

Coarse-Grain Molecular Modelling of Water/Propylene Oxide to Determine Transport Properties

Property

Diffusivity (D) is chosen as the transport property calculated to inform the reactor model. Pure water, pure propylene oxide, and the water - propylene oxide system are considered. Diffusivity is described as

Method

As diffusivity is a transport property, a molecular dynamics approach is taken. In order to mimic the complex binary system, two approaches were considered: a coarse grain model or an all-atom model. All-atom approaches consider each atom that makes up the molecule, giving rise to many different factors such as conformational changes and specific packing orientations, which lead to higher computational costs (?). The SAFT γ -Mie coarse grain approach is adopted in this design. The SAFT γ -Mie approach applies a top-down model in which potential parameters are adjusted to ensure the model matches experimental thermophysical data (?). Statistical associating fluid theory (SAFT) is used to estimate the exponent parameters (λ and a) of the Mie force field. Molecules considered in this study are water and propylene oxide. Water is modelled as a single segment ($m = 1$) (?). Propylene oxide is however modelled as 2 homonuclear beads due to the number of atoms being above 3 and below 6 (excluding hydrogens), the force field parameters were obtained using the correlation in (?), as implemented in the *Bottled SAFT* application (?).

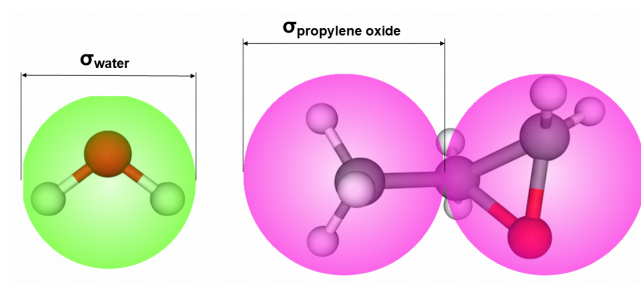


Figure 1: Segments for each species.

The parameters used are seen in appendix 1.3 in table []. The Mie equation gives us potential energy due to intermolecular forces and can be negatively differentiated to provide the force equation as a function of intermolecular radius. The Mie equation is seen below in appendix 1.4 in equations 1 (?).

Justification

Appendix

1.1 Accuracy and Literature Comparison

As discussed, the diffusivity for each mixture (pure water, pure propylene oxide and the reaction mixture) is determined for a series of temperatures. As temperature increases, the particles have more kinetic energy and means there is a higher chance of the system to overcome intermolecular bonds, giving rise to a higher diffusivity. Diffusivity as a function of temperature for each system is seen below in figure []. It should be noted that every system was run for 27 particles and 50,000 steps at a time step (dt) of 1e-15s, except the reaction mixture at 313.15K. This system was run for 216 particles and 100,000 steps at a time step of 1e-15s as this will increase the accuracy of the determined value for use within the next part of the coursework. The reason all systems are not run with these parameters is discussed below in section 1.2.

Table 1: Comparison of literature and calculated diffusivity values.

Mixture	T (K)	$D_{lit}(m^2/s)$	$D_{calc}(m^2/s)$	Ref
Pure water	298	2.9		()
	313			()
	330			()
Pure propylene oxide	298			()
	313			()
	330			()
Reactor inlet	298			()
	313			()
	330			()

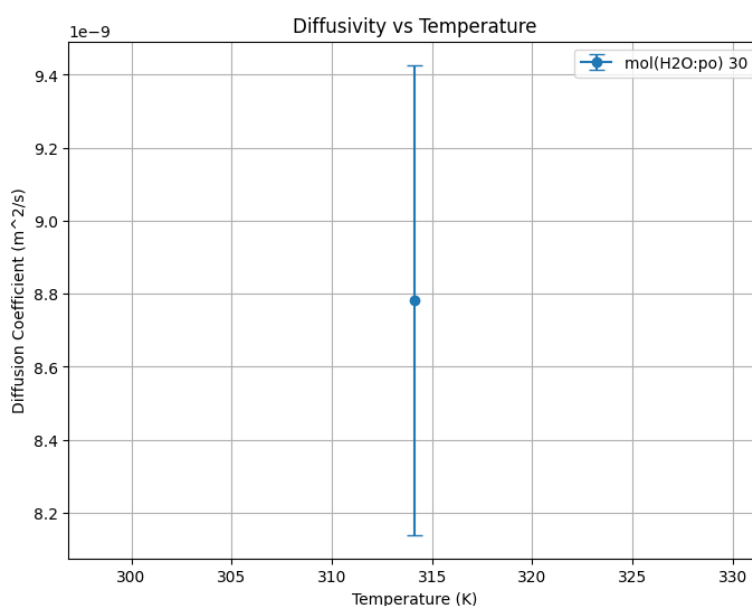


Figure 2: Diffusivity at different temperatures.

1.2 Generalisation and Discussion

Description and analysis of generalisation due to temperature...

rdf is too low, mimics a gas - probs number of particles.. Neighbour list too slow

1.3 Parameters Used

Table 2: SAFT- γ Mie parameters for water and propylene oxide used in this study.

Species	m	σ (m)	ϵ (J)	λ_r	λ_a	Ref
Water	1	2.915×10^{-10}	$378.87k_B$	8.395	6	(?)
Propylene oxide	2	3.4505×10^{-10}	$336.96k_B$	17.079	6	(?)

1.4 Equations Used

$$U(r) = C\epsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^6 \right] \text{ Where } C = \left(\frac{\lambda_r}{\lambda_r - 6} \right) \left(\frac{\lambda_r}{6} \right)^{\left(\frac{6}{\lambda_r - 6} \right)} \quad (1)$$