ELSEVIER

Journal of Chromatography A, 718 (1995) 357–369

JOURNAL OF CHROMATOGRAPHY A

# Characterization of cyano-functionalized stationary gas chromatographic phases by linear solvation energy relationships

Wentong Tian, David S. Ballantine, Jr.*

*Department of Chemistry, Northern Illinois University, DeKalb, IL 60115-2862, USA*

First received 28 March 1995; revised manuscript received 9 June 1995; accepted 20 June 1995

**Abstract**

The characterization of four cyano-containing gas chromatography stationary phases using a linear solvation energy relationship (LSER) of the type $\log K = c + r_1R_2 + s_1\pi_2^{*H} + a_1\sum \alpha_2^H + b_1\sum \beta_2^H + l_1 \log L^{16}$ was performed, and the results compared with LSER coefficients for other, previously studied phases. The coefficients obtained indicate that the presence of CN groups in these phases contributes significantly to the dipolarity–polarizability and H-bond acceptor ($s$ and $a$ values in the above LSER, respectively), but that these phases have very low or statistically insignificant $r$ values and $b$ values. The results are evaluated in terms of the development of quantitative structure solubility relationships to predict LSER coefficients.

## 1. Introduction

With the development of new materials there is a need for rapid characterization techniques to provide insight into the properties and capabilities of these materials. Because of the importance of solubility and solvation properties in many areas of chemistry, the characterization of solubility properties is of particular interest. Chromatographic techniques have been used extensively for the characterization and classification of liquid and polymeric phases since chromatographic partition coefficients, $K$, can be directly related to solute–solvent interactions [1–8]. The retention data can then be used to develop predictive equations which relate the $K$ values to a variety of physico-chemical parameters, including Gibbs free energies [9,10], quantum chemical descriptors [11], structural descriptors [12–15], and various solubility–solvation parameters [3,5,6,16–19].

Probably the most extensively utilized approach for characterization of chromatographic materials and related solvation processes is the use of linear solvation energy relationships, or LSERs [20]. Developed by Kamlett, Abraham and Taft, the LSER generally takes the form

$$\log K = c + r_1R_2 + s_1\pi_2^{*H} + a_1\sum\alpha_2^H + b_1\sum\beta_2^H + l_1 \log L^{16} \quad (1)$$

where each term in the equation refers to the ability of the solute and solvent to engage in specific interactions [19,20]. Those terms with the subscript 2 refer to solute properties. Specifically, $\alpha$ and $\beta$ represent H-bond donor acidity

* Corresponding author.

0021-9673/95/$09.50 
*SSDI* 0021-9673(95)00697-4

and H-bond acceptor basicity respectively, $\pi$ represents dipolarity and polarizability interactions, $R$ is the excess molar refraction, and $L^{16}$ is the solute gas–liquid partition coefficient into hexadecane at 25°C. The coefficients indicated by the subscript 1 represent the ability of the solvent phase to engage in complementary interactions, and are obtained by the MLR analysis, along with the regression constant, $c$. The strength of the LSERs is that they provide a model of the solvation process, with individual terms in the LSER describing the ability of the solute and solvent to engage in specific types of interactions. A prior knowledge of the solute parameters and solvent coefficients permits reliable prediction of the retention behavior of that solute. The labor-intensive nature of the LSER approach represents a significant disadvantage; a typical characterization of a single solvent phase often involves preparation of a chromatographic column with the phase of interest, followed by the determination of retention times for a large number of probe solutes. These retention data are then used in an MLR analysis to determine the coefficients for the solvent phase.

Alternatively, quantitative structure–retention studies (QSRR) have been used [12–15]. The QSRR methods correlate observed retention properties of a set of compounds (usually a homologous series or class) with a set of structural descriptors. These descriptors can include physical and/or chemical properties, (i.e., refractive index, dipole moment) or calculated indexes that encode structural information (i.e., molecular connectivity indexes). With the advanced computational power of personal computers, these structural descriptors can usually be routinely determined for even complicated molecular formulas. The advantage of the QSRR approach is the relative ease with which the descriptor sets can be developed. These approaches are still largely empirical, however, with no intuitive connection between the descriptors and the properties to be predicted. While the QSRR results can be extended to predict the retention behavior of other members of the series or class under study, application of the results to compounds outside the set is not advisable.

A recent study reported the successful application of QSRR methodology to prediction of LSER solvent coefficients [21]. Since the ability of solvent phases to engage in specific interactions is related to the molecular structure (i.e., types and arrangement of functional groups in the molecule), some correlation between solubility properties and molecular structure, and hence structural descriptors, would be expected. The advantage of such an approach is that it eliminates the need for extensive experimental studies. It permits the prediction of LSER coefficients that describe the solubility properties of the solvent phases from a simple set of molecular descriptors that are readily calculated.

Several factors limit the general applicability of this approach. First, development of the desired predictive relationships requires a large data base containing the LSER coefficients for representative solvent phases. The number of solvent phases that have been characterized by LSER methods is growing [17–19,22], but the functional groups that are adequately represented in this data set are limited. Another limitation is the identification of appropriate structural descriptors. The preliminary study used a simplistic set of descriptors consisting of the simple weight percents of the representative functional groups in the solvent molecular formula. While the final regression relationship had excellent predictive value, the descriptor set did not account for possible steric and/or inductive effects. The development of a better set of descriptors is needed. Current studies in our lab are focusing on these two areas.

The work reported here addresses the first problem by expanding the functional group representation of the solvent phase data set. Specifically, we have performed LSER characterization on a set of cyano-containing gas chromatographic (GC) stationary phases. This functional group is among those that were not adequately represented in the original data set [21]. Chromatographic determination of partition coefficients was performed following methods similar to

those described by Abraham et al. [23], followed by MLR determination of LSER coefficients as described previously. The LSER coefficients for a set of cyano-functionalized stationary phases are reported.

## 2. Experimental

### 2.1. Materials

The cyano-functionalized stationary phases characterized in this work are listed in Table 1, along with relevant information on stationary phase loading and densities at the GC operating temperature (120°C). The stationary phases and support (Chromosorb W-AW, 100/120 mesh) were obtained from Alltech. The probe solutes are listed in Table 2, along with relevant solvation parameters. These solutes were obtained from Aldrich Chemical. All materials were 95–99% purity and were used as received.

Stationary phases were selected based on the presence of cyano groups. Of the phases listed in Table 1, tris(cyanoethoxy) propane (TCEP) had been previously characterized by LSER methods [8,17,20,22,23]. It was included in the test group to serve as a control and to validate our methodology and results.

The solute probes were selected from over 200 solvents for which solvation parameters were known [20]. Several factors were considered in selecting the final 34 solutes. First, they represent a wide variety of compounds and functional groups. Second, the values of the solvation parameters span the entire range of known values for a given parameter. Finally, the retention times of the solutes were not impractically long under the experimental conditions as to make the measured retention times unreliable. The final set of solute probes met these criteria for most experimental conditions, although a modified subset was used for retention studies at lower temperatures, as described below.

### 2.2. Column preparation

Column packings were prepared by dissolving approximately 3 g of the stationary phase in 100 ml of chloroform and adding 15 to 25 g of support to create a slurry. The solvent was slowly evaporated with gentle agitation to leave the stationary phase coated on the support. Coated supports were then packed into glass columns (182.88 × 0.635 cm O.D., 2.0 mm I.D.).

Table 1
Stationary phases and percent loads during study

| Coating | Molecular formula | Density (g/ml) (at 393 K) | Load (%) (range)[a] |
|---|---|---|---|
| Tris(cyanoethoxy) propane (TCEP) | $CH_2-O-CH_2CH_2CN$<br>$\vert$<br>$CH-O-CH_2CH_2CN$<br>$\vert$<br>$CH_2-O-CH_2CH_2CN$ | 1.029 | 10.7–8.96 |
| Tetra(cyanoethoxy) pentaerythritol (TCEPE) | $C(CH_2-O-CH_2CH_2CN)_4$ | 1.048 | 15.1 |
| Sebaconitrile | $NC-CO(CH_2)_6-COCN$ | 0.843 | 12.3–9.5 |
| Benzyl cyanide | $C_6H_5-CH_2-CN$ | 0.932 | 11.5–1.2 |

[a] Loss of stationary phases noted over a period of 3 months for TCEP. No losses noted for TCEPE during analysis time of 20 h. Losses for other stationary phases are provided in Figs. 1 and 2.

Table 2
Summary of solute parameters and coating log $K$ values

| Solute | $R$ | $\pi$ | $\alpha$ | log ($L^{16}$) | $\beta$ | log $K$ values | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | TCEP 120 | SB 120 | TCEPE 120 | BC | | | |
| | | | | | | | | | 60 | 75 | 90 | 120 |
| 2-Butanone | 0.166 | 0.7 | 0 | 2.287 | 0.51 | | 1.767 | 1.527 | | | | |
| Decane | 0 | 0 | 0 | 4.686 | 0 | | 2.145 | 1.585 | | | | |
| Dodecane | 0 | 0 | 0 | 5.696 | 0 | | 2.616 | 2.026 | | | | |
| Triethylamine | 0.101 | 0.15 | 0 | 3.04 | 0.79 | 0.759 | 1.444 | 1.017 | | | | |
| Butanol | 0.224 | 0.42 | 0.37 | 2.601 | 0.48 | 1.787 | 2.096 | 1.927 | | | | |
| Chlorobenzene | 0.718 | 0.65 | 0 | 3.657 | 0.07 | 1.971 | 2.424 | 2.061 | | | | |
| Pyridine | 0.631 | 0.84 | 0 | 3.022 | 0.52 | 2.098 | 2.347 | 2.102 | | | | |
| Nonyl aldehyde | 0.15 | 0.65 | 0 | 4.859 | 0.45 | 2.199 | 3.063 | 2.575 | | | | |
| Cyclohexanol | 0.46 | 0.54 | 0.32 | 3.758 | 0.57 | 2.367 | 2.738 | 2.562 | | | | |
| $n$-Octanol | 0.199 | 0.42 | 0.37 | 4.619 | 0.48 | 2.401 | 3.162 | 2.772 | | | | |
| Propanoic acid | 0.233 | 0.65 | 0.6 | 2.29 | 0.45 | 2.499 | 2.592 | 2.543 | | | | |
| N',N-DMF | 0.367 | 1.31 | 0 | 3.173 | 0.74 | 2.959 | 3.001 | 2.872 | | | | |
| N',N-DMA | 0.363 | 1.33 | 0 | 3.717 | 0.78 | 3.16 | 3.227 | 3.054 | | | | |
| Nitrobenzene | 0.871 | 1.11 | 0 | 4.557 | 0.28 | 3.253 | 3.507 | 3.291 | | | | |
| Aniline | 0.955 | 0.96 | 0.26 | 3.934 | 0.41 | 3.297 | 3.412 | 3.267 | | | | |
| Phenol | 0.805 | 0.89 | 0.6 | 3.766 | 0.3 | 3.493 | 3.681 | 3.563 | | | | |
| Cyclohexane | 0.305 | 0.1 | 0 | 2.964 | 0 | 0.637 | 1.324 | 0.933 | 2.091 | 1.926 | 1.753 | 1.471 |
| Methanol | 0.278 | 0.44 | 0.43 | 0.97 | 0.47 | 1.428 | 1.267 | 1.277 | 2.163 | 1.887 | 1.675 | 1.253 |
| Heptane | 0 | 0 | 0 | 3.173 | 0 | 0.429 | 1.32 | 0.861 | 2.166 | 1.944 | 1.781 | 1.447 |
| Ethanol | 0.246 | 0.42 | 0.37 | 1.485 | 0.48 | 1.397 | 1.428 | 1.384 | 2.387 | 2.068 | 1.894 | 1.453 |
| Acetone | 0.179 | 0.7 | 0.04 | 1.696 | 0.49 | 1.449 | 1.502 | 1.384 | 2.396 | 2.124 | 1.922 | 1.511 |
| Isopropanol | 0.212 | 0.36 | 0.33 | 1.764 | 0.56 | 1.339 | 1.525 | | 2.43 | 2.144 | 1.918 | 1.479 |
| Butylamine | 0.224 | 0.35 | 0.16 | 2.618 | 0.61 | 1.312 | 1.605 | 1.456 | 2.536 | 2.302 | 2.068 | 1.674 |
| Tetrahydrofuran | 0.289 | 0.52 | 0 | 2.636 | 0.48 | 1.354 | 1.596 | 1.433 | 2.572 | 2.303 | 2.081 | 1.66 |
| Trichloromethane | 0.425 | 0.49 | 0.15 | 2.48 | 0.02 | 1.514 | 1.702 | | 2.603 | 2.397 | 2.177 | 1.821 |
| Ethylacetate | 0.106 | 0.62 | 0 | 2.314 | 0.45 | 1.342 | 1.606 | 1.411 | 2.605 | 2.347 | 2.115 | 1.699 |
| Benzene | 0.61 | 0.52 | 0 | 2.786 | 0.14 | 1.391 | 1.781 | 1.514 | 2.612 | 2.35 | 2.138 | 1.729 |
| Dichloroethane | 0.416 | 0.64 | 0.1 | 2.573 | 0.11 | 1.678 | 1.933 | 1.761 | 2.796 | 2.532 | 2.293 | 1.866 |
| Toluene | 0.601 | 0.52 | 0 | 3.325 | 0.15 | 1.577 | 2.093 | 1.705 | 2.975 | 2.693 | 2.486 | 2.059 |
| 1,4-Dioxane | 0.329 | 0.75 | 0 | 2.892 | 0.64 | 1.842 | 2.082 | 1.954 | 3.067 | 2.777 | 2.525 | 2.062 |
| Acetic acid | 0.265 | 0.65 | 0.61 | 1.753 | 0.44 | 2.334 | 2.243 | 2.359 | 3.204 | 2.881 | 2.618 | 2.114 |
| N-hexylamine | 0.197 | 0.35 | 0.16 | 3.655 | 0.61 | 1.624 | 2.215 | 1.981 | 3.296 | 2.976 | 2.717 | 2.219 |
| 1-Nitropropane | 0.242 | 0.95 | 0 | 2.894 | 0.31 | 2.241 | 2.499 | 2.259 | 3.494 | 3.174 | 2.861 | 2.328 |
| Anisole | 0.708 | 0.75 | 0 | 3.89 | 0.29 | 2.289 | 2.734 | 2.457 | 3.758 | 3.402 | 3.106 | 2.546 |

Both the columns and packing materials were treated with a silanizing agent prior to coating to eliminate active sites and minimize interfacial adsorption contributions to observed retention. The packed columns were conditioned for 24 h at 150°C prior to performing retention studies.

The weight percent of stationary phase on the column was determined by packing 0.5 g of coated support into a vessel and weighing accurately ($\pm$ 0.0002 g). The support was then washed with 50 ml of chloroform to dissolve and remove the adsorbed stationary phase. The remaining support was then dried, and the mass determined. This process was repeated until a constant support mass was obtained. Percent loading determinations were performed both before and after the retention studies. In addition, blank studies were performed on uncoated

support to verify the reliability of the procedures.

It has been reported that vigorous extraction methods (e.g., Soxhlet) may be needed to quantitatively remove stationary phases from the adsorbent support [25]. However, initial mass loadings determined using the simple extraction method described above agreed very well with loadings calculated from the masses of support and stationary phase used to prepare the packings. In addition, the blank studies showed little or no change in mass of the adsorbent support during extraction. This indicates that fine powders did not contribute significantly to the mass loading determinations. These observations tend to support the reliability of the mass loading data used in the calculation of $K$ values.

### 2.3. Retention studies

All retention studies were performed on an HP-5880A gas chromatograph with a heated on-column injector and a flame ionization detector. Helium carrier pressure was adjusted to 40–55 p.s.i. (275.79–379.21 kPa) to provide a column flow-rate of approximately 25 ml/min. The column oven temperature was maintained at 120°C for all phases except the benzyl cyanide. Significant bleeding losses of benzyl cyanide were observed at this elevated temperature, so retention studies were performed at 60°C, 75°C, and 90°C, and results were extrapolated to 120°C as described in the section Results and Discussion.

Solute retention times were used to calculate the specific retention volumes and partition coefficients for the solute probes on the stationary phase using the following relationship,

$$V_g = \frac{jFt_r' 273}{W \quad T_c} = \frac{K 273}{\rho_s \quad T_c} \qquad (2)$$

where $j$ is a 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 corrected solute retention time, $W$ is the weight of stationary phase, $K$ is the partition coefficient, and $\rho_s$ is the density of the stationary phase at the column temperature, $T_c$. The solute retention time is corrected for both the dead volume of the column and for retention due to adsorption on the solid support material. Adsorption contributions were determined by performing retention studies on a column packed only with the GC support material. Since the column and packing were previously deactivated these effects were generally small, $>2\%$ compared to the observed $K$ values for the solutes on the stationary phase coatings.

Other workers have reported that chromatographic retention is influenced by factors other than the gas–liquid partition coefficient, $K_L$, and that the retention data must be corrected for these factors in order to accurately determine the partition coefficient [8,26]. These factors can include adsorption at the gas–liquid interface, and adsorption at the liquid–solid interface. Interfacial adsorption is less significant at higher temperatures ($>100$°C) and at larger phase loadings ($>10\%$) [26]. Given that the majority of these studies were performed at 120°C with phase loadings ca. 10% or greater, and that the support materials were deactivated prior to use, we have assumed that the effect of interfacial adsorption on the results reported here are minimal.

The stationary phase densities at the operating column temperature(s) were determined by a thermal expansion technique. A graduated glass tube was attached to the neck of a glass bulb of known volume. A known mass of the stationary phase was then placed in the glass bulb, and the volume change was measured as a function of temperature as the bulb was heated in a water bath. The density of the stationary phase at the operating column temperature was measured, or calculated by extrapolation. Density values provided in Table 2 were used in the calculation of $K$ via Eq. 2. The reliability of the above method can be evaluated by comparing the density of TCEP reported in Table 2 (1.029 g/ml) with a literature value of 1.028 g/ml obtained using data from Ref. [26]. The results are in excellent agreement.

### 2.4. Correction for stationary phase bleed losses during analysis

Since the reliability of the LSER results requires an accurate calculation of the thermodynamic retention property (either partition coefficient, $K$, or specific retention volume, $V_g$), the mass of the stationary phase on the column at any time during the retention studies must be known. Two of the stationary phases, benzyl cyanide and sebaconitrile, exhibited significant bleeding losses during the retention studies. To permit accurate calculation of the partition coefficient it was necessary to correct for stationary phase loss during the retention studies. Corrections were accomplished by tracking the retention time of a standard solute (isopropanol) during the course of the retention studies. Once the studies were concluded and the column was removed, the weight percentage and total mass of stationary phase on the column at the conclusion of the study were determined. From the final mass of stationary phase and the final corrected retention time for isopropanol the partition coefficient for isopropanol on that phase was calculated. The mass of stationary phase on the column at any point in the analysis could then be calculated from the value of $K$ and the retention time of isopropanol on the column at that point in the analysis.

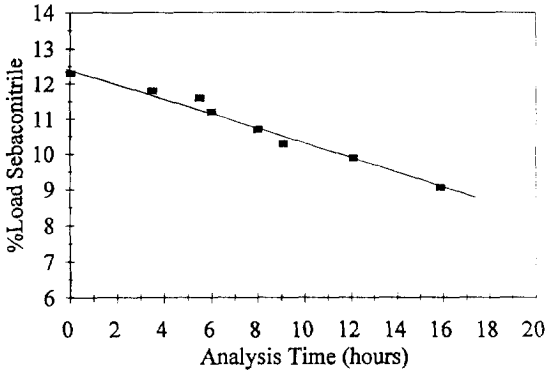


Fig. 1. Plot of % load of sebaconitrile on the GC packed column versus analysis time at 120°C (back-calculated from retention times of isopropanol).

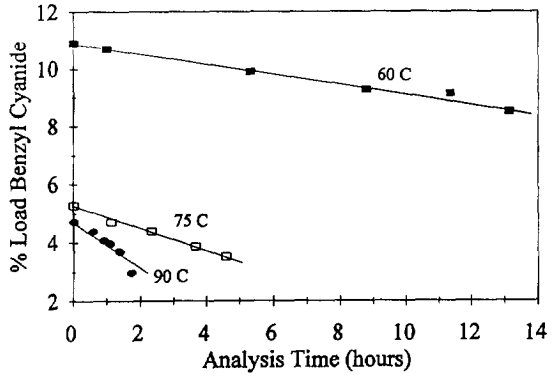


Fig. 2. Plot of % load of benzyl cyanide on the GC packed column versus analysis time at 60°C (■), 75°C (□), and 90°C (●).

Plots of stationary phase loss versus analysis time are presented in Fig. 1 for sebaconitrile (at 120°C), and in Fig. 2 for benzyl cyanide (at 60°C, 75°C, and 90°C). The other two stationary phases, TCEP and TCEPE, did not exhibit significant losses during the course of the retention studies.

## 3. Results and discussion

### 3.1. Multiple linear regression analysis

The retention data for the solutes in Table 2 were used to calculate partition coefficients, $K$, on a particular stationary phase using Eq. 2. These $K$ values were then used as the dependent variable in an LSER of the form

$$\log K = c + r_1 R_2 + s_1 \pi_2^{*H} + a_1 \sum \alpha_2^H + b_1 \sum \beta_2^H + l_1 \log L^{16} \quad (3)$$

where the terms with the subscript 2 are the solvation parameters for the solutes found in Table 2, and are taken from Ref. [20]. The experimentally determined $\log K$ values are summarized in Table 2, and were used to obtain the LSER coefficients for the stationary phases by MLR using Eq. 3.

Table 3
Comparison of LSER coefficients[a] for TCEP

| Phase = TCEP | $c$ | $r$ | $s$ | $a$ | $b$ | $l$ | $n$ | $R^2$ | S.D. | $F$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Patte et al.(1) | −1.76 | 0.36 | 1.84 | 1.81 | 0.45 | 0.374 | 168 | 0.968 | 0.15 | 980 | [17] |
| | (0.04) | (0.07) | (0.08) | (0.08) | (0.11) | (0.009) | | | | | |
| | −1.75 | 0.23 | 2.12 | 1.94 | – | 0.38 | 168 | 0.964 | 0.16 | 1091 | [20] |
| | (0.04) | (0.06) | (0.06) | (0.08) | | (0.01) | | | | | |
| (2) | −1.69 | 0.26 | 1.93 | 1.88 | – | 0.37 | 199 | 0.996 | 0.06 | 12067 | [20] |
| Poole(1) | −0.489 | 0.278 | 1.913 | 1.678 | – | 0.290 | 40 | 0.997 | 0.056 | 1449 | [22] |
| (2) | −0.670 | 0.202 | 1.816 | 1.792 | 0.244 | 0.332 | 62 | 0.9978 | 0.041 | 5080 | [24] |
| (3) | −0.744 | 0.116 | 2.088 | 2.095 | 0.261 | 0.370 | 39 | 0.998 | 0.025 | 4177 | [8] |
| | (0.029 | (0.017) | (0.025) | (0.038) | (0.031) | (0.005) | | | | | |
| | −0.697 | 0.050 | 2.215 | 2.267 | – | 0.365 | 39 | 0.996 | 0.042 | 1742 | [8] |
| | (0.049) | (0.026) | (0.034) | (0.055) | | (0.008) | | | | | |
| This work | −0.58 | 0.328 | 1.81 | 1.75 | 0.098 | 0.317 | 31 | 0.997 | 0.042 | 2044 | |
| | (0.03) | (0.05) | (0.03) | (0.04) | (0.043) | (0.0096) | | | | | |
| | −0.56 | 0.27 | 1.86 | 1.77 | – | 0.36 | 31 | 0.997 | 0.045 | 2160 | |
| | (0.03) | (0.04) | (0.03) | (0.04) | | (0.01) | | | | | |

[a] LSER coefficients obtained from references indicated. Standard error associated with individual coefficients provided in parentheses.

### 3.2. Results for TCEP

Our LSER results for TCEP are summarized in Table 3. The TCEP phase was included in this study to validate the methodology. Previous LSER characterizations were performed by several groups using chromatographic retention data reported by Patte et al. [5] and Poole and coworkers [10,24]. Results of those studies are included in Table 3 for comparison.

There are some significant differences between the LSER results reported in Table 3. The coefficient values in the first line [Patte et al. (1)] were reported by Abraham et al. [17] using a previous set of solute parameters ($\alpha$, $\beta$, $\pi^*$), whereas the latter results, also reported by Abraham [20], were obtained using updated solvation parameters which are based on a more effective scale of hydrogen-bond acidity and basicity ($\alpha^H$, $\beta^H$, $\pi^{*H}$) [5]. Thus, the coefficient values reported for Patte et al. (1) cannot be directly compared with our results. These data are included here because they include standard error values associated with the LSER coefficients and they demonstrate how the coefficient values change when the regression analyses are performed without inclusion of the $\beta$ term. Such insights are useful when interpreting the results of the current study. Another difference involves the solubility property used in the LSER calculations. For the Patte et al. data sets the solubility property used was $\log SP = \log K(\text{solute}) - \log K(\text{decane})$, whereas for the other studies $\log SP = \log K(\text{solute})$. This difference does not affect the calculated coefficient values but appears as a significant difference in the regression constant, $c$.

The LSER results of Poole in Table 3 can be found in the references indicated in the table and were obtained using retention data reported in Refs. [10,24]. It is worth noting that the Poole data set has been rigorously corrected for interfacial adsorption, whereas the Patte et al. data set and the data reported in this work were not. In spite of this, the LSER results for TCEP in Table 3 are in very good agreement, with the exception of Poole (3). Given that the LSER results of Poole (1) and Poole (2) were obtained using (nominally) the same data sets as Poole (3), these differences cannot be adequately ex-

plained. The fact that our results are generally in good agreement with previously reported values supports the assumption that interfacial adsorption effects were negligible under the experimental conditions used in this study.

It should be noted that the $b_1\beta_2$ was found to be not statistically significant in this study, as well as in most of the previously reported results listed in Table 3, so that exclusion of this term from the final regression analysis is justified. The small $b_1$ coefficient is consistent with the molecular structure of TCEP, provided in Table 1, which contains no acidic protons. The standard errors, correlation coefficients ($R^2$) and $F$-statistics associated with the LSER equation from the current study compare favorably with those obtained in previous studies, even though we are using a smaller solute set ($n = 31$). The values of the coefficients also compare favorably with results of previous studies, with the exception of Poole (3) noted above. Given the range of values reported from other studies, the results presented here appear quite reasonable.

Obtaining LSER coefficients comparable to previously reported values provides confidence regarding the representative nature of the solute subset used in our studies, and the validity of our methodology.

### 3.3. Results for TCEPE, sebaconitrile, and benzyl cyanide

Results for TCEPE and sebaconitrile are presented in Table 4. As was the case for TCEP, the $b_1\beta_2$ term was found to be not statistically significant. In addition, the $r_1R_2$ term was found to be not significant for sebaconitrile, and marginally significant for TCEPE.

The benzyl cyanide was found to be more volatile than the other coatings, so that significant bleed losses were noted at higher column operating temperatures. The rapid loss of stationary phase at 120°C made accurate experimental determination of $K$ values difficult, since the actual weight percentage of stationary phase on the column during a given analysis was in doubt. More reliable retention data were obtained for a selected subset of solutes at lower temperatures (60, 75, and 90°C) and these data were used to calculate $K$ values for these solutes at 120°C by extrapolation using the relationship

$$\log K = c_1 + c_2\frac{1}{T} \quad (4)$$

where $c_1$ and $c_2$ are regression constants. The $\log K$ values obtained at the lower temperatures were plotted versus $1/T$ in Kelvin, and the best-fit equation was used to calculate $\log K$ at 393 K (120°C). The $R^2$ values for the regression results were $>0.992$ for all solutes tested, with the exception of ethanol ($R^2 = 0.959$). All experimentally obtained $\log K$ values are included in Table 2, along with the $\log K$ values at 120°C calculated by extrapolation using Eq. 4.

The $\log K$ values from Table 2 were then used in the MLR calculation of the LSER coefficient values for benzyl cyanide at these temperatures. The results are summarized in Table 5. Alter-

Table 4
LSER coefficients for TCEPE and sebaconitrile

| Phase | $c$ | $r$ | $s$ | $a$ | $b$ | $l$ | $n$ | $R^2$ | S.D. | $F$ |
|---|---|---|---|---|---|---|---|---|---|---|
| TCEPE | −0.57 | 0.09 | 1.51 | 1.77 | −0.001 | 0.453 | 32 | 0.995 | 0.048 | 1370 |
| | (0.04) | (0.05) | (0.04) | (0.05) | (0.05) | (0.009) | | | | |
| | −0.57 | 0.09 | 1.51 | 1.77 | – | 0.453 | 32 | 0.996 | 0.047 | 1778 |
| | (0.03) | (0.05) | (0.03) | (0.04) | | (0.009) | | | | |
| Sebaconitrile | −0.42 | 0.03 | 1.32 | 1.46 | −0.048 | 0.541 | 34 | 0.995 | 0.051 | 1248 |
| | (0.04) | (0.05) | (0.04) | (0.05) | (0.049) | (0.009) | | | | |
| | −0.44 | 0.05 | 1.30 | 1.45 | – | 0.543 | 34 | 0.995 | 0.051 | 1561 |
| | (0.04) | (0.04) | (0.03) | (0.05) | | (0.009) | | | | |

Table 5
LSER coefficients for benzyl cyanide versus temperature

| Temp. | LSER coefficients | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (°C) | *c* | *r* | *s* | *a* | *l* | *b* | $R^2$ | S.D. | *F* |
| 60 | 0.120** | −0.173** | 1.575 | 1.647 | 0.636 | 0.089** | 0.985 | 0.059 | 221 |
| | (0.088) | (0.103) | (0.077) | (0.114) | (0.028) | (0.080) | | | |
| | 0.133** | −0.223* | 1.612 | 1.688 | 0.639 | – | 0.984 | 0.059 | 271 |
| | (0.088) | (0.094) | (0.068) | (0.109) | (0.028) | | | | |
| 75 | 0.033** | −0.189 | 1.463 | 1.501 | 0.604 | 0.016** | 0.992 | 0.040 | 442 |
| | (0.06) | (0.070) | (0.053) | (0.078) | (0.019) | (0.055) | | | |
| | 0.036** | −0.198 | 1.471 | 1.508 | 0.605 | – | 0.992 | 0.039 | 554 |
| | (0.057) | (0.061) | (0.045) | (0.071) | (0.018) | | | | |
| 90 | −0.010** | −0.149* | 1.317 | 1.387 | 0.564 | 0.0004** | 0.992 | 0.037 | 402 |
| | (0.056) | (0.066) | (0.049) | (0.073) | (0.018) | (0.051) | | | |
| | −0.010** | −0.149 | 1.318 | 1.387 | 0.564 | – | 0.992 | 0.036 | 545 |
| | (0.053) | (0.057) | (0.041) | (0.066) | (0.017) | | | | |
| 120[a] | −0.125* | −0.143* | 1.108 | 1.162 | 0.504 | −0.085* | 0.991 | 0.033 | 264 |
| | (0.049) | (0.057) | (0.043) | (0.063) | (0.015) | (0.044) | | | |
| | −0.138 | −0.095** | 1.069 | 1.123 | 0.502 | – | 0.990 | 0.036 | 418 |
| | (0.053) | (0.056) | (0.041) | (0.065) | (0.017) | | | | |
| 120[b] | – | −0.914 | 1.073 | 1.123 | 0.502 | – | | | |

Values marked with asterisks are either statistically insignificant (**: $P > 0.1$) or marginally significant (*: $P > 0.02$). In all cases, $n = 18$.

[a] Values obtained from extrapolated log *K* values.

[b] Values obtained by extrapolation from LSER coefficients at lower temperatures.

natively, the LSER coefficients for benzyl cyanide at 120°C could be estimated by extrapolation from the coefficients obtained at the lower experimental temperatures. These estimated LSER coefficient values are also included in Table 5, and are in good agreement with those obtained from extrapolated log *K* values. As was noted for TCEPE and sebaconitrile, the $b_1\beta_2$ and $r_1R_2$ terms were found to be insignificant or marginally significant in many cases. In addition, the significance of the regression constant, $c_1$, is questionable for this coating.

### 3.4. Residual analyses and correlation matrix

The correlation matrix for the solute set is presented in Table 6 and indicates no significant correlation among the variables used in the regression. Residuals analyses were performed to ensure that there were no correlations be-

Table 6
Correlation matrix for solute set

| | $R_2$ | $\pi_2^H$ | $\alpha_2^H$ | $\beta_2^H$ | $\log L^{16}$ |
|---|---|---|---|---|---|
| $R_2$ | 1.00 | | | | |
| $\pi_2^H$ | 0.572 | 1.00 | | | |
| $\alpha_2^H$ | 0.057 | −0.015 | 1.00 | | |
| $\beta_2^H$ | −0.113 | 0.408 | 0.179 | 1.00 | |
| $\log L^{16}$ | 0.155 | −0.129 | −0.323 | −0.261 | 1.00 |

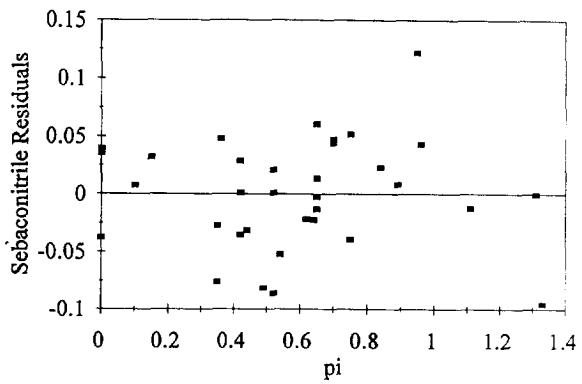


Fig. 3. Plot of $\log K$ residuals (observed − calculated) for sebaconitrile versus $\pi$.

tween residuals and the regression variables. The residual values (i.e., the difference between calculated and observed $K$ values) were plotted versus the various experimental parameters to check for correlations. The existence of a correlation indicates a possible systematic bias in the data set. Calculated residuals for all $\log K$ values on all stationary phases were plotted versus $\log K$, $\alpha$, $\beta$, $\pi$, $s$, and $l$. Examples of typical residual plots are provided in Figs. 3 and 4 for the residuals of sebaconitrile versus $\pi$ (Fig. 3) and TCEPE versus $\log K$ (Fig. 4). These plots indicate no significant correlation with these variables. Similarly, random residual plots were obtained for all coatings/parameters in this study, indicating that the LSER results are statistically valid.

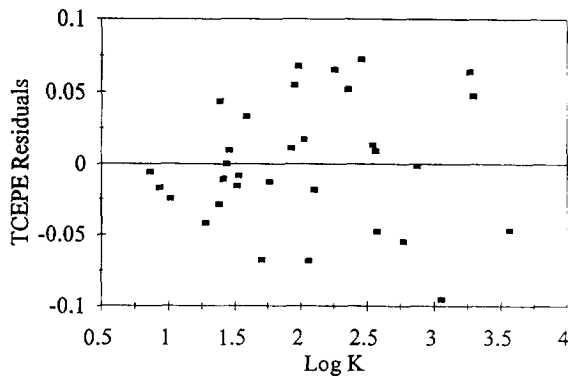


Fig. 4. Plot of $\log K$ residuals (observed − calculated) for TCEPE versus $\log K$.

### 3.5. Interpretation of LSER coefficient values

The calculated LSER coefficient values for the coatings characterized in this study are summarized in Table 7 along with other relevant data, including molecular masses and the fraction CN (by mass) in the compound. In addition, we have included values for other CN-functionalized materials, obtained from a literature search. The other coatings are siloxane polymers with varying percentages of CN functionalization, as indicated in the table. The majority of coatings were characterized at 120°C ( ± 1.4) and can be compared directly. The coefficient values for SXCN were obtained at lower temperatures, and there are insufficient determinations to permit reliable extrapolation to 120°C, so that direct comparison of the SXCN results with other coatings is not possible. The SXCN results are included in the table for general interest.

Structurally, the CN functional groups represent a significant percentage of the total mass of these coatings, ranging from 3.3% (OV105) up to 31% (TCEP). Other polar functional groups represented in these coatings include ether linkages (TCEP, TCEPE), carbonyl (sebaconitrile), and siloxane (OV105, OV225, OV275, XF1150, SXCN). Because of its polarity and its terminal position in the molecular structures, the cyano groups would be expected to have a significant impact on those coefficients which reflect polarity interactions.

With the exception of TCEP and OV275, these coatings exhibit very small and/or statistically insignificant $r$ values. This indicates that these coatings have little ability to interact with solute lone-pair and $\pi$ electrons. These coatings do exhibit relatively large $s$ and $a$ values, representative of dipolarity–polarizability and H-bond acceptor interactions, respectively. As expected, the values of these coefficients correlate with the relative fraction of CN in the coating, as seen in Fig. 5 (for $a$) and Fig. 6 (for $s$). The relatively large regression slopes, provided in the figures,

Table 7
Summary of LSER coefficients for cyano-functionalized coatings

| Coating[a] | $M_r$[b] | $r$ | $s$ | $a$ | $l$ | $n$ | CN (fraction) | Ref. |
|---|---|---|---|---|---|---|---|---|
| TCEP | 252 | 0.27 | 1.86 | 1.77 | 0.36 | 31 | 0.3095 | |
| TCEPE | 348 | 0.09 | 1.51 | 1.77 | 0.453 | 32 | 0.299 | |
| Sebaconitrile | 192 | 0.05 | 1.3 | 1.45 | 0.543 | 34 | 0.271 | |
| Benzyl cyanide | 117 | −0.095 | 1.07 | 1.123 | 0.502 | 18 | 0.222 | |
| OV105 | 30000 | −0.038 | 0.395 | 0.368 | 0.499 | 39 | 0.0332 | [22] |
| (5% cyanoethyl) | | −0.062 | 0.364 | 0.407 | 0.494 | 62 | | [8] |
| OV225 | 8000 | 0.015 | 1.214 | 0.964 | 0.462 | 39 | 0.0969 | [22] |
| (25% cyanopropyl/25% phenyl) | | −0.036 | 1.226 | 1.065 | 0.466 | 62 | | [8] |
| OV275 | 5000 | 0.388 | 1.902 | 1.644 | 0.241 | 32 | 0.283 | [22] |
| (100% cyanoallyl) | | | | | | | | [8] |
| XF1150 | ??? | 0.018 | 1.443 | 1.445 | 0.424 | 203 | 0.228 | [28] |
| (50% cyanoethyl) | | | | | | | | |
| SXCN (at 298 K) | ??? | 0 | 2.283 | 3.032 | 0.773 | 52 | 0.283 | [19] |
| (100% cyanopropyl) (at 343 K) | | 0.28 | 1.518 | 2.110 | 0.555 | 52 | | [19] |

[a] LSER values for TCEP, TCEPE, sebaconitrile, and benzyl cyanide taken from current study. Values for OV105, OV225, and OV275 from references indicated.
[b] Molecular mass values for OV phases taken from Ref. [29].

are indicative of the effect of CN on these values.

The CN-group contribution to the observed $a$ value can be estimated in the following manner. Previously reported results provided a predictive equation for calculation of the LSER $a$ coefficient based on the relative abundance of polar atoms and/or functional groups [21]. This relationship was given as

$$coef.a = 1.412(Si\text{–}O) + 3.517(ester) + 3.872(ether) + 8.969(OH) + 0.514(CH_2) \quad (5)$$

As noted earlier, most of the coatings used in this study contained small fractions of the functional groups in Eq. 5, with the exception of the hydroxyl (OH) which is not present in any of these coatings. Use of the above equation per-

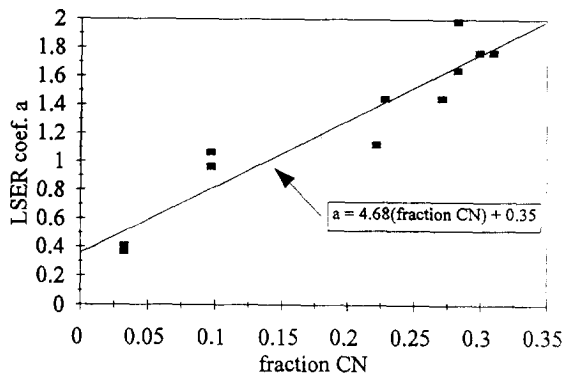


Fig. 5. Plot of LSER $a$ values for stationary phases in Table 6 versus fraction of CN in the coatings. Linear regression results shown in box.

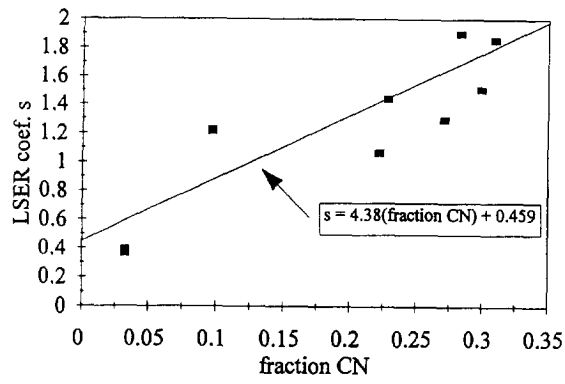


Fig. 6. Plot of LSER $s$ values for stationary phases in Table 6 versus fraction of CN in the coatings. Linear regression results shown in box.

mits calculation of the contributions to the value of $a$ from these groups. We define $a_{excess}$ as the difference between the observed $a$ value (from Table 7) and the estimated $a$ contributions from Eq. 5. This $a_{excess}$ can be attributed to the CN groups in these coatings. A plot of $a_{excess}$ versus fraction CN is provided in Fig. 7. Five of the seven coatings (OV105, OV225, OV275, XF1150, and benzyl cyanide) exhibit a nearly linear correlation versus CN ($R^2 = 0.91$, slope = 5.4). The siloxane and phenyl groups present in these coatings are very weak H-bond acceptors, so that the majority of the $a$ value would be expected to arise from the CN groups. The three outlier coatings (TCEP, TCEPE, and sebaconitrile) contain significant fractions of other strong H-bond acceptor groups, including carbonyl and ether linkages. As was noted in the previous study [1], steric and inductive effects and the presence of other functional groups would be expected to mediate the influence of the CN groups on these values, and could account for the deviation observed for these coatings.

The slopes observed in Figs. 5–7 indicate that the CN group contributes more to the observed $a$ values for GC coatings than any of the functional groups represented in Eq. 5. Evaluation of additional functional groups is clearly needed before fully applicable predictive equations can be developed for estimation of LSER coefficient values from structural descriptors.

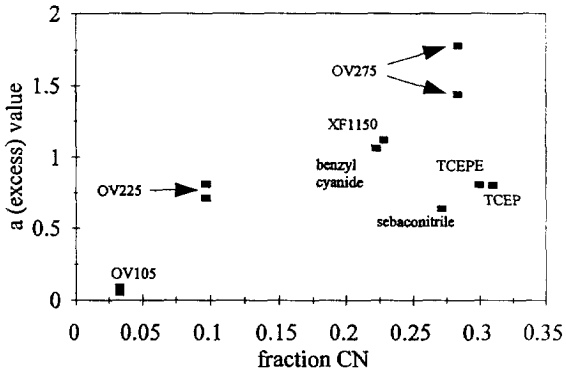


Fig. 7. Plot of $a_{excess}$ versus fraction CN for coatings in Table 6. The value of $a_{excess}$ represents the CN contributions to the observed $a$ values.

## Acknowledgement

The work reported herein was performed in partial fulfillment of degree requirements for the M.S. degree from Northern Illinois University (W.T.).

## References

[1] S.K. Poole and C.F. Poole, Chem. Rev., 89 (1989) 377.
[2] F.W. Karasek, F.I. Onuska, F.J. Yang and R. Clement, Anal. Chem., 56 (1984) 174R.
[3] R. Fellous, L. Lizzanicuveleier and R. Luft, Anal. Chim. Acta, 174 (1985) 53.
[4] W.O. McReynolds, J. Chromatogr. Sci., 8 (1970) 685.
[5] F. Patte, M. Etcheto and P. Laffort, Anal. Chem., 54 (1982) 2239.
[6] B.L. Karger, L.R. Snyder and C. Eon, J. Chromatogr., 125 (1976) 71.
[7] J.F.K. Huber and G. Reich, J. Chromatogr., 294 (1984) 15.
[8] S.K. Poole and C.F. Poole, J. Chromatogr. A, 697 (1995) 415.
[9] C.F. Poole, T.O. Kollie and S.K. Poole, Chromatographia, 34 (1992) 281.
[10] B.R. Kersten, S.K. Poole and C.F. Poole, J. Chromatogr., 468 (1989) 235.
[11] C.J. Cramer, G.R. Famini and A.H. Lowery, Acc. Chem. Res., 26 (1993) 599.
[12] P.J. Doherty, R.M. Hoes, A. Robbat and C.M. White, Anal. Chem., 56 (1984) 2697.
[13] M.N. Hasan and P.C. Jurs, Anal. Chem., 60 (1988) 978.
[14] T. Kleinert, W. Ecknig and J. Novak, J. Chromatogr., 315 (1984) 85.
[15] A. Robbat, N.P. Corso, P.J. Doherty and D. Marshall, Anal. Chem., 58 (1986) 2072.
[16] P.J. Schoenmakers, H.A.H. Billiet and L. de Galan, Chromatographia, 15 (1982) 205.
[17] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, J. Chem. Soc. Perkin Trans. 2, (1990) 1451.
[18] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, J. Chromatogr., 518 (1990) 329.
[19] M.H. Abraham, J. Andonian-Haftvan, C.M. Du, V. Diart, G.S. Whiting, J.W. Grate and R.A. McGill,, J. Chem. Soc. Perkin Trans. 2, (1995) 369.
[20] M.H. Abraham, Chem. Soc. Rev., 22 (1993) 73.
[21] D.S. Ballantine, J. Chromatogr., 628 (1993) 247.
[22] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, J. Chromatogr., 587 (1991) 229.
[23] M.H. Abraham, P.L. Grellier and R.A. McGill, J. Chem. Soc. Perkin Trans. 2, (1987) 79.
[24] C.F. Poole and T.O. Kollie, Anal. Chim. Acta, 282 (1993) 1.

[25] E.F. Sanchez, J.A.G. Dominguez, J.G. Munoz and M.J. Molera, J. Chromatogr., 299 (1984) 151.
[26] S.K. Poole, T.O. Kollie and C.F. Poole, J. Chromatogr. A, 664 (1994) 229.
[27] S.K. Poole and C.F. Poole, J. Chromatogr., 500 (1990) 329.
[28] M.H. Abraham and D. Ballantine, Re-characterization of McReynold's 77 Phase Data Set Using New H-bond Based Solvation Parameters, in preparation.
[29] OV GC Supplies, Catalog No. 42, Ohio Valley Specialty Company, 1992, pp. 22–23.