Selective absorption phenomena of longer-chain alkanes

into nano- and sub-nano-porous space

A. Chiba^A, H. Ito^A, H. Murashige^A, R. Inoue^B, K. Morishima^B, K. Matsuda^C, H. Kyakuno^C

A_{Keio} Univ., B_{Kyoto} Univ., C_{Kanagawa} Univ.

The most energy-consuming part of the chemical industry is the separation and purification process. Some data show that about 60% of the energy used in chemical engineering is spent on distillation. If similar alkanes can be separated without heating, this could be industrially important.

Recently we have found a phenomenon in which a film of polyolefin, when immersed in a mixture of alkanes of different chain lengths, selectively absorbs the longer chain length. Such selective absorption phenomenon provides useful insights into separation methods for chemically similar molecules. Specifically, an isotactic poly(4-methyl-1-pentene) (P4MP1) film selectively absorbs decane from a mixture of decane and hexane [1]. Infrared spectroscopy was used in previous studies by Uda et al. [2] that firstly reported similar selective absorption as well as our studies [1,3]. Thus the microscopic picture of this selective absorption was not known. The purpose of our small-angle neutron scattering (SANS) experiment is thus to clarify the spatial scale on which selective absorption is occurring.

Experiments were performed on decane and hexane as guest molecules and some host modelues such as carbon nanotubes as well as P4MP1. Measurements were conducted with SANS-U at an incident wavelength of 7 Å and camera lengths from 1 m to 16 m. In order to distinguish the scattering by each solvent, measurements were performed with two different mixtures of solvents: a mixture of hexane(H) and decane(D) and a mixture of hexane(D) and decane(H). Here, H and D stand for natural and deuterated solvents, respectively. Figure 1 shows the scattering profiles of P4MP1 films immersed in decane (D)-hexane mixed solvent and decane-hexane (D) mixed solvent. If there were no selectivity in absorption, both signals should coincide. However, the SANS intensity was clearly higher when the P4MP1 film was immersed in the mixture of hexane(H) and decane(D), which suggests that decane(D) is selectively absorbed in the nmscale and sub-micron range. Interestingly, similar results were obtained when the host was a carbon nanotube, suggesting that long-chain alkane absorption from mixed alkanes is a generalizable phenomenon for nano- and subnano-porous space immersed in alkane mixtures.

[1] A. Chiba, A. Oshima, R. Akiyama, Langmuir **35**, 17177 (2019).

[2] Y. Uda, *et al.*, Macromol. Rapid Commun. **25**, 1900 (2004).

[3] H. Murashige, *et al.*, Macromol. Symp. **408**, 2200090 (2023).



Fig. 1. SANS profiles of P4MP1 films immersed in solvent mixtures of decane and hexane. Black solid and red dashed lines indicate the profile of the film immersed in the mixtures of deuterated decane and hexane, and decane and deuterated hexane, respectively. Note that the scattering profile of the pristine film without solvent immersion shows much lower signal since the densities of crystalline and amorphous P4MP1 are almost same and does not have contrast.