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**Proposal of a New Liquid Separation Method Using Sub-Nanopores  
—Separation of Alkanes with Different Chain Lengths  
Using the Internal Pores of Polyolefin Crystal—**

Assistant Professor Ayano Chiba of the Keio University Faculty of Science and Associate Professor Ryo Akiyama and Akio Oshima (graduate school student; completed master's program in 2019) of the Kyushu University Faculty of Science discovered a liquid separation method that makes use of crystalline polyolefin(\*1) film and proposed a theory on its mechanism. In general, liquid separation refers to the extraction of specific molecules from a mixture containing multiple types of molecules. In liquid separation using a conventional porous film, a strategy of only allowing molecules smaller than the pores to pass through is employed. In this study, however, it was revealed that there is a strong tendency for large molecules to selectively enter a porous medium in a liquid mixture. This can be explained by a statistical mechanics theory called the Asakura-Oosawa model. In fact, when a crystalline film made of polyolefin called isotactic poly(4-methyl-1-pentene) was immersed in a binary mixture of normal (straight-chain) alkanes, the longer of the normal alkanes(\*2) were selectively absorbed by the pores in the crystal. This can be thought to be a spontaneous liquid separation due to molecular volume. Of the conventional separation methods based on volume, a method called gel permeation chromatography (GPC), which separates macromolecules based on the degree of polymerization, that is, the effective volume, is well known. This study provides a new perspective on separating low-mass molecules by their volume.

The outcomes of this research were published in the online version of the American scientific journal "Langmuir" on November 18 (Mon.), 2019 (US time), ahead of its publication in the printed version of the same journal.

1. Background of research

Many studies have been conducted up to now on the separation of specific molecules in liquid and gas mixtures with nanoscale pores. The idea was to separate smaller molecules that would easily pass through the pores from larger molecules that would not easily pass through them, just like a kitchen strainer. In this study, it was discovered experimentally that the larger of the molecules that can go inside the mesh pores of the strainer, so to speak, are spontaneously absorbed by the pores, and this phenomenon was theoretically explained.

## 2. Content of research and results

The liquid separation method proposed in this study can be viewed as being driven by entropy. A common image for the term entropy would be, for example, to picture large and small particles mixing together as the entropy of a system increases. However, the liquid separation being proposed in this study originates from the increase in entropy of the entire system due to the larger particles fitting into the pores. In other words, it can be expressed as liquid separation driven by entropy. Here, the explanation presented above assumes that the volume of the entire system is constant.

The effective force between the low-mass molecules, such as alkanes, and the wall surface of the macromolecular crystal pores is called depletion interaction, and is a concept that has been widely used to date in the study of phase separation of colloid systems and in the field of biophysics. In this study, a new liquid separation method using confined space was proposed by applying this concept to low-mass molecules such as alkanes.

### <Reference>

(Reference 1) Sho Asakura and Fumio Oosawa, "On Interaction between Two Bodies Immersed in a Solution of Macromolecules", *The Journal of Chemical Physics* 22, 1255-1256 (1954).

### <Details of original paper>

#### • Title

"Confined Space Enables Spontaneous Liquid Separation by Molecular Size: Selective Absorption of Alkanes into a Polyolefin Cast Film"

#### • Authors

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#### • Journal

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### <Glossary>

#### \*1 Polyolefin

A general term for the world's most widely used resin, as represented by polyethylene and polypropylene. In this research, a polyolefin called isotactic poly(4-methyl-1-pentene) is used.

#### \*2 Normal alkane

An alkane in which the carbon atoms are bonded in a straight chain. For example, pentane (C<sub>5</sub>H<sub>12</sub>) and decane (C<sub>10</sub>H<sub>22</sub>).

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