

# Retention of C<sub>60</sub> and C<sub>70</sub> fullerenes on reversed-phase high-performance liquid chromatographic stationary phases

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## ABSTRACT

The separation of C<sub>60</sub> and C<sub>70</sub> fullerenes on four different polysiloxane stationary phases was examined. It was determined that polar solvents can be used as mobile phases effectively for the separation of fullerene molecules. Unlike previously published work, a polymeric octadecyl siloxane (ODS) stationary phase provided higher separation factors for C<sub>70</sub>/C<sub>60</sub> than did monomeric ODS stationary phases or phenyl substituted stationary phases. For example, for a methanol-diethyl ether (50:50, v/v) mobile phase and C<sub>60</sub>,  $k' \approx 5.0$  separation factors,  $\alpha = 3.3$ , were achieved with polymeric ODS compared to  $\alpha = 2.2$ , with a monomeric ODS stationary phase. A linear solvation energy relationship (LSER) was used to model the importance of solvent interactions and stationary phase interaction to solute retention.

## INTRODUCTION

The development of a bulk method to produce the third allotrope of carbon, buckminsterfullerenes [1] has caused the development of completely new areas of chemistry and materials science. The surge of new fullerene-related discoveries continues [2]. Optical isomers of C<sub>76</sub>, C<sub>78</sub>, C<sub>82</sub>, C<sub>84</sub> were theoretically predicted [3,4] and recently experimentally separated and identified [5]. Numerous compounds with one or more metal atoms inside the fullerene cage have been produced [6].

To facilitate these new developments, various chromatographic techniques were used to separate the fullerenes. For high efficiency separations different types of HPLC columns were used. Early chromatographic separations involved use of alumina or silica stationary phases [7-9]. However, the fuller-

ene capacity factors on these columns were low and degradation of the fullerenes was occurring when silica was used. Hawkins *et al.* [10] reasoned that a  $\pi$ -acid type high-performance liquid chromatographic (HPLC) stationary phase would work well for the separation of the  $\pi$ -basic fullerenes. To test this they separated the fullerenes on a Pirkle phenylglycine column which contains dinitrobenzamide groups on the surface of the stationary phase. With hexane as the solvent they obtained a separation factor,  $\alpha = k'_{C_{70}}/k'_{C_{60}} = 2.25$  ( $k'$  is capacity factor). Cox *et al.* [11] used a dinitroanilinopropyl (DNAP) silica column (300 Å pore size, 5- $\mu$ m particles) with a gradient from *n*-hexane to 60% methylene chloride to achieve baseline separation of C<sub>60</sub> and C<sub>70</sub>. Other attempts to enhance the separation of the fullerenes involved the use of a carbon stationary phase [12], multi-legged phenyl phases [13], and a size-exclusion stationary phase [14]. However, the most commonly used HPLC stationary phase is octadecyl polysiloxane (ODS). Both monomeric and polymeric ODS phases are successfully

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used for the separation of fullerenes [14–16]. Polymeric ODS is known to exhibit selectivity based on the nonplanarity of the molecule in addition to the expected dispersive interactions with ODS. However, Jinno *et al.* [13] suggested that C<sub>60</sub> and C<sub>70</sub> are so bulky that their retention characteristics on monomeric and polymeric should be similar.

All of the previously reported fullerene separations using ODS as the stationary phase used a nonpolar solvent such as hexane or a gradient of hexane with methylene chloride as the mobile phase. Under these conditions the separation mechanism cannot be classified as a classical normal- or reversed-phase separation. Both the stationary phase and the mobile phase are nonpolar. The fullerenes are separated solely by small differences in solubility in the nonpolar solvent and the nonpolar stationary phase. Fullerene solubility was the reason for the common preference of such nonstandard HPLC conditions. Fullerenes are most soluble in aromatic solvents (5 mg/ml); slightly soluble in hexane, pentane, chloroform and diethyl ether [9].

We report here a comparison of the separation of C<sub>60</sub> and C<sub>70</sub> fullerenes on five different columns with four different types of polysiloxane-based stationary phases. Commonly used solvents, such as hexane or mixtures of hexane and methylene chloride are compared to more polar mobile phases, such as, methanol and diethyl ether mixtures. Also the specific type of molecular level interactions involved in the separation of these fullerenes was evaluated. A linear solvation energy relationship (LSER) which correlates Kamlet–Taft solvent parameters with retention was used to identify these interactions.

## EXPERIMENTAL

### Columns

The columns included an end-capped monomeric octadecyl polysiloxane, ODS-Hypersil (Shandon Scientific), C18; an end-capped phenyl dimethylpolysiloxane, phenyl-2 Hypersil (Shandon Scientific), Phen; an experimental non end-capped diphenyl methylpolysiloxane, diphenyl Hypersil, DP-K. All the columns contained 5- $\mu$ m particles with 120 Å pore size, and dimensions of 250 x 4.6 mm I.D. as supplied by Keystone Scientific, Bellefonte, PA, USA. In addition two end-capped diphenylmethyl-

polysiloxane, Supelcosil columns (Supelco, Bellefonte, PA, USA), with 5- $\mu$ m particles, 100 Å pore size were studied. One of these columns was analytical scale with 250 x 4.6 mm I.D. dimensions, DP-S; and the other was semiprep scale with dimensions of 250 x 21.2 mm I.D. A polymeric ODS, Vydac 201TP (The Separations Group, Hesperia, CA, USA) with 5- $\mu$ m particle size, 300 Å pore size, P18, was also studied.

### Instrumentation

The chromatographic system included an ISCO LC-2600 syringe pump (ISCO, Lincoln NE, USA), a Valco W-series high-pressure injection valve (Valco Instruments, Houston, TX, USA) with a 20- $\mu$ l injection volume and a Millipore 991 Photodiode Array Detector (Millipore, Waters Chromatography Division, Milford, MA, USA). All separations were done at room temperature, *ca.* 27°C.

### Fullerene production

The raw fullerene soot was prepared by the arc welding technique which was first developed by Hauffer *et al.* [17]. Detailed information on the design and operating conditions of the device have been previously published [18]. An amount of 0.5 g of raw soot was placed in a round bottom flask which was connected to a water-cooled condenser. An aliquot of 100 ml boiling benzene for 3 h was used to extract the fullerenes from the raw soot. Typical extraction yields for the fullerenes were 8% (w/w) fullerenes in soot.

### Materials

All chemicals used in this study were used as delivered without further purification. Diethyl ether (>99.99%), and benzene (>99.99%) were purchased from J. T. Baker, Phillipsburgh, NJ, USA. Methanol (99.9% purity) was obtained from Mallinckrodt (Paris, KY, USA). The dyes used to determine the Kamlet–Taft solvent parameters were 4-nitroaniline (99+%), 2-nitroanisole (99+%), obtained from Aldrich and N,N-dimethyl-*p*-nitroaniline was purchased from Eastman Kodak (Rochester, NY, USA). A standard test mixture of polynuclear aromatic hydrocarbons purchased from Supelco was also used in the study. This test mix included: acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene,

benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene and pyrene.

#### Density measurements

The molar volume of the methanol–diethyl ether mixtures were determined by measuring the solution densities with a DMA 512 density meter (Anton Paar USA, Warminster, PA, USA) and a TU16D constant temperature bath (Techne, Princeton, NJ, USA). The density meter was calibrated with distilled water at atmospheric pressure and 27°C.

#### Data analysis

A NEC 386SX PowerMate-Plus computer was used for data collection and analysis. The multivariate linear regression of the chromatographic data and the solvatochromic data was obtained using SYSTAT software (SYSTAT, Evanston, IL, USA). The statistical data provided complies with the "Recommendation for Reporting Results of Correlation Analysis in Chemistry using Regression Analysis [19]".  $R$ , the coefficient of multiple correlation is reported. An  $R$  value approaching 1 indicates excellent correlation. The standard deviation of the regression,  $s$ , is reported. The  $F$  test at the 95% confidence level is used to indicate the statistical significance of the model and the Student's  $t$  test at the 95% level was used to indicate the significance of the independent variable's coefficients. In addition to these recommendations, the adjusted coefficient of multiple determination ( $R_a^2$ ) is also reported. This variable is substantially lower than the coefficient of multiple determination ( $R^2$ ) when too many independent variables are used in a model. A more detailed description of the regression analysis of LSER was previously published [20].

#### RESULTS AND DISCUSSION

Our initial separations of fullerenes used phenyl polysiloxane columns. We anticipated that the retention and the separation factor might be higher for the phenyl columns than other reversed-phase columns, because of  $\pi$ – $\pi$  interactions between the phenyl rings on the stationary phase and the condensed rings of the different fullerenes. Hexane and

pentane were initially used as the mobile phases. The fullerenes could be separated with these mobile phases, but the efficiency was low. Fig. 1 is a sample chromatogram using a phenyl column, Phen, as stationary phase and pentane as mobile phase. Under these conditions the efficiency was low and separation factor was  $\alpha = 1.33$ . Mixed mobile phases which contained a low percentage of cosolvent, such as ethanol, methanol, tetrahydrofuran and diethyl ether, improved the efficiency substantially. Fig. 2 demonstrates the increased efficiency found when diethyl ether–pentane mixtures were used as the mobile phase with the Phen column. In addition, the retention of the fullerenes was practically unaffected by the addition of substantial quantities of diethyl ether to the pentane (see Fig. 3) and the selectivity decreased slightly.

Neat diethyl ether also worked well as a mobile phase for the separation of fullerenes. All five columns were tested with diethyl ether as a mobile phase. Short retention times and improved efficiency (2000–4000 plates) were achieved. Fig. 4A is a

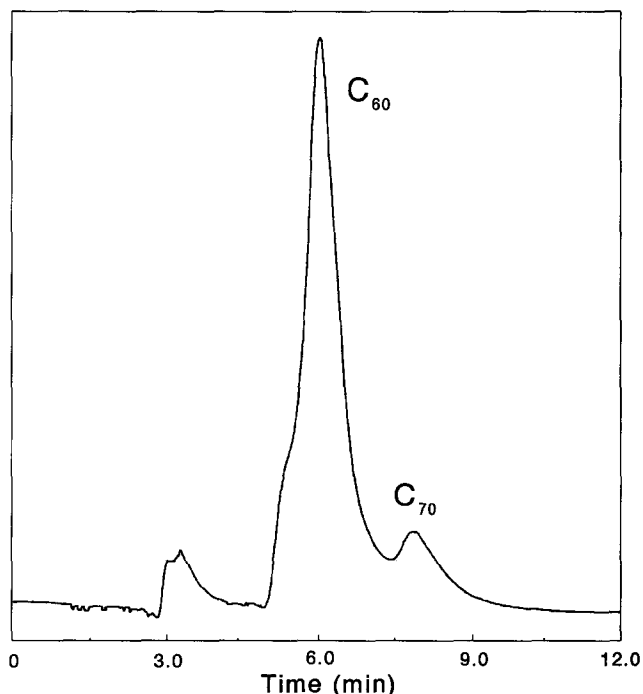


Fig. 1. Separation of  $C_{60}$  and  $C_{70}$  on the phenyl polysiloxane column (Phen). Mobile phase: pentane; flow-rate: 1 ml/min; detection wavelength: 330 nm.

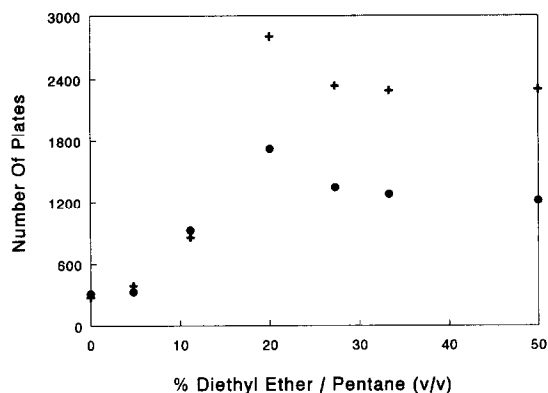


Fig. 2. Dependence of column efficiency (number of theoretical plates) on percent diethyl ether in pentane for fullerene separations on the Phen column. ● = C<sub>60</sub>; + = C<sub>70</sub>.

sample chromatogram of a high-molecular-weight fraction of the fullerene extract. This fullerene fraction was obtained by first extracting the soot with hot trichlorobenzene. An aliquot of 20  $\mu$ l of the supernatant was injected onto and separated by the monomer ODS column. As described later, the ODS column was used because it provided the highest efficiency with diethyl ether. The high molecular weight fraction of the fullerene chromatogram (portion of the chromatogram with retention time > 4.2 min) was collected for 15 injections. The resulting 250 ml sample was desolvated with a stream of N<sub>2</sub>. The residue was then dissolved in 100  $\mu$ l benzene. An aliquot of 20  $\mu$ l of this yellow solution was in-

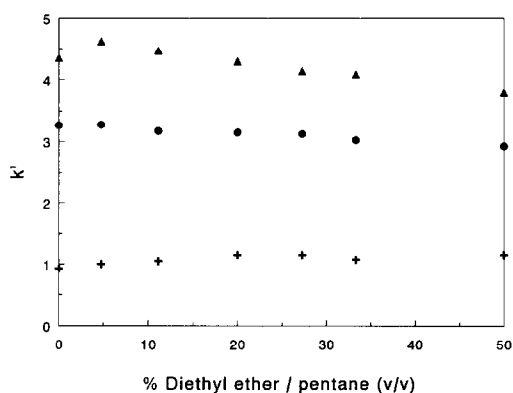


Fig. 3. Variation of capacity factor with percent diethyl ether in pentane using the phenyl polysiloxane stationary phase (Phen). + = Benzene; ● = C<sub>60</sub>; ▲ = C<sub>70</sub>.

jected onto and separated by the same column and the chromatogram in Fig. 4A was obtained. The identity of C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, and C<sub>84</sub> chromatographic peaks were determined from published UV-Vis spectra. Mass spectrometry was used to confirm the identification of the fullerene extract. Fig. 4B shows the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrum of the concentrated high-molecular-weight fraction before the final separation shown in Fig. 4A. (Note: The relative abundance of the ions in the mass spectrum may not be indicative of the relative proportions of fullerenes because the

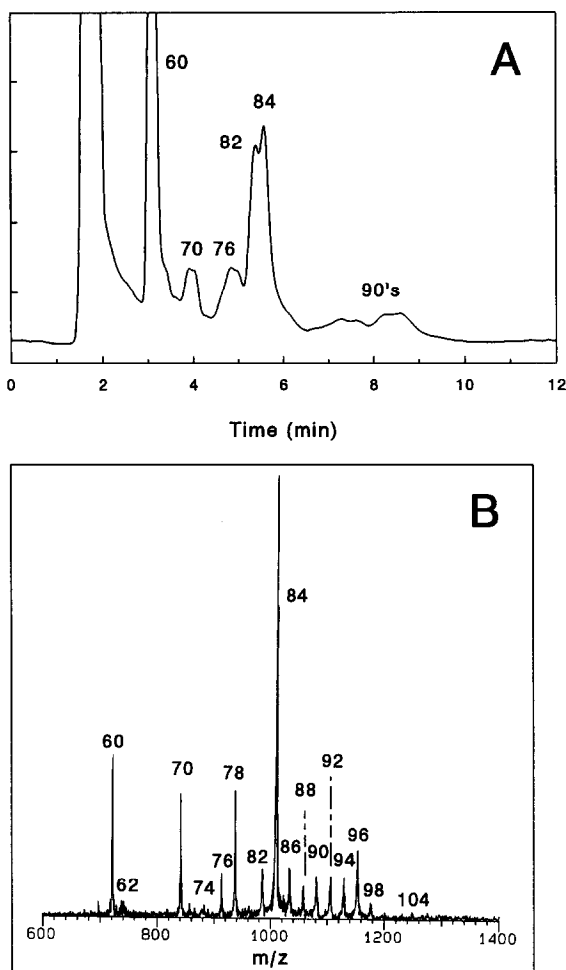


Fig. 4. (A) Chromatogram of higher molecular weight fullerenes. Mobile phase: diethyl ether; flow-rate: 1 ml/min; column: monomeric C<sub>18</sub>; detector wavelength: 330 nm. (B) Laser desorption, negative ion FT-ICR mass spectrum of the sample used in (A).

relative ionization efficiencies of fullerenes are unknown).

Because diethyl ether was a good mobile phase for fullerene separations more polar co-solvents with diethyl ether were also considered. Mixtures of 20% alcohol–diethyl ether were considered. Because fullerene solubility in polar solvents was expected to be low, hexanol–diethyl ether was first considered followed by more polar alcohols such as ethanol and methanol. Of the solvents considered, methanol provided the greatest control of mobile phase solvent strength and therefore the retention and selectivity. The efficiency of  $C_{60}$  on the C18 column increased from 1400 to 2600 theoretical plates when the proportion of methanol in the mobile phase was increased from 0 to 20% and was

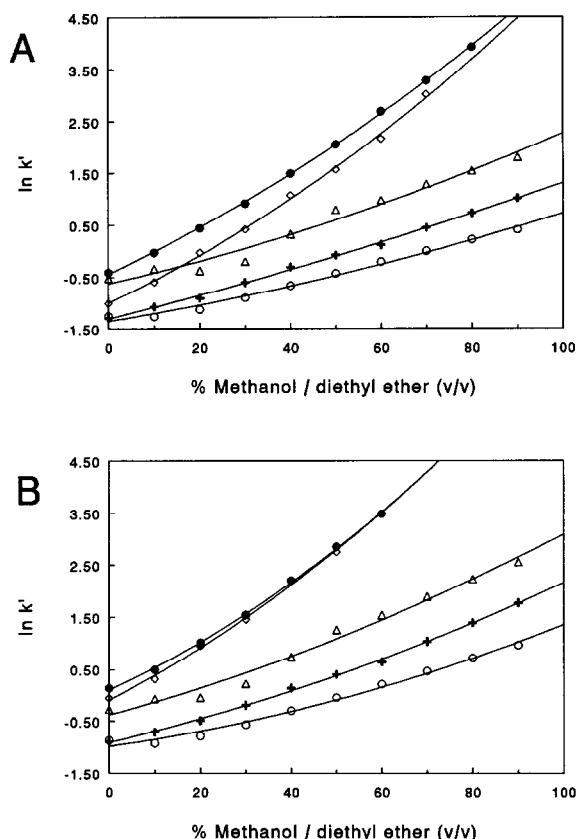


Fig. 5. Variation of capacity factors of (A)  $C_{60}$  and (B)  $C_{70}$  with percent methanol in diethyl ether mobile phase on different columns.  $\diamond$  = Polymeric ODS, P18;  $\bullet$  = monomeric ODS, C18;  $\triangle$  = diphenyl, DP-S;  $\circ$  = diphenyl, DP-K; + = phenyl, Phen.

invariant for mobile phase compositions that ranged from 20 to 70% methanol. Only for compositions  $>70\%$  methanol did the efficiency lower and tailing begin due to lowered solubility in the mobile phase. Fig. 5A and B illustrates how the retention of  $C_{60}$  and  $C_{70}$  is affected by the addition of increasing amounts of methanol to diethyl ether. The  $\ln k'$  increased with the percentage methanol added to the mobile phase for both  $C_{60}$  and  $C_{70}$  on all of the stationary phases studied. Cox *et al.* [11] reported that retention of  $C_{60}$  and  $C_{70}$  closely resembled the retention of planar molecules with similar molecular “footprints”. They showed that under their chromatographic conditions the retention of  $C_{60}$  was similar to that of triphenylene and the retention of  $C_{70}$  was intermediate between that of benzo[*a*]pyrene and coronene. However, with the 0–50% methanol–diethyl ether mobile phases, all of the polynuclear aromatic hydrocarbon standards (listed in the experimental section), were unretained on all five columns.

Fig. 6 shows the variation of the separation factor for the methanol–diethyl ether solvent system on all five columns. Surprisingly, the separation factors were higher when ODS stationary phases were used as opposed to phenyl or diphenyl columns. The separation factors obtained with the methanol–diethyl ether ODS system were significantly higher than those previously reported by Jinno *et al.* [13] for a  $C_{60}$  and  $C_{70}$  separation using monomeric and polymeric ODS with *n*-hexane as the mobile phase. In addition, Fig. 5 and Fig. 6 show the polymeric

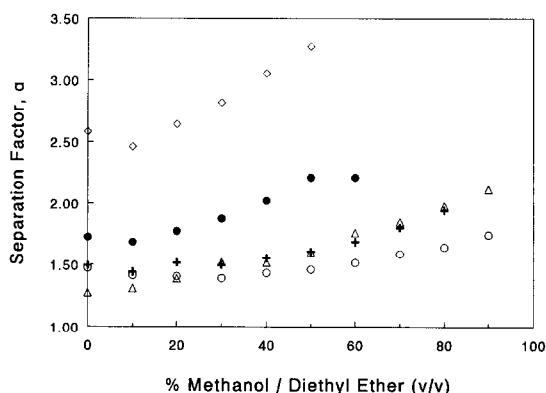


Fig. 6. Variation of separation factors with percent methanol in diethyl ether mobile phase on different columns. Symbols same as in Fig. 5.

TABLE I

NUMBER OF PLATES REQUIRED TO ACHIEVE RESOLUTION OF 1.5 WITH A 20% METHANOL-DIETHYL ETHER MIXTURE

Column	<i>N</i>
C18	351
Phen	2142
DP-K	4405
DP-S	1936
P18	179

phase, Vydac 201 TP, was more retentive and more selective than monomeric ODS for the separation of the fullerenes. Exactly opposite trends were found in the previous study [13] when *n*-hexane was used as the mobile phase. In the previous study, the same polymeric ODS was practically nonretentive toward C<sub>60</sub> and C<sub>70</sub>, while the monomer ODS provided capacity factors of 0.58 and 0.92 for C<sub>60</sub> and C<sub>70</sub>, respectively, and a separation factor of 1.65. The observed differences in fullerene retention and selectivity between this work and that of Jinno *et al.* is primarily caused by marked difference in the observed behavior of the polymeric ODS stationary phase. The monomeric ODS columns used in both studies performed similarly. The distinctly different behavior of the polymeric ODS is quite interesting. The different retention characteristics of the polymeric stationary phase were most likely caused by the different mobile phases use in the two studies. The observed differences cannot be explained by variation in mobile phase shielding of surface silanols. Hexane would afford minimum shielding of surface silanols compared to methanol-diethyl ether; however when hexane was used as the mobile phase lesser fullerene retention was observed. Perhaps the two mobile phases affect the surface structure of the polymeric ODS phase differently. Further investigations are needed to completely understand this phenomenon.

Using the data in Figs. 5 and 6 a comparison of the different columns was made. Table I shows a comparison of the number of theoretical plates required to achieve baseline separation ( $R_s = 1.5$ ) for the five chromatographic columns using the data in Figs. 5 and 6 for a solvent composition of 20% methanol-diethyl ether. Due to the higher observed

separation factors, the polymeric and monomeric ODS columns require the least theoretical plates to achieve baseline separation. The Phen and DP-S stationary phases require approximately 10 times the number of theoretical plates as P18 and due to the low separation factor, DP-K requires approximately double the number of theoretical plates as DP-S. However, under the experimental conditions described in Figs. 5 and 6 and for the 20% methanol-diethyl ether mobile phase composition, the measured efficiency of C<sub>60</sub> and C<sub>70</sub> was approximately 3000 for the C18 column and 1500–1800 for the P18, DP-K, DP-S, and Phen columns. These chromatographic conditions were scaled-up to semiprep scale using the diphenyl column described in the experimental section. This column was used because it was readily available in our laboratory. The extract used in the analytical-scale separations was first doubly concentrated. We were able to inject 100  $\mu$ l of this concentrated extract directly onto the semiprep scale column and obtain resolution of 0.8–1.0 for flow velocities of 15 ml/min. From the previous discussion it is obvious that the diphenyl polysiloxane columns are the poorest choice for fullerene separations under these chromatographic conditions. Therefore much better performance should be expected when semiprep polymeric or monomeric ODS columns are used under these chromatographic conditions.

To better understand the retention mechanism involved in the separation of fullerenes with the methanol-diethyl ether mixtures on polysiloxane-based stationary phases, a linear solvent free energy relationship (LSER) between retention ( $\ln k'$ ) and measured solvent strength parameters was developed. LSERs assume that attractive interactions can be correctly categorized by a nonspecific interaction term that measures the effect of dipolarity and specific terms that describe the effect of hydrogen bond donor and acceptor interactions on solvent properties. In addition, the aforementioned independent variables must be orthogonal and the assumption is made that there is a linear free energy relationship between the each attractive term and the specified solvent effect. Finally to complete the description of the solvent effect, an endothermic term that describes the formation of a cavity in the solvent to accommodate the solute must also be included in this model [21]. Kamlet, Taft and co-

workers [22,23] described the adsorption of gases and liquids on solids using LSER. In addition, Sadek *et al.* [24] demonstrated that LSERs can be quite useful in describing the partitioning of solutes in HPLC. Eqn. 1 is a generalized LSER that describes the transfer of a solute from mobile phase to stationary phase in HPLC.

$$\ln k' = A + B\Omega + C\pi^* + D\alpha + E\beta \quad (1)$$

Kamlet–Taft solvatochromic parameters ( $\pi^*$ ,  $\alpha$ ,  $\beta$ ) were used to describe the exoergic interactions. The  $\pi^*$  measures the ability of the medium to stabilize charged or dipolar solutes by virtue of dipolar or induced dipolar interactions. The  $\alpha$  parameter measures hydrogen bond donation capability and  $\beta$  measures the ability of solvent to accept hydrogen bonds. The most common method of modeling the cavity formation term,  $\Omega$ , is to use the cohesive energy density which is the square of the Hildebrand solubility parameter [22]. We chose to use (molar volume)<sup>-1</sup> to represent the variation in cohesive energy density (and therefore the cavity formation term) of this mixed solvent. This is a reasonable approximation when the attractive portion of the interaction potential controls the cohesive energy density of the solvent [25].

The  $\pi^*$ ,  $\alpha$ ,  $\beta$  parameters of the solvent mixture were experimentally determined by measuring the variation of the UV–Vis spectrum of solvatochromic dyes which are listed in the experimental section. More detail on the measurement of the solvent strength parameters was previously published [26]. The molar volume of the mixtures was determined from experimentally measured solution density. The cavity formation parameter used in the model was generated by dividing all the (molar volume)<sup>-1</sup> values by that of methanol. This was necessary to keep the cavity formation parameter in the same range as the other solvent strength parameters. Fig. 7A and B illustrates the variation in the solvent strength and cavity formation parameters as a function of percent methanol in the mixture. The hydrogen bond donor strength,  $\alpha$ , and the hydrogen bond acceptor strength,  $\beta$ , of the mixture increased substantially over the composition range of 0–20% methanol, then with increasing proportions of methanol the lewis acidity and basicity varied minimally. As more diethyl ether is added methanol–methanol hydrogen bonds must break to maintain

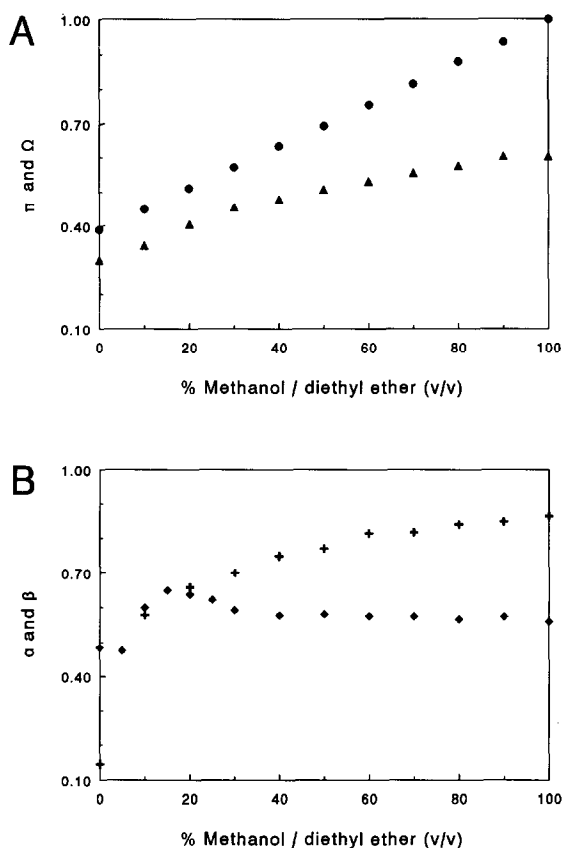


Fig. 7. Measured solvent strength parameters of methanol–diethyl ether mixtures. In A: ▲ =  $\pi^*$ ; and ● =  $\Omega$ ; and in B: + =  $\alpha$ ; ◆ =  $\beta$ .

the polarity of the mixture at close to a constant value. The cavity formation term varies linearly with added methanol.

The relative values of the coefficients  $B$ ,  $C$ ,  $D$ , and  $E$  describe the relative importance of cavity formation, dipolarity, hydrogen bond accepting or donating properties of the solvent to the retention of the fullerenes. When the capacity data shown in Fig. 5A and B were fit to solvent strength parameters, models that included the  $\alpha$  and  $\beta$  parameters were inadequate. They did not pass the  $F$  test even at the 75% confidence level. Only models which included exclusively the cavity formation term and the dipolarity term fit the data well. These models were valid at the 97% confidence level using the  $F$  test. For all columns, the regression coefficients for the cavity formation parameter,  $B$ , and dipolarity,

TABLE II  
MODEL DESCRIBING RETENTION OF C<sub>60</sub> ON DIFFERENT COLUMNS

$$\text{Model } \ln k' = A + B\Omega + C\pi^*$$

Column	<i>n</i> <sup>a</sup>	<i>N</i> <sup>b</sup>	Coefficient ( <i>t</i> test) <sup>c</sup>			Statistics					
			<i>A</i>	<i>B</i>	<i>C</i>	<i>R</i>	<i>s</i>	<i>R</i> <sub>a</sub> <sup>2</sup>	<i>t</i> <sub>95</sub>	<i>F</i>	<i>F</i> <sub>95</sub>
C18	9	6	-3.472 (48.0)	12.072 (39.7)	-5.570 (10.3)	1.000	0.029	1.000	2.447	1095	5.14
Phen	10	7	-2.815 (29.2)	5.019 (13.8)	-1.482 ( 2.2)	0.999	0.038	0.998	2.365	1853	4.74
DP-K	10	7	-2.374 (16.0)	4.799 ( 8.5)	-2.789 ( 2.7)	0.996	0.059	0.991	2.365	483	4.74
DP-S	10	7	-1.802 ( 5.8)	7.683 ( 6.5)	-5.808 ( 2.7)	0.992	0.124	0.979	2.365	214	4.74
P18	8	5	-4.238 (17.6)	12.651 ( 9.8)	-5.704 ( 2.7)	0.998	0.093	0.996	2.571	777	5.79

<sup>a</sup> Number of data points.

<sup>b</sup> The degrees of freedom.

<sup>c</sup> Number in parentheses is Student's *t* test value for the coefficient.

*C*, were positive and negative, respectively. Table II and Table III list the regression coefficients for all five columns. Fig. 8A and B shows the relative magnitude of the regression coefficients. This indicates that increased energy necessary to form a cavity in the solvent caused increased retention and increasing solvent dipolarity decreased retention. The signs of these coefficients are as expected from the endothermic and exothermic nature of the respective terms. However, the relative magnitude of these regression coefficients is interesting. For all five stationary phases the cavity formation regression coefficient was the larger of the two. However, for the monomeric and polymeric phases the cavity formation coefficient predominates. This suggests that

solvophobic forces control the fullerene retention with ODS and these mobile phase mixtures.

Since the involvement of the mobile phase in retention is described by the cavity term and solvent strength parameters, the intercept term, *A*, of the model should represent the interaction between a solute molecule and the stationary phase. In other words, *A* could be treated as a measure of "pure" retention of a solute on a specific stationary phase when no mobile phase is applied, therefore all four other terms would be zero. By comparing the relative size of the *A* term for different columns, the retention of the fullerenes on the stationary phases is expected to decrease in the following order: diphenyl, DP-S > diphenyl, DP-K > phenyl, Phen

TABLE III  
MODEL DESCRIBING RETENTION OF C<sub>70</sub> ON DIFFERENT COLUMNS

$$\text{Model } \ln k' = A + B\Omega + C\pi^*$$

Column	<i>n</i> <sup>a</sup>	<i>N</i> <sup>b</sup>	Coefficient ( <i>t</i> test) <sup>c</sup>			Statistics					
			<i>A</i>	<i>B</i>	<i>C</i>	<i>R</i>	<i>s</i>	<i>R</i> <sub>a</sub> <sup>2</sup>	<i>t</i> <sub>95</sub>	<i>F</i>	<i>F</i> <sub>95</sub>
C18	7	4	-3.235 (21.2)	13.464 (12.8)	-6.455 (4.0)	0.999	0.059	0.998	2.776	1329	6.94
Phen	10	7	-2.488 (18.7)	6.766 (13.4)	-3.547 (3.8)	0.999	0.053	0.997	2.365	1306	4.74
DP-K	10	7	-1.950 (11.6)	6.192 ( 9.7)	-4.768 (4.0)	0.996	0.067	0.990	2.365	463	4.74
DP-S	10	7	-1.897 ( 6.8)	8.842 ( 8.4)	-6.225 (3.2)	0.996	0.111	0.988	2.365	387	4.74
P18	7	4	-3.682 (16.9)	14.072 ( 9.4)	-6.404 (2.8)	0.999	0.084	0.996	2.776	745	6.94

<sup>a</sup> Number of data points.

<sup>b</sup> The degrees of freedom.

<sup>c</sup> Number in parentheses is Student's *t* test value for the coefficient.



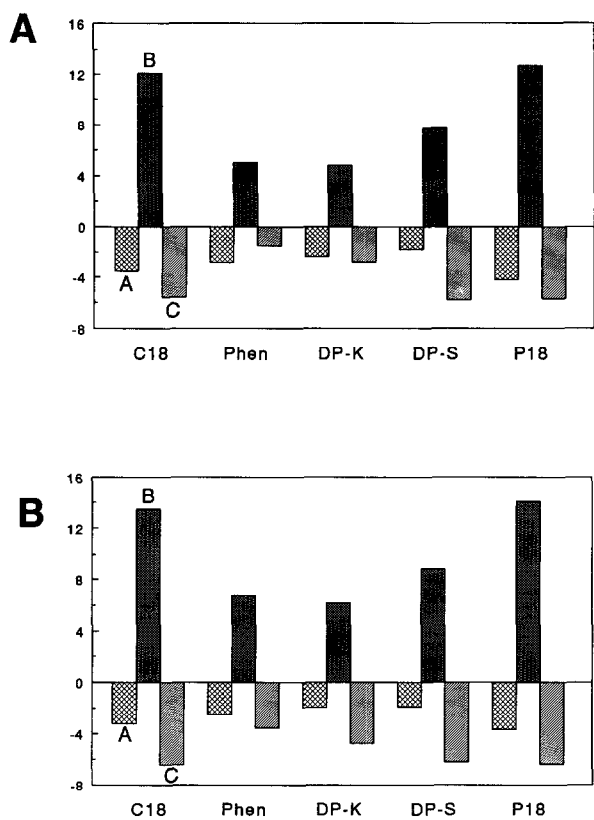


Fig. 8. Comparison of the relative values of model coefficients for different columns. (A) C<sub>60</sub>; (B) C<sub>70</sub>. A = model intercept; B = the coefficient for the cavity formation term; C = the coefficient for the dipolarity term.

> ODS, C18 > ODS, P18. This is exactly the order of retention that Jinno *et al.* [13] found for fullerenes with *n*-hexane as a mobile phase. We had also originally anticipated that the fullerenes would be more retentive on phenyl columns. However with the diethyl ether–methanol mobile phases the reverse retention order was observed for phenyl and ODS phases. As mentioned above, coefficients *B* and *C* describe different interactions between the solvent and the solute. However, for a chromatographic separation these parameters would be describing solvent–solute interaction in the bulk fluid and near the surface of stationary phase. Different *B* and *C* values from different columns may indicate that the solute and the solvent interactions near the surface were different. In both Table II and Table III, C18 and P18 had similar cavity formation and

dipolarity coefficients; DP-K and Phen, both from the same vendor, also had similar *B* and *C* values. Therefore similar surfaces gave similar solvent–solute interaction indicators, *B* and *C*.

## CONCLUSIONS

This paper demonstrates that the fullerenes are soluble enough to use solvents as polar as methanol in their separation. A nonaqueous reversed-phase method of separating C<sub>60</sub> and C<sub>70</sub> is described. A linear solvation energy relationship (LSER) provided significant evidence to support the proposed retention mechanism. With the methanol–diethyl ether mobile phase, monomeric and polymeric ODS provided the highest selectivity.

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