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Characterization of olefinic gas chromatographic stationary phases by linear solvation energy relationships

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Abstract

Three olefinic gas chromatographic stationary phases were characterized using a linear solvation energy relationship (LSER) of the type $\log V_g = c + r_1 R_2 + s_1 \pi_2^H + a_1 \Sigma \alpha_2^H + b_1 \Sigma \beta_2^H + l_1 \log L^{16}$, and the results were compared with the LSER coefficients for other, previously characterized, olefinic stationary phases. Based on the coefficients obtained, the presence of olefinic functional groups tends to contribute to the hydrogen bond acceptor basicity, molar refractivity, and dipolarity–polarizability interactions (a_1, r_1, and s_1 values, respectively, in the above equation). It is also shown that the presence of the electron withdrawing chlorine atom in polychloroprene contributes to its ability to act as a hydrogen bond donor acid. The results are viewed from the perspective of using quantitative structure–solubility relationships in the determination of LSER coefficients. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solubility phenomena play a significant role in various areas of chemistry and biology; hence, characterization of material properties relevant to the solvation process is crucial to understanding solute/solvent interactions and to optimizing the performance of these chemical systems [1]. Inverse gas–liquid chromatography (GLC), also known as molecular probe chromatography (MPC), has been used extensively to characterize a variety of materials utilized as solvents in the solvation process, including polymers [2–4]. Unlike conventional GLC, in which analytes are evaluated on a solvent (stationary phase) which has known chemical properties, inverse

GLC utilizes a set of probe solutes, for which certain properties are known, and seeks to characterize or quantify the solvent properties – in our case, to determine the extent to which various intermolecular interactions take place. The retention of a given solute on a particular stationary phase can be correlated directly to intrinsic properties of the solute–solvent system. Such intrinsic parameters include the specific retention volume, V_g, or, more fundamentally, the thermodynamic partition coefficient, K. Once the retention data have been acquired, the corresponding partition coefficients can be used to derive numerous physico-chemical predictive relationships. One of the more successful models involves the use of linear solvation energy relationships (LSERs).

A typical LSER, developed by Abraham and coworkers [5–7] and Poole et al. [8] and applied in

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various forms for extensive gas chromatographic characterizations, is given as follows:

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

Each term in Eq. (1) describes the contribution of various intermolecular interactions to the solvation process. Log SP refers to some solubility related phenomenon, typically GC retention parameters including K and V_g (above) or t_r', the adjusted retention time. Terms with subscript 2 refer to probe solute solubility properties. Specifically, $\sum \alpha_2^H$ and $\sum \beta_2^H$ describe the solute's H-bond donor acidity and H-bond acceptor basicity, respectively. R_2 relates to the excess molar refractivity of the solute, π_2^H refers to the dipolarity/polarizability of the solute, and log L^{16} is the Ostwald partition coefficient referenced to 25°C; i.e., the GC partition coefficient of a solute into hexadecane. This term accounts for dispersion/cavity formation. These solute descriptors are either determined experimentally or are calculated and are available for a very large set of probe solutes [6]. The terms with subscript 1 refer to solvent (stationary phase) complementary interactions, and these terms are usually obtained by multiple linear regression analysis (MLR) via Eq. (1).

LSERs are extremely useful for predicting the solubility behaviour of any solute–solvent pair for which solute descriptors and the LSER coefficients of the solvent are known. Moreover, the relative magnitude of the terms in the LSER provides insight into the contribution of each interaction in the overall solvation process. Unfortunately, characterization of solvents (stationary phases) by inverse GLC is time and labour intensive. The preparation of the column is the most time consuming step in the process as well as the most critical step. Care must be taken to ensure that the stationary phase is coated uniformly on the support. After injection of a large enough probe solute set to make the data statistically meaningful, MLR analysis must be performed using Eq. (1), where the terms with subscript 2 are the independent variables and the dependent variable, SP, is represented by t_r', the adjusted retention time; V_g, the specific retention volume; or K, the thermodynamic partition coefficient. The coefficients obtained (r_1, s_1, a_1, b_1, and l_1) represent the com-

plementary interactions of the solvent (stationary phase) described above. In these relationships, the coefficients obtained from the MLR analysis are the same for a given phase regardless of which SP data is used; using K instead of V_g for each probe solute only changes the regression constant, c. LSER coefficients have been published for a substantial number of phases [7–10].

Because the solute–solvent interactions are influenced significantly by the structure of the solvent, predictive relationships which correlate the structure of the solvent with the LSER coefficients would be useful to characterize the solvent in a more efficient manner. While following the general approach of quantitative structure–retention relationship (QSRR) [11] studies, relationships correlating the structure of the solvent with a specific solubility interaction could more correctly be known as quantitative structure–solubility relationships (QSSRs). A variety of structural descriptors (topological [12], constitutional [13], etc.) can be readily obtained or calculated for the materials to be characterized [14]. A subset of descriptors which can be utilized in a predictive manner can be identified by principle component factor analysis and/or a correlation matrix. A predictive equation can then be developed via MLR analysis. Ideally, the structural factors ultimately selected will contain chemical information which is relevant to the property being predicted. Because QSSRs involve *a priori* estimation of these solubility properties, this approach eliminates the need for time consuming characterization of solvents by inverse GLC. In addition, because the solubility interactions are directly related to the structure of the solvent, a more fundamental understanding of the solvation process is gained. QSSRs also permit the determination of LSER coefficients for newly synthesized compounds and for compounds which are not easily analyzed by inverse GLC. In addition, a knowledge of the relative contribution of structural/conformational features to observed solubility properties permits rational design of new materials. Preliminary results from our lab have demonstrated the utility of the QSSR approach in the prediction of LSER coefficients [15].

Current research in our laboratory focuses on two phases in the development of QSSRs. The first phase involves expansion of the existing database [16,17].

This requires the LSER characterization of materials containing functional groups which are not represented (or are under-represented) in the current data set [15]. The second phase involves the identification/development of structural descriptors which can ultimately be used predictively in QSSRs.

The results presented here address the first step in the process, i.e., expansion of the functional group representation of the current database. Three olefinic stationary phases were analyzed by inverse GLC with approximately 30 to 40 probe solutes and multiple linear regression analyses performed to determine the characteristic LSER coefficients for the stationary phase. Results for three phases will be presented, as well as an interpretation of the LSER coefficients based on the structure of the phases. Comparison of these three phases to olefinic phases which have previously been characterized will be performed and a relative determination of the extent to which the olefinic functional group participates in various interactions will be discussed.

2. Experimental

The olefinic stationary phases characterized in this work are listed in Table 1, including relevant information regarding stationary phase loading at the GC operating temperature (120°C). The stationary phases were obtained from Aldrich and the support (Chromosorb W-AW, 80–100 mesh) was obtained from Alltech. The probe solutes are listed in Table 2, along with the appropriate solute descriptors [6]. All solutes were obtained from Aldrich (95–99% purity) and were used as received.

Three criteria were used to select approximately 30–40 probe solutes from over 200 for which solute

descriptors are known. First, a wide variety of functional groups is represented. In addition, the values for each solute descriptor span the range of known values for that parameter. [Note: a cross-correlation matrix is included (Table 3) to verify that the values of all solute descriptors are independent.] Finally, from a practical standpoint, retention times for the solutes were within a reasonable range to ensure reliability of the experimental data. Due to variations between different stationary phases, certain probe solutes were not analyzed on all stationary phases.

Column packing materials were prepared by dissolving an appropriate amount (for a 15% load) of stationary phase in approximately 100 ml of methylene chloride and then adding 10 to 15 g of support to create a slurry. The solvent was slowly evaporated leaving the support coated with stationary phase. The coated support was then packed into a glass column (4 ft×4.3 mm I.D.) and conditioned for 24 hours at 150°C prior to analysis (1 ft=30.48 cm).

The mass percent of coating in the stationary phase was determined by placing approximately 0.5 g ($\pm$0.0002 g) into a tared crucible. The contents were heated in air to completely combust the stationary phase, leaving behind only the solid support. Uncoated support was run as a blank and appropriate corrections were made to calculate the mass percent of stationary phase. Alternatively, mass percents of coating can be determined by solvent stripping; however, due to the length of time required to dissolve the coating in the solvent used for stripping, the ashing technique described above is the preferred method for these polymers. Comparison of the percent load for polybutadiene by both the solvent stripping technique (12.60%) and the ashing technique (13.85%) illustrates the improved efficiency of

Table 1
Stationary phases and percent loads during study

Coating	Molecular formula	Approximate molecular mass	Load (%)
Polybutadiene (PBD)	$[-CH_2-CH=CH-CH_2-]_n$	420 000	13.85
Polychloroprene (PCP)	$[-CH_2-CH=CCl-CH_2-]_n$	200 000	10.95
Polyisoprene (PIP)	$[-CH_2-CH=CCH_3-CH_2-]_n$	800 000	13.33

Table 2
Summary of solute parameters and coating log V_g values

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\log L^{16}$	$\Sigma\beta_2^H$	$\log V_g$ values		
						PBD	PCP	PIP
Isopropanol	0.212	0.36	0.33	1.764	0.56	0.876	0.765	0.755
Hexanol	0.210	0.42	0.37	3.610	0.48	2.064	1.856	1.868
1,4-Dioxane	0.329	0.75	0	2.892	0.64	1.620	1.541	1.457
Heptane	0	0	0	3.173	0	1.445	1.093	1.345
Dodecane	0	0	0	5.696	0	2.869	–	–
Toluene	0.601	0.52	0	3.325	0.14	1.847	1.665	1.694
Acetone	0.179	0.70	0.04	1.696	0.49	0.895	0.899	0.720
Tetrahydrofuran	0.289	0.52	0	2.636	0.48	1.369	1.264	1.200
Acetonitrile	0.237	0.90	0.07	1.739	0.32	0.905	0.979	0.698
Ethyl acetate	0.106	0.62	0	2.314	0.45	1.210	1.090	1.041
1-Butanol	0.224	0.42	0.37	2.601	0.48	1.433	1.287	1.256
Anisole	0.708	0.75	0	3.890	0.29	2.314	2.178	2.117
Nitromethane	0.313	0.95	0.06	1.892	0.31	1.125	1.171	0.928
Chlorobenzene	0.718	0.65	0	3.657	0.07	2.116	1.953	1.959
Cyclohexane	0.305	0.10	0	2.964	0	1.467	1.145	1.357
Cyclohexanol	0.460	0.54	0.32	3.758	0.57	2.200	–	–
Triethylamine	0.101	0.15	0	3.040	0.79	1.451	–	1.321
Decane	0	0	0	4.686	0	2.313	1.904	2.207
1-Hexyne	0.166	0.23	0.12	2.510	0.10	1.272	1.002	1.126
2-Butanone	0.166	0.70	0	2.287	0.51	1.194	1.172	1.028
1-Bromopropane	0.366	0.40	0	2.620	0.12	1.382	1.197	1.231
Butyl ether	0	0.25	0	3.924	0.45	1.980	1.665	1.854
Pyridine	0.631	0.84	0	3.022	0.52	1.797	1.829	1.615
Isobutyraldehyde	0.144	0.62	0	2.120	0.45	1.137	1.010	0.950
1,2-Dichloroethane	0.416	0.64	0.10	2.573	0.11	1.480	1.324	1.317
Aniline	0.955	0.96	0.26	3.934	0.41	2.566	–	–
n-Nonane	0	0	0	4.182	0	2.047	1.627	1.921
Ethyl ether	0.041	0.25	0	2.015	0.45	0.912	–	0.745
Benzene	0.610	0.52	0	2.786	0.14	1.533	1.359	1.379
Butylamine	0.224	0.35	0.16	2.618	0.61	1.408	–	1.222
n-Octanol	0.199	0.42	0.37	4.619	0.48	2.637	–	–
Heptanal	0.140	0.65	0	3.865	0.45	2.116	–	1.935
Nitrobenzene	0.871	1.11	0	4.557	0.28	2.831	–	–
Benzonitrile	0.742	1.11	0	4.039	0.33	2.519	–	–
p-Xylene	0.613	0.52	0	3.839	0.16	2.156	1.935	1.987
N–Hexylamine	0.197	0.35	0.16	3.655	0.61	1.983	-	1.815
Chloroform	0.425	0.49	0.15	2.480	0.02	1.385	1.183	1.244
1-Nitropropane	0.242	0.95	0	2.894	0.31	1.655	1.660	1.475
Cyclohexene	0.395	0.20	0	3.021	0.10	1.548	1.261	1.414
Acetophenone	0.818	1.01	0	4.501	0.48	2.766	–	–
2,2,4-Trimethylpentane	0	0	0	3.106	0	1.375	1.017	1.319
Ethanol	0.246	0.42	0.37	1.485	0.48	–	0.701	–
Carbon tetrachloride	0.458	0.38	0	2.823	0	–	1.265	–

the ashing technique. It is useful to note that seldom are the results of the percent load determination of these polymers equal to the nominal percent loads determined when the stationary phase was prepared; in fact, the actual percent load is usually less than the nominal percent load. This occurs because a small amount of the polymer sticks to the flask when drying takes place. The actual percent load, determined as described above, is used in all subsequent calculations of V_g or K. Table 4 summarizes the percent load data for each stationary phase analyzed.

Table 3
Cross-correlation matrix for solute descriptors

	R_2	π_2^{H}	$\Sigma\ \alpha_2^{\mathrm{H}}$	$\log L^{16}$	$\Sigma\ \beta_2^{\mathrm{H}}$
R_2	1				
π_2^{H}	0.682	1			
$\Sigma\alpha_2^{\mathrm{H}}$	-0.026	-0.031	1		
$\log L^{16}$	0.211	-0.087	-0.116	1	
$\Sigma\ \beta_2^{\mathrm{H}}$	-0.032	0.342	0.361	-0.217	1

Inverse gas chromatographic studies were performed on a Varian Star 3400 CX series gas chromatograph equipped with a thermal conductivity detector. All studies were conducted at 120°C, and the column flow rate was maintained at approximately 25 ml/min. The specific retention volumes for each probe solute were calculated from the solute retention times using the following relationship,

$$V_g = [jFt'_r 273]/[WT_c] \qquad (2)$$

where j is the James Martin carrier gas compression correction, F is the average column flow rate (corrected for ambient temperature and water vapour pressure from the bubble meter measurement), t'_r is the adjusted solute retention time, W is the mass of stationary phase, and T_c is the operating column temperature. Because specific retention volumes were used as the dependent variable instead of thermodynamic partition coefficients, phase densities at 120°C are not included in Table 1.

Isopropanol was injected periodically throughout the course of the characterization of each coating to determine if any shift in retention time was occurring, which would indicate a loss of stationary phase due to column bleed. In all three cases, no significant loss of coating was observed; hence, no correction was necessary in order to calculate specific retention volumes. Because no significant variations in retention times occurred during the analysis, percent load determinations were unnecessary after completion of the inverse GLC analysis. However, the mass of packing material was determined before the analysis by weighing the column with no packing material and subsequently with packing material. After the analysis, the column containing the packing material was again weighed; no changes in mass were observed for the packed columns during these studies.

After the retention data were acquired, MLR analyses were performed using Eq. (1), as described previously. The coefficients obtained from the MLR analyses (r_1, s_1, a_1, b_1, and l_1) describe the electronic interactions which take place during the solvation process. Once these coefficients are obtained, they are used to calculate or predict the retention behaviour of the probe solutes that were analyzed on the stationary phase under investigation. Residuals are then calculated, which are the difference between the experimental log SP and the predicted log SP. Small residuals for a large majority of the probe solutes indicate good predictive ability of the relationship.

3. Results and discussion

The LSER coefficients (r_1, s_1, a_1, b_1, and l_1) obtained from the MLR analyses are summarized in Table 5 along with data from previously characterized olefinic stationary phases [18]. Abraham and others have previously characterized several olefinic polymers [19] using gas chromatographic data obtained by Munk [20]; however, these data were acquired at 100°C. For comparison with other data sets previously characterized, our polymers were analyzed at 120°C.

For polybutadiene and polyisoprene, examination of the coefficients shows that the $b_1\ \Sigma\ \beta_2^{\mathrm{H}}$ term was statistically insignificant; this is reasonable in light of the fact that both phases are unsaturated hydrocarbons with no acidic protons. The vinyllic protons

Table 4
Summary of percent load data for three olefinic stationary phases

Stationary phase	Nominal load (%)	Load determination (%)	n	S.D.
PBD	15.00	13.85	3	0.098
PCP	14.55	10.95	3	0.127
PIP	15.13	13.33	3	0.249

Table 5
Summary of LSER coefficients for various olefinic stationary phases

	c_1	r_1	s_1	a_1	l_1	b_1	Adj. R^2	S.E.	n
Polybutadiene	−0.39	0.27	0.30	0.36	0.578	0.03	0.9972	0.03	41
	(0.02)	(0.03)	(0.03)	(0.04)	(0.006)	(0.03)			
Polybutadiene	−0.38	0.27	0.32	0.38	0.578	–	0.9972	0.03	41
(w/o β term)	(0.02)	(0.03)	(0.02)	(0.04)	(0.006)				
Polychloroprene	−0.60	0.29	0.60	0.29	0.532	0.17	0.9935	0.03	32
	(0.03)	(0.03)	(0.03)	(0.05)	(0.009)	(0.03)			
Polyisoprene	−0.46	0.23	0.25	0.30	0.573	−0.03	0.9982	0.02	33
	(0.02)	(0.02)	(0.02)	(0.03)	(0.005)	(0.02)			
Polyisoprene	−0.47	0.24	0.23	0.28	0.573	–	0.9981	0.02	33
(w/o β term)	(0.02)	(0.02)	(0.02)	(0.03)	(0.005)				
SE-30	−0.34	−0.01	0.31	0.33	0.525	–	0.9968	0.03	249
(w/o β term)	(0.01)	(0.01)	(0.01)	(0.01)	(0.002)				
SE-31	−0.36	−0.02	0.25	0.21	0.521	–	0.9967	0.03	249
(w/o β term)	(0.01)	(0.01)	(0.01)	(0.01)	(0.002)				
Hallcomid M18	−0.35	0.13	0.58	1.49	0.592	–	0.9928	0.05	244
(w/o β term)	(0.02)	(0.02)	(0.02)	(0.02)	(0.003)				
Hallcomid M18OL	−0.41	0.14	0.65	1.50	0.584	–	0.9912	0.05	244
(w/o β term)	(0.02)	(0.02)	(0.02)	(0.02)	(0.004)				

in these two polymers are too weakly acidic to significantly act as H-bond donor acids. Because this term was statistically insignificant, the LSER coefficients were recalculated eliminating this term. With polychloroprene, all terms were included; the $b_1 \sum \beta_2^H$ term was found to be small but statistically significant. Because the chlorine substituent is strongly electronegative, electron density is pulled away from the double bond resulting in a more acidic vinyllic proton which may act as a weak H-bond donor acid ($b_1 = 0.17$).

A significant r_1 value is expected because each stationary phase investigated has π-electrons which can participate in interactions involving excess electron density. For all three phases these values are of similar magnitude, probably attributable to similar molecular mass fractions of double bonds in each polymer.

A significant s_1 term is indicative of the polarizable nature of the π-bond in the olefinic stationary phases. In the case of polychloroprene the dipolar nature of the polymer (attributable to the chlorine substituent and its extra electron pairs) accounts for the increased magnitude of s_1. All three phases act as weak-to-moderate H-bond acceptor bases (significant a_1). The electron density of the double bond interacts with the acidic hydrogens of solutes which can act as H-bond donors.

The residuals (predicted value minus observed value) for log V_g were plotted versus all five solute descriptors and versus log V_g to determine if the residuals are completely random or if any trends exist which would indicate bias in the data set. As an example, Fig. 1 shows a plot of residuals for polybutadiene versus the π_2^H solute descriptor. Examination of these residual plots for the three stationary phases shows no apparent trends in the
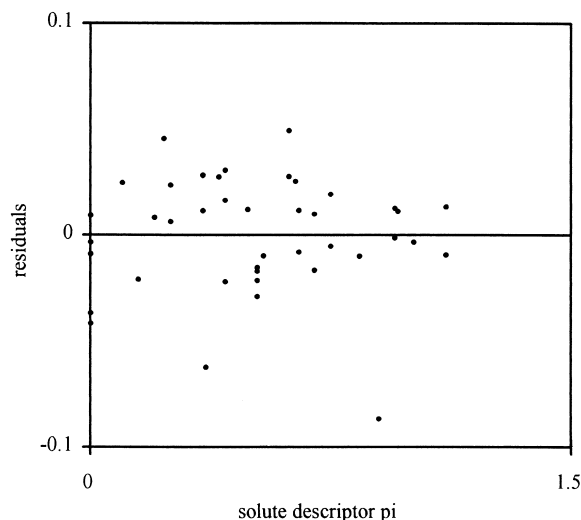

Fig. 1. Plot of residuals for polybutadiene versus π_2^H.

data. An observable trend would indicate that the residuals are biased either by one of the solute descriptors or by the magnitude of $\log V_g$. Residuals were also plotted versus functional groups to see if trends exist within a given functional group (e.g., increasing number of carbons in a straight-chain alcohol). These plots also showed no observable trends.

Comparison of the LSER values of the phases characterized in this study with previously analyzed olefinic stationary phases reveals several interesting trends. The r_1, s_1, and a_1 coefficients for the phases characterized in this study were plotted versus the percentage of functional group contained in the phase. Included in these plots were the results of two previously characterized olefinic stationary phases SE-31 and Hallcomid M18OL. SE-31 is a dimethyl siloxane-based polymer with approximately one percent of the methyl substituents replaced by a vinyl substituent. Hallcomid M18OL (N,N-di-methyloleylamide) is an amide containing one double bond in the hydrocarbon chain attached to the carbonyl carbon. For all three plots, the fraction of functional group was determined to be the ratio of the formula mass of the two carbons contributing to each double bond in the polymer and the molecular mass of the entire compound. For the plots of r_1 and s_1, the mass of the chlorine atom in polychloroprene was included because the lone pairs of electrons from chlorine contribute to the excess molar refractivity as well as the dipolar nature of the polymers. In the cases of SE-31 and Hallcomid M18OL, the portion of the coefficient that was primarily due to the olefinic character of the polymer was determined by subtracting the coefficient of the corresponding non-olefinic stationary phase; for SE-31, SE-30 was used, and, for Hallcomid M18OL, Hallcomid M18 was used. This approach is feasible because the structure of SE-30, a poly(dimethylsiloxane) polymer, differs from SE-31 only by the replacement of one methyl substituent in SE-30 with a vinyl substituent in approximately every fifty monomer units. In the case of the Hallcomids, Hallcomid M18OL differs from Hallcomid M18 (N,N-dimethyl-stearamide) by only one double bond in the hydrocarbon chain. This approach assumes that the contributions to r_1, s_1, and a_1 in the newly characterized polymers are due only to the olefinic functional

group and, with polychloroprene, the chlorine substituent as well. These phases are also listed in Table 5.

Examination of Fig. 2 shows a definite increase in magnitude for the r_1 coefficient with increasing percentage of olefinic character for each stationary phase. SE-31, has a statistically insignificant r_1 value (-0.02 ± 0.01). Hallcomid M18OL has a somewhat larger r_1 value (0.14); however, when compared to Hallcomid M18 ($r_1 = 0.13$), virtually all of the intermolecular interactions due to excess electron density result from the lone electron pairs on the oxygen and nitrogen atoms. With polybutadiene, polychloroprene, and polyisoprene, the values range from 0.24 to 0.29, higher than any of the other olefinic stationary phases. Examination of the structures of these three phases (Table 1) shows that not only does all of the excess electron density result from the π-electrons of the double bonds (and lone pair electrons of the chlorine for polychloroprene), but also, the percentage of olefinic character for these polymers is much greater.

The values of the r_1 coefficient for the previously characterized Apiezon greases were compared with the three phases currently being investigated. Comparison of these newly characterized phases with the Apiezons is more difficult (no definite structures are
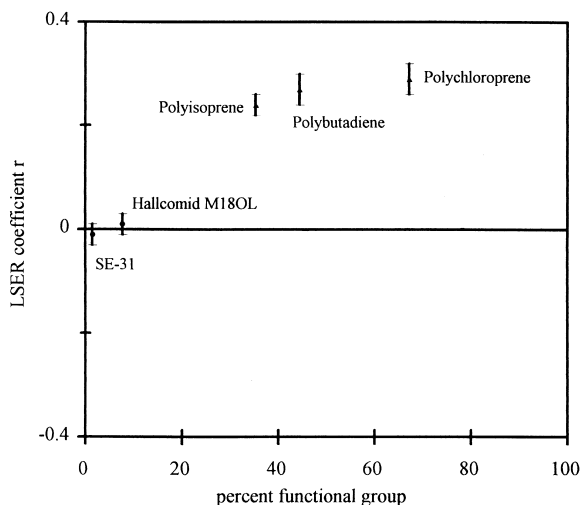

Fig. 2. Plot of r_1 versus percent functional group for several olefinic stationary phases. Previously characterized phases = ●. Newly characterized phases = ▲.

Table 6
LSER coefficients for the Apiezon greases (for comparison purposes)

	r_1	s_1	a_1	l_1
Apiezon M	0.23	0.11	0.12	0.600
Apiezon N	0.24	0.13	0.11	0.600
Apiezon J	0.24	0.14	0.12	0.595
Apiezon L	0.25	0.09	0.07	0.600

Note: Because these values are shown only for qualitative comparisons, the c_1 values are not listed as well as the statistics for each set of coefficients. Also, the b_1 coefficient is not given; in each case, it was statistically insignificant.

available) but values ranging from 0.23 to 0.25 are consistent with the fact that Apiezons are unsaturated hydrocarbons containing only double bonds and aromatic groups. The Apiezons are summarized in Table 6.

Fig. 3 shows an increasing trend for the s_1 coefficient when plotted against the percentage of functional group in the polymer. The s_1 values for all of the olefinic phases are consistent with the structures of these materials. Phases with strongly electronegative atoms or substituents or phases which contain a significant dipole moment (polychloroprene, Hallcomid M18OL) show significantly higher s_1 values (0.60, 0.65, respectively) than phases which are either unsaturated hydrocarbons
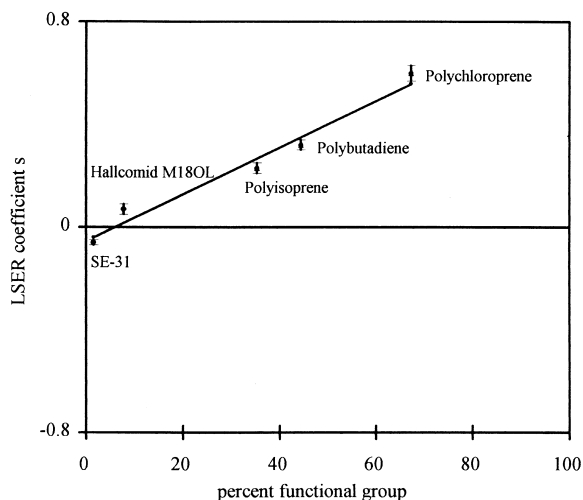
(Apiezons, $s_1 = 0.09$–0.14; polybutadiene, $s_1 = 0.32$; polyisoprene, $s_1 = 0.23$) or have electronegative atoms but not a significant dipole moment (SE-31, $s_1 = 0.25$).

When comparing the a_1 values of all olefinic phases characterized, the extent to which the phase participates in interactions as an H-bond acceptor base can be rationalized by the structure of each phase. Fig. 4 illustrates the relationship between a_1 and the percentage of olefinic functional group. The Apiezons (not included in the plot) have very small a_1 values (0.07–0.12), apparently due to the small percentage of olefinic character in the phase and the lack of any significant H-bond acceptor atoms in the phase (e.g., oxygen, nitrogen, etc.). In the case of polybutadiene, polychloroprene, and polyisoprene, the percentage of olefinic character is significantly greater; as a result, more electron density is available for solutes with acidic hydrogens to H-bond to these phases ($a_1 = 0.28$–0.38). In the case of Hallcomid M18OL, virtually all of the H-bond acceptor capability of the phase is due to the amide functionality in the phase. Comparing Hallcomid M18OL ($a_1 = 1.50$) with Hallcomid M18 ($a_1 = 1.49$) there is probably an insignificant contribution from the olefinic moiety to the H-bond acceptor basicity of this phase.

In order to determine the extent to which the olefinic moiety contributes to the a_1 coefficient, the

Fig. 3. Plot of s_1 versus percent functional group for several olefinic stationary phases. Previously characterized phases = ●. Newly characterized phases = ▲.
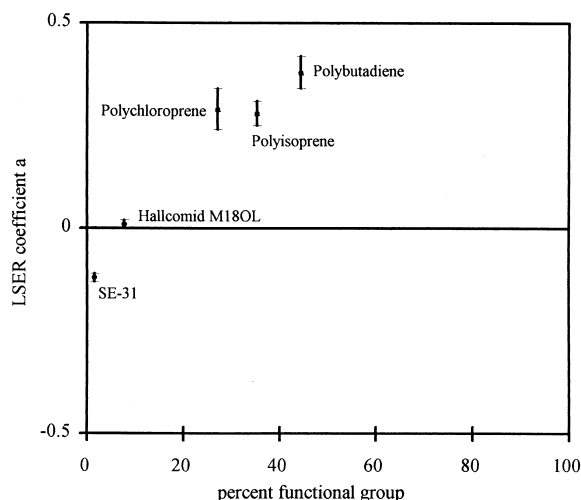

Fig. 4. Plot of a_1 versus percent functional group for several olefinic stationary phases. Previously characterized phases = ●. Newly characterized phases = ▲.

a_1 coefficient is calculated based on the structure of the polymer by a previously described method [15]. In this approach, the percent fractions of functional groups which were determined to significantly contribute to the H-bond acceptor basicity of the phase were used in a linear predictive relationship to calculate a_1, similar to the approach of LSER. The predictive relationship, which contains descriptors for the fractions of siloxane, ester, ether, hydroxyl, and methylene groups (descriptors determined to be statistically significant) is limited by the fact that several phases could not be used in the training set to develop the predictive model because these phases contained functional groups which were under-represented in the database. As a result, several functional groups (e.g., olefinic) which may contribute to the H-bond acceptor basicity of the stationary phase are not included in the relationship. Therefore, once the a_1 values for the phases containing olefinic moieties are calculated based on the above approach, this calculated a_1 is subtracted from the experimentally determined a_1; the difference is termed a_{excess}, which is a measure of the olefinic contribution to a_1. Comparing a_{excess} for each polymer with the percentage of olefin shows an increasing trend in a_{excess} with increasing olefinic character. It is worth noting that the a_{excess} value for polychloroprene contains contributions from both the double bond and also from the chlorine substituent. In the case of Hallcomid M18OL, the contribution to a_{excess} also includes the amide functionality. Table 7 lists these values along with the values for SE-31 and Hallcomid M18OL.

In the case of the plot of the s_1 coefficients versus percentage of functional group for each phase, linear regression was performed to determine the slope, which represents the extent to which the percentage of olefinic character increases the coefficient. The slope of this line was determined to be 0.0092 and the y-intercept was found to be -0.056. Thus a change in the olefinic character of ten percent would result in a change in the s_1 coefficient of approximately 0.09.

4. Conclusions

Three olefinic stationary phases have been characterized by inverse GLC in order to expand the current database of functional groups. With a greater variety of functional groups represented in the database, (QSSRs) can be developed which predict the LSER coefficients and, more fundamentally, the solubility interactions which occur in the solvation process. Through analysis of the residuals, it was determined that the LSER coefficients which were calculated by MLRA were reliable and not subject to any bias from the solute descriptors, log V_g, or the functional groups represented by the probe solutes. Comparison of these three olefinic stationary phases with those already characterized in the literature reveals consistent trends in the values of the r_1, s_1, and a_1 coefficients with the percentage of functional group in the polymer. Finally linear regression was performed on the s_1 versus percent functional group data to determine to what extent s_1 changes with a corresponding change in the percent olefinic character in the polymer.

Acknowledgements

Table 7
Summary of a_1, a_{excess}, and percent olefinic character for three olefinic stationary phases

	a_1	a_{excess}	percent olefin	percent functional group
Polyisoprene	0.28	0.07	35.3	35.3
Polybutadiene	0.38	0.11	44.4	44.4
Polychloroprene	0.29	0.13	27.1	7.2
SE-31	0.21	-0.08	0.6	0.6
Hallcomid M18OL	1.50	1.17	7.8	21.5

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