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Supercritical Fluid Extraction of Fullerenes C_{60} and C_{70} from Carbon Soot

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ABSTRACT

A new branch of organic chemistry has begun to emerge following the development of a carbon-arc electric discharge process by Krätschmer et al. which produced a carbon soot containing a series of caged buckminsterfullerene C_{60},C_{70}, and higher homologues. While these compounds are normally recovered either by sublimation in an inert atmosphere or by extraction with benzene, toluene, or a higher boiling aromatic, enhanced selectivity can be achieved by operating at supercritical conditions. The ability of supercritical fluid solvents to fractionate the extractable material of the carbon soot by pressure and/or temperature tuning of the solvent power appears to be possible due to the significant molecular weight and size difference between C_{60} and C_{70} which yield different threshold solubility densities. While CO_2 is unable to extract any fullerenes, selective extraction of C_{60} is obtained when using a nonaromatic modifier such as cyclopentane. Quantitative recoveries are achieved by employing moderate concentrations of an aromatic solvent modifier such as toluene at pressures imparting solvent densities greater than 0.8 g/cm^3.

INTRODUCTION

Although the existence of a new molecular structure, i.e., buckminsterfullerene, comprised of 60-carbon atoms organized into a round and hollow geodesic sphere-shaped molecule was proposed in 1985 by Kroto et al. (1), it was not until 1990 that measurable quantities of this molecule were prepared by Krätschmer et al. (2). Mixtures of buckminsterfullerene C_{60} and higher homologue, or simply fullerene, complexes in carbon soot, were prepared by resistive heating of carbon rods.

By far the most abundant of all fullerenes in the raw carbon soot are C_{60} and C_{70}. However, besides the normally occurring carbon soot contaminants such as benzene, anthracene, and other polynuclear aromatics, a variety of other carbon complexes are also formed, including less round, yet hollow, molecules such as C_{32}, C_{50}, C_{70}, C_{84}, and other molecules possibly larger than C_{960} (3). This new form of carbon complements the well-known pyramidal shape of diamond carbon and the hexagonal shape of graphite sheets. C_{60} is stable to pressures up to 2.5×10^6 psi (4) and, like carbon graphite, is stable in many organic solvents for several weeks. The reported reactivity of fullerenes opens broad avenues for new applications and products such as superconductors, high-temperature lubricants, and catalysts.

Mixtures of fullerenes, as prepared by the contact arc method, are available from MER Corporation of Tucson, Arizona. Fractional content of C_{60} and C_{70} in the carbon soot obtained by this method can vary between approximately 3 and 33% by weight. It is thus highly desirable to find a general separation technique that provides substantially pure fractions of C_{60} and C_{70} in order to expand the use of such compounds.

Fullerenes are generally recovered from carbon soot by either liquid extraction or sublimation. Liquid extraction generally consists of exposing a quantity of the solid matrix to a liquid solvent for a time period long enough to transfer most soluble material into the liquid phase (5). Hexane, heptane, benzene, pyridine, and tetramethylbenzene were all used as extraction solvents in a Soxhlet apparatus (6). While hexane and heptane preferentially extract C_{60} and C_{70}, tetramethylbenzene appears to recover the higher molecular weight (MW) fullerenes also. Successive extraction with hexane or heptane, and then with tetramethylbenzene, offers the possibility of fractionating the carbon soot extract into different classes of fullerenes. Preparative amounts of C_{60} and C_{70} can also be obtained by separation with a series of organic solvents of different solvent power on an alumina column (5).

Sublimation of the fullerenes essentially involves evaporation of the volatile material under vacuum and/or in an inert atmosphere into a gas phase maintained at a temperature above the sublimation temperature of the desired fullerenes (7). Reported sublimation temperatures for C_{60} range from 400 to 600°C (8), depending on the purity of C_{60} and the source of the soot. Following sublimation, the fullerenes are recovered in nearly pure form on separate regions of a cooled collector.

While liquid extraction is most efficient at recovering the bulk of the extract, it is time consuming and generally requires further solvent evaporation and fractionation of the extract. Supercritical fluid extraction (SFE) may be used to increase selectivity toward a desired fullerene (patent pending). In order to increase selectivity toward a given fullerene (i.e., C_{60}), a dilute, homogeneous mixture of a strong organic solvent in a low solvent power medium such as CO_2 can be used. The use of CO_2 as a solvent medium is practical because it is inexpensive, nontoxic, and volatilizes upon expansion to atmospheric pressure; however, its lack of polarity and aromaticity limits its utility as an SFE solvent to small or relatively nonpolar and hydrophobic molecules, and it is thereby not expected to recover quantitative amounts of fullerenes. In order to increase recovery and selectivity toward a given fullerene of interest, a dilute, homogeneous mixture of a strong organic solvent such as toluene in a low solvent power medium such as CO_2 can be used. Other supercritical fluids of stronger solvent power than CO_2 may be employed in their pure form.

Supercritical fluid mixtures appear to be suitable for such a purpose since both modifier concentration as well as temperature and pressure can be used to adjust solvent power and selectivity. The ability of supercritical fluid solvents to fractionate the extractable material of the carbon soot by pressure and/or temperature tuning of the solvent power appears to be possible due to the relatively large difference in molecular size of the fullerenes which yields different threshold solubility densities. However, combined quantitative extraction and fractionation of complex multicomponent mixtures by SFE may not be feasible (9).

Chromatographic analysis and further cleanup of the SFE extract is performed on a polystyrene divinylbenzene (PSDVB) resin Envirosep-ABC column (patent pending). Conventionally, these columns are used for separation by size-exclusion chromatography, a preparative separation technique based on different rates of permeation into surface pores of the size-exclusion resin. Elution order is thus theoretically inverse to increasing molecular volume (10). However, an additional interaction force results from the pi–pi electron interaction between the aromatic fullerenes and the resin, which causes the C_{70} to elute after C_{60}. Hence, while C_{70} is larger than C_{60}, its stronger interaction with the PSDVB resin brought about by its greater aromaticity causes it to elute first. Separation of species of both fullerenes is thus achieved by a combination of adsorption chromatography and steric exclusion chromatography, and can be accomplished within as little as 12 minutes. C_{60} and C_{70} are well separated by this method.

EXPERIMENTAL APPARATUS

Experiments were conducted to assess the ability of CO_2 and dilute supercritical fluid mixtures of cyclopentane and toluene in CO_2 to selectively extract soluble fullerenes (i.e., mainly C_{60} and C_{70}) and other extractable materials (i.e., naphthalene, anthracene, and other low MW material) from carbon soot prepared by the contact arc method. The carbon soot was supplied by MER Corporation.

An integrated multiple sample SFE unit was utilized in this study. The unit allows for simultaneous extraction of up to 4 samples of 100 g or less, and provides independent temperature, pressure, and flow rate control for each extraction subunit. The unit permits delivery of a liquid modifier at specified volume ratios by means of controlling the number of pump strokes for both CO_2 and modifier.

A simplified flow diagram of the integrated SFE unit is shown in Figure 1. A detailed description of the unit is given elsewhere (11); however, a brief description of the unit is given here.

The CO_2 and modifier pumps are both air-driven liquid pumps capable of generating volumetric pressure of 20,000 and 12,000 psig, respectively. Automatic cycling of the pumps is eliminated, and a complete cycle is accomplished by momentary pneumatic impulse at their signal ports.

The process starts by pumping a mixture of CO_2 and modifier of a desired volumetric ratio (0–1) at a controlled rate. The fluids then flow into a 573-mL heated receiver vessel. This high capacity vessel is used as 1) a preheater

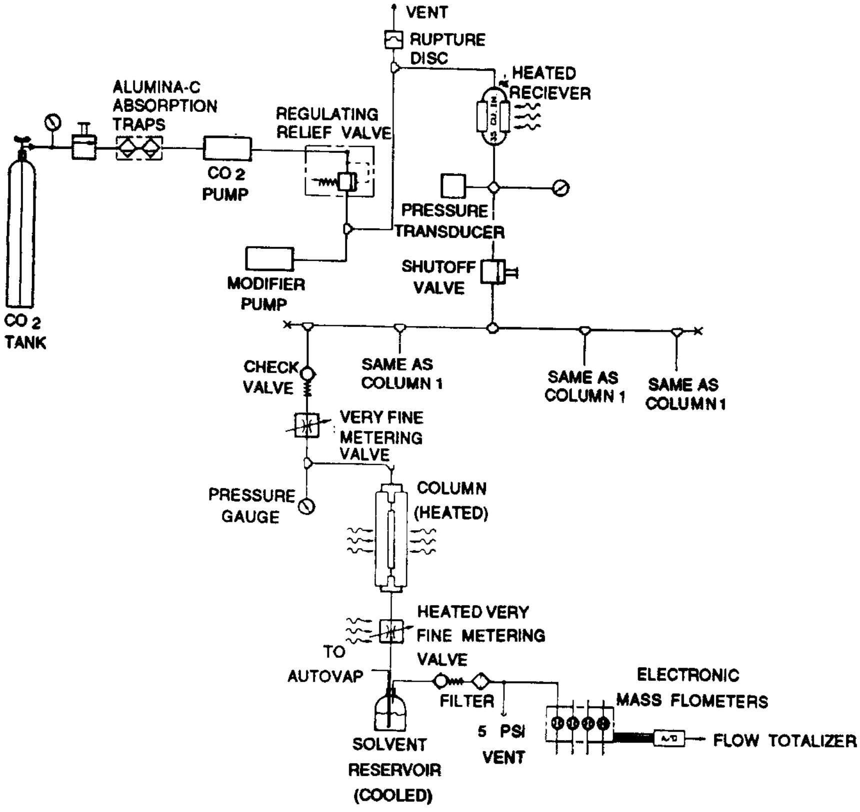


FIG. 1 Flow diagram of SFE of fullerenes from carbon soot (patent pending).

of the solvent mixture, 2) for delivery of a continuous, nonpulsating flow of fluid, and 3) to accelerate start-up of the extraction process.

The fluid mixture exiting the receiver is then distributed into four essentially identical extraction sections. The solvent passes through a check valve and then through a very fine metering valve designed to create a pressure drop from the receiver pressure down to any desired operating column pressure. The solvent then flows to heated extraction columns containing the carbon soot samples where pressure and temperature are controlled within ±200 psi and ±2°C of their respective set points. In these runs, column pressure is set identical to receiver pressure, and it is controlled by a momentary pulse of the pumps at their signal ports when the pressure in the receiver becomes lower than the set point value. The accuracy of the pressure control is thus limited by the large CO_2 pump volumetric displacement/stroke (4.5 mL saturated liquid CO_2 at 830 psig).

Expansion of the supercritical mixture of solvent and extract through the downstream heated metering valves to atmospheric pressure causes CO_2 to volatilize and the extract to precipitate. The extract is collected in a cooled collection vessel preloaded with an organic solvent to solubilize the extract, and CO_2 is vented out.

The metering valves are used to adjust the flow rate from total shutoff to essentially no flow resistance, and are kept heated to adequate temperatures (50–150°C) to avoid freezing of CO_2 and/or modifier that may cause blockage of flow. Flow rate through any one desired column is controlled by a step motor assembly mounted on the respective metering valve, and it is monitored with an electronic mass flow indicator with a 0–5-V dc output proportional to the flow rate. The flow rates through other columns are controlled manually and are monitored with rotameters.

EXPERIMENTAL RESULTS

The fractional content of C_{60} and C_{70} in the carbon soot was first determined because MER Corporation cannot provide this information due to large differences between production batches of carbon soot (3 to 33%). This information is needed to evaluate the fraction of C_{60} and C_{70} extracted by the supercritical fluid mixture. For this purpose, two 20-mg samples of soot were extracted by sonication into 50 and 100 mL toluene, respectively. Sonication was conducted in a water bath for about 3 hours. Since the solubility of $C_{60} + C_{70}$ in toluene is relatively large at ambient conditions (3.95 mg/mL), the 50-mL toluene solution should dissolve all C_{60} and C_{70} in the soot sample and form an unsaturated solution.

Figure 2 shows the HPLC chromatogram of 50 μL of the above solution, obtained by elution with 2 mL/min dichloromethane through a 300-mm long × 7.8 mm i.d. Envirosep-ABC column maintained at 40°C. We first

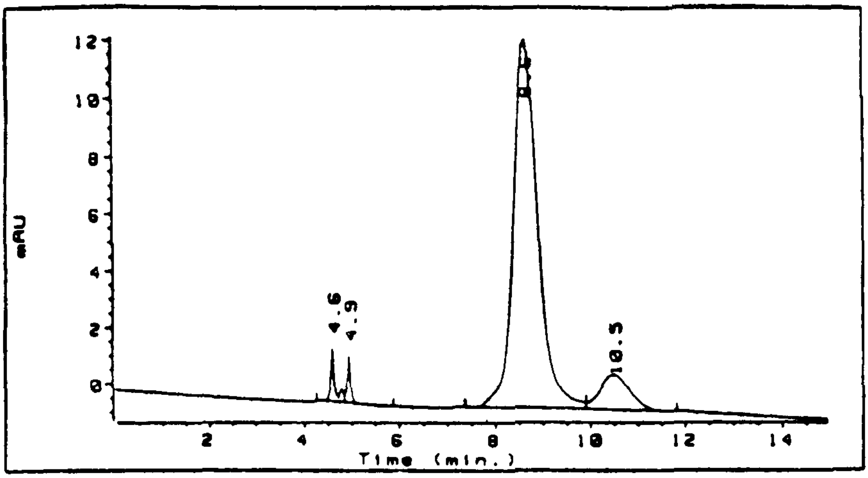


FIG. 2 HPLC of an unsaturated solution of carbon soot in toluene (20 mg soot in 50 mL toluene). C_{60} and C_{70} are well separated by the Envirosep-ABC columns (patent pending).

note that C_{60} elutes before C_{70}. This elution order indicates that adsorption chromatography dominates exclusion chromatography due to strong pi–pi electron interaction of the fullerenes with the PSDVB resin.

The quantity of C_{60} and C_{70} dissolved in the 50-mL toluene solution amounted to 5.95 and 0.73% of the original soot sample, respectively, while the amounts dissolved in the 100-mL toluene solution amounted to 5.78 and 0.83% of the original soot sample, respectively. The amounts dissolved in both toluene solutions are thus similar. Assuming that the rate of solute transfer from the carbon soot matrix phase into the bulk toluene solution phase is proportional to the difference in concentration between these two phases, incomplete solubilization would have resulted in a greater amount of solutes solubilized in the 100-mL solution than in the 50-mL one. Hence, it appears that all C_{60} and C_{70} contained in the soot is accessible for extraction, and that the soot was totally depleted of its extractable material. Average fullerene content in the carbon soot is thus roughly 5.86% C_{60} and 0.78% C_{70} by weight.

SFE OF FULLERENES WITH PURE CO_2 AND MODIFIED CO_2 WITH 8.6 MOL% CYCLOPENTANE OR 14.0 MOL% TOLUENE

The abilities of supercritical CO_2 and of supercritical fluid mixtures of cyclopentane in CO_2 and toluene in CO_2 to selectively extract soluble fullerenes from carbon soot samples were assessed at different pressures and temperatures. The carbon soot samples and Hydromatrix (Analytichem International, Inc., Harbor City, California), a diatomaceous earth adsorbent, were loaded into the columns by the pour and tap method as follows: 0.259 and 0.255 g of carbon soot samples thoroughly mixed with Hydromatrix, and sandwiched between two layers of Hydromatrix, were poured and tapped into Columns 2 and 3, respectively. The column content was then covered with a paper filter and a 4-in. long cylindrical stainless steel (ss) annular rod. The total quantity of Hydromatrix used per column amounted to about 28 g. The ss rod is used to uniformly compact the sample and Hydromatrix so that equal resistance flow channels through the matrix are established. The filter paper is used to provide a flat base for the compaction rod. Hydromatrix serves as support for the fluffy carbon soot. In these runs, heated metering valves were maintained at the same temperature as the respective columns, and the receiver temperature was 60°C. The CO_2 pump piston chamber was kept cool by using a vortex tube. All separator vessels were kept cool at around 0°C by immersion in water cooled with dry ice. Columns 1 and 4 were not used.

SFE with CO_2

Samples 2 and 3 were first extracted with 5 mL/min supercritical CO_2 for about 75 minutes at a pressure of 7500 psi and at temperatures of 90 and 60°C, respectively. Analysis of extract showed no detectable amounts of fullerenes, and no apparent difference in the nature of extracted lower MW compounds.

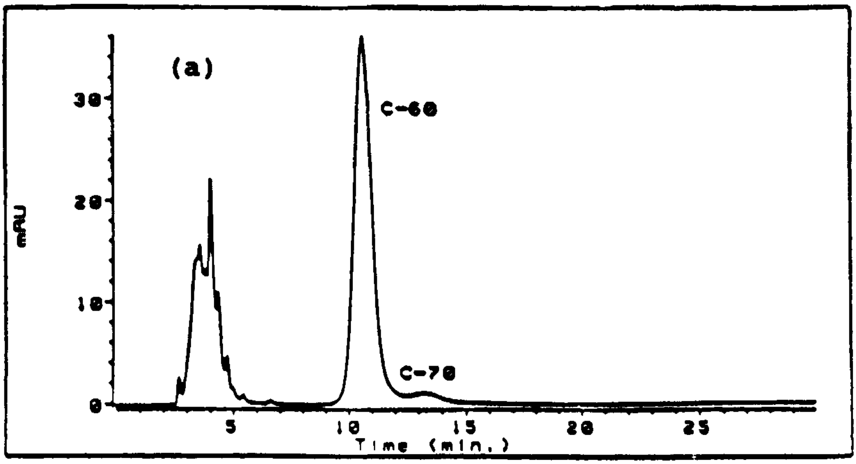
The inability of pure CO_2 to extract the fullerenes is attributed to its low solvent power and its low degree of interaction with the pi electronic cloud of the 5 and 6 carbon ring units composing fullerene molecules.

SFE with 8.6 mol% Cyclopentane/CO_2 Mixture

Cyclopentane was employed as a CO_2 modifier (8.6 mol%) to determine the effect of a slightly better solvent on recovery. Although it is not expected to significantly enhance recovery due to its lack of aromaticity and polarity, because it is planar the cyclopentane molecule should provide greater wetting and interaction with the fullerenes than CO_2, and thereby increase their recovery.

Samples 2 and 3 were thus extracted once more at 7500 psig with 2.5 mL/min of this mixture for 75 minutes, at 90 and 110°C, respectively. These conditions are supercritical since the critical temperature and pressure of the solvent mixture, evaluated by using the Gibbs energy minimization method and the Peng–Robinson (P-R) EOS (12), with a binary interaction parameter k_{12} of 0.1, were determined to be 57°C and 1340 psi, respectively. Figures 3(a) and 3(b) show the HPLC chromatograms of concentrated extracts of Samples 2 and 3, respectively.

The weight response factors of C_{60} and C_{70} were determined in the following manner. Given the unavailability of pure C_{60} or C_{70} reference standards, a mixture of unknown composition of C_{60} + C_{70} in toluene was first



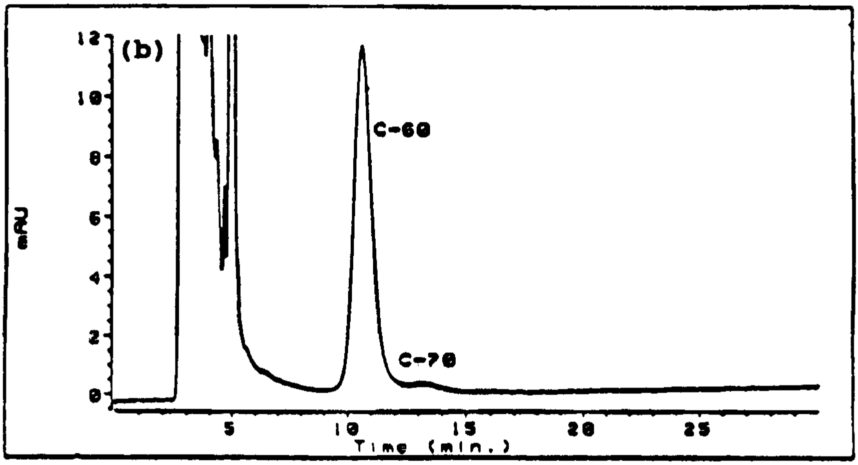


FIG. 3 Selective SFE of C_{60} from carbon soot with an 8.6-mol% cyclopentane/CO_2 mixture at 7000 psig: (a) 90°C, (b) 110°C.

prepared, and the weight of C_{60} + C_{70} in 1 mL of this mixture was determined by evaporation of the solvent. The UV spectra of C_{60} and C_{70} were then determined. The response factors for C_{60} and C_{70} at 330 nm were established by assuming that the UV molar absorptivity of C_{60} and C_{70} are equal around this absorption band. This assumption is acceptable because of the low concentration of C_{70} in the sample and the wide absorption band. C_{60} extracts from Samples 2 and 3 were thus found to amount to 13.1 and 7.8 μg, respectively. The quantity of lower MW compounds (i.e., naphthalene, anthracene, and other low MW material) extracted from Sample 3 was appreciably higher than from Sample 2 due to its higher extraction temperature. Thus, while solubility of low MW compounds increased with increasing temperature due to their relatively higher volatility, solubility of the fullerenes decreased with increasing temperature, as expected for the SFE of solids at temperatures well below their melting points. Little C_{70} was extracted from either sample, indicating that a high extraction selectivity for C_{60} can be achieved under these conditions. Recovery may be increased by allowing for more extraction time.

SFE with 14 mol% Toluene/CO_2 Mixture

Since only a small amount of fullerenes has been extracted from the soot sample so far, and, as mentioned previously, pressure has no effect on the fullerene molecular structure in our pressure range, we may assume that the soot sample is essentially unaltered by the previous extraction runs. In order to enhance recovery of the fullerenes, a mixture of roughly 14 mol% toluene in CO_2 is now employed as the SFE solvent. Toluene was selected as modifier because of the high affinity for fullerenes brought about by the pi–pi interaction between the pi-electron clouds of toluene and the fullerenes.

Based on simple Kay's rules (13), this mixture has a critical temperature of about 71°C (344 K). The critical temperature and pressure of this mixture, evaluated by using the Gibbs energy minimization method and the P-R EOS with a binary interaction parameter of 0.1, were determined to be 88°C (361 K) and 2137 psi, respectively.

The effects of pressure and temperature on recovery were investigated by simultaneous further extraction of each of Samples 2 and 3 for successive periods of 30 minutes at pressures of 4000, 5000, 6000, 7000 and 7500 psi. Transition to a new pressure level consisted of shutting off column flow at the end of the extraction period, allowing pressure in the column to reach the new level, and then reestablishing flow at the desired rate. Samples 2 and 3 were reextracted at temperatures of 70 and 110°C, respectively. Sample 2 is thus extracted at a temperature below the critical point of the solvent and, hence, the concentration of toluene in the supercritical fluid phase will be lower than 14% (close to 11%). Except for a static period of 20 minutes between the extractions at 4000 and 5000 psig, all extractions were dynamic. The saturated liquid CO_2 (at ambient temperature) flow rate was 2.5 mL/min.

Analysis of HPLC chromatograms of extracts show that the ratio of extracted C_{60}/C_{70} at all pressures is close to the ratio in the original carbon matrix (about 7/1), indicating that little selectivity is achieved with this extraction mixture under these conditions. Figure 4 and 5 show the change in the amount of C_{60} and C_{70} recovered from Samples 2 and 3, respectively. First, we note that recoveries show the same trend with temperature as with extraction with the cyclopentane/CO_2 mixture; however, though still low, recoveries of fullerenes are higher than in the previous runs with the cyclopentane/CO_2 mixture.

The precise reasons for the decrease in recovery between 4000 and 6000 psig are not known, but it may be speculated that it is due to an increase in mass transfer resistance brought about by both the increased viscosity of the solvent and the reduced diffusivity of the solvent and fullerenes, as well as the ensuing lowering of fullerene vapor pressure. These effects were reported elsewhere for the extraction of coking compounds from catalyst pellets (14). Also, the closeness of the extraction temperatures to the critical temperature of the binary mixture solvent may also cause a change

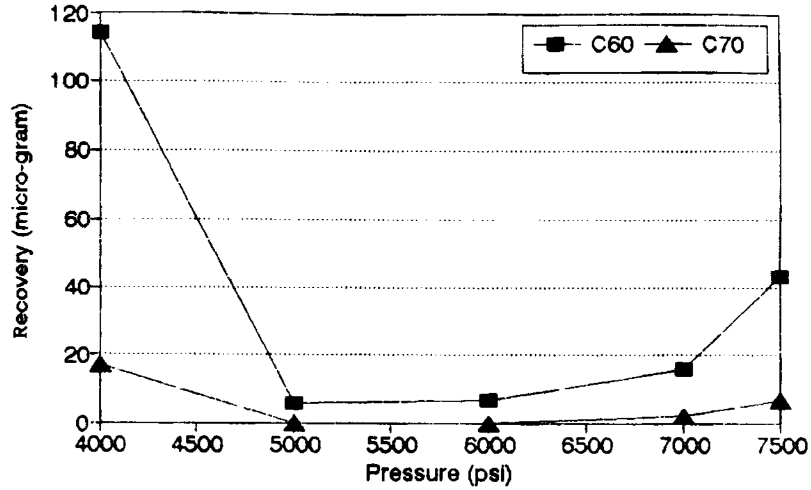


FIG. 4 Pressure effects on recovery of C_{60} and C_{70} from carbon soot with a 14-mol% toluene/CO_2 mixture at 70°C.

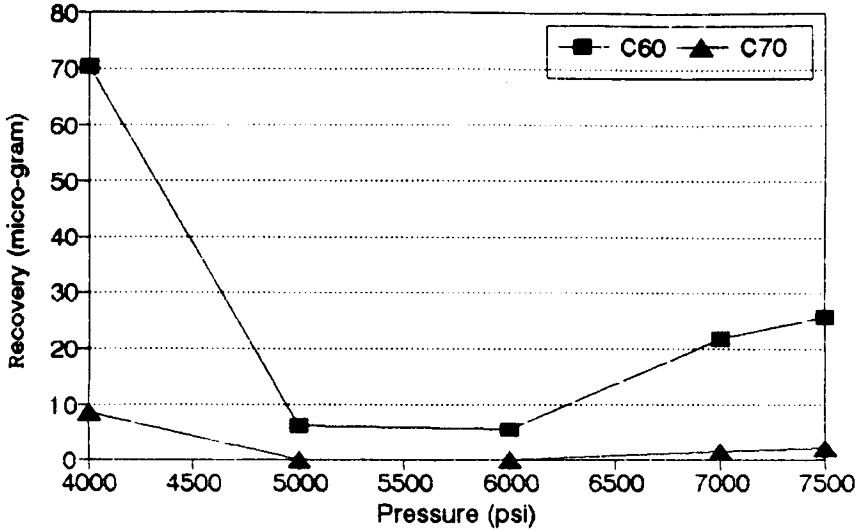


FIG. 5 Pressure effects on recovery of C_{60} and C_{70} from carbon soot with a 14-mol% toluene/CO_2 mixture at 110°C.

in the phase behavior of the solvent/fullerene mixture which could engender such effects. These effects appear to be slightly overcome as pressure reaches 6000–7000 psig. The density of the solvent mixture at 110°C in this pressure range is 0.80–0.84 g/cm^3. Thus, it appears that around this pressure range, the reduction in transport properties and vapor pressure brought about by the increased pressure is now compensated by the increase in solvent power. A further increase in pressure to beyond 7500 to assess fullerene recovery limits with this mixture was not attempted due to the fact that some components of the SFE unit are rated at only 10,000 psi at ambient temperature.

SFE of Fullerenes with 8.8 mol% Toluene/CO_2 Mixture

The effect of pressure on the ability of a more dilute supercritical fluid mixture of toluene in carbon dioxide (8.8 mol% toluene) to selectively extract C_{60} from the carbon soot matrix was then evaluated. The critical temperature and pressure of this mixture, evaluated, by using the Gibbs energy minimization method and the P-R EOS, are determined to be 63°C (336 K) and 1616 psi, respectively. Operation at 110°C (383.2 K) and 5000 psig corresponds to operation at a reduced temperature of 1.16, a reduced pressure of 3.33, and an approximate density (evaluated with the P-R EOS) of 0.73 g/cm^3.

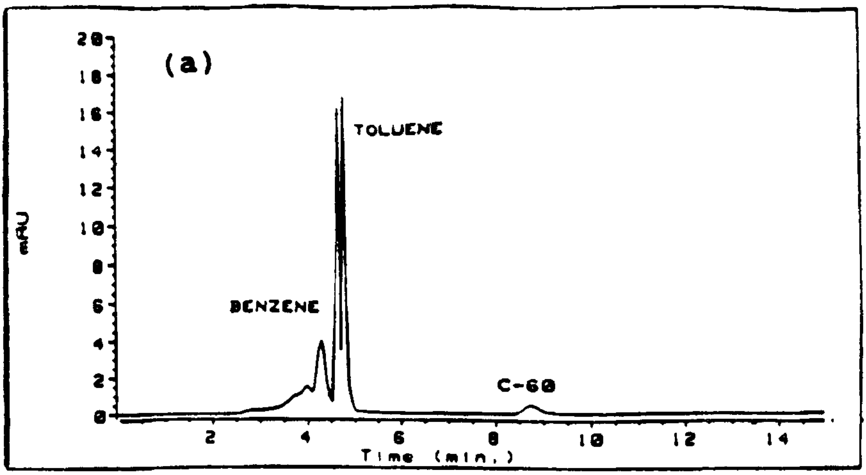
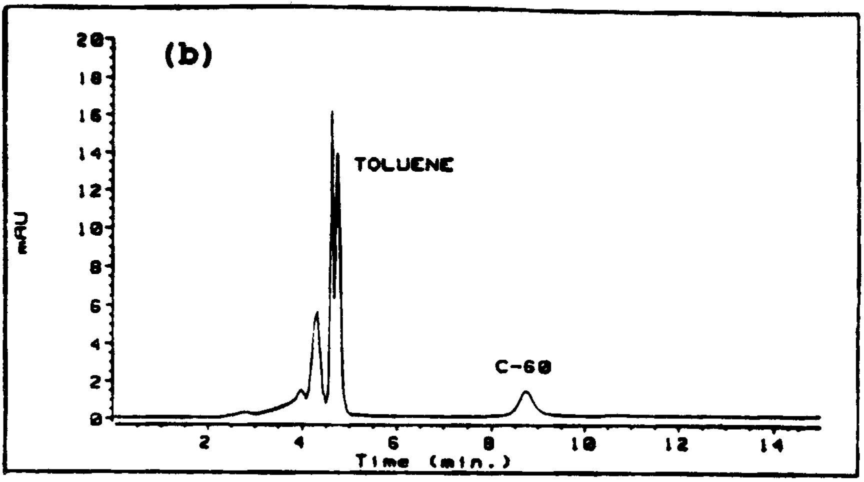


FIG. 6 Selective SFE of C_{60} from carbon soot with an 8.8-mol% toluene/CO_2 mixture at 5000 psig, 110°C: (a) Sample 2, (b) Sample 3, (c) Hydromatrix.

In this run (5000 psi, 110°C), Column 1 was not used, Column 4 was filled with blank Hydromatrix to determine whether any cross-contamination between samples occurs, and Columns 2 and 3 were loaded with carbon soot samples and Hydromatrix by the pour and tap method as described previously. Both Samples 2 and 3 consisted of 45 mg soot thoroughly mixed with 1 g Hydromatrix material.

The flow rate through Column 2 was difficult to control due to plugging of the metering valve by the extracted material, and it required constant supervision and adjustment of the micrometering valve flow opening. The flow rates through Columns 3 and 4 were easily controlled. The better flow control through Column 3 was achieved by adding a soft seat Butech (Erie, Pennsylvania) micrometering valve downstream of the expansion micrometering valve. The flow through Column 4 was easily controlled because no material that would temporarily restrict flow through the micrometering valve was being extracted.

Solvent flow rates through Columns 2, 3, and 4 averaged 2.3, 2.3, and 3.2 mL/min, respectively. The flow rate through Column 4 was monitored by an electronic flowmeter. Continuous flow through Columns 2, 3, and 4 was maintained for 75 minutes. Total volumes of toluene solutions of extracted material (mainly C_{60} and C_{70}) in Columns 2, 3, and 4 amounted to 40, 40, and 56 mL, respectively. Figures 6(a–c) and Table 1 show the HPLC chromatograms of the three SFE sample extracts and fullerene recovery results from this run, respectively.



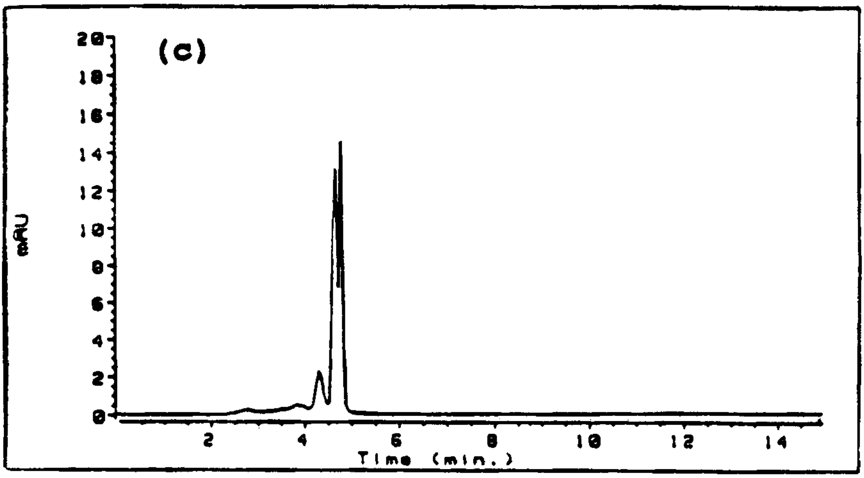


FIG. 6 (*continued*)

TABLE 1

Extraction of C_{60} and C_{70} from a Carbon Soot at 5000 psig, 110°C[a]

Sample or column number	C_{60} in sample (mg)	C_{70} in sample (mg)	Recovery of C_{60} (mg)	Recovery of C_{70} (mg)	Recovery of C_{60} (%)
2	2.64	0.35	0.0224	N.D.	0.85
3	2.64	0.35	0.0650	N.D.	2.46
4	0	0	N.D.	N.D.	N.D.

[a] N.D. = not detected.

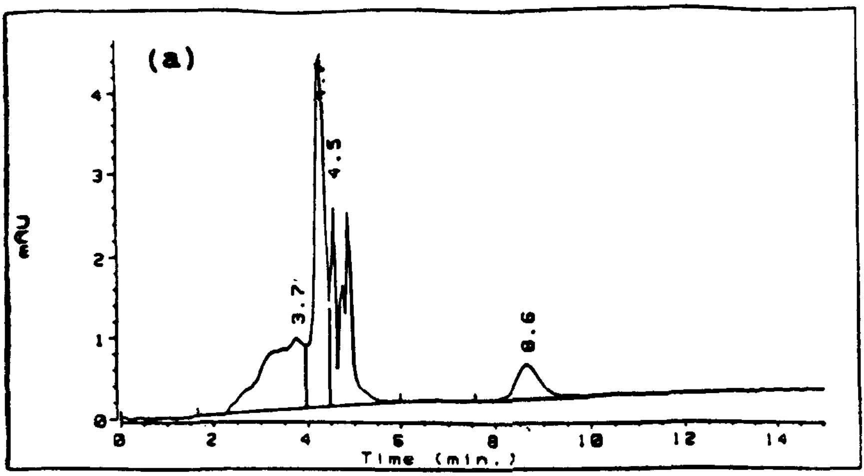


FIG. 7 SFE of C_{60} and C_{70} from carbon soot with an 8.8-mol% toluene/CO_2 mixture at 7000 psig, 110°C: (a) batch SFE of Sample 2, (b) dynamic SFE of Sample 3, (c) batch SFE of Hydromatrix.

It is evident from Table 1 that the supercritical fluid mixture was unable to quantitatively extract C_{60} or C_{70} from the carbon soot. C_{60} concentrations in SFE extract Samples 2 and 3 (0.5×10^{-3} and 1.6×10^{-3} mg/mL) are small compared to its solubility in liquid toluene (3.53 mg/mL). Several factors may have contributed to this low recovery, including the low density of the supercritical fluid, which may be below the threshold solubility density of either fullerene, and the short contact time between the supercritical fluid phase and the carbon soot (the solvent contacts the carbon soot layer in Columns 2 and 3 for about 40 seconds). The difference in recovery between Samples 2 and 3 is believed to be due to the somewhat erratic flow rate through Column 2. It is interesting to note, however, that essentially no C_{70} was recovered in either sample, indicating the possibility of fractionation of the extractable material by selective extraction of C_{60}. No cross-contamination between samples occurred throughout the run as evidenced by the purity of the extract from Sample 4 (blank sample).

The remaining samples in Columns 2, 3, and 4 were extracted once more with the same mixture (8.8 mol% toluene in CO_2) and at the same temperature (110°C) as in the previous experiment, but at a higher pressure (7000 psi), imparting a supercritical fluid solvent density of 0.82 g/cm^3. Samples 2 and 4 were extracted in the batch mode, while Sample 3 was extracted continuously at a flow rate of 2.5 mL/min. Total run time was 42 minutes. Figures 7(a–c) and Table 2 show the HPLC chromatograms

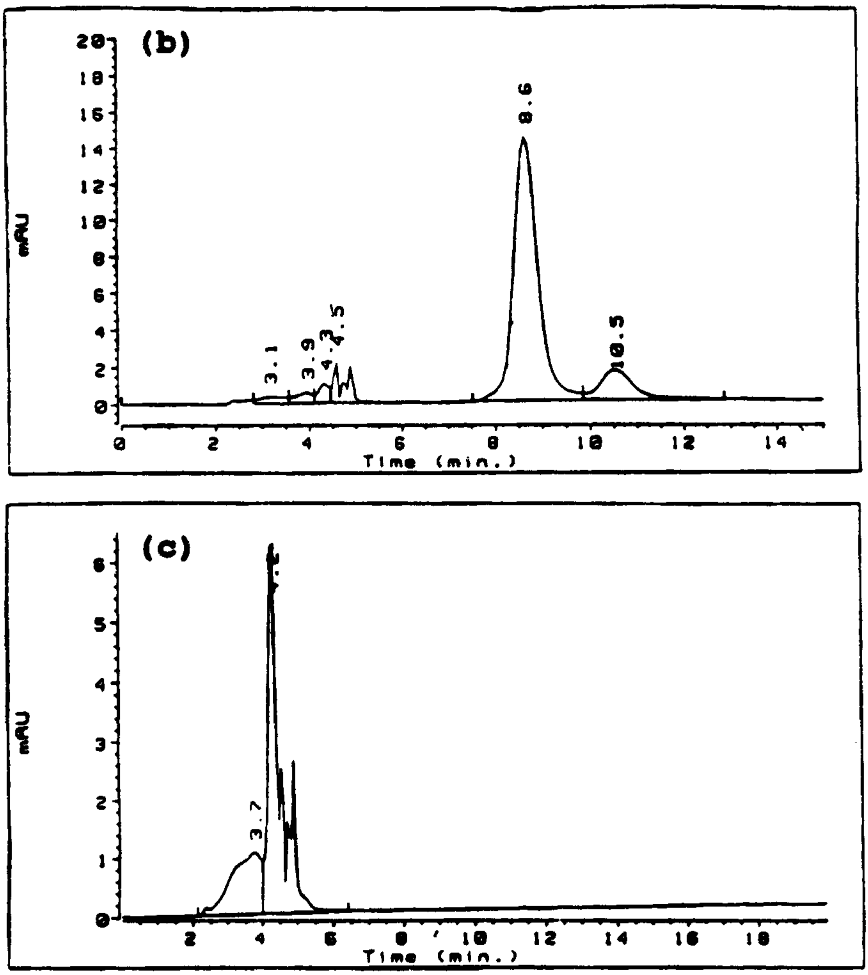


FIG. 7 (*continued*)

TABLE 2

Extraction of C_{60} and C_{70} from a Carbon Soot at 7000 psig, 110°C

Sample or column number	C_{60} in sample (mg)	C_{70} in sample (mg)	Recovery of C_{60} (mg)	Recovery of C_{70} (mg)	Recovery of C_{60} (%)	Recovery of C_{70} (%)
2	2.62	0.35	0.0136	N.D.	3.9	N.D.
3	2.57	0.35	1.2600	0.2120	49.0	60.4
4	0	0	N.D.	N.D.	N.D.	N.D.

of the three SFE sample extracts and other fullerene recovery results from this run, respectively.

We note that the amount of C_{60} extracted from Sample 3 is now about 20-fold the amount extracted in the 5000 psi run from the fresh carbon soot sample. As in the previous runs with the 14% toluene/CO_2 mixture, a marked increase in recovery occurs at pressures higher than 5000 psig where the density of the solvent mixture is greater than 0.8 g/cm^3. Recoveries of both C_{60} and C_{70} from Sample 3 are now quantitative, indicating that the density of the solvent mixture is now above the threshold solubility densities of the solutes, and the phase behavior is now favorable for transfer of the fullerenes into the solvent phase. Hence, this lower concentration of toluene appears to have a favorable effect on the solubility of the fullerenes in the binary solvent mixture, and appears to be closer to optimum concentration for the solubility of the fullerenes in the range of temperature and pressure employed in our experiments. This optimum concentration is expected to vary with the operating temperature and pressure ranges.

Single pass batch extracts from Sample 2 contained no detectable amounts of C_{70} and, as expected, contained little C_{60} due to lack of mixing and the small volume of the carbon soot sample ($\approx$ 1 mL) in contact with the supercritical fluid mixture inside the column. Extract from Sample 4 contained no contaminant, indicating once again that no cross-contamination between samples took place.

CONCLUSION

The ability to adjust recovery or selectivity of SFE for fullerenes from a carbon soot was demonstrated for different solvent mixtures, temperatures, and pressures. CO_2 is unable to extract any fullerenes. Selective extraction of C_{60} is obtained when using a nonaromatic modifier such as cyclopentane. Quantitative recoveries are achieved by employing moderate concentrations of an aromatic solvent modifier such as toluene at pressures imparting solvent densities greater than 0.8 g/cm^3.

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