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Journal of Chromatography A, 932 (2001) 171–177

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Short communication

Selectivity assessment of DB-200 and DB-VRX open-tubular capillary columns

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Received 2 April 2001; received in revised form 24 August 2001; accepted 24 August 2001

Abstract

The solvation parameter model is used to study the influence of composition and temperature on the selectivity of two poly(siloxane) stationary phases used for open-tubular capillary column gas chromatography. The poly(methyltrifluoropropyltrimethylsiloxane) stationary phase, DB-200, has low cohesion, intermediate dipolarity/polarizability, low hydrogen-bond basicity, no hydrogen-bond acidity, and repulsive electron lone pair interactions. The DB-VRX stationary phase has low cohesion, low dipolarity/polarizability, low hydrogen-bond basicity and no hydrogen-bond acidity and no capacity for electron lone pair interactions. The selectivity of the two stationary phases is complementary to those in a database of 11 stationary phase chemistries determined under the same experimental conditions. © 2001 Published by Elsevier Science B.V.

Keywords: Solvation parameter model; Stationary phases, GC; Selectivity; Polysiloxanes; DB-200; DB-VRX

1. Introduction

A number of approaches have been used to characterize the retention properties of stationary phases for gas chromatography and are reviewed elsewhere [1,2]. Surprisingly, few of these studies relate to the use of modern stationary phase chemistry employed for the manufacture of open-tubular columns [3–7]. To remedy this problem we commenced the construction of a database consisting of the system constants obtained from the solvation

parameter model for representative column chemistries used in the manufacture of contemporary open-tubular columns. In earlier studies we have published system constants for 11 stationary phase chemistries represented by 17 commercially available open-tubular capillary columns over the temperature range 60–140°C [8–12]. These studies include an assessment of the selectivity equivalence of poly(ethylene glycol) [9] and poly(dimethyldiphenylsiloxane) [11] stationary phases from different manufacturers and an appraisal of the selectivity space available for the larger number of characterized packed column stationary phases that is occupied by the open-tubular capillary columns in the database [12]. To make the database as comprehensive as possible we will add system constants for additional stationary phases

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that expand the range of chemistries represented in the database as dictated by the needs and changing workloads of our respective laboratories. To this end we report system constants for poly(methyltrifluoropropyl)dimethylsiloxane stationary phase containing 20% methyltrifluoropropylsiloxane groups, DB-200, and the poly(siloxane) phase DB-VRX. The composition of DB-VRX is considered proprietary information. Its composition was engineered for the separation of purgeable volatile organic compounds identified in US Environmental Protection Agency (EPA) methods 502.2 and 524.2.

The solvation parameter model provides a suitable framework for the selectivity characterization of gas chromatographic stationary phases and their further use for the determination of solute physicochemical properties, for simulating separations in computer-aided method development and for the identification of surrogate chromatographic models for biological and environmental processes [1,2,13]. The solvation parameter model in a form suitable for characterizing the retention properties of stationary phases in gas–liquid chromatography is set out below [1,7]:

$$\log k = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l \log L^{16} \quad (1)$$

The equation is made up of product terms containing system constants (r , s , a , b , l) and solute descriptors (R_2 , π , $\sum\alpha_2^H$, $\sum\beta_2^H$, $\log L^{16}$). The system constants are obtained by multiple linear regression analysis of the retention factors, $\log k$, for a varied group of solutes selected to conform to the chemical and statistical requirements of Eq. (1). Each product term represents a contribution from a defined intermolecular interaction to the correlated solute property ($\log k$). 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; $a\sum\alpha_2^H$ the contribution from solute hydrogen-bond acid stationary phase hydrogen-bond base interactions; and $b\sum\beta_2^H$ 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 $\sum\alpha_2^H$ and $\sum\beta_2^H$ the solute's effective hydrogen-bond acidity and basicity, respectively [2,14–16].

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 refers to the capacity of the stationary phase for interactions with solute n- or π -electrons; the s system constant to the stationary phase's capacity for dipole-type interactions; the a system constant characterizes the stationary phase's hydrogen-bond basicity (because a basic phase will interact with an acidic solute); the b system 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.

2. Experimental

The DB-200 (30 m×0.25 mm, film thickness 0.5 μm) and DB-VRX (30 m×0.25 mm, film thickness 1.4 μm) fused-silica open-tubular capillary columns were obtained from Agilent Technologies (Novi, MI, USA). Both columns were unused prior to evaluation and were conditioned overnight following the manufacturers' instructions. Prior to use each column was tested using a column evaluation test mixture [8] to ensure that the column conformed to the expected quality criteria for efficiency and chemical inertness. Upon completion of the retention measurements the column evaluation test was repeated under the same conditions to confirm that no changes in column properties had occurred during the study.

Gas chromatographic measurements were made using an Agilent Technologies HP-5890 SERIES II gas chromatograph, a 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 20 p.s.i. and a linear velocity of about 50 cm/s (1 p.s.i. = 6894.76 Pa). 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.

Multiple linear regression analysis and statistical calculations were performed on a Gateway E-4200 personal computer (North Sioux City, SD, USA) using the program SPSS v10.0 (SPSS, Chicago, IL, USA). The solute descriptors used in the solvation parameter model were from a laboratory database and are summarized in Table 1 together with the experimental retention factors.

3. Results and discussion

The system constants from the solvation parameter model and the statistics for the model fit for the DB-200 and DB-VRX columns are summarized in Table 2 for the temperature range 60–140°C. All models are statistically sound and make chemical sense. The DB-200 stationary phase is of low cohesion (large l system constant), of intermediate dipolarity/polarizability (s system constant), has low hydrogen-bond basicity (small a system constant) and is not a hydrogen-bond acid ($b=0$). Electron lone pair interactions are repulsive (negative r system constant), which is a characteristic property of fluorocarbon-containing stationary phases [2,4,12, 17], and results from the selection of the more polarizable n -alkanes as the zero point for the R_2 solute descriptor. The DB-VRX stationary phase has low cohesion (large l system constant), low dipolarity/polarizability (small s system constant) and low hydrogen-bond basicity (small a system constant). It is neither an electron lone pair donor nor hydrogen-bond acid ($r=b=0$). These conclusions are based on a comparison with the system constants at 120°C for the other open-tubular column stationary phases in the database ($l=0.42$ to 0.62 , $r=-0.34$ to 0.23 , $s=0.21$ to 2.00 , and $a=0$ to 2.10) [12]. A comparison of the system constants in the open-tubular column database with those for DB-200 and DB-VRX indicates that other columns in the database do not duplicate the selectivity of either DB-200 or DB-VRX. Since we do not know the composition of DB-VRX its closest selectivity match in the database is the poly(dimethyldiphenylsiloxane) stationary

phases containing 5% diphenylsiloxane groups [11,12]. DB-VRX, however, is less cohesive and a weaker hydrogen-bond base than the poly(dimethyldiphenylsiloxane) stationary phases.

As found for other stationary phases [12], the system constants for DB-200 and DB-VRX can be represented approximately by a linear correlation with temperature over the range 60–140°C and can be fitted to a general equation of the form:

$$\text{system constant} = p - qt \quad (2)$$

where p and q are regression constants and t the column temperature in Celsius. To avoid uncertainties associated with extrapolation the intercept, p , is calculated for 60°C, as before [12]. The slope and intercept values for DB-200 and DB-VRX are summarized in Table 3. 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 each system constant to influence selectivity. These relationships are useful for the construction of retention maps for method development [12]. Although dipole-type and hydrogen-bonding interactions are weak for DB-VRX, of note is the persistence of these interactions at higher temperatures (shallow slope for s and a system constants).

The only other fluorine-containing stationary phase in the database is the poly(methyltrifluoropropylsiloxane) stationary phase, DB-210 [6]. DB-200 and DB-210 differ in the number of methyltrifluoropropylsiloxane groups (20 vs. 100%) and the presence of dimethylsiloxane groups in DB-200. For the temperature range 60–140°C the difference in selectivity for DB-210 and DB-200 can be evaluated from the following series of linear equations:

$$l_{\text{DB-210}} = 0.583l_{\text{DB-200}} + 0.162 \quad r^2 = 0.989 \quad n = 5 \quad (3)$$

$$r_{\text{DB-210}} = 1.220r_{\text{DB-200}} + 0.052 \quad r^2 = 0.935 \quad n = 5 \quad (4)$$

$$s_{\text{DB-210}} = 0.674s_{\text{DB-200}} + 0.591 \quad r^2 = 0.890 \quad n = 5 \quad (5)$$

$$a_{\text{DB-210}} = 1.393a_{\text{DB-200}} - 0.193 \quad r^2 = 0.991 \quad n = 4 \quad (6)$$

The slope indicates the temperature dependent change in selectivity associated with the structural

Table 1
Solute descriptors and experimental (log *k*) values

| Solute | Descriptor | | | | | Dependent variable (log <i>k</i>) | | | | | | | | | |
|----------------------|------------|-----------|--------------------|-------------------|--------------|------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | R_2 | π_2^H | $\Sigma\alpha_2^H$ | $\Sigma\beta_2^H$ | Log L^{16} | Stationary phase | | | | | | | | | |
| | | | | | | DB-VRX | | | | | DB-200 | | | | |
| | | | | | | Temperature (°C) | | | | | | | | | |
| | | | | | 60 | 80 | 100 | 120 | 140 | 60 | 80 | 100 | 120 | 140 | |
| Hexane | 0 | 0 | 0 | 0 | 2.668 | 0.157 | -0.086 | -0.304 | -0.496 | -0.668 | | | | | |
| Heptane | 0 | 0 | 0 | 0 | 3.173 | 0.528 | 0.249 | 0.007 | -0.205 | -0.389 | -0.364 | -0.624 | -0.865 | | |
| Octane | 0 | 0 | 0 | 0 | 3.677 | 0.891 | 0.576 | 0.304 | 0.064 | -0.145 | -0.272 | -0.315 | -0.567 | -0.804 | -1.001 |
| Nonane | 0 | 0 | 0 | 0 | 4.182 | 1.249 | 0.897 | 0.592 | 0.327 | 0.094 | 0.289 | -0.029 | -0.309 | -0.548 | -0.775 |
| Decane | 0 | 0 | 0 | 0 | 4.686 | | 1.216 | 0.878 | 0.584 | 0.327 | 0.605 | 0.254 | -0.057 | -0.322 | -0.562 |
| Undecane | 0 | 0 | 0 | 0 | 5.191 | | | 1.161 | 0.838 | 0.556 | 0.915 | 0.530 | 0.192 | -0.102 | -0.361 |
| Dodecane | 0 | 0 | 0 | 0 | 5.696 | | | | 0.927 | 0.621 | 0.936 | 0.570 | 0.252 | -0.026 | -0.269 |
| Tridecane | 0 | 0 | 0 | 0 | 6.200 | | | | | | | 1.082 | 0.686 | 0.344 | 0.045 |
| Hexadecane | 0 | 0 | 0 | 0 | 7.714 | | | | | | | | | 0.995 | 0.631 |
| Methyl cyclohexane | 0.244 | 0.10 | 0 | 0 | 2.433 | 0.603 | 0.331 | 0.093 | -0.115 | -0.307 | -0.248 | -0.506 | -0.768 | | |
| 1-Hexyne | 0.166 | 0.23 | 0.13 | 0.10 | 2.510 | 0.204 | -0.052 | -0.277 | -0.49 | -0.681 | -0.521 | | | | |
| Ethyl propionate | 0.087 | 0.58 | 0 | 0.45 | 2.807 | 0.553 | | -0.003 | -0.223 | -0.433 | 0.118 | -0.191 | -0.482 | -0.734 | |
| Propyl formate | 0.132 | 0.63 | 0 | 0.38 | 2.433 | 0.223 | -0.041 | -0.264 | -0.483 | | -0.148 | -0.428 | | | |
| Methyl hexanoate | 0.080 | 0.60 | 0 | 0.45 | 3.874 | 1.324 | | 0.642 | 0.368 | 0.127 | 0.813 | 0.443 | 0.118 | -0.162 | -0.408 |
| Methyl octanoate | 0.065 | 0.60 | 0 | 0.45 | 4.838 | | | 1.215 | 0.884 | 0.595 | | | 0.620 | 0.289 | 0.001 |
| Methyl nonanoate | 0.056 | 0.60 | 0 | 0.45 | 5.321 | | | | 1.135 | 0.822 | | 1.270 | 0.860 | 0.506 | 0.197 |
| Methyl decanoate | 0.053 | 0.60 | 0 | 0.45 | 5.803 | | | | | 1.051 | | | 1.109 | 0.729 | 0.397 |
| Butanal | 0.187 | 0.65 | 0 | 0.45 | 2.270 | 0.112 | -0.129 | -0.532 | -0.532 | -0.698 | -0.143 | -0.396 | -0.634 | -0.839 | |
| 2-Methylpropanal | 0.144 | 0.62 | 0 | 0.45 | 2.120 | -0.019 | -0.251 | -0.460 | -0.645 | | | -0.522 | -0.768 | 0.975 | |
| Valeraldehyde | 0.163 | 0.65 | 0 | 0.45 | 2.851 | 0.502 | 0.225 | -0.017 | -0.223 | -0.413 | 0.203 | -0.089 | -0.353 | -0.574 | -0.783 |
| Hexanal | 0.146 | 0.65 | 0 | 0.45 | 3.350 | 0.878 | 0.565 | 0.293 | 0.056 | -0.153 | 0.536 | 0.211 | -0.078 | -0.331 | -0.551 |
| Heptanal | 0.140 | 0.65 | 0 | 0.45 | 3.860 | 1.242 | 0.893 | 0.590 | 0.326 | 0.097 | 0.857 | 0.498 | 0.182 | -0.095 | -0.330 |
| Octanal | 0.160 | 0.65 | 0 | 0.45 | 4.360 | | 1.215 | 0.880 | 0.590 | 0.336 | 1.170 | 0.779 | 0.435 | 0.137 | -0.124 |
| Nonanal | 0.150 | 0.65 | 0 | 0.45 | 4.856 | | | 1.165 | 0.847 | 0.569 | | | | | |
| 2-Pentanone | 0.143 | 0.68 | 0 | 0.51 | 2.755 | 0.476 | 0.198 | -0.042 | -0.254 | -0.441 | 0.241 | -0.058 | -0.324 | -0.563 | -0.771 |
| 2-Hexanone | 0.136 | 0.68 | 0 | 0.51 | 3.262 | 0.849 | 0.537 | 0.267 | 0.031 | -0.178 | 0.575 | 0.243 | -0.051 | -0.307 | -0.535 |
| Cyclohexanone | 0.403 | 0.86 | 0 | 0.56 | 3.792 | 1.215 | 0.886 | 0.601 | 0.352 | 0.133 | 0.989 | 0.640 | 0.331 | 0.062 | -0.177 |
| Ethyl acetate | 0.106 | 0.62 | 0 | 0.45 | 2.314 | 0.195 | -0.067 | -0.297 | -0.505 | -0.682 | -0.160 | -0.433 | -0.695 | -0.941 | |
| Propyl acetate | 0.092 | 0.60 | 0 | 0.45 | 2.819 | 0.567 | | 0.016 | -0.207 | -0.404 | 0.178 | -0.127 | -0.410 | -0.651 | -0.867 |
| Butyl acetate | 0.071 | 0.60 | 0 | 0.45 | 3.353 | 0.934 | 0.605 | 0.320 | 0.070 | 0.146 | 0.504 | 0.164 | -0.135 | -0.403 | -0.629 |
| Propan-1-ol | 0.236 | 0.42 | 0.37 | 0.48 | 2.031 | -0.048 | 0.301 | | | | -0.539 | -0.805 | | | |
| Butan-1-ol | 0.224 | 0.42 | 0.37 | 0.48 | 2.601 | 0.359 | 0.080 | -0.159 | -0.369 | -0.555 | -0.158 | -0.430 | -0.691 | -0.919 | -1.157 |
| 2-Methylpropanol | 0.217 | 0.39 | 0.37 | 0.48 | 2.413 | 0.216 | -0.046 | -0.273 | -0.474 | -0.666 | -0.302 | -0.557 | -0.807 | -1.045 | |
| Pentan-1-ol | 0.219 | 0.42 | 0.37 | 0.48 | 3.106 | 0.737 | 0.427 | 0.160 | -0.072 | -0.275 | 0.182 | -0.123 | -0.395 | -0.636 | -0.848 |
| Pentan-2-ol | 0.198 | 0.36 | 0.33 | 0.56 | 2.840 | 0.491 | 0.207 | -0.039 | -0.254 | -0.449 | -0.044 | -0.328 | -0.589 | -0.819 | -1.049 |
| Pentan-3-ol | 0.218 | 0.36 | 0.33 | 0.56 | 2.860 | 0.492 | 0.211 | -0.031 | -0.243 | -0.433 | -0.063 | -0.339 | -0.598 | -0.826 | -1.038 |
| 2-Methylbutanol | 0.219 | 0.39 | 0.37 | 0.48 | 3.011 | 0.631 | 0.333 | 0.077 | -0.145 | -0.341 | 0.077 | -0.216 | -0.481 | -0.712 | -0.921 |
| 3-Methylbutanol | 0.192 | 0.39 | 0.37 | 0.48 | 3.011 | 0.618 | 0.332 | 0.063 | -0.156 | -0.357 | 0.084 | -0.214 | -0.485 | -0.712 | -0.941 |
| 2-Methyl-2-butanol | 0.194 | 0.30 | 0.31 | 0.60 | 2.630 | 0.281 | 0.021 | -0.205 | -0.403 | -0.584 | -0.223 | -0.489 | -0.739 | -0.963 | -1.179 |
| Hexanol | 0.210 | 0.42 | 0.37 | 0.48 | 3.610 | 1.107 | 0.761 | 0.463 | 0.206 | -0.020 | 0.512 | 0.175 | -0.124 | -0.382 | -0.613 |
| Cyclohexanol | 0.460 | 0.54 | 0.32 | 0.57 | 3.758 | 1.158 | 0.825 | 0.538 | 0.289 | 0.069 | 0.604 | 0.275 | -0.018 | -0.270 | -0.500 |
| Octan-1-ol | 0.199 | 0.42 | 0.37 | 0.48 | 4.619 | | | 1.048 | 0.735 | 0.461 | 1.149 | 0.746 | 0.394 | 0.087 | -0.183 |
| 2-Methoxyethanol | 0.269 | 0.50 | 0.30 | 0.84 | 2.490 | 0.270 | 0.005 | -0.227 | -0.199 | -0.395 | 0.131 | -0.171 | -0.439 | -0.674 | -0.894 |
| 2-Ethoxyethanol | 0.237 | 0.50 | 0.30 | 0.83 | 2.815 | 0.557 | 0.268 | 0.018 | -0.319 | -0.502 | 1.010 | 0.646 | 0.331 | 0.053 | -0.189 |
| Dioxane | 0.321 | 0.75 | 0 | 0.64 | 2.892 | 0.546 | 0.269 | 0.028 | -0.185 | -0.384 | | | | | |
| Tetrahydrofuran | 0.289 | 0.52 | 0 | 0.48 | 2.636 | 0.254 | 0.002 | -0.219 | -0.417 | | | | | | |
| Dichloromethane | 0.387 | 0.57 | 0.10 | 0.05 | 2.019 | -0.146 | | | | | | | | | |
| Chloroform | 0.425 | 0.49 | 0.15 | 0.02 | 2.480 | 0.198 | -0.146 | -0.265 | -0.456 | -0.619 | | | | | |
| Carbon tetrachloride | 0.458 | 0.38 | 0 | 0 | 2.823 | 0.396 | 0.142 | -0.079 | -0.276 | -0.459 | -0.397 | -0.637 | -0.871 | | |
| Acetonitrile | 0.237 | 0.90 | 0.07 | 0.32 | 1.739 | | | | | | -0.254 | -0.507 | -0.757 | | |
| Triethylamine | 0.101 | 0.15 | 0 | 0.79 | 3.040 | 0.452 | 0.179 | -0.059 | -0.276 | -0.456 | | | | | |
| 1-Nitropropane | 0.242 | 0.95 | 0 | 0.31 | 2.894 | 0.661 | 0.369 | 0.117 | -0.108 | -0.307 | 0.559 | 0.235 | -0.047 | -0.302 | -0.529 |
| 2-Nitropropane | 0.216 | 0.92 | 0 | 0.32 | 2.550 | | | | | | | | | -0.380 | -0.610 |
| Benzene | 0.610 | 0.52 | 0 | 0.14 | 2.786 | 0.403 | 0.147 | -0.078 | -0.276 | -0.447 | -0.244 | -0.498 | -0.775 | -0.970 | |

Table 1. Continued

| Solute | Descriptor | | | | | Dependent variable (log <i>k</i>) | | | | | | | | | |
|----------------------------|-----------------------|---------|------------------|-----------------|----------------------------|------------------------------------|-------|-------|--------|--------|--------|--------|--------|--------|--------|
| | <i>R</i> ₂ | π^H | $\Sigma\alpha^H$ | $\Sigma\beta^H$ | Log <i>L</i> ¹⁶ | Stationary phase | | | | | | | | | |
| | | | | | | DB-VRX | | | | | DB-200 | | | | |
| | Temperature (°C) | | | | | | | | | | | | | | |
| 60 | 80 | 100 | 120 | 140 | 60 | 80 | 100 | 120 | 140 | | | | | | |
| Toluene | 0.601 | 0.52 | 0 | 0.14 | 3.325 | 0.791 | 0.497 | 0.243 | 0.016 | -0.177 | 0.116 | -0.174 | -0.428 | -0.675 | -0.883 |
| Styrene | 0.849 | 0.65 | 0 | 0.16 | 3.856 | 1.228 | 0.893 | 0.601 | 0.346 | 0.122 | 0.569 | 0.237 | -0.057 | -0.316 | -0.545 |
| <i>o</i> -Xylene | 0.663 | 0.56 | 0 | 0.16 | 3.939 | 1.240 | 0.904 | 0.613 | 0.358 | 0.134 | 0.538 | 0.217 | -0.079 | -0.333 | -0.562 |
| <i>m</i> -Xylene | 0.623 | 0.52 | 0 | 0.16 | 3.839 | 1.162 | 0.830 | 0.542 | 0.290 | 0.069 | 0.440 | 0.118 | -0.171 | -0.426 | -0.651 |
| <i>p</i> -Xylene | 0.613 | 0.52 | 0 | 0.16 | 3.839 | 1.162 | 0.831 | 0.543 | 0.292 | 0.071 | 0.427 | 0.108 | -0.178 | -0.432 | -0.656 |
| Ethylbenzene | 0.613 | 0.51 | 0 | 0.15 | 3.778 | 1.115 | 0.838 | 0.508 | 0.261 | 0.044 | 0.397 | 0.081 | -0.202 | -0.451 | -0.675 |
| Chlorobenzene | 0.718 | 0.65 | 0 | 0.07 | 3.657 | 1.059 | 0.745 | 0.473 | 0.233 | 0.024 | 0.417 | 0.110 | -0.165 | 0.409 | -0.620 |
| 1,2-Dichlorobenzene | 0.872 | 0.78 | 0 | 0.04 | 4.518 | | 1.320 | 0.998 | 0.717 | 0.470 | 1.030 | 0.672 | 0.357 | 0.082 | -0.164 |
| 1,2,4-Trichlorobenzene | 0.980 | 0.81 | 0 | 0 | 5.248 | | | | | | | 0.790 | 1.021 | 0.674 | 0.370 |
| 1,2,4,5-Tetrachlorobenzene | 1.160 | 0.86 | 0 | 0 | 5.926 | | | | | | | 1.383 | 1.003 | 0.671 | 0.379 |
| Acetophenone | 0.818 | 1.01 | 0 | 0.49 | 4.501 | | | 1.097 | 0.799 | 0.538 | | 1.087 | | 0.414 | 0.138 |
| Benzaldehyde | 0.820 | 1.00 | 0 | 0.39 | 4.008 | | 1.100 | 0.793 | 0.545 | 0.290 | 1.100 | 0.734 | 0.412 | 0.129 | -0.120 |
| Nitrobenzene | 0.871 | 1.11 | 0 | 0.28 | 4.511 | | | 1.164 | 0.850 | 0.590 | | 1.188 | | 0.521 | 0.248 |
| Aniline | 0.955 | 0.96 | 0.26 | 0.53 | 3.993 | | 1.140 | 0.823 | 0.545 | 0.304 | 1.027 | 0.657 | 0.329 | 0.042 | -0.210 |
| 4-Fluoroaniline | 0.760 | 1.09 | 0.28 | 0.40 | 4.007 | | 1.206 | 0.878 | 0.593 | 0.344 | | | 0.447 | 0.156 | -0.111 |
| 2-Chloroaniline | 1.033 | 0.92 | 0.25 | 0.31 | 4.674 | | | | | 0.666 | | | | | 0.110 |
| Phenol | 0.805 | 0.89 | 0.60 | 0.31 | 3.766 | | | 0.775 | 0.486 | 0.238 | 0.851 | 0.494 | 0.175 | -0.102 | -0.334 |
| 2,6-Dimethylphenol | 0.860 | 0.79 | 0.39 | 0.39 | 4.680 | | | 1.179 | 0.867 | 0.594 | 1.290 | 0.886 | 0.535 | 0.229 | -0.041 |
| Pyridine | 0.794 | 0.87 | 0 | 0.62 | 3.003 | 0.682 | 0.399 | 0.153 | -0.063 | -0.255 | 0.279 | -0.017 | 0.284 | -0.520 | -0.737 |

differences for the compared phases. The intercept is a temperature independent contribution to the selectivity difference for the compared phases. The most significant selectivity difference between DB-200 and DB-210 is their capacity for dipole-type interactions. The temperature dependent change in selectivity for all interactions, except hydrogen-bond acidity ($b=0$), are significantly different for the compared phases. Thus DB-200 provides complementary selectivity to DB-210, which is temperature dependent, making DB-200 a useful stationary phase for bridging the selectivity space of the stationary phases included in the database. Because of the significant selectivity differences and the different change in selectivity with temperature, it will be difficult to predict separation differences, except by using Eqs. (3) to (6), for the compared phases from a knowledge of the separation order on either phase alone.

A similar comparison can be made between the poly(dimethyldiphenylsiloxane) stationary phase containing 5% diphenylsiloxane groups, taking HP-5 as an example of this type of phase [11], and DB-VRX:

$$l_{\text{DB-VRX}} = 0.913l_{\text{HP-5}} + 0.079 \quad r^2 = 0.999 \quad n = 5 \quad (7)$$

$$s_{\text{DB-VRX}} = 1.436s_{\text{HP-5}} - 0.131 \quad r^2 = 0.924 \quad n = 5 \quad (8)$$

$$a_{\text{DB-VRX}} = 0.569a_{\text{HP-5}} + 0.035 \quad r^2 = 0.989 \quad n = 5 \quad (9)$$

The separation of members of a homologous series will be quite similar on DB-VRX and HP-5. For a more varied group of solutes with significant differences in their capacity for dipole-type interactions and hydrogen-bond acidity (but not differences in electron lone pair interactions or hydrogen-bond basicity since $r=b=0$) selectivity differences and the temperature dependence of these differences are significant. The properties of DB-VRX are not duplicated by other phases in the database.

4. Conclusions

The system constants for DB-200 and DB-VRX columns for the temperature range 60–140°C are determined under the same conditions used to con-

Table 2

System constants for DB-200 and DB-VRX for the temperature range 60–140°C ($b=0$ at all temperatures)

| Temperature (°C) | System constant | | | | | Statistics | | | |
|---------------------|------------------|-------------------|------------------|------------------|-------------------|------------|-------|----------|----------|
| | <i>l</i> | <i>r</i> | <i>s</i> | <i>a</i> | <i>c</i> | ρ | SE | <i>F</i> | <i>n</i> |
| DB-200 | | | | | | | | | |
| 60 | 0.631 (0.007) | −0.515 (0.026) | 1.289 (0.007) | 0.341 (0.038) | −2.343 (0.031) | 0.997 | 0.039 | 2077 | 53 |
| 80 | 0.566 (0.007) | −0.473 (0.026) | 1.230 (0.028) | 0.288 (0.035) | −2.415 (0.029) | 0.997 | 0.044 | 2383 | 59 |
| 100 | 0.508 (0.005) | −0.395 (0.021) | 1.073 (0.024) | 0.243 (0.030) | −2.440 (0.025) | 0.997 | 0.038 | 2643 | 58 |
| 120 | 0.464 (0.006) | −0.34 (0.026) | 1.010 (0.031) | 0.203 (0.038) | −2.520 (0.030) | 0.996 | 0.046 | 1714 | 58 |
| 140 | 0.424 (0.006) | −0.278 (0.026) | 0.953 (0.031) | 0.137 (0.038) | −2.578 (0.032) | 0.996 | 0.044 | 1450 | 53 |
| DB-VRX | | | | | | | | | |
| 60 | 0.712 (0.010) | 0 | 0.356 (0.026) | 0.244 (0.039) | −1.741 (0.037) | 0.996 | 0.039 | 1661 | 49 |
| 80 | 0.650 (0.006) | 0 | 0.326 (0.014) | 0.212 (0.024) | −1.826 (0.020) | 0.998 | 0.025 | 5086 | 51 |
| 100 | 0.593 (0.004) | 0 | 0.317 (0.011) | 0.183 (0.018) | −1.893 (0.014) | 0.999 | 0.023 | 8578 | 61 |
| 120 | 0.543 (0.003) | 0 | 0.304 (0.009) | 0.159 (0.016) | −1.956 (0.012) | 0.999 | 0.020 | 11 038 | 63 |
| 140 | 0.493 (0.003) | 0 | 0.292 (0.010) | 0.130 (0.018) | −1.988 (0.013) | 0.999 | 0.022 | 9645 | 63 |

ρ = Overall multiple linear regression correlation coefficient; SE = standard error in the estimate; *F* = Fischer statistic; *n* = number of solutes. The values in parentheses are the standard deviation in the system constants.

Table 3

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

| Stationary phase | System constant | Intercept at 60°C | Slope ($\cdot 10^3$) (system constant/°C) |
|------------------|-----------------|-------------------|---|
| DB-200 | <i>l</i> | 0.622 | −2.58 |
| | <i>r</i> | −0.522 | 3.04 |
| | <i>s</i> | 1.289 | −4.46 |
| | <i>a</i> | 0.341 | −2.47 |
| DB-VRX | <i>l</i> | 0.707 | −2.73 |
| | <i>s</i> | 0.349 | −0.75 |
| | <i>a</i> | 0.242 | −1.41 |

struct a database of 11 different stationary phase chemistries (17 column types). These phases provide a useful extension of the available selectivity represented by the 11 stationary phase chemistries. The data in Tables 2 and 3 are in the same form reported previously and can be merged with the database.

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