Quantitative structure–retention relationship approach to prediction of linear solvation energy relationship coefficients

I. H-Bond acceptor capability of gas chromatography stationary phases in McReynolds data set

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ABSTRACT

Linear solvation energy relationships (LSER) have been used successfully in the characterization of GC stationary phases. The various terms in the LSER are related to the ability of the stationary phase to engage in different types of intermolecular interactions. Using the 77 phase McReynolds set, structural features of the stationary phases have been correlated with the a value in an LSER, which reflects the H-bond acceptor capabilities of the stationary phase. Structural descriptors consisted of the fraction of each phase that was represented by a given functional group. For the coatings in this data set, only five descriptors were identified as contributing to the observed acceptor behavior: siloxane, ester, ether, hydroxyl and methylene (CH_2). These terms were included in the equation $a = c_1(\text{siloxane}) + c_2(\text{ester}) + c_3(\text{ether}) + c_4(\text{OH}) + c_5(CH_2)$, where the coefficients (c_i) were determined by multiple linear regression analysis. The R^2 for the above equation was 0.990. The values of the first four coefficients are a direct indication of the ability of these functional groups to act as H-bond acceptors, while the fifth term is believed to contribute via inductive effects.

INTRODUCTION

The importance of solubility, solvation processes, and solvent-mediated interactions in nearly all fields of chemistry has fueled research directed toward the development of predictive methods to enhance our understanding of such phenomena. Because the retention of solutes in chromatographic separations provides a quantitative measure of solute-solvent interactions, chromatographic methods have been used extensively for the investigation of solubility processes. Consequently, the character-

ization of stationary phases for chromatography is an active research area. The ability to predict the solubility/retention behavior of these materials facilitates the process of selecting a stationary phase for a given application.

The various approaches for predicting chromatographic behavior can be categorized as either theoretical or empirical. The theoretical approaches attempt to explain the interactions that give rise to retention by way of fundamental chemical theory, especially the thermodynamics of solubility behavior [1–4]. In addition to their predictive ability, such models also assist in our understanding of the chromatographic process; the better the model is at accounting for the relevant factors in the system, the

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greater its predictive accuracy. Empirical approaches rely on the statistical correlation of known or measurable characteristics of the compounds under study with their observed retention behavior. Such correlations usually take the form of multiple linear regression relationships [5,6]. In the majority of cases, the properties used for correlation are molecular structural descriptors, and these studies have been labelled as quantitative structure–retention relationships (QSRRs) [7–12]. While these methods do not enjoy the same fundamental theoretical basis as the former approach, their predictive ability has been well demonstrated. Unfortunately, the QSRR results are only valid for compound classes that have been included in the original correlation. Use of the derived regression equation to predict the behavior of *other* compound classes produces questionable results.

A compromise between the two approaches discussed above is the development of solubility factors or parameters to approximate or describe the solvation process [13–17]. Like the empirical approaches, these methods rely on the development of a regression relationship with terms and coefficients that are characteristic of the individual components in the system . However, they have a more fundamental, theoretical basis in that the terms in the regression equation represent the relative ability of the components to engage in solubility interactions. By far, the most successful and widely applied of these methods is the linear solvation energy relationships (LSER) of Kamlet, Abraham and Taft and co-workers which utilize solvatochromic parameters [18–22]. The LSER usually take a form similar to the following,

$$\log SP = c + r_1 R_2 + s_1 \pi_2^* + a_1\alpha_2 + \\ b_1\beta_2 + l_1 \log L^{16} \quad (1)$$

where SP refers to the solvation property under study, which in chromatographic investigations is usually the specific retention volume (V_g) or the partition coefficient (K_c). The coefficients with the subscript 1 are descriptors for the solvent (or stationary phase), and the terms with subscript 2 are descriptors for the solutes. For example, the α and β terms refer to the ability of a given solute to act as a hydrogen bond donor (acid) and hydrogen bond acceptor (base), respectively. The L^{16} term is the Ostwald solubility (partition) coefficient of the solute in hexadecane, and provides a measure of the dispersion interaction. The π^* measures the dipolarity/polarizability interactions, and the R term represents non-bonded electron interactions. The coefficients r, s, a, b and l represent the corresponding ability of the solvent phase to engage in these interactions, while c is a regression constant. Hence, the overall equation represents a model of the solvation process. The number and identity of parameters included in the LSER varies with the system under study.

The advantage of the LSER approach is that, once the relevant terms and coefficients have been determined for the solutes and solvents/phases in question, the solubility behavior of any solute/solvent pair can be calculated, *i.e.* the results are not necessarily limited to a closed system as in other empirical methods. The development of the terms (α, β, π^*, L^{16}, R) and coefficients (a, b, r, s, l) requires extensive data collection and reduction, and every compound/stationary phase must be studied in order to be characterized.

In this paper we demonstrate an alternative approach to the calculation of the coefficient in the LSER equation above for chromatographic stationary phases. Since the ability of a compound to engage in solubility interactions is determined largely by its molecular structure and functionality, we propose to use a simplified QSRR approach to the calculation/prediction of these values. The advantages of such an approach are that it permits rapid prediction of solubility behavior based on structural features, and it may assist in the rational design of materials for applications where solubility behavior is relevant.

METHODOLOGY

The approach demonstrated herein consists of correlating, via multiple linear regression, the coefficients determined for an LSER with structural features of the stationary phase materials. For the work reported here, we have focused on prediction of the coefficient a, which is a measure of H-bond acceptor basicity of a stationary phase interacting with an H-bond donor solute (characterized by α). In order for a material to act as an H-bond acceptor it must contain atoms that have lone electrons (*e.g.* oxygen, nitrogen) or functional groups that have

sufficient electron density (*i.e.* multiple bonds, aromatic rings).

The first requirement of this approach is a fully characterized set of stationary phases, *i.e.*, a set for which the LSER coefficient values have already been determined. A variety of GC stationary phases have recently been characterized using solvatochromic LSERs [23,24], including the McReynolds 77-phase set [25], which is probably the most extensively documented set of GC stationary phases. The second requirement is documentation of the structural features of these phases so that these materials can be adequately represented by a set of descriptors. A thorough description of the materials, by general chemical class, included in the McReynolds set is given below. In cases where a material could be listed under more than one class, it is included under the heading which represents the more significant contribution to the observed solubility behavior.

Hydrocarbons

Included in this class are squalane and the Apiezon greases. Squalane, a saturated hydrocarbon, contains no functional groups capable of engaging in H-bond acceptor interactions and thus has an *a* value of 0.0. The Apiezon phases contain undetermined amounts of alkene and aromatic groups which convey some weak acceptor behavior to these phases (*a* = 0.10–0.13). The actual structure(s) of these materials is not well known, however, which prevents their inclusion in the study set.

Polysiloxanes

These materials are dimethyl siloxane-based polymers, usually terminated with trimethyl silyl groups [$-Si(CH_3)_3$]. The methyl group substituents can be replaced with other functional groups to alter the solubility properties of the material. Included in this group are SE-30 (100% methyl substituted), SE-30-NPGA (same as SE-30, with neopentyl glycol adipate terminal groups), SE-31 (1% vinyl), SE-52 (5% phenyl), DCF-550 (25% phenyl), XF-1150 (50% cyanoethyl), DCFS-1265 (50% trifluoropropyl), and Versilube F-50 (chlorophenyl groups, unknown%). These phases are mostly weak acceptors, having *a* values in the range of 0.17 to 0.33; the only moderately strong acceptor is XF-1150, with an *a* value of 1.38.

Phosphates

Included in this group are tricresyl phosphate and Kroniflex-THPP, which have *a* values of 1.23 and 2.28, respectively. The relatively large *a* values are consistent with the multiple oxygens in the phosphate which are capable of acceptor behavior.

Nitrogen (amides/amines)

The only stationary phase which contains amine groups is Quadrol (N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine), which has an *a* value of 2.38. The amides in the data set include Flexol-8N8 (2,2'-(2-ethyl hexamido)diethyl di(2-ethyl)hexoate, and the Hallcomids M18/180L (N,N-dimethyl stearamide and N,N-dimethyl oleylamide). The *a* values for these phases are 1.55 and 1.59, respectively.

Oxygen (esters/ethers/hydroxyls)

This is by far the best represented set of functional groups in the data set. Within this subheading are several well-defined classes of materials, which are worth describing further.

Esters/polyesters. Most of the esters are manufactured by the reaction of aliphatic alcohols with dicarboxylic acids (adipic, sebacic and phthalic). Included in this set are dioctyl sebacate (DOSb), di-2-ethylhexyl sebacate (DEHb), di-2-ethylhexyl adipate (DEHA), isooctyl decyl adipate (IODA), diisodecylphthalate (DIDP), dioctylphthalate (DOP), bis(2-ethoxyethyl)phthalate, and dibutyl-tetrachlorophthalate. These are moderate acceptors (*a* = 0.60–1.25). Three of the phases are produced by the esterification of sucrose [sucrose diacetate hexaisobutanoate (SAIB), sucrose octaacetate, and octakis-2(hydroxypropyl) sucrose (Hyprose SP80)], which tend to be stronger acceptors (*a* = 1.29–2.40). Additional ester phases are tripelargonate, a triester produced by the reaction of glycerol with pelargonic acid (*a* = 0.82), and Citroflex A-4 (acetyl tributyl citrate) (*a* = 0.94).

Nine coatings in the set are polyesters, produced by the polymerization of various glycols with adipic (A), succinic (S) and sebacic (Sb) acids. Glycols used to produce these materials included ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and neopentyl glycol (NPG). Abbreviated names for these phases are given as NPGA (terminated and unterminated), EGSb, DEGSb, NPGS, EGA, DEGA, TEGS, and DEGS. Most of

the polymer chains terminate in –OH groups, but the terminal group for the NPGA term. phase was undetermined. While these phases were very popular until the 1970s, there is no information available as to the molecular weight range of the materials used. Attempts to obtain such information from the manufacturer(s) revealed that even they did not know for sure, and there was variation from one lot to the next.

Polyglycol ethers. Included under this heading are the Pluronic phases and the Carbowaxes (CW). The Carbowaxes are linear polyethylene glycols (PEGs), terminated by hydroxyl groups, with the phase number providing information about the approximate relative molecular mass (M_r) range. Carbowax 1000, for example, has an M_r of 950–1050, whereas Carbowax 20M has an M_r between 15 000 and 20 000.

The Pluronic phases consist of block copolymers of PEG and polypropylene glycol (PPG). The letter in the phase suffix refers to the physical appearance of the phase as liquid (L), paste (P) or flake (F). The first number in the suffix, when multiplied by 300, yields the approximate M_r of the phase represented by the PPG block, while the second number, when multiplied by 10, yields the % of the total M_r represented by the PEG. Pluronic L63, therefore, is a liquid phase having a PPG weight of approximately 1800, which represents 70% of the total M_r with 30% of the polymer being PEG. The total M_r of this phase is about 2600. There is some disagreement in the literature regarding the terminal groups on the polymer chains [15,26], but the more commonly accepted structure contains hydroxyl terminal groups.

Other PPG- and PEG-based polymer phases in this class include UCON LB-1715 and UCON HB-2000. The latter is a butoxy-terminated PPG with the average number of repeating PPG units equal to 28 or 29. In general, the PPG-based polymers tend to be water insoluble. The former is also butoxy-terminated, but is approximately 50% (w/w) in PEG and PPG units with a total M_r of about 2000; the high percentage of PEG groups renders these polymers water soluble.

Phenyl ethers. Eight of the remaining phases are characterized by ether linkages. Two of these are polyphenyl ethers (5 ring and 6 ring, PPE-5 and PPE-6). Once again, there is some variation in structures reported in the literature, with one refer-

ence reporting hydroxyl terminated chains [17], and another reported no hydroxyl terminals [15]. The most likely structure is the former. The remaining six ether phases are often used as detergents/surfactants; these include Polytergent-J300, Oronite NIW, Ethofat 60/25, Tergitol NPX, Igepal CO-880 and Triton X-305. These phases are di-substituted phenyls; one substituent consists of a saturated hydrocarbon (HC), and the other substituent is an hydroxyl terminated PEG chain. The number of carbons in the saturated HC substituent varies from 8 (Triton X-305) to 17 (Ethofat 60/25), and the number of ethylene glycol units in the PEG substituent varies from 10 (Tergitol NPX) to 30 (Triton X-305). The exact structure of the Polytergent-J300 could not be verified.

Alcohols. Included in this group are docosanol ($C_{22}H_{45}OH$), diglycerol [(HOCH$_2$CH(OH)-CH$_2$)$_2$–O], and sorbitol. The structure of sorbitol can be written either as a straight chain or as a 5-membered ring, which is formed upon the elimination of a water molecule. These phases are unique in the 77-phase set because they also exhibit significant H-bond donor acidity and, thus, have relatively large *b* values (0.34–0.52).

Miscellaneous phases

The remaining two phases can not be classified in any of the above groups. Castor wax is hydrogenated castor oil [CH$_3$(CH$_2$)$_{16}$COOH], with the carboxylic acid group providing significant H-bond acceptor ability (*a* = 1.09). The final remaining phase is Zonyl E-7 which can be described as a polyfluorinated ester of aromatic acid (1,2,4,5-tetracarboxylic acid), although the exact structure could not be verified.

DATA SET DEVELOPMENT

The *a* values used in this work were taken from Abraham *et al.* [25] for the 77-phase McReynolds data set at 120°C. Structures for as many coatings in this set as possible were obtained from a variety of literature sources and supplier documentation [15,17,26–30]. Unfortunately, structures for several of the phases in the data set could not be verified, and these coatings were not included in the final data set. Non-verified phases included Zonyl E-7, Polytergent-J300, Versilube F50, and the four Apie-

zon phases. In addition, the terminal group for NPGA-(term.) could not be verified, so this phase was also eliminated. This reduced the number of phases in the set to 69. A set of structural descriptors were calculated for the remaining coatings based on the relative abundance of individual functional groups, expressed as a percentage of the molecular mass. Potential H-bond acceptor groups include alkenes $(C=C)$, phenyls, siloxanes $(Si–O)$, phosphates (PO_4), nitriles $(C\equiv N)$, amides $(CONR_2)$, amines (NR_3), esters $(COOR)$, ethers $(C–O–C)$, and hydroxyls $(R–OH)$.

Functional groups for the remaining phases were considered as descriptors to be included in the regression equation. In order for the regression results to be statistically valid each functional groups should be adequately represented within the data set to prevent skewing of the result. Once again, several of the remaining phases were eliminated because of inadequate representation. Among the functional groups that were under-represented were the phosphates (2 phases), the amides/amines (3 phases), the alkene/vinyl (3 phases), and the cyano/ nitriles (1 phase). Phases eliminated at this stage were tricresyl phosphate, Kroniflex THPP, Flexol 8N8, the Hallcomids (18,180L), Quadrol, SE-31 and XF-1150. This reduced the data set to 61. Two of the remaining phases contained halogens (dibutyltetrachlorophthalate, DCFS-1265); because the acceptor behavior of chlorine is likely to be negligible, and the fluorine will likely affect acceptor behavior via inductive effects, these coatings were retained for the preliminary regression. Chlorine and fluorine were not, however, included among the functional groups considered for the regression equation.

The remaining 61 coatings in the data set are listed in Table I. Simplified descriptors for the functional groups in these coatings were determined as follows. Fractional representations for each functional groups were calculated by multiplying the number of functional groups in the molecule by the amu for that functional group, and dividing by the total M_r. Hydroxyls and ethers, for example, contain one oxygen at 16 amu, whereas each ester contains two oxygens for a total of 32 amu. Siloxanes $(Si–O)$ contained one oxygen at 16 amu; since Si does not participate as an acceptor, its mass was not included. Phenyls were represented as (C_6H_x) with

the total number of hydrogens being determined by the degree of substitution. Monosubstituted phenyls, for example, were C_6H_5 for 77 amu. Also included in the table are fractions of CH_3, CH_2 and CH groups. Although these CH_x functionalities cannot engage in acceptor behavior, they provide information regarding the extent of branching within the molecule, which can affect the molar volume and/or potential steric or inductive effects. The resulting fractions and the M_r used for each phase are included in Table I. It should be noted that the actual mass for the polyester phases was not known. The data for these phases are for $M_r \approx 2000$ ($n \approx 10$; n = number of monomer repeat units). The phases in the data set are predominantly represented by oxygenated functional groups (ester, ether, hydroxyl), with siloxanes and phenyl groups being marginally represented. The number of coatings containing these functional groups are given in Table II.

RESULTS

Statistical evaluation of the data set was performed using two different software packages. A complete statistical system (CSS), obtained from Statsoft (Tulsa, OK, USA), was used for correlation analysis of the regression variables, for calculation of standard and deleted residuals, and for calculation of F values. The R^2 values obtained using the CSS package used (N) rather than $(N-1)$, and were thus not reported in this work. Additional statistical analyses were performed using the regression subroutines available in Quattro Pro 3.0 (Borland International). R^2 values reported herein were obtained using the QPro software. Values for residuals, as well as for the regression coefficients and associated standard errors, were identical for both software packages. In all cases, results are for the linear regression with the intercept forced to zero.

The data in Table I were used to develop a regression equation of the following form

$$a_i = c_1 (\text{descriptor}_1)_i + c_2 (\text{descriptor}_2)_i + c_3 (\text{descriptor}_3) + \dots + c_n (\text{descriptor}_n)_i \qquad (2)$$

where a is the coefficient from the LSER from ref. 25, $c_{1,2\dots}$ are the regression coefficients, (descriptor) is the fraction of the total M_r represented by a given functionality (phenyl, siloxane, etc.) as given in Ta-

TABLE I

PHASE DATA SET WITH DESCRIPTORS (POLYESTER M_r SET TO $n = 10$)

Coating	M_r	Coef. a	Phenyl	Siloxane	Ester	Ether	OH	CH$_2$	CH	CH$_3$
DCFS-1265	24 600	0.2900	0.0000	0.1020	0.0000	0.0000	0.0000	0.1784	0.0000	0.0992
SE-52	100 000	0.2200	0.0959	0.1992	0.0000	0.0000	0.0000	0.0000	0.0000	0.3554
DCF-550	5186	0.2900	0.3563	0.1481	0.0000	0.0000	0.0000	0.0000	0.0000	0.2260
SE-30	1 998 100	0.2900	0.0000	0.2162	0.0000	0.0000	0.0000	0.0000	0.0000	0.4054
SE-30(NPGA)	10 032	0.3300	0.0000	0.2089	0.0128	0.0000	0.0000	0.0001	0.0000	0.4053
PPE-5	446	0.5400	0.8565	0.0000	0.0000	0.1435	0.0000	0.0000	0.0000	0.0000
PPE-6	538	0.5600	0.8513	0.0000	0.0000	0.1487	0.0000	0.0000	0.0000	0.0000
DBTCP	416	0.6000	0.1731	0.0000	0.1538	0.0000	0.0000	0.2019	0.0000	0.0721
DIDP	446	0.7300	0.1704	0.0000	0.1435	0.0000	0.0000	0.3139	0.1166	0.2018
DOP	390	0.7700	0.1949	0.0000	0.1641	0.0000	0.0000	0.3590	0.0667	0.1538
bis-(2EOE)Ph	310	1.2500	0.2452	0.0000	0.2065	0.1032	0.0000	0.2710	0.0000	0.0968
Oronite-NIW	906	1.4600	0.0839	0.0000	0.0000	0.2472	0.0177	0.5872	0.0143	0.0497
Tergitol NPX	660	1.4700	0.1152	0.0000	0.0000	0.2424	0.0242	0.5939	0.0000	0.0227
IgepalCO-880	880	1.6100	0.0864	0.0000	0.0000	0.2727	0.0182	0.6045	0.0000	0.0170
Triton-X305	1526	1.6500	0.0498	0.0000	0.0000	0.3145	0.0105	0.6147	0.0000	0.0098
Ethofat 60/25	988	1.5400	0.0000	0.0000	0.0324	0.2591	0.0162	0.6802	0.0000	0.0152
DOSb	426	0.7900	0.0000	0.0000	0.1502	0.0000	0.0000	0.7230	0.0000	0.0704
IODA	398	0.8100	0.0000	0.0000	0.1608	0.0000	0.0000	0.5276	0.0760	0.1884
DEHSb	426	0.8300	0.0000	0.0000	0.1502	0.0000	0.0000	0.5915	0.0610	0.1408
DEHA	370	0.8700	0.0000	0.0000	0.1730	0.0000	0.0000	0.5297	0.0703	0.1622
EGSb	2343	1.4400	0.0000	0.0000	0.2733	0.0000	0.0137	0.6097	0.0000	0.0000
DEGSb	2826	1.4500	0.0000	0.0000	0.2265	0.0623	0.0113	0.6143	0.0000	0.0000
NPGA	2244	1.4700	0.0000	0.0000	0.2852	0.0000	0.0143	0.3868	0.0000	0.1471
NPGS	1964	1.4900	0.0000	0.0000	0.3259	0.0000	0.0163	0.2994	0.0000	0.1527
DEGS	1986	1.6800	0.0000	0.0000	0.3222	0.0886	0.0161	0.4512	0.0000	0.0000
EGA	1782	1.7200	0.0000	0.0000	0.3591	0.0000	0.0180	0.4871	0.0000	0.0000
DEGA	2266	1.7300	0.0000	0.0000	0.2824	0.0777	0.0141	0.5190	0.0000	0.0000
TEGS	2470	1.8700	0.0000	0.0000	0.2591	0.1425	0.0130	0.4874	0.0000	0.0000
UCON-LB1715	1698	1.2200	0.0000	0.0000	0.0000	0.2638	0.0094	0.2556	0.2144	0.2562
PL-L81	2660	1.2900	0.0000	0.0000	0.0000	0.2767	0.0120	0.2789	0.2004	0.2312
PL-L72	2634	1.4100	0.0000	0.0000	0.0000	0.2855	0.0121	0.3189	0.1777	0.2050
PL-L61	2080	1.4200	0.0000	0.0000	0.0000	0.2769	0.0154	0.2894	0.1938	0.2236
PL-P84	3980	1.4400	0.0000	0.0000	0.0000	0.3055	0.0080	0.3975	0.1339	0.1545
PL-L42	1588	1.4500	0.0000	0.0000	0.0000	0.2821	0.0202	0.3262	0.1719	0.1984
PL-P85	4860	1.4600	0.0000	0.0000	0.0000	0.3160	0.0066	0.4407	0.1097	0.1265
PL-L63	2608	1.4600	0.0000	0.0000	0.0000	0.2945	0.0123	0.3597	0.1545	0.1783
UCON-HB2000	2028	1.4800	0.0000	0.0000	0.0000	0.3077	0.0079	0.4418	0.1090	0.1331
PL-P65	3664	1.5000	0.0000	0.0000	0.0000	0.3144	0.0087	0.4394	0.1100	0.1269
PL-L44	2027	1.5200	0.0000	0.0000	0.0000	0.3000	0.0158	0.3937	0.1347	0.1554
PL-P46	3084	1.5600	0.0000	0.0000	0.0000	0.3217	0.0104	0.4767	0.0885	0.1021
PL-F88	12 076	1.6000	0.0000	0.0000	0.0000	0.3445	0.0026	0.5576	0.0441	0.0509
PL-F68	8388	1.6100	0.0000	0.0000	0.0000	0.3433	0.0038	0.5558	0.0449	0.0519
PL-F77	6946	1.6100	0.0000	0.0000	0.0000	0.3340	0.0046	0.5160	0.0674	0.0777
CW-20M	17 508	1.7800	0.0000	0.0000	0.0000	0.3623	0.0018	0.6357	0.0000	0.0000
CW-6000	6772	1.8000	0.0000	0.0000	0.0000	0.3603	0.0047	0.6347	0.0000	0.0000
CW-4000	3362	1.8500	0.0000	0.0000	0.0000	0.3569	0.0095	0.6330	0.0000	0.0000
CW-1540	1470	1.8700	0.0000	0.0000	0.0000	0.3483	0.0218	0.6286	0.0000	0.0000
CW-1000	1008	1.8900	0.0000	0.0000	0.0000	0.3413	0.0317	0.6250	0.0000	0.0000
CW-600	612	2.1200	0.0000	0.0000	0.0000	0.3268	0.0523	0.6176	0.0000	0.0000
CW-400	414	2.1800	0.0000	0.0000	0.0000	0.3092	0.0773	0.6087	0.0000	0.0000
CW-300	304	2.2800	0.0000	0.0000	0.0000	0.2895	0.1053	0.5987	0.0000	0.1020
Hyprose-SP80	806	2.4000	0.0000	0.0000	0.0000	0.2184	0.1588	0.1911	0.2581	0.1489
SAIB	846	1.2900	0.0000	0.0000	0.3026	0.0567	0.0000	0.0496	0.1998	0.2482

TABLE I *(continued)*

Coating	M_r	Coef. a	Phenyl	Siloxane	Ester	Ether	OH	CH$_2$	CH	CH$_3$
Sucrose(Ac)$_8$	678	1.5900	0.0000	0.0000	0.3776	0.0708	0.0000	0.0619	0.1534	0.177
Citroflex A4	388	0.9400	0.0000	0.0000	0.3299	0.0000	0.0000	0.3608	0.0000	0.1546
Docosanol	327	0.7500	0.0000	0.0000	0.0000	0.0000	0.0490	0.9002	0.0000	0.0459
Diglycerol	166	2.7700	0.0000	0.0000	0.0000	0.0964	0.3855	0.3373	0.1566	0.0000
Sorbitol	164	1.7700	0.0000	0.0000	0.0000	0.0974	0.9898	0.1705	0.3167	0.0000
Squalane	422	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5308	0.1848	0.2844
Tripelargonate	512	0.8200	0.0000	0.0000	0.1875	0.0000	0.0000	0.6289	0.0254	0.0879
Castorwax	284	1.0900	0.0000	0.0000	0.0563	0.0000	0.0563	0.7887	0.0000	0.0528

ble I. The 61-phase data set was used to develop a preliminary regression equation. Of the 8 functionality factors in the table, only 5 were determined to be significant. These 5 were siloxane, ester, ether, hydroxyl, and methylene (CH$_2$). The regression coefficients and their respective standard errors are given in Table III. Examination of residuals using this equation revealed that the a values for two coatings (sorbitol and Citroflex A4) were severely over-predicted, while one coating (Hyprose SP80) was severely under-predicted. The over-predictions could be partly due to steric effects; some of the oxygens in these compounds may have limited accessibility. In addition, the sorbitol has a high b val-

ue due to its ability to act as a H-bond donor. The possibility of intramolecular interactions, *i.e.* self-association, may reduce the availability of the hydroxyls for H-bond acceptor behavior with solutes. An iterative process of regression, followed by eliminating of outliers due to steric hinderance and/or self-association, reduced the data set to 55 coatings. Eliminated at this round were the three alcohol phases (docosanol, diglycerol, sorbitol), Citroflex A4, and tripelargonate. The elimination of the first three coatings can be justified due to self-association; each has a significant b value. The latter two coatings were eliminated on the basis of unusual steric hinderance. It is worth noting that these 5 coatings tend to be of low M_r (164 – 512) compared with the majority of coatings in the data set. Any steric or self-association phenomena are likely to have a larger effect on smaller molecules than on larger ones. One additional coating, squalane, was eliminated due to the fact that it contained no H-bonding capability ($a = 0.00$), yet had a CH$_2$ fraction of 0.52. Inclusion of this coating would skew the coefficient for CH$_2$.

Upon elimination of these coatings the regression coefficients were redetermined and are given in Ta-

TABLE II

REPRESENTATION OF FUNCTIONAL GROUPS IN 61-PHASE DATA SET

No. of coatings	Functional groups				
	Phenyl	Siloxane	Ester	Ether	OH
	12	5	23	40	41

TABLE III

COMPARISON OF REGRESSION RESULTS FOR 61-PHASE AND 55-PHASE DATA SETS

Data set	R^2 (standard error)	Siloxane	Ester	Ether	OH	CH$_2$	F
61 phases	0.922 (0.167)	1.409 (0.415)	3.423 (0.189)	4.090 (0.170)	5.009 (0.295)	0.549 (0.088)	902
55 phases	0.990 (0.054)	1.412 (0.134)	3.517 (0.068)	3.872 (0.064)	8.969 (0.275)	0.514 (0.036)	7893

ble III for comparison. The R^2 for the regression improved from 0.922 (standard error = 0.167) to 0.990 (standard error = 0.054). The regression coefficients for siloxane and ester increased slightly, whereas the coefficients for ether and CH_2 decreased slightly. The largest effect was observed for the coefficient for hydroxyl, which increased dramatically from 5.009 to 8.969. As a result of this large increase in the hydroxyl coefficient some of the coatings that were under-predicted using the original regression equation, most notably Hyprose SP80, were now more accurately predicted. Using these coefficients yields the following regression equation

$$a = 1.412 \text{ (siloxane)} + 3.517(\text{ester}) + \\ 3.872(\text{ether}) + 8.969(\text{OH}) + 0.514(\text{CH}_2) \quad (3)$$

The F value of 7893 for eqn. 3 strongly indicates that this equation is statistically significant and a useful predictor for a. A plot of predicted a values using the regression equation *versus* observed a values from the LSER study [25] is given in Fig. 1.

The factors used in developing the regression equation were evaluated for correlation between factors; the correlation data for the 55-phase set are presented in Table IV. The only sizable positive correlation is between siloxane and CH_3; such a correlation is not unusual since most of the siloxanes have a large number of methyl substituents. Among the five factors included in the final regression equation several negative correlations are indicated, but the only one worthy of note is between ester and ether and is a consequence of the coating structures within the data set. Whereas there are a large number of coatings that have either ester *or* ether groups
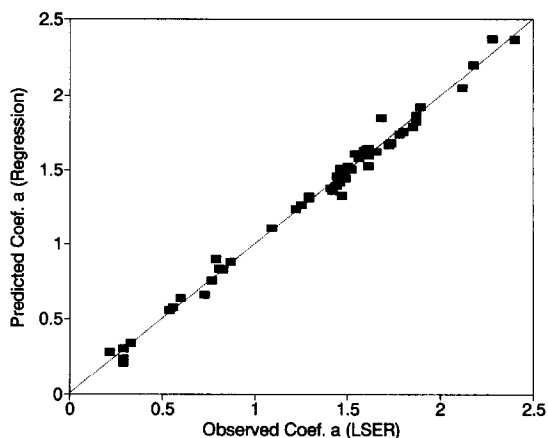

Fig. 1. Plot of the a values calculated using eqn. 3 (predicted) *versus a* values determined for the LSER from ref. 25 (observed). R^2 for the regression is 0.990, with a standard error of 0.054.

(23 and 40, respectively) only 8 coatings have *both* an ester and ether groups. Thus, intercorrelation of the regression factors was not considered to be above an acceptable level.

The residuals from the regression were examined to determine if they were truly random, or whether there was some systematic bias in the data. The average and standard deviation for the calculated residuals (using eqn.3) were 0.0007 and 0.051, respectively. Of the 55 coatings in the data set, 29 coatings were over-predicted while 26 were under-predicted. A plot of the residuals *versus a* in Fig. 2 indicates that there is no systematic trend as a function of a. Plots of residuals *versus* the various regression factors and *versus* M_r resulted in similarly random plots. Finally, the coatings were arranged in groups

TABLE IV

REGRESSION FACTOR CORRELATION TABLE

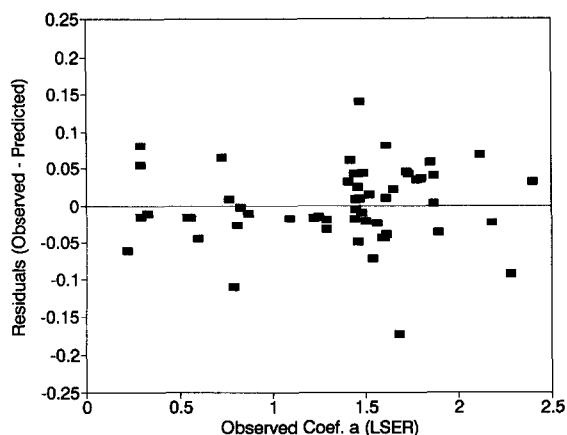| Variable	Phenyl	Siloxane	Ester	Ether	OH	CH_2	CH	CH_3
Phenyl	1.000							
Siloxane	0.0407	1.000						
Ester	−0.1157	−0.1970	1.000					
Ether	−0.1633	−0.3811	−0.6466	1.000				
OH	−0.1789	−0.1777	−0.1759	0.2269	1.000			
CH_2	−0.4608	−0.5556	−0.0357	0.3721	0.1966	1.000		
CH	−0.2076	−0.2240	−0.1212	0.2324	0.1467	−0.3023	1.000	
CH_3	−0.1358	0.6375	−0.0918	−0.3181	−0.1604	−0.6625	0.4826	1.000

Fig. 2. Plot of residual values for *a* (observed − predicted) *versus* observed value, indicating random ditribution of errors.
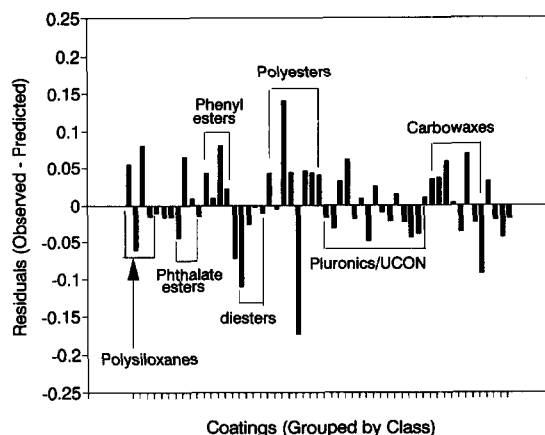

Fig. 3. Residuals for 55-phase data set grouped according to coating compound classes.

based on chemical class to determine if there were trends in residuals as a function of coating class. The results are presented in Fig. 3. While most of the coating classes exhibit fairly random distribution of residuals, some of the ester classes exhibit systematic behavior. The four diesters, for example, are over-predicted, whereas the phenyl esters tend to be under-predicted. The polyesters are, for the most part, under-predicted even though the largest *over*-predicted coating (DEGS) is a member of this class. For the most part, the number of coatings in each class is rather limited and the magnitude of the residuals is small; any conclusions regarding systematic trends in the residuals as a function of chemical class would be tenuous. The influence of

any individual coating class on the regression results was investigated further.

The first coating class investigated was the polyesters. As stated in the introduction, the actual M_r for the 8 polyester coatings was not known; the regression results given above were calculated using estimated M_r of 2000 ($n = 10$) . Additional calculations were performed to determine what effect the M_r of the polyester coatings would have on the regression results. The functionality fraction descriptors in Table I were recalculated for the 8 polyester coatings using estimated M_r of approximately 5000 and 10 000. Most of the descriptors change only slightly, on the order of 1–3%. The hydroxyl fractional descriptor, however, decreases dramatically

TABLE V

COMPARISON OF REGRESSION RESULTS (POLYESTER M_r VARIABLE)

M_r	R^2	Standard error	Siloxane	Ester	Ether	OH	CH$_2$
2000	0.990	0.0539	1.412 (0.134)	3.517 (0.068)	3.872 (0.064)	8.969 (0.275)	0.513 (0.036)
5000	0.989	0.0579	1.409 (0.144)	3.619 (0.073)	3.868 (0.069)	8.948 (0.297)	0.517 (0.038)
10000	0.988	0.0601	1.409 (0.149)	3.654 (0.075)	3.866 (0.072)	8.919 (0.309)	0.0520 (0.040)
−[a]	0.994	0.0438	1.414 (0.109)	3.423 (0.075)	3.899 (0.054)	8.906 (0.225)	0.502 (0.030)

[a] Regression results for 48 coating set after elimination of polyester coatings.

TABLE VI

RESIDUAL (STANDARD AND DELETED) FOR 55-PHASE DATA SET

Coating	a		Standard residual	Deleted residual	% change residual
	Observed	Predicted			
DCFS-1265	0.2900	0.23558	0.05442	0.05893	8.3
SE-52	0.2200	0.28117	− 0.06117	− 0.08097	− 32.4
DCF-550	0.2900	0.20904	0.08096	0.09361	156
SE-30	0.2900	0.30517	− 0.01517	− 0.02130	− 40.4
SE-30(NPGA)	0.3300	0.33993	− 0.00993	− 0.01360	− 36.9
PPE-5	0.5400	0.55566	− 0.01566	− 0.01613	− 3.0
PPE-6	0.5600	0.57580	− 0.01580	− 0.01631	3.2
DBTCP	0.6000	0.64461	− 0.04461	− 0.04558	− 2.2
DIDP	0.7300	0.66590	0.06410	0.06580	2.6
DOP	0.7700	0.76151	0.00849	0.00879	3.5
Bis-(2EOE)Ph	1.2500	1.26506	− 0.01506	− 0.01588	− 5.4
Oronite-NIW	1.4600	1.41748	0.04252	0.04426	4.1
Tergitol-NPX	1.4700	1.46063	0.00937	0.00977	4.2
IgepalCO-880	1.6100	1.52959	0.08041	0.08381	42
Triton-X305	1.6500	1.62762	0.02238	0.02348	49
Ethofat 60/25	1.5400	1.61182	− 0.07182	− 0.07547	− 5.1
DOSb	0.7900	0.89953	− 0.10953	− 0.12778	− 16.7
IODA	0.8100	0.83648	− 0.02648	− 0.02842	− 7.3
DEHSb	0.8300	0.83201	− 0.00201	− 0.00221	− 10.0
DEHA	0.8700	0.88047	− 0.01047	− 0.01123	− 7.3
EGSb	1.4400	1.39719	0.04281	0.04717	10.2
DEGSb	1.4500	1.45466	− 0.00466	− 0.00499	− 7.1
NPGA	1.4700	1.32997	01.4003	0.15109	7.9
NPGS	1.4900	1.44617	0.04383	0.04892	11.6
DEGS	1.6800	1.85239	− 0.17239	− 0.19088	− 10.7
EGA	1.7200	1.67457	0.04543	0.05139	13.1
DEGA	1.7300	1.68708	0.04292	0.04614	7.5
TEGS	1.8700	1.82996	0.04004	0.04282	6.9
UCON-LB1715	1.2200	1.23704	− 0.01704	− 0.01768	− 3.7
PL-L81	1.2900	1.32228	− 0.03228	− 0.06654	− 106.2
PL-L72	1.4100	1.37779	0.03221	0.03344	3.8
PL-L61	1.4200	1.35894	0.06106	0.06336	38
PL-P84	1.4400	1.45882	− 0.01882	− 0.01960	− 4.1
PL-L42	1.4500	1.44102	0.00898	0.00930	3.5
PLP85	1.4600	1.50911	− 0.04911	− 0.05128	− 4.4
PL-L63	1.4600	1.43538	0.02462	0.02554	3.7
UCON-HB2000	1.4800	1.48919	− 0.00919	− 0.00956	− 4.0
PL-P65	1.5000	1.52108	− 0.02108	− 0.02197	− 4.2
PL-L44	1.5200	1.50553	0.01447	0.01500	3.7
PL-P46	1.5600	1.58375	− 0.02375	− 0.02476	− 4.3
PL-F88	1.6000	1.64362	− 0.04362	− 0.04617	− 5.8
PL-F68	1.6100	1.64881	− 0.03881	− 0.04101	− 5.7
PL-F77	1.6100	1.59954	0.01046	0.01100	5.1
CW-20M	1.7800	1.74547	0.03453	0.03696	7.0
CW-6000	1.8000	1.76322	0.03678	0.03919	6.6
CW-4000	1.8500	1.79223	0.05777	0.06118	5.9
CW-1540	1.8700	1.86699	0.00301	0.00316	4.9
CW-1000	1.8900	1.92682	− 0.03682	− 0.03860	− 4.8
CW-600	2.1200	2.05163	0.06837	0.07285	6.6
CW-400	2.1800	2.20312	− 0.02312	− 0.02606	− 12.7
CW-300	2.2800	2.37283	− 0.09283	− 0.11770	− 26.8
Hyprose-SP80	2.4000	2.36803	0.03197	0.07790	143.7
SAIB	1.2900	1.30932	− 0.01932	− 0.02298	− 19.0
Sucrose(Ac)8	1.5900	1.63402	− 0.04402	− 0.05857	− 33.1
Castorwax	1.0900	1.10794	− 0.01794	− 0.02406	− 3.41

by a factor of between 4 and 6 as the M_r increases from *ca.* 2000 to 10 000. Since the coefficient for the hydroxyl is the largest factor in the regression equation, such variations in this factor may significantly affect the regression results.

Regression equations were developed for the 55 coating data set using the three different M_r ranges for the polyesters, independently. Regression results for the three data sets are compared in Table V. The effect on siloxane, ether and CH_2 coefficients is relatively small, but the effect on ester and hydroxyl coefficients is larger. As the M_r of the polyester increases the value for the hydroxyl coefficient decreases and the value for the ester coefficient increases. Such an effect is reasonable in light of the large decrease in the hydroxyl fractional descriptor as M_r increases. Increasing the M_r of the polyester decreases the hydroxyl fraction of the molecule, and the relative weight given to this factor (the coefficient) decreases accordingly, while the ester coefficient increases to make up the difference. The standard error for all coefficients increases as M_r increases. The R^2 for the regression equation decreases only slightly, from 0.990 to 0.988.

Elimination of the polyester coatings from the data set improved the regression equation dramatically. The R^2 improved to 0.994 (standard error = 0.0438), and the standard error for 4 out of 5 of the regression coefficients decreased. The standard error for ester increased slightly from 0.068 to 0.075. These results are also included in Table V.

Other classes of coatings were removed from the data set and regression results were compared with eqn. 3. In most cases, removal of a given class re-sulted in a slight improvement in the R^2, but with an increase in the standard error of the regression coefficients. The only exception occurred upon removal of the siloxanes. Removal of this class necessitated reducing the number of factors in the regression equation by 1. The R^2 for the resulting 4-term regression was 0.986 (standard error = 0.0534), although the values for the 4 remaining coefficients differ by 2% or less from the values in eqn. 3.

A complete list of the residuals for the 55-phase data set is given in Table VI. Included in this list are deleted residuals, *i.e.* the residual that would be calculated for that particular coating if that coating were eliminated from the training set. The deleted residuals provide an indication of the relative importance of that particular coating in the regression. For most of the coatings in the set the deleted residual differs from the standard residual by 10% or less. Only 13 of the 55 coatings had deleted residuals that differed by greater than 10%. Of these, 4 were siloxanes which are marginally represented in the data set. All three of the sucrose esters also exhibited changes in the deleted residual greater than 10%, with the deleted residual for Hyprose SP80 changing by 144%. The only other unusually large variation was observed for Pluronic-L81 which changed by 106%. It should be noted that, even though the % change in the residual appears to be large, the absolute change in the predicted *a* value was rather small in most cases.

To test the validity of the regression model the coatings in the data set were divided into two subsets. This was accomplished by placing the coatings in order of increasing *a* value, and then assigning

TABLE VII

SUMMARY OF SUBSET REGRESSION PREDICTIVE UTILITY

Training set		$+/-$ [a]	R^2 for Regression[b] (standard error)	Residuals average ± S.D.
Subset I	I	15 / 13	0.991 (0.056)	0.0029 ± 0.051
	II	16 / 11	0.989 (0.054)	0.0206 ± 053
Subset II	I	9 / 19	0.987 (0.064)	−0.0233 ± 0.062
	II	13 / 14	0.993 (0.044)	−0.0027 ± 0.044

[a] + is the number of coatings under-predicted (residual is positive); − is the number of coatings over-predicted (residual is negative).
[b] R^2 and standard error values for the subset used as the training set are taken from the regression results. Values for the predicted subset are calculated as regression results of observed (LSER) values *versus* predicted (regression) *a* values.

alternating coatings to subset I or subset II. Subset I had 28 coatings ($a = 0.22$–2.40), while subset II had 27 coatings ($a = 0.29$–2.28). Subset I was then used to generate regression coefficients, which were used to calculate a values for the coatings in subset II. This process was then reversed, and subset II was used to generate regression coefficients, which were used to calculate a values for the coatings in subset I. The results are summarized in Table VII. Even though the R^2 values for the predicted set are lower than for the training set, the results are still well within acceptable limits.

DISCUSSION

Although the statistical results indicate that the regression equation provides an accurate prediction for a values of the GC stationary phases, it would be more intellectually satisfying if these results (*i.e.*, regression coefficients) made sense on a molecular level. On a strictly qualitative basis, we can compare the values for the regression coefficients in eqn. 3 in light of the relative abilities of these functional groups to act as H-bond acceptors.

The coefficients for the oxygen-containing functional groups increase in the order

siloxane < ester < ether < OH

We can rationalize this trend, keeping in mind that the ability of a functional group to act as a H-bond acceptor will depend on the number and availability of lone pairs of electron. The siloxane is structurally similar to the ether, in that both are systems exhibit a tetrahedral bond arrangement around the Si or C atom. The decreased ability of the Si–O–Si functionality to act as a H-bond acceptor can be explained in terms of the extent of association of the non-bonding electron pairs with the O atom. In the siloxane system there is some back-bonding of these lone-pair electrons with the *d*-orbitals of the Si. This is evident in the Si–O bond strength (370 kJ/mol) compared to the C–O bond (336 kJ/mol) in which there is no back-bonding. This back-bonding decreases the availability of the lone-pair electrons and, hence, significantly decreases their tendency for H-bond acceptance.

The value for ester (3.517) is slightly less than that for ether (3.872). These coefficient values are normalized against the number of O atoms in each

functional group, so that the ability of an ester group to accept H-bonds is actually a factor of two greater than indicated by the coefficient. The fact that the H-bond acceptor ability of an *individual* O atom in an ester group is less than that of an O in ether is likely due to the bond orders. In ethers, the average bond order for a C–O bond is 1; in esters, the average C–O bond order is 1.5. This increase in bond order decreases the availability of electrons for H-bonding. Finally, the tremendous ability of hydroxyls to act as H-bond acceptors is consistent with the large coefficient (8.969) in eqn. 3.

It should be noted that the values of the regression coefficients are somewhat dependent on the structural descriptors used to represent these functional groups. In this work we chose to only consider those atoms which actively engaged in H-bond acceptor behavior, *i.e.*, oxygens. Alternatively, these descriptors could have included the secondary atoms (*i.e.* Si and C), which may exert inductive effects on H-bond behavior. The esters, for example, could have been represented as $-CO_2-$, having a mass of 44 amu. While use of alternative descriptors in developing the regression equation would produce different coefficient values, the relative rankings of functional groups in terms of H-bond acceptor behavior would not change. In addition, the predictive value of the resulting relationship, implied by the R^2 values, is not affected.

The fact that CH_2 was determined to be a statistically significant factor in the regression equation was, initially, disconcerting. Obviously, there are no lone electron pairs or any other structural feature that would permit CH_2 to engage in H-bond interactions directly. Removing the CH_2 term from the regression, however, decreases the R_2 for the resulting equation to 0.951 (standard error = 0.121). Clearly, this term contains information relevant to the H-bonding ability of the coatings, although the nature of this information is not intuitively obvious. A possible explanation for this observation would be the inductive effect of CH_2 on the acceptor behavior of other functional groups in the coating structure. As the length of hydrocarbon chains increases (*i.e.* as the fraction of CH_2) the polarizability of the oxygen-containing functional groups increases and, as a consequence, their acceptor behavior increases. The positive sign and relatively small magnitude of the CH_2 coefficient in eqn. 3 are consistent with such inductive effects.

CONCLUSIONS

Clearly, the regression equation discussed above permits the accurate prediction of the ability of GC stationary phases to act as H-bond acceptors, as indicated by their *a* values in the LSER of Abraham *et al.* [25]. The general applicability of this approach is currently limited by the fact that several functional groups (nitrile, amide, amine, phosphate, etc.) were not adequately represented, which precludes determination of statistically significant regression coefficients. Furthermore, this approach is constrained to those coating materials that have been characterized by LSERs. Before universal applicability can be demonstrated, both of these limitations must be addressed; subsequent refinements of the regression equation(s) may be necessary. The success of this approach for the oxygen-containing coatings is remarkable in light of the relatively simple model and the fact that the structures for many of the coatings were approximated.

The ability of a given functional group to engage in H-bonding is likely to be sensitive to changes in the structure of the molecule. More sophisticated computer modeling methods are available which permit the calculation of electron density maps, which allow for refinement of the molecular descriptors used in the development of our regression equation. Such refinements would possibly obviate the need for the CH_2 term by correcting for inductive effects. The major advantage of the approach presented here is that results can be obtained relatively quickly (and easily) without requiring access to sophisticated modelling software.

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