**Safe operation of reactors:
an investigation on the thermal stability of hydroxylamine solutions.**

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**1.Introduction**

The knowledge of the substance behavior under atypical conditions is essential when dealing with the safe operability of chemical reactors, storage systems and the sizing step of safety and control devices. In this framework, the processing of hydroxylamine (HA) and HA-derived compounds may pose hazards and additional complexity, being intrinsically unstable under specific operative and storage conditions [1,2]. These are often responsible for a thermal decomposition leading to uncontrolled mechanisms that may affect inherent safety and equipment integrity. Investigating runaway conditions in chemical reactors processing HA and HA-derived compounds is essential to obtain the set of safe operative conditions to be maintained to avoid uncontrolled reactions. In addition, detailed calorimetric studies can be used to provide guidance concerning safe conditions and appropriate storage [4,5].

This work focuses on the behavior of solutions of HA in water at a concentration of 10%-50%w, respectively. A thermal screening unit, arranged with different cells made of stainless steel and Hastelloy, is used to collect batch data on the thermal stability of HA.

**2. Methods**

Reported measurements are made with a *TSU* – *thermal screening unit* apparatus that allows for the collection of temperature and pressure profiles during the time of a closed-cell environment [3]. A specified thermal profile can be imposed in order to analyze the sample response to increasing temperatures that may trigger thermal decompositions. Different heating methods are used, namely an isothermal mode and an increasing ramp mode. The latter is employed to search for the onset of *runaway* conditions that are then investigated while keeping the system under constant temperature.

In this study, heating rates of 2 °C min-1 and 5 °C min-1 are adopted along with isothermal steps around the onset temperature. The selected rates are representative of external failures leading to respectively - uncontrolled - moderate and severe temperature increases. Besides, isothermal conditions may apply to operational storage targets.

Related cell internal temperature and time derivatives (dT/dt and d2T/dt2) are considered in the *onset* temperature evaluation according to [3]. The temperature is monitored through a type K thermocouple placed in the test cell while a pressure sensor tracks the cell internal pressure. HA aqueous solutions at 50, 30, 20 and 10 % on an HA mass basis (at 99.99 % purity) are used in addition to diluted systems.

**3. Results and discussion**

Collected data show that HA solutions may undergo *runaway* scenarios once subjected to external thermal perturbations. Results are reported in Table 1 for the HA solution heated at 2 °C min-1 and 5 °C min-1.

*Table 1. Sample mass variation, maximum sample temperature Tmax,
sample pressure (Pmax-Pv)/Pv and onset temperature Ton of HA solutions.*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Mass variation** /g | **Tmax** /°C | **(Pmax-Pv)/Pv** /- | **Ton** /°C | **Mass variation** /g | **Tmax** /°C | **(Pmax-Pv)/Pv** /- | **Ton** /°C |
|  | **Heating rate: 2 °C min-1** | **Heating rate: 5 °C min-1** |
| HA 10 % | 0.46 ± 0.26 | 202 ± 3 | 0.02 ± 0.01 | n/a | 0.04 ± 0.01 | 253 ± 5 | 0.03 ± 0.01 | n/a |
| HA 20 % | 0.45 ± 0.12 | 215 ± 3 | 0.09 ± 0.06  | 175 ± 5 | 0.15 ± 0.03 | 249 ± 4 | 0.13 ± 0.05 | 198 ± 7 |
| HA 30 % | 0.43 ± 0.23 | 239 ± 4 | 0.13 ± 0.03 | 143 ± 3 | 0.20 ± 0.05 | 245 ± 8 | 0.15 ± 0.04 | 158 ± 4 |
| HA 50 % | 0.31 ± 0.04 | 230 ± 9 | 0.10 ± 0.04 | 153 ± 5 | 0.36 ± 0.09 | 264 ± 8 | 0.11 ± 0.02 | 163 ± 4 |

First, it should be noted that for all tests, the increase in the pressure up to *Pmax* is only ascribed to the water pressure. In addition, a difference between the maximum cell pressure (*Pmax*) and the related mixture saturation pressure (*Pv*) at experimental conditions exists. The discrepancy is almost negligible for 10 % HA solution while more concentrated solutions lead to a difference increase up to 15 percent. Within the experimental error, results for 20, 30 and 50 % HA solutions are comparable, and the pressure increase with respect to *Pv* can be ascribed to HA decomposition mechanisms.

On the other hand, as reported in Figure 1, the onset of a runaway reaction is clearly observed for all the tests but the 10 % HA solution, which does not exhibit uncontrolled dynamics. This behavior is due to the hydroxylamine decomposition, which can be defined by the following set of reactions (in the absence of oxygen), producing a large increase of moles ([6; 7]):

$NH\_{2}OH\rightarrow HNO+H\_{2}$ $H\_{2}$ elimination forming nitroxyl and $H\_{2}$

2$HNO\rightarrow N\_{2}O+H\_{2}O$ rapid decomposition of $HNO $(1)

$2NH\_{2}OH\rightarrow NH\_{2}-O∙+OH∙+NH\_{3}$ bimolecular, intermolecular $H$ shift $NH\_{2}-O∙+ OH∙\rightarrow HNO+H\_{2}O$ termination, followed by (1)

$2NH\_{2}OH\rightarrow ∙NH-OH+NH\_{3}+OH∙$ bimolecular, two intermolecular $H$ shift

 $∙NH-OH+ OH∙\rightarrow HNO+H\_{2}O$ termination, followed by (1)

$NH\_{2}OH\leftrightarrow NH\_{3}^{+}-O^{-}$ mono (or bimolecular) $H∙$shift from $O$ to $N$, forming ammonia oxide (zwitterionic tautomer of $NH\_{2}-OH$)$$4NH\_{2}OH\rightarrow N\_{2}O+2NH\_{3}+3H\_{2}O$$



*Figure 1. Thermal behaviour of aqueous solutions of HA at different concentrations (%w) at oven heating rate of 2 °C min–1 (left) and 5 °C min–1 (right).*

**4. Conclusions**

The thermal decomposition of HA in aqueous systems is investigated. Runaway events are observed in the range of concentration considered, except for the 10 % HA solutions. Onset temperatures range from 143 to 198 °C depending on solution concentration and imposed heating rate, with lower onset temperatures at 2 °C min-1. The maximum temperature is observed in the 50 % HA solutions sample with an associated maximum pressure of 50 ± 5 bar.

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