Gas chromatography system constant database over an extended temperature range for nine open-tubular columns

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ABSTRACT

The solvation parameter model is used to characterize the retention properties of poly(octylmethylsiloxane), poly(dimethyldiphenylsiloxane), silphenylene-dimethylsiloxane copolymer, poly(dimethylmethyltrifluoropropylsiloxane), poly(3-cyanopropylphenyldimethylsiloxane), and poly(ethylene glycol) (SPB-Octyl, HP-5, Rxi-17, Rxi-5Sil MS, Rtx-OPP, DB-1701, DB-225, Rtx-440 and HP-INNOWAX) stationary phases over an extended temperature range from 60 °C to close to the maximum column operating temperature. System maps constructed from the system constant database are used to evaluate the influence of temperature on the contribution of intermolecular interactions to differences in selectivity. None of the stationary phases are hydrogen-bond acids. Increasing temperature reduces the contribution from cavity formation/dispersion, dipole-type interactions and hydrogen-bond basicity in a stationary phase specific manner with their preservation to the highest temperature studied for each column. Electron lone pair interactions are generally repulsive at lower temperatures becoming attractive and leading to an increase in retention at higher temperatures.

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1. Introduction

Gas chromatography is widely recognized as the premier technique for the separation of thermally stable and volatile compounds [1–4]. With few exceptions, virtually all separations by gas chromatography today are performed on open-tubular columns obtained from commercial sources. For general applications, these columns are coated with a limited range of poly(siloxane), poly(ethylene glycol) and ionic liquid stationary phases or a thin layer of adsorbent [1,5–8]. For column selection the solvation parameter model has largely replaced unsuitable methods, such as the system of phase constants proposed by Rohrshneider and further developed by McReynolds [9,10]. Ambiguities and incorrect assumptions that underlie the measurement and use of the Rohrshneider/McReynolds phase constants for column selection are reviewed elsewhere [11–14] and need not be repeated here in detail. The salient features are that the prototypical compounds employed for phase characterization are not retained by a single dominant intermolecular interaction : the magnitude of the phase constants is determined largely by the solubility of the n-alkane retention index standards and only to a lesser extent by the solubility of the prototypical compounds: on polar stationary phases interfacial adsorption is an important retention mechanism for the n-alkane retention index standards: and the prototypical compounds have inadequate retention on some stationary phases at the reference temperature for measurements. The Rohrschneider/McReynolds and other approaches, in general, adopted a single temperature for column characterization. The capability of a stationary phase for specific intermolecular interactions responsible for its selectivity needs to consider temperature as a variable, since temperature is used to moderate retention in gas chromatography and temperature affects the intensity of intermolecular interactions in a stationary phase specific manner [14–17]. It cannot be assumed that selectivity differences at one temperature provide insight into the retention mechanism at a different temperature. To adequately characterize the separation properties of a stationary phase it is necessary to establish its capability for all intermolecular interactions contributing to retention over the useful temperature operating range for the stationary phase. This can be conveniently visualized using system maps, which are two-dimensional plots of the system constants of the solvation parameter model as a continuous function of temperature [5,18–20].

To overcome the difficulties of ranking stationary phases based on retention index differences attention initially shifted to scales based on the Gibbs free energy of solution, initially for a select group of compounds assigned specific intermolecular interactions, and eventually to solute-independent scales employing linear free

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energy relationships [14,22]. These evolved from the initial studies of Kamlet and Taft on the solvatochromic comparison method [21,22]. Abraham and co-workers [23–25] and Carr and co-workers [26–28] realized that the difficulty in applying the solvatochromic parameters to retention in gas chromatography was that the spectroscopic methods used to assign descriptors to compounds were defined by excited state interactions and not equilibrium free energies responsible for retention in gas chromatography. There were also experimental difficulties in the determination of the solvatochromic parameters for solid compounds. General evolution of these approaches led to the modern form of the solvation parameter model set out in Eq. (1) to describe retention at a set temperature in gas-liquid chromatography [5,14,29,30]

$$\log k = c + eE + sS + aA + bB + lL \tag{1}$$

where k is the retention factor for a specific compound, E, S, A, B and L are descriptors that describe the capability of a compound to interact with the complementary properties of the stationary phase described by the system constants e, s, a, b, l. The equation constant, c, is not solely a column property as it incorporates contributions from the lack-of-fit of the model to the experimental retention factors. When these contributions are minor it provides an indication of the column phase ratio. The equation constant is a system property required to estimate retention factors for a specific column and temperature but is not a characteristic property of the solvation properties of the stationary phase. The capability of the stationary phase for individual intermolecular interactions are defined as contributions from electron lone pair interactions (the excess dispersion interactions that result from the presence of polarizable electrons), e, interactions of a dipole-type (both orientation and induction), s, hydrogen-bonding interactions in which the stationary phase acts as a hydrogen-bond acceptor, a, or hydrogen-bond donor, b, and the contribution of cavity formation in the stationary phase and the set up of dispersion interactions, both of which are size dependent, l. The system constants are estimated using Eq. (1) by multiple linear regression analysis after inputting experimental retention factors for a suitable number of varied compounds that simultaneously satisfy experimental requirements for accessible retention factors and statistical requirements for model assessment [29,30]. This approach differs from the Rohrshneider/McReynolds approach in that the identity of the compounds employed for column characterization is not pre-defined. The compounds are selected to facilitate experimental measurements of the retention factors and to achieve a reasonable distribution over the descriptor space with minimal descriptor cross-correlation. This requires that the descriptor quality for the selected compounds is reasonably uniform. It also facilitates column characterization at different temperatures as the compounds employed at each temperature need not be the same as long as they meet the general requirements discussed above. This is the approach used in this study to obtain system maps for stationary phases with different retention properties over a wide temperature range. The calibrated columns were subsequently utilized together with liquid-liquid partition constants for the estimation of compound descriptors [31–33].

The solvation parameter model is based on a cavity model of partition from an ideal gas phase to a stationary liquid phase. A mixed retention mechanism comprising concurrent adsorption at the gas-liquid interface and/or liquid-column wall interface as well as gas-liquid partition is a possibility for some experimental conditions. Adsorption at the column wall is hopefully controlled by adequate column deactivation but adsorption at the gas-liquid stationary phase interface remains a possibility and is likely enhanced by low temperatures and for compounds of significantly different polarity to the stationary phase [26,34–36]. Under these circum-

stances a general retention mechanism for open-tubular columns can be written as [37]

$$k = K_L/\beta + K_A A_L/V_M \tag{2}$$

where K_L is the gas-liquid partition constant, β the column phase ratio, K_A the gas-liquid adsorption constant, A_L the interfacial surface area of the stationary phase and V_M the column hold-up volume corrected for gas compressibility. The system constants of the solvation parameter model will be independent of system (column) properties when either K_A is close to zero or A_L is negligible. It is generally argued that the stationary phase surface area for open-tubular columns is very small and this ameliorates the importance of interfacial adsorption compared with packed columns, which have been studied more extensively [17,35]. Since the liquid surface is likely corrugated and its surface area not easily measured this remains an assumption. For mixed retention mechanisms on packed columns it was shown that Eq. (1) can be used to model retention but the system constants are a function of the phase ratio [38]. As a unifying framework it was suggested that the retention characteristics of the interfacial region resemble those of the bulk liquid except that the interfacial region is less cohesive and the intensity of polar interactions are reduced. To ascertain the importance of gas-liquid interfacial adsorption on the precision of the system constants a screening evaluation described in section 3.6 was performed as part of the quality control procedure for the experimental data collected in this manuscript. For systems with a mixed retention mechanism the system constants are not expected to be independent of column properties because the stationary phase volume and surface area are unlikely to be correlated for changes in the phase ratio.

The specific aims of this study were to collate a database of system constants over the full operating temperature range for nine stationary phase chemistries commonly used for gas chromatography, and which are representative of the selectivity space available for separations by gas-liquid chromatography [1,5]. A unique feature of this study is that the system constants are based on a single-laboratory retention factor database using a standard measurement protocol and evaluated for contributions from interfacial adsorption to the retention mechanism. Compared with previous studies [5,18–20] we have increased the number and variety of compounds employed, extended the temperature range covered in some cases, and used updated values for the solute descriptors demonstrated to be more precise for characterizing intermolecular interactions in chromatographic and liquid-liquid partition systems [31–33].

2. Experimental

2.1. Materials

Common organic chemicals and solvents were of the highest purity available and obtained from several sources. Organosiloxane compounds were obtained from Gelest (Morrisville, PA, USA). The wall-coated open-tubular columns were obtained from Agilent (Folsom, CA, USA), Restek (Bellefonte, PA, USA) and Supelco (Bellefonte, PA, USA) and are summarized in Table 1.

2.2. Gas chromatography

Retention factors at 20 °C intervals over the temperature range indicated in Table 1 were obtained with an Agilent Technologies HP-6890 gas chromatograph (Wilmington, DE, USA) fitted with a split/splitless injector and flame ionization detector. Nitrogen was used as the carrier gas at a constant velocity of about 40 cm / s. Samples (≈ 1 mg / mL) were introduced by split injection (split ratio 30:1 to 100:1) with a purge flow of 1 mL / min. The injector temperature

Table 1
Wall-coated open-tubular columns and temperature range evaluated in this study.

Name	Manufacturer	Dimensions			Temperature	Stationary Phase
		Length (m)	Internal diamter (mm)	Film thickness (μm)	range (°C)	
SPB-Octyl	Supelco	30	0.25	0.25	60-140	Poly(methyloctylsiloxane)
		30	0.25	1	160-260	
HP-5	Agilent	30	0.32	0.25	60-140	Poly(dimethyldiphenylsiloxane)[1]
		30	0.25	0.1	160-300	
Rxi-5Sil MS	Restek	30	0.25	0.5	60-320	1,4-Bis(dimethylsiloxy)phenylene-dimethylsiloxane
Rxi-17	Restek	30	0.25	0.5	60-260	Poly(dimethyldiphenylsiloxane)[2]
Rtx-440	Restek	30	0.25	0.25	60-140	Proprietary structure (see section 3.4)
		30	0.25	0.5	160-300	
DB-1701	Agilent	30	0.25	0.25	60-140	Poly(3-cyanopropylphenyldimethylsiloxane)[3]
		30	0.25	1	160-260	
Rtx-OPP	Restek	30	0.32	0.5	60-140	Proprietary structure (see section 3.3)
		30	0.32	0.15	160-300	
DB-225	Agilent	15	0.25	0.25	60-240	Poly(3-cyanopropylphenyldimethylsiloxane)[4]
HP-Innowax	Agilent	60	0.25	0.5	60-140	Poly(ethylene glycol)
		60	0.53	1	160-220	

[1] Contains 5% diphenylsiloxane monomer.
[2] Contains 50% diphenylsiloxaane monomer.
[3] Contains 14% 3-cyanopropylphenylsiloxane monomer.
[4] Contains 50% 3-cyanopropylphenylsiloxane monomer.

was varied between 200–260 °C depending on the volatility of the compounds with a detector temperature of 320 °C. Methane was used to determine the column hold-up time.

For retention factor measurements compounds of similar volatility were batched together and injected individually. A suitable reference standard was injected as the fifth, tenth, fifteenth, etc., sample in each sequence and its retention factor charted. If the retention factor for the reference standard fell outside the range established as two standard deviations of the mean for repeat injections of the reference standard then the sequence of samples since the last acceptable retention factor were re-measured after an instrument check. Retention factors for each compound were determined at several temperatures and fit to the general model

$$\log k = a_0 + a_1 T + a_2 T^2 \qquad (3)$$

where a_0, a_1 and a_2 are numerical constants not assigned any physical meaning and T is the column temperature (° C). Individual retention factors deviating from the best fit line through the data were re-measured. Finally, the collection of retention factors was used to calculate a retention model using the solvation parameter model as discussed in Section (2.3). Individual retention factors with a residual value > 2 times the standard deviation of the residuals for each model were re-measured. Compounds selected for re-measurement at each step were replicated to ensure repeatability and retained in the database if there was no experimental reason to support removal. The concentration of some compounds was varied to ensure that measurements occurred in a linear region of the sorption isotherm and a few compounds were removed at the onset because they failed to provide suitable asymmetry factors (outside the range 0.75–1.2 using the 5% peak height method). The retention factor database used for the columns in Table 1 is provided as supplementary material (Table S-1 to S-9).

2.3. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Dell Optiflex 9200 computer (Austin, TX, USA) using the program PASW v24.0 (SPSS, Chicago, IL, USA). The descriptors used in the solvation parameter model were taken from an in-house database and are summarized in Table 2 [31–33,39–43]. In some cases the descriptor values may differ from those in the

cited sources as further experimental results have been used in their optimization.

3. Results and discussion

3.1. Poly(methyloctylsiloxane) stationary phase

The poly(methyloctylsiloxane) stationary phase SPB-Octyl was included in the database as a low-selectivity stationary phase. It has been used for the direct measurement of the L descriptor, although as shown below, weak polar interactions contribute to the retention mechanism [44,45]. Ulrich et al. studied the temperature dependence of the system constants for SPB-Octyl over the temperature range 120–180 °C in the context of retention prediction in non-target analysis [46]. The system constants for the temperature range 60–260 °C are summarized in Table 3. The poly(methyloctylsiloxane) stationary phase is a non-hydrogen-bond acid ($b = 0$) and a weak hydrogen-bond base at temperatures < 100 °C only. It is weakly dipolar/polarizable with an s system constant that changes slightly with temperature from about 0.1 to 0.03 over a 200 °C temperature range. Retention is dominated by dispersion interactions (l system constant) with a small and variable contribution from electron lone pair interactions (e has values from 0.14 – 0.20 over a 200 °C temperature range). The fluctuations in the e and s system constants reflect the greater relative uncertainty in the determination of these small values compared with the l system constant. In addition, the retention factors used to obtain the models in Table 3 were obtained on two columns with a different phase ratio (see Table 1). The extent of crosslinking for the two columns is not necessarily the same nor is are the relative contributions from interfacial adsorption, if an applicable retention mechanism. The poly(methyloctylsiloxane) stationary phase is useful as a low-selectivity stationary phase having a small capacity for polar interactions. It represents the minimum point on the selectivity scale for pre-coated open-tubular columns with poly(siloxane) and poly(ethylene glycol) stationary phases [5,45]. Compared with poly(dimethysiloxane) stationary phases over the temperature range 60–140 °C, SPB-Octyl is a weaker hydrogen-bond base and less dipolar/polarizable making it a better candidate for a low-selectivity reference stationary phase [5,27,45–47].

Table 2
Descriptor values for compounds used for column characterization.

Compound	Descriptors				
	E	S	A	B	L
1-Acetonaphthone	1.517	1.436	0	0.557	6.649
1-Bromododecane	0.332	0.374	0	0.3	7.287
1-Bromonaphthalene	1.594	1.033	0	0.151	6.558
1-Chloronaphthalene	1.419	0.964	0	0.131	6.188
1-Hexyne	0.167	0.275	0.091	0.118	2.541
1-Hydroxyanthraquinone	1.502	1.489	0.049	0.542	9.077
1-Methylnaphthalene	1.332	0.916	0	0.196	5.699
1-Naphthol	1.407	1.101	0.758	0.332	6.192
1-Nitronaphthalene	1.392	1.482	0	0.288	6.842
1-Nitropropane	0.243	0.926	0.046	0.267	2.882
1-Nitropyrene	2.789	2.063	0	0.336	10.474
1-Phenylethanol	0.782	0.725	0.424	0.66	4.473
1-Phenyl-1-propanol	0.81	0.866	0.395	0.665	5.159
1-Phenyl-2-propanol	0.787	0.782	0.316	0.7	4.835
1,2-Dichlorobenzene	0.872	0.775	0	0.04	4.507
1,2-Dimethylbenzene	0.663	0.547	0	0.178	3.948
1,2,4-Trichlorobenzene	1.022	0.746	0	0.024	5.198
1,2,4,5-Tetrachlorobenzene	1.022	0.695	0	0.02	5.957
1,2,5,6-Dibenzoanthracene	3.837	2.286	0	0.54	12.53
1,3-Dibromobenzene	1.198	0.798	0	0.074	5.218
1,3-Dichlorobenzene	0.852	0.692	0	0.004	4.421
1,3-Dihydroxybenzene	0.973	0.963	1.286	0.498	4.877
1,3-Dimethylbenzene	0.625	0.504	0	0.183	3.845
1,3-Dinitrobenzene	0.985	1.715	0	0.424	5.971
1,3,5-Triethylbenzene	0.67	0.5	0	0.19	5.511
1,4-Dimethylbenzene	0.615	0.494	0	0.165	3.852
1,3-Bis(trimethylsiloxy)-1,3-dimethylsilane	−0.631	−0.182	0.073	0.473	4.535
1,3-Dichloro-1,1,3,3-tetramethyldisiloxane	−0.066	−0.012	0	0	4.168
1,5-Dichloro-1,1,3,3,5,5-hexamethyltrisiloxane	−0.234	0.313	0	0	4.539
1,5-Divinyl-1,1,3,3,5,5-hexamethyltrsiloxane	−0.26	0.028	0	0.588	4.689
1,12-Dodecanediol	0.456	0.807	0.817	1.217	7.531
2-(1-Naphthyl)ethanol	1.583	1.247	0.426	0.74	6.984
2-Acetonaphthone	1.481	1.478	0	0.6	6.765
2-Chloroacetamide	0.617	1.211	0.408	0.678	3.292
2-Chloroaniline	1.026	0.991	0.243	0.315	4.685
2-Chlorophenol	0.879	0.66	0.535	0.342	4.124
2-Ethoxyethanol	0.237	0.554	0.324	0.785	2.793
2-Heptanone	0.123	0.657	0	0.487	3.789
2-Hexanone	0.136	0.668	0	0.502	3.273
2-Methoxycinnamaldehyde	1.143	1.517	0	0.589	6.322
2-Methoxyethanol	0.268	0.591	0.362	0.84	2.338
2-Methoxynaphthalene	1.476	1.161	0	0.354	6.232
2-Methyl-2-butanol	0.193	0.388	0.247	0.657	2.538
2-Methylaniline	0.771	1.022	0.208	0.443	4.321
2-Methylbenzothiazole	1.075	0.953	0	0.558	5.78
2-Methylbutanol	0.217	0.429	0.336	0.52	2.981
2-Methylnaphthalene	1.197	0.921	0	0.19	5.778
2-Methylphenol	0.772	0.748	0.607	0.355	4.281
2-Methylpropanol	0.206	0.386	0.362	0.508	2.401
2-Naphthol	1.467	1.187	0.773	0.347	6.144
2-Nitroaniline	1.215	1.467	0.346	0.353	5.771
2-Nitrophenol	0.942	1.107	0.033	0.374	4.731
2-Nitropropane	0.216	0.898	0.01	0.312	2.707
2-Nitrotoluene	0.866	1.115	0	0.269	4.989
2-Nonanone	0.113	0.676	0	0.467	4.764
2-Octanone	0.109	0.661	0	0.509	4.277
2-Pentanone	0.143	0.681	0	0.485	2.731
2-Phenylacetamide	1.294	1.729	0.345	0.944	5.376
2-Phenylethanol	0.808	0.821	0.409	0.629	4.698
2-Phenyl-1-propanol	0.81	0.866	0.395	0.665	5.159
2-Undecanone	0.105	0.679	0	0.494	5.721
2,3-Dimethylphenol	0.851	0.8	0.564	0.402	4.862
2,4-Dimethylaniline	1.003	0.726	0.373	0.65	5.003
2,4-Dinitroaniline	1.496	2.351	0.284	0.507	7.681
2,6-Dichloro-4-nitroaniline	1.078	1.247	0.492	0.352	7.443
2,6-Dimethylphenol	0.752	0.774	0.413	0.406	4.635
2,2,4,4,6,6-Hexamethylcyclotrisilazane	0.203	0.296	0.124	0.682	4.762
2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclo-tetrasiloxane	−0.095	0.215	0	0.67	5.736
3-Aminopropyltriethoxysilane	−0.021	0.477	0.085	1.348	5.539
3-Methylaniline	0.779	1.058	0.195	0.457	4.404
3-Methylbutanol	0.198	0.423	0.35	0.513	2.968
3-Methylphenol	0.776	0.771	0.695	0.339	4.327
3-Nitroaniline	1.234	1.535	0.49	0.429	6.034

Table 2 (*Continued*)

Compound	Descriptors				
	E	S	A	B	L
3-Nitrotoluene	0.874	1.121	0	0.252	5.241
3-Phenylpropan-1-ol	0.81	0.866	0.395	0.665	5.159
3,3'-Dichlorobenzidine	1.737	1.921	0.752	0.436	10.025
3,4-Dichloroanilne	1.218	1.21	0.421	0.247	5.973
3,5-Dimethylphenol	0.786	0.799	0.662	0.337	4.759
4-Acetylbiphenyl	1.505	1.526	0	0.611	7.661
4-Bromoacetanilide	1.065	1.537	0.806	0.451	6.89
4-Chloro-2-nitroaniline	0.985	1.425	0.453	0.184	6.781
4-Chloroaniline	0.979	1.11	0.341	0.322	4.977
4-Chlorophenol	1.032	0.81	0.873	0.202	4.795
4-Cyanophenol	1.099	1.261	0.824	0.385	5.486
4-Dimethylaminoazobenzene	2.057	1.748	0	1.532	8.516
4-Fluoroaniline	0.723	0.958	0.331	0.41	4.063
4-Hydroxybenzaldehyde	1.156	1.263	0.913	0.467	5.243
4-Hydroxybezyl alcohol	1.24	1.285	0.989	0.764	5.119
4-Methoxy-2-nitroaniline	1.294	1.577	0.314	0.418	6.791
4-Methoxybenzyl alcohol	0.888	0.968	0.544	0.765	5.326
4-Methylphenol	0.828	0.791	0.664	0.364	4.314
4-Nitroaniline	1.233	1.813	0.591	0.346	6.383
4-Nitrobenzyl alcohol	1.008	1.356	0.51	0.584	6.347
4-Nitrotoluene	0.858	1.153	0	0.268	5.282
4-Phenylphenol	1.537	1.187	0.794	0.45	7.058
4,4'-Dibromobiphenyl	2.126	1.173	0	0.247	8.674
4,4'-Methylenedianiline	2.013	1.696	0.662	0.861	8.522
8-Hydroxyquinoline	1.037	1.082	0.196	0.388	5.967
Acenaphthene	1.44	0.941	0	0.219	6.727
Acenaphthylene	1.566	1.15	0	0.201	6.382
Acetamide	0.268	1.076	0.718	0.69	2.722
Acetoacetanilide	2.055	0.187	0.602	1.65	4.805
Acetophenone	0.806	1.057	0	0.496	4.488
alpha-Isomethyl ionone	0.721	0.843	0	0.812	6.485
alpha-Pinene	0.441	0.191	0	0.226	4.345
Amyl cinnamal	1.212	1.046	0	0.74	7.132
Androsterone	1.327	1.699	0.394	1.592	10.745
Aniline	0.955	1.021	0.239	0.424	3.944
Anisaldehyde	0.92	1.35	0	0.47	5.304
Anisole	0.712	0.761	0	0.313	3.81
Anthracene	1.995	1.309	0	0.259	7.723
Anthraquinone	1.735	1.504	0	0.563	8.572
Azulene	1.466	1.085	0	0.21	5.736
Benz[a]anthracene	2.735	1.678	0	0.368	10.124
Benzaldehyde	0.813	1.027	0	0.395	4.003
Benzamide	1.268	1.383	0.637	0.659	5.244
Benzene	0.608	0.506	0	0.144	2.784
Benzenesulfonamide	1.14	1.871	0.658	0.671	6.055
Benzidine	1.116	1.567	0.228	1.018	9.166
Benzodioxane	0.884	1.064	0	0.304	4.952
Benzo[a]pyrene	3.033	1.846	0	0.418	11.54
Benzo[e]pyrene	3	1.89	0	0.41	11.436
Benzo[ghi]perylene	3.612	2.11	0	0.436	12.707
Benzonitrile	0.742	1.128	0	0.332	4.055
Benzophenone	1.21	1.295	0	0.58	7.059
Benzothiazole	1.08	1.109	0	0.488	5.333
Benzyl 2-ethylhexyl phthalate	1.405	1.303	0	1.341	10.823
Benzyl alcohol	0.804	0.872	0.409	0.557	4.248
Benzyl cinnamate	1.206	1.509	0	0.622	8.997
Benzyl salicylate	1.317	1.263	0.041	0.438	8.073
beta-Pinene	0.525	0.233	0	0.208	4.584
Bis(trimethylsiloxy)methylsilane	−0.448	−0.149	0.066	0.365	3.794
Biphenyl	1.342	0.987	0	0.284	6.044
Borneol	0.671	0.638	0.201	0.634	5.135
Bromobenzene	0.882	0.729	0	0.092	4.038
Butan-1-ol	0.219	0.446	0.336	0.48	2.577
n-Butylbenzene	0.595	0.484	0	0.139	4.75
Butyl acetate	0.079	0.565	0	0.476	3.417
Butyl benzoate	0.668	0.877	0	0.389	5.954
Butyl benzyl phthalate	1.296	1.72	0	1.007	9.803
Butyl cyclohexyl phthalate	1.083	1.423	0	0.911	9.6
Butyl decyl phthalate	0.742	1.354	0	1.689	8.397
Butyl 2-ethylhexyl phthalate	0.722	1.144	0	1.045	11.287
Butyl octyl phthalate	0.751	1.593	0	0.938	8.32
Butyl oleate	0.024	0.628	0	0.582	10.855
Butyl stearate	0.051	0.52	0	0.645	11.001
Camphor	0.573	0.846	0	0.664	5.031

Table 2 (*Continued*)

Compound	Descriptors				
	E	S	A	B	L
Carbazole	2.271	1.633	0.393	0.157	7.39
Carvone	0.638	0.928	0	0.611	5.406
Chlorobenzene	0.718	0.656	0	0.058	3.622
Cholestane	1.186	0.391	0	0	13.004
Cholesterol	1.353	1.097	0.212	0.558	13.389
Cholesteryl acetate	1.234	0.977	0	0.334	14.276
Chrysene	2.593	1.66	0	0.294	10.142
Cinnamyl alcohol	1.1	0.97	0.469	0.598	5.465
Citronellal	0.287	0.674	0	0.756	5.076
Coumarin	1.426	1.649	0	0.525	5.966
Cyclohexanol	0.474	0.638	0.246	0.583	3.722
Cyclohexanone	0.403	0.887	0	0.531	3.771
Cyclohexanone oxime	0.73	0.677	0.45	0.596	4.442
Decaethylcyclopentasiloxane	−0.309	0.21	0	0.974	9.115
Decamethylcyclopentasiloxane	−0.698	−0.099	0	0.647	5.243
Decamethyltetrasiloxane	−0.717	−0.167	0	0.559	4.873
Decan-1-ol	0.26	0.444	0.318	0.549	5.611
n-Decane	0	0	0	0	4.7
Di-(2-Methoxyethyl) phthalate	0.788	1.742	0	1.507	8.35
Di-2-Ethylhexyl phthalate	0.693	1.157	0	1.401	11.255
Di-n-Butyl phthalate	0.694	1.321	0	0.93	8.508
Di-n-Butyl succinate	0.091	0.94	0	0.963	6.867
Di-n-Octyl phthalate	0.662	1.291	0	1.13	11.957
Di(2-Ethoxyethyl) phthalate	0.619	1.559	0	1.495	9.043
Di(2-n-Butoxyethyl) phthalate	1.084	1.505	0	1.458	10.546
Dibenzofuran	1.633	1.112	0	0.105	6.619
Dibenzyl ether	1.21	1.1	0	0.727	7.17
Dibenzylamine	1.418	1.005	0.068	0.99	7.529
Dicyclohexyl phthalate	1.464	1.516	0	1.064	10.722
Dicyclohexylamine	0.576	0.419	0	0.667	6.665
Dicylcohexyl adipate	0.649	1.275	0	1.073	10.052
Diethoxydimethylsilane	−0.15	0.176	0	0.699	3.29
Diethyl adipate	0.085	1.063	0	0.835	5.891
Diethyl diethylmalonate	0.01	0.729	0	0.867	5.645
Diethyl phthalate	0.725	1.393	0	0.887	6.68
Diethyl sebecate	0.043	1.058	0	0.981	7.871
Dihydrocholesterol	1.333	1.046	0.207	0.638	13.525
Diisobutyl phthalate	0.672	1.246	0	0.939	8.094
Dimethyl phthalate	0.795	1.502	0	0.798	5.965
Dioxane	0.329	0.739	0	0.592	2.833
Diphenyl ether	1.168	0.936	0	0.329	6.107
Diphenylamine	1.432	1.223	0.186	0.461	6.892
Dodecamethylcyclohexasiloxane	−0.88	−0.045	0	0.752	6.065
Dodecamethylpentasiloxane	−0.936	−0.175	0	0.717	5.729
n-Dodecane	0	0	0	0	5.685
Dodecan-1-ol	0.19	0.433	0.346	0.53	6.655
Ethyl benzoate	0.694	0.897	0	0.451	5.022
Ethyl 2-methylbutyrate	0.319	0.427	0	0.45	3.699
Ethyl oleate	0.144	0.582	0	0.625	9.978
Ethyl propionate	0.092	0.533	0	0.45	2.889
Ethylbenzene	0.613	0.509	0	0.147	3.8
Eugenol	1.076	0.82	0.398	0.572	5.765
Fluoranthene	2.402	1.51	0	0.292	8.719
Fluorene	1.659	1.103	0	0.255	6.952
Geranial	0.612	0.938	0	0.659	5.463
Geraniol	0.493	0.635	0.282	0.573	5.416
Glycidoxypropyltrimethoxysilane	0.067	1.12	0	0.981	6.202
Heptanal	0.14	0.643	0	0.435	3.855
n-Heptane	0	0	0	0	3.173
Heptan-1-ol	0.202	0.45	0.335	0.531	4.132
Hexachlorobenzene	1.53	0.819	0	0.126	7.73
n-Hexadecane	0	0	0	0	7.714
Hexaethylcyclotrisiloxane	−0.111	0.044	0	0.524	6.618
Hexamethylcyclotrisiloxane	−0.246	0.013	0	0.509	3.623
Hexamethyldisilane	0.101	0.083	0	0.173	3.26
Hexamethyldisilathiane	0.374	0.311	0	0.246	4.292
Hexamethyldisilazane	−0.038	−0.049	0.274	0.139	3.493
Hexamethyldisiloxane	−0.27	−0.187	0	0.299	3.115
Hexanal	0.146	0.639	0	0.45	3.35
n-Hexane	0	0	0	0	2.668
Hexan-1-ol	0.21	0.432	0.35	0.535	3.646
Hydroxycitronellal	0.54	0.562	0.68	1.08	5.496
Iodobenzene	1.182	0.782	0	0.135	4.549
Isocyanatopropyltriethoxysilane	−0.049	0.654	0	0.853	5.948

Table 2 (*Continued*)

Compound	Descriptors				
	E	S	A	B	L
Lilial	0.775	0.994	0	0.599	6.659
Limonene	0.497	0.338	0	0.164	4.689
Linalool	0.325	0.524	0.199	0.693	4.783
Methacryloxypropyltrimethoxysilane	0.046	0.873	0	1.051	6.208
Methyl abietate	1.164	1.091	0	1.108	10.268
Methyl benzoate	0.738	0.916	0	0.441	4.681
Methyl Cyclohexane	0.244	0.118	0	0	3.318
Methyl decanoate	0.057	0.558	0	0.489	5.872
Methyl eugenol	0.939	0.991	0	0.827	5.977
Methyl hexanoate	0.084	0.566	0	0.47	3.967
Methyl nonanoate	0.054	0.557	0	0.449	5.421
Methyl octanoate	0.069	0.557	0	0.448	4.955
Methyl phenyl ether	0.71	0.77	0	0.31	3.808
Methylbis(trimethylsiloxy)vinylsilane	−0.424	−0.07	0	0.441	4.327
Methyltriethoxysilane	−0.23	0.249	0	0.751	3.869
Methyltris(trimethylsiloxy)silane	−0.739	−0.156	0	0.528	4.803
N-Methylacetamide	0.263	1.293	0.157	0.663	3.133
N-Methylaniline	0.95	0.9	0.17	0.48	4.478
N,N-Diethyl-4-nitroaniline	1.316	1.722	0	0.621	7.965
N,N-Diethylcarbanilide	1.735	1.265	0	1.346	7.948
N,N-Diethyldodecamide	0.394	0.934	0	0.966	8.719
N,N-Dimethyl-4-nitroaniline	1.029	1.917	0	0.339	7.208
N,N-Dimethylaniline	0.865	0.798	0	0.42	4.842
N,N-Diphenyl-4-phenylenediamine	2.67	1.847	0.524	1.106	10.369
Naphthalene	1.241	0.921	0	0.188	5.144
Neral	0.589	0.901	0	0.65	5.391
Nicotinamide	1.227	1.804	0.43	0.779	5.342
Nicotine	0.882	0.959	0	1.082	5.92
Nitrobenzene	0.846	1.143	0	0.268	4.53
Nonanal	0.121	0.635	0	0.399	4.84
n-Nonane	0	0	0	0	4.201
Nonan-1-ol	0.199	0.406	0.356	0.542	5.15
n-Octadecane	0	0	0	0	8.722
Octaethylcyclotetrasiloxane	−0.266	0.016	0	0.785	7.938
Octamethylcyclotetrasiloxane	−0.471	−0.084	0	0.513	4.473
Octamethyltrisiloxane	−0.498	−0.074	0	0.372	3.936
Octan-1-ol	0.199	0.464	0.327	0.543	4.635
Octan-2-ol	0.176	0.413	0.275	0.528	4.335
Octanal	0.148	0.629	0	0.415	4.364
n-Octane	0	0	0	0	3.689
Octanophenone	0.779	0.995	0	0.498	7.384
Octyltriethoxysilane	−0.255	−0.002	0	0.953	6.986
Pentachlorophenol	1.732	0.989	0.554	0.355	7.525
Pentan-1-ol	0.219	0.44	0.35	0.526	3.116
Pentan-2-ol	0.198	0.387	0.302	0.564	2.818
Pentan-3-ol	0.218	0.4	0.275	0.577	2.833
Perylene	2.896	1.853	0	0.431	11.652
Phenanthrene	1.961	1.309	0	0.278	7.709
Phenol	0.776	0.772	0.713	0.317	3.83
Phenyl acetate	0.661	1.13	0	0.54	4.414
Phenylcyclohexane	0.879	0.59	0	0.239	6.072
Phenylsilane	0.69	0.407	0	0.148	3.48
Phenyltrimethoxysilane	0.487	0.804	0	0.687	5.221
Phthalimide	1.394	1.561	0.334	0.591	5.874
Phthalonitrile	0.772	1.953	0	0.391	5.234
Progesterone	1.585	2.213	0	1.388	11.665
Propyl acetate	0.092	0.568	0	0.45	2.887
Pyrene	2.27	1.505	0	0.276	8.966
Pyridine	0.63	0.838	0	0.525	3.011
Quinine	1.832	1.272	0.808	1.27	12.025
Quinoline	1.415	1.103	0	0.687	5.302
Styrene	0.845	0.671	0	0.166	3.856
p-Terphenyl	1.816	1.285	0	0.742	9.513
Terpinen-4-ol	0.494	0.523	0.181	0.626	5.262
n-Tetradecane	0	0	0	0	6.655
Tetraethylorthosilicate	−0.343	0.343	0	0.766	4.338
Tetrahydofuran	0.295	0.529	0	0.476	2.541
Tetrakis(trimethylsiloxy)silane	−0.989	−0.155	0	0.664	5.441
Tetramethylorthosilicate	−0.139	0.54	0	0.689	3.124
Thioacetamide	0.64	1.816	0.003	0.293	3.853
Toluene	0.606	0.508	0	0.139	3.332
trans-Stilbene	1.658	1.219	0	0.296	7.289
Tri-n–Butyrin	0.22	1.235	0	1.292	7.962
Tribenzylamine	1.531	1.196	0	0.599	9.897
n-Tridecane	0	0	0	0	6.157

Table 2 (*Continued*)

Compound	Descriptors				
	E	S	A	B	L
Triethylamine	0.101	0.14	0	0.784	3.017
Triisopropanolamine	0.773	1.421	0.359	1.517	5.801
Tris(trimethylsiloxy)silane	−0.693	−0.173	0.047	0.457	4.671
Trimethoprin	2.055	2.065	0.029	2.095	10.429
Triphenylamine	2.379	0.877	0	0.815	8.889
Triphenylene	2.96	1.773	0	0.425	9.911
Triphenylmethane	1.714	1.1	0	0.565	8.704
n-Undecane	0	0	0	0	5.184
Valeraldehyde	0.079	0.649	0	0.45	2.804
Valerophenone	0.795	0.983	0	0.512	5.925
Vanillin	1.128	1.484	0.301	0.731	5.625
Vinylpentamethyldisiloxane	−0.188	−0.031	0	0.282	3.493
Vinyltrimethoxysilane	−0.005	0.478	0	0.67	3.317

Table 3
System constants for the poly(methyloctylsiloxane) SPB-Octyl column (b = 0 at all temperatures).

Temperature	System constant					Statistics*			
(°C)	e	s	a	l	c	r	SE	F	n
60	0.142 (0.008)	0.092 (0.009)	0.088 (0.015)	0.775 (0.003)	−2.598 (0.012)	0.999	0.021	20410	88
80	0.169 (0.009)	0.093 (0.010)	0.040 (0.017)	0.701 (0.003)	−2.664 (0.013)	0.999	0.025	14885	96
100	0.192 (0.008)	0.087 (0.009)	0	0.640 (0.003)	−2.737 (0.012)	0.999	0.030	19522	117
120	0.198 (0.010)	0.088 (0.012)	0	0.588 (0.003)	−2.815 (0.015)	0.999	0.039	13321	121
140	0.200 (0.010)	0.097 (0.013)	0	0.528 (0.003)	−2.812 (0.014)	0.999	0.033	13486	104
160	0.169 (0.007)	0.061 (0.008)	0	0.430 (0.002)	−1.977 (0.013)	0.999	0.026	15980	116
180	0.180 (0.005)	0.054 (0.006)	0	0.389 (0.002)	−1.982 (0.010)	0.999	0.026	21844	140
200	0.175 (0.005)	0.051 (0.006)	0	0.350 (0.001)	−1.962 (0.009)	0.999	0.026	31552	162
220	0.190 (0.005)	0.054 (0.007)	0	0.339 (0.001)	−2.016 (0.036)	0.999	0.031	27948	167
240	0.187 (0.005)	0.044 (0.007)	0	0.291 (0.001)	−1.991 (0.008)	0.999	0.029	31109	171
260	0.199 (0.007)	0.037 (0.011)	0	0.263 (0.002)	−2.002 (0.015)	0.998	0.039	10360	113

* r = multiple correlation coefficient, SE = standard error of the estimate, F = Fisher statistics and n = number of compounds. Numbers in parentheses are the standard deviation for the system constants.

3.2. Poly(siloxane) stationary phases prepared from phenyl-containing monomers

The introduction of diphenylsiloxane monomers into a poly(dimethylsiloxane) is expected to influence selectivity due to the weak dipolarity/polarizability and hydrogen-bond basicity of the phenyl ring compared with an alkyl group [18,26,28,46,48–50]. System constants for the temperature range 60–300 °C were determined for the poly(dimethyldiphenylsiloxane) stationary phase HP-5 containing 5% diphenylsiloxane monomer, Table 4, and from 60 to 260 °C for the poly(dimethyldiphenylsiloxane) stationary phase Rxi-17 containing 50% diphenylsiloxane monomer, Table 5. The system constants for a 1,4-bis(dimethylsiloxy)phenylene-dimethylsiloxane copolymer Rxi-5Sil MS over the temperature range 60–320 °C, Table 6, were determined for comparison with HP-5. The Rxi-5Sil MS column is engineered to have higher thermal stability but similar separation characteristics to poly(dimethyldiphenylsiloxane) stationary phases prepared from 5% diphenylsiloxane monomer [51]

The system map for the HP-5 column is shown in Fig. 1. The discontinuity in the c term results from the difference in the phase ratio for the two columns used to measure the retention factors over the extended temperature range. The system constants appear to be independent of the phase ratio and are drawn as continuous plots.
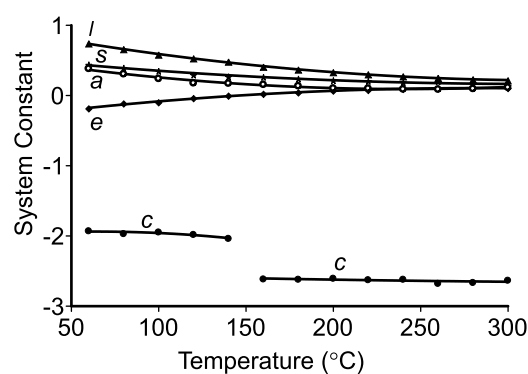

Fig. 1. System map for the poly(dimethyldiphenylsiloxane) stationary phase HP-5.

Dispersion interactions are important for this phase, being only slightly weaker than those for the poly(methyloctylsiloxane) stationary phase. The influence of temperature affects the value of the e system constant for poly(siloxane) stationary phases in a typical manner with small negative values at low temperatures changing to positive values at higher temperatures, albeit the range is small ($e \approx$ -0.2 to 0.1). Compared with the poly(methyloctylsiloxane) stationary phase, dipole-type interactions (s system constant) and

Table 4
System constants for the poly(dimethyldiphenylsiloxane) HP-5 column ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.191	0.436	0.380	0.735	−1.934	0.999	0.032	11493	85
	(0.013)	(0.016)	(0.024)	(0.004)	(0.016)				
80	−0.131	0.390	0.303	0.653	−1.974	0.999	0.027	19786	105
	(0.009)	(0.010)	(0.015)	(0.002)	(0.011)				
100	−0.104	0.345	0.237	0.576	−1.951	0.999	0.031	17014	118
	(0.010)	(0.012)	(0.018)	(0.003)	(0.011)				
120	−0.045	0.290	0.174	0.522	−1.986	0.999	0.030	22476	132
	(0.008)	(0.010)	(0.015)	(0.002)	(0.009)				
140	−0.010	0.265	0.170	0.476	−2.042	0.999	0.028	20992	130
	(0.008)	(0.010)	(0.014)	(0.002)	(0.009)				
160	0.016	0.260	0.153	0.403	−2.620	0.999	0.023	28893	138
	(0.004)	(0.006)	(0.007)	(0.001)	(0.009)				
180	0.036	0.234	0.133	0.363	−2.624	0.999	0.023	25892	140
	(0.004)	(0.006)	(0.008)	(0.001)	(0.009)				
200	0.062	0.211	0.100	0.325	−2.610	0.999	0.025	27613	151
	(0.004)	(0.006)	(0.008)	(0.001)	(0.009)				
220	0.071	0.202	0.098	0.295	−2.631	0.999	0.025	26384	150
	(0.004)	(0.006)	(0.008)	(0.001)	(0.009)				
240	0.086	0.184	0.087	0.266	−2.624	0.999	0.024	27322	148
	(0.004)	(0.006)	(0.008)	(0.001)	(0.008)				
260	0.092	0.196	0.085	0.245	−2.683	0.999	0.029	12487	110
	(0.005)	(0.008)	(0.013)	(0.001)	(0.012)				
280	0.104	0.165	0.094	0.224	−2.678	0.999	0.026	9317	82
	(0.005)	(0.009)	(0.020)	(0.001)	(0.014)				
300	0.099	0.135	0.112	0.210	−2.638	0.999	0.018	15420	83
	(0.003)	(0.006)	(0.011)	(0.001)	(0.010)				

Table 5
System constants for the poly(dimethyldiphenylsiloxane) Rxi-17 column ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	0.006	0.977	0.597	0.692	−2.397	0.999	0.028	6741	63
	(0.015)	(0.015)	(0.024)	(0.005)	(0.020)				
80	0.041	0.920	0.478	0.644	−2.567	0.998	0.042	5464	89
	(0.016)	(0.016)	(0.022)	(0.006)	(0.023)				
100	0.069	0.849	0.405	0.594	−2.666	0.998	0.041	6000	98
	(0.016)	(0.017)	(0.020)	(0.004)	(0.024)				
120	0.110	0.774	0.345	0.552	−2.76	0.998	0.038	5606	93
	(0.015)	(0.017)	(0.016)	(0.004)	(0.022)				
140	0.143	0.710	0.304	0.496	−2.761	0.998	0.035	4369	86
	(0.019)	(0.022)	(0.019)	(0.005)	(0.028)				
160	0.145	0.532	0.296	0.401	−2.461	0.998	0.034	4851	81
	(0.011)	(0.011)	(0.012)	(0.004)	(0.023)				
180	0.154	0.510	0.260	0.371	−2.536	0.998	0.032	5961	82
	(0.010)	(0.011)	(0.011)	(0.003)	(0.020)				
200	0.167	0.494	0.218	0.333	−2.544	0.998	0.037	7243	109
	(0.009)	(0.011)	(0.013)	(0.002)	(0.017)				
220	0.171	0.464	0.195	0.302	−2.546	0.998	0.038	8582	121
	(0.008)	(0.010)	(0.012)	(0.002)	(0.016)				
240	0.188	0.422	0.180	0.278	−2.577	0.998	0.037	9003	120
	(0.007)	(0.011)	(0.012)	(0.002)	(0.015)				
260	0.182	0.380	0.180	0.240	−2.449	0.999	0.036	7958	90
	(0.007)	(0.012)	(0.018)	(0.002)	(0.018)				

interactions as a hydrogen-bond base (a system constant) are more important These interactions are diminished at higher temperatures but persist to the highest temperature, 300 °C, employed in this study. These are weak polar interactions, and it is interesting that while temperature dependent, they still contribute to the retention mechanism at high temperatures.

Similarities in selectivity are expected for the poly(dimethyldiphenylsiloxane) stationary phase HP-5 and the 1,4-bis(dimethylsiloxy)phenylene-dimethylsiloxane Rxi-5Sil MS stationary phase because the later is intentionally engineered to have similar retention characteristics to the former [51]. The system constants for the HP-5 stationary phase are plotted against those for Rxi-5Sil MS for the temperature range 60–300 °C, Fig. 2.

If the stationary phases are selectivity equivalent the system constants at all temperatures would fall on a single line with a slope of 1 and an intercept of 0. The regression model for the plot with SC used to indicate any system constant value (e, s, a, l) at the same temperature on the compared phases over the explored temperature range is
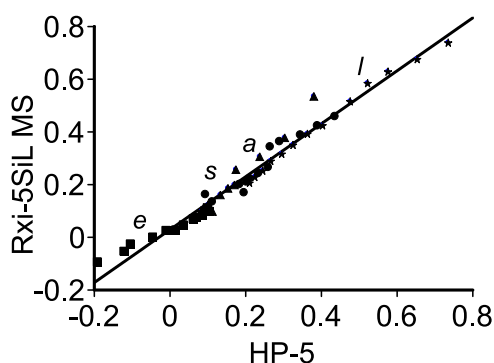
$$SC_{HP-5} = 0.966\,(\pm0.024)\,SC_{Rxi\text{-}5Sil\,MS} - 0.022\,(0.007)$$
$$r^2 = 0.970 \quad SE = 0.032 \quad F = 1631 \quad n = 52$$
(4)

where r^2 is the coefficient of determination, SE the standard error of the estimate, F the Fisher statistic, and n the number of paired system constant values. The 95% confidence interval for the slope (0.918–1.014) includes one but the intercept is different to zero

Table 6
System constants for 1,4-bis(dimethylsiloxy)phenylene-dimethylsiloxane co-polymer Rxi-5Sil MS column ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.094	0.458	0.535	0.739	−2.29	0.999	0.024	9716	69
	(0.013)	(0.013)	(0.018)	(0.004)	(0.016)				
80	−0.054	0.423	0.378	0.676	−2.404	0.998	0.035	6592	90
	(0.013)	(0.016)	(0.017)	(0.005)	(0.020)				
100	−0.026	0.388	0.306	0.629	−2.530	0.999	0.027	13730	107
	(0.009)	(0.010)	(0.011)	(0.003)	(0.013)				
120	0	0.363	0.257	0.585	−2.649	0.998	0.036	10047	108
		(0.012)	(0.014)	(0.004)	(0.017)				
140	0.025	0.343	0.199	0.516	−2.607	0.998	0.036	5087	103
	(0.012)	(0.014)	(0.014)	(0.004)	(0.020)				
160	0.027	0.265	0.186	0.425	−2.393	0.999	0.026	13429	120
	(0.006)	(0.007)	(0.008)	(0.002)	(0.013)				
180	0.046	0.242	0.161	0.393	−2.461	0.999	0.026	12565	122
	(0.006)	(0.008)	(0.009)	(0.002)	(0.012)				
200	0.069	0.222	0.122	0.351	−2.447	0.999	0.028	15323	145
	(0.005)	(0.007)	(0.009)	(0.002)	(0.011)				
220	0.075	0.210	0.107	0.317	−2.440	0.999	0.026	25623	159
	(0.004)	(0.006)	(0.008)	(0.001)	(0.009)				
240	0.085	0.200	0.105	0.290	−2.470	0.999	0.026	23642	149
	(0.004)	(0.007)	(0.008)	(0.001)	(0.009)				
260	0.099	0.169	0.100	0.253	−2.374	1.000	0.020	32611	124
	(0.003)	(0.005)	(0.008)	(0.001)	(0.008)				
280	0.098	0.162	0.104	0.229	−2.361	0.999	0.021	22713	114
	(0.004)	(0.006)	(0.009)	(0.001)	(0.008)				
300	0.111	0.134	0.098	0.207	−2.340	0.999	0.026	11667	106
	(0.005)	(0.008)	(0.008)	(0.001)	(0.011)				
320	0.111	0.121	0.133	0.185	−2.287	0.997	0.036	4700	105
	(0.006)	(0.011)	(0.016)	(0.002)	(0.015)				

Fig. 2. Correlation plot of the system constants for the poly(dimethyldiphenylsiloxane) stationary phase HP-5 and the 1,4-bis(dimethylsiloxy)phenylene-dimethylsiloxane stationary phase Rxi-5Sil MS. The range for each system constant is indicated by the lower case letters on the plot.

(confidence interval -0.037 to -0.008). The a system constant at 60 °C is clearly visible as a poor fit to the best linear model but whether included or excluded from the regression model, it does not affect the interpretation of the results. Fourty-eight out of the fifty-two absolute deviations (SC_{HP-5} - $SC_{Rxi-5Sil\ MS}$) have a negative sign and are evenly distributed among the four system constants. The absolute deviations, however, are small and subject to statistical fluctuations and some caution is called for to avoid over interpretation. It would seem safe to conclude that the HP-5 and Rxi-5Sil MS stationary phases have similar separation properties over a wide temperature range but are not selectivity equivalent.

The Rxi-17 stationary phase is prepared with a higher percentage of diphenylsiloxane monomer than HP-5 and is expected to have a greater contribution from interactions characteristic of the phenyl group. The relationship between the two sets of system constants is approximately linear and nearly independent of tem-

perature for the full temperature range explored (60–260 °C). The linear models are:

$$e_{Rxi-17} = 0.640\,(0.030)\,e_{HP-5} + 0.131\,(0.003)$$
$$r^2 = 0.981 \quad SE = 0.009 \quad F = 465 \quad n = 11 \tag{5}$$

$$s_{Rxi-17} = 2.448\,(0.023)\,s_{HP-5} - 0.031\,(0.066)$$
$$r^2 = 0.926 \quad SE = 0.061 \quad F = 113 \quad n = 11 \tag{6}$$

$$a_{Rxi-17} = 1.388\,(0.048)\,a_{HP-5} + 0.072\,(0.009)$$
$$r^2 = 0.990 \quad SE = 0.009 \quad F = 851 \quad n = 11 \tag{7}$$

$$l_{Rxi-17} = 0.953\,(0.036)\,l_{HP-5} + 0.025\,(0.017)$$
$$r^2 = 0.987 \quad SE = 0.019 \quad F = 701 \quad n = 11 \tag{8}$$

At the 95% confidence level the slope includes 1 and the intercept 0 for the l system constant indicating that increasing the relative amount of diphenylsiloxane monomer in Rxi-17 has little effect on the contribution from cavity formation and dispersion interactions for the two stationary phases. Because the confidence interval for the intercept for Eqs. (6) and (7) includes zero for the s system constant and is close to 0 for the a system constant the increase in the amount of diphenylsiloxane monomer increases the contribution of dipole-type interactions, s system constant, by about 2.4 fold and hydrogen-bond basicity, a system constant, by about 1.4 fold for Rxi-17 independent of temperature. The difference in electron lone pair interactions, e system constant, indicate stronger interactions for the Rxi-17 stationary phase but these difference are small (0.197 to 0.09) with an average of 0.135 (standard deviation = 0.035). There is thus a weak temperature dependence for the difference in the e system constant but the small numerical values and retention of the sign over the temperature range indicate that electron lone pair interactions are always more favorable for Rxi-17. This being said, the difference in the e system constant makes only a relatively small contribution to the difference in selectivity for HP-5 and Rxi-17. The main contribution from increasing the
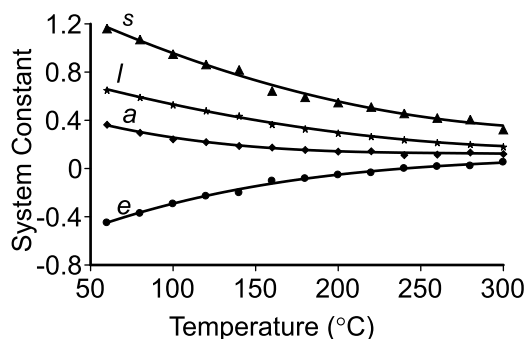
Fig. 3. System map for the Rtx-OPP stationary phase.

amount of diphenylsiloxane monomer in poly(dimethylsiloxane) stationary phases is to selectively increase retention through interactions of a dipole-type and to a lesser extent as a hydrogen-bond base, with only modest changes in dispersion and electron-lone pair interactions.

3.3. Rtx-OPPesticides

Rtx-OPPesticides (or Rtx-OPP) is an application-specific stationary phase with an undisclosed structure. A comparison of its system constants over the temperature range 60–140 °C with a large database of system constants for open-tubular columns indicated that it had separation properties similar to a poly(dimethylmethyltrifluoropropylsiloxane) stationary phase with about 20% methyltrifluoropropylsiloxane monomer units [5]. The poly(siloxane) stationary phases containing methyltrifluoropropylsiloxane substituents have a characteristic ratio for the s / a system constants and large values for the e system constant at low to moderate temperatures that distinguished them from other common poly(siloxane) stationary phases prepared from polar monomers [52,53]. Its extended temperature range compared with typical poly(dimethylmethyltrifluoropropylsiloxane) stationary phases as well as its characteristic separation properties were the main reason for its inclusion in this study.

The system constants for Rtx-OPP over the temperature range 60–300 °C are summarized in Table 7 and are plotted as a system map in Fig. 3 The Rtx-OPP column is generally more dipolar/polarizable and a weaker hydrogen bond base than the poly(dimethyldiphenylsiloxane) stationary phases in Section 3.2. This behavior is assigned to the inductive effect of the 3,3,3-trifluoropropyl group in known poly(siloxane) stationary phases prepared with methyltrifluoropropylsiloxane monomers [5,52,53]. In addition, electron lone pair interactions are more important and repulsive for temperatures < 240 °C. This reflects the fact that both the disiloxane and fluorocarbon groups bind electrons more strongly than n-alkanes selected as the scale origin for the E descriptor [13,31].The Rtx-OPP stationary phase has useful complementary separation properties to the poly(siloxanes) prepared with diphenylsiloxane monomer. Dipole-type interactions are enhanced while interactions as a hydrogen-bond base are suppressed and electron lone pair interactions are more important and generally reduce retention.

3.4. Poly(siloxane) stationary phases prepared from 3-cyanopropyl-containing monomers

Tello et al. studied the temperature dependence of nine self-made poly(methylcyanopropylsiloxane) stationary phase over the temperature range 75–120 °C [54,55]. Li and Carr studied the temperature dependence of three pre-coated poly(3-cyanopropylphenyldimethylsiloxane) stationary phases over the
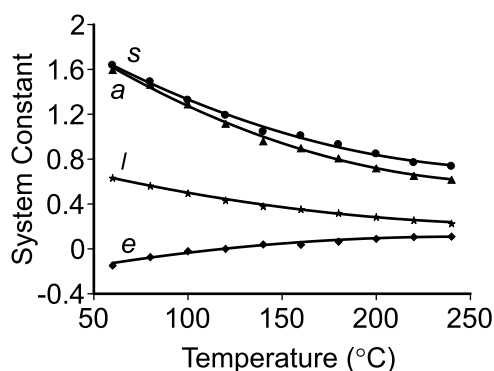

Fig. 4. System map for the poly(3-cyanopropylphenyldimethylsiloxane) stationary phase DB-225.
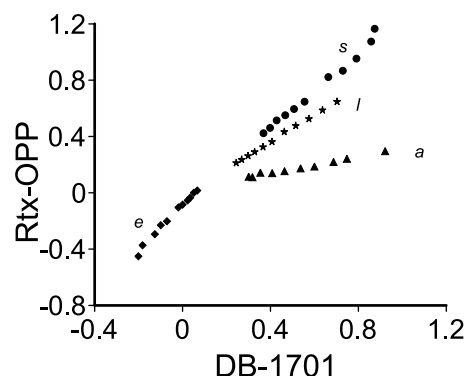

Fig. 5. Correlation plot of the system constants for Rtx-OPP and the poly(3-cyanopropylphenyldimethylsiloxane) stationary phase DB-1701. The range for each system constant is indicated by the lower case letters on the plot.

temperature range 45–150 °C using a linear solvation energy relationship model with different descriptors to the modern version of the solvation parameter model [27]. System constants for the poly(3-cyanopropylphenyldimethylsiloxane) stationary phase DB-1701 prepared from 14% 3-cyanopropylphenylsiloxane monomer were determined over the temperature range 60–260 °C, Table 8, and for DB-225 prepared from 50% 3-cyanopropylphenylsiloxane monomer over the temperature range 60–240 °C, Table 9 [56–58]. The system map for DB-225 is shown in Fig. 4. DB-225 is more cohesive than the poly(alkylsiloxane) and poly(dimethyldiphenylsiloxane) stationary phases and is also significantly more dipolar/polarizable and hydrogen-bond basic. Electron lone pair interactions are weak. The selectivity of the poly(3-cyanopropylphenyldimethylsiloxane) stationary phases is complementary to Rtx-OPP as illustrated by the correlation plot for the system constants of Rtx-OPP and DB-1701over a 200 °C temperature range in Fig. 5. The construction of a single line passing through all system constants is not possible in this case and the dispersion of the slopes for individual system constant is a measure of the multiple differences in selectivity and their different temperature dependence. A characteristic feature of the difference in selectivity for the poly(siloxane) stationary phases containing diphenylsiloxane and 3-cyanopropylphenylsiloxane monomers and Rtx-OPP is the s / a system constant ratio, Fig. 6. The s / a system constant ratio for DB-1701 (similar to DB-225) is about 1.1 and for Rtx-OPP about 3.3. Both stationary phases are strongly dipolar/polarizable while Rtx-OPP is a significantly weaker hydrogen-bond base. For both stationary phases the system constant ratios are weakly temperature dependent with a slight positive slope. The s/a system constant ratio for HP-5 has a stronger temperature dependence with a range from 1.1 to 2.3 over the

Table 7
System constants for the Rtx-OPP column ($b = 0$ at all temperatures).

Temperature	System constant					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.451 (0.015)	1.161 (0.019)	0.363 (0.022)	0.650 (0.005)	−2.470 (0.022)	0.997	0.046	5550	121
80	−0.373 (0.013)	1.070 (0.010)	0.296 (0.017)	0.590 (0.004)	−2.559 (0.019)	0.998	0.042	6566	130
100	−0.294 (0.013)	0.949 (0.016)	0.242 (0.017)	0.528 (0.004)	−2.581 (0.020)	0.997	0.046	5962	137
120	−0.230 (0.015)	0.863 (0.019)	0.219 (0.020)	0.479 (0.004)	−2.632 (0.023)	0.996	0.055	3834	136
140	−0.202 (0.012)	0.818 (0.016)	0.187 (0.018)	0.436 (0.004)	−2.694 (0.022)	0.996	0.047	4006	125
160	−0.104 (0.009)	0.643 (0.012)	0.174 (0.016)	0.365 (0.003)	−2.535 (0.019)	0.998	0.045	6257	125
180	−0.084 (0.008)	0.591 (0.009)	0.154 (0.013)	0.328 (0.002)	−2.531 (0.014)	0.998	0.041	10859	149
200	−0.054 (0.007)	0.547 (0.010)	0.140 (0.013)	0.293 (0.002)	−2.532 (0.013)	0.998	0.045	12305	175
220	−0.036 (0.007)	0.510 (0.010)	0.143 (0.013)	0.265 (0.002)	−2.539 (0.012)	0.998	0.043	11634	169
240	0	0.457 (0.008)	0.111 (0.013)	0.238 (0.002)	−2.522 (0.074)	0.998	0.045	10829	166
260	0.016 (0.007)	0.419 (0.012)	0.115 (0.019)	0.215 (0.002)	−2.528 (0.021)	0.997	0.042	3895	108
280	0.021 (0.009)	0.406 (0.016)	0.133 (0.023)	0.200 (0.003)	2.596 (0.029)	0.995	0.050	2018	87
300	0.052 (0.007)	0.323 (0.014)	0.120 (0.019)	0.180 (0.002)	2.516 (0.020)	0.997	0.038	3154	81

Table 8
System constants for the poly(cyanopropylphenyldimethylsiloxane) DB-1701 stationary phase ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.201 (0.013)	0.877 (0.013)	0.984 (0.019)	0.703 (0.003)	−2.694 (0.016)	0.999	0.023	11930	58
80	−0.182 (0.011)	0.861 (0.013)	0.922 (0.022)	0.637 (0.005)	−2.802 (0.022)	0.999	0.030	6038	63
100	−0.126 (0.011)	0.794 (0.013)	0.748 (0.020)	0.575 (0.004)	−2.855 (0.022)	0.999	0.031	5625	66
120	−0.099 (0.011)	0.732 (0.013)	0.687 (0.020)	0.515 (0.004)	−2.864 (0.023)	0.999	0.031	4863	59
140	−0.071 (0.012)	0.666 (0.016)	0.600 (0.021)	0.463 (0.006)	−2.871 (0.035)	0.997	0.032	1891	48
160	−0.019 (0.008)	0.558 (0.009)	0.537 (0.012)	0.407 (0.003)	−2.110 (0.017)	0.999	0.030	9042	92
180	0	0.510 (0.007)	0.464 (0.011)	0.366 (0.002)	−2.102 (0.015)	0.999	0.030	13985	100
200	0.023 (0.005)	0.470 (0.007)	0.408 (0.010)	0.328 (0.001)	−2.096 (0.010)	0.999	0.027	22950	135
220	0.034 (0.004)	0.431 (0.007)	0.354 (0.010)	0.298 (0.001)	−2.086 (0.010)	0.999	0.027	20942	134
240	0.051 (0.004)	0.401 (0.007)	0.318 (0.008)	0.269 (0.001)	−2.087 (0.009)	0.999	0.025	26455	138
260	0.067 (0.004)	0.371 (0.006)	0.301 (0.010)	0.244 (0.001)	−2.089 (0.010)	1.000	0.019	23025	92

temperature range 60–260 °C. The dominant effects of introducing the 3-cyanopropylphenylsiloxane monomer into poly(siloxane) stationary phases is a significant increase in interactions of a dipole-type and hydrogen-bond basicity [more hydrogen-bond basic than poly(siloxane) stationary phases prepared from diphenylsiloxane monomers and Rtx-OPP], a small increase in the cohesion of the stationary phase and minor changes in electron lone pair interactions.

The structure for the Rtx-440 stationary phase is undisclosed but a comparison of its system constants over the temperature range 60–140 °C with a large database of system constants for open-tubular columns indicated that it had separation properties similar to a poly(3-cyanopropylphenyldimethylsiloxane) prepared from 6% 3-cyanopropylphenylsiloxane monomer but was a signifi-

cantly weaker hydrogen-bond base [5,59]. This change in selectivity made it an appropriate choice for method development, particularly as an alternative to DB-1301 for the separation of overlapping compounds with different hydrogen-bond acidity. The system constants for Rtx-440 over the temperature range 60–300 °C are summarized in Table 10. The system map is presented in Fig. 7. Rtx-440 has low cohesion [similar to a poly(dimethylphenylsiloxane) stationary phase containing 5% diphenylsiloxane monomer such as HP-5] and is moderately polar with a modest capability for dipole-type interactions and as a hydrogen-bond base. Its s/a ratio is larger than for a typical poly(3-cyanopropylphenyldimethylsiloxane) stationary phase like DB-1701 reflecting its relatively weaker hydrogen-bond basicity.

Table 9
System constants for the poly(cyanopropylphenyldimethylsiloxane) DB-225 stationary phase ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.149	1.636	1.595	0.632	−2.920	0.999	0.032	7969	63
	(0.014)	(0.019)	(0.040)	(0.004)	(0.021)				
80	−0.074	1.489	1.464	0.562	−2.958	0.999	0.036	9259	85
	(0.012)	(0.017)	(0.029)	(0.004)	(0.020)				
100	−0.021	1.325	1.288	0.495	−2.922	0.999	0.043	8610	98
	(0.013)	(0.018)	(0.026)	(0.004)	(0.022)				
120	0	1.191	1.119	0.432	−2.849	0.998	0.045	9699	96
		(0.012)	(0.022)	(0.004)	(0.021)				
140	0.039	1.044	0.959	0.379	−2.759	0.998	0.043	6072	89
	(0.013)	(0.017)	(0.019)	(0.004)	(0.024)				
160	0.036	1.008	0.897	0.353	−2.866	0.999	0.035	17345	142
	(0.007)	(0.009)	(0.012)	(0.002)	(0.014)				
180	0.064	0.929	0.807	0.319	−2.888	0.999	0.035	17997	149
	(0.007)	(0.009)	(0.012)	(0.002)	(0.013)				
200	0.089	0.846	0.718	0.284	−2.858	0.999	0.038	18109	164
	(0.006)	(0.010)	(0.012)	(0.002)	(0.013)				
220	0.105	0.768	0.651	0.255	−2.824	0.999	0.041	14881	163
	(0.006)	(0.010)	(0.013)	(0.002)	(0.014)				
240	0.109	0.735	0.617	0.226	−2.815	0.999	0.038	12106	143
	(0.006)	(0.010)	(0.013)	(0.002)	(0.014)				

Table 10
System constants for the proprietary stationary phase Rtx-440 ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	−0.097	0.541	0.480	0.733	−2.346	0.999	0.025	12139	99
	(0.008)	(0.010)	(0.014)	(0.003)	(0.014)				
80	−0.048	0.498	0.394	0.670	−2.452	0.999	0.021	20080	114
	(0.006)	(0.008)	(0.010)	(0.003)	(0.011)				
100	0	0.436	0.333	0.604	−2.476	0.999	0.029	17420	131
		(0.007)	(0.011)	(0.003)	(0.014)				
120	0.032	0.409	0.296	0.556	−2.576	0.999	0.022	24965	131
	(0.006)	(0.007)	(0.008)	(0.002)	(0.010)				
140	0.065	0.365	0.259	0.503	−2.598	0.999	0.031	11900	134
	(0.009)	(0.010)	(0.011)	(0.003)	(0.014)				
160	0.057	0.305	0.202	0.422	−2.377	0.999	0.024	18390	127
	(0.006)	(0.007)	(0.009)	(0.002)	(0.011)				
180	0.066	0.281	0.173	0.383	−2.309	0.999	0.022	26776	143
	(0.004)	(0.005)	(0.007)	(0.002)	(0.009)				
200	0.082	0.257	0.151	0.345	−2.385	0.999	0.021	39452	164
	(0.004)	(0.005)	(0.007)	(0.001)	(0.007)				
220	0.087	0.246	0.140	0.320	−2.443	0.999	0.024	38794	174
	(0.004)	(0.005)	(0.007)	(0.001)	(0.007)				
240	0.106	0.213	0.125	0.287	−2.400	0.999	0.022	38369	166
	(0.003)	(0.005)	(0.007)	(0.001)	(0.007)				
260	0.119	0.206	0.123	0.266	−2.467	0.999	0.027	17382	107
	(0.005)	(0.008)	(0.011)	(0.001)	(0.011)				
280	0.123	0.192	0.107	0.244	−2.476	0.999	0.026	14101	103
	(0.005)	(0.008)	(0.010)	(0.001)	(0.011)				
300	0.131	0.179	0.095	0.226	−2.505	0.999	0.030	8459	95
	(0.005)	(0.010)	(0.014)	(0.002)	(0.014)				

3.5. Poly(ethylene glycol) stationary phase

Several techniques including physical coating, stabilization, immobilization and sol-gel chemistry are used to prepare open-tubular columns coated with poly(ethylene glycol) stationary phases [60]. The method of column preparation affects the thermal stability of the column but does not seem to have a significant effect on the retention properties [5,27,46,47,61,62]. The system constants over the temperature range 60–220 °C for the immobilized poly(ethylene glycol) stationary phase HP-INNOWAX are summarized in Table 11. The HP-INNOWAX stationary phase is moderately cohesive, similar to DB-225, slightly more dipolar/polarizable and a significantly stronger hydrogen-bond base. Electron lone pair interactions are weak but more important than for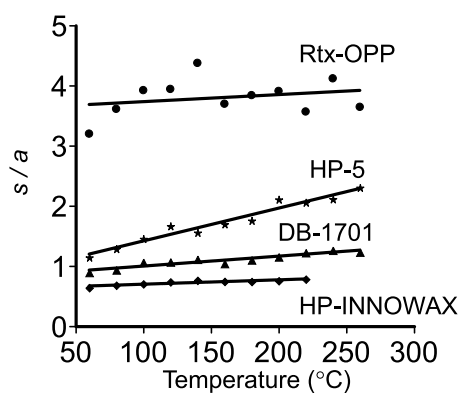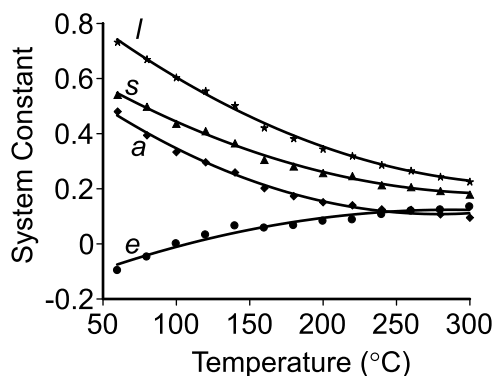 typical poly(siloxane) stationary phases containing polar monomers. They are also generally attractive (positive sign) compared with poly(siloxane) stationary phases, for which the e system constant is positive only at high temperatures. The poly(ethylene glycol) stationary phase can be distinguished from the poly(3-cyanopropylphenyldimethylsiloxane) stationary phases and Rtx-OPP by its distinctive s / a system constant ratio of about 0.72, Fig. 6, which is only weakly temperature dependent.

3.6. Interfacial adsorption

Interpretation of the system constants depends on the prescribed retention mechanism. For gas-liquid chromatography this is generally presumed to be partition although a combination of partition and interfacial adsorption might be appropriate in some cases [14,17,26,35,36,38]. The retention mechanism depends on

Table 11
System constants for the poly(ethylene glycol) HP-INNOWAX stationary phase ($b = 0$ at all temperatures).

Temperature	System constants					Statistics			
(°C)	e	s	a	l	c	r	SE	F	n
60	0.203	1.682	2.638	0.600	−2.482	0.998	0.036	2458	45
	(0.028)	(0.030)	(0.042)	(0.008)	(0.034)				
80	0.216	1.589	2.357	0.556	−2.596	0.999	0.026	5866	50
	(0.018)	(0.019)	(0.029)	(0.005)	(0.021)				
100	0.205	1.471	2.097	0.503	−2.619	0.999	0.028	5363	57
	(0.017)	(0.019)	(0.029)	(0.004)	(0.020)				
120	0.211	1.349	1.888	0.454	−2.618	0.999	0.029	5364	62
	(0.017)	(0.019)	(0.030)	(0.004)	(0.019)				
140	0.231	1.256	1.653	0.418	−2.666	0.999	0.026	8954	67
	(0.015)	(0.016)	(0.022)	(0.003)	(0.015)				
160	0.169	1.152	1.552	0.350	−2.526	0.997	0.045	2367	67
	(0.016)	(0.022)	(0.03)	(0.005)	(0.036)				
180	0.210	1.010	1.360	0.311	−2.476	0.998	0.040	4564	85
	(0.012)	(0.015)	(0.024)	(0.003)	(0.024)				
200	0.232	0.895	1.189	0.279	−2.429	0.998	0.042	6124	105
	(0.010)	(0.013)	(0.021)	(0.003)	(0.020)				
220	0.232	0.834	1.068	0.246	−2.393	0.998	0.040	7643	110
	(0.009)	(0.012)	(0.018)	(0.002)	(0.016)				

Fig. 6. Variation with temperature for the s / a system constant ratios for selected poly(siloxane) and poly(ethylene glycol) stationary phases.

Fig. 7. System map for the poly(siloxane) stationary phase Rtx-440. The structure of the stationary phase has not been disclosed.

the solute identity for any specified stationary phase and for varied compounds it is difficult to predict its overall affect on the system constants of the solvation parameter model. Presumably it increases the uncertainty in the model fit to the experimental data and in the prediction of retention factors for compounds not employed to build the model. As an extreme case the retention factors of n-alkanes on polar stationary phases was considered [17,38,63]. The retention factors of n-dodecane, n-tetradecane, n-hexadecane and n-octadecane on DB-225 and HP-INNOWAX as

examples of polar stationary phases in the database were evaluated. The retention factors for these n-alkanes at several temperatures were estimated by the solvation parameter models obtained for varied compounds with exclusion of the n-alkanes and cholestane from the dataset and compared with the experimentally measured retention factors. Plots of the two sets of retention factors as a function of temperature were linear with slopes that included one and intercepts that included zero at the 95% confidence level. The models described in this report are adequate to predict retention factors for compounds of a wide polarity range with an acceptable overall precision as indicated by the models and their statistics in Tables 3–11. There are no specific compounds given in Table 2 with persistent standard residuals > 2 SE as a function of temperature or column type for the columns indicated in Table 1.

4. Conclusions

Except as noted, the columns employed in this study were selected based on their monomer composition to confer differences in selectivity on their retention properties and where utilized to determine descriptor values for a variety of compounds not studied previously [31–33,39–43]. This has increased the number of compounds available for column characterization and facilitated extending the temperature range covered for each column. Several features of this study are notable. Polar interactions, even for weakly polar stationary phases, persist to the highest temperatures used in this study. This means that selectivity differences are still present at high temperatures but may be of a different relative intensity compared with lower temperatures due to the difference in temperature sensitivity for individual intermolecular interactions. The introduction of polar monomers has most influence on the cohesive energy of the stationary phase and the ratio of the s / a system constants, which tend to dominate relative retention properties. Electron lone pair interactions are weak for all stationary phases studied here but become relatively more important at higher temperatures. None of the poly(siloxane) and poly(ethylene glycol) stationary phases are hydrogen-bond acids. Since most compounds are hydrogen-bond bases, for example see Table 2, this is a missing opportunity to vary selectivity as was noted previously [64,65]. Among pre-coated, open-tubular columns only ionic liquid stationary phases have been identified as weak hydrogen-bond acids so far [6,7,20,66].

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2019.01.028.

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