous series, but with higher absolute values for those with larger dipole moments, or for the more polar ones, i.e.,  $\Delta G(P) = -860, -744, -655, -558$  and  $-899$  cal mol<sup>-1</sup> for 1-nitropropane, aniline, pyridine, *N,N*-dimethylaniline and benzonitrile, respectively.

Table 4 shows results of  $I_i$ ,  $\Delta G(C/D)$ ,  $\Delta G(P)$  and

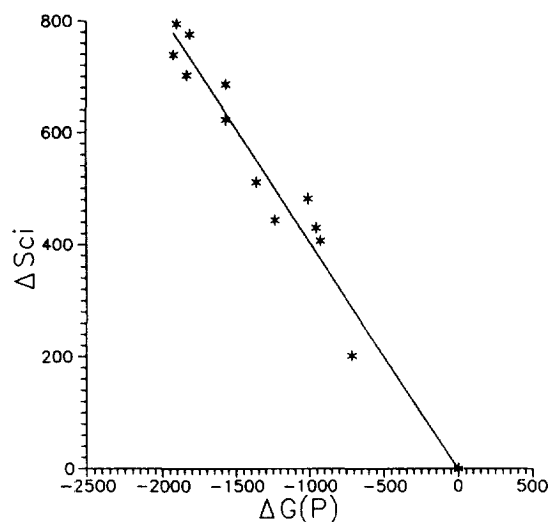


Fig. 2. Plot of  $\Delta S_{ci}$  against  $\Delta G(P)$ , the solute-solvent polar contribution to the Gibbs solution energy, for 13 solutes on TFPS50 (see Table 2).

$y_i$  for 33 solutes, some of them from chemical functions too (see Table 6), on the PP1 stationary phase of Tian and Munk's at 383.2 K. Identical considerations can be put forward.

### 3.2.2. Dependence of $\Delta y_i(RX)$ on solute polarity

The so-called 'polar group constant',  $\Delta y_i(RX)$ , for the RX function was calculated with Eq. (18), where RH is the parent *n*-alkane with the same carbon atom number; Fig. 3 is the plot of  $\Delta y_i(RX)$  against  $\Delta G(P)$  for 12 solutes derived from *n*-hexane on TFPS15 at 393.2 K (see Table 3). Least-mean-square regression yields the straight line:  $\Delta y_i(RX) = -0.00539\Delta G(P) - 0.00292$ , with a correlation coefficient of 0.83, i.e., there is a modest correlation in spite of the different van der Waals molecular volumes of the solutes, estimated according to Abraham and McGowan [32]. Similar correlations were observed with the data of Table 5 for *n*-octane and six derivatives and for benzene and derivatives, together with the characteristic van der Waals volumes, calculated by McGowan's method [32]. Although the solutes have unequal (but close) molecular volumes, there is a correlation between  $\Delta G(P)$ , the polar solute-solvent contribution, to the solvation free energy of solution, and the polar group constant  $\Delta y_i(RX)$ :  $\Delta y_i(RX) = -0.00494[\Delta G(P)] -$

Table 3

Retention index,  $I_i$ , cavity/dispersion Gibbs energy of solution,  $\Delta G(C/D)$ , polar Gibbs energy of solution,  $\Delta G(P)$ , and relative partial molar Gibbs energies,  $y_i$ , of 42 solutes on TFPS15 at 393.2 K

Compound	$I_i$	$\Delta G(C/D)$ (cal mol <sup>-1</sup> )	$\Delta G(P)$ (cal mol <sup>-1</sup> )	$y_i$
<i>n</i> -Octane	800	-2627	0	6.88
<i>n</i> -Nonane	900	-3062	0	8.89
<i>n</i> -Decane	1000	-3775	0	9.89
<i>n</i> -Undecane	1100	-3932	0	10.88
<i>n</i> -Dodecane	1200	-4368	0	11.88
Oct-2-yne	867	-2776	-235	7.55
<i>cis</i> -Hydrindane	1013	-3453	-121	9.02
Benzene	696	-1858	-342	5.85
Methyl benzene	802	-2323	-344	6.90
Ethyl benzene	892	-2714	-330	7.80
<i>n</i> -Propyl benzene	984	-3104	-323	8.72
<i>n</i> -Butyl benzene	1083	-3535	-334	9.72
<i>n</i> -Pentyl benzene	1181	-3966	-336	10.70
Butan-2-one	672	-1428	-654	5.61
Pentan-2-one	764	-1832	-641	6.52
Hexan-2-one	870	-2269	-643	7.58
Heptan-2-one	972	-2698	-647	8.60
Octan-2-one	1074	-3127	-651	9.63
Cyclohexanone	999	-3770	-744	8.87
Butanol-1	686	-1699	-443	5.75
Pentanol-1	792	-2134	-445	6.80
Hexanol-1	895	-2569	-447	7.83
Heptanol-1	999	-3004	-432	8.87
Octanol-1	1101	-3439	-451	9.90
Cyclohexanol	929	-2697	-480	8.17
2-Methyl-2-pentanol	769	-2113	-321	6.57
<i>n</i> -Propyl formate	673	-1554	-595	5.62
<i>n</i> -Butyl formate	778	-2007	-598	6.66
Ethyl acetate	657	-1451	-593	5.46
<i>n</i> -Propyl acetate	761	-1887	-576	6.49
<i>n</i> -Butyl acetate	863	-2347	-582	7.51
Pyridine	809	-2062	-655	6.97
Aniline	1026	-2848	-744	9.15
<i>N,N</i> -Dimethylaniline	1140	-3510	-558	10.29
Butyronitrile	773	-1653	-853	6.61
Valeronitrile	881	-2136	-856	7.69
Hexanenitrile	985	-2567	-860	8.73
Benzonitrile	1090	-2939	-899	9.79
1-Nitropropane	840	-1951	-888	7.28
Nitrobenzene	1191	-3386	-860	10.80
1-Chlorobutane	688	-1803	-341	5.77
1-Iodobutane	854	-2584	-214	7.42
1,1,1-Trichloroethane	685	-1813	-304	5.74
Chlorobenzene	891	-2610	-442	7.79
1,4-Dioxane	759	-1950	-654	6.47

0.2617, with  $r=0.82$  for *n*-octane and derivatives. For benzene and derivatives it is  $\Delta y_i(RX) = -0.00691[\Delta G(P)] - 1.6688$ , with  $r=0.90$ ; and for all the 12 solutes in Table 5 (*n*-octane not included) it is

$\Delta y_i(RX) = -0.00592[\Delta G(P)] - 0.919$ , with  $r=0.84$ . It seems demonstrated that  $\Delta y_i(RX)$  of the described chemical functions with respect to an *n*-alkane parent (RH) agrees quite well with the polar Gibbs solution



Table 4

Retention index,  $I_i$ , cavity/dispersion and polar partial molar Gibbs energy of solution,  $\Delta G(C/D)$  and  $\Delta G(P)$ , respectively, and relative partial molar Gibbs energy,  $y_i$ , for 33 solutes on PPI (polypropylene) at 383.2 K

Compound	$I_i$	$\Delta G(C/D)$ (cal mol <sup>-1</sup> )	$\Delta G(P)$ (cal mol <sup>-1</sup> )	$y_i$
<i>n</i> -Decane	1000	-4391	0	9.46
Cyclopentane	587	-2065	-121.5	4.47
Cyclohexane	696	-2638	-137	6.05
Cycloheptane	830	-3357	-154	7.60
Cyclooctane	953	-4015	-178	8.89
Cyclohexene	705	-2638	-152	6.17
Benzene	670	-2391	-347	5.79
Toluene	774	-2958	-344	6.86
Ethylbenzene	861	-3435	-346	7.91
Methyl chloride	373	-684	-181.8	1.87
Methylene chloride	516	-1583	-275.7	3.76
Chloroform	610	-2068	-271.4	5.19
Carbon tetrachloride	681	-2430	-284	5.90
Butyl chloride	639	-2323	-170	5.48
Pentyl chloride	747	-2851	-169.5	6.59
Chlorohexane	843	-3434	-167	7.73
Chlorooctane	1042	-4482	-163.2	9.88
1,1-Dichloroethane	568	-1896	-232.5	4.28
1,2-Dichloroethane	628	-2166	-302	5.37
Methylchloroform	648	-2335	-232	5.57
Chlorobenzene	852	-3308	-418.3	7.82
Propanone	465	-1243	-225	3.24
Pentan-2-one	555	-1865	-220	4.15
Tetrahydrofuran	609	-2233	-224	5.18
Dioxane	675	-2502	-291	5.84
Methyl acetate	503	-1469	-197.4	3.63
Ethyl acetate	555	-1894	-179.3	4.15
<i>n</i> -Propyl acetate	658	-2426	-169.4	5.67
<i>n</i> -Butyl acetate	752	-2988	-161.6	6.64
Ethanol	396	-1021	-183	2.10
Propanol-1	524	-1596	-167.6	3.84
Butanol-1	596	-2196	-163.1	4.56
Pentanol-1	708	-2728	-161.3	6.20

energy contribution,  $\Delta G(P)$ , deduced from Abraham's model [11], although the solutes involved have different molecular volumes.

Table 6 contains  $y_i$ ,  $\Delta y_i(RX)$  and the cavity/dispersion and polar components of the Gibbs solution energy calculated according to Eqs. (13) and (14), respectively, for the chemical functions of Table 4: chloroalkyl compounds, chloromethanes, cycloalkenes, cycloalkanes, alkanols, acetates and chloroethanes. It is observed that the Gibbs energy cavity/dispersion term increases in absolute value as the carbon chain length increases for all the solutes within each series. Just the opposite trend is found for the polar Gibbs energy contribution, since it

decreases slightly in absolute value with increasing carbon chain length in chloroalkyl compounds. The value of  $-418$  cal mol<sup>-1</sup> for chlorobenzene can be considered as normal, because the benzyl radical is expected to be much more polar than the other *n*-alkyl radicals, cycloalkenes and dioxane, alkanols and esters. However,  $\Delta G(P)$  increases in absolute value for chloromethanes (for which chain length remains unchanged), and also increases slightly for cycloalkanes, due to the slightly increasing  $R_2$  descriptor for higher terms in Abraham's equation [11]. Besides, a remarkable difference between the two dichloroethanes can be seen at the bottom of Table 6.

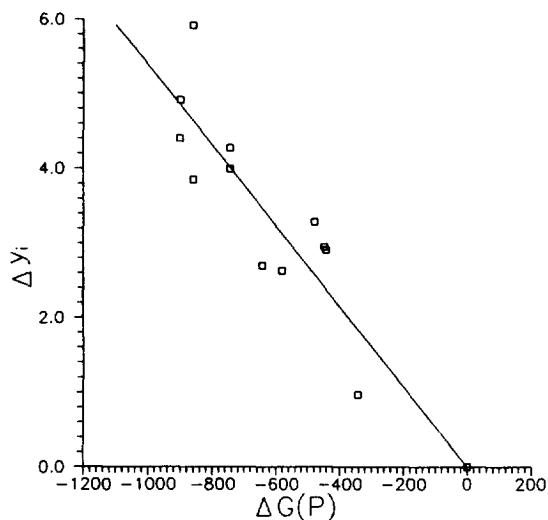


Fig. 3. Plot of  $\Delta y_i(\text{RX})$  against  $\Delta G(\text{P})$  on  $t=\text{TEPS15}$  at 393.2 K for  $n$ -hexane and 12 chemical functions, RX, of increasing polarity:  $n$ -butyl acetate, hexan-2-one, cyclohexanone, aniline, hexanenitrile, 1-nitrohexane, benzonitrile and nitrobenzene ( $-900 \text{ cal mol}^{-1}$ ).

There exists a good correlation between  $y_i/\Delta y_i(\text{RX})$  and  $\Delta G(\text{P})$  and between  $y_i/\Delta y_i(\text{RX})$  and  $\Delta G(\text{C/D})$  for these series:

(a) chloroalkyl compounds:  $y_i = 0.412[\Delta G(\text{P})] + 76.49$  ( $r = 0.96$ ) and  $y_i = -0.0020[\Delta G(\text{C/D})] + 0.494$  ( $r = 0.95$ );  $\Delta y_i = -0.00213[\Delta G(\text{C/D})] - 1.3639$  ( $r = 1.00$ ) and  $\Delta y_i = 0.4083[\Delta G(\text{P})] + 75.94$  ( $r = 0.96$ ) after the removing of chlorobenzene;

(b) methane and chloromethanes:  $\Delta y_i = -0.0169[\Delta G(\text{P})] - 0.4367$  ( $r = 0.80$ ) and  $\Delta y_i = -0.00167[\Delta G(\text{C/D})] + 1.0177$  ( $r = 0.95$ );

(c) chloroalkanes and chlorobenzene:  $y_i = 0.412[\Delta G(\text{P})] + 76.49$  ( $r = 0.96$ ) and  $y_i = -0.0020[\Delta G(\text{C/D})] + 0.494$  ( $r = 0.95$ );

(d) cycloalkanes:  $y_i = -0.0781[\Delta G(\text{P})] - 4.783$  ( $r = 0.98$ ) and  $y_i = -0.00225[\Delta G(\text{C/D})] - 0.0356$  ( $r = 0.99$ );

(e) alkanols:  $y_i = 0.1592[\Delta G(\text{P})] + 31.03$  ( $r = 0.85$ ) and  $y_i = -0.0023[\Delta G(\text{C/D})] - 0.104$  ( $r = 0.97$ );

(f) esters:  $y_i = 0.0841[\Delta G(\text{P})] + 19.9$  ( $r = 0.88$ ) and  $y_i = -0.00208[\Delta G(\text{C/D})] + 0.455$  ( $r = 0.98$ ); and

(g) for benzene and derivatives, worse correlations were obtained:  $y_i = 0.00162[\Delta G(\text{P})] + 0.877$  ( $r = 0.88$ ) and  $y_i = -0.00091[\Delta G(\text{C/D})] - 1.84$  ( $r = 0.67$ ).

So, it is demonstrated that  $y_i$  and  $\Delta y_i(\text{RX})$  are, as  $S_{ci}$  and  $\Delta S_{ci}(\text{RX})$ , parameters with a strong relationship to solute–solvent interactions of polar type. Therefore, it is basically correct to characterize a chemical function by means of its polar group constant  $\Delta y_i(\text{RX})$  value.

### 3.3. Gibbs solution energy and stationary phases polarity

The strength or power [3] (the more widespread name is polarity) of the SP affects the Gibbs solution energy of the solutes, i.e., the solute–solvent interac-

Table 5

$\Delta y_i(\text{RX})$ , polar group constant, Gibbs solution energy polar contribution,  $\Delta G(\text{P})$ , calculated with Abraham's equation, and Van der Waals molecular volumes for six solutes derived from  $n$ -octane and for five solutes derived from benzene

Compound	$\Delta y_i(\text{RX})$	$\Delta G(\text{P})$ (cal mol $^{-1}$ )	$V_i(\text{RX})$ (cm $^3$ mol $^{-1}$ )
$n$ -Octane	0	0	117
Octyn-2-e	0.67	-235	112.7
Ethylbenzene	0.92	-330	99.8
$n$ -Hexyl acetate	2.63	-588	124.5
Octan-2-one	2.75	-652	118.6
Octanol-1	3.02	-451	122.9
Octanenitrile	3.85	-861	122.5
Benzene	0	-342	71.6
Methylbenzene	0.95	-344	85.7
Chlorobenzene	1.94	-442	83.9
Aniline	3.30	-744	87.1
Benzonitrile	3.94	-899	87.1
Nitrobenzene	4.95	-860	89.1

SP, TFPS15; temperature, 393.2 K.

Table 6

$y_i$ ,  $\Delta y_i(\text{RX})$  and cavity/dispersion and polar contributions to the Gibbs free energy of solution,  $\Delta G(\text{C/D})$  and  $\Delta G(\text{P})$ , respectively, for several RX chemical functions on PP1 at 383.2 K

Solute	$y_i$	$\Delta y_i(\text{RX})$	$\Delta G(\text{C/D})$ (cal mol <sup>-1</sup> )	$\Delta G(\text{P})$ (cal mol <sup>-1</sup> )
CH <sub>3</sub> Cl	1.87	0	-684	-182
C <sub>4</sub> H <sub>9</sub> Cl	5.48	3.61	-2323	-170
C <sub>5</sub> H <sub>11</sub> Cl	6.59	4.72	-2851	-169
C <sub>6</sub> H <sub>13</sub> Cl	7.73	5.86	-3434	-167
C <sub>6</sub> H <sub>5</sub> Cl	7.82	5.95	-3308	-418
C <sub>8</sub> H <sub>17</sub> Cl	9.88	8.01	-4482	-163
CH <sub>4</sub>		0	883	0
CH <sub>3</sub> Cl		1.41	-684	-182
CH <sub>2</sub> Cl <sub>2</sub>		3.30	-1583	-276
CHCl <sub>3</sub>		4.73	-2068	-271
CCl <sub>4</sub>		5.44	-2430	-284
Benzene		0.33	-2391	-347
1,4-Dioxane		0.38	-2502	-291
Cyclohexane		0.59	-2758	-137
Cyclohexene		0.71	-2638	-152
Cyclopentane	4.47		-2065	-121.5
Cyclohexane	6.05		-2638	-137
Cycloheptane	7.60		-3357	-154
Cyclooctane	8.89		-4015	-178
Ethanol	2.10		-1021	-183
<i>n</i> -Propanol	3.84		-1596	-168
<i>n</i> -Butanol	4.56		-2196	-163
<i>n</i> -Pentanol	6.20		-2728	-161
Methyl acetate	3.63		-1469	-197
Ethyl acetate	4.15		-1894	-179
<i>n</i> -Propyl acetate	5.67		-2425	-169
<i>n</i> -Butyl acetate	6.64		-2988	-162
1,1-Dichloroethane	4.28		-1896	-232
1,2-Dichloroethane	5.37		-2166	-302
1,1,1-Trichloroethane	5.57		-2335	-232

tions, depending on which SP the analyte is chromatographed. Table 7 shows the dependence of  $y_i$  on the cavity/dispersion Gibbs solution energy term,  $\Delta G(\text{C/D})$ , and on the polar Gibbs energy of solution term,  $\Delta G(\text{P})$ , of eight solutes on 10 SPs of different polarity increasing from top to bottom, at 393.2 K. It is shown that: (a) for *n*-hexane,  $y_i$  decreases with increasing SP polarity, while  $\Delta G(\text{C/D})$  increases in the same way; (b) for the other solutes, even for the non-polar benzene,  $\Delta G(\text{P})$  decreases as the SP polarity increases, but the contrary occurs for the cavity/dispersion term and  $y_i$ , the two increasing with increasing SP polarity. From Table 7, good  $y_i$  vs.  $\Delta G(\text{C/D})$  and  $y_i$  vs.  $\Delta G(\text{P})$  correlations can be expected. The arithmetic mean of the correlation coefficients were 0.85 and 0.98, respectively, i.e., the

latter correlations are much better. Fig. 4a,b show the variation of  $y_i$  of *n*-hexane and some other polar solutes against the polarity of five methyl(3,3,3-TFP)siloxanes. It can be inferred that the more polar the SP, the larger the  $y_i$  value will be, except for *n*-hexane, for which  $y_i$  decreases with increasing SP polarity.

Table 8 shows the  $y_i$  dependence on the cavity/dispersion and polar terms of the Gibbs energy of solution of three hydrocarbons and another nine polar solutes on four of Tian and Munk's SPs at 383.2 K: PEE, PBMA, PCL and PECH, ordered by increasing polarity. It is found that: (a)  $y_i$  decreases with increasing SP polarity for *n*-undecane, and  $\Delta G(\text{C/D})$  increases (less negative values) with increasing SP polarity; (b) for the remaining solutes,  $y_i$

Table 7  
 $y_i$  and Gibbs solution energy cavity/dispersion and polar contributions,  $\Delta G(C/D)$  and  $\Delta G(P)$ , respectively, for 10 stationary phases at 393.2 K

SP	<i>n</i> -Hexane		Benzene		Butanol-1		Pentane 2-one		Pyridine		Ethyl acetate		<i>N,N</i> -Dimethylamine		Butyronitrile									
	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$								
OV-101	4.96	-1922	0	5.66	-2027	-287	5.58	-1863	-397	5.82	-1586	-369	6.71	-2235	-467	4.84	-1610	-324	9.39	-3716	-480	-1817	-443	
OV-105	4.84	-1993	0	5.73	-2095	-232	5.78	-1934	-501	6.02	-1662	-418	6.68	-2300	-443	4.83	-1685	-375	8.77	-3759	-394	-1888	-515	
TPPS00	4.88	-2018	0	5.56	-2122	-193	5.32	-1959	-263	5.58	-1682	-240	6.22	2330	-304	4.83	-1705	-210	8.77	-3811	-316	5.10	-1912	-299
TPPS09	5.01	-1900	0	5.83	-2003	277	5.67	-1841	-388	6.26	-1566	-486	6.78	2209	-504	5.32	-1590	-439	10.12	-3679	-445	6.22	-1795	-642
TPPS15	4.91	-1757	0	5.87	-1858	-342	5.77	-1699	-654	6.56	-1428	-655	5.48	-1451	-592	5.48	-1451	-592	10.31	-3510	-558	6.64	-1653	-853
TPPS25	4.72	-1582	0	5.96	-1680	-439	6.05	-1527	-633	7.12	-1266	-902	7.60	-1876	-877	5.94	-1288	-819	10.69	-3270	-717	7.41	-1483	-1180
TPPS26	4.69	-1502	0	5.93	-1602	-455	6.03	-1445	661	7.09	-1180	-952	7.56	-1801	-919	5.92	-1203	-865	10.67	-3219	-750	7.38	-1401	-1236
TPPS50	4.47	-1214	0	6.31	-1300	-695	6.39	-1165	944	8.08	-935	-1434	8.26	-1473	-1400	7.04	-954	-1300	11.83	-2704	-1154	9.17	-1126	-1844
TPPS50	4.06	-1064	0	6.52	-1153	-710	6.80	-1014	-943	8.42	-778	-1384	8.73	-1330	-1371	6.39	-798	-1255	11.39	-2591	-1154	8.70	-974	-1818
Superox-20M	3.72	-1168	0	7.33	-1262	-1427	8.86	-1114	-2197	8.62	-862	-1585	8.73	-1451	-1928	6.39	-884	-1418	11.39	-2591	-2014	8.70	-974	-1818

Table 8  
 $y_i$ , cavity/dispersion Gibbs solution energy contribution,  $\Delta G(C/D)$ , and polar Gibbs solution energy contribution,  $\Delta G(P)$ , of 12 solutes on four Tian and Munk's stationary phases

Solute	Poly(ethylene)		Poly( <i>n</i> -Butylmethacrylate)		Polycaprolactone		Polypicthorhydrin	
	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$	$y_i$	$\Delta G(C/D)$
<i>n</i> -Undecane	9.94	-4913	9.78	-4285	9.20	-3787	8.78	-3173
Cyclooctane	8.63	-4042	8.68	-3450	8.48	-3010	8.60	-2443
Benzene	5.65	-2484	6.56	-1956	7.05	-1658	7.37	-1138
Butanone	4.31	-1980	5.88	-1473	6.46	-1168	7.33	-715
Ethyl acetate	4.36	-2008	5.32	-1499	7.12	-1192	6.73	-738
<i>n</i> -Butanol	4.94	-2298	6.91	-1777	8.07	-1451	7.87	-981
Tetrahydrofuran	5.09	-2333	5.95	-1811	6.39	-1483	7.15	-1011
Chloroform	5.07	-3362	5.97	-1660	7.21	-1342	6.73	-879
Dioxane	5.69	-2591	7.19	-2059	8.05	-1714	8.89	-1227
1,1-Dichloroethane	4.53	-2010	5.07	-1501	6.20	-1194	6.11	-740
Chlorohexane	7.45	-3485	8.26	-2916	8.35	-2512	8.46	-1956
Chlorobenzene	7.55	-3362	8.91	-2798	9.46	-2402	9.64	-1873

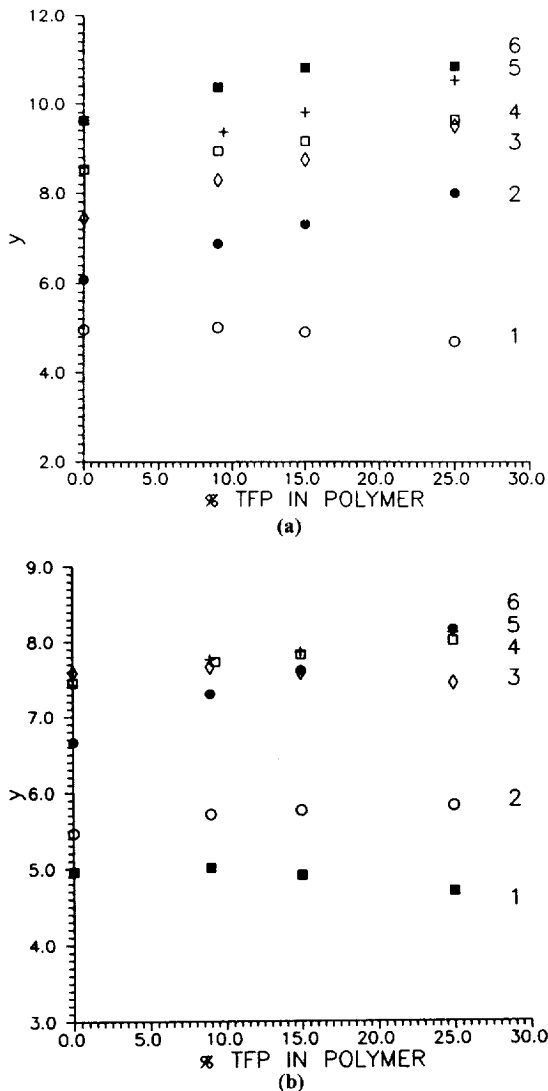


Fig. 4. Plot of  $y_i$ , relative Gibbs solution energy, of *n*-hexane and other derived polar solutes, versus the polarity of methyl(3,3,3-trifluoropropyl)siloxanes, expressed as their percentage of 3,3,3-TFP substitution at 393.2 K. (a) Solutes: 1, *n*-hexane; 2, 1-nitropropane; 3, hexanenitrile; 4, aniline; 5, benzonitrile; and 6, nitrobenzene. (b) Solutes: 1, *n*-hexane; 2, 1,1,1-trichloroethane; 3, oct-2-yne; 4, chlorobenzene; 5, hexanol-1; and 6, hexan-2-one.

and  $\Delta G(C/D)$  increase with increasing SP polarity; while (c)  $\Delta G(P)$  decreases (more negative values) with increasing SP polarity.

From Table 8, good  $y_i$  vs.  $\Delta G(C/D)$  and  $y_i$  vs.  $\Delta G(P)$  correlations should be obtained. Mean correlation coefficients evaluated as the arithmetic mean

of the correlation coefficients for each of the 13 solutes (one less for the correlations of  $y_i$  and  $\Delta G(P)$ ) were 0.87 and 0.944, respectively. Again, the correlations between  $y_i$  and  $\Delta G(P)$  are better. Cyclooctane was discarded because of its poor correlations.

### 3.4. The relationship between $S_{ci}$ and $y_i$

Table 9 shows density,  $\rho$ ;  $b$  value; Kováts coefficients,  $K_c$ ; partial molar Gibbs energy per methylene,  $\Delta G_{kCH_2}^0$  (in  $J mol^{-1}$ ); and  $E_R$  values, calculated with Eq. (7), of 20 SPs. A first group, with seven methyl(3,3,3-TFP) siloxanes; a second group, with OV-101, OV-25, OV-225, Superox 20M and Carbowax 20M; and a third group, with eight Munk's SPs and squalane, calculated with data taken from Ref. [7].

There is a close relationship between the molecular structural coefficient of a solute and 100 times its relative partial molar Gibbs energy,  $100y_i$ , for a given SP and temperature. According to Eq. (8),  $100y_i$  exceeds  $S_{ci}$  by the  $E_R$  term, which depends on both the density and the polarity of the SP, i.e., only on the chromatographic column for a given temperature and carrier gas. From Table 9,  $\rho$  increases with increasing polarity, while  $b$  decreases with increasing polarity for each of the five listed group of SPs. From Eq. (6), the polarity of the SPs contributes to  $E_R$  with the reciprocal of the  $b$  value, while the density is part of the sum [ $\log \rho + 0.15816$ ]. The mean percentage of  $\log \rho$  with respect to  $(1/b)$  is 3.9, 3.8 and 2.7%, respectively, for the above three groups, with an average value of 3.5%, i.e., the weight of the density in Eq. (7) is negligible. The difference between  $100y_i$  and  $S_{ci}$  is mostly due to the SP polarity ( $b$  value, as long as *n*-alkanes are used as markers).  $E_R$  for squalane is the lowest value, being the less polar SP.

$E_R$  increases with increasing SP polarity. Therefore,  $100y_i$  will be very close to  $S_{ci}$  for apolar SPs, while their difference will increase with increasing polarity of the SP.

## 4. Conclusions

The following conclusions have been reached:

(1) The molecular structural coefficient increment,

Table 9

Density,  $\rho$  (g ml<sup>-1</sup>);  $b$  value; Kováts coefficients,  $K_i$ ; partial molar Gibbs energy per methylene,  $[\Delta G_{kCH_2}]$  (J mol<sup>-1</sup>), and  $E_R$  for 20 SPs at 393.2 K

SP	$\rho$ (g ml <sup>-1</sup> )	$b$	$K_i$	$\Delta G_{kCH_2}^0$ (J mol <sup>-1</sup> )	$E_R$
PS-255	0.8836	0.2501	144	-1873	41.7
TFPS09	0.9563	0.2418	156	-1814	57.4
TFPS15	0.9843	0.2355	173	-1768	64.2
TFPS25	1.0552	0.2303	212	-1710	78.8
TFPS26	1.0580	0.2257	208	-1697	80.9
QF-1	1.1665	0.2058	302	-1542	109.3
OV-215	1.1665	0.2050	270	-1534	109.8
OV-101	0.9026	0.2499	146	-1860	45.4
OV-25	1.1061	0.2429	231	-1818	83.1
OV-225	1.0572	0.2294	293	-1718	79.5
Superox 20M	1.0351	0.2267	301	-1701	76.4
CW 20M	1.1026	0.2157	429	-1860	93.0
PDMS <sup>a</sup>	0.7529	0.2598	60	-1952	13.4
PPI	0.7838	0.2622	69	-1969	20.0
PEE	0.7890	0.2780	135	-2086	19.9
PBMA	0.9890	0.2550	182	-1914	63.9
PCL	0.9395	0.2404	219	-1806	54.5
PEA	1.0278	0.2229	220	-1676	76.3
PECH	1.2123	0.2227	337	-1676	108.5
PMA	1.1364	1.1970	367	-1497	108.5
SQ <sup>b</sup>	0.7506	0.2899	146	-2178	11.6

<sup>a</sup>Values obtained by extrapolation [21].

<sup>b</sup>Squalane, data taken from Ref. [7].

$\Delta S_{ci}(RX)$ , of a solute  $i$  and the parent  $n$ -alkane of the same carbon atom number  $Z$  increases with increasing RX group polarity for a given SP.

(2) For the same RX,  $\Delta S_{ci}(RX)$  increases with increasing SP polarity. There are good correlations between these increments and the Gibbs solution energy polar contribution,  $\Delta G(P)$ , given by Abraham's solvation model [11]. Therefore, it is correct to say  $\Delta S_{ci}(RX)$  as accounting for the polar solute-solvent interactions taking place in retention.

(3) The use of  $y_i$  instead of  $\Delta G_{ki}^0$  is advantageous, because the minus sign disappears from the modified Golovnya et al. equation.

(4) For a given SP, one more methylene in a given chemical function produces a shift of one unit on  $y_i$ .

(5) The  $y_i(RX)$  of a polar solute is larger than the  $y_Z$  of the  $n$ -alkane with the same carbon atom number from which it derives.

(6) The more polar the solute, the larger the  $y_i$  for a given SP, and for a given solute, the more polar the SP, the larger the  $y_i$ .

(7) The  $\Delta y_i(RX)$  increment between  $y_i$  of a solute  $i$  (of a given chemical function) and  $y_Z$  or  $y(RH)$  of the parent  $n$ -alkane, called constant of polar group, is useful for a qualitative evaluation of the solute-stationary-phase interactions.  $\Delta y(RX)$  and  $\Delta G(P)$  were linearly correlated for six chemical functions derived from  $n$ -octane, although the solutes involved do not have equal molecular volumes, as Poole demonstrated [8]. The unaccounted for cavity/dispersion contributions for functional groups are, therefore, correctly assigned to the polar solute-solvent interactions.

(8) The  $y_i$  and  $\Delta y_i(RX)$  and  $S_{ci}$  and  $\Delta S_{ci}(RX)$  parameters correlate fairly well with the Gibbs solution energy non-polar and polar contributions deduced from Abraham's equation [11]. On the other hand, they are easily and directly calculated from the retention data.

(9)  $100y_i$  and  $S_{ci}$  are closely related through the Gibbs solution energy. The two parameters tend to become equal the less polar the SP.

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