

Short communication

System constants for the bis(cyanopropylsiloxane)-*co*-methylsilylene HP-88 and poly(siloxane) Rtx-440 stationary phases

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Abstract

The solvation parameter model is used to characterize the retention properties of the bis(cyanopropylsiloxane)-*co*-methylsilylene, HP-88, and poly(siloxane), Rtx-440, stationary phases over the temperature range 60–140 °C. HP-88 is among the most cohesive, dipolar/polarizable and hydrogen-bond basic of stationary phases for open-tubular column gas chromatography. It has no hydrogen-bond acidity or capacity for electron lone pair interactions. It exhibits similar selectivity to the poly(cyanopropylsiloxane) stationary phase SP-2340. Rtx-440 is a low-polarity, low-cohesion stationary phase with a moderate capacity for dipolar/polarizable and hydrogen-bond base interactions. It has no hydrogen-bond acidity and possesses weak electron lone pair interactions. It has unique selectivity when compared against a system constants database for 28 common stationary phase compositions. Cluster analysis indicated that the poly(cyanopropylphenyldimethylsiloxane) stationary phase containing 6% cyanopropylphenylsiloxane monomer, DB-1301, the poly(dimethyldiphenylsiloxane) stationary phase containing 20% diphenylsiloxane monomer, Rtx-20, the poly(siloxane) stationary phase of unknown composition, DB-624, and DX-1 [a mixture of poly(dimethylsiloxane) and poly(ethylene glycol) 9:1] are the closest selectivity matches in the database. The selectivity of DB-1301 and Rtx-440 are very similar for solutes with weak hydrogen-bond acidity allowing one stationary phase to be substituted for the other with likely success. For strong hydrogen-bond acids, such as phenols, DB-1301 and Rtx-440 exhibit different selectivity.

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1. Introduction

In 2000, we began construction of a system constants database for open-tubular columns using Abraham's solvation parameter model to establish the contribution of defined intermolecular interactions to the retention mechanism. The current database contains information for 28 stationary phase compositions over the temperature range 60–140 °C. Early studies are reviewed in [1–3] with more recent results for sol-gel phases [4], solvated β -cyclodextrin derivatives [5], and DB-608 and DB-624 [6] provided in the references indicated. A consistent approach for data collection and analysis facilitates a straightforward comparison of stationary phase

properties for all phases in the database. As new stationary phase chemistries are developed we intend to add these to the database with a view to establishing whether these phases provide useful separation characteristics or merely duplicate the properties of phases already in the database. With this in mind, in the current communication system constants over the temperature range 60–140 °C are provided for the new stationary phases HP-88 and Rtx-440.

HP-88 is a copolymer of bis(cyanopropyl)siloxane and methylsilylene monomers in a ratio of approximately 9:1, Fig. 1 [7]. The stationary phase is described as “stabilized” but is neither crosslinked nor immobilized. Methylsilylene monomers are introduced into the backbone of the bis(cyanopropyl)siloxane polymer to improve thermal stability, reproducibility of column preparation and to increase efficiency. Rtx-440 is a general-purpose, low-polarity,

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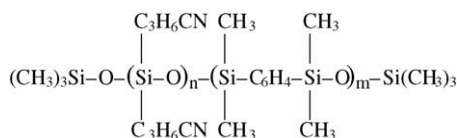


Fig. 1. Reported structure for the bis(cyanopropylsiloxane)-*co*-methylsilylene stationary phase HP-88.

crosslinked poly(siloxane) stationary phase optimized for the fast separation of pesticides, polycyclic aromatic hydrocarbons and other semivolatiles. The manufacturer describes Rtx-440 as a low-bleed stationary phase with unique selectivity, but has not disclosed its structure [8].

The solvation parameter model in a form suitable for characterizing the retention properties of stationary phases in gas chromatography is set out below [2,9,10].

$$\log k = c + lL + eE + sS + aA + bB \quad (1)$$

where k is the retention factor, c the model intercept (which is dominated by the phase ratio), the lower case letters (l , e , s , a and b) are the system constants representing the stationary phase contribution to intermolecular interactions, and the capital letters (L , E , S , A and B) are the solute descriptors for the complementary interactions with the system constants of the stationary phase. The system constants are identified as the contribution from cavity formation and dispersion interactions, l , the contribution from interactions with solute n - or π -electrons, e , the contribution from dipole-type interactions, s , the contribution from hydrogen-bond basicity (because a basic phase will interact with an acidic solute), a , and b the contribution from hydrogen-bond acidity. The system constants and their variation with temperature are used to characterize stationary phase selectivity and the effect of temperature on selectivity.

2. Experimental

2.1. Materials

The 25 m \times 0.25 mm I.D. (film thickness 0.20 μm) HP-88 open-tubular column was obtained from Agilent Technologies (Folsom, CA, USA). The 30 m \times 0.25 mm I.D. (film thickness 0.50 μm) Rtx-440 open-tubular column was obtained from Restek Corporation (Bellefonte, PA, USA). Solutes for column evaluation were obtained from Sigma-Aldrich (Milwaukee, WI, USA) and dissolved in ethyl acetate to a final concentration of about 0.5–2.0 mg/ml.

2.2. Instrumentation

Gas chromatographic measurements were made with an Agilent Technologies (Wilmington, DE, USA) HP 5890 SERIES II gas chromatograph fitted with a flame ionization detector, 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 psi and linear velocity of 35–40 cm/s. Methane was used to determine the column hold-up time. Sample volumes of 2 μl were introduced by split injection (split vent flow rate 10 ml/min and septum purge 5 ml/min), at an injection temperature of 240 $^\circ\text{C}$. Measurements of the retention factor ($\log k$) were made isothermally at 60, 80, 100, 120 and 140 $^\circ\text{C}$.

2.3. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Dell Dimension 4600 computer (Austin, TX, USA) using the program SPSS v12.1 (SPSS, Chicago, IL, USA). The solute descriptors were taken from an in-house database and are compiled in [1,11]. The solutes were selected to evenly occupy a wide selectivity space (E 0–1.34; S 0–1.11; A 0–0.67; B 0–0.84; and L 2.0–6.2). Because of the wide temperature range studied, it is necessary to use different solute sets for each measurement. The solute sets are selected according to the following criteria: the retention factors are distributed over a wide range without significant clustering; the solute descriptors are distributed throughout the descriptor space without significant clustering; cross-correlation of the solute descriptors is minimal; and the number of solutes included in each model is sufficient to ensure that the system constants are adequately defined by statistical tests (the data sets described here are over fitted by this criterion). The number of solutes that meet the above criteria for each column and temperature are indicated for all models in the data summary tables.

3. Results and discussion

The system constants for the HP-88 stationary phases at equally spaced temperatures in the range 60–140 $^\circ\text{C}$ are summarized in Table 1. The models are statistically sound and make chemical sense. The HP-88 stationary phase has no hydrogen-bond acidity ($b=0$) or capacity for electron lone pair interactions ($e=0$). Poly(siloxane) stationary phases containing 3-cyanopropylphenylsiloxane monomers are weakly electron lone pair repulsive [3] and this characteristic seems to have been lost by introducing a second 3-cyanopropyl group on silicon in HP-88, similar to observations for the poly(cyanopropylsiloxane) stationary phase SP-2340 [1]. The HP-88 stationary phase is strongly dipolar/polarizable and hydrogen-bond basic (large s and a system constants). It is clustered among the most dipolar/polarizable and hydrogen-bond basic of the stationary phases in the system constants database. HP-88 is also among the most cohesive stationary phases in the database (small l system constant). These results are not surprising given the high concentration of bis(cyanopropylsiloxane) monomers in the stationary phase.

The system constants in the database are entered with their temperature dependence to allow interpolation to any temper-

Table 1
System constants for the HP-88 stationary phase ($b = e = 0$)

Temperature (°C)	System constants				Statistics ^a			
	<i>s</i>	<i>a</i>	<i>l</i>	<i>c</i>	ρ	SE	<i>F</i>	<i>n</i>
60	1.943 (0.034)	2.246 (0.042)	0.562 (0.006)	−3.001 (0.034)	0.998	0.032	3846	48
80	1.981 (0.026)	2.098 (0.048)	0.520 (0.006)	−3.241 (0.039)	0.997	0.046	3144	57
100	1.927 (0.027)	1.899 (0.034)	0.475 (0.006)	−3.371 (0.039)	0.997	0.047	3395	60
120	1.881 (0.033)	1.711 (0.035)	0.426 (0.008)	−3.442 (0.051)	0.996	0.047	2124	51
140	1.887 (0.040)	1.556 (0.035)	0.380 (0.009)	−3.532 (0.057)	0.996	0.047	1639	46

^a ρ : overall multiple linear regression correlation coefficient; SE: standard error in the estimate; *F*: Fischer statistic; *n*: number of solutes with retention factors in an appropriate range ($-0.85 < \log k < 1.4$). The values in parentheses are the standard deviation in the system constants.

ature in the range of the measurements. For the *l* and *a* system constant the relationship is linear

$$l_{\text{HP-88}} = 0.702 (\pm 0.004) - 2.29 \times 10^{-3} (\pm 3.51 \times 10^{-5})T, \\ r^2 = 0.999 \quad (2)$$

$$a_{\text{HP-88}} = 2.786 (\pm 0.026) - 8.84 \times 10^{-3} (2.46 \times 10^{-4})T, \\ r^2 = 0.998 \quad (3)$$

where *T* is the temperature in Celsius. The *s* system constant can be represented by a linear relationship but the fit is not as good

$$s_{\text{HP-88}} = 2.03 (\pm 0.05) - 1.06 \times 10^{-3} (\pm 4.58 \times 10^{-4})T, \\ r^2 = 0.657 \quad (4)$$

The *s* system constant is only weakly temperature dependent for the range 60–140 °C with a maximum value of 1.98 and a minimum value of 1.88. The average standard deviation in the *s* system constant is 0.03 so that a better fit for the trendline cannot be expected. The model constant, *c* term, is not a system constant related to intermolecular interactions, but is required for the prediction of retention on a given column. It is dominated by the phase ratio for the column and its change with temperature. It is adequately described by a second order model

$$c = -2.096 (\pm 0.18) - 1.914 \times 10^{-2} (\pm 3.89 \times 10^{-3})T \\ + 6.411 \times 10^{-5} (\pm 1.93 \times 10^{-5})T^2, \quad r^2 = 0.990 \quad (5)$$

The nearest neighbor to HP-88 in the system constants database is the poly(cyanopropylsiloxane) stationary phase SP-2340, Fig. 2. The values and trends for the system constants as a function of temperature are similar. Neither stationary phase is hydrogen-bond acidic or enters into electron lone pair interactions. SP-2340 is slightly more cohesive over the temperature range studied

$$l_{\text{SP-2340}} = 0.95 (\pm 0.06)l_{\text{HP-88}} + 0.01 (\pm 0.03), \\ r^2 = 0.989, \quad \text{SE} = 0.008, \quad F = 265, \quad n = 5 \quad (6)$$

Ignoring the fact that there is a trend indicated by the above regression equation, differences in the *l* system constant for the compared phases are small, and from this perspective, if an average value is computed for the difference in *l* system constants, its value of 0.011 corresponds to 2.4% of the average value for the *l* system constant for HP-88. SP-2340 is slightly more dipolar/polarizable than HP-88. The difference in *s* system constants for the compared phases shows no discernible temperature dependence and can be represented as an average difference of 0.08 (± 0.04 , $n = 5$), corresponding to about 4.1% of the average value for the *s* system constants for HP-88. There is a small but more significant difference in the *a* system constant. This difference is non-linear and increases with temperature from 0.12 to 0.35

$$a_{\text{SP-2340}} = 0.73 (\pm 0.17)(a_{\text{HP-88}})^2 - 2.11 (\pm 0.63)(a_{\text{HP-88}}) \\ + 3.43 (\pm 0.59), \quad r^2 = 0.996 \quad (7)$$

Thus, SP-2340 and HP-88 are not selectivity equivalent but have similar separation properties. This is illustrated by the plot of retention factors at 60 °C for a varied group of 41 compounds on the two columns, Fig. 3 (compounds listed in the legend). The two sets of data are highly correlated and described by the relationship

$$k_{\text{SP-2340}} = 0.972 (\pm 0.009)k_{\text{HP-88}} + 0.05 (\pm 0.04), \\ r^2 = 0.997, \quad \text{SE} = 0.206, \quad F = 11678, \quad n = 41 \quad (8)$$

At the 95% confidence level, the confidence interval for the intercept includes 0 while the range for the slope is 0.95–0.99 and, thus, distinguishable from 1. However, the separation characteristics for the two columns are close, and for many separations it is likely that one column could be substituted for the other. It is interesting that replacing roughly 10% of the bis(cyanopropylsiloxane) monomers by methylsilylene monomers in the compared stationary phases changes the separation characteristics by only a small amount, and for many applications the claimed improved coating characteristics and thermal stability of the HP-88 stationary phase are likely to be the main reason to adopt this stationary phase over stationary phases like SP-2340.

The system constants for the Rtx-440 stationary phase over the temperatures range 60–140 °C are summarized in

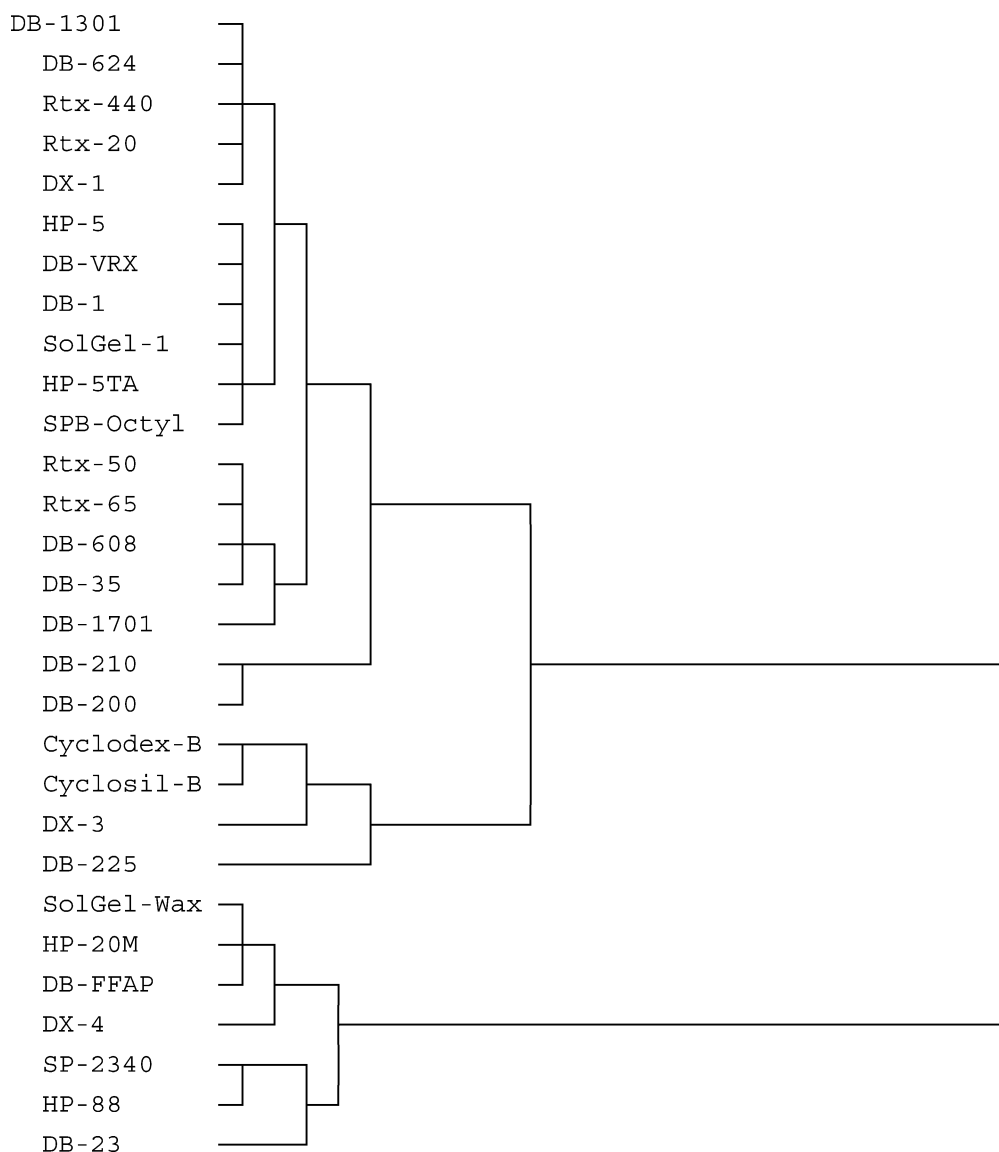


Fig. 2. Average-linkage dendrogram for hierarchical cluster analysis of representative columns for the different stationary phase compositions contained in the database of system constants for the temperature range 60–140 °C. DB, HP, DX, Cyclodex and CycloSil columns are from Agilent Technologies; Rtx from Restek corporation; sol-gel from SGE Incorporated; and SP and SPB from Supelco Incorporated.

Table 2. The models are statistically sound and make chemical sense. The Rtx-440 stationary phase has no hydrogen-bond acidity ($b = 0$) and only a weak capacity for electron lone pair interactions. It is moderately polar with a small capacity for dipolar/polarizable and hydrogen-bond basic interactions (intermediate values for s and a system constants) and has low cohesion (large l system constant). The temperature dependence of the system constants is summarized below:

$$e_{\text{Rtx-440}} = 1.505 \times 10^{-3} (\pm 5.85 \times 10^{-5})T - 0.179 (\pm 0.006), \quad r^2 = 0.996 \quad (9)$$

$$s_{\text{Rtx-440}} = -1.970 \times 10^{-3} (\pm 1.28 \times 10^{-4})T + 0.675 (\pm 0.013), \quad r^2 = 0.999 \quad (10)$$

$$a_{\text{Rtx-440}} = 2.893 \times 10^{-5} (\pm 2.04 \times 10^{-6})T^2 - 8.666 \times 10^{-3} (\pm 4.11 \times 10^{-4})T + 0.936 (\pm 0.019), \quad r^2 = 0.999 \quad (11)$$

$$l_{\text{Rtx-440}} = -2.930 \times 10^{-3} (\pm 9.45 \times 10^{-5})T + 0.914 (\pm 0.010), \quad r^2 = 0.997 \quad (12)$$

$$c_{\text{Rtx-440}} = 2.500 \times 10^{-5} (\pm 1.20 \times 10^{-5})T^2 - 7.640 \times 10^{-3} (\pm 2.40 \times 10^{-3})T - 2.039 (\pm 0.11) \quad r^2 = 0.979 \quad (13)$$

These results are statistically well defined and can be used for estimating system constants by interpolation for tem-

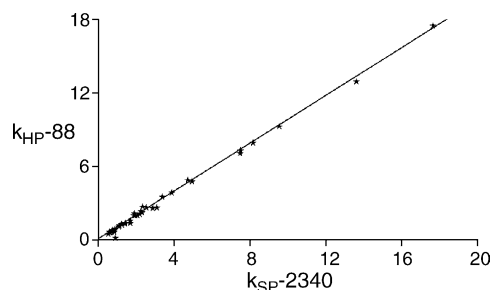


Fig. 3. Plot of retention factors for a varied group of compounds on HP-88 and SP-2340 at 60 °C. The compounds are: undecane, dodecane, tridecane, methyl hexanoate, methyl octanoate, methyl nonanoate, 2-methylpropanal, valeraldehyde, heptanal, octanal, nonanal, 2-pentanone, 2-hexanone, cyclohexanone, propyl acetate, propan-1-ol, butan-1-ol, pentan-1-ol, pentan-2-ol, pentan-3-ol, 2-methylbutanol, 3-methylbutanol, 2-methyl-2-butanol, hexanol, cyclohexanol, octan-1-ol, 2-methoxyethanol, 2-ethoxyethanol, dioxane, acetonitrile, toluene, styrene, *o*-xylene, *p*-xylene, ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, pyridine, 1-nitropropane and 2-nitropropane.

peratures other than those used for the original measurements.

Cluster analysis indicates that the nearest neighbors to Rtx-440 in the system constants database are DB-1301, DB-624, DX-1 and Rtx-20, Fig. 2. Of this group, DB-1301 and DB-624 are virtually selectivity equivalent [6], and although small selectivity differences between DX-1 and DB-1301 exist [3], these two stationary phases are interchangeable for many applications. The separation properties of this subgroup of three stationary phases can be adequately represented by the poly(cyanopropylphenyldimethylsiloxane) stationary phase containing 6% cyanopropylphenylsiloxane monomer groups (DB-1301). In addition, the composition of DB-624 is unknown and DX-1 is a mixture of poly(dimethylsiloxane) and poly(ethylene glycol) in the approximate ratio 9:1. It will be more difficult, therefore, to assign chemical differences to structural features between these phases and Rtx-440 than for DB-1301. Rtx-20 is a poly(dimethyldiphenylsiloxane) stationary phase containing 20% diphenylsiloxane monomer groups. The separation differences between Rtx-20 and DB-1301 are greater than among the subgroup DB-1301, DB-624 and DX-1 and, thus, Rtx-20 should be compared with Rtx-440 independently of DB-1301 to establish its selectivity relationship to Rtx-440.

The difference in system constants (Δ) at each temperature and the average value of the differences for all temperatures ($\Delta\Delta$) for Rtx-440 and DB-1301, and Rtx-440 and Rtx-20 are summarized in Table 3. The system constants for DB-1301 were taken from [3] and Rtx-20 from [11]. In all cases, the differences in the system constants are small but generally significant at the 95% confidence level. The main differences are that Rtx-440 is slightly more hydrogen-bond basic and less dipolar/polarizable than Rtx-20 and slightly less hydrogen-bond basic and dipolar/polarizable than DB-1301. All three stationary phases have similar cohesive properties. Differences in electron lone pair interactions are less significant because this interaction makes only a minor contribution to retention for the compared stationary phases. In summary, the three stationary phases show small selectivity differences with the properties of Rtx-440 falling between those of Rtx-20 and DB-1301. For compounds that are weak hydrogen-bond acids DB-1301 is likely to be a suitable replacement for Rtx-440 and for compounds of moderate polarity Rtx-20 is likely to be a suitable replacement for Rtx-440. For difficult separations Rtx-440 affords small selectivity differences to either Rtx-20 or DB-1301 that might be useful for separations where compounds differ in their hydrogen-bond acidity.

As a further indication of selectivity differences, regression methods can be used to describe correlation plots of the retention factors for a varied group of compounds on the compared columns. The regression models are summarized in Table 4 and a representative correlation plot for 51 varied solutes at 100 °C on Rtx-440 and DB-1301 is shown in Fig. 4. There are two general relationships illustrated by the plot. A high level of correlation exists for the two columns for solutes that are weak hydrogen-bond acids. The strong hydrogen-bond acids (e.g. phenols) are displaced from the trendline and clustered below it. This is anticipated based on the interpretation of the system constant differences discussed above and summarized in Table 3. For compounds with either no or weak hydrogen-bond acidity, if DB-1301 is able to substitute for Rtx-440 then a high coefficient of determination together with a slope of 0.5 (the ratio of film thickness for the DB-1301 and Rtx-440 columns is 1:0.5) and an intercept of zero is required for the correlation plots. The data in Table 4 indicates that this is generally the case. The slopes vary from 0.460 to 0.519 for compounds with either no or weak hydrogen-bond acidity with an average value of 0.494 ± 0.026 ($n=5$). At the 95% confidence level most slopes are statistically different to

Table 2
System constants for the Rtx-440 stationary phase ($b=0$)

Temperature (°C)	System constants					Statistics			
	<i>e</i>	<i>s</i>	<i>a</i>	<i>l</i>	<i>c</i>	ρ	SE	<i>F</i>	<i>n</i>
60	-0.085 (0.014)	0.558 (0.015)	0.519 (0.016)	0.741 (0.005)	-2.399 (0.019)	0.999	0.024	7912	59
80	-0.063 (0.012)	0.522 (0.015)	0.431 (0.016)	0.682 (0.004)	-2.508 (0.018)	0.999	0.024	8655	69
100	-0.028 (0.020)	0.481 (0.010)	0.356 (0.015)	0.615 (0.004)	-2.550 (0.018)	0.999	0.025	9757	69
120	0	0.444 (0.010)	0.313 (0.014)	0.558 (0.004)	-2.582 (0.019)	0.999	0.022	8213	65
140	0.034 (0.011)	0.400 (0.016)	0.290 (0.017)	0.510 (0.005)	-2.626 (0.024)	0.998	0.024	3828	60

Table 3

Differences in the systems constants (Δ) and the average difference ($\Delta\Delta$) over the temperature range 60–140 °C for the compared stationary phases

System constant	Temperature					Average ($\Delta\Delta$)
	60	80	100	120	140	
(i) $\Delta[(\text{Rtx-440})-(\text{DB-1301})]$						
<i>l</i>	0.022	0.025	0.019	0.011	0.010	0.017 (± 0.007)
<i>e</i>	0.110	0.076	0.059	0.057	0.082	0.077 (± 0.021)
<i>s</i>	-0.076	-0.055	-0.073	-0.054	-0.076	-0.067 (± 0.011)
<i>a</i>	-0.138	-0.138	-0.190	-0.137	-0.118	-0.144 (± 0.027)
(ii) $\Delta[(\text{Rtx-440})-(\text{Rtx-20})]$						
<i>l</i>	0.027	0.026	0.017	0.009	0.004	0.017 (± 0.010)
<i>e</i>	-0.085	-0.063	-0.028	0	0.034	-0.028 (± 0.048)
<i>s</i>	-0.091	-0.091	-0.124	-0.120	-0.097	-0.105 (± 0.016)
<i>a</i>	0.086	0.078	0.065	0.054	0.070	0.071 (± 0.010)

0.5 but the closeness of the slopes to the target value indicates similar selectivity for the DB-1301 and Rtx-440 stationary phases (for compounds that are not strong hydrogen-bond acids). In all cases, the confidence interval for the intercept includes zero for the regression models. The coefficient of

determination for the regression models varies from 0.983 to 0.994 (with four of the five values >0.992 for the models with strong hydrogen-bond acids deleted) with an average value $r_{\text{av}}^2 = 0.991 \pm 0.005$ ($n = 5$). Inclusion of the phenols in the correlation plot results in a lower coefficient of determina-

Table 4

Correlation models for the retention factors of a varied group of compounds on Rtx-440 and either DB-1301 or Rtx-20

Temperature (°C)	Slope/intercept	Value	Confidence limit		Statistics			
			Upper	Lower	r^2	SE	<i>F</i>	<i>n</i>
(i) DB-1301								
60	Slope	0.460 ± 0.009	0.479	0.442	0.983	0.526	2573	46
	Intercept	-0.048 ± 0.107	0.168	-0.263				
80	Slope	0.475 ± 0.006	0.487	0.464	0.993	0.332	6624	47
	Intercept	-0.095 ± 0.067	0.039	-0.229				
100	Slope	0.490 ± 0.014	0.519	0.461	0.961	0.683	1178	49
	Intercept	-0.209 ± 0.142	0.077	-0.494				
120	Slope	0.480 ± 0.014	0.508	0.450	0.963	0.363	1097	44
	Intercept	-0.091 ± 0.086	0.083	-0.265				
140	Slope	0.486 ± 0.011	0.408	0.464	0.980	0.123	1908	41
	Intercept	-0.042 ± 0.033	0.026	-0.109				
(ii) DB-1301 after removal of phenols ^a								
100	Slope	0.519 ± 0.007	0.533	0.504	0.992	0.319	5357	44
	Intercept	-0.210 ± 0.067	-0.076	-0.345				
120	Slope	0.515 ± 0.007	0.528	0.501	0.994	0.152	6025	37
	Intercept	-0.109 ± 0.037	-0.034	-0.183				
140	Slope	0.501 ± 0.007	0.514	0.488	0.994	0.123	1908	35
	Intercept	-0.051 ± 0.019	-0.013	-0.089				
(iii) Rtx-20								
60	Slope	0.834 ± 0.024	0.881	0.786	0.962	1.153	1249	51
	Intercept	0.048 ± 0.211	0.473	-0.377				
80	Slope	0.871 ± 0.023	0.917	0.826	0.966	0.996	1459	54
	Intercept	0.014 ± 0.186	0.388	-0.360				
100	Slope	0.891 ± 0.023	0.937	0.846	0.969	0.631	1533	52
	Intercept	-0.106 ± 0.128	0.153	-0.364				
120	Slope	0.889 ± 0.014	0.917	0.862	0.989	0.291	4143	47
	Intercept	-0.058 ± 0.059	0.063	-0.178				
140	Slope	0.836 ± 0.018	0.873	0.800	0.981	0.207	2164	46
	Intercept	0.029 ± 0.044	0.118	-0.061				

^a Phenols: phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,3-dimethylphenol, 2,6-dimethylphenol and 2-nitrophenol.

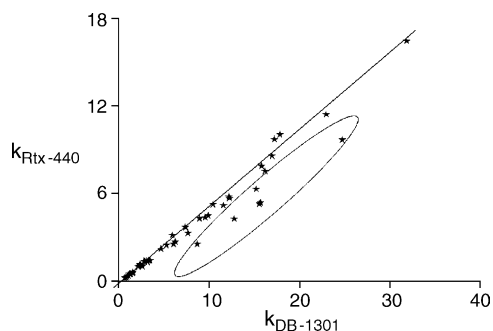


Fig. 4. Plot of the retention factors for a varied group of compounds on Rtx-440 and DB-1301 at 100 °C. The compounds indicated by the ellipse below the trend line are the phenols: phenol; 2-, 3- and 4-methylphenol; 2,3-dimethylphenol; and 2,6-dimethylphenol. The compounds indicated by the trendline are: heptane, octane, nonane, decane, undecane, dodecane, tridecane, methyl hexanoate, methyl octanoate, methyl nonanoate, valeraldehyde, heptanal, octanal, nonanal, 2-hexanone, cyclohexanone, propyl acetate, butyl acetate, pentan-1-ol, pentan-3-ol, 2-methylbutanol, 3-methylbutanol, hexanol, cyclohexanol, octan-1-ol, 2-ethoxyethanol, toluene, styrene, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, acetophenone, benzaldehyde, nitrobenzene, aniline, 4-fluoroaniline, 2-chloroaniline, 1,4-benzodioxane, benzyl alcohol and 2-nitrophenol.

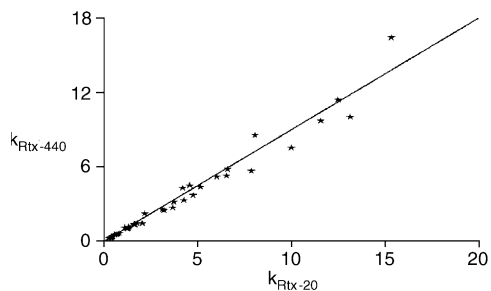


Fig. 5. Plot of the retention factors for a varied group of compounds on Rtx-440 and Rtx-20 at 100 °C. The solutes are identified in the legend to Fig. 4.

tion, Table 4, as expected, since the selectivity of DB-1301 and Rtx-440 for retention of hydrogen-bond acids is characteristically different.

A representative correlation plot for 51 varied solutes at 100 °C on Rtx-440 and Rtx-20 is shown in Fig. 5. In this case there is general scatter around the trendline indicating greater selectivity differences. The target slope in this case is 1.0 (columns have the same film thickness) for the correlation model if both columns have similar selectivity.

The average slope observed, 0.864 ± 0.028 ($n = 5$), is significantly different from 1.0. The confidence interval for the intercepts includes zero. The average coefficient of determination at 0.973 ± 0.011 indicates a modest correlation model reflecting the selectivity differences between the compared columns. The statistically significant difference in dipolarity/polarizability and hydrogen-bond basicity, discussed previously, result in a general retention dispersion between the two columns.

4. Conclusions

The above results indicate that HP-88 should be a useful substitute for poly(cyanopropylsiloxane) stationary phases, such as SP-2340. The different structures of HP-88 and SP-2340 does not result in large changes in separation characteristics while addressing column stability, activity, efficiency and thermal stability issues with poly(cyanopropylsiloxane) stationary phases. Further, it is shown that Rtx-440 is a useful low-polarity stationary phase with complementary separation characteristics to DB-1301 and Rtx-20. While DB-1301, in particular, might be a suitable replacement for Rtx-440 for many separations, mixtures containing strong hydrogen-bond acids are likely to exhibit significant selectivity differences, legitimizing a role for Rtx-440 in method development.

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