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PRE-CHROMATOGRAPHY CRUDE SEPARATION OF LIGHT FULLERENES BY POLY-TERMICAL (RE)CRYSTALLIZATION METHOD

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The pre-chromatography method of crude separation of light fullerenes (C_{60} and C_{70}) is based on multistage processes of (re)crystallization — the solution of fullerenes solid solutions in liquid solvent (o-xylene) or in liquid o-xylene solutions at high temperature (85 °C) and crystallization of solid solutions from saturated liquid solutions at low temperature (–20 °C). As a result, for example, the initial standard fullerene extract may be efficiently divided into two different solid solutions — the first, considerably enriched in C_{60} fullerene and the second, considerably enriched by the C_{70} fullerene. In this separation process, the concentrate enriched by C_{60}, is also enriched in C_{84}. In that process, 98.6 mass % of C_{60} was contained in the C_{60}-enriched concentrate (from the sum content of C_{60} in the initial extract), simultaneously, 65.9 mass % of C_{70} contained in the C_{70}-enriched concentrate (from the sum content of C_{70} in the initial extract).

Keywords: light fullerenes, heavy fullerenes, o-xylene, separation, solution, (re)crystallization, temperature, counter-current, pre-chromatography, high efficiency.

1. Introduction

The most important current technological process of fullerenes production of consists of 3 consequent stages: synthesis of fullerene soot, extraction of fullerenes from the soot and separation of the extract into individual fullerenes [1–3]. Fullerene soot is usually provided by the sublimation of carbon electrodes in an inert atmosphere. Extraction of fullerenes from this soot usually is accomplished with the use of aromatic solvents. The fullerenes extract, which consists of light fullerenes (C_{60} and C_{70}) and heavy (high) fullerenes (C_{76}, C_{78} and C_{84} etc) may be separated into individual fullerenes with discrete molecular masses by different methods. For separation and production of individual fullerenes, the following methods are used: chromatography [4], crystallization [5], combined method, which can include additional stages, such as thermal vacuum sublimation [6–8]. Only light fullerenes (C_{60} and C_{70}) may be provided using these methods. Heavy fullerenes are distributed in some different products or by-products [6] or stay in activated carbon, used as the absorbent in separation processes for light fullerenes [7, 8].

In this work, we were interested in processes for the (re)crystallization of fullerene extracts with the aim of separating the initial extract into two concentrates (all light and heavy fullerenes in such process will be naturally distributed between these concentrates).

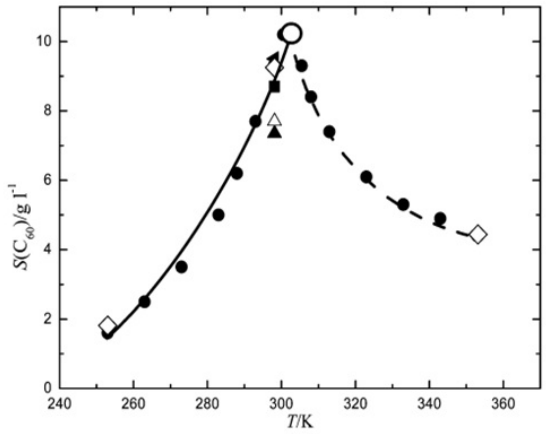

Fig. 1. Solubility of the C_{60} fullerene in o-xylene (S) against temperature (T)

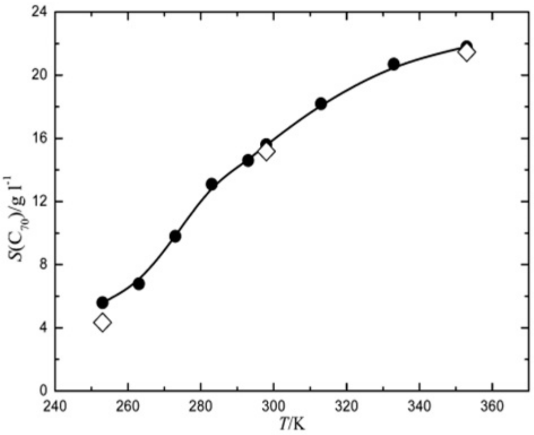

Fig. 2. Solubility of the C_{70} fullerene in o-xylene (S) against temperature (T)

In the final processes of chromatographic separation and purification of concentrates, the latter may be provided with an efficiency considerably higher than in the initial processes of extract separation and purification [9]. In different patents and papers, the processes which were realized during the interaction of the fullerene extract (or fullerene mixture) with aromatic solvents, for example o-xylene, are named differently and the titles of the stages depend on the conditions and goals of the experiments: crystallization [5], fractional concentrating at 80 to 85 °C [6–8], fractional crystallization at −20 to −24 °C [8], (re)crystallization [10, 11] and polythermal (re)crystallization [11]. Phase processes, realized in such cases are the following:

— solution of fullerene solid solutions in aromatic solvent or unsaturated liquid solutions,

— crystallization fullerenes solid solutions from saturated liquid solutions.

2. Experiment and results discussion

The (re)crystallization processes of fullerene extracts are based on the different solubilities of light fullerenes (C_{60} and C_{70}) in o-xylene at different temperatures [12–14]. An actual description of the processes for fullerene extract (re)crystallization was the investigation of solubility diagrams in ternary systems of C_{60}–C_{70} — o-xylene at 80 °C and −20 °C [15]. The dependence of individual fullerenes C_{60} and C_{70} solubilities in o-xylene on temperature is represented in Fig. 1 and Fig. 2, correspondingly [13].

The solubility of the individual fullerene C_{60} in o-xylene at temperatures T∼28–30 °C crosses through the maximum, and further warming decreases the solubility. Simultaneously, the solubility of the individual fullerene C_{70} in o-xylene at the same experimental conditions monotonously increases along with temperature. The first experiments concerning the solubility of heavy fullerenes in o-xylene were made at 28 °C and 84 °C. It is well-known that the fullerene extract composition (when fullerene soot is provided by the method of carbon rods sublimation with the help of an electric arc in He-plasm) can vary widely, for example (in mass %): $C_{60} \sim 55$–88, $C_{70} \sim 10$–45, heavy fullerenes $C_{n>70} > 1$ [16]. The fullerene extract used in these studies had the following composition: (in mass %): $C_{60} \sim 73.3$, $C_{70} \sim 24.9$, $C_{76} \sim 0.90$, $C_{78} \sim 0.26$, $C_{84} \sim 0.64$. The fullerene extract, representing a solid solution of fullerenes in each other, and o-xylene was magnetically stirred (at 28 °C, the time of saturation was 3 hours). Then, the temperature was increased to 84 °C and mixing was continued for a longer period (for example 24 hours), during which the fullerene concentration in the solution was continuously monitored by express spectrophotometry. For more exact analysis of light fullerenes (C_{60} and C_{70}) and heavy fullerenes content, HPLC analysis was used. Experiments were done at different combinations of quantitative characteristics of Liquid and Solid phases (L:S), where L — is volume of o-xylene in ml, S — is mass of fullerene extract in grams. In Table 1 the data are shown for the dynamics of the selective solution-extraction of light fullerenes from the initial fullerene extract at the temperatures T ∼ 28 °C and T ∼ 84 °C at L:S = 10 and L:S = 50 ml/g.

Table 1. Dynamics of the selective solution-extraction of light fullerenes from the initial fullerene extract at L:S = 10 and L:S = 50 ml/g

Time (min)	T °C	Extraction into liquid solution at L:S = 10 ml/g, %		Extraction into liquid solution at L:S = 50 ml/g, %	
		C_{60}	C_{70}	C_{60}	C_{70}
30	28	21.3	37.3	54.7	81.8
60	28	22.6	37.9	56.9	83.3
120	28	22.5	38.5	54.6	77.0
180	28	23.4	39.9	54.2	75.8
235	84	8.4	46.5	52.5	77.6
295	84	7.9	45.4	54.7	83.5
355	84	9.6	47.9	53.8	79.2

In the first case, the fullerene extract was treated with o-xylene at 28 °C and L:S = 10 ml/g, into liquid solution were extracted not more than 25 mass % of C_{60} and 40 mass % of C_{70}, other light fullerenes remained in the solid state. During treatment of the heterogeneous system at 84 °C, (re)crystallization of fullerene solid solutions was realized, the solid solution was enriched by C_{60} and liquid solution was enriched by C_{70}. In the second case, the fullerene extract was treated with o-xylene at 28 °C and L:S = 50 ml/g, one can get a more concentrated liquid solution of C_{60} and C_{70}, but (re)crystallization, unfortunately, practically did not occur. According to literature data, the high temperature (re)crystallization of fullerenes in o-xylene is done, using the following conditions — at L:S = 30 g/g [5], L:S = (11±1) ml/g [8]. In Table 2, data are represented concerning the change of the fullerene (including heavy fullerenes) liquid soutions' compositions in the treatment of the fullerene extract with o-xylene at L:S = 10 ml/g.

According to the results of the experiment one can conclude the following: during (re)crystallization at 84 °C, the liquid solution is enriched by the fullerene C_{70} (light) and C_{76}, C_{78} (heavy), and simultaneously, the solid solution is enriched by the fullerene C_{60} (light) and C_{84} (heavy). On the basis of previous experimental data, the method for crude high-efficiency pre-chromatography separation of fullerenes was developed. As a result of these methods, the initial fullerene extract was separated into two fullerenes extracts basically and unequivocally enriched by light fullerenes C_{60} and C_{70}, but also differently enriched by various heavy fullerenes. The main processes in these methods are: high temperature (re)crystallization (further high temperature process — HTP), low temperature (re)crystallization (further low temperature process — LTP). The high temperature process was developed in stages by mixing for 60–120 min at 70 to 90 °C, while the low temperature process utilized stirring for 10–30 hours at –25 to –15 °C. Separation

Table 2. Dynamics of the change of the composition of fullerene liquid solutions in the process of treatment of fullerene extract by o-xylene at L:S = 10 ml/g

Time (min)	T ° C	Concentration in liquid solution (mg/liter)					Mass fraction of fullerene in the relation to sum mass of all fullerenes in solution (mass %)				
		C_{60}	C_{70}	C_{76}	C_{78}	C_{84}	C_{60}	C_{70}	C_{76}	C_{78}	C_{84}
30	28	15628	9281	256	56	87	61.8	36.7	1.00	0.20	0.30
60	28	16546	9436	221	78	147	62.6	35.7	0.84	0.30	0.56
120	28	16457	9596	213	74	164	62.1	36.2	0.80	0.28	0.62
180	28	17179	9923	202	34	152	62.5	36.1	0.73	0.12	0.55
235	84	6118	11570	150	44	28	34.2	64.6	0.8	0.25	0.15
295	84	5763	11306	149	44	25	33.3	65.4	0.9	0.25	0.15
355	84	7025	11925	149	58	22	36.6	62.2	0.8	0.3	0.1

of liquid and solid fullerene solutions in HTP was effected by filtration at the temperature of HTP, however, for separation in LTP simple decantation was used. The multistage process of fullerene separation was accomplished by producing concentrates, enriched by C_{60}, and enriched by C_{70} at each stage of the whole process. The movement of fullerene liquid solutions formed in LTP, countercurrent to the direction of the movement of solid solutions formed in HTP, was organized also. In the first stage of HTP, was pure solvent — o-xylene was used. In subsequent stages of HTP, the solid fullerene extract was mixed with the liquid fullerene solution from the previous stage of HTP. If such scheme of technological process is realized, one does not need any additional intermediate products, and all fullerenes are distributed between the two concentrates. Correction of the o-xylene volume used in the case of the change of the initial fullerene extract composition or in the case of technical losses was developed mainly in the last stage of HTP. Fig.3 shows the scheme of the n-stage of the fullerene separation process with 2-stage HTP, while in Fig. 4, the scheme of n-stage of the fullerene separation process with 3-stage HTP is depicted.

The following example highlights the data concerning the realization of the n-stage of fullerene separation with the production of the concentrate, enriched by the light fullerenes C_{60} and C_{70}. For analysis of fullerene-containing phases we used chromatography — HPLC (Shimadzu LC-20 with spectrophotometric detection at 300 and 315 nm).

The composition of the initial extract was slightly different from the previous one: (in mass %): $C_{60} \sim 73.5$, $C_{70} \sim 22.8$, $C_{76} \sim 1.09$, $C_{78} \sim 0.37$, $C_{84} \sim 1.83$ (some “oxides” of fullerene C_{60} were also determined — $C_{60}O \sim 1.07$, $C_{60}O_2 \sim 0.16$. There was no information, concerning the “oxides” of the second light fullerene $C_{70}O_n$ or “semi-oxides” of light fullerenes $(C_{60})_2O$ and $(C_{70})_2O$, because the content of the last ones in initial fullerene extract was comparatively low ($\leqslant$ 0.03 mass %). The first HTP stage was the mixing of 100 g of the initial fullerene extract in the returned from the second HTP stage previous (n–1)-stage solution at 85 ° C over 90 min. The volume of the returned solution was 1000 ml. After filtration, we got solid fullerene product enriched by C_{60} and a liquid fullerene solution which was then subjected to LTP. LTP was performed for 20 hours at –20 ° C. After decantation, we obtained the C_{70}-enriched concentrate and a solution, which was then used in the second HTP stage. The second HTP stage was performed with mixing of solid fullerene product after the first HTP stage and the liquid fullerene solution after

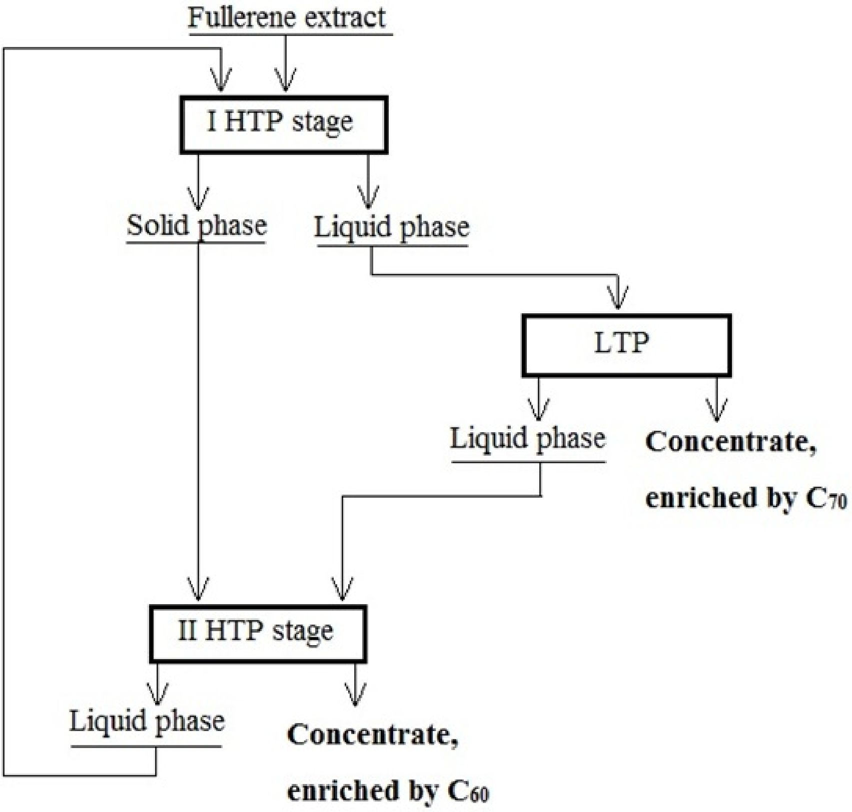

Fig. 3. Scheme of n-stage of the process of fullerene separation with 2-stage HTP

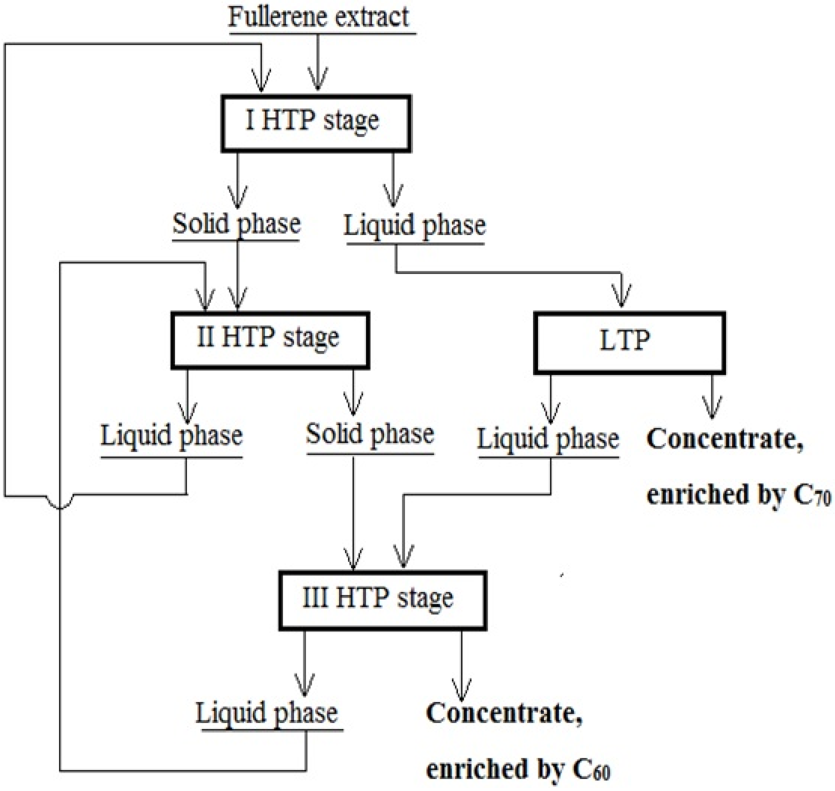

Fig. 4. Scheme of n-stage of the process of fullerene separation with 3-stage HTP

LTP again at 85 ° C over 90 min. After filtration, we obtained the C_{60}-enriched concentrate and the solution which was given for the first HTP stage of the next (n+1)-stage. So, as a result of the n-stage separation process, we were afforded two concentrates: a C_{70}-enriched concentrate, consisting of 84.2 mass.% C_{70}, 5.6 mass.% C_{60} and enriched by heavy fullerenes in comparison with the initial fullerene extract and a C_{60}-enriched concentrate, consisting of 9.4 mass.% C_{70}, 88.3 mass.% C_{60}, while the heavy fullerenes content in it was considerably lower than the previous concentrate. Characteristics of fullerene products in n-stage of process of fullerene separation are represented in Tables 3–5.

Table 3. Characteristics of fullerene solid products in n-stage of process of fullerene separation

Name of product	Fullerenes content in products (mass.%)						
	C_{60}	C_{70}	C_{76}	C_{78}	C_{84}	$C_{60}O$	$C_{60}O_2$
Initial fullerene extract	73.52	22.76	1.09	0.37	1.03	1.07	0.16
Solid fullerene product after the first HTP stage	79.4	17.4	0.8	0.3	1.0	1.0	0.1
Concentrate, enriched by C_{60}	88.3	9.4	0.1	0.2	1.0	0.9	0.1
Concentrate, enriched by C_{70}	5.6	84.2	5.4	1.3	1.3	1.8	0.4

Table 4. Characteristics of fullerene liquid solutions in n-stage of process of fullerene separation

Name of product	Individual fullerenes concentrations in the sum fullerene mass (mass.%)						
	C_{60}	C_{70}	C_{76}	C_{78}	C_{84}	$C_{60}O$	$C_{60}O_2$
Returned solution	36.1	56.7	3.4	0.9	0.8	1.9	0.2
Solution after the first HTP stage	17.4	74.0	4.4	1.0	1.0	1.8	0.4
Solution after LTP	58.2	38.8	0.6	0.2	0.1	1.9	0.2

In this process, as mentioned above, in HTP, the C_{60}-enriched concentrate is also enriched by C_{84}. In our separation process, 98.6 mass % C_{60} was contained in that concentrate(from the sum content of C_{60} in the initial extract), simultaneously, 65.9 mass % C_{70} was contained in the C_{70}-enriched concentrate (from the sum content of C_{70} in the initial extract). “Oxides” of C_{60} were mainly isolated in the C_{70}-enriched concentrate, which is natural, since the specific electronic configuration of the last one, for example has both higher asymmetry and electric polarizability than C_{60}. The solutions after both HTP stages, after removing from the (re)crystallization system the C_{60}-enriched concentrate, naturally contained less C_{60} than the initial fullerene extract and enriched by C_{70} and heavy fullerenes. The solutions after the LTP, after removing from the (re)crystallization system the C_{70}-enriched concentrate, naturally contained less C_{70} than initial fullerene extract and was enriched by C_{60} but not by heavy fullerenes. The two-stage (re)crystallization process for producing the C_{60}-enriched concentrate, with the returning of counter-current liquid fullerene solutions, permitted us to get a concentrate, considerably more enriched by C_{60} than was obtained for a one-stage (re)crystallization process. We could also considerably increase the mass of C_{70} obtained in the C_{70}-enriched concentrate. One can easily understand that, using the (re)crystallization method of fullerene pre-chromatography crude

Table 5. Calculated characteristics of concentrates, got in the n-stage of fullerene separation

Characteristics	Concentrate, enriched by C_{60}	Concentrate, enriched by C_{70}
Content of C_{60} (mg)	72520	1000
Content of C_{70} (mg)	7760	15000
Content of C_{76} (mg)	120	970
Content of C_{78} (mg)	139	231
Content of C_{84} (mg)	796	234
Content of $_{60}$ (mg)	750	320
Content of $_{602}$ (mg)	90	70
Mass (mg)	82175	17825
Distribution of C_{60} (mass.%)	98.6	1.4
Distribution of $_{70}$ (mass.%)	34.1	65.9
Distribution of $_{76}$ (mass.%)	11.0	89.0
Distribution of $_{78}$ (mass.%)	37.6	62.4
Distribution of $_{84}$ (mass.%)	77.3	22.7

fullerene separationdescribed above, we may produce fullerene concentrates with compositions, considerably varying from the above-described example. The factors, which can rule such (re)crystallization process are the following: composition of the initial fullerene extract, phases masses – L:S, temperature of HTP, temperature of LTP etc. Changing of other factors, such as time of HTP or LTP, regimes of mixing or saturation, to our opinion, make the process a-equilibrium, non-static and thus, not easily controlled.

3. Conclusion

We have elaborated an original, highly efficienct method of pre-chromatography crude separation of light fullerenes (C_{60} and C_{70}), based on the multistage processes of (re)crystallization — the solution of fullerenes solid solutions in liquid solvent (o-xylene) or in liquid o-xylene solutions and the crystallization of solid solutions from saturated liquid solutions. The process is developed in a poly-thermal regime in the temperature ranges from $-20\,^\circ$C to $85\,^\circ$C. As a result, the initial fullerene extract (solid solution) may be efficiently divided into two different solid solutions — the first considerably enriched by fullerene C_{60} and the second considerably enriched by fullerene C_{70}. Heavy fullerenes — C_{76}, C_{78}, C_{84} … are distributed between these solid solutions.

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