Physical Properties of Degraded Aqueous Amine Solutions

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There has been an emphasis placed on the effects of degradation of amine solvents used in post-combustion CO₂ capture (PCC), particularly from the viewpoint of reaction mechanisms and the role of degradation species. Whilst this understanding is essential, a broader view is key to assess how degradation impacts the operation, performance, and efficiency of process operations. The determination of optimal processing parameters is guided by the solution physical properties, rather than by the changing solution species. As such, quantifying the changes to solution physical properties due to degradation is vital. This work studies changes to the physical properties of model degraded aqueous amine solvents and compares these results to various correlations and models developed to describe fresh solvent systems.

The exemplar solution described in this abstract is 5 M monoethanolamine (MEA) degraded at 80 °C for 28 days in the presence of a constant CO₂ flow. A reflux condenser was used to minimize solvent losses. Additional aqueous amine solutions (including methyldiethanolamine, MDEA, and piperazine, PZ) have also been tested; various degradation conditions have been employed including the presence or absence of O₂. The composition of the degraded solutions has been assessed at the conclusion of the 28-day period by means of GC-MS and IC. Comparable fresh solvents are also tested before and after loading with CO₂, where the loading was quantified using both the standard BaCO₃ titration method and a calibrated GC-TCD. The density (Anton Paar 5000 M) and viscosity (calibrated capillary viscometers) of these solutions were measured from 298.15 K up to 353.15 K, except where degassing restricted the temperature range.

The experimental data is considered in the context of various correlations and models currently used in literature and industry for prediction of the density and viscosity. One such model is examined in detail here: the Weiland correlations [1]. These empirically-derived expressions describe density and viscosity behaviours for CO₂-loaded solutions of MEA, DEA, and MDEA. The data used by Weiland et al. in the development of these correlations was collected at a temperature of 298 K (only) for solutions of amine mass fraction between 10 and 40 mass % for MEA and with CO₂ loadings (α) ranging from 0 to 0.5 mol(CO₂)/mol(amine). The resulting expression for density is

$$\rho = \frac{x_A M_A + x_{H_2O} M_{H_2O} + x_{CO_2} M_{CO_2}}{V}$$

where x denotes mole fraction, M is molar mass and subscripts denote species (A = amine). The molar volume V of the solution was corrected as

$$V = x_A V_A + x_{H_2O} V_{H_2O} + x_{CO_2} V_{CO_2} + x_A x_{H_2O} V^* + x_A x_{CO_2} V^{**}.$$
Table 1: MEA Density and Viscosity Parameters (Weiland et al.)

<table>
<thead>
<tr>
<th>Density Parameters</th>
<th>Viscosity Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$0$</td>
</tr>
<tr>
<td>$b$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c$</td>
<td>$21.186$</td>
</tr>
<tr>
<td>$d$</td>
<td>$2373$</td>
</tr>
<tr>
<td>$e$</td>
<td>$0.01015$</td>
</tr>
<tr>
<td>$f$</td>
<td>$0.0093$</td>
</tr>
<tr>
<td>$g$</td>
<td>$-2.2589$</td>
</tr>
</tbody>
</table>

Here, $V_{H_2O}$ is the molar volume of pure $H_2O$, $V_{CO_2}$ is the effective partial molar volume of dissolved $CO_2$ and the remaining terms were correlated as follows:

$$V_A = \frac{M_A}{aT^2 + bT + c}$$

and $V^* = d + ex_A,$

where $T$ is the temperature in K.

Both the density and viscosity expressions can be reliably extrapolated to 398 K for all systems, and to $\alpha = 0.6$ for MEA. The viscosity, $\eta$, is expressed as follows, where $\Omega$ is the mass % amine in solution and $\alpha$ is loading, as before.

$$\ln \left( \frac{\eta}{\eta_{H_2O}} \right) = \frac{[(a\Omega + b)T + (c\Omega + d)][(e\Omega + fT + g) + 1]\Omega}{T^2}$$

The results for two 5 M aqueous MEA solutions, one fresh and one degraded, are presented in Figure 1. For the fresh unloaded ($\alpha = 0$) and loaded ($\alpha = 0.34$) solutions, the experimental density and viscosity data obtained are in good agreement with Weiland’s correlation; the density data also agree with Hartono et al. [2]. Similarly, the viscosity predictions made by the Weiland’s correlation prove to be very accurate for both the unloaded and loaded MEA solutions.

The significant increases observed, in both the density and viscosity, for the degraded solutions are notable. For the density, the increase is about 2.7 % at all temperatures, while the viscosity is observed to increase by between about 9 % (at the lowest temperature) and 22 % (at the highest temperature). Two phenomena are occurring during the degradation process which account for these dramatic changes. Firstly, during the degradation process it can be expected that there is some (albeit small) loss of solvent due to both flow and elevated temperatures. This is likely an oversimplified interpretation given that, to explain the increase, Weiland’s density correlation would suggest that the amine concentration had increased to approximately 6.9 M MEA (42 mass %). More likely, is that this significant change in physical properties is due to the formation of degradation products. This is supported by a similar exploration of the Weiland viscosity correlation which shows that the degraded solution has the same viscosity as a 5.2 M (31.5 mass %) fresh MEA solution.

In theory, the Weiland correlations have been developed to accommodate multi-amine systems to more accurately reflect solution mixtures. However, the essential data (Table 1) on individual components is likely elusive given the multitude of degradation products known to form. As such, this study addresses whether approximations using the Weiland (or alternative) correlations can be used to provide an improved prediction to an evolving system due to solvent loss and degradation. With this understanding of the changing physical properties in the operating aqueous amine systems, process operations can be modified to enhance process efficiency and output.
Figure 1: Solution (a) density and (b) viscosity for 5 M MEA where 5 M MEA was measured without degradation for (▲) α=0 and (●) α=0.34 and (♦) with degradation for α=0.34. The comparable un-degraded system was modeled using the Weiland correlation for (…) α=0 and (---) α=0.34.