

PARTITION OF AMMONIUM ION BETWEEN WATER AND CLATHRATE HYDRATE IN A SUBSURFACE OCEAN OF ICY BODIES. R. Nishitani¹, A. Tani¹, and S. Sasaki¹, ¹Department of Earth and Space Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka, 560-0043, Japan (tanishi@astroboy-jp.com)

Introduction: Clathrate hydrates are crystalline inclusion compounds where water molecules incorporate guest molecules into hydrogen-bonded water cages. Clathrate hydrates may be easily formed in a subsurface ocean in icy bodies because they are stable at low-temperature and high-pressure condition of the ocean [1-2].

A recent study shows that one of cage-forming water molecule could be replaced by an ammonium ion [3]. Another research shows that ammonia molecule can be enclathrated in the water cage as a guest molecule [4]. Such incorporation of ammonium ion and/or ammonia into clathrate hydrates may occur in the interior ocean of icy bodies. Ammonia has been important species as it contains nitrogen atom that is essential to life. So it is crucial to know how much ammonium ion in the sea is included into clathrate hydrates. We, therefore, investigated partition coefficient of ammonium ion in formation of clathrate hydrate.

Experimental: Tetrahydrofuran (THF) was used as a guest molecule as an analog of CO₂ or methane because THF solution easily formed clathrate hydrate under warmer condition in atmospheric pressure [5]. Ammonia chloride was used as ammonium ion source. Four different solutions (i-iv) were prepared. Final concentration of ammonium chloride in all solutions were 0.01 mol/L. In this concentration, any ammonium chloride hydrates are not formed over -15°C [6]. Concentrations of THF solution were 11.9 wt% in (i), 1.0 wt% in (ii), and 0 in (iii) and (iv). In solution (i), approximately 50 vol% of the solution is crystallized as THF hydrate at 0°C [5]. In solution (ii), THF hydrate is not formed and water ice is formed at the same temperature. Solutions (iii) and (iv) were ammonium chloride solution without THF. These conditions are summarized in Table 1.

Microtubes filled with 1 mL of solution (i), (ii), and (iii) were kept at -20°C in a freezer for a few days. These samples were transferred to a thermostatic chamber. After heated up to melting points, the samples were partially recrystallized for a few days at specific temperatures (0.5°C below the melting points), respectively. It is noted that melting points were different in solution (i), (ii), and (iii) because of different concentrations of THF. The residual liquid in the microtubes was collected by syringe to analyze ammonium ion concentration in the liquid (C_L). The volume of liquid part was also determined (V_L). Solution (iv) was

a control sample and ammonium ion concentration in the solution was measured without the above processes.

Determination of the ammonium ion concentrations was followed by indophenol method [7]. In this method, if solution contains ammonium ion, the transparent solution becomes blue-colored after mixed with reagents such as sodium salicylate and sodium dichloroisocyanurate. The ammonium ion concentrations are determined from the absorption (maximum absorption was at 637 nm). In this study, absorption spectrum of each solution was measured by UV-vis spectrometer after diluted appropriately with milli-Q water. The concentration of ammonium ion was calculated using a calibration curve.

Table 1: The conditions of samples. Solution (iv) is a control sample.

	NH ₄ Cl (mol/L)	THF wt%	Formed crystal in solution
(i)	0.01	11.9	THF clathrate hydrate
(ii)	0.01	1.0	Water ice
(iii)	0.01	0	Water ice
(iv)	0.01	0	-

Results and Discussion: Absorption spectra of solutions (i-iv) are shown in Fig. 1. The spectrum shapes are concordant with those in the other indophenol method. Absorption maximum appeared at 637 nm and its absorbance (Abs_{637}) was used for further discussion. Ammonium ion concentration in the residual liquid (C_L) was determined using the calibration curve.

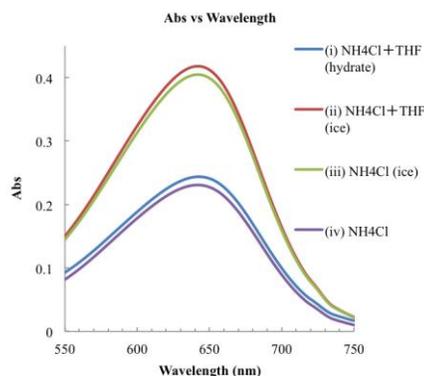


Fig. 1: Absorption spectra of the residual liquid in the samples after recrystallization.

Furthermore, concentration in solid part (C_s) was determined by the following equation

$$C_s = \frac{\text{Abs}}{\epsilon} C_0 - C_L \frac{V_L}{V} \frac{1}{1 - V_L/V}, \quad (1)$$

where C_0 is an initial concentration of ammonium ion (0.01 mol/L) and V is a total sample volume (1 mL). Partition coefficient, $K_D = C_s/C_L$, shows how much ammonium ion is included into the solid phase. All values including Abs_{637} are summarized in Table 2.

Table 2: Summary of the obtained results. THF clathrate hydrate was formed in solution (i), whereas water ice was formed in solutions (ii) and (iii). In the control sample (iv), C_s and K_D were not evaluated due to no solid formation.

	Abs_{637}	C_L (mol/L)	V_L/V	C_s (mol/L)	K_D
(i)	0.24	0.011	0.55	0.0092	0.87
(ii)	0.42	0.020	0.40	0.0035	0.18
(iii)	0.40	0.019	0.40	0.0040	0.21
(iv)	0.23	0.010	-	-	-

As indicated in Table 2, K_D in solution (i) is much larger than those of the others. This means that more ammonium ion was included into the solid in solution (i) than those of solution (ii) and (iii). In short, THF hydrate can include ammonium ion more than water ice. The reason why K_D of solution (ii) and (iii) are smaller than that of solution (i) is probably that water ice excludes other species such as ammonium ion. If so, the K_D should be 0, but is not. One of the reasons may be due to inclusion of ammonium ion into the voids and/or grain boundaries. In order to understand the details like dynamics of ammonium ion inclusion in formation of clathrate hydrate and water ice, further experiment is needed.

Our results show that ammonium ion may be included into clathrate hydrates if any hydrates are formed in the interior ocean of icy bodies. Nevertheless, K_D is lower than 1, which suggests that ammonium ion is slightly concentrated in the interior ocean even in clathrate hydrate formation.

Conclusion: Partition coefficient of ammonium ion between water and THF clathrate hydrate was investigated to consider the amount of ammonium ion included into clathrate from the ocean. We found that much more ammonium ion is captured into clathrate hydrate than in water ice. Our study shows that formation of clathrate hydrate affects ammonium ion concentration in icy bodies. In another study, how ammo-

nium ion is included into solid phase should be considered. When the subsurface ocean is evaluated as a chemical or biological environment, the effect of clathrate might be taken into consideration.

References: [1] Prieto-Ballesteros O. et al. (2005) *Icarus*, 177, 491–505. [2] Bouquet A. et al. (2015) *Geophys. Res. Lett.*, 42, 1334–1339. [3] Park S. et al. (2015) *Chem. Commun.*, 51, 8761–8764. [4] Shin K. (2012) *PNAS*, 109(37), 14785–14789. [5] Ross R. G. (1981) *Can. J. Chem*, 60, 881–892. [6] Beckermann C. and Viskanta R. (1989) *Experimental Thermal and Fluid Science*, 2(1), 17–26. [7] Krom M. D. (1980) *Analyst*, 105(1249), 305–316.