Electronic Supplementary Information

Memory effect in tetra-\textit{n}-butyl ammonium bromide semiclathrate hydrate reformation: the existence of solution structures after hydrate decomposition

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Procedure for the preliminary experiments on the memory effect of TBAB semiclathrate hydrate with differential scanning calorimetry (DSC)

Memory effect of TBAB semiclathrate hydrate was investigated with the microDSC (Setaram, µDSC VII evo). Approximately 20 mg of the TBAB aqueous solution with the mass fraction of $w_{TBAB} = 0.040$ was loaded in a DSC cell. The precise mass of the loaded sample was measured with the electric balance (A&D, BM-22) with an uncertainty of 0.02 mg. In the DSC measurement, the furnace temperature was programmed to have the following three sections.

1) The furnace temperature was decreased to 263.2 K at a cooling rate of 0.5 K/min. During the initial cooling process, the TBAB semiclathrate hydrate was always formed at 267.4±0.7 K. This spontaneous formation temperature agrees well with that reported previously $^1$.

2) After the temperature was held at 263.2 K for 10 min and then increased to 278.2 K at a heating rate of 2.0 K/min. In this section, there was no characteristic behavior in DSC curves.

3) After the temperature was held at 278.2 K for 40 min and then increased to a holding temperature (286.2 K or 287.2 K) at a heating rate of 0.1 K/min. Finally, the temperature was held at each holding temperature for 30 min. The TBAB semiclathrate hydrate was decomposed at 285.1 K$^{1-6}$. The offset point of the endothermic peak derived from the hydrate decomposition was located at 285.9-286.0 K during the heating process. Considering the offset point, the hydrate in the DSC cell was completely decomposed until the furnace temperature reached to a holding one.

After the sections 1) to 3), they were repeated four times to investigate the memory effect of the hydrate reformation in every target temperature. If the memory effect appears, the reformation temperature should become higher than 267.4±0.7 K without the memory effect.
Results

Figures S1 and S2 show the results and the programmed temperature profiles in the case of the holding temperature of 286.2 K and 287.2 K, respectively. The difference of the programmed temperature between them is just 1.0 K of the holding temperature after complete decomposition of TBAB semiclathrate hydrate.

In the case of 286.2 K as the holding temperature, as shown in Figure S1, the 1st reformation temperature was 279.8 K, which is higher than the spontaneous formation temperature of 267.4±0.7 K\(^1\). The 2nd, 3rd, and 4th reformation temperatures (not shown) were 279.9 K, 274.4 K, and 276.1 K respectively. The memory effect appears in all temperature cycles, though, as the temperature cycles repeat three or more times, the reformation temperature seems to get lower.

In the case of 287.2 K as the holding temperature, as shown in Figure S2, the 1st reformation temperature was 267.0 K. The 2nd, 3rd, and 4th reformation temperatures (not shown) were 267.0 K, 267.1 K, and 266.9 K respectively. The temperatures agree with the spontaneous formation temperature of 267.4±0.7 K\(^1\). The holding at 287.2 K for 30 min lost the memory effect.
Figure S1. Schematic illustration of the programmed furnace temperature (top). DSC curves of the TBAB semiclathrate hydrate reformation (bottom, left) and decomposition (bottom, right) in the case of the holding temperature of 286.2 K after complete decomposition of TBAB semiclathrate hydrate. The reformation temperature of TBAB semiclathrate hydrate was 279.8 K that is much higher than the spontaneous formation temperature of approximately 267 K, that is, the memory effect appears. $T_{\text{onset}}$ stands for the onset temperature of the DSC peak.
Figure S2. Schematic illustration of the programmed furnace temperature (top). DSC curves of the TBAB semiclathrate hydrate reformation (bottom, left) and decomposition (bottom, right) in the case of the holding temperature of 287.2 K after complete decomposition of TBAB semiclathrate hydrate. Slight holding-temperature difference of 1.0 K from that in Figure S1 results in the disappearance of the memory effect.
REFERENCES


