Short communication

System maps for retention of small neutral compounds on a superficially porous particle column in reversed-phase liquid chromatography

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ABSTRACT

The system constants of the solvation parameter model are used to prepare system maps for the retention of small neutral molecules on the ocadecylsiloxane-bonded silica superficially porous particle stationary phase (Kinetex C18) for aqueous-organic solvent mobile phases containing 10–70% (v/v) methanol or acetonitrile. A comparison of the system constants with eight commercially available octadecylsiloxane-bonded silica columns for the same separation conditions confirms that the general retention properties of Kinetex C-18 are similar to totally porous octadecylsiloxane-bonded silica stationary phases and that method transfer should be no more difficult than that usually observed when substituting one octadecylsiloxane-bonded silica column for another.

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1. Introduction

Recent developments in liquid chromatography have concentrated on improvements in column technology and instrumentation with a view to improving its intrinsic performance and to reduce the separation time compared with the standards set in the previous decade [1–4]. One attractive approach to achieving these goals is the development of superficially porous particles, also known as fused-core or core-shell particles, consisting of a solid impenetrable core surrounded by a thin layer of porous stationary phase. Compared with totally porous particles, columns packed with superficially porous particles provide smaller plate heights for the same particle diameter, a more homogeneous packing density, a lower column operating pressure for the same performance, and can utilize higher column flow rates in larger diameter columns compatible with a wider range of instruments [3,5–7]. They have moved from an experimental product to a commodity item in a short time indicating that the claims made at the beginning for this technology were well founded. They are used routinely in many laboratories today.

The purpose of this report is not to discuss further the kinetic characteristics and structural optimization of superficially porous particles, which are documented in several reviews [1–3]. The current study was undertaken to characterize the retention properties of a commercially available superficially porous particle material, Kinetex C-18, to establish whether columns of this type are similar in retention properties to octadecylsiloxane-bonded totally porous silica stationary phases. If so, this will facilitate method transfer, and if not, to explore how differences in the manufacturing process lead to observed changes in retention properties.

The hydrophobic subtraction model has been used to characterize a large number of reversed-phase columns with the results assembled in a large database for the identification of columns with (near) equivalent or (most) different selectivity [8,9]. While allowing for a rapid evaluation of new columns according to a defined protocol and a comparison with existing columns in the database, all measurements are referenced to a single mobile phase composition. This method, therefore, fails to provide insight into the retention properties for other conditions than those specified in the protocol and for different organic modifiers. The retention properties of reversed-phase sorbents are subject to variation

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Table 1
Solute descriptors used in the solvation parameter model.

Compound	Descriptors				
	E	S	A	B°	V
4-Aminobenzonitrile	1.087	1.780	0.460	0.500	0.9710
2-Aminobiphenyl	1.488	1.480	0.260	0.480	1.4240
2-Aminophenol	1.110	1.310	0.610	0.600	0.8750
Aniline	0.955	1.019	0.236	0.483	0.8162
Anisole	0.712	0.762	0	0.313	0.9160
Benzaldehyde	0.813	1.027	0	0.395	0.9730
Benzamide	1.262	1.387	0.642	0.655	0.9728
Benzene	0.608	0.507	0	0.143	0.7176
Benzenesulfonamide	1.173	1.862	0.674	0.679	1.0971
Benzophenone	1.204	1.294	0	0.580	1.4808
2-Bromoacetophenone	1.048	1.391	0	0.470	1.1889
3-Bromophenol	1.081	0.774	0.948	0.205	0.9501
Caffeine	1.596	1.694	0.050	1.246	1.3632
4-Chlorophenol	1.007	0.788	0.856	0.212	0.8975
Cinnamyl alcohol	1.092	0.972	0.486	0.597	1.1546
Coumarin	1.397	1.647	0	0.525	1.7106
4-Cyanophenol	1.084	1.268	0.820	0.381	0.9298
1,3-Dibromobenzene	1.177	0.800	0	0.054	1.0664
Diethyl phthalate	0.725	1.393	0	0.888	1.7106
N,N-Diethylaniline	0.961	0.808	0	0.404	1.3798
N,N-Dimethylaniline	0.956	0.913	0	0.404	1.0980
1,3-Dimethylbenzene	0.625	0.504	0	0.183	0.9982
1,4-Dimethylbenzene	0.615	0.494	0	0.165	0.9982
2,4-Dinitrophenol	1.500	1.427	0.011	0.679	1.1236
Diphenylamine	1.623	1.268	0.140	0.520	1.4240
Diphenyl ether	1.221	0.947	0	0.307	1.3829
4-Fluoroaniline	0.780	0.974	0.314	0.436	0.8339
4-Hydroxybenzaldehde	1.124	1.256	0.956	0.454	0.9317
8-Hydroxyquinoline	1.057	1.085	0.239	0.548	1.1030
Indole	1.129	1.314	0.376	0.225	0.9464
Iodobenzene	1.182	0.782	0	0.135	0.9747
2-Methoxybenzaldehyde	0.956	1.120	0	0.590	1.0730
2-Methylbenzaldehyde	0.870	0.960	0	0.400	1.0140
4-Methylphenol	0.808	0.762	0.672	0.354	0.9160
Methyl salicylate	0.850	0.820	0.010	0.480	1.1310
2-Naphthaldehyde	1.979	1.732	0	0.375	1.2420
Naphthalene	1.228	0.906	0	0.190	1.0854
Nicotinamide	1.564	1.918	0.317	0.921	0.9317
4-Nitroaniline	1.226	1.833	0.599	0.341	0.9904
2-Nitrophenol	0.925	1.081	0.052	0.357	0.9493
3-Nitrophenol	1.077	1.244	1.072	0.240	0.9493
4-Nitrophenol	1.137	1.297	1.223	0.229	0.9493
Pentafluorophenol	0.297	0.830	0.790	0.090	0.8631
2-Phenylethanol	0.787	0.815	0.419	0.628	1.0569
1-Phenyl-2-propanol	0.787	0.815	0.291	0.691	1.1978
Phthalimide	1.182	1.658	0.282	0.577	1.0208
Pyridine	0.635	0.842	0	0.454	0.6753
Quinoline	1.268	1.096	0	0.554	1.0443
Toluene	0.606	0.507	0	0.137	0.8573
Vanillin	1.202	1.475	0.313	0.716	1.1313

as a result of the selective adsorption of the organic modifier with formation of an interphase region responsible for retention [10,11]. Consequently, the hydrophobic subtraction model is limited in its ability to describe retention for varied mobile phase conditions. Our preferred method for studying retention as a function of mobile phase composition and type of organic modifier is through the use of system maps [11,12]. System maps are a continuous plot of the system constants derived from the solvation parameter model against a selected experimental variable, such as mobile phase composition or temperature for reversed-phase liquid chromatography. The simultaneous variation of the system constants as a function of mobile phase composition and temperature or the study of ternary mobile phase compositions results in a 3-D surface plot used mainly to predict retention maps for method development [11,13]. The simpler 2-D system maps are used in this study to evaluate the parameters that contribute to retention for binary mobile phase compositions from 10 to 70% (v/v) methanol and acetonitrile as organic modifiers for Kinetex

C-18 and subsequently to project these results onto the selectivity space occupied by octadecylsiloxane-bonded totally porous silica stationary phases studied previously [14–22]. The general use of system maps in reversed-phase liquid chromatography is reviewed in [11,12] for thin-layer chromatography in [23], for micellar electrokinetic chromatography in [24], and for gas chromatography in [25–27]. In addition, several studies have compared multiple octadecylsiloxane-bonded silica columns with a single or few mobile phase compositions [28–34], which are reviewed in [11,12,35,36].

The solvation parameter model in the form suitable for modeling retention in reversed-phase liquid chromatography is set out below [12,36–39]:

$$\log k = c + eE + sS + aA + bB° + vV \qquad (1)$$

where k is the retention factor. The lower case letters on the right-hand side of Eq. (1) are system constants that describe the complementary interactions of the system with the solute descrip-