PHASE BEHAVIOR OF TETRAHYDROFURAN CLATHRATES IN AQUEOUS AMMONIA SOLUTIONS, V. Muñoz-Iglesias, T. H. Vu, W. Smythe, C. Sotin, R. Hodyss and M. Choukroun, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Pasadena, CA 91109 (mathieu.choukroun@jpl.nasa.gov)

**Introduction:** Titan’s icy crust is likely composed mainly of water ice $I_h$, clathrate hydrates (of methane and ethane) and ammonia hydrated minerals (ammonia mono- and di-hydrates) [e.g. 1, 2, and therein]. It is well known that ammonia affects the stability of both water ice and clathrates, by decreasing their melting temperature [e.g., 3, 4, and therein]. Thermal evolution may promote the melting of the ammonia hydrates at shallow depths, and subsequently allow for the resulting ammonia-rich aqueous solution to be in contact with crustal ice and clathrates. Interactions between these solutions and surrounding icy materials may result in dissociation of clathrates and outgassing of methane in the atmosphere [5]. This process may contribute to methane replenishment in the atmosphere over geologic timescales, and could thus explain the presence of methane in large amounts at present-day [6], despite its fast photochemical destruction [7].

In this work we investigate experimentally how ammonia aqueous solutions at a concentrations up to 30 wt% alter the stability of tetrahydrofuran (THF)-clathrates at 1 bar and within a temperature range from 77 to 298 K. THF-clathrates are a commonly used proxy for $CH_4$-clathrates since they form at atmospheric pressure. Before using $CH_4$-clathrates that are more challenging because of the pressure requirements, the present study permits us to determine the temperature at which transformations in this ternary system occur.

**Experimental equipment and procedures:** The ternary system $H_2O$-THF-NH$_3$ is being studied in two facilities: a Setaram BT 2.15 Calvet calorimeter and a Linkam LTS 350 cryostage coupled to a Horiba Jobin Yvon LabRaman HR confocal dispersive spectrometer (Figure 1). Both equipments allow cooling down to 77 K. For the future work with $CH_4$-clathrates that require high pressure, the calorimeter is prepared for doing runs up to 10 MPa. A detailed explanation of the solution preparation can be found in [8]. Aqueous ammonia solutions are prepared by direct dilution of a mother solution at 30 wt%. Next, 33 vol% of THF is added. This allows the solutions to be supersaturated in THF with respect to THF-clathrates, thus ensuring that all available $H_2O$ molecules are incorporated in clathrate hydrates and prevents formation of water ice in addition. Experiments consist in monitoring cooling-heating cycles.

**Results:** The phase diagram of the system $H_2O$-THF-NH$_3$ is being built by cooling the samples to 80 K, then heating at a constant rate of 0.1 K/min. Figure 2 shows some typical thermograms obtained upon heating, and illustrates the various phase transitions observed. At the conditions of this work, with a THF-ammonia aqueous solution mass ratio of 0.8:2.5, it has been observed that, after THF-clathrate formation when the system is cooled, chemical interactions between part of the remained THF and the ammonia molecules occur. When the system is warmed, the first melting at 165 K corresponds with the pure THF that did not enter the clathrate cages or interact with ammonia. From temperatures around 200 K for the ammonia concentration range studied (0 - 30 wt%), THF-NH$_3$ interactions disappear and, finally, the THF-clathrate starts a partial dissociation until complete melting. It is noted that the increase in ammonia concentration causes a higher drop in THF-clathrate melting temperature in parallel form as it does to water ice. Specifically, this temperature decreases by 7, 31 and 68 K for NH$_3$ concentrations of 10, 20 and 29 wt%, respectively. The eutectic point is found at the last NH$_3$ concentration mentioned.

Figure 3 shows the phase diagram of the $H_2O$-THF-NH$_3$ system that results from all our experiments. We express ammonia concentration in weight fraction relative to water, so that a direct comparison with the phase diagram of the $H_2O$-NH$_3$ system is possible. In the NH$_3$ concentration range studied, we distinguish three zones before reaching the eutectic: a) 0-10 wt%, b) 10-20 wt% and c) 20-29 wt%. At low NH$_3$ concentrations the THF-NH$_3$ interactions are almost negligible, while the amplitude of the THF-clathrate partial dissociation...
increases gradually with the NH\textsubscript{3} concentration. In the middle zone (b), THF and NH\textsubscript{3} stabilize a presumed solid that melts at 218 K and promotes the start of clathrate destabilization. At concentrations higher than 20 wt%, the putative THF-NH\textsubscript{3} solid becomes unstable and THF-clathrate starts to melt at lower temperatures. Above the eutectic (29 wt%), the THF-NH\textsubscript{3} solid seems to recrystallize around 160 K; the new phase melts at 185 K followed by the THF-clathrate dissociation.

**Implications:** The fact that ammonia promotes that clathrates start to decompose partially before reaching the equilibrium curve at a certain ammonia concentration means that melting processes at Titan’s shell can occur at lower temperatures than initially expected. The amplitude of this partial melting, according to the temperature and pressure, may be well determined for CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}-clathrates in the ammonia range concentration of interest and included in evolution models.

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**References:**