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Note	

Separation of propane and propylene by urea clathrate formation

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Keywords. Clathrate compound, Urea, Separation, Phase equilibria, Propane, Propylene

ABSTRACT

Separation of propane and propylene is an important issue in the chemical industry due to their similar properties. In this study, the proof-of-concept of propane-propylene separation using urea clathrates has been demonstrated from a thermodynamic viewpoint. We found that thermodynamic stability of urea clathrate including propane (hereafter, propane/urea clathrate, which means "guest(s)/host clathrate") is significantly different from that of propylene/urea clathrate, which provides us with the possibility of propane-propylene separation by urea clathrate formation. When the urea clathrates were prepared from the mixtures of propane and propylene, propane was concentrated in the (propane+propylene)/urea clathrates, whereas propylene was concentrated in guest fluid phase under the coexistence with urea clathrates. The separation of propane by urea clathrate formation would be better suited for the pre-separation before other separation techniques.

1. Introduction

Propane and propylene have similar chemical and physical properties, but they are used for different purposes. Propane, used as a fuel, has the advantage of providing the heat of combustion twice as large as methane [1]. Propylene is mainly used as a material for polypropylene synthesis. Polypropylene has a wide range of applications in the field of research, daily necessities, and medical materials such as plastic containers, syringes, and raw materials for 3D printers [2]. Propane and propylene have been separated by distillation. More than 100 separation stages, however, are required because the relative volatility of propane to propylene is close to unity. Therefore, the separation with only distillation process needs enormous costs [3-5]. Several studies on the efficient separation of propane and propylene have been conducted [3-10]. Membrane separation and adsorption/desorption by zeolites and metal organic frameworks have been considered to be promising methods, but they still have many problems such as structural defects and durability [6-10]. Therefore, they are hard to put to practical use.

Clathrate compound is another candidate for separation medium. Clathrate compound has a three-dimensional structure and physically confines another molecule within the interior of the space. It has been reported that clathrate hydrate (or gas hydrate) would be available as a gas supply, storage, and separation medium [11,12]. Studies on the propane-propylene separation using clathrate hydrates have been reported to be thermodynamically quite efficient. [11]

Urea is known as one of the host substances that form clathrate compounds. Unlike clathrate hydrates with the cage structure, urea clathrates form a hexagonal channel structure [13-16]. The encapsulated guest molecules have less restriction on molecular translational motion, compared to clathrate hydrates with a cage structure [14-16]. Therefore, there is a possibility that urea clathrate is superior to clathrate hydrate in the propane-propylene separation. Typically, urea clathrates are formed by dissolving urea in an auxiliary solvent and recrystallizing it in contact with guest molecules. Yamazaki et al. [17] revealed that urea clathrates can be prepared by directly pressurizing urea with guest molecules (including propane and propylene) at low temperatures. The method without auxiliary solvents allows linear hydrocarbons longer than ethane to be included as guest molecules in the urea clathrate. In this study, using the direct pressurization method [17], the possibility of propane-propylene separation using urea clathrates was investigated from a thermodynamic perspective.

2. Experimental

2.1. Urea clathrate preparation and characterization

The chemicals used in the present study are summarized in Table 1. All of them were used without further purifications after purchase. The urea clathrates were prepared by directly pressurizing urea with propane (C_3H_8), propylene (C_3H_6), or C_3H_8+C_3H_6 mixtures as reported previously [17]. After the fine-powdered urea was loaded in a high-pressure cell, the cell was placed in a thermostatic bath kept at 253 K or 283 K. The urea powder was pressurized with liquefied C_3H_8 and/or C_3H_6 by a deliver pump (JASCO, SCF-Get). After the cell was kept at the temperature for a week, it was quenched and kept in liquefied nitrogen for at least 10 min. Note that the formation duration for a week is long enough for urea clathrate formation. The pressure in the cell was then released and allowed to reach atmospheric pressure at low-temperature room kept at 253 K for analyses by high-pressure differential scanning calorimetry (DSC, Setaram MicroDSC VIIevo) and TCD gas chromatography (TCD-GC, Shimadzu, GC-14B). The sample was placed in a freezer at 223 K for a day to remove unreacted solid C_3H_8 and C_3H_6 that remained in the sample when quenching at liquefied nitrogen temperature of 77 K. The quenched urea clathrate was decomposed at room temperature and atmospheric pressure. Equilibrium compositions were analyzed by using TCD-GC with the packed column (SUS 6.0 m x 3.0 mm i.d.) of DBM+ODPN (95:5) 35 % Shinwasorb-U 60/80.

2.2 DSC measurements of urea clathrates enclathrating single gas at high pressures

Approximately 60 mg of the prepared urea clathrate including C_3H_8 or C_3H_6 (hereafter, "guest(s)/host clathrate") was loaded in a high-pressure DSC cell (maximum working pressure, 40 MPa) precooled to 223 K. The DSC cell was set in a DSC furnace precooled to 228 K. Both the sample and reference DSC cells were connected with the pressure control apparatus (homemade) and the air was purged with C_3H_8 or C_3H_6 precooled to 228 K. After liquefied C_3H_8 or C_3H_6 (precooled to 228 K) was introduced into both sample and reference cells simultaneously to a given pressure, the furnace temperature was increased to 313 K (for C_3H_8/urea clathrate) or 288 K (for C_3H_6/urea clathrate) at a heating rate of 0.1 K/min. The onset temperature of endothermic peak was adopted as the equilibrium temperature of urea clathrate. In addition, water and naphthalene were adopted as references. The uncertainty of the temperature based on the melting temperatures of water and naphthalene is 0.06 K at a heating rate of 0.1 K/min. When the decomposition temperature of urea clathrate is determined with DSC, the effect of the heating rate should be unable to be ignored. We have measured the decomposition temperature of clathrate hydrates with similar DSC setup [18-20], where the onset temperature at 0.1 K/min was 0.6-1.0 K higher than the real equilibrium temperature. According to these results, the maximum uncertainty of the equilibrium temperature of urea clathrate measured with DSC in the present study was 1 K. The pressure was measured with a pressure gauge (Valcom, VPRT, maximum uncertainty 0.4 MPa). The equilibrium pressure was recorded when the decomposition peak appeared. The pressure fluctuation caused by the temperature ramping was relatively large because the pressure media were liquefied gases. The maximum uncertainty of the equilibrium pressure was 1 MPa. In the present study, we did not evaluate the enthalpy of urea clathrate decomposition because the DSC samples included solid urea as well as urea clathrates.

2.3. DSC measurements of (C_3H_8+C_3H_6)/urea clathrates at atmospheric pressure

Approximately 40 mg of the prepared (C_3H_8+C_3H_6)/urea clathrate was loaded in a batch-type DSC cell precooled to 223 K. The DSC cell was set in a DSC furnace precooled to 228 K. DSC measurements of (C_3H_8+C_3H_6)/urea clathrates were performed at atmospheric pressure without pressurization. The furnace temperature was increased to 273 K at a heating rate of 0.1 K/min. The cell volume was enough large that the pressure change in the urea clathrate decomposition could be ignored. The maximum uncertainty of the equilibrium temperature measured with batch-type DSC in the present study was 1 K for essentially the same reason as the DSC measurements at high pressures.

3. Results and discussion

3.1 Thermodynamic stabilities of C_3H_8/urea clathrate and C_3H_6/urea clathrate.

Thermodynamic stabilities of the C_3H_8/urea clathrate and the C_3H_6/urea clathrate were investigated by DSC measurements. Typical DSC thermograms are shown in Figure 1. The observed endothermic peak was derived from urea clathrate decomposition, where the guest molecules (C_3H_8 or C_3H_6) were released from the channel of urea clathrates, after which the framework of the urea clathrates collapsed and returned to the solid urea. As shown in Figure 1(a), the endothermic peak was split into a doublet in the C_3H_8/urea clathrates only during high-pressure measurements. We adopted the onset temperature of the peak detected on the low-temperature side as the equilibrium temperature of the C_3H_8/urea clathrate. The endothermic peak was shifted to the high-temperature region with an increase in pressure. Figure 2 shows the thermodynamic stability boundaries, that is, three-phase equilibrium curves of (urea clathrate + solid urea + guest-rich liquid phases) and (urea clathrate + solid urea + gas phases) of C_3H_8/urea clathrate and C_3H_6/urea clathrate. In Figure 2, the saturated vapor-pressure curves of pure C_3H_8 and pure C_3H_6 were drawn by dashed-dotted curves [21]. The three-phase equilibrium curves of (urea clathrate + guest-rich liquid + gas phases) and (solid urea + guest-rich liquid + gas phases) should lie slightly below the saturated vapor-pressure curve of guest species. The intersection of the four three-phase equilibrium curves is a quadruple point of (urea clathrate + solid urea + guest-rich liquid + gas phases), which is located around 298 K and 0.94 MPa (C_3H_8/urea clathrate system) and 261 K and 0.40 MPa (C_3H_6/urea clathrate system).

The equilibrium temperature of the C_3H_8/urea clathrate is approximately 40 K higher than that of the C_3H_6/urea clathrate at the same pressure above the pressure of the quadruple point. At pressures lower than the pressure of the quadruple point, the difference in the thermodynamic stability between C_3H_8/urea clathrate and C_3H_6/urea clathrate becomes small, which was approximately 16 K at 0.1 MPa. The difference in the thermodynamic stability of these urea clathrates is larger than that of C_3H_8 and C_3H_6 clathrate hydrates [11] and much larger than the difference in the vapor-liquid equilibria of C_3H_8 and C_3H_6 [11]. The large difference in the thermodynamic stability of these urea clathrates suggests the possibility of C_3H_8-C_3H_6 separation using urea clathrates. The reason why the C_3H_6/urea clathrate is less thermodynamically stable than the C_3H_8/urea clathrate might be the difference in the interaction between guest (C_3H_6 or C_3H_8) and the channel structure of urea clathrate. C_3H_6 has a more linear bond angle, due to the double bond, compared with C_3H_8. The thin molecular structure of the C_3H_6 molecule would cause a decrease in thermodynamic stability of the C_3H_6/urea clathrate.

3.2. (C_3H_8+C_3H_6)/urea clathrate formation and their equilibrium relationships

Equilibrium relationships in the (C_3H_8+C_3H_6)/urea clathrates with various guest compositions were investigated under conditions where both clathrates are thermodynamically stable (10 and 40 MPa at 253 K) and under conditions where only the C_3H_8/urea clathrate is stable (10 and 20 MPa at 283 K). Typical DSC thermograms of the (C_3H_8+C_3H_6)/urea clathrates prepared with various compositions at (253 K, 40 MPa) or (283 K, 20 MPa) are shown in Figure 3. The symbol z stands for the mole fraction in urea clathrates on a urea-free basis. These thermograms were recorded at atmospheric pressure. The endothermic DSC peak corresponding to (C_3H_8+C_3H_6)/urea clathrate decomposition was located at a temperature between those of C_3H_8/urea clathrate and C_3H_6/urea clathrate decomposition. With an increase in the C_3H_8 composition in urea clathrate, the decomposition temperature of the (C_3H_8+C_3H_6)/urea clathrates became high, which was independent of the preparation conditions. This result means the (C_3H_8+C_3H_6)/urea clathrate formation, not physically mixture of C_3H_8/urea clathrate and C_3H_6/urea clathrate.

Figure 4 shows the relations between the feed composition (y, before urea clathrate formation) and the equilibrium composition in urea clathrate (z). Under every condition in the present study, the composition of C_3H_8 in the (C_3H_8+C_3H_6)/urea clathrates was higher than each feed composition (Tables 2 and 3), that is, C_3H_8 was concentrated in the (C_3H_8+C_3H_6)/urea clathrate. At 253 K, where both C_3H_8/urea clathrate and C_3H_6/urea clathrate are stable, the equilibrium composition in the (C_3H_8+C_3H_6)/urea clathrate was gradually varied and dependent on the feed composition, as shown in Figure 4a. The pressure effect on the equilibrium composition was small or almost nothing because the composition in urea clathrate prepared at 40 MPa was almost the same as that at 10 MPa. This means that the pressure (at least in a pressure range from 10 MPa to 40 MPa) has no effect on the occupancy of the C_3H_8 and C_3H_6 molecules in urea clathrate.

At 283 K and 10 MPa (or 20 MPa), where only C_3H_8/urea clathrate is stable, the behavior of the equilibrium composition in urea clathrate (Figure 4b) was different from that of 253 K (Figure 4a). Even in a feed-C_3H_8 compositional range lower than 0.2, the equilibrium C_3H_8 composition in the (C_3H_8+C_3H_6)/urea clathrate above 0.8 was maintained at 283 K, whereas it varied from 0.5 to zero at 253 K. Due to the instability of the C_3H_6/urea clathrate at 283 K, a C_3H_8 composition above 0.8 was required to keep urea clathrate stable. In other words, we can concentrate the mole fraction of C_3H_8 from 0.1 (in feed) to 0.8 or more (in urea clathrate) at 283 K in the first step of the separation by urea clathrate formation. In case of low initial composition of C_3H_8 in a C_3H_8+C_3H_6 mixture, urea clathrate formation could be one of the prominent methods for pre-separation and concentration of C_3H_8. After a pre-separation step by urea clathrate formation, the usage of other separation methods would be better because the separation efficiency in urea clathrate gets worse under C_3H_8-rich conditions higher than the C_3H_8 mole fraction of 0.8.

4. Conclusion

In the present study, we demonstrated that urea clathrate can be used to separate C_3H_8 from C_3H_8+C_3H_6 mixtures. The significant difference between the thermodynamic stabilities of C_3H_8/urea clathrate and C_3H_6/urea clathrate makes the C_3H_8-C_3H_6 separation possible. In a pressure-temperature range in which only C_3H_8/urea clathrate is thermodynamically stable, C_3H_8 was separated with considerable efficiency, where C_3H_8 was concentrated from the mole fractions of 0.1 in feed mixture to 0.8 in urea clathrate. The present findings reveal that the C_3H_8-C_3H_6 separation by urea clathrate formation is expected to be a pre-separation method combined with other separation techniques.

Table 1. Information on the Chemicals Used in the Present Study[a]

chemical name	CAS RN	source	mole fraction purity
urea	57-13-6	Merck	> 0.995
propane	74-98-6	Sumitomo Seika Chemicals	> 0.995
propylene	115-07-1	Sumitomo Seika Chemicals	> 0.995

[a] All of the chemicals were used without further purifications after purchase.

Table 2. Relations between Feed Composition (*y*, before Urea Clathrate Formation) and Equilibrium Composition (*z*, after Urea Clathrate Formation) in Urea Clathrates at 253±1 K[a]

y_{C3H8}	z_{C3H8}	y_{C3H8}	z_{C3H8}
10±1 MPa		40±1 MPa	
0	0	0	0
0.12	0.39	0.05	0.07
0.17	0.68	0.06	0.48
0.24	0.53	0.10	0.57
0.27	0.57	0.19	0.54
0.29	0.57	0.25	0.67
0.35	0.91	0.44	0.81
0.45	0.91	0.47	0.90
0.48	0.84	0.56	0.79
0.57	0.84	0.58	0.88
0.70	0.95	0.61	0.84
0.71	0.91	0.73	0.82
0.81	0.99	0.74	0.93
0.91	0.99	0.88	0.94
0.93	0.98	1	1
0.95	0.99		
1	1		

[a] Both standard uncertainties *u*(*y*) and *u*(*z*) were 0.01.

Table 3. Relations between Feed Composition (y, before Urea Clathrate Formation) and Equilibrium Composition (z, after Urea Clathrate Formation) in Urea Clathrates at 283±1 K[a]

y_{C3H8}	z_{C3H8}	y_{C3H8}	z_{C3H8}
10±1 MPa		20±1 MPa	
0	0	0	0
0.15	0.92	0.05	0.82
0.24	0.86	0.18	0.89
0.59	0.94	0.21	0.88
0.66	0.89	0.31	0.86
0.81	0.97	0.35	0.93
1	1	0.44	0.91
		0.44	0.87
		0.44	0.87
		0.55	0.91
		0.63	0.93
		0.75	0.87
		1	1

[a] Both standard uncertainties $u(y)$ and $u(z)$ were 0.01.

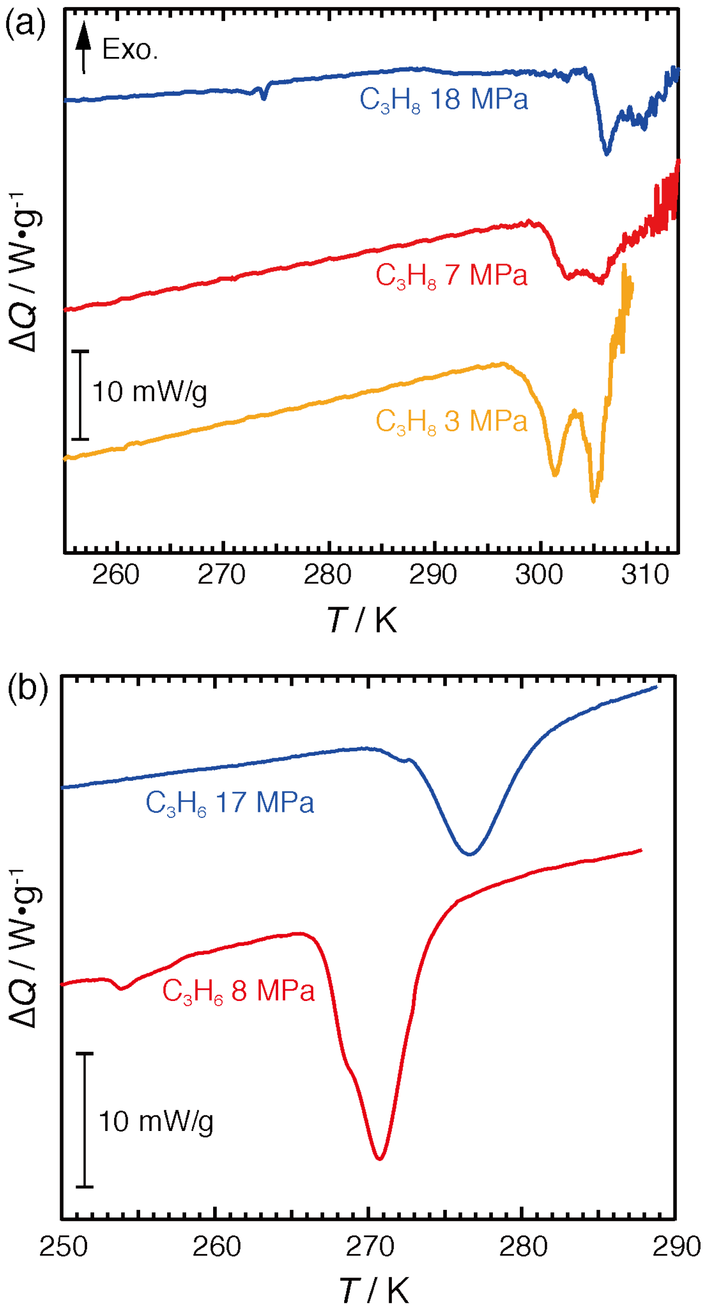

Figure 1. Typical high-pressure DSC thermograms of (a) C_3H_8/urea clathrate and (b) C_3H_6/urea clathrate decomposition at various pressures.

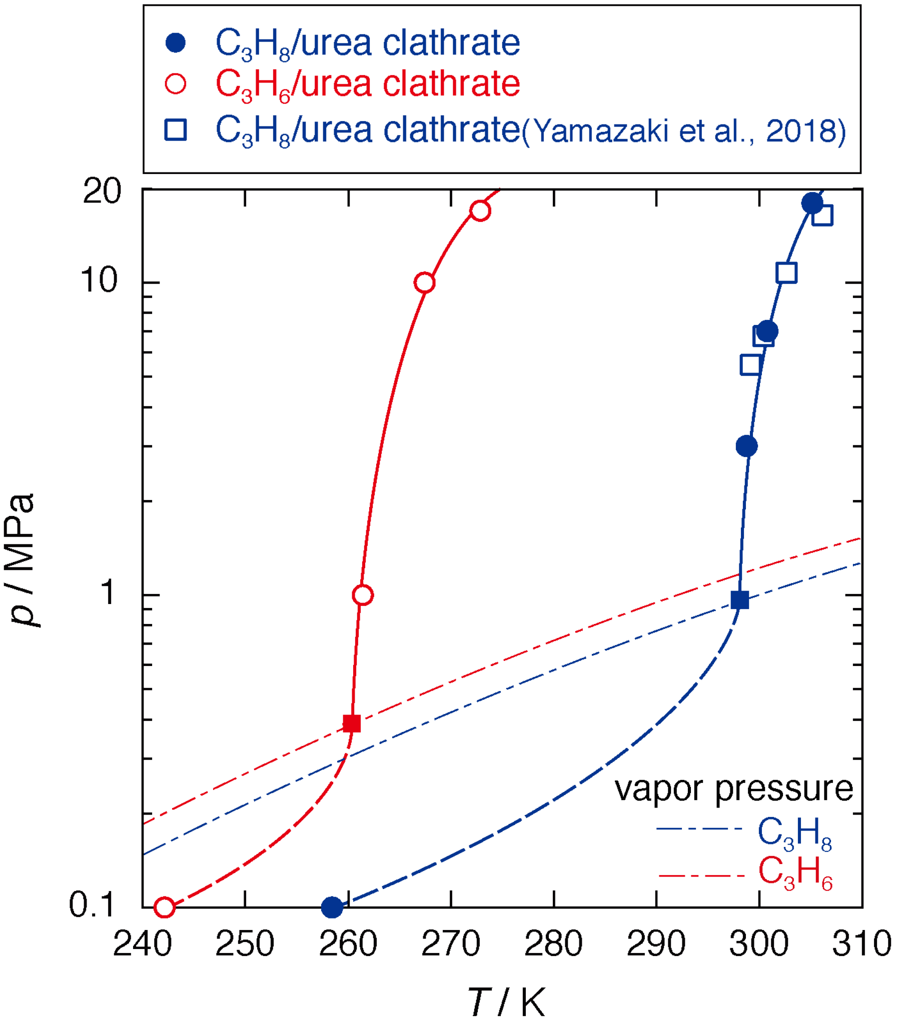

Figure 2. Three-phase equilibrium curves and quadruple point (urea clathrate +solid urea + guest-rich liquid + gas phases) of C_3H_8/urea clathrate and C_3H_6/urea clathrate.

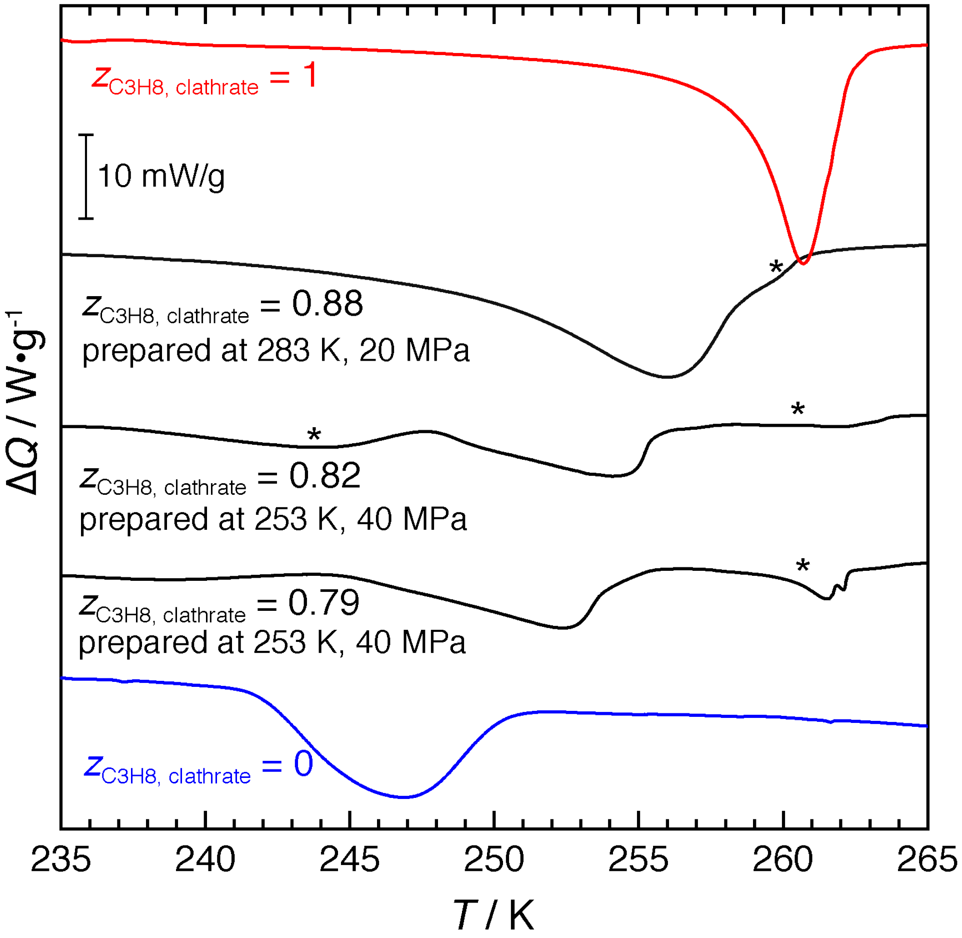

Figure 3. Typical DSC thermograms of the (C_3H_8+C_3H_6)/urea clathrates with various compositions. The symbol *z* stands for the mole fraction in urea clathrate on a urea-free basis. All thermograms were measured at 0.1 MPa. The asterisks represent the C_3H_8/urea clathrate around 260 K and the C_3H_6/urea clathrate around 245 K.

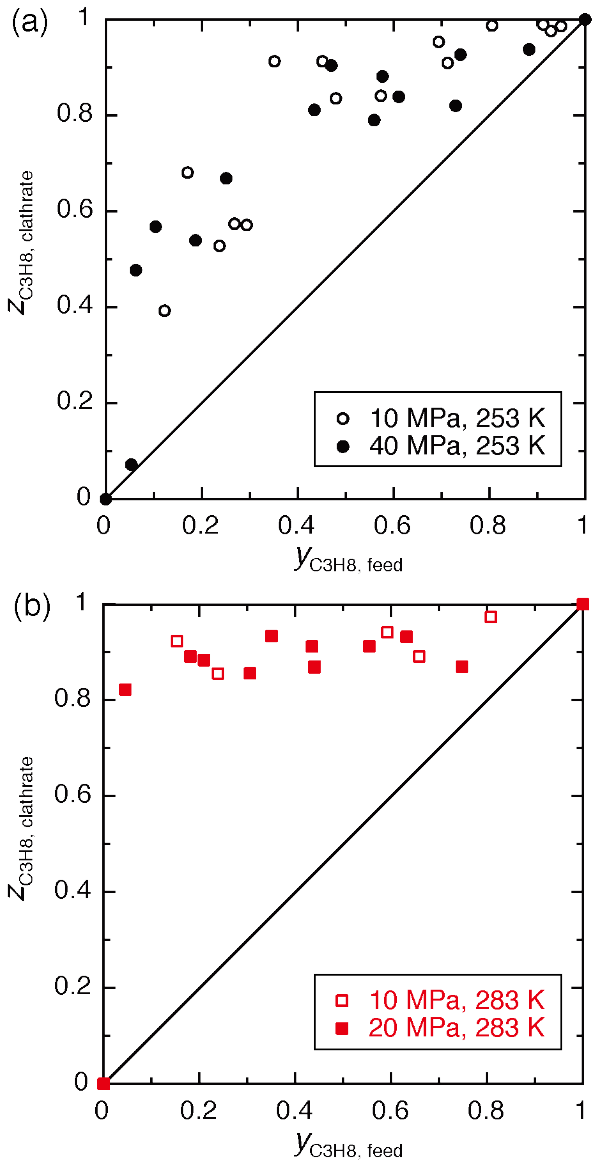

Figure 4. Relation of equilibrium C_3H_8 composition in urea clathrate ($z_{\mathrm{C3H8,\ clathrate}}$) with feed C_3H_8 composition ($y_{\mathrm{C3H8,\ feed}}$) at (a) 253 K (10 or 40 MPa) and (b) 283 K (10 or 20 MPa).

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Notes

The authors declare no competing financial interest.

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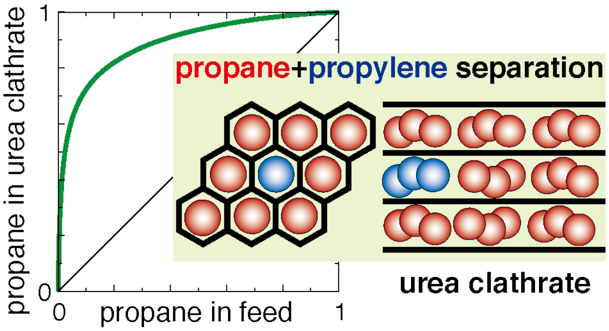
propane in urea clathrate
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