Supporting Information

Dissecting Dynamics near the Glass Transition

*Khalil Akkaoui, Joseph B. Schlenoff**

Department of Chemistry and Biochemistry

The Florida State University, Tallahassee, FL 32306 USA

*jschlenoff@fsu.edu

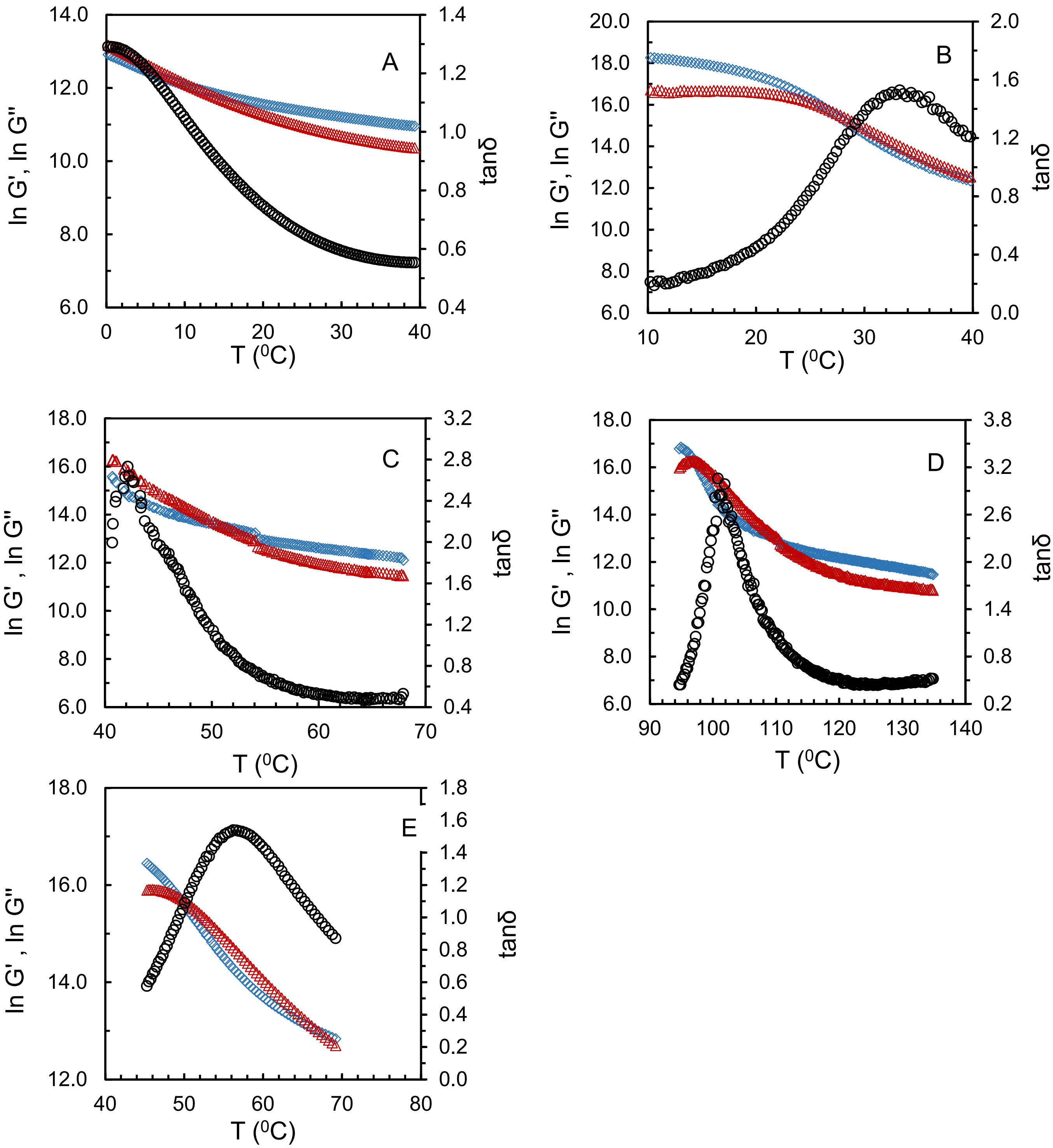

Figure S1. Storage modulus, G’ (in Pa, blue diamonds), loss modulus G’’ (in Pa, red triangles) and the tanδ (black circles) of PDADMA/PSS (A) and PVBT/PAMS (B) in 0.01 M NaCl and PVA (C), PS (D) and P(iBM) (E) at 0.62 rad s^{-1}. At T_g the modulus drops significantly. The location of T_g is typically identified by a maximum in tanδ (= G”/G’).

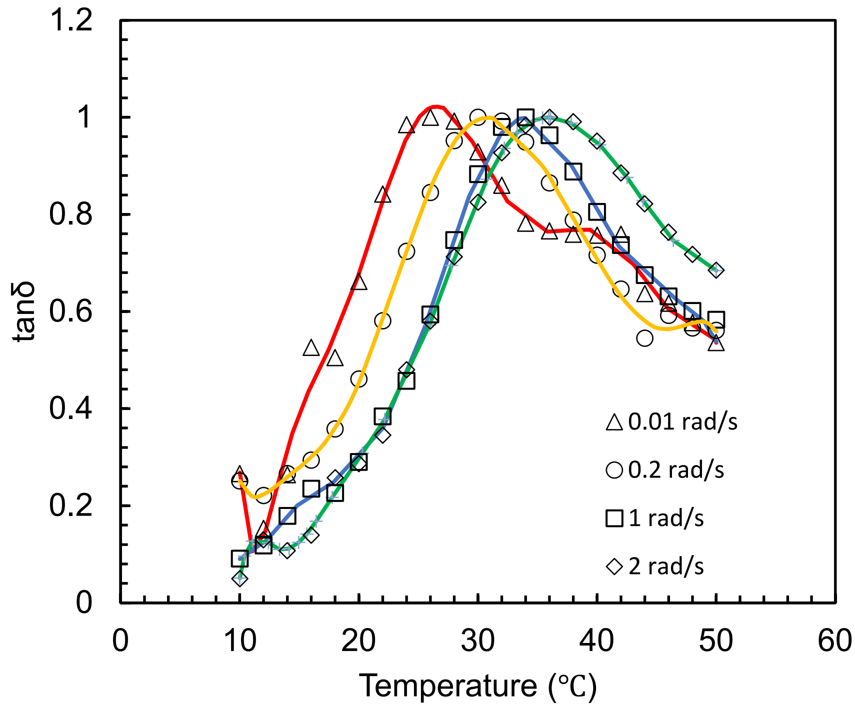

Figure S2. Examples of tanδ fits using MatLab as a function of temperature. Three frequencies are presented as an example to illustrate the fit to the data points (0.01, 0.2, 1 and 2 rad s^{-1}). The T_g was acquired from the maximum of the fits.

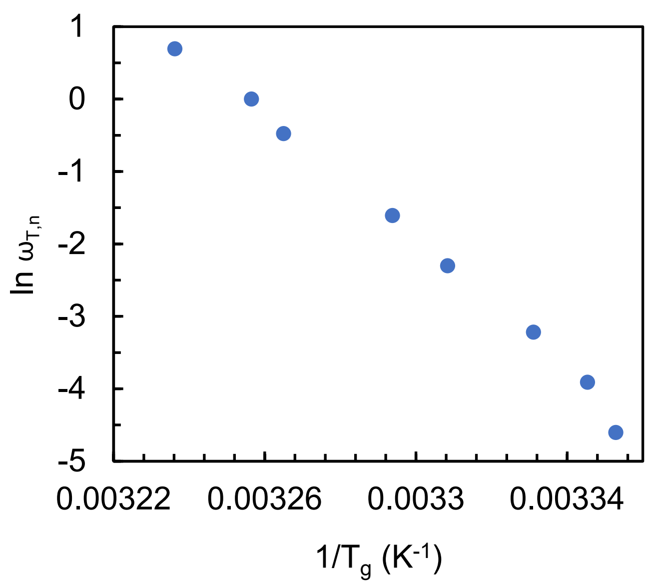

Figure S3. The variation of T_g in PDADMA/PSS PEC in 0.01 M [NaCl] as a function of the applied frequency.

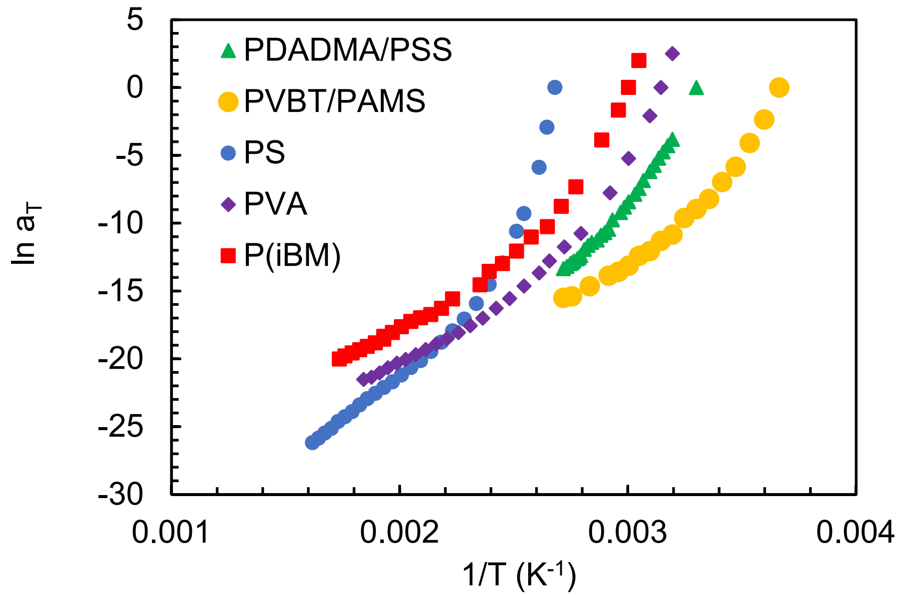

Figure S4. Frequency shift factor a_T as a function of 1/T for the two PECs in 0.01 M NaCl and the three neutral polymers. The reference temperature is at the T_g of each.

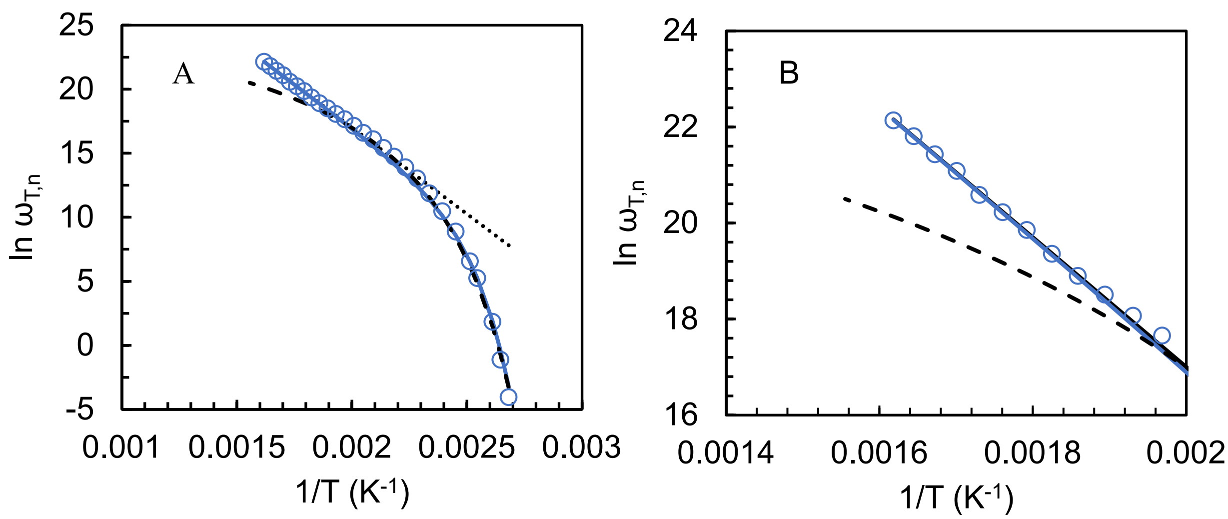

Figure S5. Panel A: VFT fit of PS using $\omega_{0,VFT}$ = 6.0 x 10^{10}, D = 4.25 and T_o = 324 K as the best fit parameters (dashed line) according to the experimental data, carried to temperatures well into the Arrhenius region. The dotted line denotes Arrhenius behavior, the solid line is the fit according to Equation S11 and the open circles are the experimental data. **Panel B**: A closer look at the deviation of the VFT equation (dotted line) at temperatures into the Arrhenius region.

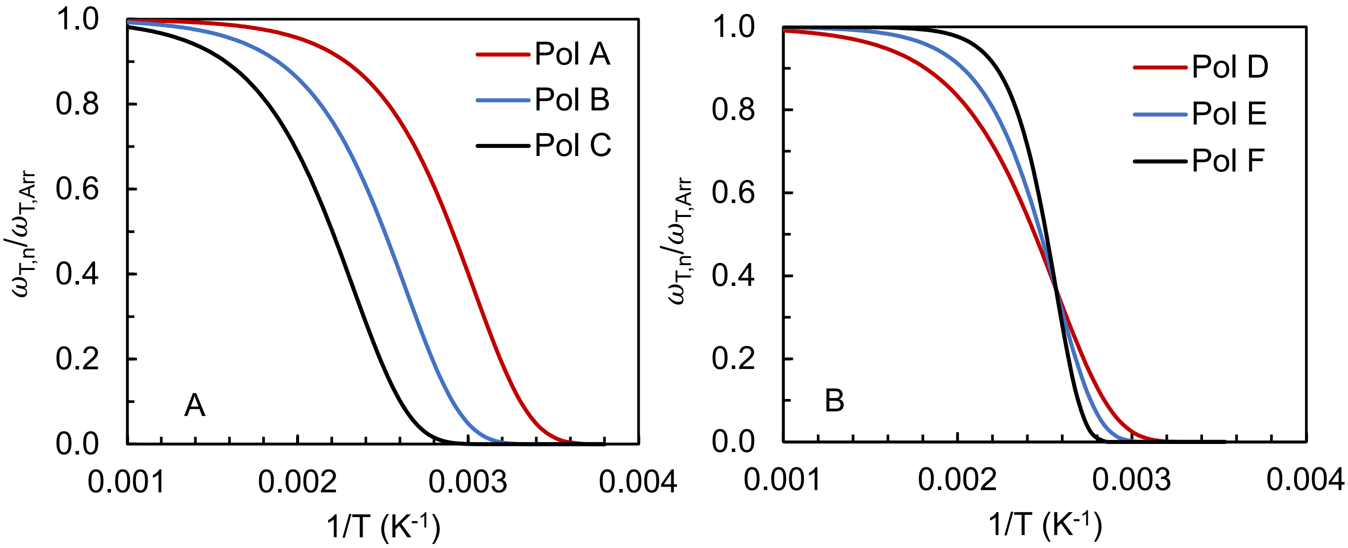

Figure S6. The deviation from Arrhenius described as the ratio between the actual relaxation frequency ($\omega_{T,n}$) and the Arrhenius frequency ($\omega_{T,Arr}$) for six polymers with simulated conditions described in Table S1.

Table S1. Parameters used to simulate the frequency response for six polymers in Figure S6.

	$\omega_{0,arr}$ (s^{-1})	$E_{a,u}$ (kJ mol^{-1})	T_c (K)	T_g (K)	T_c/T_g	U (J $mol^{-1}K^{-1}$)
Pol A	1.27×10^{19}	25.0	330	261	1.26	20.0
Pol B	1.27×10^{19}	25.0	380	291	1.3	20.1
Pol C	1.27×10^{19}	25.0	430	320	1.34	20.0
Pol D	1.14×10^{16}	25.0	390	297	1.31	20.1
Pol E	1.14×10^{16}	35.0	390	319	1.22	20.0
Pol F	1.14×10^{16}	55.0	390	342	1.14	19.8

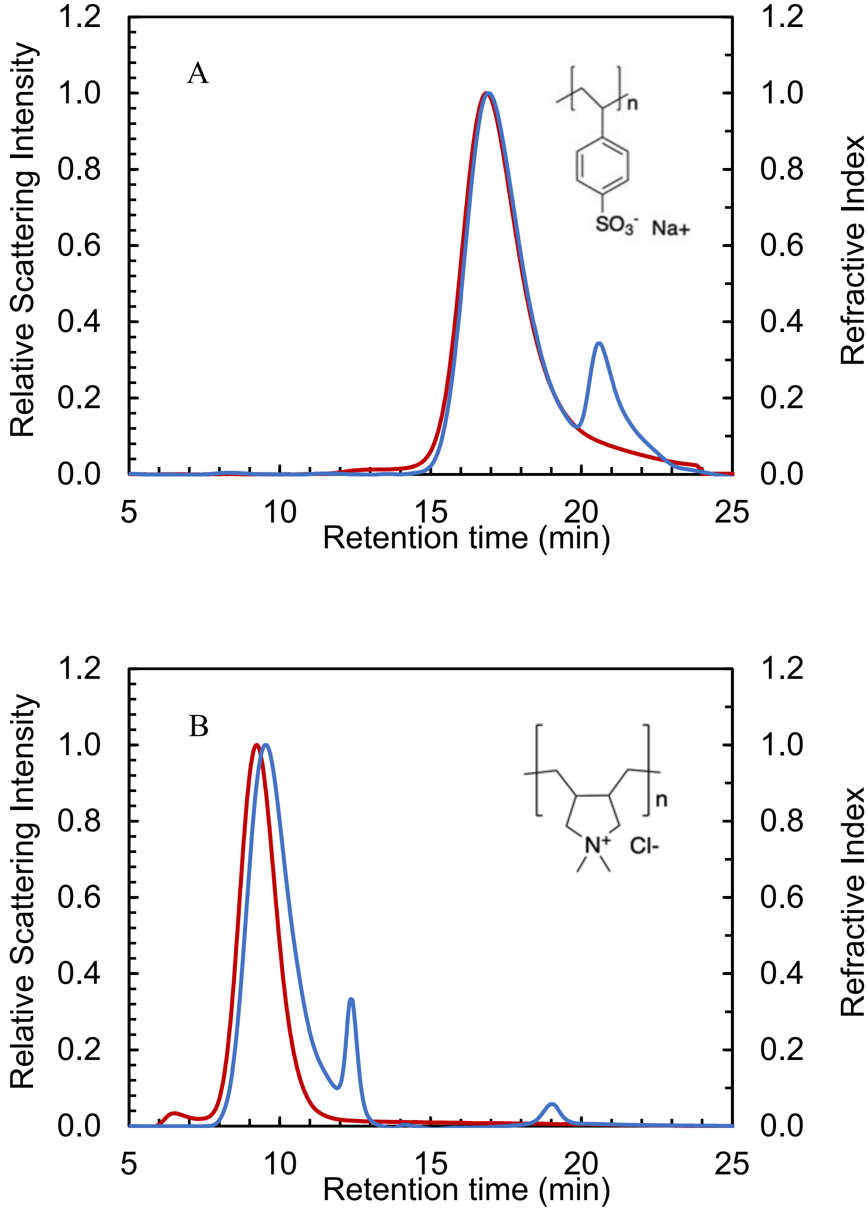

Figure S7. Panel A and B show the SEC chromatograms of isolated fractions of PSSNa (M_w = 94.8 kg mol^{-1}, Đ = 1.02) and PDADMAC (M_w = 70.0 kg mol-1, Đ = 1.13) respectively. SEC conditions: mobile phase 0.3 M $NaNO_3$ with 200 ppm NaN_3, 1 mL min^{-1}, with an injection volume of 50 µL.

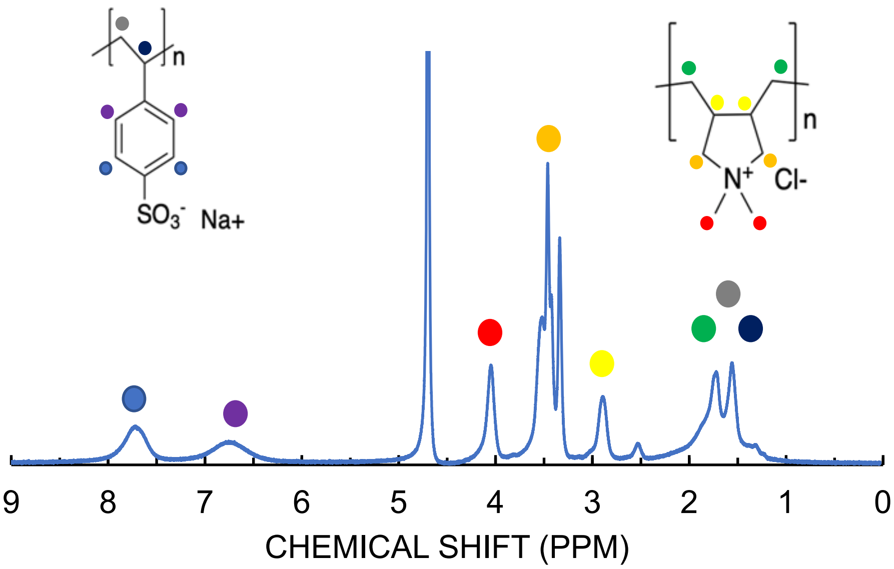

Figure S8. [1]H solution NMR spectra of PDADMA/PSS PEC with an average number of 446 repeat units made using the fractions of PDADMAC and PSS with respective M_w of 70.0 and 94.8 kg mol^{-1} in 2.5 M KBr in D_2O. H_2O is at 4.75 ppm. A PSSNa/PDADMAC ratio of 0.98 indicates that the complex is nearly stoichiometric with 2 % excess PDADMAC.

Derivation of Equation 14

At any temperature the slope of $\ln\omega_T$ versus 1/T is given by

$$\frac{d}{d}\frac{\ln\omega_{T,n}}{T^{-1}} = -\frac{nE_{a,u}}{R} \quad \text{[S1]}$$

Also,

$$\ln\left(\frac{\omega_{T,arr}}{\omega_{T,n}}\right) = n - 2 \quad \text{[S2]}$$

The Arrhenius region is given by

$$\omega_{T,arr} = \omega_{0,arr} e^{\frac{-2E_{a,u}}{RT}} \quad \text{[S3]}$$

Combining Equation S1 with S2 gives:

$$-\frac{d}{d}\frac{ln\omega_{T,n}}{T^{-1}}=\frac{nE_{a,u}}{R}=\frac{E_{a,u}}{R}\left(\ln\omega_{T,arr}-\ln\omega_{T,n}+2\right) \quad [S4]$$

And substituting the Arrhenius Equation S3 into S4 we obtain:

$$-\frac{d}{d}\frac{ln\omega_{T,n}}{T^{-1}}=\frac{E_{a,u}}{R}\left(\ln\omega_{0,arr}-\frac{2E_{a,u}}{RT}-\ln\omega_{T,n}+2\right) \quad [S5]$$

Consider y = ln $\omega_{T,n}$ and x = T^{-1}

We can then re-write the equation as:

$$y'-\frac{E_{a,u}}{R}y-\frac{2E_{a,u}^2}{R^2}x+\frac{E_{a,u}}{R}\ln\omega_{o,2}+\frac{2E_{a,u}}{R}=0 \quad [S6]$$

Let A = $\frac{E_{a,u}}{R}$, B = $\frac{2E_{a,u}^2}{R^2}$ and C = $\frac{E_{a,u}}{R}\ln\omega_{o,2}+\frac{2E_{a,u}}{R}$

Substituting the terms A, B and C into Equation S6 provides a differential equation with the form:

y' - Ay -Bx + C = 0

The solution of this differential equation is expressed as: $y=\frac{-B}{A^2}-\frac{B}{A}x+c_1e^{Ax}+\frac{C}{A}$

Substituting for the values of the constants provides solution S7 to the differential equation S6:

$$\ln\omega_{T,n}=\ln\omega_{0,arr}-\frac{2E_{a,u}}{RT}+c_1e^{\frac{E_{a,u}}{RT}} \quad [S7]$$

Or, using Equation S3

$$\ln\omega_{T,n}=\ln\omega_{T,arr}+c_1e^{\frac{E_{a,u}}{RT}} \quad [S8]$$

To find c_1, set a boundary condition, define $T_c = T_{conv}$ as the temperature where n = 3.

At T = T_{conv}, from Equation S2

$$\omega_{T,n}=\frac{\omega_{T,arr}}{e} \quad [S9]$$

Solve for c_1 by applying this condition to Equation S8 to obtain:

$$c_1=-e^{\frac{E_{a,u}}{RT_C}} \quad [S10]$$

Substitute c_1 into Equation S8.

$$\ln\omega_{T,n}=\ln\omega_{T,arr}-e^{\frac{E_{a,u}}{R}\left(\frac{1}{T}-\frac{1}{T_C}\right)} \quad [S11]$$