Study on Separation of Structural Isomer with Magneto-Archimedes method

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Abstract. Organic compounds are refined by separating their structural isomers, however each separation method has some problems. For example, distillation consumes large energy. In order to solve these problems, new separation method is needed. Considering organic compounds are diamagnetic, we focused on magneto-Archimedes method. With this method, particle mixture dispersed in a paramagnetic medium can be separated in a magnetic field due to the difference of the density and magnetic susceptibility of the particles. In this study, we succeeded in separating isomers of phthalic acid as an example of structural isomer using MnCl₂ solution as the paramagnetic medium. In order to use magneto-Archimedes method for separating materials for food or medicine, we proposed harmless medium using oxygen and fluorocarbon instead of MnCl₂ aqueous solution. As a result, the possibility of separating every structural isomer was shown.

1. Introduction

Organic compounds are used in many fields such as industrial products, foods and medicines. They are refined by separating their structural isomers contained in the raw materials. The separation methods are distillation, crystallization and extraction. However, distillation consumes the large amount of energy. The crystallization and the extraction have a problem in the low separation accuracy [1]. These problems could be remarkable in separating structural isomers, etc. that have very similar physical properties. Therefore, new separation method is needed from the viewpoint of environmental conservation.

In this study, we focused on the difference of magnetic susceptibility and density between organic compounds and their structural isomers, that is, we used a magnetic separation method. Considering organic compounds are diamagnetic, we proposed magneto-Archimedes method which is effective for separation of diamagnetic mixture. There are some reports studying magneto-Archimedes separation for metals, foods or plastics [2, 3, 4]. However, the separation of the organic compound and its structural isomers has not been reported before. In this work, we chose isomers of phthalic acid (figure 1) as the separation objects. Each of them is white particle whose size is about 50 µm.
2. Magneto-Archipedes method

2.1. Magneto-Archipedes effect [5]
Particle mixture dispersing in the medium can be separated in the magnetic field with magneto-Archipedes method, using the difference of levitation or sedimentation height of each particle. Levitation or sedimentation is induced by magneto-Archipedes effect.

In figure 2, z axis was set to vertical direction where upward is positive. The resultant force acting on the particle in the medium which is placed in the magnetic field, \( F_z \), is the sum of the magnetic force, gravity force and buoyancy. Based on the Archimedes’ principle, buoyancy is the reaction force of the resultant force acting on the medium which has the same volume as the particle. Thus, \( F_z \) can be expressed as equation (1). Here, \( \chi \) (-), \( \mu_0 \) (N/A²), \( B \) (T), \( \rho \) (kg/m³) and \( g \) (m/s²) are magnetic permeability, magnetic flux density, density and gravitational acceleration, respectively. The subscripts \( p \) and \( m \) correspond to particle and medium. Magnetic force acting on the particle is expressed in the first term. Considering \( \partial B_z/\partial z \) is negative, magnetic force acting on the paramagnetic particle (\( \chi_p > 0 \)) is negative, which corresponds to attractive force. On the other hand, the force acting on the diamagnetic particle (\( \chi_p < 0 \)) is positive, which corresponds to repulsive force.

\[
F_z = \frac{\chi_p}{\mu_0} B_z \frac{\partial B_z}{\partial z} - \rho_p g + \left( \frac{\chi_m}{\mu_0} B_z \frac{\partial B_z}{\partial z} - \rho_m g \right)
\]  

(1)

Since paramagnetic medium is usually used in magneto-Archipedes method, \( \chi_m \) is positive. Since \( \partial B_z/\partial z \) is negative, and then the magnetic force acting on the medium is negative, corresponding to the third term in the parentheses. Therefore, buoyancy acting on the particle placed in the magnetic field is positive and becomes larger than that without the magnetic field, which results in the particle levitation. This effect is called magneto-Archipedes effect.

2.2. The mechanism of magneto-Archipedes method
Here, the particle levitation mechanism of magneto-Archipedes method is explained. When buoyancy is larger than the sum of magnetic and gravity force (\( F_z \geq 0 \)), the particle levitates. When the three forces balance (\( F_z = 0 \)), the particle keeps levitation at certain height. Because \( \chi_p < \chi_m \) in this work, the levitation condition (\( F_z \geq 0 \)) can be shown in equation (2).
\[ B_z \frac{\partial B_z}{\partial z} \leq \frac{\rho_p - \rho_m}{\chi_p - \chi_m} \mu_0 g \tag{2} \]

Usually, \( \chi_p \) of the diamagnetic material is negative and its magnitude is much smaller than \( \chi_m \), therefore \( \chi_p \chi_m \) of equation (2) can be approximated as \( -\chi_m \). When equation (2) is satisfied, the relationship between \( \rho_p \) and \( B_z \partial B_z/\partial z \) can be shown in figure 3(a).

\( B_z \partial B_z/\partial z \) required for levitation of each particle, denoted as 1 and 2, having density of \( \rho_1 \) and \( \rho_2 \) are calculated and presented in the figure 3(b). Figure 3(b) shows \( B_z \partial B_z/\partial z \) as a function of height from the magnet used in this experiment. According to figure 3(b), particle 1 and 2 levitate at \( h_1 \) and \( h_2 \) respectively. Using the difference of levitation heights, each particle can be separated.

![Figure 3](image_url)

**Figure 3.** Mechanism of separation. Relation between density of particle and \( B_z \partial B_z/\partial z \) for levitation is shown in (a). \( B_z \partial B_z/\partial z \) distribution against height from magnet center is shown in (b).

When the concentration or composition of the medium is changed, the right-hand side of equation (2) is also changed. Thus, the inclination and the intercept of figure 3(a) depends on the medium, which affects the levitation height of each particle. In addition, the profile of figure 3(b) depends on the magnet, which also affects the levitation height. Effective separation is possible when the appropriate medium and magnet are chosen.

2.3. Flowchart for Magneto-Archimedes method

Based on above discussion, we proposed the procedure of Magneto-Archimedes separation was shown in figure 4. It consists of determining the physical property of separation objects, choice of medium, calculation of \( B_z \partial B_z/\partial z \) for levitation, choice of magnet, estimation of levitation height, and then separation experiment. The separation conditions in this study were determined based on the flowchart presented in figure 4.

![Figure 4](image_url)

**Figure 4.** Flowchart for magneto-Archimedes method.
3. Separation of isomers of phthalic acid

3.1. Choice of the medium and magnet

The density and susceptibility of isomers of phthalic acid are shown in table 1[6, 7, 8].

| Structural isomer       | Density (kg/m³) | Susceptibility (-) |
|-------------------------|-----------------|--------------------|
| Phthalic acid           | 1590            | -1.00×10⁻⁵         |
| Isophthalic acid        | 1540            | -9.85×10⁻⁶         |
| Terephthalic acid       | 1510            | -9.53×10⁻⁶         |

We chose MnCl₂ aqueous solution which shows paramagnetism as the medium. Due to high solubility in water, the density and susceptibility of MnCl₂ solution can be controlled by its concentration. Figure 5 shows the relation between concentration of MnCl₂ solution and \( B_z \frac{\partial B_z}{\partial z} \) for levitation of each particle which are calculated by equation (2) and table 1.

![Figure 5](image)

**Figure 5.** Relation between concentration of MnCl₂ solution and \( B_z \frac{\partial B_z}{\partial z} \) for levitation of each particle.

Figure 5 shows that the difference of \( B_z \frac{\partial B_z}{\partial z} \) for levitation between three structural isomers, demonstrating the largest difference at 10-15 wt. % MnCl₂ solution. Thus, 12 wt. % MnCl₂ solution, whose density was 1100 kg/m³ and magnetic susceptibility was \( 2.10 \times 10^4 \), was chosen as the medium. However, even in case 12 wt. % MnCl₂ solution was used, the difference of \( B_z \frac{\partial B_z}{\partial z} \) for levitation among three acids was too small to separate with permanent magnet. Therefore, superconducting solenoidal magnet shown in figure 6 (model number: JMTD-10T100E3, maximum magnetic flux density: 10 T) was used.

![Figure 6](image)

**Figure 6.** Superconducting solenoidal magnet.
3.2. Estimation of levitation heights

Figure 7(a) shows $B_z \partial B_z / \partial z$ for levitation of the particle as a function of $\rho_p$ with 12 wt. % MnCl$_2$ solution. In this case, each isomer gets on the same line because $(\chi_p - \chi_m)$ of each isomer can be approximated as “- $\chi_m$”, in other words, $\chi_m$ is much larger than $\chi_p$ as shown in table 1. Figure 7(b) shows $B_z \partial B_z / \partial z$ distribution against height from the center of magnet which generates 3 T in the maximum magnetic flux density. Based on figure 7(a) and table 1, $B_z \partial B_z / \partial z$ for levitation of each particle was estimated by figure 7(a) and levitation height was estimated by figure 7(b). Each particle was estimated to levitate at the height in the order of terephthalic (0.079 m), isophthalic (0.064 m) and phthalic acid (0.071 m).

![Figure 7](image)

**Figure 7.** Estimation of levitation height of each object. $B_z \partial B_z / \partial z$ for levitation as a function of density of particle is shown in (a). $B_z \partial B_z / \partial z$ distribution against height from magnet center is shown in (b).

3.3. Separation experiment

Based on above estimation, we conducted separation experiment. Firstly, 12 wt. % MnCl$_2$ solution and mixture of separation objects were put into the glass vessel and installed near the center of superconducting solenoidal magnet. As a result, due to the density difference between the medium and each particle, all the isomers settled to the bottom. Then, the vessel was elevated slowly and each isomer levitated at the different height in the order of terephthalic (0.074 m), isophthalic (0.085 m) and phthalic acid (0.092 m). Figure 8 shows the result. This phenomenon was simulated by the calculation with satisfactory accuracy, indicating that we succeeded in separating isomers of phthalic acid.

![Figure 8](image)

**Figure 8.** Separation experimental result with 12 wt. % MnCl$_2$ solution.
4. Separation without heavy metal solution

4.1. Choice of the medium and magnet
Foods and medicines are also the subjects of the interest. Paramagnetic medium including heavy metals such as MnCl$_2$ solution should not be suitable for separation of foods or medicines, because heavy metal is harmful to human body. In order to separate materials of foods or medicines, paramagnetic medium without heavy metals should be examined. Oxygen gas is paramagnetic, however the density is very small and magneto-Archimedes effect is hard to be observed.

We focused on oxygen dissolved fluorocarbon as new medium. Fluorocarbon has carbon-fluorine bonds. Due to the bond, intermolecular force is smaller than that of hydrocarbon, and oxygen gas can be dissolved into fluorocarbon easily. Therefore, when high pressure oxygen gas is dissolved in fluorocarbon, it becomes paramagnetic [9]. Moreover, many fluorocarbons is volatile, so oxygen dissolved fluorocarbon is suitable for foods and medicines. Physical property of fluorocarbon used in this study (C$_4$F$_9$OCH$_3$) is shown in table 2 [10].

| Density (kg/m$^3$) | Susceptibility (-) | Boiling point (℃) | Melting point (℃) | Oxygen solubility (mL/L) |
|-------------------|--------------------|-------------------|-------------------|-------------------------|
| 1520              | -7.75×10^{-6}      | 61                | -135              | 300                     |

Magnetic susceptibility of oxygen dissolved fluorocarbon was calculated, based on the assumption that oxygen gas was ideal gas which follows Henry’s law. The calculation result is shown in figure 9. Magnetic susceptibility increased linearly against the pressure of oxygen gas and became positive at 1.5 MPa.

![Figure 9. Relation between pressure of oxygen gas and the calculated susceptibility of oxygen dissolved fluorocarbon.](image)

In this chapter, pellets (φ3×1.5 mm) of isomers of phthalic acid prepared with tablet forming device were separated. The density of each pellet measured with an analytical valance (model number: AUX-220) with a specific gravity measurement kit (model number: SMK-401) is shown in table 3. According to table 1 and 3, the magnitude relation of the density of each isomer in pellet form differs from that in powder form. That may be caused by air included in each pellet, but the clear reason is currently under investigation.

| Density (kg/m$^3$) | Phthalic acid | Isophthalic acid | Terephthalic acid |
|-------------------|---------------|-----------------|------------------|

Based on table 3, $B_z/\partial B_z/\partial z$ for levitation as a function of density of particle at 1.5 MPa oxygen dissolved fluorocarbon is calculated and presented in figure 10(a). In this case, isophthalic acid was
excluded because it was estimated to float in the medium without magnetic field due to the difference of density between isophthalic acid and fluorocarbon. Moreover, each isomer does not get on the same line. The difference between figure 7(a) and figure 10(a) is brought about by the difference of \((\chi_p - \chi_m)\) in equation (2). In this case, \((\chi_p - \chi_m)\) cannot be approximated as \(\chi_m\). This is because magnitude of \(\chi_m\) is smaller than that of \(\chi_p\) as shown in figure 9 and table 3. From figure 10(a), \(B_z \partial B_z / \partial z\) for levitation of each isomer was calculated as -48.1 and -60.0 T²/m respectively for phthalic and terephthalic acid. The difference between -48.1 and -60.0 T²/m was very small to separate pellets with permanent magnet. On the basis of the calculation, superconducting solenoidal magnet shown in figure 6 was also used.

4.2. Estimation of levitation heights

Figure 10(b) shows the distribution of \(B_z \partial B_z / \partial z\) against the height from the center of the magnet which generates 8 T at the center of the magnet. From figure 10, each isomer was estimated to levitate at 0.192 m for terephthalic and 0.199 m for phthalic acid.

\[
\frac{B_z \partial B_z}{\partial z} = \frac{\rho_p - \rho_m}{\chi_p - \chi_m} \mu_0 g
\]

Figure 10. Estimation of levitation height of each pellet. \(B_z \partial B_z / \partial z\) for levitation as a function of density of particle is shown in (a). \(B_z \partial B_z / \partial z\) distribution against height from magnet center is shown in (b).

4.3. Separation experiment

Firstly, the pressure resistant vessel consisting of glass and polycarbonate vessels shown in figure 11(a) and (b) are prepared, and fluorocarbon and three different pellets were encapsulated in the vessel. Then, isophthalic acid floated on the surface of medium, whereas other two pellets settled at the bottom of vessel. After that, 1.5 MPa oxygen gas was fed into the vessel as shown in figure 11(c). Then the vessel was put at 0.12 m height from the center of the magnet. Each pellet was expected to levitate at different height as shown in figure 11(d). The experimental photograph is shown in figure 11(e). Each pellet levitated at different height from the center of magnet in the order of terephthalic (0.19 m), phthalic (0.20 m) and isophthalic acid (surface of medium) similar to the estimation as figure 11(d). The result indicates the possibility of separation of isomers of phthalic acid with oxygen dissolved fluorocarbon.
5. Conclusion
In this study, we developed a new method to separate structural isomers, and tried to separate isomers of phthalic acid by magneto-Archimedes method. Based on calculation for effective separation, 12 wt. % MnCl₂ solution as a medium and superconducting solenoidal magnet generating 3 T were used. As a result, isomers of phthalic acid were separated as predicted by calculation.

Moreover, considering the application of magneto-Archimedes method for foods and medicines, we proposed oxygen dissolved fluorocarbon as the medium without heavy metals. 1.5 MPa oxygen dissolved fluorocarbon and superconducting solenoidal magnet generating 8 T were used, based on the designing for the effective separation. As a result, we succeeded in separating pellets of isomers of phthalic acid. In progress, we are trying to separate powdered isomers of phthalic acids with oxygen dissolved fluorocarbon.

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