Selectivity assessment of popular stationary phases for open-tubular column gas chromatography

Colin F. Poole[a],*, Qinglin Li[a], Waruna Kiridena[b], Wladyslaw W. Koziol[b]

[a]*Department of Chemistry, Rm. 171 Chemistry, Wayne State University, Detroit, MI 48202, USA*
[b]*Flint Ink North America, Analytical Division, 4600 Arrowhead Drive, Ann Arbor, MI 48105, USA*

Abstract

The solvation parameter model is used to study the influence of temperature and composition on the selectivity of nine poly(siloxane) and two poly(ethylene glycol) stationary phase chemistries for open-tubular column gas chromatography. A database of system constants for the temperature range 60–140°C was constructed from literature values with additional results determined for HP-50+, DB-210, DB-1701, DB-225 and SP-2340 columns. The general contribution of monomer composition (methyl, phenyl, cyanopropyl, and trifluoropropyl substituents) on the capacity of poly(siloxane) stationary phases for dispersion, electron lone pair, dipole-type and hydrogen-bond interactions is described. The selectivity coverage of the open-tubular column stationary phases is compared with a larger database for packed column stationary phases at a reference temperature of 120°C. The open-tubular column stationary phases provide reasonable coverage of the range of dipole-type and hydrogen-bond base interactions for non-ionic packed column stationary phases. Deficiencies are noted in the coverage of electron lone pair interactions. None of the open-tubular column stationary phases are hydrogen-bond acids. The system constants are shown to change approximately linearly with temperature over the range 60–140°C. The intercepts and slopes of these plots are used to discuss the influence of temperature on stationary phase selectivity. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

There is a reasonable understanding of the kinetic properties of open-tubular columns and column manufacturers often provide specific information for individual columns. Knowledge of column kinetic properties, however, is only one component of the information required for column selection and to optimize separations. By comparison, there is little information of either a general or specific nature for column selectivity, although this is as import as kinetic properties for method development. Traditional methods of characterizing column selectivity, such as Rorschneider/McReynolds phase constants, fail to determine selectivity correctly [1–4]. More recent and credible methods are based on the solvatochromic [5–7] or solvation parameter [4,8] models. These models are often mistaken for each other, but are different, connected only by the common use of a cavity model for the solvation

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*Corresponding author. Tel.: +1-313-577-2881; fax: +1-313-577-1377.

E-mail address: cfp@chem.wayne.edu (C.F. Poole).

process. The solvatochromic model employs a different basis set of solute descriptors to the solvation parameter model and an empirical correction factor to account for differences in solute polarizability [4,8–10]. In addition, not all-solute descriptors in the solvatochromic model are derived from free energy properties and cannot be considered reliable [8]. The solvation parameter model, on the other hand, is free from these objections and has been widely used to evaluate partition properties in chromatographic systems [8,11,12], including gas–liquid chromatography [4,8,13–18]. Most studies, however, refer to the less popular packed column stationary phases. In this report a database of system constants is provided for a varied group of open-tubular column stationary phases to assist in the assessment of the selectivity range available for separations by open-tubular column gas chromatography. These results should be immediately useful for method development applications as well as suggesting further needs for additional stationary phases to extend the selectivity coverage.

The solvation parameter model in a form suitable for characterizing the retention properties of stationary phases in gas–liquid chromatography is given by Eq. (1) [4,8]:

$$\log SP = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H$$
$$+ l \log L^{16} \tag{1}$$

SP is some free energy related solute property such as a gas–liquid partition coefficient or retention factor. The remainder of the equation is made up of product terms called system constants (r, s, a, b, l) and solute descriptors (R_2, π, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, $\log L^{16}$). Each product term represents a contribution from a defined intermolecular interaction to the correlated solute property (log SP). The $l \log L^{16}$ term represents the contribution from cavity formation and solute-stationary phase dispersion interactions; rR_2 the contribution from lone pair n- and π-electron interactions; $s\pi_2^H$ the contribution from interactions of a dipole-type; $a\Sigma\alpha_2^H$ the contribution from solute hydrogen-bond acid stationary phase hydrogen-bond base interactions; and $b\Sigma\beta_2^H$ the contribution from solute hydrogen-bond base stationary phase hydrogen-bond acid interactions.

The solute descriptors used in Eq. (1) are $\log L^{16}$

the solute gas–liquid partition coefficient on hexadecane at 298 K, R_2 the excess molar refraction, π_2^H the ability of the solute to stabilize a neighboring dipole by virtue of its capacity for orientation and induction interactions, and $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ the solute's effective hydrogen-bond acidity and basicity, respectively. Experimental solute descriptors are available for over 3000 compounds [8,19]. A computer program has been described for the calculation of additional values from structure [20].

Differences in selectivity between compared phases are indicated by statistically meaningful differences in the system constants defined by Eq. (1). For typical experimental conditions the gas phase can safely be assumed to be ideal, and the system constants, therefore, describe stationary phase properties alone. The r system constant, therefore, refers to the capacity of the stationary phase for interactions with solute n- or π-electrons; the s constant to the stationary phase's capacity for dipole-type interactions; the a constant characterizes the stationary phase's hydrogen-bond basicity (because a basic phase will interact with an acidic solute); the b constant the stationary phase's hydrogen-bond acidity; and the l constant incorporates contributions from stationary phase cavity formation and solute-stationary phase dispersion interactions.

Santiuste [21] used the solvation parameter model to characterize the retention properties of seven poly(trifluoropropylmethylsiloxane) stationary phases coated on glass open-tubular columns. The database described here was developed in our respective laboratories using commercially available fused-silica open-tubular columns with coated or (generally) immobilized stationary phases. Initial studies have been reported for the selectivity equivalence of poly(dimethyldiphenylsiloxane) columns containing 5% diphenylsiloxane groups [22,23] and poly-(ethylene glycol) columns [22,24] from different manufacturers. The five poly(dimethyldiphenylsiloxane) columns were shown to be virtually identical with respect to selectivity with minor differences in hydrogen-bond basicity. Greater selectivity differences were noted for four poly(ethylene glycol) stationary phases, which resulted from a combination of chemical differences and from differences in the relative contribution of interfacial adsorption to the retention mechanism. Contributions from interfacial

adsorption depend on the column phase ratio. Columns coated with immobilized poly(dimethylsiloxane) and poly(methyloctylsiloxane) stationary phases were evaluated for the determination of log L^{16} [25]. The poly(methyloctylsiloxane) stationary phase was shown to be less cohesive and hydrogen-bond basic than the poly(dimethylsiloxane) stationary phase, while both phases had similar dipolarity/polarizability. Both stationary phases were more polar (selective) than squalane but suitable for the determination of log L^{16} descriptors for solutes of low volatility using the defined regression models.

2. Experimental

The wall-coated open-tubular (WCOT) fused-silica capillary columns were obtained from different sources. The HP-50+ column (30 m×0.32 mm I.D., $d_f = 0.50$ μm) was from Agilent Technologies (Novi, MI, USA). The DB-210 (30 m×0.32 mm I.D., $d_f = 0.50$ μm), DB-225 (15 m×0.32 mm I.D., $d_f = 0.25$ μm) and DB-1701 (15 m×0.32 mm I.D., $d_f = 0.25$ μm) columns were from J&W Scientific (Folsom, CA, USA). The SP-2340 column (30 m×0.25 mm I.D., $d_f = 0.20$ μm) was from Supelco (Bellefonte, PA, USA). All solvents were OmniSolv grade from EM Science (Gibbstown, NJ, USA).

2.1. Determination of open-tubular column retention factors

For the SP-2340 WCOT fused-silica capillary column gas chromatographic measurements were made using an Agilent Technologies HP 5890 SERIES II gas chromatograph, HP 7673 automatic sampler and HP chemstation software (v. 6.03) for data acquisition. Helium was used as carrier gas at a column inlet pressure of 30 p.s.i. and a linear velocity of 25–30 cm/s. Samples were introduced by split injection (split vent flow 10 ml/min and septum purge 5 ml/min) at an injection temperature of 240°C. Methane was used to determine the column hold-up time.

For the HP-50+, DB-1701, DB-210 and DB-225 WCOT fused-silica capillary columns, gas chromatographic measurements were made using an Agilent Technologies HP-6890 gas chromatograph with

manual injection and HP chemstation software (v. 4.02) for data acquisition. Nitrogen was used as carrier gas at a constant linear velocity of 30 cm/s using the EPC (electronic pressure control) feature of this instrument. Samples were introduced by split injection (split vent flow 16 ml/min and septum purge 3.5 ml/min) at an injection temperature of 220°C. Methane was used to determine the column hold-up time.

All WCOT fused-silica capillary columns were unused prior to evaluation and were conditioned overnight following the manufacturers' recommendations. Prior to use each column was tested with a column evaluation mixture consisting of decane, undecane, dodecane, methyl undecanoate, methyl dodecanoate, 1-octanol, 1-dodecanol, nonanal, 2,6-dimethylaniline, and 2,6-dimethylphenol to ensure that the columns conformed to expected quality criteria for efficiency and chemical inertness. Upon completion of all retention measurements the column evaluation test was repeated under the same conditions to confirm that no changes in the column properties had occurred during the study.

2.2. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Gateway E-4200 computer (North Sioux City, SD, USA) using the program SPSS v. 10.0 (SPSS, Chicago, IL, USA). The solute descriptors used in the solvation parameter model were from an in-house database and identical to those used in earlier studies [22–25].

3. Results and discussion

To establish the relationship between the selectivity range of packed column stationary phases and those available as WCOT fused-silica capillary columns a database of system constants for a varied group of WCOT fused-silica columns was required. System constants databases for over 100 varied packed column stationary phases at a reference temperature of 120°C [8,15,17,26] and for a smaller number of stationary phases at other temperatures [8,27] already exist. Our laboratories have reported system constants for a limited number of WCOT

fused-silica capillary columns over the temperature range 60–140°C at increments of 20°C using a consistent experimental protocol [22–25]. To make this data collection more representative of the selectivity range of open-tubular column stationary phases in common use we report the system constants for an additional five chemically varied stationary phases determined with the same protocol in this report.

Our main interest in this report is the general solvation chemistry of the stationary phases and not the small differences that may exist between nominally identical stationary phases from different vendors. These differences are expected to be less than the differences between stationary phases prepared from different chemical monomers. To allow a description of stationary phase properties in general terms a generic description and abbreviation for the stationary phases in the database is presented in Table 1. When appropriate this nomenclature will be used throughout the remainder of this report.

3.1. System constants for additional stationary phases

The system constants from the solvation parameter model for the HP-50+, DB-1701, DB-210, DB-225 and SP-2340 columns over the temperature range 60–140°C are summarized in Table 2. All models are statistically sound and make chemical sense. The

poly(dimethyldiphenylsiloxane) stationary phase (HP-50+) has intermediate dipolarity/polarizability, weak hydrogen-bond basicity and intermediate cohesion. Exchanging diphenylsiloxane groups for dimethylsiloxane groups has most affect on the selectivity of the stationary phases for dipole-type (s system constant) and electron lone pair interactions (r system constant). The poly(cyanopropylphenyldimethylsiloxane) stationary phase (DB-1701) differs from the poly(dimethyldiphenylsiloxane) stationary phase in having no capacity for electron lone pair interactions (r system constant is zero) and is significantly more hydrogen-bond basic (larger a system constant). Exchanging cyanopropylphenylsiloxane groups for diphenylsiloxane groups results in a significant increase in the selectivity of the stationary phase (DB-225) for dipole-type interactions and in its hydrogen-bond basicity (larger s and a system constants). For the poly(cyanopropylsiloxane) stationary phase (SP-2340) these trends are maximized with the whole solution chemistry of the poly(cyanopropylsiloxane) stationary phase explained by its extreme cohesion (small l constant), strong dipole-type interactions (large s constant) and strong hydrogen-bond basicity (large a system constant). Exchanging the trifluoropropylmethylsiloxane group for the diphenylsiloxane group has a significant affect on the selectivity of the stationary phase (DB-210) for dipole-type interac-

Table 1
General description of the chemical composition of WCOT stationary phases entered in the open-tubular column database

Chemical description	Abbreviation	Column identity
Poly(dimethylsiloxane)	PMS	DB-1
Poly(methyloctylsiloxane)	PMOS	SPB-Octyl
Poly(dimethyldiphenylsiloxane)	PMPS-5	HP-5, OV-5, SPB-5, PTE-5
(5% diphenylsiloxane groups)		DB-5
Arylene-Siloxane copolymer	AS-5	HP-5TA
(nominally similar to HP-5)		
Poly(dimethyldiphenylsiloxane)	PMPS-50	HP-50+
(50% diphenylsiloxane groups)		
Poly(methyltrifluoropropylsiloxane)	PMTS	DB-210
(50% trifluoropropylsiloxane groups)		
Poly(cyanopropylphenyldimethylsiloxane)	PCPM-14	DB-1701
(14% cyanopropylphenylsiloxane groups)		
Poly(cyanopropylphenyldimethylsiloxane)	PCPM-50	DB-225
(50% cyanopropylphenylsiloxane groups)		
Poly(cyanopropylsiloxane)	PCPS	SP-2340
Poly(ethylene glycol)	PEG	HP-20M, HP-INNOWAX, AT-Wax
Nitroterephthalic acid-modified PEG	NPEG	DB-FFAP

Table 2
System constants for additional WCOT columns[a]

Temperature (°C)	System constants					Statistics[b]			
	l	r	s	a	c	ρ	SE	F	n
(i) HP-50+									
60	0.669	0.075	0.886	0.606	−2.466	0.999	0.027	2858	37
	(0.007)	(0.017)	(0.019)	(0.046)	(0.030)				
80	0.608	0.106	0.795	0.431	−2.532	0.998	0.029	2822	42
	(0.007)	(0.017)	(0.021)	(0.030)	(0.032)				
100	0.546	0.124	0.728	0.336	−2.558	0.998	0.032	3201	50
	(0.005)	(0.018)	(0.022)	(0.026)	(0.028)				
120	0.474	0.160	0.623	0.281	−2.484	0.997	0.042	2589	58
	(0.005)	(0.020)	(0.026)	(0.030)	(0.029)				
140	0.428	0.185	0.555	0.215	−2.499	0.997	0.047	2315	60
	(0.005)	(0.020)	(0.028)	(0.033)	(0.031)				
(ii) DB-1701									
60	0.696	0	0.755	0.959	−2.666	0.996	0.056	2589	64
	(0.008)		(0.023)	(0.055)	(0.041)				
80	0.617	0	0.694	0.861	−2.687	0.997	0.051	3114	68
	(0.007)		(0.021)	(0.040)	(0.036)				
100	0.548	0	0.658	0.744	−2.709	0.997	0.042	3644	66
	(0.005)		(0.018)	(0.032)	(0.032)				
120	0.487	0	0.593	0.636	−2.682	0.997	0.034	3177	59
	(0.005)		(0.016)	(0.025)	(0.032)				
140	0.443	0	0.569	0.547	−2.741	0.996	0.030	2200	51
	(0.006)		(0.016)	(0.023)	(0.036)				
(iii) DB-210									
60	0.529	−0.607	1.455	0.429	−2.068	0.996	0.050	887	36
	(0.010)	(0.036)	(0.036)	(0.047)	(0.048)				
80	0.496	−0.482	1.401	0.212	−2.292	0.998	0.034	2020	45
	(0.006)	(0.022)	(0.025)	(0.030)	(0.031)				
100	0.452	−0.453	1.367	0.147	−2.425	0.996	0.044	1469	51
	(0.007)	(0.026)	(0.029)	(0.035)	(0.034)				
120	0.439	−0.343	1.278	0.077	−2.648	0.995	0.052	1057	51
	(0.007)	(0.027)	(0.036)	(0.044)	(0.040)				
140	0.407	−0.299	1.197	0.004	−2.734	0.994	0.051	907	48
	(0.008)	(0.027)	(0.035)	(0.042)	(0.044)				
(iv) DB-225									
60	0.624	0	1.517	1.598	−2.879	0.996	0.057	1664	41
	(0.011)		(0.031)	(0.071)	(0.052)				
80	0.552	0	1.414	1.474	−2.904	0.997	0.047	2162	43
	(0.008)		(0.026)	(0.049)	(0.043)				
100	0.484	0	1.255	1.179	−2.832	0.996	0.049	1720	44
	(0.008)		(0.028)	(0.038)	(0.047)				
120	0.438	0	1.208	1.175	−2.895	0.997	0.039	1699	39
	(0.007)		(0.026)	(0.033)	(0.044)				
140	0.369	0	1.080	0.961	−2.726	0.998	0.030	1586	27
	(0.007)		(0.019)	(0.028)	(0.044)				
(v) SP-2340									
60	0.552	0	2.048	2.370	−3.029	0.996	0.041	1769	46
	(0.008)		(0.035)	(0.048)	(0.045)				
80	0.508	0	2.020	2.236	−3.214	0.995	0.046	1509	47
	(0.008)		(0.037)	(0.055)	(0.048)				
100	0.451	0	1.961	2.040	−3.285	0.995	0.044	1275	43
	(0.008)		(0.038)	(0.059)	(0.051)				
120	0.418	0	1.993	1.960	−3.478	0.995	0.047	1386	42
	(0.008)		(0.037)	(0.053)	(0.047)				
140	0.378	0	1.986	1.911	−3.604	0.994	0.052	830	36
	(0.009)		(0.044)	(0.063)	(0.060)				

[a] At all temperatures $b = 0$.
[b] ρ, overall multiple linear regression correlation coefficient; SE, standard error in the estimation; F, Fischer statistic; and n, number of solutes. The values in parenthesis are the standard deviation in the system constants.

tions (larger s system constant), electron lone pair interactions (negative r system constant) and hydrogen-bond basicity (small a system constant). The characteristic negative value for the r system constant is a product of the method of scaling the R_2 solute descriptor, resulting from the selection of the more polarizable n-alkanes as the zero point [8,9]. Negative values for the other system constants for gas–liquid chromatography would be chemically indefensible, suggesting stronger interactions with the carrier gas than with the stationary phase.

The c term in Table 2 is not a fundamental constant and is not interpreted here. It is dominated by the column phase ratio and is required for the simulation of retention on the characterized columns.

3.2. Selectivity range for all stationary phases in the database

The capacity of a stationary phase for intermolecular interactions is temperature dependent. Any meaningful comparison of phase properties must be made at a constant temperature, but this will only provide a snapshot suitable for ranking phases for a particular intermolecular interaction over a narrow temperature window. The change in system constants with temperature depends on the composition of the stationary phase. To take both factors into account the stationary phases in the database are described at a reference temperature of 120°C and then the change in system constants over the temperature range 60–140°C are considered (Section 3.3). A reference temperature of 120°C was selected based on historical precedent (the reference temperature used for the McReynolds' database) and because at this temperature the contribution of interfacial adsorption to the retention mechanism of the solutes used to characterize stationary phase properties is minimized [4,24,28,29].

The system constants for all stationary phase types in the database at 120°C are summarized in Table 3. For the poly(dimethyldiphenylsiloxane) stationary phases containing 5% diphenylsiloxane groups an average value for the five columns (Table 1) is entered in Table 3 [23]. In chemical terms this is of little consequence since the stationary phases have similar system constants (range $l = 0.51–0.50$, $s = 0.31–0.28$, and $a = 0.22–0.19$). The three poly-

Table 3
System constants at 120°C for different types of WCOT column stationary phases in the database

Stationary phase	System constants				
	l	r	s	a	b
PMOS	0.618	0	0.231	0	0
PMS	0.504	0	0.207	0.185	0
PMPS-5	0.506	0	0.292	0.209	0
AS-5	0.595	0	0.361	0.304	0
PMPS-50	0.474	0.160	0.623	0.281	0
PMTS	0.439	−0.343	1.278	0.077	0
PCPM-14	0.487	0	0.593	0.636	0
PCPM-50	0.438	0	1.208	1.176	0
PCPS	0.418	0	1.993	1.960	0
PEG	0.450	0.218	1.335	1.928	0
NPEG	0.428	0.214	1.424	2.077	0

(ethylene glycol) columns are treated in the same way [24]. Small chemical differences between columns were identified in this case, but the range of system constant values ($l = 0.46–0.40$, $r = 0.22–0.21$, $s = 1.35–1.32$, and $a = 2.01–1.88$) is small and an average value is acceptable for the present purpose.

The data in Table 3 enables an assessment of the range of selectivity space occupied by the stationary phases and their relationship to each other to be made. The l system constant characterizes the importance of the difficulty of cavity formation (solvent–solvent interactions) and non-selective dispersion solute–solvent interactions to retention. The variation in the l system constant at a constant temperature is assumed to result mainly from changes in the cavity term related to the cohesive energy of the stationary phase. The stationary phases in Table 3 cover a wide range of cohesion properties with PMOS the least and PCPS the most cohesive. Increasing stationary phase polarity opposes cavity formation. The l constant is also an indication of the ability of the stationary phase to separate individual members of a homologous series. A relatively large value expands the separation potential of the system for solutes of similar size (or boiling point) but reduces the size (or boiling point) range of compounds that can be separated at a constant temperature. The stationary phases entered in the database provide a reasonable range for this system constant. The significant difference between the selectivity of the poly(methyloctylsiloxane) and poly(dimethyl-

siloxane) stationary phases for size separations should be noted.

There is limited selectivity for electron lone pair interactions among the stationary phases in Table 3. The *r* system constant is zero for most phases with small values observed for the phenyl- and trifluoro-propyl-containing poly(siloxanes) (PMPS-50, PMTS) and for the poly(ethylene glycols) (PEG and NPEG). Electron lone interactions are repulsive for fluorine-containing phases and selectively result in lower retention. The limited options presented by the stationary phases in Table 3 means that for most separations, electron lone pair interactions make a small contribution to the retention mechanism and provide only a limited scope for selectivity optimization.

The stationary phases in Table 3 span a wide range of dipolarity/polarizability (*s* system constant). The *s* system constant increases significantly with the introduction of either trifluoroproylsiloxane or cyanopropylsiloxane monomer groups into the poly(methylsiloxane) backbone. The poly(ethylene glycol) stationary phases are also significantly dipolar/polarizable and roughly equivalent to the poly(siloxane) phases containing slightly more than about 50 mol% of cyanopropylphenylsiloxane or trifluoropropylmethylsiloxane groups. The cyanopropylsiloxane stationary phases are simultaneously strong hydrogen-bond bases and differ from the trifluoropropylsiloxane stationary phases, which are weak hydrogen-bond bases (e.g., compare PMTS and PCPM-50).

The capacity of the stationary phases in Table 3 for hydrogen-bond interactions is dominated by two considerations. None of the stationary phases are hydrogen-bond acids. All stationary phases that are strong hydrogen-bond bases are strongly dipolar/polarizable as well. This is a significant deficiency for selectivity optimization. With the exception of the *n*-alkanes and similar compounds all solutes are hydrogen-bond bases. Hydrogen-bond acid stationary phases, therefore, should have great utility for selectivity optimization. This problem was addressed recently with the development of a strong hydrogen-bond acid poly(siloxane) stationary phase for packed column gas chromatography [9]. This stationary phase should be compatible with open-tubular column technology. The poly(ethylene glycol) and poly(methyltrifluoropropylsiloxane) stationary phases provide the best options for varying the *a/s* system constant ratio for the phases found in Table 3.

Hierarchical cluster analysis, Fig. 1, provides a convenient tool to visualize the selectivity grouping of the stationary phases in Table 3. The largest cluster contains the phases PMS, PMPS-5, AS-5 and PMOS. These are all low polarity phases and thus possess a limited range for selectivity adjustment. Their nearest neighbors are the weakly polar PMPS-50 and PCPM-6 phases, which are more dipolar/polarizable and cohesive than the first group. PMTS, PCPS and PCPM-50 are polar phases identified as behaving independently. PEG and NPEG are grouped together but differentiated from the other polar phases. In terms of method development PMS (or PMOS, PMPS-5), PMTS, PEG (or NPEG), PCPS and PCPM-50 are suitable phases for selectivity optimization of the phases included in the database.

3.3. Influence of temperature on selectivity

The capacity of a stationary phase for specific intermolecular interactions depends on its composition and temperature. Higher temperatures are expected to reduce the capacity of the stationary phase for polar interactions. Fig. 2 presents a representative example of the influence of temperature on the system constants for a poly(methyltrifluoropropylsiloxane) stationary phase. The change in system constants over the temperature range 60–140°C is approximately linear for all stationary phases identified in Table 1. This allows the system constants to be fit to a relationship of the form:
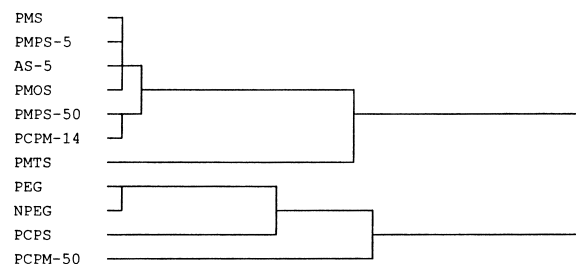
$$\text{system constant} = p - qt \tag{2}$$

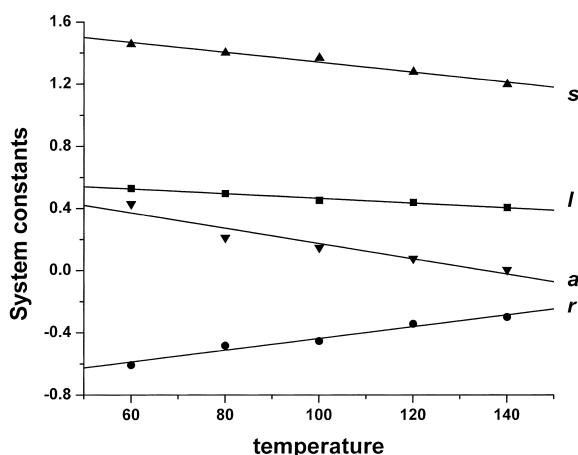Fig. 1. Single linkage dendrogram for the stationary phases in Table 3 at 120°C.

Fig. 2. Plot of the system constants as a function of temperature for the poly(methyltrifluoropropylsiloxane) stationary phase (DB-210).

where p and q are regression constants and t the column temperature in Celsius. The regression constants are summarized in Table 4 with the intercept value indicated for $t = 60°C$. The intercept value serves as a rough guide to the relative importance of a particular interaction to the selectivity of the stationary phase. For each system constant the larger the numerical value of the intercept the greater its potential to influence selectivity. The slope indicates the affect of increasing temperature on the capacity of the stationary phase for a particular interaction. A negative slope represents declining selectivity at higher temperatures (for the temperature range 60–140°C) and a positive slope an increase in selectivity. The r system constant is not expected to have a large influence on selectivity, except for PMTS, and has either a zero or small positive slope. The s system constant has a small slope indicating persistence of dipole-type interactions at higher temperatures. The large intercept and small slope observed for PCPS is particularly noteworthy. At higher temperatures the relative magnitude of the a/s system constant ratio changes significantly for PCPS due to the greater reduction in hydrogen-bond basicity compared with the dipolarity/polarizability of this phase. Similar observations apply to PEG and NPEG, which have particularly large negative slopes for the a system constant compared with the s system constant. In general, the a system constant has the largest nega-

tive slope of the system constants and its contribution to selectivity is the most dependent on temperature. The slopes for the l system constant are closely grouped, and although the intercepts for the various stationary phases are significantly different, the influence of increasing temperature is similar for all phases. The fact that the sign of the slope is negative and similar for all phases indicates that increasing ease of cavity formation at higher temperatures is not the primary contribution to the l system constant. A possibility is that expansion of the stationary phase volume at higher temperatures results in an increase in the average distance between solute and solvent molecules and a smaller contribution from dispersion interactions. Alternatively, if the thermal (entropic) effect associated with cavity formation is greater than the work (enthalpy) of cavity formation then the net effect will be to reduce the l system constant. The above results parallel findings for packed column stationary phases and a more detailed discussion can be found in [8].

3.4. Comparison with the selectivity range of packed column stationary phases

The chemistry required for the preparation of stable liquid films for open-tubular columns is more demanding than that used for the preparation of coated supports for packed columns. Consequently, a wider range of chemical types is employed as stationary phases in packed column gas chromatography compared with open-tubular column gas chromatography. The existence of a large database for packed column stationary phases at 120°C [8,15,17,26] allows a comparison of the selectivity range of the packed and open-tubular column stationary phases to be made. The range of system constants in packed column stationary phase database at 120°C is: $l = 0.67–0.24$; $r = -0.49–0.40$; $s = 0–2.10$; and $a = 0–5.70$. The b system constant is zero except for a small number of stationary phases specifically synthesized to function as hydrogen-bond acids [9] and for some polar phases, such as poly(esters), where it seems likely that the small b system constants result from phase impurities rather than from properties of the stationary phase itself [15,17,29]. If we compare these values with the system constants in Table 3 there is good coverage

Table 4
Variation of system constants with temperature (60–140°C)

Stationary phase type	System constant	Intercept at 60°C	Slope ($\times 10^3$) (system constant/°C)
PMOS	l	0.785	−3.0
	s	0.166	1.2
PMS	l	0.698	−3.2
	s	0.209 (±0.003)	
	a	0.307	−2.0
PMPS-5	l	0.692	−3.1
	s	0.321	−0.5
	a	0.380	−2.8
AS-5	l	0.743	−2.5
	s	0.370	−0.2
	a	0.442	−2.7
PMPS-50	l	0.667	−3.1
	r	0.077	1.4
	s	0.882	−4.2
	a	0.588	−4.7
PMTS	l	0.525	−1.5
	r	−0.586	3.8
	s	1.467	−3.2
	a	0.372	−4.9
PCPM-14	l	0.684	−3.2
	s	0.746	−2.4
	a	0.962	−5.2
PCPM-50	l	0.619	−3.1
	s	1.511	−5.4
	a	1.590	−7.9
PCPS	l	0.548	−2.2
	s	2.035	−0.7
	a	2.340	−6.0
PEG	l	0.605	−2.5
	r	0.220 (±0.003)	
	s	1.680	−5.7
	a	2.665	−12.1
NPEG	l	0.593	−2.8
	r	0.217	0.4
	s	1.785	−6.1
	a	2.791	−11.9

of the upper range of the l system constant, reasonable coverage of the low and intermediate region for the r system constant, and near complete coverage of the range for the s system constant. There is near complete coverage of the range for the a system constant if only non-ionic packed column stationary phases are considered ($a = 0$–2.40). The liquid organic salts are unique in their range of hydrogen-bond basicity ($a = 1.40$–5.70) [26]. Thus, it is reasonable to assume that the chemistry available for the preparation of open-tubular columns is able to provide stationary phases with a general coverage of solvation properties exploiting dipole-type and solvent hydrogen-bond base interactions, as well as solvent cohesion. Although open-tubular columns coated with liquid organic salts have been prepared

[30,31], their low viscosity limited their temperature operating range. If it proves possible to reinvent this class of stationary phase by marriage to poly(siloxane) chemistry this would provide an expansion of the current selectivity range of open-tubular columns by further optimization of the a/s system constant ratio.

3.5. Selectivity equivalence of packed and open-tubular columns of a similar type

The chemical composition of a number of packed and open-tubular column stationary phases in the databases are nominally similar. Their selectivity equivalence can be assessed by comparison of their system constants at 120°C (Table 5). There are small differences in selectivity for the polar phases and the description ''of similar'' rather than ''equivalent'' selectivity is justified. Open-tubular column phases are synthesized to different specifications than packed column phases and then further treated to induce immobilization after coating. The packed column stationary phases have been corrected for interfacial adsorption while the open-tubular column data is not. Any of these factors could contribute to the small differences observed in system constants for phases with nominally similar chemistry. In general, packed column separations on nominally equivalent phases should transfer to the ''selectivity similar'' open-tubular columns without great difficulty.

4. Conclusions

The results in this report demonstrate that contemporary stationary phases for open-tubular column gas chromatography provide an adequate coverage of the selectivity range for dipole-type interactions and for hydrogen-bond basicity. The open-tubular column stationary phases have similar cohesion properties to packed column stationary phases. Exploitation of selectivity differences due to electron lone pair interactions are under-represented by the stationary phases in the open-tubular database and none of the stationary phases are hydrogen-bond acids. In addition, none of the stationary phases in the open-tubular column stationary phase database have hydrogen-bond basicity equivalent to the liquid organic salts. These deficiencies indicate potential for the development of new stationary phases useful for method development.

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Table 5
Comparison of system constants at 120°C for nominally similar packed and open-tubular column stationary phases

Stationary phase type	Column	System constants				
		l	r	s	a	b
Poly(dimethylsiloxane)	DB-1	0.50	0	0.21	0.19	0
(PMS)	SE-30	0.50	0.02	0.19	0.13	0
Poly(methylphenylsiloxane)[a]	HP-50+	0.47	0.16	0.61	0.28	0
(PMPS-50)	OV-17	0.52	0.07	0.65	0.26	0
Poly(methyltrifluoropropylsiloxane)	DB-210	0.44	−0.34	1.28	0.08	0
(PMTS)	QF-1	0.42	−0.45	1.16	0.19	0
Poly(cyanopropylphenyldimethylsiloxane)	DB-225	0.44	0	1.21	1.18	0
(PCPM-50)	OV-225	0.47	0	1.23	1.07	0
Poly(ethylene glycol)	AT-Wax	0.44	0.23	1.32	1.89	0
(PEG)	CW-20M	0.45	0.32	1.26	1.88	0

[a] HP-50+ is a poly(dimethyldiphenylsiloxane) and OV-17 a poly(methylphenylsiloxane).

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