System maps for retention of neutral organic compounds under isocratic conditions on a reversed-phase monolithic column

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Abstract

The solvation parameter model is used to create systems maps for the separation of neutral organic compounds on a Chromolith Performance RP-18e octadecylsiloxane-bonded silica-based monolithic column for water–acetonitrile and water–methanol mobile phase compositions from 10 to 70% (v/v) organic solvent. These results demonstrate that the retention properties of the monolithic column are similar to those of conventional octadecylsiloxane-bonded silica particle-packed columns. It is further shown that the selectivity for the monolithic column falls within the selectivity range for typical particle-packed columns at two mobile phase compositions for which a direct comparison is possible.
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Keywords: Retention properties; Monoclinic columns; System maps; Organic compounds, neutral

1. Introduction

Monoliths (or continuous bed columns) are a new concept in column technology, that affords an alternative choice to conventional particle-packed columns for analytical and preparative liquid chromatography [1,2]. Polymeric monoliths have a small surface area and are used for the separation of macromolecules where a large surface area is not required. Silica monoliths, on the other hand, are easily prepared with a bimodal pore structure, providing a larger surface area suitable for the separation of small molecules. Silica monoliths are prepared by a sol–gel method from alkoxysilanes in the presence of a water-soluble organic polymer contained in a mold. After aging the silica rods are subjected to a controlled pore redistribution process using aqueous ammonia at elevated temperatures followed by strengthening of the pore network by thermal treatment. Modification of the silica surface by reaction with conventional organosilane reagents allows the preparation of monoliths for use in different separation modes. Silica rod columns for analytical separations with through pores of 1.5–2 μm, diffusion pores of about 12 nm, a specific surface area of 300–350 m^2/g, and a total porosity of 0.87 were introduced in about 1999 [3,4]. These columns produce a minimum plate height of about 10–15 μm, similar to conventional particle-packed columns containing 5 μm particles, and can be operated at higher flow-rates without a significant loss of separation efficiency compared with particle-packed columns [4–6]. The lower pressure drop and favorable mass transfer properties of silica monoliths

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at high flow-rates is the main advantage of these columns, allowing exploitation for fast separations [5–7].

All monoliths contain macropores to provide convective transport through the continuous bed. Convective transport affords an increase in the rate of mass transfer but its implementation in particle beds is limited by the presence of interparticle voids that provide an alternative flow path of low resistance compared with particle macropores. Employing a continuous structure with convective pores responsible for mobile phase flow connected to mesopores to control the surface area for stationary phase interactions circumvents this problem.

Most studies of silica-based monoliths so far have focused on column preparation techniques and the influence of pore network properties on separation efficiency [1–7]. The separation of standard mixtures under reversed-phase conditions has been widely demonstrated in these studies. This information, however, affords only a qualitative picture of retention properties for the silica-based monoliths. An exception is the paper by McCalley [8], which deals specifically with interactions contributing to retention and peak shape of weak and strong bases on an octadecylsiloxane-bonded silica monolith. The purpose of this study, then, is to provide a comprehensive account of the retention properties of neutral organic compounds on an octadecylsiloxane-bonded silica monolith over a range of mobile phase compositions. The selection of solutes and experimental conditions is made in such a manner as to allow a quantitative comparison of retention properties with conventional octadecylsiloxane-bonded silica particles. For this purpose, comparisons are made within the framework of the solvation parameter model using system maps to illustrate changes in the capacity of the solvated monolith for defined fundamental intermolecular interactions as a function of mobile phase composition [9,10].

The solvation parameter model in a general form suitable for characterizing the retention properties of column packings in reversed-phase chromatography is set out below [9–12]:

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

where k is the solute retention factor. The model equation is made up of product terms representing solute properties (descriptors), indicated by capital letters, and the complementary system properties characteristic of the sorbent and mobile phase, indicated by the lower case letters in italics. Each product term defines the relative contribution of a defined intermolecular interaction to the correlated property, in this case $\log k$. The contribution from electron lone pair interactions is defined by eE, interactions of a dipole type by sS, hydrogen-bond interactions by aA and bB, and differences in cavity formation and dispersion interactions for transfer of the solute from the mobile phase to the solvated stationary phase by vV. The solute descriptors are formally defined as the excess molar refraction, E, dipolarity/polarizability, S, effective hydrogen-bond acidity, A, effective hydrogen-bond basicity, B, and McGowan's characteristic volume, V. Solute descriptors are available for about 4000 compounds with others accessible through calculation and estimation methods [9,11–14].

The system constants characterize the sorption properties of the solvated stationary phase in contact with an identified mobile phase. They are defined as the difference in contributions from electron lone pair interactions, e, dipole-type interactions, s, hydrogen-bond basicity, a, hydrogen-bond acidity, b, and cohesion and dispersion interactions, v, for the mobile phase and solvated stationary phase. The system constants are calculated by multiple linear regression analysis for a varied group of solutes selected to satisfy the statistical and chemical requirements of the model [9,13,15,16].

2. Experimental

Acetonitrile, methanol and water were OmniSolv grade from EM Science (Gibbstown, NJ, USA). Other common chemicals were reagent grade or better and obtained from several sources. The 10 cm × 4.6 mm I.D. Chromolith Performance RP-18e column was obtained from EM Science.

For liquid chromatography, a Hitachi D-7000 liquid chromatograph (Hitachi Instruments, San Jose, CA, USA) fitted with a L-7100 pump, L-7455 diode array detector and L-7300 column oven was used. The column hold-up time was determined by in-

Table 1
Solute descriptors used in the solvation parameter model

Solute	Descriptor				
	V	E	S	A	B
Acetanilide	1.113	0.870	1.40	0.50	0.67
Acetophenone	1.014	0.820	1.01	0	0.48
2-Aminophenol	0.875	1.110	1.10	0.60	0.66
Aniline	0.816	0.955	0.96	0.26	0.50
Anisole	0.916	0.710	0.75	0	0.29
Benzamide	0.973	0.990	1.50	0.49	0.67
Benzene	0.716	0.610	0.52	0	0.14
Benzonitrile	0.871	0.740	1.11	0	0.33
Benzophenone	1.481	1.447	1.50	0	0.50
Benzyl alcohol	0.916	0.832	0.97	0.37	0.56
Benzyl benzoate	1.680	1.264	1.42	0	0.51
Biphenyl	1.324	1.360	0.99	0	0.26
1-Bromonaphthalene	1.260	1.598	1.13	0	0.13
3-Bromophenol	0.950	1.060	1.15	0.70	0.16
Butyrophenone	1.300	0.800	0.95	0	0.51
Caffeine	1.363	1.500	1.60	0	1.33
4-Chloroaniline	0.939	1.060	1.13	0.30	0.35
1-Chloronaphthalene	1.208	1.417	1.06	0	0.13
4-Chlorophenol	0.898	0.920	1.08	0.67	0.20
Cinnamyl alcohol	1.155	1.152	0.90	0.58	0.60
Coumarin	1.062	1.060	1.79	0	0.46
Dibutyl phthalate	2.270	0.700	1.40	0	0.86
3,4-Dichloroaniline	1.061	1.158	1.24	0.35	0.25
Diethyl phthalate	1.711	0.729	1.40	0	0.88
2,6-Dimethylphenol	1.057	0.860	0.79	0.39	0.39
N-Ethylaniline	1.099	0.945	0.88	0.17	0.51
Ethylbenzene	0.998	0.613	0.51	0	0.15
Fluorene	1.357	1.588	1.06	0	0.25
Hexanophenone	1.580	0.720	0.95	0	0.50
4-Hydroxybenzyl alcohol	0.975	0.998	1.15	0.88	0.85
4-Hydroxybenzaldehyde	0.932	1.010	1.54	0.79	0.40
2-Methoxynaphthalene	1.285	1.390	1.13	0	0.35
2-Methylphenol	0.916	0.840	0.86	0.52	0.30
4-Methylphenol	0.916	0.820	0.87	0.57	0.31
Naphthalene	1.085	1.340	0.92	0	0.20
1-Naphthol	1.144	1.520	1.05	0.61	0.37
2-Naphthol	1.144	1.520	1.08	0.61	0.40
2-Nitroaniline	0.990	1.180	1.37	0.30	0.36
4-Nitroaniline	0.990	1.220	1.91	0.42	0.38
Nitrobenzene	0.891	0.871	1.11	0	0.28
4-Nitrobenzyl alcohol	1.090	1.064	1.39	0.44	0.62
4-Nitrotoluene	1.032	0.870	1.11	0	0.28
Octanophenone	1.859	0.720	0.95	0	0.50
Phenanthrene	1.454	2.055	1.29	0	0.26
Phenol	0.775	0.810	0.89	0.60	0.30
2-Phenylethanol	1.057	0.811	0.91	0.30	0.65
4-Phenylphenol	1.383	1.560	1.41	0.59	0.45
Progesterone	2.620	1.450	3.30	0	1.10
Propriophenone	1.160	0.800	0.95	0	0.51
Propylbenzene	1.139	0.604	0.50	0	0.15
Pyridine	0.675	0.631	0.84	0	0.47
Quinoline	1.044	1.268	0.97	0	0.51
Toluene	0.857	0.601	0.52	0	0.14
o-Toluidine	0.957	0.966	0.92	0.23	0.45
m-Toluidine	0.957	0.946	0.95	0.23	0.55
p-Toluidine	0.957	0.923	0.95	0.23	0.52
1,2,3-Trimethylbenzene	1.139	0.728	0.61	0	0.19
Valerophenone	1.440	0.800	0.95	0	0.50

jection of an aqueous solution of sodium nitrate (26 mg/ml).

Multiple linear regression analysis and statistical calculations were performed on a Gateway E-4200 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 an in-house database and are summarized in Table 1. Solutes were selected to minimize cross-correlation and to provide a reasonable distribution of descriptors throughout the descriptor space, as indicated by histogram plots. Subsets of the solutes provide a reasonable range of retention properties in reversed-phase chromatography with a wide range of solvent strength and retain the characteristics of low cross-correlation and effective distribution across the descriptor space. The solutes in Table 1 should be useful for determining system maps for additional reversed-phase columns.

3. Results and discussion

There are several hallmarks of a separation by reversed-phase chromatography that distinguishes them from other liquid chromatographic methods [17]. One of the most symbolic being a decrease in polarity of the mobile phase, equivalent to increasing the volume fraction of organic solvent in an aqueous mixture, leads to a decrease in retention that can be described by:

$$\log k = \log k_{\mathrm{w}} + a_1 \phi + a_2 \phi^2 \tag{2}$$

and if only a limited range of binary mobile phase compositions is considered, by:

$$\log k = \log k_{\mathrm{w}} + S\phi \tag{3}$$

where ϕ is the volume fraction of organic solvent (binary mobile phase), $\log k_{\mathrm{w}}$ the retention factor for water as the mobile phase (usually estimated by an extrapolation method), S the slope of the experimental data after fitting to a linear regression model (sometimes taken as a general measure of the solvent strength of the organic solvent), and a_1 and a_2 are regression constants for the second-order model, which are not usually assigned any physical significance [10,17–19]. In theory it should be possible to

compare stationary phase properties using $\log k_{\mathrm{w}}$ for select solutes. In practice, general errors in estimating this parameter and its ambiguous relationship to a defined two-phase system make this choice unacceptable [10,20,21]. Instead, we have fit Eqs. (2) and (3) to the retention data measured in this study and used it as a check for confirmation with general expectations for a reversed-phase chromatographic system for acetonitrile and methanol as the mobile phase strength adjusting solvent. The data in Table 2 for acetonitrile and Table 3 for methanol are re-

stricted to those compounds that had accessible retention factors over the full composition range investigated of 10 to 70% (v/v) organic solvent. These results are representative of the other compounds in Table 1, for which a smaller composition range was appropriate based on practical considerations. For acetonitrile–water mobile phase compositions, the variation of the retention factor with mobile phase composition conforms to a non-linear model, Eq. (2), with a coefficient of determination >0.99 in all cases. For methanol–water mobile

Table 2
Fit of the experimental retention factors ($\log k$) to Eq. (2) or (3) for acetonitrile–water mobile phase compositions (10–70% v/v)

Solute	Non-linear model Eq. (2)				Linear model Eq. (3)		
	$\log k_{\mathrm{w}}$	a_1	a_2	r^2	$\log k_{\mathrm{w}}$	$-S$	r^2
Acetanilide	1.02	−4.84	3.21	0.989	0.64	2.27	0.933
Acetophenone	1.54	−4.55	2.16	0.996	1.28	2.82	0.978
2-Aminophenol	0.41	−3.44	2.48	0.993	0.11	1.46	0.914
Aniline	0.74	−2.90	1.13	0.998	0.60	2.00	0.988
Anisole	1.82	−4.13	1.41	1.000	1.65	3.00	0.993
Benzene	1.62	−3.15	0.57	1.000	1.55	2.69	0.998
Benzonitrile	1.39	−3.66	1.24	0.999	1.24	2.67	0.992
Benzyl alcohol	0.93	−4.38	2.80	0.992	0.59	2.15	0.944
3-Bromophenol	2.11	−5.86	2.85	0.999	1.77	3.59	0.980
Butyrophenone	2.71	−6.49	3.33	0.999	2.31	3.83	0.977
4-Chloroaniline	1.62	−4.51	1.91	0.998	1.39	2.98	0.986
4-Chlorophenol	1.90	−5.44	2.55	0.998	1.59	3.40	0.981
Cinnamyl alcohol	1.89	−6.44	3.90	0.996	1.42	3.32	0.957
Coumarin	1.50	−4.99	2.64	0.994	1.18	2.88	0.970
3,4-Dichloroaniline	2.47	−6.35	3.19	1.000	2.09	3.79	0.979
Diethyl phthalate	3.08	−8.31	4.96	0.997	2.48	4.34	0.960
2,6-Dimethylphenol	1.98	−5.36	2.64	0.999	1.67	3.25	0.980
N-Ethylaniline	1.75	−3.74	1.11	0.998	1.62	2.85	0.994
4-Hydroxybenzaldehyde	0.85	−4.54	3.02	0.983	0.48	2.13	0.927
2-Methylphenol	1.54	−4.60	2.08	0.997	1.29	2.94	0.982
4-Methylphenol	1.53	−4.75	2.21	0.997	1.26	2.99	0.981
1-Naphthol	2.50	−6.73	3.34	0.997	2.10	4.06	0.978
2-Naphthol	2.47	−7.21	4.15	0.998	1.97	3.89	0.965
2-Nitroaniline	1.50	−4.33	1.76	0.998	1.29	2.92	0.987
4-Nitroaniline	1.17	−3.97	1.66	0.999	0.97	2.64	0.987
4-Nitrobenzyl alcohol	1.26	−5.24	3.31	0.998	0.87	2.59	0.951
Nitrobenzene	1.61	−3.75	1.07	1.000	1.48	2.90	0.995
4-Nitrotoluene	2.23	−5.02	1.93	1.000	2.00	3.48	0.990
Phenol	1.01	−3.99	2.12	0.999	0.76	2.29	0.974
2-Phenylethanol	1.36	−5.25	3.16	0.996	0.98	2.73	0.957
Propriophenone	2.12	−5.42	2.65	0.999	1.80	3.31	0.980
Pyridine	0.54	−3.28	2.13	0.985	0.29	1.57	0.934
Quinoline	1.88	−6.37	4.31	0.994	1.36	2.93	0.933
Toluene	2.25	−4.38	1.33	0.999	2.09	3.31	0.995
o-Toluidine	1.21	−3.65	1.46	0.996	1.04	2.48	0.985
m-Toluidine	1.27	−3.87	1.24	0.996	1.07	2.56	0.984
p-Toluidine	1.27	−3.84	1.59	0.997	1.08	2.57	0.986

Table 3

Fit of the experimental retention factors (log k) to Eq. (2) or (3) for methanol–water mobile phase compositions (10–70% v/v)

Solute	Non-linear model Eq. (2)				Linear model Eq. (3)		
	$\log k_{\mathrm{w}}$	a_1	a_2	r^2	$\log k_{\mathrm{w}}$	$-S$	r^2
Acetanilide	1.16	2.89	0.994				
Acetophenone	1.82	−4.00	0.89	1.000	1.72	3.29	0.998
2-Aminophenol	0.46	2.25	0.999				
Aniline	0.74	−2.09	−0.29	1.000	0.77	2.33	0.999
Anisole	1.80	−2.61	−0.35	1.000	1.84	2.89	0.999
Benzene	1.62	−3.15	0.57	1.000	1.55	2.69	0.998
Benzamide	0.91	−3.57	0.98	1.000	0.79	2.78	0.996
Benzonitrile	1.49	3.07	1.000				
Benzyl alcohol	1.09	2.71	1.000				
3-Bromophenol	1.98	−2.73	−0.83	1.000	2.08	3.40	0.998
4-Chlorophenol	1.75	−2.49	−0.88	1.000	1.86	3.19	0.997
Cinnamyl alcohol	1.99	3.61	0.994				
Coumarin	1.89	−4.78	1.53	1.000	1.70	3.55	0.970
2,6-Dimethylphenol	2.00	3.32	1.000				
2-Methylphenol	1.57	2.97	1.000				
4-Methylphenol	1.59	3.08	1.000				
1-Naphthol	2.44	3.88	1.000				
2-Naphthol	2.41	3.96	1.000				
2-Nitroaniline	1.50	3.07	1.000				
4-Nitroaniline	1.09	2.98	0.999				
4-Nitrobenzyl alcohol	1.32	−3.47	0.62	0.999	1.25	2.97	0.998
Nitrobenzene	1.59	2.83	0.999				
4-Nitrotoluene	2.20	3.43	1.000				
Phenol	0.96	−2.12	−0.58	1.000	1.03	2.59	0.998
2-Phenylethanol	1.50	3.06	1.000				
Propriophenone	2.34	−4.34	0.81	1.000	2.24	3.69	0.998
Quinoline	2.28	−4.66	1.10	1.000	2.14	3.78	0.997
Toluene	2.07	−1.89	−1.36	1.000	2.23	2.98	0.993
m-Toluidine	1.33	2.81	1.000				

phase compositions a linear model, Eq. (3), is preferred in most cases, with a few compounds better represented by a non-linear model. This difference in fit for acetonitrile–water and methanol–water mobile phase compositions is not unusual [10]. The results in Tables 2 and 3 indicate that the retention data for a group of solutes selected for their variation in solvation properties is distributed in a typical fashion for reversed-phase chromatography.

Greater details of the retention mechanism are available from the system maps obtained from the solvation parameter model. The system constants for each acetonitrile–water and methanol–water composition are summarized in Table 4. System maps for acetonitrile–water and methanol–water compositions are presented in Figs. 1 and 2, respectively. In both cases, the dominant contribution to retention is the cavity and dispersion interaction term (v constant) with a small contribution from electron lone pair interactions (e constant). Both system constants have a positive sign for all mobile phase compositions. As the volume fraction of organic solvent increases the v system constant decreases. This is a reflection of the fact that the difference in cohesion and dispersion interactions between the mobile and stationary phases is smaller at higher volume fractions of organic solvent. This provides the basis for the observation that increasing the volume fraction of organic solvent in the mobile phase results in reduced retention in reversed-phase chromatography. Polar interactions are more favorable in the mobile phase and reduce retention (s, a, b system constants have a negative sign). The dominant characteristic property of the mobile phase is its hydrogen-bond

Table 4
System constants for a Chromolith RP-18e column with different acetonitrile–water and methanol–water mobile phase compositions

Organic solvent % (v/v)	System constants						Statistics[a]			
	v	e	s	a	b	c	ρ	SE	F	n
Acetonitrile										
10	3.28	0.35	−0.59	−0.45	−2.39	−0.64	0.995	0.062	654	39
	(0.07)	(0.06)	(0.04)	(0.04)	(0.06)	(0.07)				
20	2.76	0.30	−0.58	−0.50	−2.40	−0.50	0.995	0.071	738	45
	(0.07)	(0.06)	(0.05)	(0.05)	(0.06)	(0.06)				
30	2.26	0.22	−0.53	−0.58	−2.14	−0.46	0.996	0.066	1260	54
	(0.05)	(0.04)	(0.03)	(0.04)	(0.05)	(0.04)				
40	1.81	0.13	−0.43	−0.56	−1.77	−0.49	0.996	0.058	1218	55
	(0.03)	(0.03)	(0.03)	(0.04)	(0.05)	(0.04)				
50	1.49	0.07	−0.33	−0.52	−1.55	−0.57	0.996	0.049	1087	53
	(0.03)	(0.03)	(0.03)	(0.03)	(0.05)	(0.03)				
60	1.19	0.09	−0.32	−0.48	−1.17	−0.66	0.992	0.057	575	54
	(0.03)	(0.03)	(0.04)	(0.04)	(0.05)	(0.04)				
70	1.03	0.09	−0.32	−0.50	−1.01	−0.82	0.986	0.067	329	53
	(0.04)	(0.03)	(0.04)	(0.04)	(0.05)	(0.05)				
Methanol										
10	3.83	0	−0.51	−0.26	−2.18	−0.91	0.984	0.091	224	34
	(0.16)	(0.06)	(0.06)	(0.10)	(0.14)					
20	3.33	0.21	−0.63	−0.27	−2.24	−0.79	0.991	0.081	368	38
	(0.10)	(0.09)	(0.05)	(0.07)	(0.09)	(0.09)				
30	2.91	0.31	−0.69	−0.34	−2.19	−0.70	0.993	0.076	555	43
	(0.08)	(0.06)	(0.05)	(0.05)	(0.08)	(0.08)				
40	2.48	0.34	−0.72	−0.43	−1.98	−0.63	0.993	0.091	555	46
	(0.07)	(0.06)	(0.06)	(0.06)	(0.07)	(0.07)				
50	2.10	0.30	−0.67	−0.41	−1.77	−0.67	0.992	0.087	540	47
	(0.06)	(0.06)	(0.06)	(0.05)	(0.07)	(0.07)				
60	1.78	0.23	−0.62	−0.34	−1.69	−0.72	0.993	0.070	561	46
	(0.05)	(0.05)	(0.05)	(0.05)	(0.07)	(0.05)				
70	1.49	0.20	−0.58	−0.36	−1.47	−0.84	0.991	0.068	459	50
	(0.05)	(0.05)	(0.04)	(0.04)	(0.07)	(0.05)				

[a] ρ, overall multiple correlation coefficient; SE, standard error in the estimate; F, Fischer's statistic; n, number of solutes; values in parentheses are the standard deviations in the system constants.

acidity, which is (largely) a fundamental property of water, and is responsible for the (relatively) low retention of hydrogen-bond basic solutes in reversed-phase chromatography. There is good general agreement in the form of the system maps for the Chromolith RP-18e column and system maps for chemically bonded silica-based particle stationary phases [9,10].

To place the retention properties of the Chromolith RP-18e column into perspective the system constants can be compared with a peer group of octa-decylsiloxane-bonded silica particle-packed columns. System constants have generally been determined for a limited range of mobile phase compositions, with

acetonitrile–water (30:70) and methanol–water (50:50) being the most common [10]. The available data for octadecylsiloxane-bonded silica particle-packed columns are summarized in Table 5. The system constants for the Chromolith RP-18e column fall within the range of the octadecylsiloxane-bonded silica particle-packed columns or are close in value to the largest or smallest value for the octa-decylsiloxane-bonded silica particle-packed columns. The difference in system constants for the Chromolith RP-18e column and its nearest neighbor in Table 5 is less than the range of system constant values for the octadecylsiloxane-bonded silica par-ticle-packed columns for both mobile phase com-
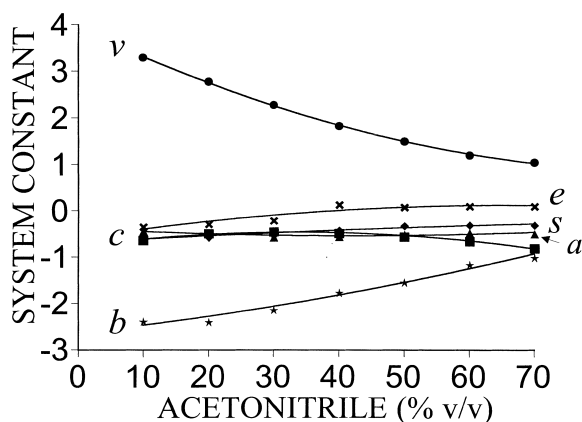
Fig. 1. System map for acetonitrile–water mobile phase compositions.

positions. Thus, selectivity differences for the Chromolith RP-18e column and its nearest neighbor are no greater than differences that exist among the group of octadecylsiloxane-bonded silica particle-packed columns.

Selectivity equivalence of stationary phases is generally demonstrated by comparison of the system constant ratios (e/v, s/v, a/v, b/v) [9,10,13,17]. The retention of solutes on columns with similar system constant ratios is highly correlated. The band order and band spacing is expected to be (largely) the same, even if the absolute retention for the solutes on the compared columns is different. The results in Table 5 are easily recast in terms of the system constant ratios, not shown here. The retention properties of the Spherisorb ODS-2 column for the methanol–water mobile phase composition are expected to provide a good prediction of the separation characteristics of the Chromolith RP-18e column. The sum of the differences for the system constant ratios equals 0.07, and the largest difference in any single system constant ratio is only 0.03. For the acetonitrile–water mobile phase compositions, the same treatment indicates that LiChrospher 100 RP-18e and LiChrospher 100 RP-18 should provide a good prediction of the separation characteristics of the Chromolith RP-18e column. The sum of the differences for the system constant ratios equals 0.10 for LiChrospher 100 RP-18 (0.11 for LiChrospher 100 RP-18e) and the largest difference in any single system constant ratio is only 0.06 for both LiChrospher columns. Building a regression model for the retention factors on LiChrospher 100 RP-18 [26] in common with the measured values for the Chromolith RP-18e column gave the results shown in Fig. 3 and below:
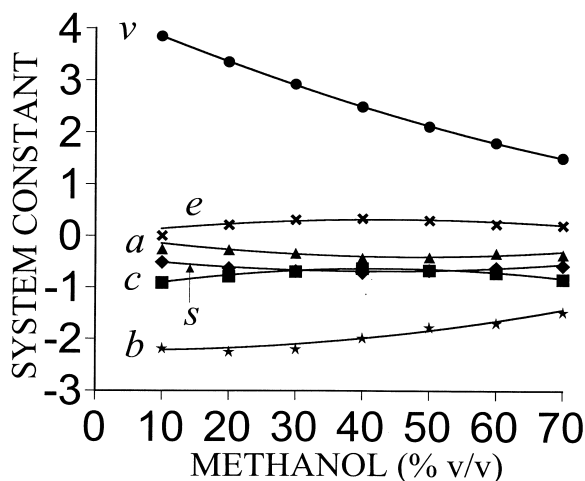
$$\log k \text{ (Chromolith RP-18e)}$$
$$= 1.13(\pm 0.03) \log k \text{ (LiChrospher 100 RP-18)}$$
$$- 0.75(\pm 0.03), \ r^2 = 0.992, \text{SE} = 0.048, F$$
$$= 1912, n = 17 \quad\quad\quad\quad (4)$$

These results indicate the favorable prospects for selectivity transfer of separations on the LiChrospher 100 RP-18 column to the Chromolith RP-18e column, at least for the 30% (v/v) acetonitrile–water mobile phase composition. Since the chromatographic efficiency of the monolith column is about the same as that anticipated for a 5 μm particle-packed column, method transfer should be reasonably straightforward with the added advantage that faster separations without a significant loss of chromatographic efficiency are possible for monolithic columns. Our observations on peak tailing of bases are by no means as extensive as those of McCalley [8] but are in keeping with his conclusions. Compounds that tail on high-purity silica-based octadecylsiloxane columns were also found to show similar properties on the Chromolith RP-18e column. For the sepa-

Fig. 2. System map for methanol–water mobile phase compositions.

Table 5
System constants for contemporary octadecylsiloxane silica-bonded stationary phases at a fixed mobile phase composition for comparison with the Chromolith RP-18e column

| Stationary phase	System constants					Ref.
	v	e	s	a	b	
Methanol–water (50:50)						
Chromolith RP-18e	2.10	0.30	−0.67	−0.41	−1.77	
Hypersil ODS	2.46	0.17	−0.66	−0.20	−1.84	[10]
Zorbax ODS	2.68	0.38	−0.83	−0.29	−2.17	[10]
Spherisorb ODS-2	2.14	0.36	−0.68	−0.47	−1.84	[10]
Capcell Pak C18	2.23	0.18	−0.47	−0.76	−2.03	[22]
J.T. Baker ODS	2.03	0.16	−0.40	−0.34	−1.51	[23]
Nucleosil C18	1.78	0.20	−0.52	−0.45	−1.62	[10]
Nucleosil C18 (HD)	2.37	0.20	−0.38	−0.20	−2.01	[24]
Partisil ODS	2.28	0.44	−1.07	−0.48	−2.07	[25]
Acetonitrile–water (30:70)						
Chromolith RP-18e	2.26	0.22	−0.53	−0.58	−2.14	
LiChrospher 100 RP-18e	1.95	0.30	−0.48	−0.59	−1.95	[26]
LiChrospher 100 RP-18	1.84	0.26	−0.45	−0.57	−1.84	[26]
Purospher RP-18e	1.97	0.31	−0.50	−0.62	−1.97	[26]
Purospher	1.89	0.27	−0.33	−0.60	−2.06	[26]
LiChrospher PAH	1.76	0.28	−0.52	−0.55	−1.61	[26]
SymmetryShield RP-C18	2.01	0.39	−0.45	−0.43	−2.10	[26]
Aquapore OD-300	1.62	0.23	−0.40	−0.48	−1.59	[26]
Synchropak RP-C18	1.38	0.19	−0.34	−0.45	−1.30	[26]
J.T. Baker ODS	2.11	0.17	−0.27	−0.49	−1.90	[23]
Inertsil ODS2	1.78	0.09	−0.32	−0.41	−1.73	[27]
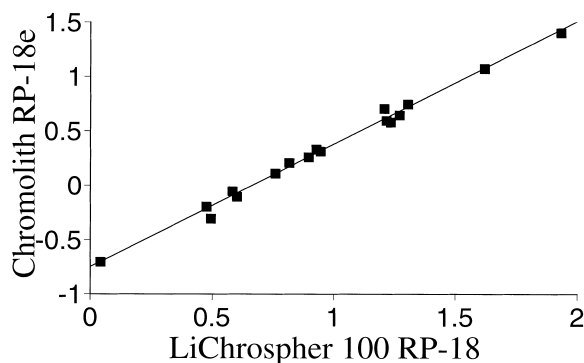
Fig. 3. Plot of retention factors ($\log k$) for a varied group of solutes on the Chromolith RP-18e monolithic column against the LiChrospher 100 RP-18 particle-packed column for the mobile phase 30% (v/v) acetonitrile–water. Solutes plotted on the figure are acetophenone, aniline, anisole, benzyl alcohol, caffeine, 2,6-dimethylphenol, ethylbenzene, 2-methylphenol, 4-methylphenol, 1-naphthol, 2-naphthol, 4-nitroaniline, nitrobenzene, phenol, pyridine, toluene, and *o*-toluidine.

ration of nitrogen-containing bases we see no specific advantage for the Chromolith RP-18e column over conventional silica-based, particle-packed columns.

4. Conclusions

System maps are provided for the Chromolith RP-18e monolithic column for acetonitrile–water and methanol–water mobile phase compositions. These maps should be useful for predicting the retention properties of thousands of compounds with known or estimated descriptor values in isocratic mobile phase compositions containing from 10 to 70% (v/v) acetonitrile or methanol. Although the technology used to prepare silica-based monolithic columns is different to conventional silica-based particle columns, it results in materials for reversed-phase chromatography with similar retention characteristics. The main advantage of the monolithic columns is their superior performance for fast sepa-

rations. The similar retention properties to particle stationary phases should be advantageous for method transfer.

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