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# Characterization of amine functionalized stationary phases using linear solvation energy relationships

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**Abstract**

In a continuing effort to develop quantitative structure–solubility relationships, this work describes the characterization of four amine functionalized stationary phases: Quadrol, tetraethylene pentamine, phenyldiethanolamine succinate, and triethanolamine. Solubility properties of these materials were examined using linear solvation energy relationship of the following form:

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

in which the coefficients (subscript 1) represent the ability of the stationary phase to engage in specific interactions. These coefficient values were correlated with the fraction of amine functionalities in the phase, and were quantitatively compared with literature values for similar nitrogen containing (amide) stationary phases. 

*Keywords:* Stationary phases, GC; Linear solvation energy relationships

## 1. Introduction

Solute–solvent interactions play a major role in many areas of chemistry, including chemical synthesis, pharmaceuticals, coatings development, and the development/optimization of analytical separations and spectrophotometric methods. Characterization of materials in terms of solubility properties facilitates the selection of appropriate materials and conditions for a given application, and provides insight into the rational design of new materials. A priori prediction of chemical properties, based on known chemical and/or structural information, would be particularly useful for the latter.

Chromatographic methods have been used extensively to characterize the solubility properties of both solutes and solvent stationary phases [1–5]. In these studies, the retention behavior of a solute (or class of solutes) on a given solvent phase is correlated with chemical descriptors which are related to the molecular or solubility properties of the solute and/or solvent. The most common approaches can be classified as linear solvation energy relationships (LSERs) or quantitative structure–retention relationships (QSRRs). The LSER approach typically involves molecular probe chromatography, sometimes referred to as inverse chromatography, in which the retention behavior of a series of probe solutes are

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measured on a given stationary phase. Using known descriptors for the probe solutes as independent variables and the retention parameter for the solutes (typically the thermodynamic partition coefficient, *K*, or a related value) as the dependent variable, linear regression analyses are performed to obtain descriptors for the stationary phase [3,4]. The advantage of the LSER approach is that it provides a theoretical model to describe the solvation process, so that the regression results provide direct insight into the solvation properties of the stationary phases. Knowledge of the solute and solvent parameters permits reliable prediction of retention behavior.

Obtaining characterization data for a solvent material, however, is labor intensive. In QSRR methods, observed retention behavior of the solute on a given phase is correlated with a set of structural descriptors, which may include physical/chemical properties (e.g., refractive index, dipole moment) or calculated indexes that encode molecular structural information (e.g., topological or connectivity indexes, surface area, shape parameters) [6–10]. The advantage of the QSRR is that it permits prediction of retention behavior based solely on known or measurable physico–chemical properties. The disadvantage is that results are generally only valid for members of the solute set on a single solvent phase. While the results may be correlated with the properties of the solutes, they generally provide little or no insight into the solubility properties of the solvent phases.

Previous studies in this laboratory focussed on combining the LSER and QSRR approaches [11,12]. Since the solubility properties of the solvent phases should logically be related to molecular structure, it should be possible to predict the LSER coefficients for a stationary phase based on relevant structural descriptors. Such a QSSR has the advantage of eliminating extensive chromatographic characterization of the solvent phases. The general applicability of this approach has been hampered by the need for a representative data set that includes characterization data for stationary phases containing a wide variety of functional groups. Current work in our laboratory strives to expand the data base by obtaining characterization data for stationary phases containing underrepresented functionalities, and the identification and/or development of descriptor sets for the prediction of LSER coefficient values. In this work we describe the LSER characterization of nitrogen-containing stationary phases (amines/amides), and correlate the presence of these functional groups with specific solvation properties of these phases.

## 2. Methodology

Probably the most widely utilized LSER are those developed by Kamlet, Abraham, and Taft, and subsequently used in various forms [3,5,12,14–16]. As used in this work, the LSER takes the form

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

where each term in the equation refers to the ability of the solute and solvent to engage in specific interactions. The solute terms, identified with a subscript 2, represent the hydrogen bond donor acidity ($\alpha_2^{\mathrm{H}}$), acceptor basicity ($\beta_2^{\mathrm{H}}$), dipolarity/polarizability ($\pi_2^{\mathrm{H}}$), excess molar refractivity ($R_2$), and gas–liquid partition coefficient into hexadecane ($L^{16}$) for the solute (referenced to 25°C). The coefficients having a subscript 1 represent the ability of the solvent phase to engage in complementary interactions with the solute. For example, $a_1$ represents the tendency of the solvent phase to act as a H-bond acceptor base when interacting with a H-bond donor acid ($\alpha_2^{\mathrm{H}}$) solute. These coefficient values are obtained by multiple linear regression (MLR), along with the regression constant, *c*.

In order for the LSER results to be statistically meaningful certain criteria must be met. First, the number of cases used in the regression should be sufficiently large, taking into consideration the number of variables in the regression. Second, the selected probes should represent a broad spectrum of solubility behavior, i.e., the solute descriptors should be known and span the range of values for each of the five parameters used in the LSER. The solutes used in this study, along with their solute descriptors (obtained from Ref. [18]), are listed in Table 1.

Solute retention parameters that could be used in the above LSER equation include corrected retention time ($t_r'$), specific retention volume ($V_g$), and partition

Table 1
Probe solutes and solute descriptors

| Solutes | $R_2$ | $\pi_2^H$ | $\alpha_2^H$ | Log $L^{16}$ | $\beta_2^H$ |
|---|---|---|---|---|---|
| Cyclohexanol | 0.460 | 0.54 | 0.32 | 3.758 | 0.57 |
| *n*-Butanol | 0.224 | 0.42 | 0.37 | 2.601 | 0.48 |
| Toluene | 0.601 | 0.52 | 0.00 | 3.325 | 0.14 |
| Benzene | 0.610 | 0.52 | 0.00 | 2.786 | 0.14 |
| N-Hexylamine | 0.197 | 0.35 | 0.16 | 3.655 | 0.61 |
| 1,2-Dichloroethane | 0.416 | 0.64 | 0.10 | 2.573 | 0.11 |
| Trichloromethane | 0.425 | 0.49 | 0.15 | 2.480 | 0.02 |
| *n*-Decane | 0.000 | 0.00 | 0.00 | 4.686 | 0.00 |
| 2-Butanone | 0.166 | 0.70 | 0.00 | 2.287 | 0.51 |
| Tetrahydrofuran | 0.289 | 0.52 | 0.00 | 2.636 | 0.48 |
| *n*-Dodecane | 0.000 | 0.00 | 0.00 | 5.696 | 0.45 |
| Anisole | 0.708 | 0.73 | 0.00 | 3.859 | 0.29 |
| Butylamine | 0.224 | 0.35 | 0.16 | 2.618 | 0.61 |
| Triethylamine | 0.101 | 0.15 | 0.00 | 3.04 | 0.79 |
| Nitromethane | 0.313 | 0.95 | 0.06 | 1.892 | 0.31 |
| N,N-Dimethylformamide | 0.367 | 1.31 | 0.00 | 0.173 | 0.74 |
| Chlorobenzene | 0.718 | 0.65 | 0.00 | 3.657 | 0.07 |
| 1,4-Dioxane | 0.329 | 0.75 | 0.00 | 2.892 | 0.64 |
| Ethanol | 0.246 | 0.42 | 0.37 | 1.485 | 0.48 |
| Methanol | 0.278 | 0.44 | 0.43 | 0.970 | 0.47 |
| Isopropanol | 0.212 | 0.36 | 0.33 | 1.764 | 0.56 |
| Acetone | 0.179 | 0.70 | 0.04 | 1.696 | 0.49 |
| Pyridine | 0.631 | 0.84 | 0.00 | 3.022 | 0.52 |
| Acetonitrile | 0.237 | 0.90 | 0.07 | 1.739 | 0.32 |
| Acetophenone | 0.818 | 1.01 | 0.00 | 4.501 | 0.48 |
| Benzylamine | 0.829 | 0.88 | 0.10 | 4.319 | 0.72 |
| Aniline | 0.955 | 0.96 | 0.26 | 3.934 | 0.41 |
| N,N-Dimethylacetamide | 0.363 | 1.33 | 0.00 | 3.717 | 0.78 |
| *n*-Heptane | 0.000 | 0.00 | 0.00 | 3.173 | 0.00 |
| Ethylacetate | 0.106 | 0.62 | 0.45 | 2.314 | 0.45 |
| Cyclohexane | 0.305 | 0.10 | 0.00 | 2.964 | 0.00 |
| Dibutyl ether | 0.000 | 0.25 | 0.00 | 3.924 | 0.45 |
| Benzylaldehyde | 0.820 | 1.00 | 0.00 | 4.008 | 0.39 |
| Heptanal | 0.140 | 0.65 | 0.00 | 3.865 | 0.45 |
| Hexanol | 0.210 | 0.42 | 0.37 | 3.610 | 0.48 |
| Isobutyraldehyde | 0.144 | 0.62 | 0.00 | 2.120 | 0.45 |
| Diethyl ether | 0.041 | 0.25 | 0.00 | 2.015 | 0.45 |
| Hexyne | 0.166 | 0.23 | 0.12 | 2.510 | 0.10 |
| Bromopropane | 0.366 | 0.40 | 0.00 | 2.620 | 0.12 |
| Chloroform | 0.425 | 0.49 | 0.15 | 2.480 | 0.02 |

coefficient ($K$). These parameters are all mathematically related by

$$V_g = \left(\frac{jFt_r'}{W}\right)\left(\frac{273}{T_c}\right) = \left(\frac{K}{\rho_g}\right)\left(\frac{273}{T_c}\right) \quad (2)$$

Calculation of reliable values of $V_g$ and $K$ require accurate values of the James–Martin compressibility factor $j$, the carrier gas flow-rate $F$ (measured postcolumn with a soap-bubble meter and corrected for water vapor pressure and temperature differences), the mass of stationary phase on the packed column $W$, and the density of the stationary phase $\rho_s$ at the column temperature $T_c$. Alternatively, corrected retention times ($t_r'$) can be used providing other terms in Eq. (2), such as $W$, $F$, and $j$ are held constant or change in a predictable manner during retention studies for a given stationary phase. Identical LSER solvent coefficients should be obtained regardless of which retention parameter is used as the dependent variable. The value of the regression constant ($c$), however, will depend on the retention parameter used in the LSER.

Obtaining meaningful values for the LSER coefficients requires that the retention parameters represent the solubility properties of the bulk solvent phase. Thus, the possible influence of interfacial adsorption on solute retention must be examined. In general, it has been reported that this phenomenon is most significant for saturated hydrocarbons and tends to increase with the polarity of the solvent phase, while this mechanism tends to be less significant for polar solutes on polar phases at moderate phase loadings [5]. It is possible to correct for the contributions of interfacial adsorption to observed retention using the approach of Nikolov [13] as modified by Kersten et al. [14] using the relationship

$$\frac{V_{N^*}}{V_L} = K_L + (A_{GL} + A_{LS}K_{GLS})(1/V_L) \quad (3)$$

where $V_N^*$ is the net retention volume of the solute per gram of column packing, $V_L$ is the volume of liquid phase, $K_L$ is the gas–liquid partition coefficient, $A_{GL}$ and $A_{LS}$ are the gas–liquid and liquid–solid interfacial areas per gram of packing, respectively, and $K_{GLS}$ is the coefficient for adsorption at the gas–liquid interface. Measuring the net retention volume at more than one phase loading and plotting $V_N^*/V_L$ vs. $1/V_L$ yields an intercept of $K_L$.

In this work we wished to obtain LSER coefficients for a series of amine-containing stationary phases, a functional group that was not adequately represented in the data base of stationary phases used previously [11]. The materials selected as stationary phases for characterization included N,N,N,N-tetrakis(2-hydroxypropyl)ethylenediamine (also known by the trade name Quadrol), tetraethylene pentamine

Table 2
Stationary phase materials

| Coating | Molecular formula | Formula weight (g/ml) | Density at 393 K | Polar fraction | | Load (final) (%) |
|---|---|---|---|---|---|---|
| | | | | N | Total | |
| N,N,N,N-Tetrakis(2 -hydroxypropyl)ethylenediamine (Quadrol) | $\{CH_3CH(OH)CH_2\}_2$ $NCH_2CH_2N$ $\{CH_2CH(OH)CH_3\}_2$ | 292.42 | 0.974 | 0.0958 | 0.3146 | 9.4–16.2 |
| Tetraethylene pentamine (TEP) | $HN(CH_2CH_2NHCH_2CH_2NH_2)_2$ | 189.31 | 0.922 | 0.370 | 0.370 | 8.2–16.0 |
| Phenyldiethanolamine succinate (PDAS) | HO-[-$CH_2CH_2N(C_6H_5)$ $CH_2CH_2CO_2CH_2CH_2CO_2$-]$_n$ -H | ≈20 000 ($n$≈75) | 1.726 | 0.0532 | 0.2971 | 11.1–12.5 |
| Triethanolamine (TEA) | $(HOCH_2CH_2)_3N$ | 149.2 | 1.056 | 0.0938 | 0.4155 | 12.5–14.5 |

(TEP), triethanolamine (TEA), and phenyldiethanolamine succinate (PDAS). Of these phases, Quadrol has been characterized previously by several researchers [3,4,15,16]. It was included in this study to validate our methodology and provide a basis for comparison with prior results. The molecular formulas and formula weights of these phases are provided in Table 2, along with other relevant data. These phases were coated onto 100–120 Chromosorb AW support, and packed into glass columns. A series of probe solutes were then analyzed, and retention times were obtained at 120°C. For some phases, more than one phase loading was analyzed to evaluate the significance of interfacial adsorption using the approach outlined above. Corrected retention data were used to calculate the partition coefficients, as described below, which were then used as the dependent variables in the LSER. The values for the solvent coefficients that are representative of polar and electron interactions ($a_1$, $b_1$, $s_1$, $r_1$) were then examined to determine the relative contribution of the amine functional group to these values. The coefficients of these phases were then compared to other amine and amide stationary phases that have been previously characterized [3,17].

## 3. Experimental

### 3.1. Materials

All solute probes listed in Table 1 were 96–99% analytical grade solvents obtained from Aldrich (Milwaukee, WI, USA) and were used as received. Of the solvent phases listed in Table 2, Quadrol, TEP, and TEA were obtained from Aldrich, while PDAS was obtained from Supelco (Bellefonte, PA, USA). Solvents were also 96–99% purity and were used as received.

### 3.2. Instrumentation

The GC system employed for these studies was a Varian 3400CX gas chromatograph equipped with a heated off-column injector ($T$=220°C) with dual flame ionization/thermal conductivity detection (TCD) system. The TCD system ($T$=220°C) was utilized to permit correction of retention times vs. the unretained air peak. High-grade helium carrier gas was used as the mobile phase, with a head pressure of 27–30 p.s.i. above ambient to obtain a carrier flow-rate of 30 (±1) ml/min (1 p.s.i.=6894.76 Pa). Carrier flow-rates were measured by a soap bubble meter, and corrected for pressure differentials and water vapor pressure.

The GC column oven temperature was maintained at 120°C for all phases, except TEA, so that the LSER results could be directly compared with prior studies. The recommended temperature for TEA is 25–75°C. Triethanolamine was characterized at 55, 70, and 85°C, and results obtained were extrapolated to 120°C, as discussed in the Results and Discussion section.

### 3.3. Column preparation

Support-coated stationary phases were prepared by solvent evaporation. Approximately 0.5–0.6 g of stationary phase was dissolved in 50 ml of an appropriate solvent, and 5 g of 100–120 mesh Chromosorb AW was added to create a slurry. The slurry was gently agitated for 10–15 min to create a uniform mixture. The solvent was then removed under vacuum with occasional agitation to prevent agglomeration. The dried packing material was then placed in a glass jar and stored in a desiccator until analysis. Packed columns were prepared by loading the packing into a glass column (1.8 m×6.4 mm O.D.×2 mm I.D.) using suction and gentle agitation. The packed columns were placed in the GC oven and conditioned overnight at a temperature 15–20°C higher than the experimental temperature.

The stationary phase percent load was determined by two independent methods: solvent extraction and combustion. Percent loads were determined both before filling the column and at the completion of retention studies. In the solvent extraction method, 0.4–0.5 g of packing was placed in a clean, dry and tared micropipette. The pipette (with packing) was weighed, and the mass recorded. The pipette was then flushed with 10 ml of an appropriate solvent (acetone for Quadrol and TEA; chloroform for PDAS; methanol for TEP) to dissolve and remove the stationary phase. The pipette was then dried in an oven, and the mass was recorded. This procedure was repeated until a constant mass was obtained.

In the combustion method, 0.4–0.5 g of packing was placed in a clean, dried and tared ceramic crucible. The crucible was weighed with packing, then placed on a clay triangle and heated with a Bunsen burner to combust the stationary phase. The mass of the cooled crucible was then recorded. The procedure was repeated until a constant mass was obtained. The range of stationary phase loads used during these studies are also listed in Table 2.

## 4. Results and discussion

### 4.1. Quadrol

As mentioned previously, Quadrol was included in this study to verify our experimental methodology via direct comparison with results from previous studies. Multiple columns, packed with nominal stationary phase loadings of 10%–16%, were prepared and retention studies were performed using the probe solutes from Table 1. The log $K$ values (at 120°C) for these solutes at each of the % loads are summarized in Table 3. In addition, previously reported log $K$ values for some of these solutes are included for comparison [15]. Values for the LSER coefficients for these % loads are presented in Table 4, along with the corresponding standard errors (in parentheses). The LSER results at each % load were determined both with and without the $b_1\beta_2^H$ term to facilitate comparison with results from previous studies, summarized in Table 5. To examine the possible effects of interfacial adsorption on retention data and on the LSER coefficient values, these results were analyzed using Eq. (3). The corrected log $K$ values are included in Table 3. Substantial differences are noted for the $n$-alkanes (heptane, decane, and dodecane), with our results being significantly lower than previously reported. Results for these solutes were eliminated prior to performing the MLR analysis to obtain the LSER results in Table 4.

When the data are corrected for interfacial adsorption the LSER coefficients increase dramatically, particularly for $s_1$ and $a_1$, and a more negative intercept (regression constant, $c$) is obtained. The source of this discrepancy may be large errors in the log $K$ values for some solutes at infinite load obtained by extrapolation via Eq. (3). Comparison of the extrapolated values with log $K$ values reported by Poole and coworkers supports this possibility. In addition, the correlation coefficient and standard errors obtained for the extrapolated data indicated larger error for this set of LSER coefficients. Given that there is reasonably good agreement between the coefficient values obtained at the three different % loads, and that interfacial adsorption would be expected to be minimized at high loads (>10%) for polar solutes on a polar phase, the values reported for 16% load of Quadrol are taken as representative values for comparison with other values obtained from studies reported in the literature.

The LSER values reported in Table 5 for comparison were obtained from several previous studies. The values reported for Poole and coworkers are

Table 3
Log $K$ values for Quadrol, TEP, and PDAS

| Solute | Quadrol | | | | | TEP | | PDAS |
|---|---|---|---|---|---|---|---|---|
| | 10% | 12% | 16% | [a] | Kollie et al.[b] | 13% | 16% | 12% |
| Toluene | 1.747 | 1.724 | 1.672 | 1.549 | | 1.738 | 1.729 | 2.173 |
| 1,2-Dichloroethane | 1.706 | 1.664 | 1.600 | 1.414 | | 1.726 | 1.721 | 2.138 |
| Dimethylformamide | 2.689 | 2.685 | 2.678 | 2.610 | 2.626 | 2.349 | 2.333 | 3.018 |
| 1.4-Dioxane | 1.877 | 1.85 | 1.807 | 1.700 | 1.765 | 1.767 | 1.772 | 2.321 |
| *n*-Decane | 1.829 | 1.794 | 1.736 | 1.579 | 1.838 | 1.751 | 1.746 | 1.955 |
| Methanol | 1.616 | 1.594 | 1.52 | 1.403 | 1.352[b] | 1.794 | 1.804 | 1.738 |
| Ethanol | 1.695 | 1.670 | 1.609 | 1.479 | 1.597[b] | 1.845 | 1.850 | 1.829 |
| *n*-Butanol | 2.127 | 2.120 | 2.106 | 2.072 | 2.084 | 2.357 | 2.363 | 2.189 |
| *n*-Dodecane | 2.252 | 2.231 | 2.205 | 2.137 | 2.298 | 2.256 | 2.220 | 2.327 |
| Anisole | 2.286 | 2.263 | 2.251 | 2.191 | 2.222 | 2.318 | 2.317 | 2.790 |
| Chloroform | 1.636 | 1.588 | 1.515 | 1.279 | | 1.762 | 1.754 | 1.964 |
| Dimethylacetamide | 2.966 | 2.957 | 2.957 | 2.941 | 2.901 | 2.542 | 2.528 | 3.220 |
| Benzylamine | 2.995 | 2.988 | 2.971 | 2.936 | | 2.949 | 2.915 | – |
| Nitromethane | 1.794 | 1.787 | 1.744 | 1.676 | 1.44[b] | 1.754 | 1.763 | 2.312 |
| Butylamine | 1.810 | 1.783 | 1.74 | 1.633 | | 1.524 | 1.521 | – |
| 2-Butanone | 1.624 | 1.604 | 1.515 | 1.352 | 1.426[b] | 1.436 | 1.444 | 1.964 |
| Acetonitrile | 1.654 | 1.628 | 1.560 | 1.422 | | 1.543 | 1.540 | 2.064 |
| Benzene | 1.573 | 1.533 | 1.455 | 1.253 | 1.389 | 1.512 | 1.517 | 1.982 |
| Tetrahydrofuran | 1.611 | 1.588 | 1.492 | 1.323 | | 1.453 | 1.439 | 1.946 |
| N-Hexylamine | 2.301 | 2.246 | 2.222 | 2.062 | | 2.081 | 2.002 | – |
| Acetophenone | 2.997 | 2.998 | 2.985 | 2.971 | | – | – | 3.488 |
| Isopropanol | 1.692 | 1.673 | 1.612 | 1.478 | | 1.795 | 1.800 | 1.806 |
| Chlorobenzene | 2.049 | 2.031 | 2.003 | 1.932 | | 2.076 | 2.071 | 2.501 |
| Aniline | 3.024 | 3.034 | 3.015 | 3.006 | 2.957 | 3.217 | 3.223 | 3.504 |
| Pyridine | 2.191 | 2.18 | 2.167 | 2.127 | 2.13 | 2.004 | 2.003 | 2.610 |
| Acetone | 1.483 | 1.454 | 1.34 | 1.08 | 1.187[b] | – | – | 1.829 |
| Triethylamine | 1.489 | 1.42 | 1.315 | 0.87 | | 1.237 | 1.234 | – |
| Ethylacetate | 1.562 | 1.491 | 1.391 | 0.848 | | 1.386 | 1.396 | 1.859 |
| Cyclohexane | 1.417 | 1.351 | 1.201 | 0.498 | | 1.194 | 1.201 | 1.652 |
| *n*-Heptane | 1.366 | 1.292 | 1.114 | −0.230 | 1.156[b] | 1.220 | 1.191 | 1.597 |
| Bromopropane | – | 1.456 | 1.334 | | | 1.260 | 1.209 | 1.854 |
| Dibutyl ether | – | 1.717 | 1.656 | | | 1.672 | 1.647 | 1.943 |
| Isobutyraldehyde | – | 1.431 | 1.322 | | | – | – | 1.814 |
| Benzaldehyde | – | 2.677 | 2.670 | | | – | – | 3.217 |
| *n*-Hexanol | – | 2.628 | 2.607 | | 2.578[b] | 2.874 | 2.890 | 2.613 |
| Hexyne | – | 1.348 | 1.215 | | | 1.406 | 1.356 | 1.713 |
| Diethyl ether | – | 1.203 | 1.014 | | | – | – | – |
| Heptanal | – | 2.184 | 2.155 | | | 2.241 | 2.236 | 2.492 |

[a] Log $K$ values obtained using Eq. (3) as described in the text.
[b] Log $K$ values obtained by extrapolation from members of the homologous series; data from Ref. [15].

from two different studies [15,16] in which retention data and solute descriptors for a set of solutes were used to calculate the LSER coefficient values directly using Eq. (1). Abraham et al. used retention data originally collected and published by McReynolds for 376 solutes on 77 phases. Using specific retention volumes ($V_g$) and solute descriptors for over 150 of the solutes in the McReynolds set, LSER coefficients were published for all 77 phases, including Quadrol [3]. Since then, Abraham et al. have expanded the number of solutes from the McReynolds set for which solute descriptors are available, and have also modified the descriptors of the solutes to correct for hydrogen bonding effects. This updated set of solute descriptors has been used to obtain new LSER coefficients for the 77 phases originally characterized

Table 4
Summary of LSER coefficient values for Quadrol at various % loading

| Load (Quadrol) (%) | Constant | $r$[a] | $s$ | $a$ | $l$ | $b$ | $n$ | $R^2$ ($F$-value) | SD |
|---|---|---|---|---|---|---|---|---|---|
| 10 | −0.230 | 0.035 | 0.970 | 1.835 | 0.436 | 0.363 | 28 | 0.990 | 0.050 |
| | (0.047) | (0.052) | (0.045) | (0.090) | (0.011) | (0.047) | | (550) | |
| | −0.176 | −0.102 | 1.146 | 2.02 | 0.443 | – | 28 | 0.965 | 0.093 |
| | (0.087) | (0.092) | (0.072) | (0.16) | (0.021) | | | (214) | |
| 12 | −0.184 | 0.037 | 0.943 | 1.78 | 0.430 | 0.311 | 37 | 0.982 | 0.073 |
| | (0.051) | (0.063) | (0.053) | (0.11) | (0.014) | (0.063) | | (388) | |
| | −0.139 | −0.058 | 1.094 | 1.94 | 0.431 | – | 37 | 0.969 | 0.095 |
| | (0.066) | (0.078) | (0.057) | (0.13) | (0.018) | | | (279) | |
| 16 | −0.407 | 0.035 | 1.034 | 1.964 | 0.463 | 0.318 | 37 | 0.988 | 0.063 |
| | (0.044) | (0.054) | (0.046) | (0.092) | (0.012) | (0.055) | | (598) | |
| | −0.361 | −0.062 | 1.189 | 2.13 | 0.464 | – | 37 | 0.976 | 0.090 |
| | (0.062) | (0.073) | (0.054) | (0.12) | (0.017) | | | (368) | |
| [b] | −0.957 | 0.190 | 1.339 | 2.489 | 0.475 | 0.433 | 28 | 0.976 | 0.107 |
| | (0.093) | (0.149) | (0.093) | (0.173) | (0.036) | (0.116) | | (218) | |
| | −0.972 | −0.128 | 1.533 | 2.725 | 0.537 | – | 28 | 0.962 | 0.134 |
| | (0.116) | (0.153) | (0.096) | (0.202) | (0.040) | | | (–) | |

[a] Results for the $r$ coefficient are not statistically significant. The LSER results are tabulated including the $R$ value to facilitate comparison with previously published results.
[b] Results obtained by plotting of retention data using Eq. (3) in the text. The $K$ values at infinite load were determined as the intercept of plotting $V_N^*/V_L$ vs. $1/V_L$, and were subsequently used in the LSER Eq. (1) to obtain these coefficients.

by Abraham et al. [17]; the results for Quadrol obtained from Abraham et al.'s data are provided in Table 5.

Patte et al. published a set of solubility factors for 240 solutes and 207 stationary phases which could be used to predict Kovats indexes [4]. These data were used by Abraham to obtain LSER coefficients for five stationary phases: Carbowax 1540, diethylene glycol succinate, polyphenyl ether (6 ring), triscyanoethoxypropane, and Zonyl E7 [18]. Accurate calculation of the LSER coefficients requires use of the slope of the corrected retention times of

Table 5
Comparison of Quadrol LSER coefficient values with literature values

| | $c$ | $r_1$ | $s_1$ | $a_1$ | $l_1$ | $b_1$ | $n$ | $R^2/(F)$ | SD | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Patte et al. | | | | | | | | | | |
| $b=0.20$ | −1.88 | 0.128 | 1.049 | 2.290 | 0.395 | 9.2E-05 | 169 | 0.982 | 0.109 | [4] |
| | (0.027) | (0.043) | (0.036) | (0.043) | (0.007) | (0.0001) | | (1796) | | |
| $b=0.23$ | −2.165 | 0.147 | 1.206 | 2.633 | 0.455 | 0.00011 | 169 | 0.982 | 0.125 | [4] |
| | (0.032) | (0.049) | (0.042) | (0.050) | (0.008) | (0.00013) | | (1796) | | |
| Poole and coworkers | −0.399 | 0.093 | 1.20 | 2.01 | 0.466 | – | 54 | 0.986[a] | – | [15] |
| | −0.422 | −0.136 | 1.20 | 2.14 | 0.472 | – | 62 | 0.997[a] | 0.043 | [16] |
| Abraham et al. | −0.798 | 0.071 | 1.30 | 2.28 | 0.476 | 0.239 | 202 | 0.992 | 0.052 | [17] |
| | (0.02) | (0.03) | (0.03) | (0.04) | (0.001) | (0.04) | | | | |
| | −0.746 | −0.057 | 1.44 | 2.44 | 0.473 | – | 202 | 0.990 | 0.057 | [17] |
| | (0.02) | (0.03) | (0.03) | (0.03) | (0.001) | | | | | |
| This study[b] | −0.407 | 0.035 | 1.034 | 1.964 | 0.463 | 0.318 | 37 | 0.988 | 0.063 | |
| | (0.04) | (0.054) | (0.046) | (0.092) | (0.012) | (0.055) | | (598) | | |
| | −0.361 | −0.062 | 1.189 | 2.13 | 0.464 | – | 37 | 0.976 | 0.090 | |
| | (0.06) | (0.073) | (0.054) | (0.12) | (0.017) | | | (363) | | |

[a] Original work ([15,16]) reported $R$ values rather than $R^2$.
[b] Values in the Table are for 16% load of stationary phase.

*n*-alkanes on the stationary phase (*b*) vs. carbon number. For the five phases listed, the value of *b* published by Patte et al. varied from 0.178 to 0.262. Unfortunately, the value of *b* for Quadrol can not be obtained directly from the data published in Ref. [4]. However, using intermediate representative values of 0.20 and 0.23 for *b*, we can obtain estimated LSER values from the Patte et al. data set. These values are also listed in Table 5 for comparison.

Of the coefficients, the $r_1$ value was found to be not statistically significant in our studies, and is either insignificant or marginally significant for the Abraham and Patte et al. studies. The remaining coefficients ($s_1$, $a_1$, $l_1$, and $b_1$) for 10%, 12% and 16% loads are in good agreement within standard error. Removal of the $b_1\beta_2^H$ term results in a substantial increase in the remaining terms, and a decrease in the adjusted correlation coefficient, $R^2$. Comparison of these results with the LSER values from previous studies (Table 5) indicates generally good agreement, with some notable discrepancies. Our results and the results calculated from Abraham et al. indicate that the $b_1$ value is statistically significant, whereas the results obtained using retention data from Patte et al. indicate that $b_1$ is not statistically significant. The results reported for Poole and Kollie [16] indicate a $b_1$ value of 0.0; standard errors were not provided, so the statistical significance of the $r_1$ values are uncertain. Given the chemical structure of Quadrol, i.e., the presence of four hydroxyl groups, some H-bond donor acidity would not be unreasonable. For the remaining coefficients ($s_1$, $a_1$, $l_1$) there appears to be reasonably good agreement between the results obtained during this work, and the results reported for Abraham and Poole. The results for the Patte et al. data vary, dependent on the value of *b* used in the calculation of retention data used in the LSER Eq. (1). For $b=0.20$, there is reasonably good agreement for $s_1$ and $a_1$, but the value of $l_1$ is lower than other values in Table 5. For $b=0.23$, the value of $s_1$ has increased but is still within the range of values obtained for the other studies, and the value of $l_1$ is now comparable. The value for $a_1$, however, is now significantly larger than other values in Table 5.

Evaluation of these data indicates that the LSER results obtained during this study are comparable to values obtained previously. Furthermore, the % loading of stationary phase materials does not appear to have an identifiable effect on the values of the LSER coefficients. Given the high % loads typically used (>10%) and the polar nature of the stationary phases being characterized, correction for interfacial adsorption effects does not appear warranted.

### *4.2. TEP and PDAS.*

The molecular formulas, % loading, and other physical data for TEP and PDAS are given in Table 2. The TEP was prepared at nominal % loads of 13% and 16%, and the PDAS was prepared at a nominal load of 12%. The retention times of probe solutes from Table 1 were determined at 120°C, from which partition coefficients (*K*) were calculated. The log *K* values for probe solutes on these phases are listed in Table 3.

The TEP has one of the lowest molecular masses of the materials characterized in this study. As a result, there were substantial losses of TEP from the chromatographic column during the course of the solute retention studies at 120°C. Obtaining reliable LSER coefficients requires an accurate knowledge of the stationary phase load on the column at any time so that accurate partition coefficients can be calculated for each of the probe solutes. To correct for loss of TEP over time the retention time of a standard solute was tracked over the course of retention studies for a given column. Once retention studies on a given column were completed, the final % load of TEP on the column was determined by the ashing and/or solvent stripping. From the final % load and the final retention time the log *K* for isopropanol could be determined. Once log *K* was known, the % load of TEP on the column at any given time could be determined from Eq. (2). This assumes that the change in retention of isopropanol is due only to the decrease in the amount of stationary phase, i.e., that the retention is due predominantly to absorption in the stationary phases and only minimally affected by interfacial adsorption. For a polar solute (isopropanol) on a polar stationary phase (TEP) this is a reasonable assumption.

The data in Fig. 1 illustrate typical losses of TEP from columns having nominal initial loads of 13% and 16%. For the 13% column, the % load decreased

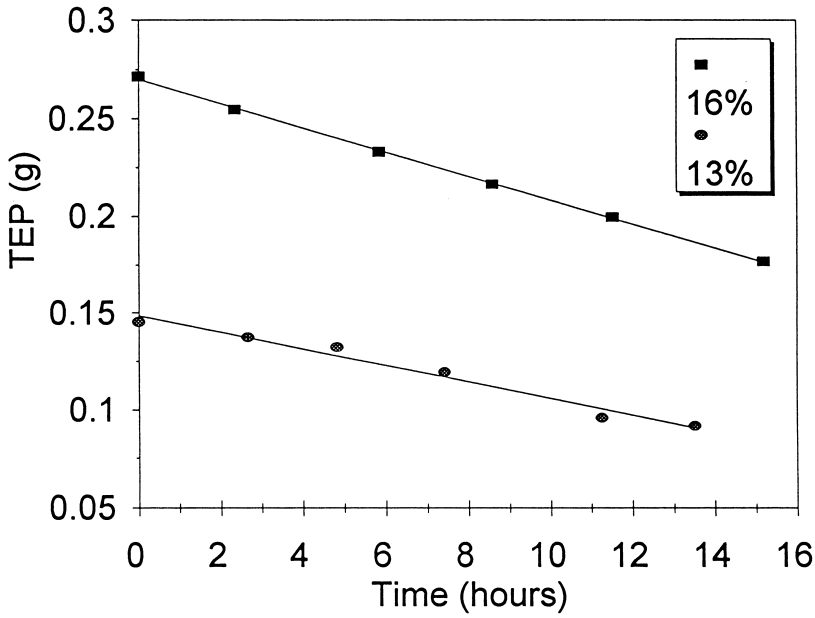


Fig. 1. Plot of TEP mass vs. analysis time, indicating the loss of stationary phase from a 16% (w/w) loaded column (■) and a 13% (w/w) loaded column (●). These data were used to correct for stationary phase loss when calculating log *K* values from retention data as discussed in the text.

from 13% to 8.4%, while the 16% column decreased from 16% to 10.4%, which corresponds to losses of approx. 35% for each column over the course of the retention studies. By noting the time at which a given solute was analyzed, the correct mass of stationary phase can be determined from Figure 1 and an accurate log *K* value can be calculated. The log *K* values in Table 3 for TEP have been corrected for stationary phase during analysis. A comparison of data for the 13% and 16% columns indicates that the final calculated log *K* values are very comparable.

The corrected log *K* values for the probe solutes were then used for the MLR analysis (Eq. (1)) to obtain LSER coefficients. The coefficients for TEP at both 13% and 16% load are provided in Table 6, as

Table 6
LSER Coefficient values for TEP and PDAS

| Coating | $c_1$ | $r_1$[a] | $s_1$ | $a_1$ | $l_1$ | $b_1$[a] | $n$ | $R^2/(F)$ | SD |
|---|---|---|---|---|---|---|---|---|---|
| TEP (13%) | −0.282 | 0.155 | 0.931 | 2.80 | 0.448 | 0.016 | 33 | 0.ad980 | 0.072 |
| | (0.059) | (0.070) | (0.060) | (0.11) | (0.015) | (0.065) | | (324) | |
| | −0.283 | 0.161 | 0.922 | 2.79 | 0.448 | – | “” | 0.981 | 0.071 |
| | (0.057) | (0.064) | (0.047) | (0.10) | (0.015) | | | (420) | |
| (16%) | −0.282 | 0.159 | 0.945 | 2.82 | 0.442 | −0.023 | 33 | 0.976 | 0.080 |
| | (0.065) | (0.078) | (0.067) | (0.12) | (0.017) | (0.073) | | (258) | |
| | −0.283 | 0.168 | 0.932 | 2.81 | 0.441 | – | “ ” | 0.977 | 0.079 |
| | (0.64) | (0.071) | (0.052) | (0.11) | (0.016) | | | (334) | |
| PDAS | 0.280 | 0.387 | 1.069 | 1.13 | 0.364 | 0.099 | 33 | 0.983 | 0.070 |
| | (0.055) | (0.075) | (0.078) | (0.12) | (0.014) | (0.095) | | (373) | |
| | 0.280 | 0.343 | 1.135 | 1.19 | 0.365 | – | “ ” | 0.983 | 0.070 |
| | (0.055) | (0.061) | (0.047) | (0.10) | (0.014) | | | (465) | |

[a] Values of $b_1$ for TEP and PDAS are not statistically significant; $r_1$ values for TEP are marginally significant.

well as coefficients for PDAS. For both TEP and PDAS the $b_1$ term was found to be statistically insignificant, so LSER coefficients were recalculated after omitting the $b_1\Sigma\beta_2^H$ term and are also included in Table 6. The coefficients for TEP at 13% and 16% are very similar and well within standard errors. For TEP the $r_1$ value is marginally significant, but is retained for comparison with coefficient values of other coatings included in this work.

### 4.3. TEA

The molecular formula for triethanolamine is included in Table 2. It has the lowest molecular mass of all stationary phases characterized in this study. The recommended temperature limit for chromatographic use is 75°C [19]. Thus, obtaining LSER coefficients for comparison with other materials at 120°C cannot be reasonably accomplished at such a high operating temperature. However, performing retention studies to obtain log $K$ values and LSER coefficients at several lower temperatures would permit us to obtain the LSER coefficients for TEA at 120°C.

TEA columns were prepared and % loads were determined as described previously. The % load of TEA varied from 12.5–14.5% for the columns used in these characterization studies. The retention times of probe solutes were obtained for column temperatures of 55°C, 70°C, and 85°C. The log $K$ values of the probe solutes at the three different temperatures are summarized in Table 7. In addition, log $K$ values at 120°C obtained by extrapolation of log $K$ vs. $1/T$ are also included in Table 7, along with $R^2$ values for the individual extrapolations. Most of the extrapolations are reliable, with $R^2$ values $>0.95$. Only three solutes (heptane, ethyl ether, and cyclohexane) exhibited $R^2$ values $<0.90$.

The LSER coefficients for TEA at the different operating temperatures are summarized in Table 8.

Table 7
Log $K$ values for probe solutes on TEA at 55°, 70°, and 85°C

| Probe solute | Log $K$ | | | | $R^2$ |
|---|---|---|---|---|---|
| | 55°C | 70°C | 85°C | 120°C[a] (extrap.) | |
| Toluene | 2.131 | 1.878 | 1.723 | 1.312 | 0.988 |
| 1,4-Dioxane | 2.474 | 2.241 | 2.083 | 1.693 | 0.993 |
| *n*-Decane | 1.922 | 1.619 | 1.463 | 0.995 | 0.976 |
| Methanol | 2.513 | 2.253 | 2.071 | 1.633 | 0.994 |
| Ethanol | 2.629 | 2.345 | 2.140 | 1.657 | 0.996 |
| *n*-Dodecane | 2.485 | 2.101 | 1.852 | 1.219 | 0.991 |
| Chloroform | 2.090 | 1.836 | 1.679 | 1.265 | 0.988 |
| 2-Butanone | 2.041 | 1.826 | 1.705 | 1.364 | 0.983 |
| Acetonitrile | 2.224 | 2.015 | 1.893 | 1.559 | 0.985 |
| Benzene | 1.880 | 1.653 | 1.537 | 1.187 | 0.975 |
| Isopropanol | 2.612 | 2.305 | 2.096 | 1.582 | 0.993 |
| Chlorobenzene | 2.616 | 2.311 | 2.113 | 1.576 | 0.986 |
| Ethyl acetate | 1.834 | 1.607 | 1.518 | 1.188 | 0.953 |
| Acetone | 1.868 | 1.639 | 1.567 | 1.247 | 0.931 |
| Triethylamine | 1.913 | 1.644 | 1.494 | 1.069 | 0.982 |
| Tetrahydrofuran | 1.971 | 1.772 | 1.653 | 1.332 | 0.986 |
| 1,2-Dichloroethane | 2.170 | 1.923 | 1.775 | 1.377 | 0.987 |
| *n*-Heptane | 1.242 | 1.037 | 1.066 | 0.853 | 0.653 |
| Diethyl ether | 1.252 | 1.083 | 1.135 | 0.981 | 0.485 |
| Cyclohexane | 1.335 | 1.138 | 1.137 | 0.910 | 0.776 |
| Bromopropane | 1.671 | 1.455 | 1.370 | 1.056 | 0.953 |
| *n*-Butanol | – | 2.841 | – | – | |
| Anisole | | 2.681 | – | – | |

[a] Log $K$ values obtained by extrapolation (log $K$ vs. $1/T$) from values at 55, 70, and 85°C. The $R^2$ values in the last column represent the regression coefficient (squared) for each extrapolation.

Table 8
LSER coefficients for TEA

| Temperature (°C) | $c$ | $r_1$ | $s_1$ | $a_1$ | $l_1$ | $b_1$ | $n$ | $R^2/(F)$ | Std. error |
|---|---|---|---|---|---|---|---|---|---|
| 55 | −0.361 | 0.273 | 1.234 | 3.526 | 0.497 | 0.672 | 21 | 0.980 | 0.060 |
| | (0.089) | (0.089) | (0.079) | (0.131) | (0.021) | (0.072) | | (203) | |
| | −0.340 | – | 1.381 | 3.590 | 0.502 | 0.570 | 21 | 0.970 | 0.074 |
| | (0.110) | | (0.078) | (0.161) | (0.026) | (0.080) | | – | |
| 70 | −0.444 | 0.308 | 1.203 | 3.230 | 0.449 | 0.657 | 23 | 0.986 | 0.057 |
| | (0.073) | (0.079) | (0.074) | (0.106) | (0.017) | (0.066) | | (300) | |
| | −0.455 | – | 1.398 | 3.309 | 0.463 | 0.547 | 23 | 0.974 | 0.076 |
| | (0.097) | | (0.072) | (0.139) | (0.023) | (0.080) | | – | |
| 85 | −0.048 | 0.206 | 1.002 | 2.549 | 0.332 | 0.498 | 21 | 0.967 | 0.060 |
| | (0.089) | (0.088) | (0.079) | (0.131) | (0.029) | (0.072) | | (120) | |
| | −0.032 | – | 1.113 | 2.597 | 0.336 | 0.421 | 21 | 0.958 | 0.067 |
| | (0.100) | | (0.071) | (0.146) | (0.024) | (0.072) | | – | |
| 120[a] | 0.203 | 0.135 | 0.800 | 1.654 | 0.178 | 0.343 | 21 | 0.920 | 0.072 |
| | (0.108) | (0.107) | (0.096) | (0.159) | (0.025) | (0.087) | | (47) | |
| | 0.213 | – | 0.872 | 1.685 | 0.181 | 0.293 | 21 | 0.918 | 0.074 |
| | (0.109) | | (0.078) | (0.160) | (0.026) | (0.079) | | – | |
| 120[b] | 0.161 | 0.167 | 0.811 | 1.684 | 0.187 | 0.357 | | | |
| | 0.162 | – | 0.913 | 1.726 | 0.193 | 0.297 | | | |

[a] Coefficients obtained by regression using Eq. (1), with log $K$ values at 120°C estimated by extrapolation from values at lower temperatures.
[b] Coefficients obtained by extrapolation from LSER values in the Table for lower temperatures.

Those values in italics ($r_1$, $c$) are either statistically insignificant ($P>0.001$) or marginally significant ($P>0.0001$). Thus, LSER equations are given in Table 8 both including and omitting the $r_1R_2$ term. The LSER coefficients at 120°C were obtained by two different methods. First, the log $K$ values at 120°C obtained by extrapolation (Table 7) were used as dependent variables in the MLR analysis via Eq. (1). Again, these results were calculated both with and without the $r_1R_2$ term. In the second method, the LSER coefficients obtained at the lower temperatures were extrapolated vs. $1/T$ to obtain estimated values for these coefficients at 120°C. Comparison of the LSER coefficient values at 120°C reveals excellent agreement between the values obtained by both methods.

Because of the lower operating temperatures the retention times of several solutes were too long, or peak shapes were too asymmetric to obtain reliable retention times. Thus, the total number of probe solutes used for characterization of TEA is less than optimal. The LSER results should therefore be considered as estimates at best; however, the $R^2$ values indicate good predictive ability for the LSER and the TEA values can be compared with the other N-containing phases in this study.

### *4.4. Correlation of LSER coefficient values with molecular structure*

In this study LSER coefficients at 120°C were obtained for four stationary phase materials with nitrogen-containing functional groups. In addition, LSER values for a few other amide-containing stationary phases have been previously reported [3,17]. Hallcomid M18(N,N-dimethyl stearamide) and Hallcomid M19/OL (N,N-dimethyl oleylamide) differ only in the presence of a C=C bond; the amide functional groups are the major contributors to polar solubility interactions. Flexol-8N8 [N,N′-bis(2-ethyl(2-ethylhexoate)-2-ethyl hexoamide)] has both amide and ester functional groups which can contribute to observed LSER coefficient values. The LSER coefficients for these phases and the fraction of total molecular mass represented by the polar functional groups are summarized in Table 9. In all cases, values for $b_1$ are statistically insignificant. Because of our interest in using structural/compositional

Table 9
LSER values and functional group fractions for amide coatings

| Coating | $c$ | $r_1$ | $s_1$ | $a_1$ | $l_1$ | $b_1$ | $n$ | $R^2$ | Std. error | Amide | Ester | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hallcomid M18OL | −0.421 | 0.092 | 0.687 | 1.56 | 0.586 | – | 202 | 0.991 | 0.040 | 0.0971 | – | 0.0971 |
| | (0.01) | (0.02) | (0.02) | (0.02) | (0.004) | | | | | | | |
| Hallcomid M18 | −0.351 | 0.091 | 0.575 | 1.52 | 0.593 | – | 202 | 0.993 | 0.042 | 0.0965 | – | 0.0965 |
| | (0.01) | (0.02) | (0.02) | (0.02) | (0.003) | | | | | | | |
| Flexol 8N8 | −0.483 | 0.024 | 0.757 | 1.27 | 0.572 | – | 202 | 0.996 | 0.035 | 0.0640 | 0.1365 | 0.2005 |
| | (0.01) | (0.02) | (0.02) | (0.02) | (0.003) | | | | | | | |

descriptors as predictors of solubility properties, preliminary correlations were performed. Specifically, the compositions of the stationary phases described above were correlated with observed values of the LSER coefficients for each phase.

Of the four phase characterized in this study, and the three others obtained from the literature, only two have significant $b_1$ values (Quadrol and TEA) which prevents meaningful correlation. Examination of these phases indicates that hydroxyl functional groups, which can act as weak to moderate H-bond donors, represent a significant fraction of the total molecular mass (23% and 34%, respectively). Similarly, the $r_1$ coefficient was determined to be statistically insignificant (or marginally significant) for all phases except PDAS ($r_1 = 0.343 \pm 0.061$) and the Hallcomids ($r_1 = 0.09 \pm 0.02$). Since the functional groups under study are more likely to affect polar interactions, the following analysis will examine the relative contribution of the N-containing functionalities to the values of $a_1$ and $s_1$.

### 4.5. Prediction of $a_1$ values

The value of the $a_1$ coefficient represents the relative H-bond basicity of the stationary phase. In general, the amines (Quadrol, TEP, TEA) exhibit greater H-bond basicity than the amides (Hallcomids, Flexol 8N8). This trend is consistent with expected basicity for N-functionalized solvents (amines > phenylamines > amides). The PDAS, a phenylamine, exhibits the lowest $a_1$ value in the set and does not follow the expected trend. This may be due to the polymeric nature of the PDAS phase – high molecular mass and possible steric hindrance may contribute to a decrease in the accessibility of the nitrogen in this compound.

The difficulty in determining the contribution of a given functional group to the value of a polar LSER coefficient lies in separating out the relative contributions of each in a compound which contains multiple and varied functionalities. PDAS, for example, is a polyester with tertiary amine and phenyl groups, as well as terminal OH or COOH groups. Evaluation of the contribution from the amines requires a method to correct for the contributions from the other functional groups in the phase. In a previous work the molecular mass fractions of a variety of polar functional groups were correlated with observed values of $a_1$ for a large set of stationary phases [11]. The value of $a_1$ could be predicted using one of the following equations:

$$a_1 = 1.409(\text{siloxane}) + 3.423(\text{ester}) + 4.090(\text{ether}) + 5.009(\text{OH}) + 0.549(\text{CH}_2) \quad (4a)$$

$$a_1 = 1.412(\text{siloxane}) + 3.517(\text{ester}) + 3.872(\text{ether}) + 8.969(\text{OH}) + 0.514(\text{CH}_2) \quad (4b)$$

Eq. (4a) was developed for a set of 61 stationary phases ($R^2 = 0.922$), which included three phases exhibiting significant H-bond donor behavior. Removal of these three phases and a few other sterically hindered phases reduced the stationary phase set to 55 phases and yielded Eq. (4b) ($R^2 = 0.990$). The coefficients in the equations represent the relative contribution of each of the functional groups to the observed $a_1$ value, while the functional groups (in parentheses) are expressed as the fraction of total molecular mass. These equations can be used to estimate the contribution $a_1$ values for the stationary phases in this work from those functional groups included in Eq. (4a and b). An $a_{\text{excess}}$ value, which represents the contributions to $a_1$ from functional

Table 10
Functional group fractions and $a_1$ values for coatings

| Coating | N | Ester[a] | OH | $CH_2$ | $a_1$ | $a_{calc.}$ | $a_{excess}$ |
|---|---|---|---|---|---|---|---|
| Hallcomid M18OL | 0.0450 | (0.0518) | – | 0.6343 | 1.56 | 0.508 | 1.052 |
| Hallcomid M18 | 0.0453 | (0.0514) | – | 0.7203 | 1.52 | 0.551 | 0.969 |
| Flexol | 0.0299 | (0.1706) | – | 0.3881 | 1.27 | 0.799 | 0.471 |
| Quadrol | 0.0958 | – | 0.2189 | 0.2873 | 1.964 | 1.254 | 0.710 |
| TEP | 0.3698 | – | – | 0.5916 | 2.81 | 0.304 | 2.506 |
| PDAS | 0.0532 | 0.2432 | 0.0016 | 0.3192 | 1.19 | 1.034 | 0.156 |
| TEA | 0.0938 | – | 0.3217 | 0.562 | 1.684 | 1.920 | −0.236 |

[a] In order to determine the contribution to observed $a_1$ values from nitrogen, the carbonyl fraction of the amides has been added to the ester values. The ester values in parentheses represent the molecular mass fraction of ester plus the amide carbonyl fraction.

groups not included in Eq. (4a and b), can be calculated by subtracting the estimated $a_1$ value from the value determined experimentally (i.e. from the LSER analysis).

The fractional compositions of the stationary phases under study here are presented in Table 10, along with $a_1$ (observed), $a_{calc.}$ (from Eq. (4a and b)), and $a_{excess}$ values. For the phases in the table, Eq. (4a) was used to obtain $a_{calc.}$ for Quadrol and TEA, since these phases exhibit significant H-bond acidity ($b_1$), while Eq. (4b) was used to obtain corresponding values of the remaining phases. When determining the $a_{calc.}$ values for the amide phases, the molecular mass fraction of the amide carbonyl was included in the ester molecular mass fraction. Thus, the $a_{calc.}$ values represent the contribution to the observed $a_1$ values solely from the nitrogen fraction. In Fig. 2, the $a_{excess}$ values are plotted vs. the fraction of N-functionality in the stationary phases. The plot indicates that the value of $a_1$ increases significantly with increasing amount of N-groups in the stationary phase, with a more dramatic increase for the amides than the amines. This observation is consistent with the differences in the chemical environment for nitrogen in an amide compared to an amine. In an amide, the nitrogen is

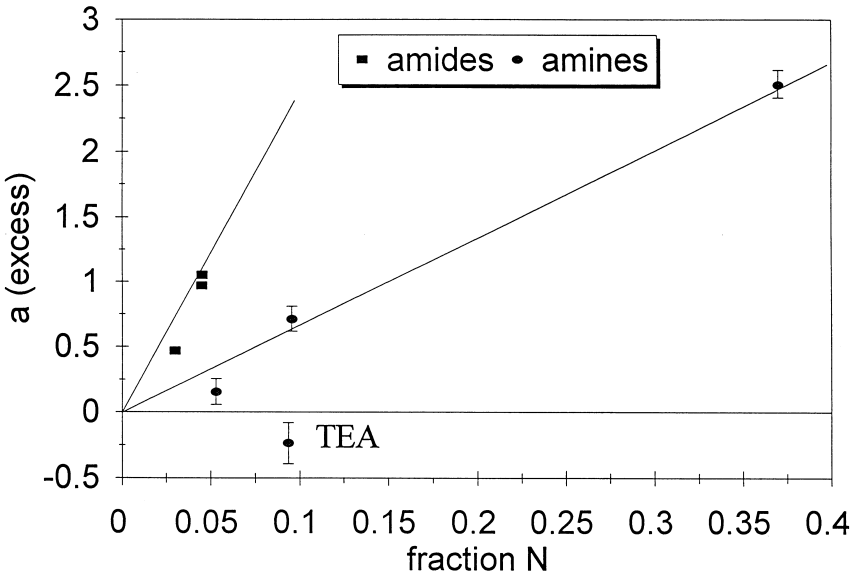


Fig. 2. Plot of $a_{excess}$ vs. the mass fraction of N-functional groups in the stationary phases. Drawn lines indicate differences in relative contribution from amide (■) and amine (●) functional groups.

bonded to a carbonyl carbon, and the basicity of the amide group is generally assigned to the carbonyl. Thus, our calculated excess $a_1$ values for the amides may reflect the increase in basicity of the carbonyl group in an amide relative to the basicity of a carbonyl in an ester. In amines, the nitrogen is bonded either to hydrogens or tetrahedral carbons, which have a much smaller effect on the nitrogen basicity. (The value for TEA is significantly over estimated; this may be due to the fact that TEA has a very low molecular mass compared to other stationary phases used in the development of Eq. (4a).

### *4.6. Prediction of $s_1$ values*

Unfortunately, predictive relationships similar to Eq. (4a and b) have not yet been developed for the prediction of $s_1$ values from structural information. However, since $s_1$ represents a combination of dipolarity and polarizability interactions then the value of $s_1$ should increase with polarizability of the functional groups in the stationary phase. Molecular and bond polarizabilities can be estimated using a method that considers average atomic polarizabilities ($\alpha$) and the atomic hybridization [20]. For our purposes, we are interested in the contribution of polar functional groups, particularly N-containing functionalities, to the observed $s_1$ values. Thus, the contribution to polarizability from the carbon–hydrogen backbones of these stationary phase materials was not considered. This is a reasonable omission since stationary phases that are exclusively saturated hydrocarbons generally have very low $s_1$ values. For example, squalane ($C_{30}H_{62}$) has an $s_1$ value of only 0.07.

The functional groups considered in the estimation of $s_1$ are given in Table 11, along with bond polarizabilities estimated using the method of Miller [20]. The relative contribution of these functional groups to the total polarizability was determined by multiplying the bond polarizability by the bond fraction (i.e. the number of each of the bonds in the functional group relative to the total number of bonds in the molecule). Carbon–hydrogen bonds were not included in the bond count for the reason discussed above. The individual bond fractions and the total polarizability for each stationary phase are given in the table.

The $s_1$ values were then plotted vs. total polarizabilities in Fig. 3. There is clearly a very strong correlation between bond polarizability and the observed $s_1$ value. TEA and Quadrol are slightly underpredicted based on the bond polarizability approach, whereas TEP is slightly overpredicted. The underprediction of the latter phases may be related to their H-bond donor capabilities. TEP is the only phase which contains primary and secondary amine moieties, whereas the nitrogens in TEP, Quadrol and PDAS are exclusively tertiary amines. Further evaluation of bond polarizabilities for estimation of $s_1$ appears warranted.

## 5. Conclusions

We present the LSER coefficients for a series of nitrogen-containing stationary phases, and compare these results with values for other similar materials previously reported. Correlation of the values of $s_1$ and $a_1$ with the structure/composition of the station-

Table 11
Bond fractions and polarizabilities

| Coatings | $s_1$ | $C_{sp4}$–O | C–N (amine) | O–H | N–H | C–O (ester) | C–N (amide) | C=O | $C_{Ar}$–$C_{Ar}$ | C=C | Total polarizability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bond polarizabilities | --> | 0.584 | 0.586 | 0.706 | 0.708 | 0.769 | 0.772 | 1.02 | 1.087 | 1.643 | |
| Hallcomid M18 | 0.687 | – | 0.0952 | – | – | – | 0.0476 | 0.0476 | – | 0.0476 | 1.002 |
| Hallcomid M18OL | 0.575 | – | 0.0952 | – | – | – | 0.0476 | 0.0476 | – | – | 0.924 |
| Flexol | 0.757 | – | 0.0606 | – | 0.0909 | 0.1212 | 0.0303 | 0.0606 | – | – | 1.057 |
| Quadrol | 1.034 | 0.1739 | 0.2609 | 0.2105 | – | – | – | – | – | – | 1.175 |
| TEP | 0.932 | – | 0.421 | – | 0.3684 | – | – | – | – | – | 1.280 |
| PDAS | 1.135 | 0.0952 | 0.0952 | 0.0013 | – | 0.0952 | 0.0476 | 0.0952 | 0.2855 | – | 1.413 |
| TEA | 0.872 | – | 0.250 | 0.250 | – | – | – | – | – | – | 1.095 |

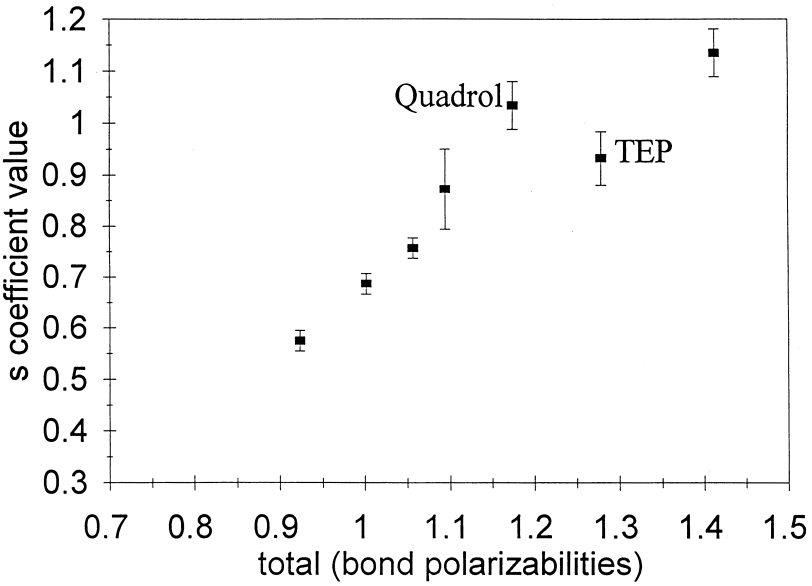


Fig. 3. Plot of $s_1$ values for amide and amine stationary phases vs. total polarizability. Polarizability was calculated as the sum of individual bond polarizabilities using data from Miller [20] as described in the text.

ary phase indicates that the N-containing functional groups contribute significantly to these values. The presence of appreciable OH fractions in two of these phases results in significant $b_1$ (H-bond donor) values, whereas the $r_1$ values were generally not statistically significant.

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