Enclathration of Ethane, Propane, and Propylene into Urea Clathrates and Roles of Methanol on Urea Clathrate Formation

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ABSTRACT: As a guest molecule of urea clathrate, a long-chain normal alkane and its derivative with low substituents in methanol solutions have been reported. To investigate the role of methanol in the urea clathrate formation, in the present study, we used propane (C₃H₈), propylene (C₃H₆), ethane (C₂H₆), and methane (CH₄) as guest molecules. Raman spectra and powder X-ray diffraction profiles revealed that, regardless of the existence of methanol, the C₂H₆, C₃H₈, and C₃H₆ molecules are enclathrated into urea clathrates with a hexagonal structure, whereas there is no urea clathrate formation enclathrating CH₄. The pressurization of the urea clathrates including C₂H₆ and C₃H₈ reveals that no pressure-induced structural phase transition occurs at pressures up to 200 MPa. In spite of the guest molecule much shorter than the lattice constant of the a-axis of the hexagonal channel structure, the urea clathrates have a fairly rigid structure against the compression. Methanol as an auxiliary solution is not always necessary for the urea clathrate formation. Methanol plays a role in decreasing the activation energy of the urea clathrate formation, although it makes urea clathrate thermodynamically unstable due to the high solubility of urea in methanol.

1. INTRODUCTION

Some organic compounds form an inclusion compound with suitable guest species. The inclusion compounds have been studied as a medium of separation and storage, a specific reaction field, and so on. It is well known, as one of them, that urea molecules form an inclusion compound (hereafter, urea clathrate) with a hexagonal channel structure in which a guest molecule is enclathrated.1−3 Host structure of urea clathrate, like a honeycomb, is hydrogen-bonded between urea molecules and commonly a hexagonal structure (space group, P6₁22).3 This host structure is stable only when the channels are filled with a dense packing of guest molecules.1 It is well known that, as a guest molecule of urea clathrate, a long-chain n-alkane or its derivative with low substituents is enclathrated. The stereoselectivity (shape and size) of urea clathrates, that is, how it can be a guest molecule of urea clathrate is still the focus of attention for chemical engineers, especially in the fields of gas separation and gas storage.

The thermodynamic stabilities of urea clathrates under atmospheric pressure have been reported.4−7 White et al.7 reported the thermodynamic stability of urea clathrates with three different alkanes (decane, dodecane, and hexadecane). The shorter the alkane in the urea clathrate, the lower the equilibrium temperature of the urea clathrate under atmospheric pressure. This literature suggests that the stability of urea clathrate depends on the melting point of the guest molecule and, at a temperature above the melting point of the guest molecule, urea clathrate becomes much less stable in competition with liquefying the guest molecule. Therefore, a short-chain molecule, having relatively low melting point, could make urea clathrates unstable at ambient temperature. Then, when the urea clathrate is formed in a saturated methanol solution of urea, instead of the formation of urea clathrate, the original urea crystal with tetragonal structure is recrystallized.1

The n-heptane (n-C₇H₁₆) has a molecular-length similar to the unit lattice of c-axis (c₁₆) of the host hexagonal structure.8 That is, in the case of an n-alkane shorter than n-C₇H₁₆, the length of n-alkane (c₁₆) as a guest molecule in the urea clathrate is shorter than that of c₁₆. The schematic illustration is shown in Figure 1. The shorter length of the guest molecule leads to structural instability in the urea clathrate. How small molecule form the urea clathrate is very interesting. In the early literature,9 propane (C₃H₈) and n-butane (n-C₄H₁₀) as the small guest molecules enclathrated into urea clathrate had been reported. Moreover, the urea clathrate with C₃H₆ (hereafter, C₃H₆/urea clathrate; G/urea clathrate (G: guest molecule)) was formed without dissociation of urea to methanol in advance, whereas the C₃H₈/urea clathrate was not formed in the presence of methanol.4,5 The formation of n-C₇H₁₆/urea clathrate is independent of the existence of methanol. The role
of methanol, which is generally considered as an auxiliary solvent, has not been understood yet.

In the present study, to clarify how small molecules can be enclathrated in urea clathrates and why the existence of methanol affects the urea clathrate formation, the urea pressurized directly with methane (CH₄), ethane (C₂H₆), C₃H₈, and propylene (C₃H₆) in the presence or absence of methanol has been investigated by means of Raman spectroscopy. The crystal structure of the formed urea clathrates has been analyzed by powder X-ray diffraction (PXRD). The stability of the formed urea clathrates against the pressure has been investigated.

2. RESULTS AND DISCUSSION

2.1. Urea Clathrate Formation without Methanol.

Figure 2 shows the Raman spectra corresponding to the intramolecular C–N and N–H stretching vibrations of urea and the intramolecular C–H stretching vibration of the guest molecule in the CH₄ + urea, C₂H₆ + urea, C₃H₈ + urea, and C₃H₆ + urea binary systems (without methanol), accompanied by those of the n-C₈H₁₈/urea clathrate and pure solid urea. Every spectrum was measured at the same condition (atmospheric pressure and 77 K). The n-C₈H₁₈/urea clathrate has a hexagonal channel structure, whose space group and lattice constants are P6₃22 and (a = 0.81874 nm, c = 1.10046 nm), respectively. The n-C₈H₁₈/urea clathrate was formed by cooling the mixture of n-C₈H₁₈ and the saturated methanol solution of urea.

The Raman spectra of urea in the C₂H₆ + urea, C₃H₈ + urea, and C₃H₆ + urea systems shown in Figure 2b–d are similar to that of n-C₈H₁₈/urea clathrate shown in Figure 2e and different from those of the CH₄ + urea system and pure solid urea shown in Figure 2a,f. Moreover, the last two spectra of Figure 2a,f are also similar. The Raman peaks detected around 3230 and 3360 cm⁻¹ of C₂H₆ + urea, C₃H₈ + urea, and C₃H₆ + urea systems are slightly shifted to lower wavenumber side and higher wavenumber side, respectively, compared to those of n-C₈H₁₈/urea clathrate. It is speculated that the enclathration of a guest molecule smaller than a unit length along the c-axis of the hexagonal structure of urea clathrate would affect the host structure of urea clathrate. The n-heptane (n-C₇H₁₆) has a similar molecular length to the unit lattice of the c-axis of the hexagonal structure. Raman shifts of the intramolecular C–H and C–C stretching vibrations of guest molecules were different from those of pure guest molecules. In the case of C₃H₈ + urea system, as a typical result, Raman shifts of the intramolecular C–C stretching vibration of C₃H₈ (detected around 995 cm⁻¹) are shown in Figure 3. These results reveal the formation of the C₈H₁₈/urea, C₃H₈/urea, and C₃H₆/urea clathrates, similar to the n-C₈H₁₈/urea one. We pressurized the CH₄ + urea system at a pressure up to 200 MPa, but the urea molecules construct no clathrate structure and remain as solid urea. The CH₄ molecule is so small that urea clathrate including CH₄ cannot be formed under the present experimental condition.

The pressure-induced structural phase transition, especially in the case of enclathrating a small guest molecule into the organic inclusion compounds with a channel structure, has been reported. Hydroquinone (HQ) has been recognized as one of them. The channel structure (α-HQ) of HQ clathrate is transformed into the cage structure (β-HQ) in the presence of an appropriate guest molecule with pressurization. For example, α-HQ is transformed to β-HQ under the coexistence of CH₄ at 12 MPa for 5 days. To investigate the pressure effect of the C₈H₁₈/urea and C₈H₁₈/urea clathrates, we pressurized the urea powder with C₈H₁₈ or C₈H₁₈ at a pressure of up to 200 MPa. Figure 3 shows the Raman spectra of the...
in Figure 4. The PXRD patterns of the C$_2$H$_6$/urea, C$_3$H$_6$/urea, and C$_3$H$_8$/urea clathrates. The PXRD patterns obtained in the present study are shown in Figure 3. Raman spectra of the intramolecular C–C (~995 cm$^{-1}$), C–N (~1030 cm$^{-1}$), and N–H (3230–3450 cm$^{-1}$) stretching vibrations of C$_2$H$_6$ + urea binary system prepared at (a) 197 MPa and 253 K, (b) 49.3 MPa and 253 K, (c) pure C$_2$H$_6$, and (d) pure solid urea. All the spectra were recorded at 77 K and atmospheric pressure.

Intramolecular C–C (~995 cm$^{-1}$), C–N (~1030 cm$^{-1}$), and N–H (3230–3450 cm$^{-1}$) stretching vibrations of the C$_2$H$_6$/urea clathrates prepared at 253 K and 49.3 MPa (Figure 3b) and 197 MPa (Figure 3a). Raman spectra of the intramolecular C–N and N–H stretching vibrations of urea are independent of pressure up to 197 MPa. Also, Raman spectra of the intramolecular C–C stretching vibration exhibited no significant pressure dependence, whereas the relative intensity of C$_2$H$_6$ to urea became large with increasing pressure. These results imply that there is no structure phase transition of C$_2$H$_6$/urea clathrate in a pressure range up to 200 MPa. Similarly, Raman spectra of the intramolecular C–C (~880 cm$^{-1}$) and N–H (3230–3450 cm$^{-1}$) stretching vibrations of the C$_3$H$_6$/urea clathrates are independent of pressure. As mentioned above, the CH$_4$ + urea system, unlike CH$_4$ + HQ system, constructs no urea clathrate even at 200 MPa. In the urea clathrate system including a small guest molecule, no pressure-induced structural phase transition occurs, unlike HQ clathrates. The channel structure of urea clathrates can withstand higher pressure, compared with that of HQ clathrates.

The PXRD patterns obtained in the present study are shown in Figure 4. The PXRD patterns of the C$_2$H$_6$/urea, C$_3$H$_6$/urea, and C$_3$H$_8$/urea clathrates were coincident with the main pattern of n-C$_3$H$_{18}$/urea clathrate. These results support the results from the Raman spectra, that is, the C$_2$H$_6$, C$_3$H$_6$, and C$_3$H$_8$ molecules work as guest molecule in urea clathrates with a hexagonal channel structure. The PXRD patterns of C$_2$H$_6$/urea, C$_3$H$_6$/urea, and C$_3$H$_8$/urea clathrates contained the profiles derived from solid urea and solid guest molecules. And those of n-C$_3$H$_{18}$/urea clathrate also contained the profiles derived from solid methanol and solid n-C$_3$H$_{18}$.

Table 1. Space Group and Lattice Constants of Urea Clathrates (Measured at 153 K and Atmospheric Pressure)

| guest               | space group | lattice constants       | present study | present study | present study |
|---------------------|-------------|-------------------------|---------------|---------------|---------------|
| n-C$_3$H$_{18}$     | P6$_2$22    | a = 0.8187 nm, c = 1.1005 nm | present study | present study | present study |
| C$_2$H$_6$          | P6$_2$22    | a = 0.8176 nm, c = 1.1051 nm | present study | present study | present study |
| C$_3$H$_6$          | P6$_2$22    | a = 0.8158 nm, c = 1.1041 nm | present study | present study | present study |
| C$_3$H$_8$          | P6$_2$22    | a = 0.8168 nm, c = 1.1042 nm | present study | present study | present study |
| n-C$_3$H$_{18}$     | P6$_2$22    | a = 0.8227 nm, c = 1.102 nm | ref 8         | ref 8         | ref 8         |

*Measured at 200 K and atmospheric pressure.

Figure 4. PXRD patterns of (a) C$_2$H$_6$/urea clathrate prepared at 137 MPa, (b) C$_3$H$_6$/urea clathrate at 66.4 MPa, (c) C$_3$H$_8$/urea clathrate at 0.8 MPa, (d) n-C$_3$H$_{18}$/urea clathrate with methanol, and (e) pure solid urea. All the samples were prepared without methanol at 253 K for a couple of days. All the patterns were recorded at 153 K and atmospheric pressure.

Figure 5 shows the Raman spectra of the intramolecular C–(C$_2$H$_6$) stretching vibrations of C$_2$H$_6$ + urea + methanol, and C$_3$H$_8$ + urea + methanol, and C$_3$H$_6$ + urea + methanol ternary systems accompanied by those of the n-C$_3$H$_{18}$/urea clathrate.
and pure solid urea. Raman spectra corresponding to the O−H and C−H stretching vibrations derived from both unreacted and/or incorporated methanol are also included in Figure 5. Every spectrum was measured at the same condition (atmospheric pressure and 77 K). As is the case in the guest + urea binary systems (without methanol, Figure 1), the Raman spectra of urea in the C2H6 + urea + methanol, C3H6 + urea + methanol, C3H8 + urea + methanol systems shown in Figure 5b−d, respectively, are similar to those of n-C8H18/urea clathrate shown in Figure 5e. That is, the C2H6, C3H6, and C3H8 molecules work as guest molecule in the urea clathrate with a hexagonal channel structure even in the presence of methanol. The presence of methanol does not prevent the urea molecules from forming urea clathrate, different from the results of the C3H8 + urea + methanol system in the literature.9

In the case of using CH4 as a guest molecule, the Raman spectrum as shown in Figure 5a is completely different from the spectra of urea clathrates (Figure 5b−d) as well as those of pure solid urea (Figure 5f) and the CH4 + urea binary system (without methanol, Figure 2a). The Raman peak corresponding to the C−H stretching vibration of CH4 in the newly formed urea compound was very weak or not detected because it is difficult to distinguish from the C−H vibrations of methanol. To confirm what kind of structure the newly formed urea compound has, the additional two samples were prepared from the saturated methanol solution of urea pressurized with hydrogen (H2) and just from the saturated methanol solution of urea without pressurization. The Raman spectra and PXRD profiles are shown in Figures 6 and 7, respectively. In spite of pressurization with H2, the Raman spectra similar to that in the CH4 + urea + methanol ternary system were detected. The very weak Raman peaks of H2 vibration in the urea complex of the H2 + urea + methanol ternary system are detected at 4110 and 4144 cm⁻¹ (not shown). The PXRD profiles suggest that the newly formed urea complex is different from the hexagonal urea clathrate, although the crystal structure could not be identified. The present results reveal that the newly formed urea complex including H2 and CH4, which seems to have neither channel- nor cage-like structure, would not be appropriate for the gas storage material like HQ clathrates.13,14

2.3. What is the Role and Effect of Methanol? To investigate the effect of methanol on the stability of urea clathrate, we have adopted C3H8 as a small guest molecule. The thermodynamic stability boundaries of the C3H8/urea clathrate with and without methanol are shown in Figure 8. In the case of coexistence with the methanol solution phase, the stability boundary of the C3H8/urea clathrate was shifted to the lower temperature (higher pressure) side. That is, C3H8/urea clathrate in the C3H8 + urea binary system is thermodynamically more stable than C3H8/urea clathrate coexisting with the methanol solution phase. These results revealed that methanol as an auxiliary solvent is not always necessary for C3H8/urea clathrate formation. Rather, instead of methanol solution, the use of liquefied propane phase leads to high stability of C3H8/urea clathrate.
lique after pressurizing the saturated methanol solution of urea with preparation way with and without methanol. Within 6 days from urea clathrate. preparation, the methanol solution of urea should be drained most important factors in utilizing urea clathrates. Urea results also indicate that the solubility of urea is one of the makes urea clathrates thermodynamically unstable. These clathrate formation, but the solubility of urea in methanol solution plays a role in decreasing the activation energy of urea

Considering the kinetics of the urea clathrate formation, methanol plays an important role in accelerating the formation of urea clathrate. Table 2 shows how high pressure was required for the C2H6/urea clathrate formation in the different preparation way with and without methanol. Within 6 days after pressurizing the saturated methanol solution of urea with liquefied C2H6 at a pressure of up to 12.0 MPa and 253 K, C2H6/urea clathrate was formed. In the case without methanol, C2H6/urea clathrate was formed neither at 17.9 MPa nor 40.1 MPa (253 K for 6 days). The pressure of more than ~50 MPa is needed for C2H6/urea clathrate formation. That is, methanol solution plays a role in decreasing the activation energy of urea clathrate formation, but the solubility of urea in methanol makes urea clathrates thermodynamically unstable. These results also indicate that the solubility of urea is one of the most important factors in utilizing urea clathrates. Urea clathrate should be prepared in methanol solution. After preparation, the methanol solution of urea should be drained from urea clathrate.

### Table 2. Effect of Methanol on C2H6/Urea Clathrate Formation at 253 K

| pressure (MPa) | urea clathrate formation |
|---------------|--------------------------|
| with methanol | 12.0 ○                    |
| without methanol | 17.9 ×                  |
|              | 40.1 ×                   |
|              | 54.8 ○                   |

4. CONCLUSIONS

By means of Raman spectroscopy and PXRD, the formation of urea clathrates including C3H6, C2H6, and C3H8 as guest molecule has been revealed. The thermodynamic stability of urea clathrates depends on the guest molecules. The crystal structure of the formed urea clathrates is similar to the hexagonal channel structure of the well-known urea clathrate with n-C6H12 and n-C7H16. The smallest limit of the guest molecule for the urea clathrate formation is laid between the sizes of CH4 and C2H6. The enclathration of CH4 to the urea clathrate is difficult even at 200 MPa. No pressure-induced phase transition from the original channel structure to a cage-like structure occurs at pressures up to 200 MPa. That is, although the guest molecule is much shorter than the lattice constant of the c-axis of the hexagonal channel structure, the urea clathrates including C3H6, C2H6, and C3H8 have a fairly rigid structure against compression.

Some researchers had believed that methanol is necessary for urea clathrate formation. The present results reveal that methanol is not always necessary. Methanol has two different roles: thermodynamic inhibitor of urea clathrate stability and kinetic promoter of urea clathrate formation. In the case without an appropriate guest molecule for urea clathrates,
methanol forms an unknown complex with urea. The methanol–urea complex would have little ability to store CH₄ and H₂.

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Notes
The authors declare no competing financial interest.

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