Adsorption Kinetics of Aqueous n-Alcohols: A New Kinetic Equation for Surfactant Transfer

Andrew M. Prpich, M. Elias Biswast, P. Chen*

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario,

Canada, N2L 3G1

* Corresponding Author E-mail: p4chen@uwaterloo.ca

† Department of Chemical and Biomolecular Engineering, Johns Hopkins University,

Baltimore, MD 21218

This file includes:

Experimental Setup and Procedure

Modified Langmuir Adsorption Isotherm Derivation

Figure S1

References

Experimental Setup and Procedure

A schematic diagram of the experimental setup for the surface tension experiments is shown in Fig. S1. An IsoStation vibration isolated workstation was used to prevent vibration of the key components during operation. An optical light source filtered by a diffuser was used to illuminate the pendant drop. The drop was formed by means of a motorized syringe pump attached to a Hamilton gas-tight syringe. The drop was formed inside a clear quartz cuvette, placed inside the environmental chamber, to allow for control of the vapor phase conditions. The environmental chamber was used to control the temperature of the system and minimize vapor leakage during operation. The drop images were captured by a high speed camera and microscope system that displayed the profile on a monochromatic monitor and exported the image files to a computer system. The digitized images were analyzed using the ADSA-P program once the experiment was completed to generate the surface tension values.



Figure S1. Schematic of ADSA-P experimental setup; (1) IsoStation vibration isolated workstation, (2) optical light source, (3) light diffuser, (4) motorized syringe pump and gas-tight syringe, (5) environmental chamber, (6) high speed camera, (7) monochromatic monitor, and (8) computer system.

For each experiment, a pendant drop of the sample under test (referred to as the drop solution) was formed inside the quartz cuvette above 1 ml of aqueous solution (referred to as the environment solution) containing the same component as the drop. The environment solution was added to facilitate adsorption from the vapor side of the

interface by creating a surfactant vapor phase surrounding the drop solution. If the two liquid solutions had different surfactant concentrations, a driving force was established for molecular transfer across the vapor/liquid interface causing the surface tension of the drop solution to evolve as a result of the exchange. Before each set of experiments, the gas-tight syringe was cleaned by ultrasonic and repeated rinsing with purified water. After cleaning, approximately 0.3-0.4 ml of aqueous solution was drawn into the syringe. The environment solution was added to the cuvette using a 1 ml micropipette. The syringe was then fed into the cuvette and the chamber was sealed. The system was allowed to equilibrate for 15 minutes after which, the drop was formed using the motorized syringe. For all experiments the temperature of the chamber was maintained at 25°C by a water cooling bath. Image capture began immediately after the drop was formed and continued until the surface tension of the drop was no longer changing (~2-5 hours).

Modified Langmuir Adsorption Isotherm Derivation

In the derivation of Langmuir's classic adsorption isotherm, adsorption from either the liquid phase or the vapor phase, to the interface, was considered. As a result the Langmuir adsorption isotherm is a relation between the interfacial concentration of a surfactant and either the concentration in the bulk liquid phase or the partial pressure in the vapor phase.¹ However, in the current systems adsorption from the liquid and the vapor phase contribute to the surface concentration simultaneously. Thus, the modified adsorption isotherm must account for dual adsorption from both sides of the vapor/liquid interface. The derivation will follow the same rational and level of assumptions as the classic Langmuir isotherm due to its broad range of applicability. The first step in the derivation is to write expressions for the rates of adsorption and desorption to and from either side of the vapor/liquid interface:

$$r_a^g = k_a^g P S_o = k_a^g P (S - S_1) \tag{S1}$$

$$r_d^g = k_d^g S_1 \tag{S2}$$

$$r_a^{l} = k_a^{l} C S_o = k_a^{l} C (S - S_1)$$
(S3)

$$r_d^l = k_d^l S_1 \tag{S4}$$

where r_a^g , r_d^g , r_a^l , r_d^1 are the rates of adsorption and desorption in the vapor and liquid phases, respectively, k_a^g , k_d^g , k_a^1 , k_d^1 , are the kinetic rate constants for adsorption and desorption in the vapor and liquid phases, respectively, P is the partial pressure of surfactant in the vapor phase, C is the concentration of surfactant in the liquid phase, S is the total number of adsorption sites at the interface, S_o is the number of free adsorption sites, and S_1 is the number of occupied adsorption sites. The model follows Langmuir kinetics where the rates of adsorption are proportional to the surfactant concentration and the number of vacant adsorption sites at the interface (S – S₁), and the rate of desorption is proportional to the surface coverage (S₁).² At steady-state or equilibrium, the overall rate of adsorption is equal to the overall rate of desorption. Equating the expressions for the rates of adsorption leads to:

$$k_a^g P(S - S_1) + k_a^l C(S - S_1) = k_d^g S_1 + k_d^l S_1$$
(S5)

Equation (S5) can be simplified to obtain the modified Langmuir adsorption isotherm:

$$\frac{S_1}{S} = \frac{\Gamma}{\Gamma_{\infty}} = \frac{K_1 P + K_2 C}{1 + K_1 P + K_2 C}$$
(S6)

$$K_1 = \frac{k_a^g}{k_d^g + k_d^l} \tag{S7}$$

$$K_2 = \frac{k_a^l}{k_d^g + k_d^l} \tag{S8}$$

where Γ is the surface concentration of surfactant, Γ_{∞} is the maximum surface concentration, and K₁ and K₂ are the equilibrium constants for adsorption from the vapor phase and the liquid phase, respectively. Equation (S6) describes the equilibrium relationship between the surface concentration of surfactant and both partial pressure in the vapor phase and concentration in the liquid phase. In order to relate the surface concentration of surfactant to surface tension, an appropriate surface equation of state must be utilized. From the Gibb's adsorption equation³ the following equation of state can be derived which is consistent with Langmuir-type kinetics and has been used extensively in the literature:⁴

$$\gamma = \gamma_o + \Gamma_{\infty} RT \ln \left(1 - \frac{\Gamma}{\Gamma_{\infty}} \right)$$
(S9)

where γ is the surface tension of the solution, γ_0 is the surface tension of the pure solvent, R is the universal gas constant, and T is the temperature. In the Gibb's adsorption equation the activity coefficients are assumed to be unity, as is the common practice for ideally dilute solutions.¹ The final form of the surface equation of state can be obtained by combining Equations (S6) and (S9) and relating the partial pressure of surfactant in the vapor phase (P) to the concentration of the environment solution (C_{env}) through Henry's law ($P = H C_{env}$):⁵

$$\gamma = \gamma_o - \Gamma_{\infty} RT \ln \left(1 + K_1 H C_{env} + K_2 C_{drop} \right)$$
(S10)

where H is the Henry's law constant for the surfactant in aqueous solution, C_{env} is the concentration of surfactant in the environment solution, and C_{drop} is the concentration of surfactant in the drop solution. The modified Langmuir adsorption isotherm [Equation (S6)] and corresponding surface equation of state [Equation (S10)] are the first of their kind for predicting the steady-state surface tension of a liquid solution as a function of surfactant concentration in both the liquid phase and the vapor phase. The equilibrium

parameters K_1 , K_2 , and Γ_{∞} , can be determined for any system by fitting Equation (S10) to experimental data through nonlinear regression. The results from parameter estimation for both systems are presented in the main text of this article.

References

1. Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*. 6 ed.; Wiley: New York, 1997; p 23.

2. Eastoe, J.; Dalton, J. S. Adv. Colloid Interface Sci. 2000, 85, 103.

3. Chattoraj, D. K.; Birdi, K. S. *Adsorption and the Gibbs Surface Excess*. 1 ed.; Plenum Press: New York, NY, 1984.

4. Biswas, M. E.; Chatzis, I.; Ioannidis, M. A.; Chen, P. J. Colloid Interface Sci. 2005, 286, 14.

5. Castellan, G. W. *Physical Chemistry*. 3 ed.; Benjamin/Cummings, Inc.: Menlo Park, CA, 1983.