SORPTION AND LIQUID CHROMATOGRAPHIC
SEPARATION OF LIGHT FULLERENES C$_{60}$ AND C$_{70}$ WITH MULTIWALL CARBON NANOTUBES

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Isotherms for the sorption of light fullerenes (C$_{60}$ and C$_{70}$) from toluene solutions with the use of multiwall carbon nanotubes (MWCNTs) were investigated. Both isotherms are of the Langmuir-type. The successful liquid chromatographic separation of light fullerenes from toluene solutions was accomplished using the above-mentioned sorbent.

Keywords: light fullerenes, C$_{60}$, C$_{70}$, isotherms of sorption, toluene solutions, chromatographic separation.

1. Introduction

One of the main (if not unique) methods of industrial fullerenes separation and purification is now the method of liquid chromatography. In this method, one typically uses an aromatic solvent — mobile phase, where the solubility of the fullerenes is relatively high [1–4] (e.g. benzene, toluene, chlorobenzene, m-, p-, or often o-xylene or o-dichlorobenzene, etc), however, some non-aromatic solvents e.g. CS$_2$, CCl$_4$, etc. can be used as well. Sometimes, the addition of a non-aromatic solvent with comparatively low fullerenes solubility (e.g. n-hexane, n-octane, 1-hexanol, acetonitrile, etc.) [1–5] to an aromatic solvent is also done to increase the efficiency of the separation. As a stationary phase — one can use different sorbents with relatively high affinity for the fullerenes (e.g. different activated carbons, modified (carbonized silicates, silochroms, aerosols, etc) [5–8]. Literature searches yielded no information about the use of single-wall or multiwall carbon nanotubes (MWCNTs) for the chromatographic separation of the light fullerenes, C$_{60}$ and C$_{70}$ as the main components of standard fullerenes mixture, produced by the most popular current method — electric arc erosion of carbon rods in a He atmosphere. Meanwhile, such a stationary phase seems to be reasonable enough, because carbon nanotubes:

— are absolutely inert and insoluble in any nondestructive solutions used for fullerenes separation,
— have considerable specific surface (m$^2$/gram),
— have high affinity for fullerenes (the main structural motif of carbon nanotubes and fullerenes is the same — carbon hexagons without any functional groups; carbon pentagons also are present in fullerenes and in the ends of carbon nanotubes),
— are relatively accessible, if we use MWCNTs, which are considerably cheaper than single wall ones and are produced in mass quantities.

So, the aim of preset work is:
Sorption and liquid chromatographic separation of light fullerenes

— to investigate the isotherms for the sorption of light fullerenes (C\textsubscript{60} and C\textsubscript{70}) from toluene solutions with the use of MWCNTs,
— to execute liquid chromatographic separation of light fullerenes with the use of the above-mentioned MWCNTs, produced by Bayer corporation (Germany).

2. Materials

1. MWCNTs used in this study were produced by Bayer corporation (Germany). Their physical properties are as follows: external diameter 50–60 nm, internal diameter 5–15 nm, specific surface area 125±35 m\textsuperscript{2}/g (BET – theory), bulk density \(\rho = 0.15±0.02\) g/cm\textsuperscript{3}, length 10–20 \(\mu\)m, temperature of phase transition 3652–3697 °C. Typical electronic photo of MWCNTs, produced by Bayer corporation (Germany) is represented in Fig. 1.

2. C\textsubscript{60} and C\textsubscript{70} fullerenes were produced by the “ILIP” corporation (Saint Petersburg) [6–8] with purities of 99.9 and 99.5 mass\%, respectively. Liquid — phase chromatograms of these products are shown in Fig. 2 and 3. The condition of UHPLC-analysis hereinafter were the following: chromatograph – Shimadzu LC-20 Prominence, solvent – toluene, detector – light absorption at wavelength \(\lambda = 335\) nm, column Agilent HC-C18(2).

3. The C\textsubscript{70}-enriched fullerene mixture C\textsubscript{60} + C\textsubscript{70} utilized in these separation studies was also produced by “ILIP” corporation [7–9]. This mixture had the following average composition: 90±3 mass\% C\textsubscript{70}, 10±3 mass\% C\textsubscript{60}, high fullerenes C\textsubscript{n>70} \(\leq 0.3\) mass\%. The fullerene mixture, enriched by the C\textsubscript{60} fullerene was not investigated, because one can produce the pure individual light fullerene C\textsubscript{60}, using the cheaper and more traditional sorbent with high exploitation characteristics, e.g. active carbon Norrit Azo [7, 8]. A typical liquid — phase chromatogram of such fullerene mixture is also represented in Fig. 4.

4. Toluene (“pure for analysis”, Rus. State Standard GOST — 5789-78) (boiling temperature (1 atm) \(T^b = 110.6\) °C, refractive index \(n_D^{20} = 1.4969\) rel.un.).

Fig. 1. Typical electronic photo of carbon multiwall nanotubes, produced by Bayer corporation (Germany) (\(\times 10^5\))
Fig. 2. Liquid — phase chromatograms of \( C_{60} \)

Fig. 3. Liquid — phase chromatograms of \( C_{70} \)

Fig. 4. Liquid — phase chromatograms of mixture \( C_{60} + C_{70} \)
3. Isotherms of sorption of light fullerenes

Experiment and discussion

The investigation of the isotherms for the sorption of individual light fullerenes — C\(_{60}\) and C\(_{70}\) separately, on Bayer MWCNTs, in toluene solutions was done using the static method. In preliminary experiments, it was established that 2–3 hours was long enough to realize sorption equilibrium — i.e. after this time, the concentration of fullerenes in the liquid solution ceased to change. So, the duration of the experiment was chosen as 4 h. The experiment was done at 25.0 ± 0.1 °C in a shaker-thermostat by the method of constant volumes. A determined mass of the sorbent was added to an aliquot of the fullerene-toluene solution with a determined concentration (20 ml), and after shaking for 4 h with an equal mass of the sorbent (0.15 g), the concentration of fullerenes in liquid solution was determined. According to the changes of fullerenes concentrations in liquid solution the concentrations of the remaining fullerenes in the sorbent were calculated. In this manner, the sorbent capacity was determined.

To measure the fullerenes concentration, we used light absorption in the near-UV and visual spectral region. These measurements were done using a UV–1800 spectrophotometer (Shimadzu), quartz cuvette (l = 1 cm), toluene as a solvent, spectral range (\(\lambda = 250 – 750\) nm). To calculate the concentration of C\(_{60}\) and C\(_{70}\), we hereafter use the following system of equations, which are the decision of Burger-Lambert-Beer equations in the maxima of light absorption wavelengths for C\(_{60}\) and C\(_{70}\) — 335.7 and 472.0 nm, respectively:

\[
C(C_{60}) = 13.10(D_{335.7} - 1.8051D_{472.0})
\]

\[
C(C_{70}) = 42.51(D_{472.0} - 0.00810D_{335.7})
\]

Where: \(C(C_{60})\), \(C(C_{70})\) concentration of fullerenes C\(_{60}\) and C\(_{70}\) in mg/l, \(D_{335.7}\), \(D_{472.0}\) — optical density at 1 = 1 cm and \(\lambda = 335.7\) nm and 472.0 nm, correspondingly [1–4]. Typical electronic spectrum of C\(_{60}\) and C\(_{70}\) are represented in Fig. 5.

Data obtained for the investigation of sorption isotherms in the C\(_{60}\) fullerene — Bayer MWCNTs — toluene and the C\(_{70}\) fullerene — Bayer MWCNTs — toluene systems are represented in Table 1 and in Fig. 6 and 7. Both isotherms are of the Langmuir-type. The graphics of the isotherms in Langmuir coordinates are also shown in Fig. 8 and 9.

One can see, that the static capacities of the sorbent for both light fullerenes are very similar and rather high — \(C_{\text{max}}\) ≈ 21 and 18 mg of C\(_{60}\) and C\(_{70}\) fullerenes per gram of sorbent, respectively. As a comparison, the capacity of traditional sorbent for C\(_{60}\) and C\(_{70}\) separation, carbon Norrit Azo, has capacities of \(C_{\text{max}}\) ≈ 14 and 8 mg of C\(_{60}\) and C\(_{70}\) fullerenes per gram of sorbent, respectively.

4. Liquid chromatographic separation of light fullerenes

Experiment and discussion

As a typical example, the chromatographic separation of light fullerenes from toluene solutions was done with Bayer MWCNTs as the sorbent. The column volume was ≈ 28 ml, height ≈ 56.5 cm (so, we used “thick” preparative column). The composition of the initial fullerene solution was as follows: C\(_{60}\) ≈ 1450 mg/l, C\(_{70}\) ≈ 178 mg/l (C\(_{60}\) ≈ 11 mass%, C\(_{70}\) ≈ 89 mass%), the volume of fullerene toluene solution was ≈ 33 ml. The mass of the sorbent was \(m \approx 4.254\) g. So, we used dynamical capacity of the sorbent \(C_{\text{dyn}}\) ≈ 12.6 mg of total light fullerenes per gram of sorbent or approximately 2/3 of its average static capacity. The results of the separation are represented in Fig. 10.

One can see the following:
FIG. 5. Electronic spectrum of $C_{60}$ and $C_{70}$

Table 1. Sorption isotherms for the $C_{60}$ fullerene – Bayer MWCNTs – toluene and the $C_{70}$ fullerene – Bayer MWCNTs – toluene systems at 25°C

<table>
<thead>
<tr>
<th>System</th>
<th>Concentration in liquid phase $C_l$(g/l)</th>
<th>Concentration in solid phase $C_s$(mg/g sorbent)</th>
<th>Degree of sorbent filling $\theta = C_s/C_{s_{max}}$(rel.un.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$ fullerene – Bayer MWCNTs – toluene</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.12</td>
<td>10.7</td>
<td>0.52</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.26</td>
<td>18.7</td>
<td>0.91</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.47</td>
<td>20.0</td>
<td>0.97</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.65</td>
<td>20.4</td>
<td>0.99</td>
</tr>
<tr>
<td>$C_{70}$ fullerene $C_{70}$ – Bayer MWCNTs – toluene</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.13</td>
<td>9.3</td>
<td>0.51</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.30</td>
<td>13.3</td>
<td>0.73</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.48</td>
<td>16.0</td>
<td>0.88</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.67</td>
<td>17.3</td>
<td>0.95</td>
</tr>
<tr>
<td>- “-”</td>
<td>0.86</td>
<td>18.0</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Sorption and liquid chromatographic separation of light fullerenes

**Fig. 6.** Sorption isotherms in the C\(_{60}\) fullerene – Bayer MWCNTs – toluene system in normal coordinates

**Fig. 7.** Sorption isotherms in the C\(_{70}\) fullerene – Bayer MWCNTs – toluene system in normal coordinates
Fig. 8. Sorption isotherms in the C$_{60}$ fullerene – Bayer MWCNTs – toluene system in Langmuir coordinates

Fig. 9. Sorption isotherms in the C$_{70}$ fullerene – Bayer MWCNTs – toluene system in Langmuir coordinates
- We produced more than 85 mass% of C\textsubscript{70} fullerene (in relation to the entered C\textsubscript{70} — dotted line in Fig. 10, nearly 3 column volumes),
- Thus, the average concentration of produced C\textsubscript{70} (3 → 8 column volumes) was more than 99 mass%,
- The losses of both fullerenes C\textsubscript{60} and C\textsubscript{70} were negligible (< 3 mass%).
So, the chromatographic separation was thus deemed successful.

A similar experiment was performed using mixed sorbent Bayer MWCNTs/granules of fluorine plastic (IV) in equal volume (1/1 v/v). We used a “thick” laboratory little column and a dynamical capacity of the mixed sorbent $C'_{dyn.} \approx 12.6$ mg of total light fullerenes per gram of Bayer MWCNTs without taking into account the fluorine plastic (which was used to allow free flow of the solution through the sorbent in the column, and simultaneously, for the consolidation of the sorbent). The initial mixed fullerene solution was the same. The results of the separation are also represented in Fig. 11. In this case, chromatographic separation was also successful and very close to the above-mentioned results, however this separation was realized more quickly (4 → 6.5 column volumes) and the concentration of the separated fullerenes were lower.
Fig. 11. Chromatographic separation of light fullerenes C$_{60}$ and C$_{70}$ with the help of the mixed sorbent Bayer MWCNTs/granules of fluorine plastic from toluene solutions

5. Conclusions

Isotherms for the sorption of light fullerenes (C$_{60}$ and C$_{70}$) from toluene solutions with the use of MWCNTs were investigated. Both isotherms were of the Langmuir-type. The static capacities of the sorbent, for both light fullerenes, are very similar and rather high. Successful liquid chromatographic separation of light fullerenes has been achieved using the above-mentioned sorbent from toluene solutions. The results showed that Bayer MWCNTs are a reasonable and effective material for the separation and purification of light fullerenes.

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References

Sorption and liquid chromatographic separation of light fullerenes


