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Selectivity equivalence of poly(ethylene glycol) stationary phases for gas chromatography

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Abstract

The solvation parameter model is used to study differences in selectivity for poly(ethylene glycol) stationary phases for packed column (Carbowax 20M) and fused-silica, open-tubular column (HP-20M, AT-Wax, HP-INNOWax and DB-FFAP) gas chromatography. All phases are dipolar, strongly hydrogen-bond basic with no hydrogen-bond acidity and of moderate cohesion. No two phases are exactly alike, however, and selectivity differences identified with cavity formation and dispersion interactions, n- and π -electron pair interactions, dipole-type interactions and hydrogen-bond interactions are quantified by differences in the system constants at a fixed temperature where retention occurs solely by gas–liquid partitioning. The system constants vary linearly with temperature over the range 60–140°C (except for n- and π -electron pair interactions which are temperature invariant) facilitating a general comparison of the importance of temperature on selectivity differences for compared phases. From a mechanistic point of view it is demonstrated that selectivity differences can result from chemical differences between the poly(ethylene glycol) stationary phases and from differences in the relative contribution of interfacial adsorption to the retention mechanism. The latter depends on both system properties and solute characteristics. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Poly(ethylene glycols) have been widely used as general purpose polar stationary phases for the separation of volatile polar compounds, such as flavors and fragrances, solvents and fatty acid esters, since the early days of gas chromatography [1–3]. The most popular phase is Carbowax 20M, a waxy

solid with a molecular mass of 14 000 to 18 000 melting at 60°C to a stable liquid with a maximum operating temperature of about 225°C [4]. Specially purified poly(ethylene glycols) of higher molecular mass, such as Superox-4 (molecular mass 4 million) [5] and Superox-20M [5,6] can be used at temperatures up to about 250–275°C. Pluronic phases have a lower polydispersity than Carbowax phases and are prepared by condensing propylene oxide with propylene glycol [7]. The resulting chain is then extended on both sides by the controlled addition of ethylene oxide until the desired molecular mass is

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obtained (usually in the range 2000–8000 for materials used in gas chromatography). The pluronic phases are not as widely used as the Carbowax phases. Condensing Carbowax 20M with 2-nitroterephthalic acid produces a new material, FFAP, with improved chromatographic properties for the separation of organic acids.

Carbowax 20M was one of the earliest phases used routinely for the preparation of wall-coated open tubular (WCOT) columns because of its good film-forming properties. In addition, the thermal decomposition products of Carbowax 20M provided a popular method of surface deactivation for subsequent coating with moderately polar stationary phases in the early development of capillary column technology [8]. The improved chemical and thermal stability of modern poly(ethylene glycol) WCOT columns is achieved through bonding the polymer to the column wall and/or through crosslinking. For commercial columns the details remain proprietary information but some general clues are contained in the literature [7,9–11]. Immobilization is possible using “autocrosslinking” poly(ethylene glycols), free radical crosslinking of copolymers of poly(ethylene glycol) and vinylsiloxanes, or by acid-catalyzed reactions with an alkyltrialkoxysilane coupling reagent. Crosslinking partially destroys the crystallinity of the poly(ethylene glycol) polymer resulting in a lower column operating temperature and improved film diffusion properties.

For the present it is unknown how useful the extensive packed column data obtained for Carbowax 20M is for predicting the selectivity of separations performed on open tubular columns prepared from poly(ethylene glycols). There are a number of reasons for this. Retention on packed and open tubular columns may be influenced to different extents by contributions from interfacial adsorption [12–21]. The chemistry used to immobilize poly(ethylene glycol) phases on open tubular columns may result in changes in selectivity that are unrelated to the properties of the free polymer. Differences in molecular mass between Carbowax 20M and the poly(ethylene glycols) used to prepare WCOT columns could result in changes in selectivity. The purpose of this paper is to establish the magnitude of column type, differences in immobilization chemis-

try and the contribution of interfacial adsorption to retention on column selectivity as a general indication of the importance of these factors on models used for structure-driven, computer-aided method development in gas chromatography [22–24].

2. Theory

With a few simplifying assumptions it is possible to state a general model for retention in gas–liquid chromatography that includes interfacial adsorption as a retention mechanism [12,21,25–30]. Assuming that: (i) individual retention mechanisms are independent and additive; (ii) the solute concentration is in a region where the infinite dilution and zero surface coverage approximations apply; and (iii) the contribution to retention from the structured liquid-phase layer in close contact with the support can be neglected (the general case for thick stationary phase films), a general expression for retention in gas–liquid chromatography can be written, Eq. (1):

$$V_N^* = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{LS} \quad (1)$$

where for a packed column V_N^* is the net retention volume per gram of column packing, V_L the volume of liquid phase per gram of column packing, K_L the gas–liquid partition coefficient, A_{GL} the gas–liquid interfacial surface area per gram of column packing, K_{GL} the adsorption coefficient at the gas–liquid interface, A_{LS} the liquid–solid interfacial surface area per gram of column packing and K_{LS} the coefficient for adsorption at the liquid–solid interface. Division of both sides of Eq. (1) by V_L allows the gas–liquid partition coefficient to be evaluated independently of the other contributions to retention by extrapolating the experimental data to obtain the intercept on the V_N^*/V_L axis corresponding to an infinite stationary phase volume. At high phase loadings ($\geq 8\%$, w/w) the contribution of gas–solid adsorption interactions for a polar phase like Carbowax 20M can be neglected and a linear extrapolation used to evaluate K_L . The proof of this is the general observation of linear fits for the experimental data for a large number of polar stationary phases [22,25–27]. If adsorption at the liquid and solid

interfaces were simultaneously important then Eq. (1), in the general case, would result in a non-linear fit as is commonly observed for experimental conditions selected to emphasize a mixed adsorption mechanism [26,31]. In addition, from the experimental data for retention at any phase loading the contribution from gas–liquid interfacial adsorption can be found by subtraction of the contribution from gas–liquid partitioning.

The interpretation of selectivity differences from the relative retention of individual solutes on compared phases is of limited value because polar solutes are capable of multiple intermolecular interactions that simultaneously contribute to the overall retention. Apart from noting that selectivity differences exist it is impossible to reveal the changes in intermolecular interactions responsible for the change. Where no net change in relative retention is noted this does not preclude changes in the relative contribution of individual intermolecular interactions that occur in a compensatory manner. This problem is solved by using the solvation parameter model, which relates the retention properties of a varied group of solutes to the contribution of intermolecular interactions responsible for the general retention mechanism [22,23,32]. This model is ostensibly a partition model. Acceptable model fits are possible for sorption interactions [23,28], however, but for a mixed retention mechanism the interpretation of the results based on an assumed partition model is compromised. Thus, there is a need to understand the retention mechanism, as discussed above, to assure that a meaningful interpretation of the results is obtained.

The solvation parameter model in a form suitable for characterizing the retention properties of stationary phases in gas–liquid chromatography is given by Eq. (2) [22,23]:

$$\log SP = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L^{16} \quad (2)$$

SP is some free energy related solute property such as a gas–liquid partition coefficient, retention factor, specific retention volume, or relative adjusted retention time. The remainder of the equation is

made up of product terms called system constants (r, s, a, b, l) and solute descriptors ($R_2, \pi_2^H, \sum\alpha_2^H, \sum\beta_2^H, \log L^{16}$). 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; $a\sum\alpha_2^H$ 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. (2) are $\log L^{16}$ the solute gas–liquid partition coefficient on hexadecane at 298 K, R_2 the excess molar refraction (in $\text{cm}^3/10$), 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. Experimental solute descriptors are available for over 3000 compounds [23,33]. A computer program has been described for the calculation of additional values from structure [34].

Differences in selectivity between compared phases are indicated by statistically meaningful differences in the system constants defined by Eq. (2). For typical experimental conditions employed in gas chromatography the gas phase can safely be assumed to be ideal, and therefore, the system constants describe stationary phase properties alone. In which case, the r constant 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 and 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. The system constants are determined by multiple linear regression analysis of experimental $\log K_L$ or $\log k$ values for a group of solutes of sufficient number and variety to establish the statisti-

cal and chemical validity of the model. In addition, the solute descriptors should not be cross-correlated and the values for individual descriptors should not be clustered if stable models are to be obtained [35].

3. Experimental

Carbowax 20M and Chromosorb W-AW (177–250 μm) were obtained from Anspec (Ann Arbor, MI, USA). The WCOT columns were obtained from different sources. The HP-20M (25 m \times 0.32 mm I.D., $d_f=0.30 \mu\text{m}$) and HP-INNOWax (60 m \times 0.25 mm I.D., $d_f=0.5 \mu\text{m}$) were from Agilent Technologies (Novi, MI, USA), AT-Wax (30 m \times 0.25 mm I.D., $d_f=0.25 \mu\text{m}$) from Alltech Associates (Deerfield, IL, USA) and DB-FFAP (15 m \times 0.32 mm I.D., $d_f=0.25 \mu\text{m}$) from J&W Scientific (Folsom, CA, USA). All solvents were OmniSolv grade from EM Science (Gibbstown, NJ, USA). The density of Carbowax 20M was determined over the temperature range 60–160°C, using a modified Lipkin bicapillary pycnometer as described previously [36]. The data were fitted to Eq. (3):

$$\rho_t = A - B(t) \quad (3)$$

where ρ_t is the liquid density at temperature t (°C) and A and B are regression constants. For Carbowax 20M $A=1.1490$ and $B=9.494 \cdot 10^{-4}$.

3.1. Determination of packed column gas–liquid partition coefficients

The protocol used to determine the gas–liquid partition coefficients is outlined in Ref. [37]. Briefly, all measurements were made on packed columns with three or four stationary phase loadings between 8 to 21% (w/w). The gas–liquid partition coefficient was determined by averaging the individual column values when retention was solely by partitioning, or by linear extrapolation to an infinite phase volume based on Eq. (1) when interfacial adsorption contributed to retention. The typical uncertainty in K_L is 2–5% relative standard deviation when the uncertainty in the phase loading is $\pm 0.15\%$ (Soxhlet extraction), carrier gas flow-rate ± 0.20 ml/min, column pressure drop ± 1 mmHg, column temperature $\pm 0.2^\circ\text{C}$, and retention time ± 0.02 min (1

mmHg = 133.322 Pa). The gas–liquid partition coefficients determined at four temperatures are summarized in Tables 1–4.

Gas chromatographic measurements for packed columns were made using a Varian 3700 gas chromatograph (Walnut Creek, CA, USA) fitted with a flame ionization detector. A mercury manometer was used to measure the column inlet pressure and a US National Institute of Standards and Technology (NIST)-certified thermometer ($\pm 0.2^\circ\text{C}$) to measure ambient and column temperatures.

3.2. Determination of open-tubular column retention factors

For the HP-INNOWax WCOT column gas chromatographic measurements were made using an Agilent Technologies HP 5890 SERIES II gas chromatography, 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 (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.

For the HP-20M, AT-Wax and DB-FFAP WCOT 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 columns were unused prior to characterization and were conditioned overnight following the manufacturers' recommendations. Prior to use each column was tested with a column evaluation mixture consisting of hexadecane, octadecane, methyl undecanoate, 1-octanol, acetophenone, 2,6-dimethylaniline, 2,6-dimethylphenol and 1-dodecanol to ensure that the columns conformed to expected quality criteria for efficiency and chemical

Table 1
Distribution constants and percent adsorption for Carbowax 20M columns at 81.2°C

Solute	Log K_L	Phase loading					
		8.84%		13.21%		20.71%	
		Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ
<i>n</i> -Undecane	2.291	2.50	9.15	2.45	6.85	2.39	4.32
<i>n</i> -Dodecane	2.564	2.79	8.63	2.73	6.48	2.67	4.11
<i>n</i> -Tridecane	2.833	3.07	8.27	3.01	6.22	2.95	3.96
Butan-2-one	1.815	1.86	2.56	1.85	1.90	1.83	1.07
Pentan-2-one	2.034	2.09	2.56	2.07	1.90	2.06	1.08
Hexan-2-one	2.307	2.37	2.74	2.35	2.02	2.33	1.16
Heptan-2-one	2.573	2.65	2.89	2.63	2.12	2.60	1.24
Octan-2-one	2.838	2.92	3.01	2.90	2.21	2.87	1.30
Butan-1-ol	2.406	2.47	2.68	2.45	1.97	2.43	1.14
Pentan-1-ol	2.679	2.75	2.73	2.73	2.01	2.71	1.17
Hexan-1-ol	2.947	3.04	3.05	3.01	2.19	2.99	1.34
Heptan-1-ol	3.225	3.32	2.83	3.29	2.08	3.26	1.23
Octan-1-ol	3.495	3.60	2.89	3.57	2.12	3.54	1.27
2-Methylpentanol	2.308	2.39	3.34	2.36	2.45	2.34	1.44
Methyl hexanoate	2.504	2.59	3.58	2.57	2.63	2.54	1.55
1-Nitropropane	2.585	2.64	2.06	2.62	1.53	2.61	0.87
1-Nitropentane	3.157	3.22	1.91	3.20	1.41	3.18	0.81
1-Nitrohexane	3.415	3.48	2.02	3.47	1.49	3.44	0.86
<i>cis</i> -Hydridane	2.508	2.64	5.21	2.60	3.84	2.57	2.33
Oct-2-yne	2.103	2.23	5.79	2.19	4.25	2.16	2.58
1,1,2,2-Tetrachlorobenzene	3.271	3.33	1.85	3.32	1.36	3.30	0.78
1,4-Dioxane	2.238	2.29	2.23	2.27	1.65	2.26	0.94
Benzene	1.982	2.03	2.30	2.02	1.73	2.00	0.96
Toluene	2.271	2.33	2.56	2.31	1.89	2.30	1.08
Ethylbenzene	2.501	2.57	2.70	2.55	1.99	2.53	1.15
<i>n</i> -Butylbenzene	3.029	3.12	2.88	3.09	2.11	3.07	1.25
Chlorobenzene	2.698	2.75	1.97	2.74	1.46	2.72	0.83
<i>o</i> -Dichlorobenzene	3.413	3.47	1.66	3.46	1.23	3.44	0.70
Bromobenzene	3.069	3.12	1.64	3.11	1.22	3.09	0.69
Iodobenzene	3.517	3.58	1.79	3.56	1.32	3.54	0.76
Benzaldehyde	3.383	3.45	2.11	3.44	1.55	3.41	0.90
Acetophenone	3.659	3.72	1.71	3.70	1.26	3.69	0.73
Methylphenyl ether	2.926	2.97	1.65	2.96	1.23	2.95	0.69
Benzonitrile	3.561	3.63	2.06	3.62	1.52	3.59	0.89
Nitrobenzene	3.897	3.96	1.58	3.94	1.12	3.94	1.10
Pyridine	2.523	2.59	2.83	2.58	2.08	2.55	1.21
2,4,6-Trimethylpyridine	3.010	3.06	1.69	3.05	1.25	3.03	0.71
Aniline	3.900	3.99	2.28	3.96	1.62	3.95	1.29
<i>N,N</i> -Dimethylaniline	3.560	3.61	1.44	3.60	1.07	3.58	0.60
<i>N,N</i> -Dimethylacetamide	3.541	3.63	2.50	3.61	1.83	3.58	1.08
<i>N,N</i> -Dimethylformamide	3.259	3.35	2.70	3.32	1.98	3.30	1.17

inertness. Upon completion of all retention measurements the column evaluation test was repeated under identical conditions to the original test to confirm that no changes in the column properties had occurred during the study.

3.3. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Gateway E-4200 computer (North Sioux City, SD, USA) using the

Table 2
Distribution constants and percent adsorption for Carbowax 20M columns at 101.2°C

Solute	Log K_L	Phase loading							
		8.84%		13.21%		16.73%		20.71%	
		Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ
<i>n</i> -Dodecane	2.251	2.34	3.97	2.33	3.52	2.31	2.51	2.29	1.49
<i>n</i> -Tridecane	2.491	2.59	4.07	2.58	3.64	2.55	2.44	2.53	1.63
<i>n</i> -Tetradecane	2.731	2.84	4.15	2.83	3.73	2.80	2.38	2.78	1.75
<i>n</i> -Pentadecane	2.970	3.10	4.23	3.08	3.81	3.04	2.33	3.03	1.86
<i>n</i> -Hexadecane	3.210	3.35	4.30	3.34	3.90	3.28	2.31	3.27	1.96
Butan-2-one	1.565	1.60	2.25	1.59	1.60	1.59	1.36	1.58	0.89
Pentan-2-one	1.770	1.79	1.23	1.78	0.83	1.78	0.77	1.78	0.47
Hexan-2-one	2.027	2.04	0.44	2.03	0.32	2.03	0.25	2.03	0.18
Heptan-2-one	2.265	2.28	0.71	2.28	0.50	2.27	0.40	2.27	0.29
Octan-2-one	2.499	2.52	1.03	2.52	0.87	2.51	0.48	2.51	0.47
Nonan-2-one	2.729	2.77	1.30	2.76	1.18	2.75	0.67	2.74	0.55
Butan-1-ol	2.095	2.14	1.94	2.12	1.31	2.12	1.03	2.11	0.86
Pentan-1-ol	2.349	2.38	1.24	2.37	0.98	2.36	0.61	2.36	0.55
Hexan-1-ol	2.601	2.62	0.76	2.62	0.56	2.61	0.43	2.61	0.31
Heptan-1-ol	2.845	2.87	0.97	2.87	0.71	2.86	0.68	2.85	0.32
Octan-1-ol	3.084	3.12	1.21	3.11	1.00	3.11	0.71	3.10	0.47
Nonan-1-ol	3.324	3.37	1.41	3.37	1.24	3.35	0.74	3.34	0.60
2-Methylpentanol	2.009	2.03	1.21	2.03	1.08	2.02	0.78	2.02	0.41
Methyl hexanoate	2.203	2.22	0.93	2.22	0.79	2.22	0.59	2.21	0.33
Nonanal	2.766	2.80	1.24	2.79	0.90	2.78	0.70	2.78	0.51
1-Nitropropane	2.279	2.31	1.38	2.31	1.17	2.30	0.91	2.29	0.47
1-Nitropentane	2.804	2.82	0.44	2.81	0.33	2.81	0.32	2.81	0.14
1-Nitrohexane	3.035	3.05	0.59	3.05	0.35	3.05	0.33	3.04	0.25
<i>cis</i> -Hydridane	2.217	2.25	1.48	2.24	1.10	2.24	0.84	2.23	0.61
Oct-2-yne	1.855	1.88	1.20	1.87	0.92	1.87	0.69	1.86	0.48
1,1,2,2-Tetrachlorobenzene	2.904	2.93	0.84	2.92	0.60	2.92	0.55	2.91	0.29
1,4-Dioxane	1.961	1.98	0.72	1.97	0.54	1.97	0.41	1.97	0.29
Benzene	1.716	1.76	2.52	1.74	1.44	1.74	1.35	1.74	1.15
Toluene	1.989	2.02	1.48	2.01	0.86	2.00	0.72	2.00	0.71
Ethylbenzene	2.203	2.22	0.93	2.22	0.66	2.22	0.57	2.21	0.35
<i>n</i> -Butylbenzene	2.684	2.70	0.73	2.70	0.54	2.69	0.41	2.69	0.30
Chlorobenzene	2.381	2.41	1.08	2.40	0.65	2.40	0.61	2.39	0.46
<i>o</i> -Dichlorobenzene	3.044	3.05	0.23	3.05	0.17	3.05	0.13	3.05	0.09
Bromobenzene	2.724	2.74	0.64	2.74	0.45	2.74	0.42	2.73	0.22
Iodobenzene	3.146	3.16	0.48	3.16	0.34	3.15	0.27	3.15	0.20
Benzaldehyde	3.020	3.05	0.91	3.04	0.66	3.04	0.61	3.03	0.32
Acetophenone	3.258	3.28	0.82	3.28	0.70	3.27	0.39	3.27	0.37
Methylphenyl ether	2.593	2.60	0.35	2.60	0.26	2.60	0.20	2.60	0.14
2,6-Dimethylphenol	3.866	3.89	0.55	3.88	0.46	3.88	0.34	3.87	0.20
Benzonitrile	3.184	3.22	0.99	3.21	0.71	3.21	0.67	3.20	0.34
Nitrobenzene	3.479	3.51	0.85	3.50	0.66	3.50	0.49	3.49	0.34
Pyridine	2.239	2.26	1.07	2.26	0.79	2.25	0.60	2.25	0.43
2,4,6-Trimethylpyridine	2.658	2.67	0.51	2.67	0.37	2.67	0.30	2.66	0.20
Aniline	3.490	3.53	1.02	3.52	0.77	3.51	0.72	3.50	0.33
<i>N,N</i> -Dimethylaniline	3.164	3.18	0.49	3.18	0.36	3.17	0.27	3.17	0.20
<i>N,N</i> -Dimethylacetamide	3.157	3.21	1.58	3.19	1.20	3.18	0.84	3.18	0.69
<i>N,N</i> -Dimethylformamide	2.873	2.92	1.79	2.91	1.24	2.91	1.18	2.89	0.67

Table 3
Distribution constants and percent adsorption for Carbowax 20M columns at 121.2°C

Solute	Log K_L	Phase loading				Phase Loading			
		8.84%		13.21%		16.73%		20.71%	
		Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ
<i>n</i> -Undecane	1.793	1.82	1.31	1.81	0.97	1.81	0.74	1.80	0.53
<i>n</i> -Dodecane	2.020	2.04	1.23	2.04	0.92	2.03	0.70	2.03	0.50
<i>n</i> -Tridecane	2.240	2.28	1.58	2.27	1.16	2.26	0.89	2.25	0.65
<i>n</i> -Tetradecane	2.460	2.51	1.88	2.49	1.37	2.49	1.06	2.48	0.79
<i>n</i> -Pentadecane	2.678	2.74	2.19	2.72	1.62	2.71	1.25	2.70	0.92
<i>n</i> -Hexadecane	2.896	2.97	2.47	2.95	1.83	2.94	1.42	2.93	1.05
Butan-2-one	1.369	1.43	4.09	1.41	2.85	1.40	2.52	1.39	1.62
Pentan-2-one	1.560	1.60	2.42	1.59	1.70	1.58	1.34	1.58	1.03
Hexan-2-one	1.800	1.82	1.00	1.81	0.79	1.81	0.56	1.81	0.41
Heptan-2-one	2.024	2.04	0.71	2.03	0.51	2.03	0.40	2.03	0.29
Octan-2-one	2.239	2.26	0.97	2.26	0.76	2.25	0.56	2.25	0.39
Nonan-2-one	2.450	2.48	1.28	2.47	0.92	2.47	0.72	2.46	0.53
Butan-1-ol	1.847	1.92	3.82	1.89	2.31	1.89	2.20	1.88	1.69
Pentan-1-ol	2.085	2.14	2.50	2.12	1.61	2.11	1.40	2.11	1.10
Hexan-1-ol	2.321	2.36	1.47	2.35	1.07	2.34	0.78	2.34	0.64
Heptan-1-ol	2.562	2.58	0.59	2.57	0.43	2.57	0.33	2.57	0.24
Octan-1-ol	2.784	2.80	0.72	2.80	0.42	2.79	0.39	2.79	0.32
Nonan-1-ol	3.001	3.03	1.04	3.02	0.79	3.02	0.59	3.01	0.42
2-Methylpentanol	1.764	1.81	2.55	1.79	1.73	1.79	1.34	1.78	1.15
Methyl hexanoate	1.968	1.98	0.65	1.98	0.46	1.97	0.36	1.97	0.27
Nonanal	2.483	2.51	1.19	2.50	0.86	2.50	0.67	2.50	0.50
1-Nitropropane	2.053	2.09	1.90	2.08	1.50	2.08	1.13	2.07	0.74
1-Nitropentane	2.535	2.55	0.68	2.55	0.50	2.54	0.38	2.54	0.28
1-Nitrohexane	2.747	2.77	0.68	2.76	0.50	2.76	0.38	2.75	0.28
<i>cis</i> -Hydridane	1.971	2.00	1.65	1.99	1.07	1.99	1.03	1.98	0.64
Oct-2-yne	1.621	1.67	2.90	1.65	1.71	1.65	1.49	1.64	1.37
1,1,2,2-Tetrachlorobenzene	2.626	2.66	1.41	2.65	0.94	2.65	0.85	2.64	0.57
1,4-Dioxane	1.749	1.77	1.03	1.76	0.77	1.76	0.59	1.76	0.42
Benzene	1.506	1.58	4.99	1.55	2.97	1.55	2.73	1.54	2.32
Toluene	1.756	1.81	3.38	1.80	2.34	1.79	1.88	1.78	1.47
Ethylbenzene	1.962	2.00	1.94	1.99	1.33	1.98	1.07	1.98	0.84
<i>n</i> -Butylbenzene	2.421	2.43	0.34	2.43	0.25	2.43	0.21	2.42	0.12
Chlorobenzene	2.135	2.18	2.05	2.16	1.27	2.16	1.14	2.15	0.91
<i>o</i> -Dichlorobenzene	2.765	2.77	0.36	2.77	0.26	2.77	0.20	2.77	0.15
Bromobenzene	2.464	2.49	1.04	2.48	0.71	2.48	0.61	2.47	0.42
Iodobenzene	2.870	2.88	0.33	2.88	0.23	2.88	0.18	2.87	0.14
Benzaldehyde	2.751	2.78	0.87	2.77	0.62	2.76	0.48	2.76	0.36
Acetophenone	2.962	2.99	1.05	2.99	0.78	2.98	0.59	2.97	0.43
Methylphenyl ether	2.341	2.35	0.53	2.35	0.39	2.35	0.30	2.35	0.22
Phenol	3.647	3.68	0.96	3.67	0.68	3.67	0.53	3.66	0.40
<i>p</i> -Cresol	3.824	3.84	0.33	3.83	0.25	3.83	0.18	3.83	0.13
2,6-Dimethylphenol	3.528	3.54	0.47	3.54	0.39	3.54	0.26	3.53	0.19
2,5-Dimethylphenol	3.856	3.87	0.43	3.87	0.34	3.87	0.24	3.86	0.18
Benzonitrile	2.906	2.94	0.99	2.93	0.77	2.92	0.51	2.92	0.43
Nitrobenzene	3.179	3.21	0.88	3.20	0.63	3.20	0.49	3.19	0.37
Pyridine	2.021	2.04	1.04	2.04	0.78	2.03	0.59	2.03	0.42
2,4,6-Trimethylpyridine	2.393	2.41	0.76	2.41	0.55	2.40	0.43	2.40	0.31
Aniline	3.194	3.22	0.70	3.21	0.50	3.21	0.39	3.20	0.29
<i>N,N</i> -Dimethylaniline	2.869	2.89	0.80	2.89	0.60	2.88	0.45	2.88	0.32
<i>N,N</i> -Dimethylacetamide	2.872	2.93	1.87	2.91	1.37	2.90	1.06	2.89	0.79
<i>N,N</i> -Dimethylformamide	2.620	2.67	1.75	2.66	1.40	2.65	0.97	2.64	0.73

Table 4
Distribution constants and percent adsorption for Carbowax 20M columns at 141.2°C

Solute	Log K_L	Phase loading				Phase Loading			
		8.84%		13.21%		16.73%		20.71%	
		Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ	Log (V_N^*/V_L)	Δ
<i>n</i> -Dodecane	1.800	1.82	1.03	1.81	0.74	1.82	1.27	1.81	0.43
<i>n</i> -Tridecane	2.007	2.01	0.30	2.01	0.21	2.02	0.79	2.01	0.13
<i>n</i> -Tetradecane	2.251	2.27	0.68	2.26	0.48	2.27	0.93	2.26	0.28
<i>n</i> -Pentadecane	2.455	2.48	1.06	2.47	0.74	2.48	1.10	2.47	0.45
<i>n</i> -Hexadecane	2.659	2.70	1.39	2.69	0.98	2.69	1.25	2.68	0.59
Butan-2-one	1.277	1.34	4.96	1.32	3.51	1.33	3.77	1.30	2.14
Pentan-2-one	1.405	1.46	4.01	1.44	2.77	1.45	3.12	1.43	1.75
Hexan-2-one	1.636	1.66	1.56	1.65	1.09	1.66	1.63	1.65	0.65
Heptan-2-one	1.846	1.87	1.11	1.86	0.79	1.87	1.30	1.85	0.47
Octan-2-one	2.048	2.07	1.28	2.07	0.89	2.07	1.32	2.06	0.54
Nonan-2-one	2.245	2.28	1.52	2.27	1.06	2.28	1.40	2.26	0.64
Butan-1-ol	1.668	1.76	5.36	1.73	3.82	1.73	3.81	1.71	2.35
Pentan-1-ol	1.895	1.96	3.55	1.94	2.51	1.95	2.67	1.92	1.54
Hexan-1-ol	2.068	2.12	2.50	2.10	1.76	2.11	2.01	2.09	1.08
Heptan-1-ol	2.280	2.31	1.30	2.30	0.91	2.31	1.27	2.29	0.55
Octan-1-ol	2.491	2.51	0.65	2.50	0.43	2.51	0.84	2.50	0.24
Nonan-1-ol	2.696	2.73	1.10	2.72	0.77	2.73	1.08	2.71	0.47
2-Methylpentanol	1.587	1.65	3.71	1.63	2.65	1.63	2.89	1.61	1.60
Methyl hexanoate	1.791	1.81	0.96	1.80	0.68	1.81	1.23	1.80	0.40
Nonanal	2.276	2.31	1.42	2.30	0.99	2.31	1.34	2.29	0.60
1-Nitropropane	1.884	1.94	2.79	1.92	1.97	1.93	2.23	1.91	1.20
1-Nitropentane	2.337	2.37	1.22	2.36	0.85	2.36	1.21	2.35	0.52
1-Nitrohexane	2.501	2.54	1.40	2.53	0.97	2.53	1.28	2.52	0.59
<i>cis</i> -Hydridane	1.782	1.83	2.71	1.82	1.89	1.82	2.21	1.80	1.17
Oct-2-yne	1.448	1.51	4.59	1.50	3.28	1.50	3.47	1.48	1.98
1,1,2,2-Tetrachlorobenzene	2.386	2.44	2.14	2.42	1.50	2.43	1.72	2.41	0.92
1,4-Dioxane	1.597	1.62	1.26	1.61	0.89	1.62	1.48	1.61	0.52
Benzene	1.402	1.49	6.25	1.46	4.43	1.46	4.45	1.44	2.76
Toluene	1.639	1.70	4.00	1.69	2.82	1.69	3.02	1.67	1.74
Ethylbenzene	1.812	1.86	2.68	1.85	1.87	1.85	2.19	1.83	1.15
<i>n</i> -Butylbenzene	2.227	2.24	0.39	2.23	0.27	2.24	0.78	2.23	0.16
Chlorobenzene	1.961	2.02	2.87	2.00	2.02	2.01	2.25	1.99	1.24
<i>o</i> -Dichlorobenzene	2.505	2.52	0.57	2.52	0.40	2.53	0.81	2.51	0.24
Bromobenzene	2.255	2.29	1.46	2.28	1.02	2.29	1.37	2.27	0.62
Iodobenzene	2.627	2.63	0.25	2.63	0.17	2.64	0.62	2.63	0.10
Benzaldehyde	2.564	2.59	0.89	2.58	0.62	2.59	0.98	2.57	0.37
Acetophenone	2.767	2.80	1.23	2.79	0.86	2.80	1.14	2.78	0.52
Methylphenyl ether	2.160	2.18	0.67	2.17	0.47	2.18	0.95	2.17	0.28
Phenol	3.268	3.31	1.45	3.30	1.02	3.31	1.20	3.29	0.62
<i>p</i> -Cresol	3.404	3.42	0.44	3.41	0.30	3.43	0.61	3.41	0.18
2,6-Dimethylphenol	3.157	3.18	0.68	3.17	0.47	3.18	0.77	3.17	0.28
2,5-Dimethylphenol	3.464	3.48	0.53	3.48	0.37	3.49	0.65	3.47	0.22
3,5-Dimethylphenol	3.595	3.62	0.56	3.61	0.39	3.62	0.66	3.60	0.24
Benzonitrile	2.705	2.74	1.12	2.73	0.78	2.73	1.08	2.72	0.47
Nitrobenzene	2.960	2.99	1.09	2.98	0.76	2.99	1.03	2.97	0.46
Pyridine	1.863	1.88	1.14	1.88	0.80	1.89	1.30	1.87	0.48
2,4,6-Trimethylpyridine	2.202	2.23	1.03	2.22	0.71	2.23	1.14	2.21	0.44
Aniline	2.924	2.95	0.78	2.94	0.54	2.95	0.86	2.93	0.33
<i>N,N</i> -Dimethylaniline	2.948	2.97	0.84	2.97	0.58	2.97	0.89	2.96	0.35
2,6-Dimethylaniline	3.238	3.29	1.59	3.27	0.97	3.28	1.28	3.26	0.66
<i>N,N</i> -Dimethylacetamide	2.693	2.76	2.48	2.74	1.75	2.74	1.87	2.72	1.08
<i>N,N</i> -Dimethylformamide	2.452	2.50	1.81	2.48	1.27	2.49	1.52	2.47	0.77

program SPSS v10.0 (SPSS, Chicago, IL, USA). The solute descriptors used in the solvation parameter model were from a laboratory database and have been published elsewhere [23,24,28,38,39].

4. Results and discussion

Previous studies have shown that interfacial adsorption can contribute to retention of some compounds on packed and open tubular columns coated with Carbowax 20M [12–20]. Typical plots of V_N^*/V_L against $1/V_L$ at 81.2°C and 141.2°C for some representative compounds with varied properties are shown in Figs. 1 and 2. A horizontal line is expected for a pure partitioning system and a line with a slope and positive intercept on the V_N^*/V_L axis for a mixed retention mechanism. The intercept for the plots corresponds to the gas–liquid partition coefficient, K_L , with increased retention (V_N^*/V_L) at the experimental phase loadings corresponding to the contribution from interfacial adsorption. For a mixed retention mechanism the relative contribution of interfacial adsorption is expected to decline as the phase loading is increased due to a larger increase in the phase volume compared with the interfacial surface area [40]. The contribution from interfacial adsorption is also expected to decline at higher temperatures due to an increase in solute partitioning

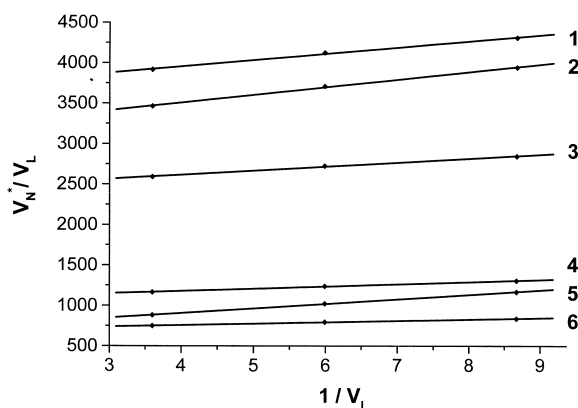


Fig. 1. Plot of (V_N^*/V_L) against $(1/V_L)$ for solutes of different polarity on Carbowax 20M coated on Chromosorb W-AW at 81.2°C. Identification: 1 = *n*-tridecane; 2 = *n*-butylbenzene; 3 = 2-octanone; 4 = octan-1-ol; 5 = benzonitrile; and 6 = benzaldehyde.

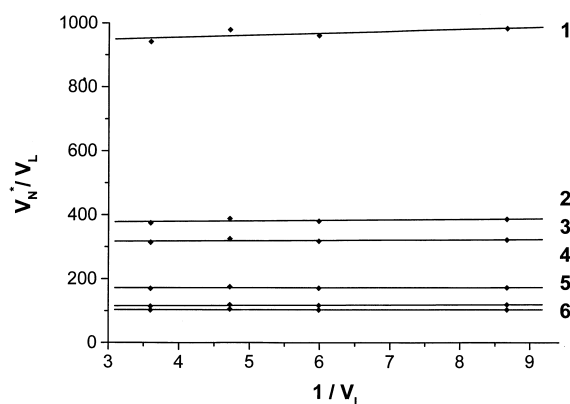


Fig. 2. Plot of (V_N^*/V_L) against $(1/V_L)$ for solutes of different polarity on Carbowax 20M coated on Chromosorb W-AW at 141.2°C. Identification: 1 = *n*-tridecane; 2 = *n*-butylbenzene; 3 = 2-octanone; 4 = octan-1-ol; 5 = benzonitrile; and 6 = benzaldehyde.

and a decrease in interfacial adsorption [25]. Qualitatively, the ratio of the slope to the intercept for the plots in Figs. 1 and 2 indicates that interfacial adsorption could be an important retention mechanism at 81.2°C on Carbowax 20M but at 141.2°C it makes a negligible contribution to retention. These observations can be put on a quantitative basis for a wider range of solutes and experimental conditions by the results summarized in Tables 1–4.

For each table $\log K_L$ is the gas–liquid partition coefficient, $\log (V_N^*/V_L)$ the experimental distribution coefficient at a specified phase loading for retention by a mixed retention mechanism, and the difference (Δ) defined by Eq. (4), serves as an index of the relative importance of interfacial adsorption to the retention mechanism:

$$\Delta (\%) = 100 [\log (V_N^*/V_L) - \log K_L] / \log K_L \quad (4)$$

The Δ values range from 0 to 10% and vary with the solute, phase loading and temperature, indicating that interfacial adsorption is both a solute and a system property. In general, interfacial adsorption influences the retention of the *n*-alkanes, higher-molecular-mass fatty acid methyl esters, oct-2-yne and *cis*-hydrindane the most. The system properties that increase the value for Δ are a low phase loading (lower volume-to-surface area ratio) and a low column temperature. Already at 101.2°C interfacial adsorption is of minor importance and at 141.2°C is

no greater than the statistical fluctuations in the retention measurements as many of the solutes, particularly at low phase loadings are weakly retained.

The use of a logarithmic function of retention tends to compress the retention scale minimizing the difference in retention values. It is justified here because we are interested in the influence of mixed retention on the use of the solvation parameter model to characterize stationary phase properties. As a free energy solvation model the correct dependent variable is $\log K_L$, $\log (V_N^*/V_L)$ or $\log k$. System constants for the solvation parameter model determined at different phase loadings and four temperatures, and from the gas–liquid partition coefficients, are summarized in Table 5. In each case the models are statistically sound and chemically sensible. Only in the case of the results for 81.2°C is there any dependence of the system constants on the phase loading, and even here it is small. The slope in the linear plot of the system constants against phase loading is small for the *r*, *s* and *l* constants and is insignificant for the *a* system constant. This reflects the greater importance of interfacial adsorption for the retention of solutes with properties opposite to those of the stationary phase, that is, compounds of low polarity. At 101.2°C and above there is no statistical difference between the system constants as a function of phase loading and at these temperatures interfacial adsorption has no detectable influence on the system constants. As well as the relatively small contribution to retention from interfacial adsorption a further contributing factor is the probable nature of interfacial interactions. It has been speculated that adsorption at the gas–liquid interface and absorption by the liquid stationary phase involve identical intermolecular interactions that differ primarily in intensity and not type [28]. When the relative contribution to retention from interfacial adsorption is small this tends to minimize selectivity differences compared with a pure partitioning system.

Table 5 also summarizes the system constants for Carbowax 20M at four temperatures calculated using the extrapolated values of $\log K_L$. At 141.2 and 121.2°C there is no statistical difference between the system constants calculated from the sorption coefficients [$\log (V_N^*/V_L)$] and the gas–liquid partition coefficient ($\log K_L$). At 81.2°C the differences in

system constants calculated from the sorption and partition coefficients, although small, are statistically significant. At 101.2°C the differences in system constants for the sorption and partition coefficients are statistically significant for the *l* and *r* system constants but not for the *s* and *a* system constants. These results confirm that interfacial adsorption has an influence on the selectivity of Carbowax 20M up to about 100°C for the compounds studied. At higher temperatures the results can be explained by a pure partitioning model within the framework of the solvation parameter model.

The importance of interfacial adsorption as a retention mechanism for WCOT columns will depend on chemical properties of the stationary phase, such as crosslinking and surface bonding, and the volume-to-surface area ratio for the WCOT columns. For simplification, if we assume that the stationary phase for a WCOT column has a smooth surface and a constant film thickness that does not change with temperature then the volume-to-surface area ratio will equal the film thickness (about $2.5 \cdot 10^{-5}$ cm for a 0.25- μ m thick film). This estimate is probably a little on the high side for stationary phase films with a reticulated surface. For a 2 m packed column with a 15% (w/w) phase loading (0.20 g of Carbowax 20M and 1.15 g of support), a liquid surface area of 10^4 cm²/g [40], at 100°C where the density of Carbowax 20M is 1.054 g/cm³, the volume-to-surface area ratio is about $1.65 \cdot 10^{-5}$. Thus the volume-to-surface area ratio of the packed and WCOT columns used in this study are quite comparable in magnitude and all other things being equal, the significance of interfacial adsorption as a retention mechanism is expected to be of similar importance for the two column types. Although not a proof, it at least establishes the likelihood that interfacial adsorption will be important for the characterization of WCOT columns coated with stationary phases similar to Carbowax 20M at temperatures below 100°C for the compounds used to characterize the selectivity of the WCOT columns.

The system constants for four Carbowax-type WCOT columns as a function of temperature are summarized in Table 6. Exact details of the chemical composition of each stationary phase and column preparation conditions are proprietary information. The manufacturers describe the WCOT columns as

Table 5
System constants for Carbowax 20M ($b=0$ in all cases)

Stationary phase		System constants					Statistics ^a			
Temperature	Loadings	c	l	r	s	a	ρ	SE	F	n
81.2°C	8.84%	-0.511 (0.028)	0.577 (0.006)	0.267 (0.015)	1.444 (0.017)	2.176 (0.033)	0.999	0.026	4624	41
	13.21%	-0.518 (0.026)	0.569 (0.005)	0.282 (0.014)	1.456 (0.016)	2.170 (0.032)	0.999	0.025	5123	41
	16.73%	-0.559 (0.025)	0.563 (0.005)	0.290 (0.014)	1.457 (0.015)	2.174 (0.030)	0.999	0.023	5574	41
	20.71%	-0.516 (0.028)	0.559 (0.006)	0.297 (0.015)	1.461 (0.017)	2.175 (0.035)	0.999	0.025	3983	41
	Log K_L	-0.511 (0.030)	0.542 (0.006)	0.324 (0.016)	1.481 (0.018)	2.185 (0.035)	0.999	0.027	4090	41
101.2°C	8.84%	-0.551 (0.021)	0.505 (0.004)	0.289 (0.013)	1.348 (0.013)	1.957 (0.026)	0.999	0.024	6222	47
	13.21%	-0.554 (0.020)	0.505 (0.003)	0.293 (0.012)	1.343 (0.012)	1.951 (0.024)	0.999	0.022	7161	47
	16.73%	-0.536 (0.021)	0.497 (0.004)	0.307 (0.013)	1.343 (0.013)	1.953 (0.026)	0.999	0.024	6194	47
	20.71%	-0.532 (0.020)	0.495 (0.004)	0.310 (0.012)	1.340 (0.012)	1.951 (0.025)	0.999	0.023	6787	47
	Log K_L	-0.522 (0.023)	0.487 (0.004)	0.326 (0.014)	1.337 (0.014)	1.962 (0.028)	0.999	0.026	5274	47
121.2°C	8.84%	-0.575 (0.021)	0.459 (0.004)	0.296 (0.013)	1.282 (0.013)	1.848 (0.020)	0.999	0.025	7441	51
	13.21%	-0.600 (0.019)	0.461 (0.003)	0.302 (0.012)	1.288 (0.012)	1.846 (0.018)	0.999	0.023	8880	51
	16.73%	-0.600 (0.020)	0.460 (0.004)	0.308 (0.012)	1.281 (0.013)	1.852 (0.019)	0.999	0.024	7921	51
	20.71%	-0.599 (0.020)	0.459 (0.004)	0.309 (0.012)	1.278 (0.012)	1.851 (0.019)	0.999	0.023	8303	51
	Log K_L	-0.624 (0.021)	0.461 (0.004)	0.317 (0.013)	1.279 (0.014)	1.854 (0.019)	0.999	0.026	7019	51
141.2°C	8.84%	-0.509 (0.026)	0.411 (0.005)	0.271 (0.016)	1.225 (0.017)	1.553 (0.020)	0.999	0.031	4220	52
	13.21%	-0.538 (0.023)	0.415 (0.004)	0.278 (0.014)	1.225 (0.015)	1.550 (0.021)	0.999	0.028	5463	52
	16.73%	-0.534 (0.021)	0.415 (0.004)	0.281 (0.013)	1.224 (0.014)	1.556 (0.020)	0.999	0.026	6265	52
	20.71%	-0.561 (0.020)	0.418 (0.004)	0.279 (0.013)	1.226 (0.013)	1.551 (0.018)	0.999	0.024	7042	52
	Log K_L	-0.606 (0.017)	0.423 (0.003)	0.289 (0.011)	1.230 (0.011)	1.554 (0.016)	0.999	0.021	10 292	52

^a ρ = Multiple correlation coefficient; SE = standard error in the estimation; F = Fischer statistic and n = number of solutes.

follows. The HP-20M column is coated with a poly(ethylene glycol) stationary phase similar to Carbowax 20M. The AT-Wax column is coated with a crosslinked poly(ethylene glycol) stationary phase similar to Carbowax 20M. The HP-INNOWax col-

umn is coated with a surface bonded and crosslinked poly(ethylene glycol) stationary phase similar to Carbowax 20M. The DB-FFAP column is coated with a surface bonded and crosslinked poly(ethylene glycol) stationary phase modified with nitro-

Table 6
System constants for WCOT columns coated with poly(ethylene glycol) stationary phases ($b=0$ for all columns)

Column	Temperature (°C)	System constants					Statistics			
		r	s	a	l	c	ρ	SE	F	n
HP-20M	60	0.214 (0.029)	1.691 (0.040)	2.681 (0.089)	0.620 (0.010)	-3.032 (0.060)	0.995	0.053	1055	47
	80	0.207 (0.024)	1.566 (0.035)	2.394 (0.058)	0.557 (0.008)	-3.060 (0.049)	0.997	0.048	1919	54
	100	0.202 (0.023)	1.441 (0.036)	2.147 (0.052)	0.501 (0.008)	-3.074 (0.048)	0.997	0.049	1970	56
	120	0.209 (0.023)	1.335 (0.038)	2.014 (0.032)	0.452 (0.008)	-3.095 (0.052)	0.997	0.045	2176	56
	140	0.210 (0.029)	1.244 (0.047)	1.818 (0.034)	0.411 (0.010)	-3.123 (0.071)	0.996	0.046	1188	47
AT-Wax	60	0.216 (0.029)	1.712 (0.034)	2.735 (0.077)	0.608 (0.010)	-2.872 (0.049)	0.996	0.052	1379	49
	80	0.239 (0.024)	1.566 (0.027)	2.414 (0.060)	0.545 (0.007)	-2.888 (0.037)	0.997	0.045	2089	57
	100	0.252 (0.022)	1.429 (0.024)	2.143 (0.052)	0.491 (0.006)	-2.900 (0.033)	0.997	0.042	2472	61
	120	0.225 (0.018)	1.318 (0.022)	1.889 (0.042)	0.440 (0.005)	-2.886 (0.027)	0.998	0.040	3997	69
	140	0.220 (0.017)	1.210 (0.022)	1.672 (0.040)	0.397 (0.005)	-2.882 (0.026)	0.998	0.038	3639	69
HP-INNOWax	60	0.220 (0.042)	1.686 (0.047)	2.712 (0.063)	0.605 (0.011)	-2.529 (0.053)	0.994	0.057	895	49
	80	0.218 (0.033)	1.554 (0.038)	2.384 (0.053)	0.551 (0.009)	-2.579 (0.041)	0.995	0.051	1351	54
	100	0.222 (0.029)	1.445 (0.032)	2.116 (0.045)	0.505 (0.007)	-2.630 (0.034)	0.996	0.046	1726	57
	120	0.219 (0.027)	1.351 (0.031)	1.882 (0.045)	0.458 (0.006)	-2.653 (0.031)	0.996	0.045	1940	60
	140	0.227 (0.025)	1.268 (0.029)	1.701 (0.041)	0.424 (0.005)	-2.706 (0.028)	0.997	0.043	2210	62
DB-FFAP	60	0.248 (0.041)	1.769 (0.059)	2.816 (0.089)	0.597 (0.013)	-3.097 (0.073)	0.996	0.059	822	31
	80	0.210 (0.033)	1.674 (0.050)	2.526 (0.069)	0.536 (0.010)	-3.143 (0.060)	0.995	0.065	851	38
	100	0.207 (0.027)	1.555 (0.044)	2.305 (0.038)	0.480 (0.008)	-3.157 (0.052)	0.996	0.059	1371	45
	120	0.214 (0.034)	1.424 (0.057)	2.077 (0.035)	0.428 (0.010)	-3.142 (0.065)	0.998	0.049	2429	47
	140	0.287 (0.040)	1.285 (0.061)	1.853 (0.049)	0.376 (0.012)	-3.140 (0.080)	0.997	0.060	683	34

terephthalic acid. A general comparison of solvation properties can be made using the system constants for 140°C, since at this temperature interfacial adsorption is unlikely to be a significant retention mechanism. All four WCOT column stationary

phases are similar to each other and to Carbowax 20M as indicated by the narrow range for the individual system constants in Tables 5 and 6. There is no statistical difference for the r , s and b system constants while some differences in cohesion (l

system constant) and hydrogen-bond basicity (a system constant) is observed. DB-FFAP is noticeably more cohesive and hydrogen-bond acidic compared with the other Carbowax-type phases, but this is also probably the most predictable result since this phase is chemically modified by introduction of nitroterephthalic acid. All the WCOT stationary phases are stronger hydrogen-bond bases than Carbowax 20M. Apart from DB-FFAP, since the most different is the coated column (HP-20M) this is not necessarily connected to the chemistry employed for crosslinking and surface bonding, but might be related to surface preparation chemistry. In general, one can state that the poly(ethylene glycol) stationary phases are strongly dipolar/polarizable and hydrogen-bond basic (large a and s system constants) with no hydrogen-bond acidity (b system constant is zero). Dispersion interactions also make an important contribution to retention (l system constant is of intermediate magnitude). These results are similar to those obtained previously for packed columns coated with poly(ethylene glycols) [22–24,32,41,42].

It is quite probable that selectivity differences will depend on the retention mechanism for the WCOT columns at low temperatures where interfacial adsorption is a likely retention mechanism. It is also possible that comparisons of stationary phase properties made at a single temperature ignore important relative changes in selectivity for compared stationary phases if their change in capacity for intermolecular interactions with temperature is different. This is not a problem when the solvation parameter model is used to determine the importance of defined intermolecular interactions to retention since there is generally a linear relationship between the system constants as a function of temperature, or slight curvature is indicated in these plots [23–25,38,39,41]. To fashion a discussion of selectivity differences we will take the HP-20M column as a reference point and compare the sorption characteristics of this column to those of the packed column Carbowax 20M and the other three poly(ethylene glycol) WCOT stationary phases. The system constants summarized in Tables 5 and 6 allow the properties of any two columns to be compared using the same general framework presented below.

For the columns studied in this report there is a good linear fit for the change in system constants as

a function of temperature, at least for the temperature range 60–140°C used for the retention measurements. The plots of the system constant over a range of common temperatures for two compared stationary phases are also linear and allow differences in stationary phase selectivity over the temperature range studied to be determined by the slope and intercept of such plots. For two phases with an identical change in selectivity with temperature a slope close to 1.0 and an intercept indistinguishable from zero is expected. In other cases temperature-induced selectivity differences are indicated.

Using the system constants obtained for the HP-20M WCOT column as a reference point a comparison can be made with the partition model for the packed column coated with Carbowax 20M. A series of linear plots are obtained as shown in Fig. 3. The regression equations are given below together with the coefficient of determination (r^2):

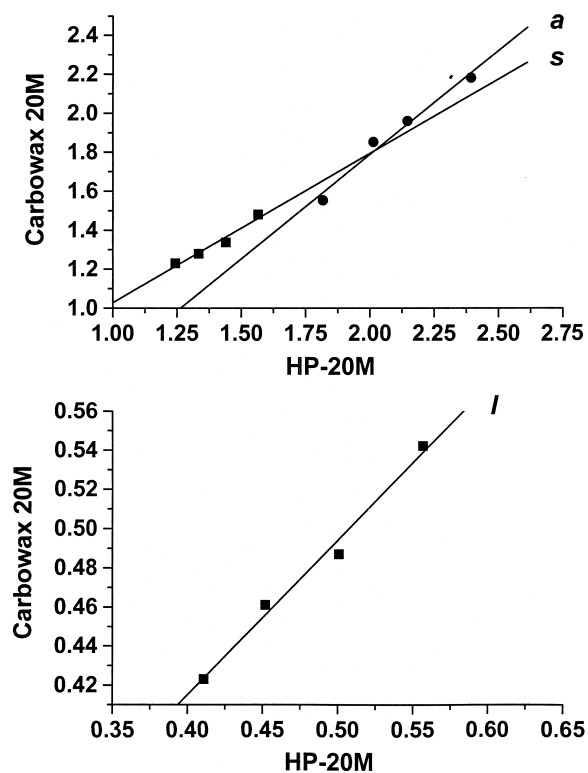


Fig. 3. Plot of the system constants for partitioning on a Carbowax 20M stationary phase against the system constants for the WCOT HP-20M column over the temperature range 80–140°C.

$$l_{\text{CW-20M}} = 0.100 + 0.788l_{\text{HP-20M}}, r^2 = 0.987 \quad (5)$$

$$s_{\text{CW-20M}} = 0.261 + 0.767s_{\text{HP-20M}}, r^2 = 0.959 \quad (6)$$

$$a_{\text{CW-20M}} = -0.354 + 1.072a_{\text{HP-20M}}, r^2 = 0.976 \quad (7)$$

The r system constant for both phases does not change with temperature, $r_{\text{CW-20M}} = 0.314 (\pm 0.017)$ and $r_{\text{HP-20M}} = 0.208 (\pm 0.004)$. The change in selectivity of the HP-20M column is different to that predicted from gas-liquid partitioning on Carbowax-20M for the temperature range 80–140°C. The change in selectivity of hydrogen-bond interactions is similar for both phases but differences exist in the changes for cohesive interactions and dipole-type interactions (slope < 1). Carbowax 20M has a slightly larger capacity for lone-pair electron interactions than HP-20M, but these interactions make only a small contribution to retention on both columns. We attribute the above differences in selectivity to a combination of chemical differences (as indicated previously) and contributions from interfacial adsorption on the HP-20M column.

A similar approach can be used to compare the selectivity of the AT-Wax and HP-INNOWax columns with that of the HP-20M column over the temperature range 60–140°C. The linearity of the plot of the system constants for AT-Wax and HP-20M, Fig. 4, is excellent providing the regression models indicated below (the r system constant is temperature invariant, $r_{\text{AT-Wax}} = 0.230 \pm 0.015$):

$$l_{\text{AT-Wax}} = -0.015 + 1.007l_{\text{HP-20M}}, r^2 = 1.000 \quad (8)$$

$$s_{\text{AT-Wax}} = -0.173 + 1.113s_{\text{HP-20M}}, r^2 = 1.000 \quad (9)$$

$$a_{\text{AT-Wax}} = -0.585 + 1.246a_{\text{HP-20M}}, r^2 = 0.993 \quad (10)$$

The two columns have a similar volume-to-surface area ratio (HP-20M/AT-Wax = 1.2), which may go part of the way in explaining the similar changes in selectivity with change in temperature for the l and s system constant (slopes close to 1). The difference in selectivity for hydrogen-bond basicity is more marked and this combined with significant intercepts for the s and a system constant, is an indication of chemical differences between the two phases. The HP-INNOWax column has a larger volume-to-sur-

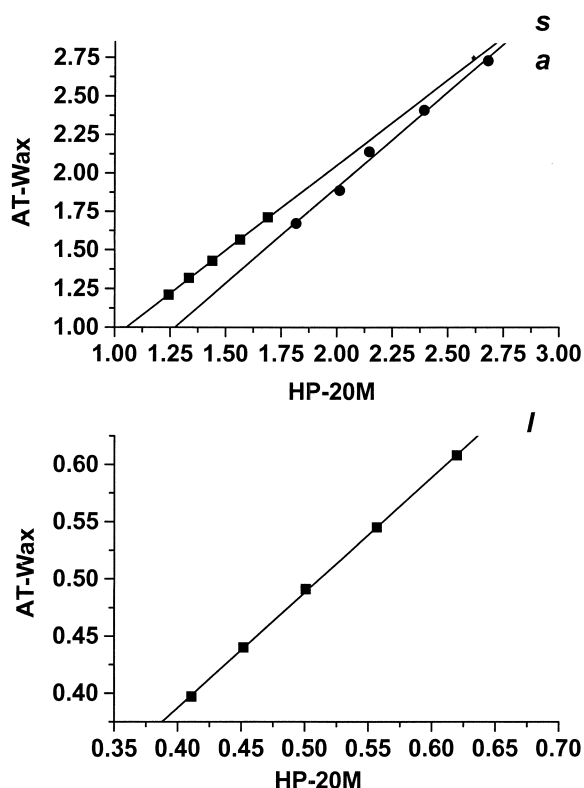


Fig. 4. Plot of the system constants for the WCOT columns AT-Wax against HP-20M over the temperature range 60–140°C.

face area ratio than the HP-20M column (HP-INNOWax \approx 1.67 HP-20M) and contributions from interfacial adsorption could be a more significant contribution to the observed selectivity differences. The regression equations for the plot of the system constants for the two phases over the temperature range 60–140°C are given below (r system constant is temperature invariant, $r_{\text{HP-INNOWax}} = 0.221 \pm 0.004$):

$$l_{\text{HP-INNOWax}} = 0.067 + 0.869l_{\text{HP-20M}}, r^2 = 0.999 \quad (11)$$

$$s_{\text{HP-INNOWax}} = 0.115 + 0.925s_{\text{HP-20M}}, r^2 = 0.999 \quad (12)$$

$$a_{\text{HP-INNOWax}} = -0.476 + 1.192a_{\text{HP-20M}}, r^2 = 0.993 \quad (13)$$

The change in selectivity as a function of temperature is significant but not large (slopes close to 1) but the large intercepts for the a and s system constants again point to chemical differences between the compared phases. It cannot be ruled out that part of this difference is due to differences in the contribution from interfacial adsorption.

Changes in selectivity as a function of temperature for DB-FFAP and HP-20M are no different in general magnitude to that observed for the poly(ethylene glycol) phases without a defined chemical modification. The slopes of the system constants as a function of temperature are close to 1, Eqs. (14–16), and the intercepts small for the plot of DB-FFAP against HP-20M. Differences in the r system constant are not statistically important or temperature dependent ($r_{\text{DB-FFAP}} = 0.233 \pm 0.034$). There are small chemical differences that effect the selectivity of DB-FFAP compared to HP-20M but the change in selectivity with temperature is similar:

$$l_{\text{DB-FFAP}} = -0.049 + 1.047l_{\text{HP-20M}}, r^2 = 0.998 \quad (14)$$

$$s_{\text{DB-FFAP}} = -0.020 + 1.073s_{\text{HP-20M}}, r^2 = 0.982 \quad (15)$$

$$a_{\text{DB-FFAP}} = -0.147 + 1.114a_{\text{HP-20M}}, r^2 = 0.991 \quad (16)$$

5. Conclusions

The solvation parameter model provides a general framework for defining the differences in selectivity for poly(ethylene glycol) stationary phases used in packed column and open-tubular column gas chromatography. The model accounts for sorptive interactions at least when interfacial adsorption makes a small contribution to the retention mechanism. Since interfacial adsorption is both a solute and system property there is no general set of conditions for which interfacial adsorption will not occur. For the compounds studied here it is reasonable to surmise that interfacial adsorption is just as likely to be important for open-tubular columns as packed columns, and that for both column types at temperatures above 100°C, it is negligible. Within this framework

it is necessary to allow that selectivity differences between columns with different volume-to-surface area ratios below 100°C can result from both differences in retention mechanism and from chemical differences. The system constants and their linear temperature dependence allow selectivity differences between compared poly(ethylene glycol) stationary phases to be quantified at any point in the temperature range studied (60 or 80 to 140°C). None of the columns studied could be described as duplicates, and although all similar in properties, small statistically significant selectivity differences were identified that would result in differences in the separation of critical compound pairs.

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