

Quantitative study on metallofullerene separation by chemical reduction

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Endohedral metallofullerene (EMF) is expected to be applied in electronics and medicine because of its excellent donor-acceptor properties and unique structure. Among these useful applications, the application in nuclear medicine using radioactive metallofullerenes is promising. However, the production yield of EMFs is generally low: for example, the yield of EMFs in whole fullerene species is less than 1% with the commonly employed arc discharge method. Therefore, the separation and purification of EMFs from a large amount of empty fullerene species are needed. In general, high-performance liquid chromatography (HPLC) is employed for the separation/purification of EMFs from empty fullerenes. Because this method is not always efficient from the viewpoint of cost and time consumption, a more efficient method is required to be developed.

Recently, low-cost separation methods for EMFs using the chemical redox reaction were reported.^{1,2)} Considering the separation of carrier-free radioactive EMFs, separations through the reduction of EMFs using an electron donor are expected to be suitable because these methods do not include a process using a large amount of carriers such as the formation of the precipitate. However, these separation methods have some problems because the separation efficiency is not very high and the number of steps is large. Currently, we are attempting to develop a separation method with higher efficiency and smaller number of steps than the other methods through the chemical reduction of EMFs. In this study, we employed the radio-tracer method to acquire quantitative data for the separation by chemical reduction for determining the best separation condition.

To obtain the radio tracer of ¹³⁹Ce, a dried La₂O₃ pellet (600 mg/cm²) was irradiated with 3 μA of 24 MeV deuteron for 2 h at the RIKEN AVF cyclotron. After the irradiation, ¹³⁹Ce and the target material La were converted into their nitrate forms, dissolved in ethanol, and then injected into porous carbon rods for fullerene generation. Radioactive ¹³⁹Ce EMFs were produced by the arc discharge method and extracted together with empty fullerenes from the soot by CS₂. Mixed solutions of polar solvents (acetonitrile: MeCN, acetone, and methanol: MeOH) and small amounts of electron donors (triethylamine: TEA, tripropylamine: TPA, tetrahydrofuran: THF, *N,N*-dimethylformamide: DMF, pyridine, and aniline) for the reduction of EMFs were added into these CS₂ so-

lutions and then stirred. To separate the produced EMF anion from the residual empty fullerene precipitate, these solutions were passed through a membrane filter. A few drops of an aqueous solution of dichloroacetic acid were added into the filtrate samples for neutralizing the EMF anion, and the neutralized EMFs were re-dissolved in chlorobenzene (F). The residual empty fullerenes on membrane filters were dissolved in CS₂ for recovery from a filter (P). The γ ray emitted from these solutions and filter were detected using a Ge detector.

Figure 1 shows the rate% of radioactivity observed in F, P, and filter for each sample. In principle, radioactivity observed in F is derived from radioactive EMFs separated from empty fullerenes and that in P is derived from radioactive EMFs that remained in the empty fullerene precipitate. Accordingly the rate% of F indicates the separation efficiency of EMFs. Considering the donor number (DN) which is known as an index indicating the strength of the electron donor properties, the electron donors used in this study can be arranged according to their performance as TEA >TPA >aniline >pyridine >DMF >THF.³⁾ In the case of MeCN as the polar solvent, a rate% greater than 80% in F was found with alkylamines such as TPA and TEA. These results indicate that good electron donors such as TPA and TEA easily reduce EMFs. From the viewpoint of the polarity of the solvent, the rate% of F for the solvents with large polarity such as MeCN is found to be larger than that for the solvents with small polarity such as acetone. On the other hand, the rate% of F for MeCN which is a non-protic solvent is superior to that for MeOH which is a protic solvent in spite of both polarities being comparable.

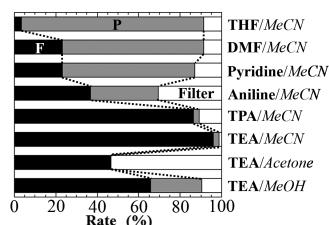


Fig. 1. Observed radioactivity in solution F (black), solution P (gray), and filter (white) for each sample.

References

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