IEAGHG Information Paper: 2017-IP38; Volatility of Amines for CO$_2$ Capture

Volatility of solvents is a key parameter on the selection of solutions to be used for carbon capture. This factor will determine the solvent losses and environmental issues, which can be dissipated with the use of water wash sections, but will impact on the size and capital charge.

The group of Gary T Rochelle (University of Texas at Austin), investigates on this topic, considering unloaded and loaded amine solutions. In their previous work released in 2010 (see link below), the volatility of MEA, MDEA+PZ, EDA and AMP were measured as their partial pressures and apparent activity coefficients. Recently, the group delivered a new study (click link below to access their paper) which included 24 amines: 18 were tertiary amines, 3 hindered amines, 2 ether amines and 1 pyridine derivative. The solutions studied were aqueous amine solutions, compound by those amines with water or in their blend with PZ and water. The properties measured were the Henry's law constant (H$_{am}$) in the case of aqueous amine solutions, and amine partial pressure (P$_{am}$) in the case of aqueous amine solutions that also contains PZ. Moreover, the partial pressure of the amines (P$_{am}$), extracted at 40ºC (benchmark temperature at which the CO$_2$ absorption in amine solutions takes place), were related to the amines pK$_a$ and correlated to their Henry's Law constants.

The set up included a stirred reactor connected to a hot gas FTIR analyser and a temperature controller, which was validated in 2010 with water and MEA for the vapour pressure measurements and with aqueous MEA and aqueous PZ for the CO$_2$ solubility measurements, from 40 to 100ºC. The results were comparable to values from literature using a wetted wall column apparatus and an equilibrium cell, what confirmed the accuracy of this set-up.

From their results in the previous study, at loaded conditions, both 7m MDEA+2mPZ (measured as MDEA) and 8m PZ solutions were considered non-volatile. 12m EDA was more volatile than those, followed by 7m MEA and 5m AMP in crescent order. However, 12m EDA was the most volatile solution at unloaded conditions, while the others stayed in the same order than at loaded conditions. It is interesting to highlight from their previous study the differences on the relation temperature-apparent activity coefficient of amines: 1) The apparent activity coefficient increased as the temperature increased (endothermic behaviour), as the cases of MDEA and PZ in the blend 7mMDEA+2mPZ, PZ in 8m PZ solutions, EDA in 8m and 12m EDA solutions and AMP in 5m AMP solutions; 2) The apparent coefficient decreased as the temperature increased, as showed by PZ in 2m PZ solutions; and 3) The temperature had not influence on the apparent activity coefficient, as the case of PZ in 5m PZ solutions.

In their recent work, the objectives were not only the measurement and prediction of volatility through the Henry's Law constants and vapour pressure at 40ºC, but to correlate the molecular structures present in the amines with their volatility. In general, it was found that polar groups (for example, -NH$_3$, -OH) reduced volatility, being the cyclic hydroxyl group the most significant one due to its strong hydrogen bond with water. Primary amino groups and cyclic secondary amino groups made the compound less volatile than non-cyclic secondary amino groups and non-cyclic tertiary amino groups. Non-polar groups (for example, -CH$_3$, -CH$_2$) increased volatility.

The partial pressure of PZ in the blends PZ+ tertiary/hindered amines decreased as the CO$_2$ loading increased due to the carbamate formation. As tertiary/hindered amines do not form carbamate, the influence of CO$_2$ loading was not that relevant. However, due to protonation, the CO$_2$ loading became more significant as the pKa of tertiary/hindered amines increased.

Finally, based on the proportionality of H_{am}-P_{am}, the use of H_{am} was recognised as a good indicator of amine volatility at operation conditions (for example, in a coal-fired flue gas, with a partial pressure of CO_2 of approximately 0.5kPa).

Volatility can impact on the operational and capital charge costs. In their work, it has been studied the influence of chemical structures and operation conditions (temperature and CO_2 loading) on the amines solutions volatility. In addition, it has been confirmed that Henry's Law constants can be used as prediction of volatility at operation conditions. Those results represent a substantial input not only on the characterization of the specific amines, but on the design of an ideal amine solution through the relation of molecular groups and volatility. While polar groups decreased volatility, non-polar groups increased it. Moreover, the CO_2 loading and temperature impact on the solution volatility. Generally, the volatility decreased as the CO_2 loading increased, with high variation on solutions containing amines with high pKa, and imperceptible influence on solutions with low pKa. As seen in loaded PZ solutions, the impact of the temperature on the volatility also depended on the amine concentration, changing from endothermic to exothermic behaviour as the amine concentration decreased. However, those changes were not observed at unloaded conditions, where the behaviour was always endothermic in PZ solutions.

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12/07/2017

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