Supporting Information for

A Kinetic Description of How Interfaces Accelerate Reactions in Micro-compartments

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This file contains supplementary Tables S1 and S2 and Figure S1-S7

Table S1: Computed fraction of molecules at the surface of a sphere with radius, R, compared with the reactangular prism simulation geometry.

	Rectangular Prism			*Sphere*		
R (µm)	**Surface #**	**Bulk #**	$f_{surface}$	**Surface #**	**Bulk #**	$f_{surface}$
1	1.66	3.011	**0.554**	2.09×10^{7}	3.78×10^{7}	**0.554**
10	1.66	30.11	**0.0554**	2.09×10^{9}	3.78×10^{10}	**0.0554**
100	1.66	301.1	$\mathbf{5.54 \times 10^{-3}}$	2.09×10^{11}	3.78×10^{13}	$\mathbf{5.54 \times 10^{-3}}$
1000	1.66	3011	$\mathbf{5.54 \times 10^{-4}}$	2.09×10^{13}	3.78×10^{16}	$\mathbf{5.54 \times 10^{-4}}$
10000	1.66	30110	$\mathbf{5.54 \times 10^{-5}}$	2.09×10^{15}	3.78×10^{19}	$\mathbf{5.54 \times 10^{-5}}$

Table S2: The set of elementary reaction and diffusion steps and rate coefficients used in stochastic simulations 1 and 2.

	Elementary Step	Simulation 1	Simulation 2		
No.	**Surface Compartment**	**Rate Coefficient**	**Rate Coefficient**	**units**	**Ref.**
1	Amine + Site → Amine_ads	0.066	See Sim. 1	$M^{-1}\ s^{-1}$	1
2	Amine_ads → Amine + Site	1.10×10^{-3}	See Sim. 1	s^{-1}	1
3	Aldehyde + Site → Aldehyde_ads	0.120	See Sim. 1	$M^{-1}\ s^{-1}$	1
4	Aldehyde_ads → Aldehyde + Site	8.0×10^{-4}	See Sim. 1	s^{-1}	1
5	Imine + Site → Imine_ads	0.120	See Sim. 1	$M^{-1}\ s^{-1}$	1
6	Imine_ads → Imine + Site	2	See Sim. 1	s^{-1}	2, a
7	Amine_ads + Aldehyde_Ads → Imine_ads + Site	1.54×10^{-3}	3.22×10^{-3}	$M^{-1}\ s^{-1}$	3
8	Imine_ads → Amine_ads + Aldehyde_Ads	1.52×10^{-3}	See Sim. 1	s^{-1}	2
	Diffusion Pathways	**Diffusion Coefficient**	**Diffusion Coefficient**		
9	Amine (Bulk) ↔ Amine (Surface)	5.02×10^{-6}	See Sim.1	$cm^2\ s^{-1}$	2
10	Aldehyde (Bulk) ↔ Aldehyde (Surface)	4.46×10^{-6}	See Sim.1	$cm^2\ s^{-1}$	2
11	Imine (Bulk) ↔ Imine (Surface)	2.39×10^{-6}	See Sim. 1	$cm^2\ s^{-1}$	2
	Bulk Compartment	**Rate Coefficient**	**Rate Coefficient**		
12	Amine + Aldehyde → Imine	2.60×10^{-5}	See Sim.1	$M^{-1}\ s^{-1}$	2
13	Imine → Amine + Aldehyde	1.52×10^{-3}	See Sim. 1	s^{-1}	2

[a] The value of this rate coefficient is selected to produce simulation results consistent with the experimental observations in Ref. [2]

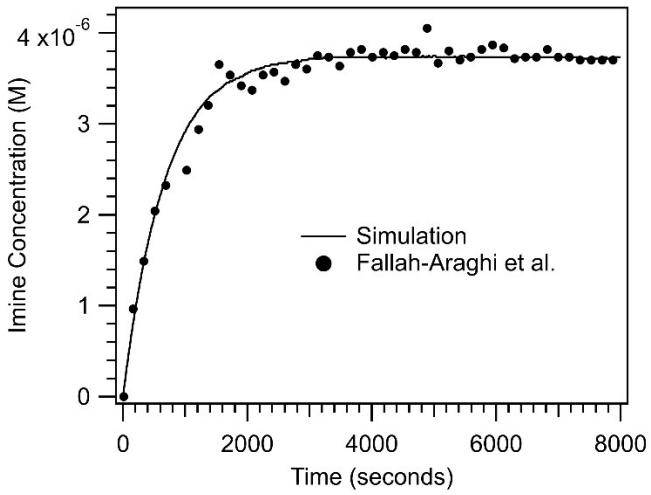

Figure S1: Imine concentration vs. reaction time measured in a bulk solution. Points are data reproduced from Ref. [2] and the line is a fit from simulations in order to constrain the forward and reverse rates for the bulk reaction (Steps 12 and 13 Table 2).

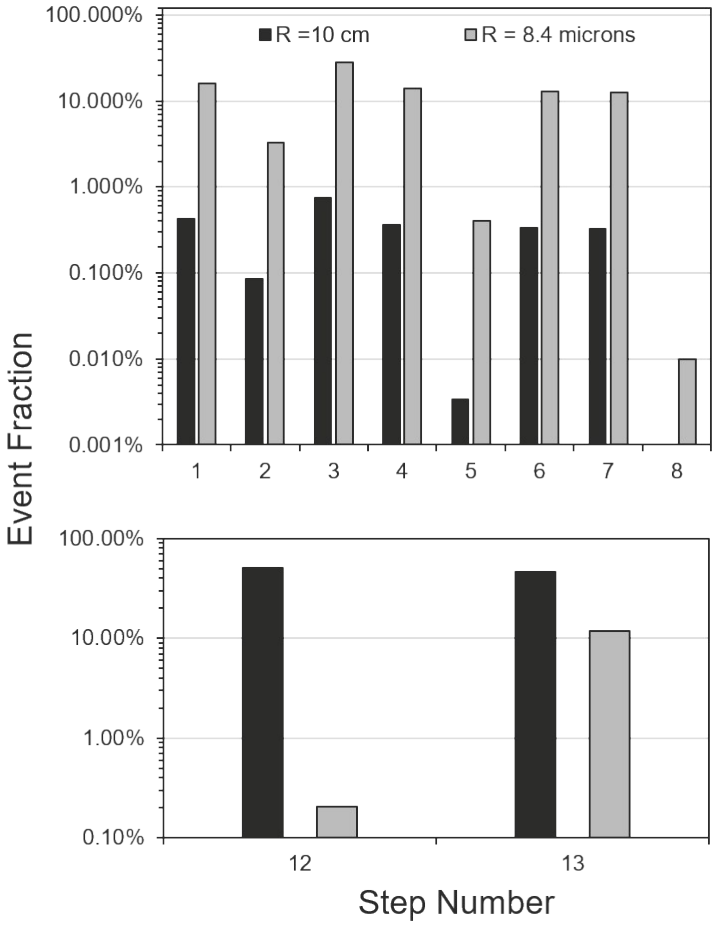

Figure S2: Event fraction in the surface (top) and bulk (bottom) compartments as a function of reaction step number (see Table 2) for R=8.4 μm and R = 10 cm.

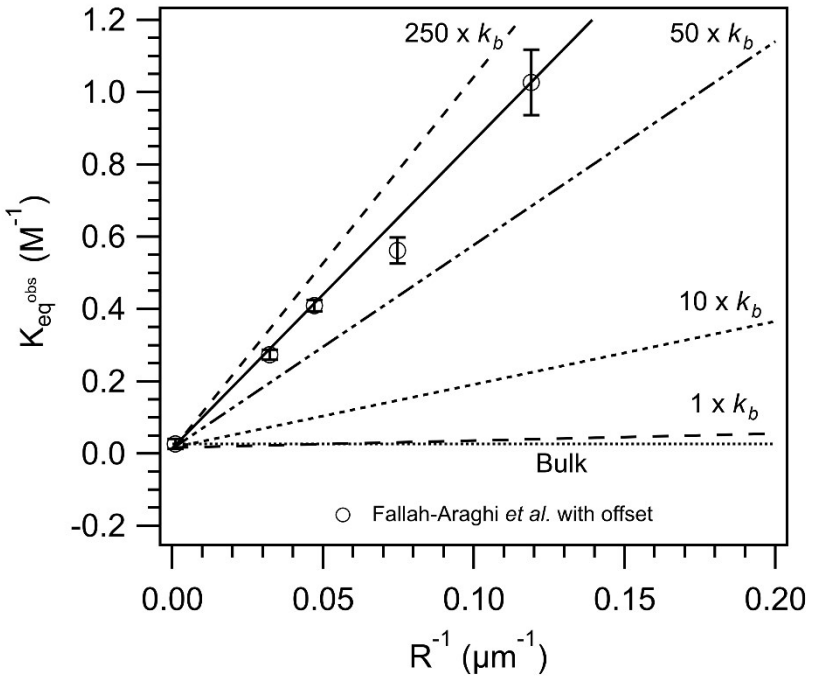

Figure S3: Sensitivity of simulated K_{eq}^{obs} vs. R^{-1} for [amine]=[aldehyde] = 15mM. Lines represent different simulated values for the surface forward rate coefficient for imine synthesis (Step 7, Table S2). These rate coefficients are expressed as multiples of the bulk value (k_b) (see Step 12, Table S2).

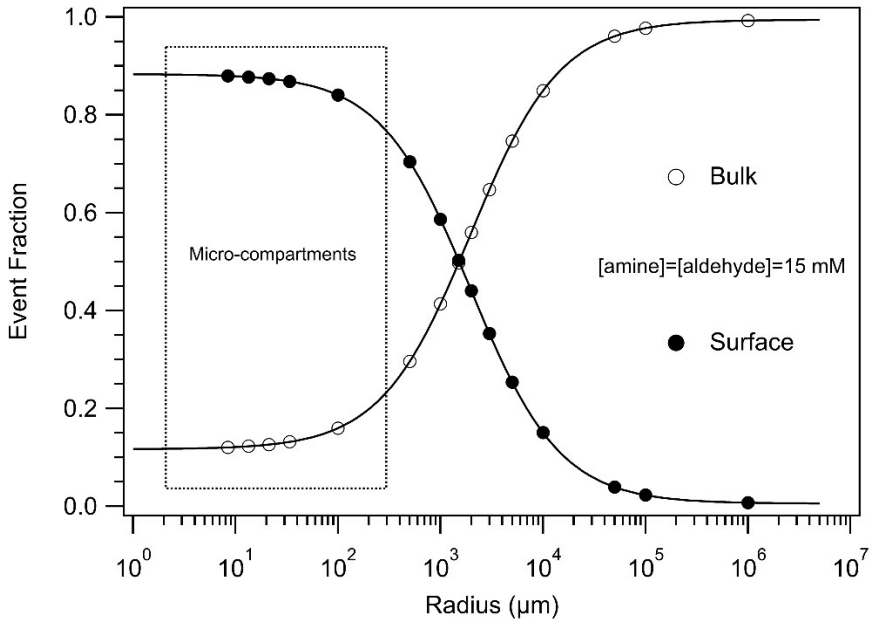

Figure S4: Bulk and surface event fractions as a function of radius for simulation 2 ([amine]=[aldehyde] =15 mM). Lines are guides for the eye.

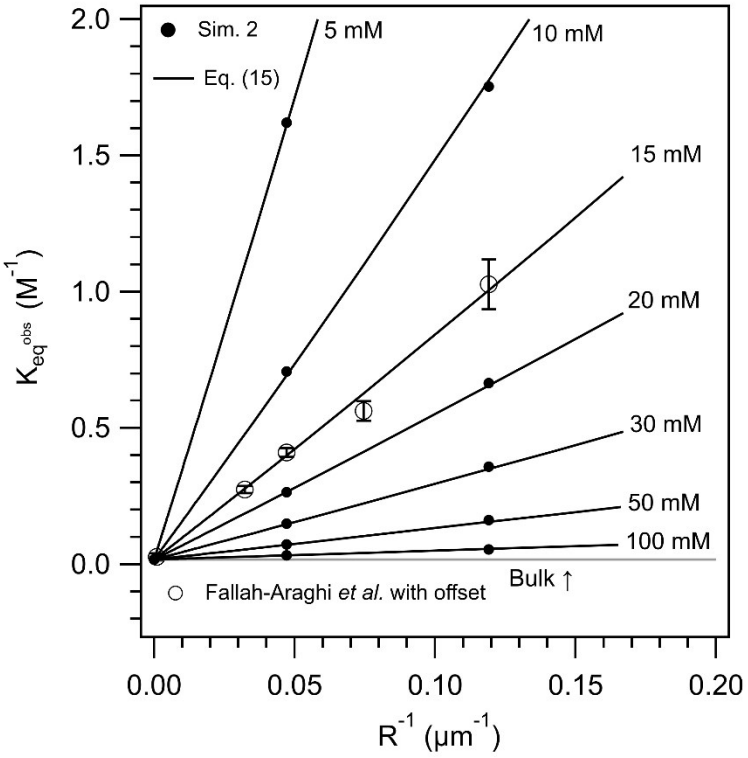

Figure S5: K_{eq}^{obs} vs. R^{-1} and concentration for [amine]=[aldehyde]. Comparison of experimental data from Ref. [2], results from simulation 2 and predictions from Eq. (15). K_{eq}^{B} = 0.017 M^{-1} and is shown in the figure as a gray line.

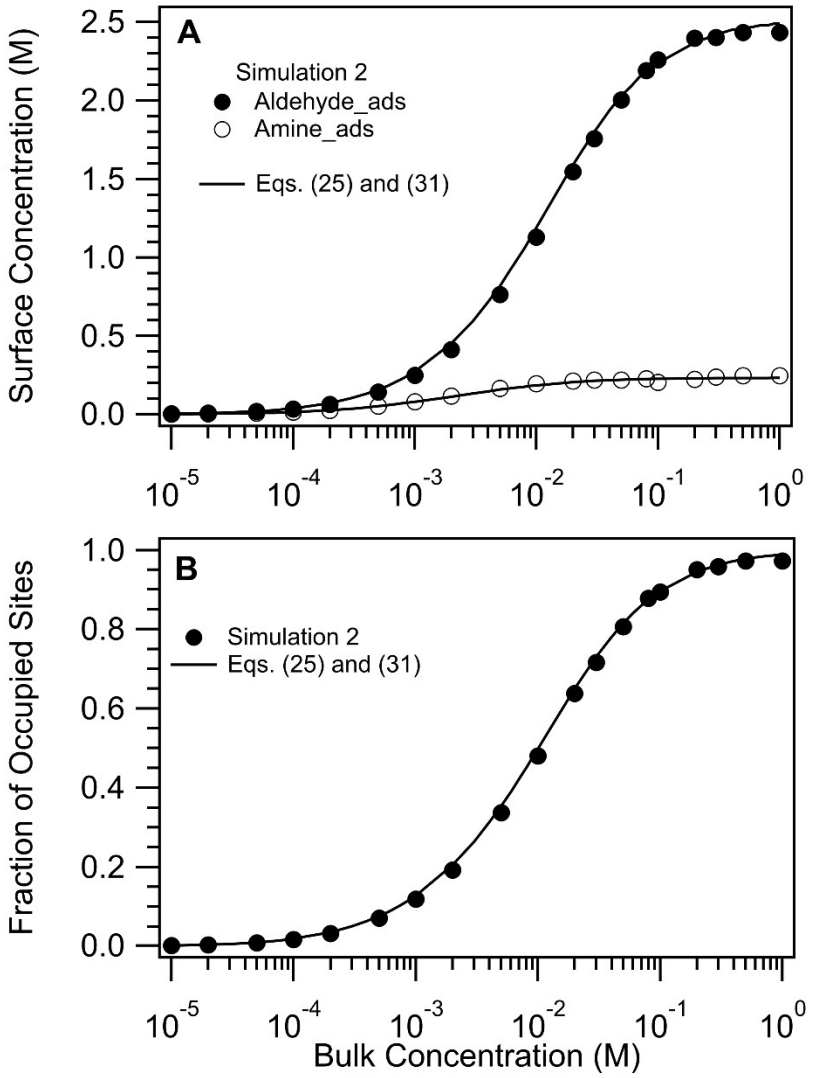

Figure S6: Surface concentrations of (A) adsorbed amine and aldehyde and (B) fraction of occupied surface sites vs. bulk concentration for R = 8.4 μm. Simulation 2 results (points) are compared with predictions from Eqs. (31) and (25).

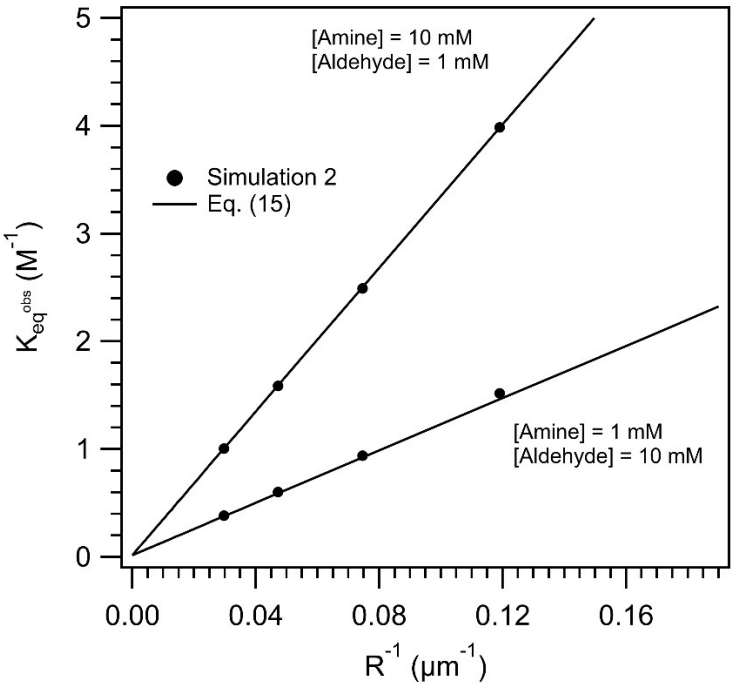

Figure S7: K_{eq}^{obs} vs. R^{-1} for non-stoichiometric reactant concentrations (i.e. [amine] ≠ [aldehyde]): simulation 2 (points) and prediction (lines) from Eq. (15).

Supporting References

1. Tomoaia, G.; Tomoaia-Cotisel, A.; Tomoaia-Cotisel, M.; Mocanu, A., Kinetic study of adsorption of some biocompounds at the oil/water interface. *Cent. Eur. J. Chem.* **2005,** *3*, (2), 347-360.

2. Fallah-Araghi, A.; Meguellati, K.; Baret, J.-C.; Harrak, A. E.; Mangeat, T.; Karplus, M.; Ladame, S.; Marques, C. M.; Griffiths, A. D., Enhanced Chemical Synthesis at Soft Interfaces: A Universal Reaction-Adsorption Mechanism in Microcompartments. *Phys. Rev. Lett.* **2014,** *112*, (2), 028301.

3. Meguellati, K.; Fallah-Araghi, A.; Baret, J.-C.; El Harrak, A.; Mangeat, T.; Marques, C. M.; Griffiths, A. D.; Ladame, S., Enhanced imine synthesis in water: from surfactant-mediated catalysis to host–guest mechanisms. *Chem. Commun.* **2013,** *49*, (96), 11332-11334.