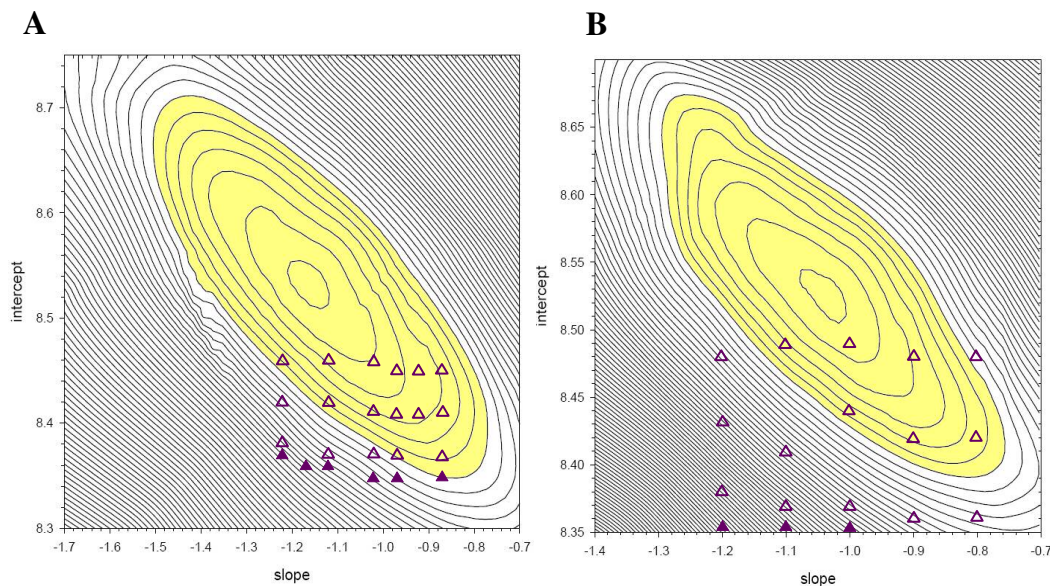


## Supplemental Information

### Determining the viscosity-dependent region for electrostatic and covalent assemblies.

The error in the regression line was ascertained by calculating goodness-of-fit ( $\chi^2$ ) values for different combinations of the slope and intercept. Figure 1 shows the result of this analysis, where the ratio  $\chi^2/\chi^2_{\min}$  is plotted as contours and  $\chi^2_{\min}$  was the smallest calculated  $\chi^2$  value. The shaded region encloses slope-intercept combinations for which  $\chi^2/\chi^2_{\min} \leq 4$ , for which the best-fit line does not visibly deviate from the data. Slope-intercept combinations that fit the D<sub>2</sub>O cell data either perfectly (closed triangles) or within one standard deviation (open triangles) were then plotted on the same graph to determine where those combinations lay with respect to the acceptable (shaded) region. From this analysis, it can be seen that, within error, the viscosity dependent model exactly accounts for the cell isotope effect in the covalent and electrostatic systems. On the other hand, the incubant viscosity effect data lies well outside the scale of the contour plots in Figure 1, indicating that viscosity does not account for this effect.

The upper and lower slope and intercept values were used to calculate the best-fit lines shown in Figure 3 of the main text for plots of  $\ln(\text{average } k^0)$  vs.  $\ln(\eta)$ . When  $\text{KIE}_{\text{cell}}$  and  $\text{KIE}_{\text{tot}}$  are plotted on the same set of axes, the same conclusions naturally follow.



**Figure 1.** Contour plots describing the goodness of fit for the viscosity dependence of the rate constant in (A) electrostatic and (B) covalent cytochrome *c*/C<sub>6</sub> acid/C<sub>4</sub>OH SAM assemblies as a function of the slope and intercept of the best fit line. Contours are fixed values of  $\chi^2/\chi^2_{\min}$ , where  $\chi^2_{\min}$  is the smallest calculated  $\chi^2$  value. The innermost contour has a value of  $\chi^2/\chi^2_{\min} = 1$ ; subsequent contours are separated by 0.5. The shaded region indicates slope-intercept combinations that acceptably fit the data set ( $\chi^2/\chi^2_{\min} \leq 4$ ). Plotted points show some slope-intercept combinations that perfectly fit the rate constant for H<sub>2</sub>O-incubated cytochrome *c* in D<sub>2</sub>O buffer (closed triangles) or fit within error (open triangles). Slope-intercept combinations that fit the rate constant for D<sub>2</sub>O-incubated cytochrome *c* in D<sub>2</sub>O are beyond the scale of both plots.