Characterization of phosphorus-containing gas chromatographic stationary phases by linear solvation energy relationships

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Abstract

Linear solvation energy relationships allow the prediction of a variety of solubility interactions based on a set of descriptors found in the following equation:

$$\log SP = c + r_1 R_2 + s_1 \pi_2^H + a_1 \sum \alpha_2^H + b_1 \sum \beta_2^H + l_1 \log L^{16}$$

SP refers to an intrinsic thermodynamic property that can be found experimentally for a series of solutes. Phases containing phosphate, phosphite and phosphine functional groups were studied in this work. Coefficients obtained during this work, as well as those available for previously characterized phases, were correlated with molecular structural descriptors. When effects of non-phosphorus functional groups are estimated and subtracted out, hydrogen bond acceptor capability, a_1, shows a positive trend when correlated with percent functional group. Correlation of the dipolarity/polarizability coefficient, s_1, with calculated atomic polarizability shows stationary phases group according to like functional groups. A similar correlation with dipole moment gives a trend of increasing dipole as s_1 increases. Further quantitative structure–solubility relationship work is planned to better describe the contributions of inner shell and valence electrons to the chemical and physical properties of these compounds.   © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solubility plays an important role in a wide range of chemical processes. Understanding solute–solvent interactions is vital in chemical synthesis and coatings development, as well as the pharmaceutical industry. Development and optimization of analytical separations and spectrophotometric methods are also dependent on a thorough understanding of solvent-mediated processes. Two basic approaches can be taken to predict solubility interactions, theoretical or empirical [1–4]. Theoretical approaches attempt to explain interactions through fundamental chemical theory, in particular the thermodynamics of solubility behavior [2]. Empirical approaches rely on statistical correlation of known or measurable characteristics of a compound, such as molecular structure, with observed properties [5]. Quantitative structure–retention relationships (QSRRs), one of the more commonly used empirical approaches, generally take

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the form of multiple linear regression relationships [1,6,7]. QSRRs describe specific chromatographic retention phenomena, and offer good predictability within a compound class on a given stationary phase. Unfortunately, the relationships obtained cannot be reliably extended to other chemical families or generalized to behavior on other stationary phases.

One of the most successful and extensively used of the theoretical methods is the linear solvation energy relationships (LSERs), of Kamlet, Abraham, and Taft [8–11]. This approach uses inverse chromatography to determine solvation parameters for a given solvent, also called the stationary phase. Eq. (1) is most often used to describe the solvation process [9]:

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

The SP term represents an intrinsic thermodynamic property such as partition coefficient or specific retention volume. The regression constant is c. Each of the other terms describe various solvent/solute interactions. Variables with the subscript 1 represent the contribution of the solute to a specific solubility interaction. Subscript 2 values refer to the solvent contribution. The R_2 term represents excess molar refraction, π_2^{*H} dipolarity and polarizability, $\sum \alpha_2^H$ and $\sum \beta_2^H$ represent hydrogen bond donor acidity and hydrogen bond acceptor basicity, respectively, and L^{16} is the solute gas–liquid partition coefficient into hexadecane at 25 °C, also known as the Ostwald partition coefficient. The values for solvation parameters for the solute portion of each term have been previously determined for over 1000 compounds [9,12–14].

The LSER approach provides a model for the solubility process, with each term describing the ability of the solute and solvent to engage in specific interactions. The relative magnitude of each of the terms also gives insight into the contribution of each interaction to the overall solvation process [12]. Results can be applied more generally than QSRRs in both chromatographic and non-chromatographic applications.

The most common approach for obtaining the corresponding coefficients for stationary phases/solvents is inverse gas–liquid chromatography. The stationary phase is packed into a column and re-

tention data collected at 120 °C. Multiple linear regression (MLR) is used to obtain the solvent coefficient terms (subscript of 2). MLR is performed with known solute parameters used as multiple independent variables, and the intrinsic thermodynamic value (log SP) as the dependent variable. Column preparation and data collection are inherently time consuming, and this is one of the major disadvantages of the LSER method. Because retention data must be collected or extrapolated at 120 °C to permit direct comparison with other literature values, characterized stationary phases are limited to compounds that are liquids at this column temperature. In addition, compounds with high vapor pressures tend to volatilize off the column, making it difficult and sometimes impossible to obtain useful retention information.

Quantitative structure–solubility relationships (QSSRs) represent a compromise between the LSER and QSRR approaches. In QSSRs, the LSER coefficients which describe the solubility behavior of the solvent phase are predicted based on molecular descriptors. Currently, QSSR studies take a two-stage approach. The first stage is expansion of the stationary phase database to include under-represented functional groups. Olefinic, cyano-, amine-, amide-, and fluorine-containing phases have been evaluated previously in our research group [15–18]. Phases containing functional groups with third quantum level elements such as sulfur [19] and phosphorus require additional characterization. LSER studies with phosphorus-containing stationary phases listed in Table 1 will be discussed in this work. Phosphorus phases are challenging to characterize because many are high vapor pressure compounds that bleed off the column at the required column temperature. Many that are thermally stable are significantly toxic, to the degree that safety issues preclude analysis. Tributyl phosphate, poly(dipropylene glycol)phenyl phosphite, and diphenyl(p-tolyl)phosphine were characterized and results presented in this work. Tritolyl phosphate had been characterized previously [20], and was used as a control to insure that our results would be comparable with previous studies. LSER data for Kroniflex THFP, triethylhexyl phosphate, cresyl diphenyl phosphate, and tributoxyethyl phosphate were obtained from previous studies and are included here for comparison purposes [20,21].

The second stage of research involves using QSSR

Table 1
Stationary phases studied

Coating	Molecular formula	Molecular mass	Ref.
Tritolyl phosphate (TTP)[a]	$(CH_3C_6H_4O)_3P=O$	368.37	[19]
Tributyl phosphate (TBP)	$[CH_3(CH_2)_3O]_3P=O$	266.32	[19]
Poly(dipropylene glycol)phenyl phosphite	$C_6H_5O[P(OC_6H_5)OC_3H_6OC_3H_6O]_n$ $P(OC_6H_5)_2$, $n \sim 7$	~2103	
Diphenyl (*p*-tolyl)phosphine	$(C_6H_5)_2PC_6H_4CH_3$	276.32	
Kroniflex THFP	$(C_4H_7OCH_2O)_3P=O$	350.35	[19]
Triethylhexyl phosphate	$[CH_3(CH_2)_4CH(CH_2CH_3)O]_3P=O$	434.64	[21]
Cresyl diphenyl[a] phosphate (CDP)	$(CH_3C_6H_4O)$ $(C_6H_4O)_2P=O$	340.32	[21]
Tributoxyethyl phosphate	$[CH_3(CH_2)_3O(CH_2)_2O]_3P=O$	398.48	[21]

[a] Mixture of *ortho*, *para*, and *meta* isomers.

studies to develop predictive relationships using data from characterized phases. QSSR studies involve correlation of structure and/or molecular descriptors with solubility properties. This would allow a priori estimation of solubility properties, eliminating the need for time-consuming characterization of stationary phases. LSER coefficients for materials whose properties make it impractical for conventional characterization can also be estimated.

2. Experimental

The molecular formulae of phosphorus-containing stationary phases studied, along with molecular masses are listed in Table 1. Stationary phases were purchased from Aldrich. The support material used was Chromosorb W AW DMCS washed, mesh size 80–100, and was obtained from Alltech. Compounds used as solutes were obtained from Aldrich and were 95–100% pure. All materials were used as received.

Retention data were collected for 30–40 solutes on each of the characterized phases. Retention time was recorded at the peak maximum which represents the point of equilibrium between the stationary phase and solute. The difference between the maxima for air and solute was taken as the adjusted retention time. Peaks showed a Gaussian appearance with no appreciable fronting. One or more probe solutes were injected at regular intervals and adjusted retention times were recorded and compared to verify that there was no substantial loss of stationary phase during the LSER characterization. The solute set

used can be found in Table 2. Representative solutes were chosen to maximize the range of values for each solvation parameter, and to represent a wide variety of functional groups. Retention times that were either too long or too short to be reliably reproduced were not used in the LSER calculations. As a result, data for all solutes in the set are not listed for all stationary phases.

Stationary phases were prepared for analysis using approximately 15% load of solvent phase on the packing material. An appropriate amount of stationary phase was weighed and dissolved in 150 ml of methylene chloride, with 10–15 g of support material to form a slurry. The methylene chloride was evaporated off over a period of days, leaving a uniform layer of stationary phase on the packing. The coated support was then packed into a deactivated glass column (1.22 m×4.3 mm I.D.).

The percent mass of stationary phase, or percent load, is verified experimentally. The experimental percent load is generally less than the nominal percent load due to stationary phase adhering to the flask wall during the drying process. Percent load is determined by removing stationary phase by ashing or solvent stripping techniques [17]. Ashing proved to be impractical for phosphorus-containing stationary phases because varying amounts of phosphorus oxides or other refractive compounds may be formed during combustion. The preferred method for these phases, therefore, was solvent stripping.

Partition coefficient or specific retention volume are commonly used as an intrinsic thermodynamic property, the SP term in the LSER equation. The

Table 2
Summary of solute parameters and log SP values

	R_2	π_2^H	α_2^H	Log L^{16}	β_2^H	TTP[a] log t'_r	TBP log V_g	Polymer log V_g	DPPP log V_g
1,2-Dichloroethane	0.416	0.64	0.10	2.573	0.11	−0.201	1.772	1.413[b]	1.415
1,4-Dioxane	0.329	0.75	0.00	2.892	0.64	−0.077	1.711	1.527[b]	1.589
1-Bromopropane	0.366	0.40	0.00	2.620	0.12	−0.453	1.455	1.120[b]	1.235
1-Hexyne	0.166	0.23	0.12	2.510	0.10	−0.618	1.378	0.973[b]	1.081
1-Nitropropane	0.242	0.95	0.00	2.894	0.31	0.254	2.149	1.857	1.747
2,2,4-Trimethylpentane	0.000	0.00	0.00	3.106	0.00	−0.686	1.380	0.795[b]	1.070
2-Butanone	0.166	0.70	0.00	2.287	0.51	−0.383	1.436	1.185[b]	1.190
2-Hexanol	0.188	0.36	0.33	3.838	0.56	0.278	2.471		1.778
Acetone	0.179	0.70	0.04	1.696	0.49	−0.678	1.171	0.921[b]	0.852
Acetonitrile	0.237	0.90	0.07	1.739	0.32	−0.420	1.462	1.219[b]	0.981
Acetophenone	0.818	1.01	0.00	4.501	0.48	1.212[c]			
Aniline	0.955	0.96	0.26	3.934	0.41	1.161[c]			
Anisole	0.708	0.75	0.00	3.890	0.29	0.586	2.506	2.182	2.258
Benzene	0.610	0.52	0.00	2.786	0.14	−0.301	1.575	1.266[b]	1.402
Benzonitrile	0.742	1.11	0.00	4.039	0.33	1.088[c]			
Butanol	0.224	0.42	0.37	2.601	0.48	−0.071	2.141	1.603[b]	1.417
Butyl ether	0.000	0.25	0.00	3.924	0.45	−0.026	2.011	1.524[b]	1.783
Butylamine	0.224	0.35	0.16	2.618	0.61		1.441		
Chlorobenzene	0.718	0.65	0.00	3.657	0.07	0.364	2.206	1.863	2.007
Cyclohexane	0.305	0.10	0.00	2.964	0.00	−0.604	1.343	1.060[b]	1.193
Cyclohexanol	0.460	0.54	0.32	3.758	0.57	0.631			2.199
Decane	0.000	0.00	0.00	4.686	0.00	0.111	2.250	1.702[b]	1.995
Dichloromethane	0.387	0.57	0.10	2.019	0.05	−0.524	1.383	0.996[b]	0.985
Dodecane	0.000	0.00	0.00	5.696	0.00	0.624		2.124	
Ethanol	0.246	0.42	0.37	1.485	0.48	−0.674	1.497	1.045[b]	0.728
Ethyl ether	0.041	0.25	0.00	2.015	0.45			0.724[b]	0.689
Ethyl acetate	0.106	0.62	0.00	2.314	0.45	−0.478	1.384	1.104[b]	1.134
Heptane	0.000	0.00	0.00	3.173	0.00	−0.635	1.382	0.881[b]	1.121
Isopropanol	0.212	0.36	0.33	1.764	0.56	−0.611	1.581	1.105	0.835
Methanol	0.278	0.44	0.43	0.970	0.47	−0.801	1.369		0.530
N',N-DMA	0.363	1.33	0.00	3.717	0.78	0.783		2.351	2.246
N',N-DMF	0.367	1.31	0.00	3.173	0.74	0.578	2.212	2.154	2.011
N-Hexylamine	0.197	0.35	0.16	3.655	0.61				
Nitrobenzene	0.871	1.11	0.00	4.557	0.28	1.404[c]			
Nitromethane	0.313	0.95	0.06	1.892	0.31	−0.182	1.775	1.517	1.239
n-Nonane	0.000	0.00	0.00	4.182	0.00	−0.143	1.945	1.433[b]	1.706
n-Octanol	0.199	0.42	0.37	4.619	0.48	1.078[c]			
p-Xylene	0.613	0.52	0.00	3.839	0.16	0.288	2.142	1.760[b]	1.995
Pyridine	0.063	0.84	0.00	3.022	0.52	0.217	1.947	1.798	1.783
Terahydrofuran	0.289	0.52	0.00	2.636	0.48	−0.426	1.362	1.186[b]	1.265
Toluene	0.601	0.52	0.00	3.325	0.15	0.026	1.872	1.545	1.712
Trichloromethane	0.425	0.49	0.15	2.480	0.02	−0.364	1.420	1.277	1.279
Triethylamine	0.101	0.15	0.00	3.040	0.79			1.064	1.201
Isobutyraldehyde	0.144	0.62	0.00	2.120	0.45				1.055

[a] Propanoic acid dropped from data set.
[b] Indicates retention data were extrapolated from a minimum of three temperatures below 120 °C.
[c] Indicates retention data were extrapolated from a minimum of three temperatures above 120 °C.

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observed retention data, t_r', can be related to specific retention volume, V_g, through this equation [22]:

$$V_g = \frac{JFt_r'273}{WT_c} \qquad (2)$$

where J is the James–Martin carrier gas compression correction, F is the average column flow-rate (corrected for ambient temperature and water vapor pressure from the bubble meter measurement), t_r' is the adjusted solute retention time, W is the mass of the stationary phase, and T_c is the column operating temperature. Adjusted retention time is not an intrinsic thermodynamic property, but is directly proportional to V_g. The adjusted retention time can be used as SP so that the dependent variable is log t_r' in the LSER/MLR if the mass of stationary phase, column temperature, compressibility correction factor and carrier gas flow-rate are held constant. Specific retention volume is, in turn, directly proportional to the partition coefficient (K), using the relationship [22]:

$$K = \frac{V_g\rho_s T_c}{273} \qquad (3)$$

In this way, the retention data obtained can be directly correlated with the free energy of the system. Density of the stationary phase at the column temperature (ρ_s), must be known if K is to be calculated. Use of any of these terms as SP will give the same regression constants with the exception of the constant c term.

A Varian Star 3400 CX gas chromatograph with a thermal conductivity detector was used for data collection. Column temperature was maintained at 120 °C with a helium flow-rate of approximately 25 ml/min. Volatility losses with some compounds made it necessary to reduce column temperatures and extrapolate data to 120 °C. Retention data for the characterized solvents are analyzed by multiple linear regression. Log SP values for solutes used to characterize each stationary phase can be found in Table 2. In the case of tritolyl phosphate, SP is the adjusted retention time (t_r'). For tributyl phosphate, poly(dipropylene glycol)phenyl phosphite, and diphenyl(p-tolyl)phosphine, the specific retention volume (V_g) is used as SP. The resulting r_1, s_1, a_1, l_1, and b_1 coefficients, along with standard errors for each coefficient are summarized in Table 3.

Volatility losses during retention data collection had to be taken into account for three of the stationary phases studied. At a stationary phase loading of less than 10%, interfacial adsorption may play a significant role in observed retention. As a result, LSER results may not represent solubility properties of the bulk solvent. Effects of interfacial adsorption are most significant for saturated hydrocarbons, and increase with increasing polarity of the stationary phase. These interactions are generally found to be insignificant at percent loadings above 10% [23–25]. Probe solutes were used to track stationary phase losses. Probe retention time losses were plotted against total analysis time, and solute retention times were adjusted by a factor calculated from the resulting regression. Retention times, t_r', for solutes were corrected back to $t = 0$ by comparison with probe solutes. If stationary phase load fell below 10%, retention data were discarded and a new column was prepared. When multiple columns were used, retention volumes were normalized versus stationary phase mass to adjust for differences between columns. An example of bleeding losses for tributyl phosphate is displayed in Fig. 1. Retention time decreases were linear with respect to time, with r^2 of 0.996 for column 1, and 0.992 for column 2.

Poly(dipropylene glycol)phenyl phosphite was the only phosphorus polymer available for characterization. Due to the hygroscopic nature of the polymer, coated phases were prepared and stored in nitrogen to minimize water adsorption. Multiple columns were needed due to volatility losses. Retention volumes were found at column temperatures at 15 °C intervals from 60 to 120 °C. Retention data were used in extrapolation to 120 °C from a minimum of three lower column temperatures. For the tritolyl phosphate phase, data were collected in 10 °C increments from 140 to 170 °C. Data from a minimum of three higher column temperatures were used to obtain retention data at 120 °C by extrapolation. Extrapolated values are given in Table 2.

To evaluate the obtained regression equation, the LSER coefficients are subsequently used to back-calculate log SP for each solute. These calculated values are then compared to the original experimentally obtained log SP values, and the difference between the two is represented by the residual. If the residual for a particular solute was greater than three

Table 3
Phosphorus stationary phase results

Coating	r_1	s_1	a_1	l_1	b_1	Adj. r^2	S.E.	n
Tributyl phosphate	−0.05	0.87	1.9	0.53	−0.22	0.949	0.085	32
	(0.095)	(0.077)	(0.15)	(0.023)	(0.082)			
Dropping R		0.85	1.9	0.53	−0.21	0.951	0.084	32
		(0.058)	(0.14)	(0.022)	(0.074)			
Dropping β	0.05	0.76	1.8	0.52		0.937	0.094	32
	(0.097)	(0.071)	(0.15)	(0.026)				
Dropping R and β		0.78	1.8	0.53		0.939	0.093	32
		(0.058)	(0.15)	(0.025)				
Diphenyl (p-tolyl)phosphine	0.24	0.63	0.45	0.54	−0.01	0.980	0.066	36
	(0.072)	(0.053)	(0.10)	(0.015)	(0.064)			
Dropping β	0.25	0.62	0.45	0.54		0.983	0.065	36
	(0.062)	(0.039)	(0.091)	(0.015)				
Poly(dipropylene glycol)phenyl phosphite	0.11	0.94	1.3	0.47	0.01	0.968	0.077	33
	(0.078)	(0.057)	(0.15)	(0.018)	(0.072)			
Dropping R		0.98	1.3	0.47	−0.03	0.967	0.078	33
		(0.049)	(0.15)	(0.018)	(0.070)			
Dropping β		0.94	1.3	0.47		0.969	0.076	33
		(0.041)	(0.15)	(0.018)				
Dropping R and β		0.97	1.3	0.47		0.968	0.077	33
		(0.041)	(0.15)	(0.018)				
Tritolyl phosphate (our results)	0.21	1.00	1.23	0.52	−0.11	0.989	0.064	39
	(0.064)	(0.061)	(0.098)	(0.011)	(0.076)			
Dropping β (our results)	0.25	0.94	1.15	0.52		0.989	0.066	39
	(0.055)	(0.040)	(0.080)	(0.011)				
Previous data	0.14	1.00	1.21	0.553	0.10	0.997	0.032	207
	(0.019)	(0.018)	(0.019)	(0.002)	(0.020)			
Dropping β (previous)	0.14	1.01	1.19	0.550		0.993	0.993	250
	(0.022)	(0.017)	(0.019)	(0.003)				
Kroniflex THFP	0.13	1.36	2.34	0.498	−0.05	0.997	0.034	200
	(0.022)	(0.020)	(0.024)	(0.002)	(0.025)			
Dropping β	0.17	1.34	2.31	0.499		0.996	0.036	235
	(0.018)	(0.014)	(0.017)	(0.002)				
Cresyl diphenyl phosphate	0.04	1.10	1.25	0.521		0.996	0.084	105
	(0.024)	(0.020)	(0.036)	(0.004)				
Triethylhexyl phosphate	−0.005	0.67	1.71	0.55		0.989	0.084	105
	(0.041)	(0.035)	(0.006)	(0.006)				
Tributoxyethyl phosphate	0.05	0.94	1.84	0.525		0.991	0.074	105
	(0.037)	(0.031)	(0.056)	(0.006)				

times the standard error for the multiple linear regression, that solute was eliminated from the data set for that particular stationary phase. Eliminated solutes are shown in Table 2. A large residual is an indication that the solute engages in an interaction not described by the LSER model. If the majority of the residuals for a given stationary phase are small, this indicates that the relationship may have good predictive value, although more statistical analysis is necessary to verify this.
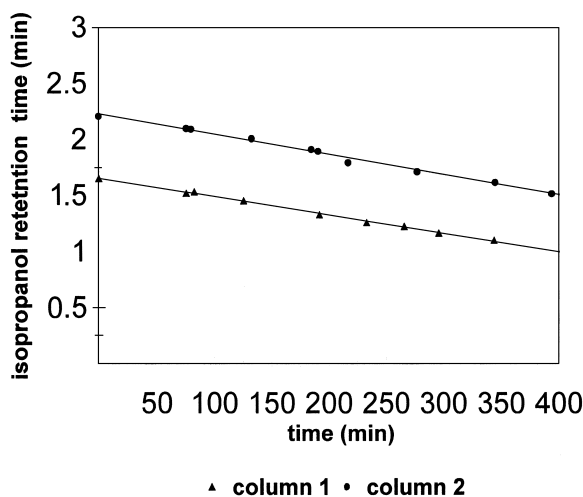
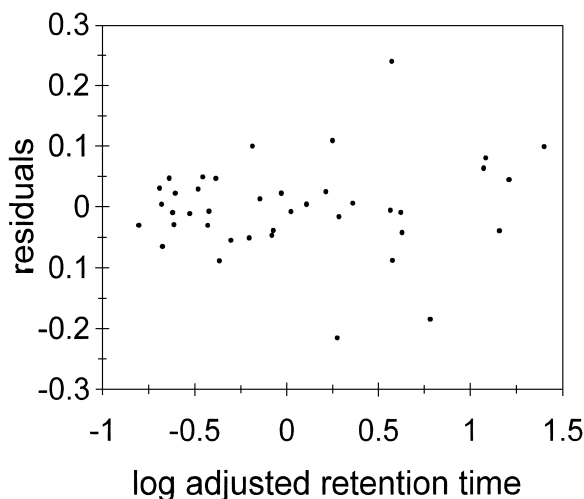Fig. 1. Tributyl phosphate volatility loss at 120 °C.

Fig. 3. Residual analysis of tritolyl phosphate adjusted retention time.

3. Results and discussion

For each characterized phase, the LSER relationship can be evaluated by plotting the experimentally obtained retention times with the retention times calculated by the LSER equation (Fig. 2). As previously noted, solutes with residual errors greater than three times the standard error for the regression are discarded from the data set. Residuals for solutes were also examined by plotting against both experimental log SP (Fig. 3), and each LSER coeffi-
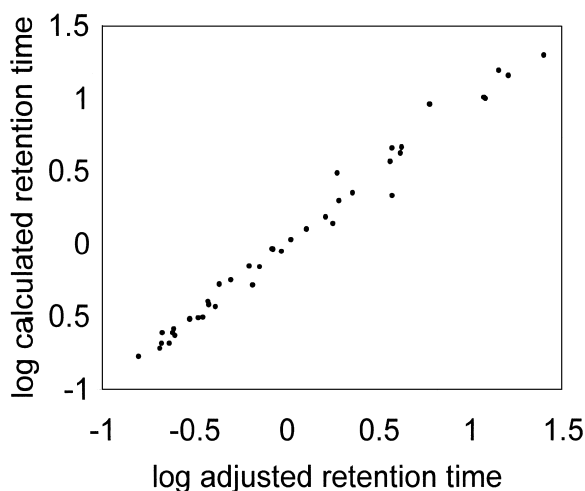
Fig. 2. Comparison of calculated and experimental values.

cient. A random scatter of points indicates that there is not substantial systematic error in the data.

The tritolyl phosphate phase had been previously characterized by Abraham et al. [27], using retention data collected by McReynolds [26], and was included for analysis in this work to insure that our solute set produced results that are comparable with previous results. Although the McReynolds set used by Abraham et al. was much larger (number of solutes = 207) compared with this study (number of solutes = 39), coefficients compare favorably and are, for the most part, within error (Table 3). Beta terms are often dropped out because they are either statistically insignificant or marginally so. This makes chemical sense in terms of the studied phosphorus phases since none contain functional groups that are hydrogen bond acids. The r_1 term, representing n and π electron interactions, was marginally significant for tributyl phosphate and poly(dipropylene glycol)phenyl phosphite. Results in Table 3 show that coefficients do not change to a great extent as terms are dropped out and the MLR is recalculated.

3.1. Correlation with a_1 coefficient

Determining the contribution of phosphorus functional groups to the a_1 coefficient is complicated by the presence of other hydrogen bond acceptor groups

within the stationary phase. Ballantine used MLR for stationary phases in the McReynold's data set to develop the following relationship to estimate contributions of oxygen-containing functional groups to the a_1 coefficient [1]:

$$a_{calculated} = 1.412(siloxane) + 3.517(ester)$$
$$+ 3.872(ether) + 8.969(OH)$$
$$+ 0.514(CH_2) \quad (4)$$

The siloxane, ester, ether, OH, and CH_2 portion of the terms represent the mass fraction of that functional group in the stationary phase. While not capable of direct hydrogen bonding behavior, the CH_2 term was shown to be statistically significant, and is thought to contain information relative to steric/inductive effects. Once corrections are made for the functional groups listed in Eq. (4) ($a_{calculated}$), the a_{excess} can be calculated using Eq. (5):

$$a_{excess} = a_1 - a_{calculated} \quad (5)$$

These values can be found in Table 4. The a_{excess} value can be attributed to interactions of phosphorus-containing groups. Oxygen atoms were included in the functional group mass because these atoms by virtue of their electron withdrawing properties will affect overall ability of a given functional group to engage in hydrogen bond interactions. In addition, the number of oxygens related to the central phosphorus atom will have steric, or space filling effects, as well as inductor effects on hydrogen bond capability. The values obtained can be found in Table 4. A plot of a_{excess} shows a positive correlation with the mass % of phosphorus functional group ($r^2 = 0.620$,
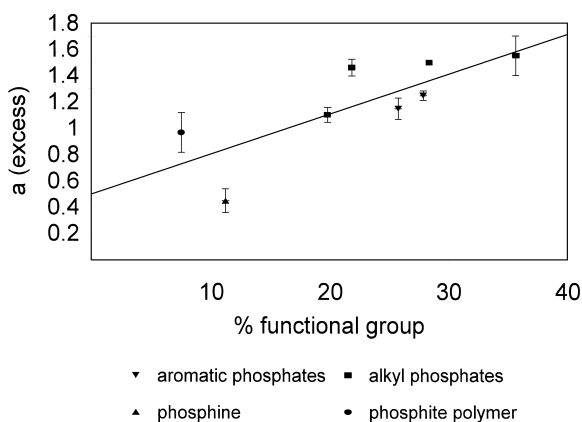

Fig. 4. Plot of a_{excess} versus % phosphorus functional group.

slope = 0.0304) (Fig. 4). Phosphate phases tend to group together and the phosphite polymer and phosphine phases are outlying at the lower end of the graph. The number of oxygen atoms and, hence, the number of lone pair electrons will affect electron density, thus H-bonding ability will vary with the type of P-containing group. Phosphates (four oxygens) will have eight lone pairs, while phosphite (three oxygens) will have seven lone pairs — six associated with the oxygen and one with the phosphorus. Phosphine, however, will have only one lone pair, analogous to amines. Factoring in the number of lone electron pairs gives a more favorable correlation ($r^2 = 0.787$, slope = 0.00346), shown in Fig. 5. While these results indicate that phosphorus atoms/functional groups do contribute to H-bond acceptor behavior, it is difficult to determine how much of the variation in contributions to a_1 are due to steric

Table 4
Functional group fractions and a_1 values for coatings

Coating	Functional group (%)	Ether	CH_2	a_1	$a_{calculated}$	a_{excess}
Tritolyl phosphate	25.78	–	–	1.151	–	1.151
Tributyl phosphate	35.66	–	0.4740	1.796	0.2436	1.552
Poly(dipropylene glycol)phenyl phosphite	7.51	0.0533	0.2801	1.318	0.3503	0.968
Diphenyl (*p*-tolyl)phosphine	11.21	–	–	0.450	–	0.450
Kroniflex THFP	27.11	0.1370	0.4804	2.314	0.7774	1.534
Triethylhexyl phosphate	21.85	–	0.4841	1.710	0.2488	1.461
Cresyl diphenyl phosphate	28.08	–	–	1.250	–	1.250
Tributoxyethyl phosphate	23.88	0.1204	0.5280	1.840	0.7376	1.102
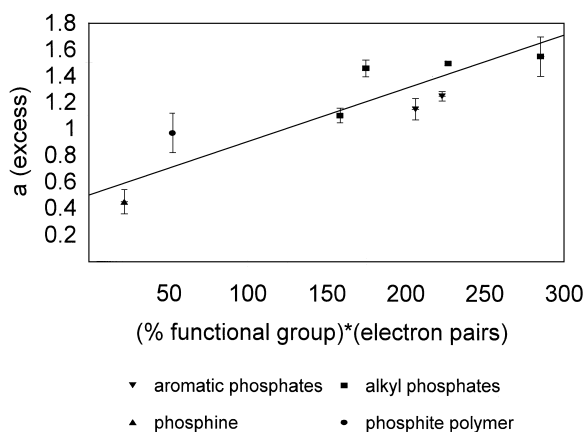
Fig. 5. Plot of a_{excess} versus % phosphorus functional group adjusted by number of electron pairs.

Fig. 6. Plot of calculated atomic polarizability with s_1 coefficient.

and/or inductive effects for each of the phosphorus-containing groups.

3.2. Correlation with s_1 coefficient

The s_1 term incorporates both polarizability and dipolarity interactions in one term, so attempts were also made to correlate this coefficient with both calculated dipole moments and polarizabilities of the stationary phases. Total atomic polarizabilities were estimated by calculating average polarizabilities for each atom in the stationary phase molecule, and summing to obtain conjugate molecular polarizability using the methods described by Miller [28]. These results are summarized in Table 5. Conjugate polarizabilities were divided by molecular mass to
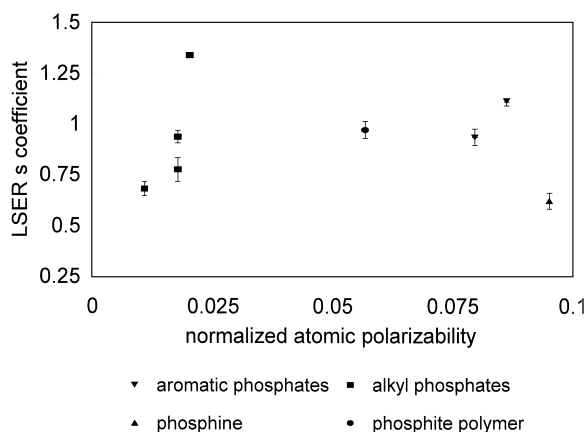
adjust for effects of size differences. Plotting these values versus s_1 does not yield a linear trend, but the phases do group together according to type (Fig. 6). The phosphates with aromatic groups, CDP and TTP are in close proximity and alkyl phosphates also group closely. Poly(dipropylene glycol)phenyl phosphite, the only phosphite phase and polymer, lies between the two major groupings. Since diphenyl(p-tolyl)phosphine is the only phosphine-containing phase, there are no similar functional groups in the data set for comparison. The reason the Kroniflex data point does not group with the rest of the phosphates is unclear, but may be due to steric/inductive effects of the oxygen-containing rings.

Calculated results for bond polarizabilities using the method by Miller [28], are shown in Table 6. Some values for relevant bond types were not

Table 5

Coating atomic polarizabilities and s_1 values

Coating	s_1	Aromatic carbon		Phosphorus		Oxygen		Oxygen (double bond)		Total α ahc	Normalized α ahc
		No. atoms	α ahc	No. atoms	α ahc	No. atoms	α ahc	No. atoms	α ahc		
Tritolyl phosphate	0.937	18	24.64	1	1.647	3	2.34	1	0.739	29.368	0.0797
Tributyl phosphate	0.776	0	0	1	1.647	3	2.34	1	0.739	4.726	0.0177
Poly(dipropylene glycol) phenyl phosphite	0.973	60	82.14	8	13.176	31	24.18	0	0	119.496	0.0568
Diphenyl (p-tolyl)phosphine	0.624	18	24.64	1	1.647	0	0	0	0	26.389	0.0951
Kroniflex THFP	1.340	0	0	1	1.647	6	4.68	1	0.739	7.066	0.0202
Triethylhexyl phosphate	0.682	0	0	1	1.647	3	2.34	1	0.739	4.726	0.0109
Cresyl diphenyl phosphate	1.114	18	24.64	1	1.647	3	2.34	1	0.739	29.368	0.0863
Tributoxyethyl phosphate	0.938	0	0	1	1.647	6	4.68	1	0.739	7.066	0.0177

Table 6
Bond fractions and polarizabilities

Coating	s_1	C–O (ether)	P–O (phosphate)	P–O (phosphite)	P=O	C_{ar}–C_{ar}	C–C_{ar}	C_{ar}–P	C_{ar}–O	Total bond polarizabilities
Bond polarizabilities		0.584	0.703	0.826	0.954	1.087	0.716	0.963	0.769	
Tritolyl phosphate	0.937	–	0.11	–	0.04	0.64	0.11	–	0.11	0.9497
Tributyl phosphate	0.776	0.19	0.19	–	0.04	–	–	–	–	0.2135
Poly(dipropylene glycol) phenyl phosphite	0.973	0.19	–	0.16	–	0.40	–	–	0.07	0.6764
Diphenyl (*p*-tolyl)phosphine	0.624	–	–	–	–	0.82	0.05	0.14	–	1.116
Kroniflex THFP	1.340	0.36	0.12	–	0.04	–	–	–	–	0.2185
Triethylhexyl phosphate	0.682	0.11	–	–	0.04	–	–	–	–	0.1220
Cresyl diphenyl phosphate	1.114	–	0.12	–	0.04	0.69	0.04	–	0.12	0.9833
Tributoxyethyl phosphate	0.938	0.36	0.12	–	0.04	–	–	–	–	0.2185

included in the reference so estimations were made using atomic hybrid polarizabilities (ahp), following examples given in Table 3 of that reference. Estimations were calculated as follows:

P=O (1/4 PTE + OTR4) = 0.954

P–O(phosphate) $(1/4 \text{ PTE} + \frac{1}{2} \text{ OTE}) = 0.703$

P–O(phosphite) (1/3 PTE + 1/2 OTE) = 0.826

C_{ar}–P (1/3 PTE + 1/3 CTR) = 0.963

C–C_{ar} (1/4 CTE + 1/3 CTR) = 0.716

Polarizabilities for each bond type were found and multiplied by the fraction of that bond type with respect to the total number of bonds in the molecule. Plotting bond polarizability values versus s_1 yields a plot with similar groupings (Fig. 7).

Dipole moments were calculated using CAChe 3.11 software for Windows from Oxford Molecular. CAChe uses a combination of molecular mechanics and quantum methods [29]. Due to computational limitations of the program, the dipole value for the repeating unit [$P(OC_6H_5)OC_3H_6OC_3H_6O$], of poly-(dipropylene glycol)phenyl phosphite was used. This approximation is probably an over-estimated value for the polymer. The calculated dipole is likely greater than the effective dipole due to the large size of the molecule. Dipole moments obtained from CAChe and corresponding s_1 values are found in Table 7. A plot of dipole with s_1, shows a positive correlation with this coefficient, with the coefficient
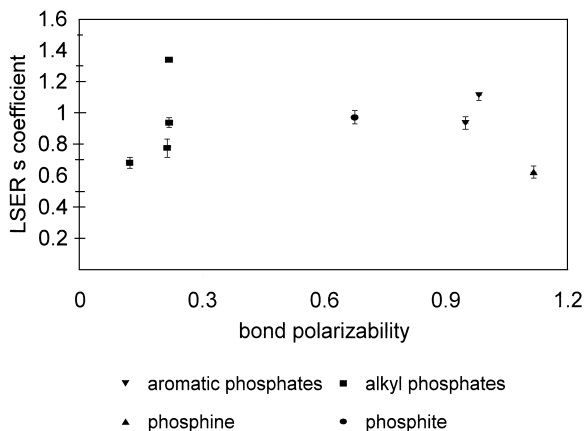

Fig. 7. Plot of calculated bond polarizability with s_1 coefficient.

Table 7
Calculated dipole moments and s_1 values

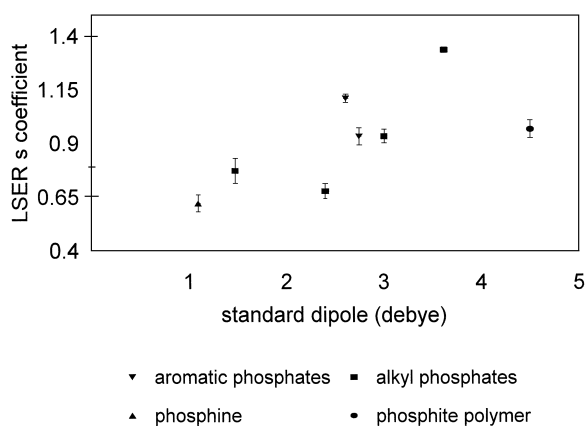| Coating	s_1	Dipole moment (debye)
Tritolyl phosphate	0.937	2.748
Tributyl phosphate	0.776	1.475
Poly(dipropylene glycol)phenyl phosphite	0.973	4.499[a]
Diphenyl (*p*-tolyl)phosphine	0.624	1.092
Kroniflex THFP	1.340	3.619
Triethylhexyl phosphate	0.682	2.398
Cresyl diphenyl phosphate	1.114	2.610
Tributoxyethyl phosphate	0.938	3.004

[a] Value for monomer unit.

Fig. 8. Plot of dipole moment and dipolarity/polarizability coefficient.

value increasing as dipole moments increase (Fig. 8). In the case of these stationary phases, dipolarity appears to be the dominant interaction described by the s_1 term.

4. Future work

Further quantitative structure–solubility relationships can also be developed using molecular connectivities, first proposed by Kier and Hall [30]. Connectivity indices provide information about relevant structural and electronic properties of compounds. The higher order connectivity indices use larger atom fragments, better describing steric and inductive effects. These calculations can be easily done with CAChe software. Preliminary calculations for the larger stationary phase database have shown problems with the way third quantum level elements (sulfur and phosphorus) are represented. Molecular connectivity calculations for third quantum level atoms need to be adjusted to take into account effects of inner shell electrons. CAChe software also has the ability to calculate a wide variety of properties including electron affinity and HOMO/LUMO, and some of these may provide promising correlations.

5. Conclusions/summary

In this work, LSER coefficients have been de-termined for several previously uncharacterized phases. Coefficients for tritolyl phosphate are comparable to previous work by Abraham et al. After estimation and elimination of hydrogen bond acceptor capability of non-phosphorus functional groups, the a_1 coefficient (a_{excess}), shows a positive correlation with phosphorus functional group content. Correlations of the dipolarity/polarizability coefficient (s_1) with calculated atomic and bond polarizability show phases group by functional type. Dipole moment correlates positively with s_1, indicating this term primarily represents dipolarity interactions rather than polarizability in the case of these phosphorus compounds. The magnitude of the contribution to the LSER coefficient values from the various phosphorus functional group types cannot be fully evaluated from the available data.

Acknowledgements

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