

A computational chemistry study of the temperature dependency of amine basicity

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Keywords: Solvents, computational chemistry

Post-combustion CO₂ capture is usually operated as a temperature swing process. Being able to understand and predict the effects of the temperature on the process is therefore of great interest when selecting solvents and optimizing the process. The key change with temperature is expected to be in the main equilibrium constants of the system: the amine basicity and the carbamate stability.

Computational chemistry models can be utilized to predict these equilibrium constants at ambient temperature with semi-quantitative accuracy. While the same type of models can in principle be utilized to predict the temperature effects, there has however so far been very little work on this type of temperature effects in computational chemistry. To predict an equilibrium constant in solution at a given set of conditions one requires a quantum mechanical method and a solvation model. Most quantum mechanical methods are expected to perform well under varying conditions, most solvation models are however semi-empirical and have only been parameterized to ambient conditions. The performance of the solvation model is therefore one of the main uncertainties in predicting equilibrium constants at higher temperatures.

Solvation models should be parameterized against experimental data to assure their performance at higher temperatures. There is however little direct experimental data, particularly for ionic species. In the present work we compare calculated amine basicities with experimental values. Based on such a comparison the solvation models can be recalibrated.

In the calculations we have utilized the SM8T solvation model and the CBS-QB3 method for calculation of the energies of the solute in vacuum.

In Figure 1 the calculated pK_a is shown together with the experimental pK_a for MDEA (N-methyl diethanolamine). The results suggest that the SM8T model overestimates the temperature dependency of the pK_a.

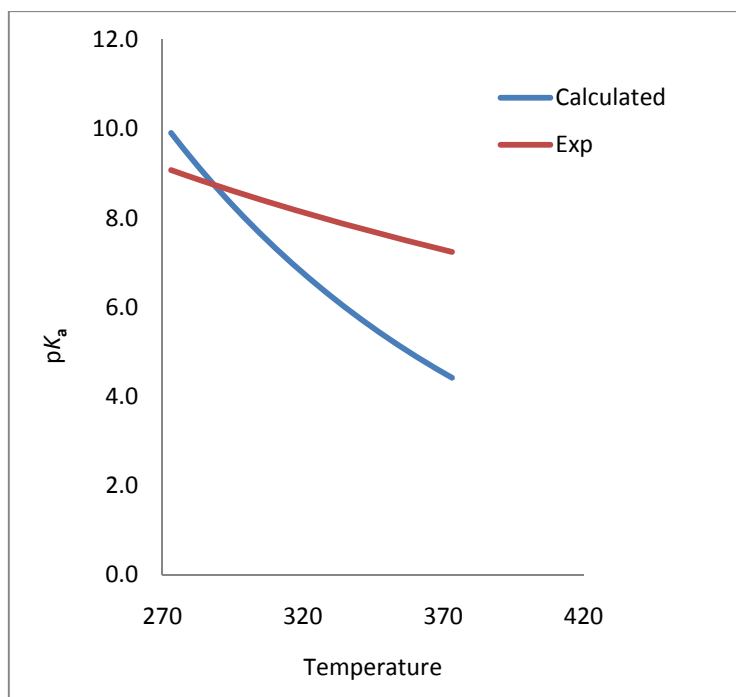


Figure 1. Experimental and calculated pK_a as a function of temperature for MDEA.

By comparing the performance with experimental data for a range of components, we will have a basis for recalibrating the SM8T model. Such a recalibrated model would be a valuable tool in predicting the performance of solvents for post-combustion CO₂ capture.