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Effect of iodide on DETA oxidation

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Abstract

The high CO_2 absorption capacity and CO_2 absorption rate of diethylenetriamine (DETA) make it a good alternative to monoethanolamine (MEA) for CO_2 capture, and it has excellent performance in biphasic absorbents [1]. However, amine solutions inevitably degrade in complex flue gas environments, and oxidation is the most prevalent type of degradation. The degradation of amine solvents may lead to reduced absorption performance, shortened reactor service life, and environmental risks, thereby increasing operating costs. Polyamines, especially long-chain amines with primary and secondary amino groups, display more severe oxidation behavior. To deploy them economically at scale for CO_2 capture, oxidation must be reduced. Previous studies have shown that potassium iodide (KI) can efficiently inhibit oxidative degradation in MEA, piperazine (PZ), and methyldiethanolamine (MDEA) [2]. However, the mechanism by which potassium iodide inhibits amine oxidation is unclear. A likely explanation is that iodide is oxidized to iodine by oxygen or free radicals in solution, and then further reduced to iodide, allowing it to function for a long time. In addition, iodides may also react with some metal ions, preventing their catalytic activity in oxidative degradation reactions [3]. The study of the effect of iodide on the oxidation of polyamines which readily oxidize is of great significance for their future large-scale application.

This work investigated the effect of different types and concentrations of iodide on the oxidation of the polyamine DETA. The oxidation experiments were conducted in a High Oxygen Pressure Reactor (HOPR) and a High Gas Flow reactor (HGF). As shown in Figure 1, the HOPR consists of four stainless steel reaction vessels, with pure oxygen entering from above. The pressure of the vessels was maintained at 300 kPa during the experiment. Electric heating was used to maintain a 60 °C environment. Each vessel was equipped with a magnetic stirring device and a port for timed sampling. Due to the high oxygen pressure in the reactor, which can accelerate the oxidation of amines, the experimental period was 4–7 days. The extent of oxidation was determined by analyzing the amine retention in the sample using Gas Chromatography. In the HGF, air mixed with a small amount of CO_2 was introduced into the amine solution from the bottom of the reactor at an inlet flowrate of 100 SCCM. Part of the gas entered a hot gas FTIR for detection and circulated at 5 L/min in the system. This experiment reflected amine oxidation by measuring the ammonia generation rate in the outlet gas. The Oxygen Depletion Batch Reactor (ODBR) measured the oxygen consumption rate of amine solutions under varied conditions. As shown in Figure 3, air was introduced into the solution, and after 10 minutes, the air inlet was closed. The consumption rate of dissolved oxygen (DO) in the solution was measured by a DO sensor and reported as the first order rate constant, k.

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Different concentrations and types of iodides were used in the HOPR experiment. As shown in Figures 4 and 5, within a certain range, the degradation rate of amines decreased with increasing salinity. All four selected iodides (KI, NaI, LiI, NH_4I) effectively inhibited DETA oxidation. In this case, the difference in their effects mainly depended on their cationic properties. 300 mmol/kg NaI completely inhibited DETA oxidation.

Experimental results with the HGF are sometimes different from those with HOPR, as shown in Figure 6. In the absence of dissolved iron, iodide maintains the ammonia generation rate at a very low level. In contrast with the results from the HOPR, iodide did not inhibit DETA oxidation after ferric or ferrous iron was added. The reason for the difference may be the importance of oxygen partial pressure, which was 300 kPa in the HOPR, almost 15 times higher than that in the HGF experiment. High oxygen pressure may change the oxidative degradation mechanism of DETA.

The results with the ODBR are shown in Table 1. The oxygen consumption rate varied with the order of adding iodide and iron ions. The inhibiting effect of iodide also depends on the degree of amine oxidation. In the degraded amine solution, the presence of some degradation products may make iodide unable to inhibit oxidation. Although the lowest oxygen consumption was achieved after adding iodide to clean DETA, it is still much higher than the rate with PZ, 0.78 h^{-1}, which may be because the addition of iodide also consumes oxygen.

Table 1. Dissolved oxygen consumption in the ODBR with 30 wt % DETA ($\alpha = 0.4$)

Additives	k (h^{-1})
None	30.1
100 mM NaI	23.7
1 mM $FeCl_3$	65.6
1 mM $FeCl_3$+100 mM NaI (in order)	58.7
100 mM NaI+1 mM $FeCl_3$ (in order)	39.5
No DETA, 30 wt % PZ, 1 mM $FeCl_3$	0.78

Keywords: amine oxidation; iodide; oxidation inhibitor.

References

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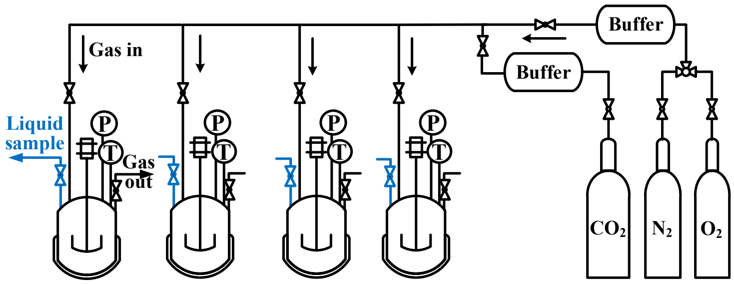


Figure 1. High Oxygen Pressure Reactor (HOPR) flow sheet

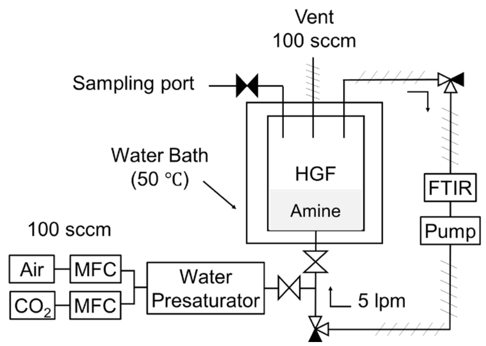


Figure 2. High Gas Flow reactor (HGF) flow sheet.

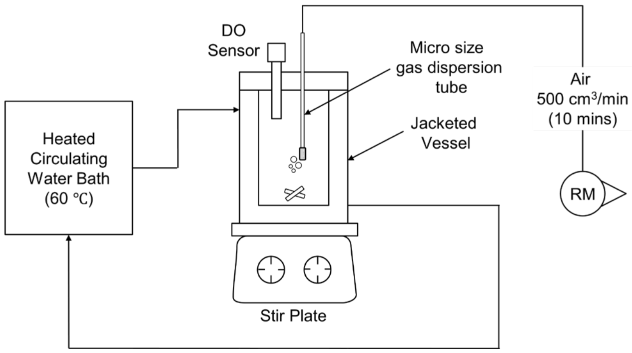
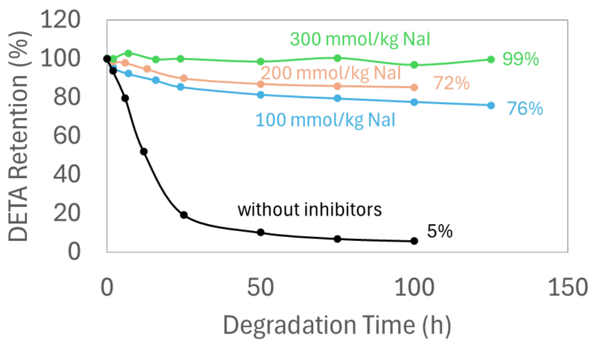


Figure 3. Oxygen Depletion Batch Reactor (ODBR)



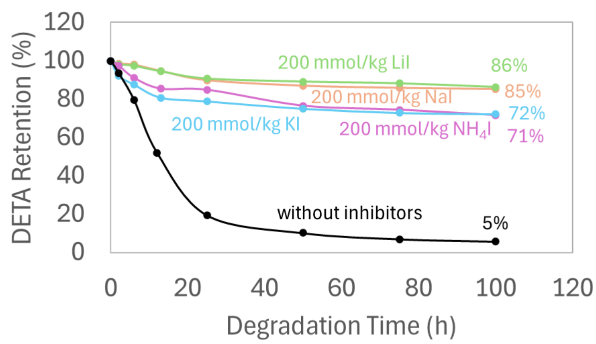


Figure 4. DETA retention with variable iodide in HOPR (30 wt % DETA, α = 0.4, 0.5 mM Fe^{2+}, 60 ℃).
Figure 5. DETA retention with different types of iodides in HOPR (30 wt % DETA, α = 0.4, 0.5 mM Fe^{2+}, 60 ℃).

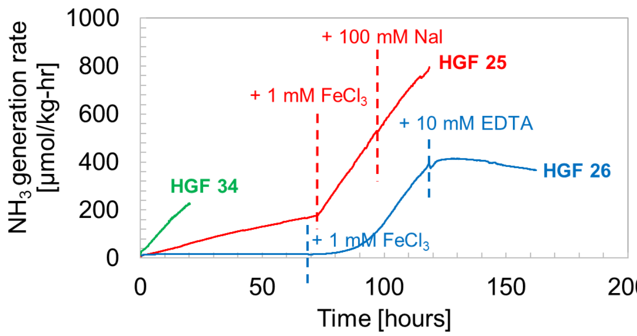


Figure 6. Ammonia generation rate in HGF 25, HGF 26 and HGF 34 (HGF 25 t = 0: 30 wt % DETA, α = 0.4; HGF 26 t = 0: 30 wt % DETA, α = 0.4, 100 mmol/kg NaI; HGF 34 t = 0: 30 wt % DETA, α = 0.4, 100 mmol/kg NaI, 0.5 mM $FeCl_2$).