Extraction of fullerenes in organic solvents and the development of superior isolation procedures

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Development of methods for the isolation of fullerenes depends to a great extent on the identification of suitable solvents. In the present work, extraction of fullerenes from carbon soot by a number of aliphatic, alicyclic and aromatic solvents has been examined at a constant temperature of 60°C. The results indicate that the extraction power of aliphatic straight chain hydrocarbons increases with increase in carbon chain length. The aromatic solvents have superior extracting power as compared to the aliphatic solvents. The higher extraction power of the aromatic solvents is attributed to their better solubilising action. Based on the experimental data, it was possible to develop efficient procedures for the chromatographic separation of \( \text{C}_{60} \) and \( \text{C}_{70} \) employing cyclohexane and a normal paraffin hydrocarbon mixture with average carbon number of 12 as solvents. \( \text{C}_{60} \) and \( \text{C}_{70} \) could both be isolated completely in pure form in much smaller volumes of eluant than in the hexane system.

The recent isolation of macroquantities of \( \text{C}_{60} \) and \( \text{C}_{70} \) has led to a veritable explosion in scientific literature on the properties of these all-carbon clusters called fullerenes. Superconductivity has been observed in alkali metal-doped \( \text{C}_{60} \), a number of chemical reactions involving \( \text{C}_{60} \) have been reported, and “endohedral complexes” of the fullerenes, where a metal atom is trapped inside the ball shaped cage of the fullerene molecule, have also been reported. These as well as many other aspects of fullerenes are covered in several reviews. The major advancement that was responsible for the developments mentioned above was the discovery of a procedure for the preparation and isolation of the fullerenes in bulk quantities. Preparation of fullerenes is carried out by the “contact arc” method or “resistance heating” method, the former being more popular. High yields (upto 40% of the soot as soluble material) have been obtained by suitable modifications in the design and operation of the arcing set up.

The procedure widely used for the isolation of fullerenes involves the soxhlet extraction of the soluble material in the soot (with toluene or benzene as solvent) followed by rotary evaporation to obtain a mixture of fullerenes. From this mixture, \( \text{C}_{60} \) is separated by chromatographic separation on neutral alumina. \( \text{C}_{60} \) is eluted from the column by using hexane-5% toluene as eluant. \( \text{C}_{70} \) is eluted by using hexane containing ~25% toluene.

The poor solubility of fullerenes in hexane makes this separation procedure tedious, and large volumes of solutions have to be handled. Further, the use of toluene means that for recycling of the solvents, fractional distillation has to be resorted to.

It has been observed that by using aromatic solvents with higher boiling points such as 1, 2, 3, 5-tetramethylbenzene, fullerenes with high carbon numbers (as high as 300) could be extracted from soot. However, in the absence of any systematic data on the solubility of various fullerenes in different solvents as a function of temperature, it cannot be concluded whether the efficient extraction of higher fullerenes is due to the nature of the solvent used, or the higher boiling points of the solvents.

In the present work, the extraction of fullerenes from carbon soot by a number of organic solvents was studied at a constant temperature (60°C), with the following objectives: (a) to examine the relative solubilities of fullerenes in these solvents and (b) to arrive at procedures for chromatographic separations based on single solvent systems. The results of our studies indicate trends in the solubilities of fullerenes based on the nature of the solvent, and thus point to better chromatographic procedures. Two new solvents for fullerene separation are also suggested.

Materials and Methods

Carbon soot obtained by the contact arc method was subjected to toluene soxhlet extraction to
recover the fullerenes. The details of the apparatus and the separation methods are reported in an earlier paper.

The paraffin solvent (Normal Paraffin Hydrocarbon-NPH) used in the present work was a mixture of \( n \)-decane, \( n \)-undecane, \( n \)-dodecane, \( n \)-tridecane and \( n \)-tetradecane, with an average carbon number of 12 supplied by M/s Tamilnadu Petroproducts Ltd., Madras. It contained less than 0.003% of aromatics, as confirmed by its absorption spectrum. The absorbance at 270 nm, usually considered as an indicator of the concentration of aromatics, was measured to be 0.150 absorbance units. All other solvents used were either of HPLC grade or AR grade. The NPH solvent, as well as \( n \)-hexane and \( n \)-octane were used without any further purification. \( n \)-Decane, \( n \)-dodecane and \( n \)-tetradecane, which were found to contain some aromatic impurities, were purified by passing through neutral alumina to remove aromatic impurities in the solvent. The absence of aromatic impurities was confirmed by measuring the UV-visible absorption spectrum.

In the experiments to study the extraction of fullerenes from soot, approximately 10 g of soot was homogenised and a 100 mg aliquot was suspended in 10 ml of the solvent taken in an equilibration tube. This tube was kept in a water bath maintained at a constant temperature of 60 ± 0.1°C by circulating water from a thermostat through a glass jacket surrounding the bath. The entire apparatus was kept on top of a magnetic stirrer, and the contents of the glass equilibration tube were mixed by using a teflon coated magnetic stirring bar. The equilibration was continued for 4 hr, after which the tube was centrifuged, and a sample of the solvent phase withdrawn for the measurement of the absorption spectrum.

UV-visible absorption spectra were measured using a Shimadzu model UV-2100 spectrophotometer.

**Results and Discussion**

Figures 1 and 2 show the absorption spectra of the solutions obtained by equilibration of the soot with various solvents. The absorbance values at appropriate wavelengths were taken to indicate the extent of extraction. Fig. 1 shows the spectra of the extracts in aliphatic solvents and Fig. 2 shows the spectra of the extracts in some aromatic solvents as well as cyclohexane and carbon tetrachloride. The spectra in Figs 1 and 2 were recorded with extract solutions as such without dilution. Table 1 gives some data on absorbance values measured from these spectra, for a more quantitative comparison.

Since the studies have been made on raw soot, the absorption spectral information obtained indicates the combined solubility of C\(_{60}\) and C\(_{70}\) (ignoring the higher fullerenes which are formed in much lower amounts). Still, the data reported here bring out clearly the role of the chemical nature of the solvent in solubilising the fullerenes.

The spectra in Fig. 1 as well as the data in Table 1 clearly show that the solubility of the fullerenes in aliphatic straight chain hydrocarbons increases with chain length. It is seen that the extraction power of \( n \)-dodecane is approximately six times that of \( n \)-hexane. This trend is contrary to that normally observed in the solubilities of organic compounds. On the basis of the theory of regular solutions, the solubility is expected to dec-
The solubility of pure C₆₀ in various solvents of differing solubility parameter has since been measured in our laboratory, and the results are being published separately. These results indicate that the solubility of C₆₀ first increases with the increase in solubility parameter, and then decreases. Such a behaviour may be explained on the basis of the regular solution theory and the solubility parameter of C₆₀ which has now been estimated. The efficiency of separation of C₆₀ and C₇₀ by chromatography is decided by the difference in the affinity of alumina for these fullerenes, as well as the difference in solubility of the fullerenes in the solvent used for chromatography. The use of a solvent with higher solvation capacity has the

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Table 1—Absorbance values for fullerene extracts in various solvents at selected wavelengths

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>468</td>
</tr>
<tr>
<td>n-Hexane (SD)</td>
<td>0.159</td>
</tr>
<tr>
<td>n-Hexane (Qualigens)</td>
<td>0.235</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.402</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>0.909</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>1.219</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>1.507</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.042</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.333</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.409</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.554</td>
</tr>
<tr>
<td>Xylene</td>
<td>1.606</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>1.761</td>
</tr>
</tbody>
</table>

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The solubility parameter of C₆₀ has now been estimated.

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† The solubility of pure C₆₀ in various solvents of differing solubility parameter has since been measured in our laboratory, and the results are being published separately. These results indicate that the solubility of C₆₀ first increases with the increase in solubility parameter, and then decreases. Such a behaviour may be explained on the basis of the regular solution theory and the solubility parameter of C₆₀ which has now been estimated.
advantage of loading the mixture and eluting the individual fullerenes in smaller volumes.

The extraction data obtained by us indicated that cyclohexane can be a good solvent for extraction/isolation of fullerenes. We have carried out a few column runs using this solvent, and excellent separation of $C_{60}$ and $C_{70}$ was realised using this solvent. Further, all the $C_{70}$ could be eluted from the column by this solvent. The solvent coming out of the column in the loading step could be directly reused for preparing feed solutions or for elution; the $C_{60}$ and $C_{70}$ eluates were evaporated in a rotary evaporator, and the solvent recovered used in elution. The complete separation of approx. 200 mg of fullerene mixture could thus be accomplished using just 4 litres of the solvent, whereas in similar runs with hexane-toluene system we had to use more than 10 litres of the solvents, with the added problem of having to separate toluene and hexane by distillation for reuse.

The aliphatic hydrocarbon NPH was also used in some column runs; it also led to complete isolation and separation of $C_{60}$ and $C_{70}$. In fact, use of NPH resulted in lesser solvent volumes due to the higher solubility of the fullerenes in NPH. However, since the boiling range of this solvent is high, high vacuum must be used with the rotary evaporator to be able to evaporate away the solvent for recovery of the fullerenes. Cyclohexane possesses an advantage in this respect, as fullerenes can be conveniently recovered from it by simple evaporation or distillation.

In conclusion, it can be said that aliphatic hydrocarbons of higher chain length extract fullerenes from soot better than hexane does, and aromatic solvents in general extract better than the aliphatic solvents. The solvents studied, in this work can be ranked in terms of their extraction power (based on the absorbance of the extract at 468 nm) as follows: $n$-hexane < $n$-octane < $n$-decane < cyclohexane < $n$-dodecane < carbon tetrachloride < toluene < $n$-tetradecane < benzene < xylene < mesitylene.

The extraction of higher percentages of soluble matter from soot by mesitylene is due to its better solvation properties. It is possible to arrive at more efficient and convenient methods for the extraction and purification of the fullerenes by a proper choice of the solvents. Two examples of such solvents are described above. More experiments are being conducted to understand the solubility behaviour of $C_{60}$ and $C_{70}$ in various solvents.

References