LETTER TO THE EDITOR

On the derivation of the Langmuir isotherm for adsorption kinetics

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Abstract. The Langmuir isotherm, essentially an equilibrium relation but often used as a boundary condition in modelling adsorption kinetics, is introduced and discussed. Starting from a more fundamental, and therefore more generally applicable, boundary condition we justify mathematically the use of the isotherm relation in this context, showing under what conditions it may be considered a valid approximation to the more fundamental relation.

In many systems exhibiting surfactant properties, e.g. soap solutions, the dependence of Γ^∞, the equilibrium concentration of the surface-active component at an interface, and C^∞, the corresponding bulk phase concentration, is observed to be given by the so-called Langmuir isotherm,

$$\Gamma^\infty = \frac{\gamma\hat{\Gamma}C^\infty}{1+\gamma C^\infty} \tag{1}$$

where $\hat{\Gamma}$ represents the saturated surface concentration, see figure 1, and the parameter γ some constant. The relation was proposed by Langmuir [1] in 1933 for his model of the formation of monolayer oil films on water.

Studies of the kinetics of adsorption from surfactants often proceed by assuming that, at any time t, a corresponding equation (2) relates $\Gamma(t)$, the adsorbed surface concentration, to $C(t)$, the 'subsurface' concentration (that is the concentration in the bulk phase adjacent to the surface), see [2–7]

$$\Gamma(t) = \frac{\gamma\hat{\Gamma}C(t)}{1+\gamma C(t)}. \tag{2}$$

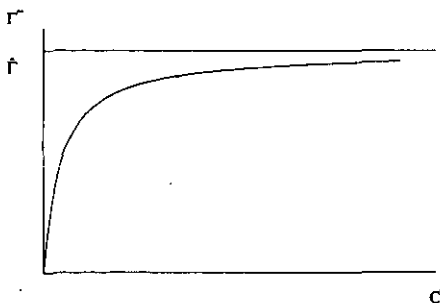The unusual justification for this 'quasi-equilibrium' assumption being that the relaxa-

Figure 1. The Langmuir isotherm relation.

tion of the surface concentration on a change in subsurface concentration is very rapid. This argument for the use of (2), whilst being intuitively plausible, is somewhat unsatisfactory in that it neither gives insight into the mechanism of the adsorption process nor indicates exactly when such a 'quasi-equilibrium' assumption is valid.

The purpose of this letter is to provide a formal derivation of the Langmuir isotherm as an approximation to a more general, and physically transparent, boundary condition and in so doing, demonstrate the conditions under which it is valid.

Representing the rate at which subsurface surfactant is adsorbed by J^+ and the rate at which adsorbed surfactant is desorbed by J^- and assuming no evaporation, then the net rate of adsorption, $\dot{\Gamma}(t)$, is simply

$$\dot{\Gamma}(t) = J^+ - J^-.$$

Taking J^+ to be proportional to both the subsurface concentration, $C(t)$, and the proportion of the surface unoccupied by adsorbed surfactant, we obtain

$$J^+ = k_1 C(t)\left(1 - \frac{\Gamma(t)}{\hat{\Gamma}}\right)$$

where k_1 is some rate constant.

The desorption rate, J^-, we take to be simply proportional to the current surface concentration, i.e.

$$J^- = k_2 \Gamma(t)$$

with rate constant k_2. Hence

$$\dot{\Gamma}(t) = k_1 C(t)\left(1 - \frac{\Gamma(t)}{\hat{\Gamma}}\right) - k_2 \Gamma(t). \tag{3}$$

Informally the 'quasi-equilibrium' condition now corresponds to setting the right-hand side of (3) to zero, whereupon (2) is obtained with $\gamma = k_1/k_2\hat{\Gamma}$. More precisely rapid equilibrium corresponds to large rate constants k_1 and k_2, and when this is the case we may proceed with some standard perturbation analysis: take $\varepsilon = 1/k_1$ and $\rho = k_1/k_2$ and assume a solution in the form

$$\Gamma(t) = \sum_{r=0}^{\infty} \varepsilon^r \Gamma^{(r)}(t). \tag{4}$$

On substituting (4) into (3) and rearranging we obtain

$$\varepsilon^0 \left[\rho C(t)\left(1 - \frac{\Gamma^{(0)}(t)}{\hat{\Gamma}}\right) - \Gamma^{(0)}(t)\right] - \sum_{r=1}^{\infty} \varepsilon^r \left[\left(1 + \frac{\rho C(t)}{\hat{\Gamma}}\right)\Gamma^{(r)}(t) + \dot{\Gamma}^{(r-1)}(t)\right] = 0.$$

So, provided $\rho \approx 1$, we obtain, as the zeroth-order approximation for $\Gamma(t)$,

$$\Gamma(t) \approx \frac{\rho \hat{\Gamma} C(t)}{\hat{\Gamma} + \rho C(t)}$$

which, of course, corresponds to the isotherm relation (2) with $\gamma = k_1/k_2\hat{\Gamma}$. Therefore (2) may be considered a valid approximation, derivable from (3), provided not only that $(k_1, k_2) \gg 1$ but also that $k_1 \approx k_2$. When this is not the case other choices of $\varepsilon \ll 1$ and $\rho \approx 1$, depending on the relative magnitudes of the rate constants, need to be considered. The following table lists the various possibilities and the resulting approximations.

1	Magnitudes		Parameters		Approximations
1	$k_1, k_2 \gg 1$	$k_1 \approx k_2$	$\varepsilon = 1/k_1$	$\rho = k_1/k_2$	$\Gamma(t) \approx \rho\hat{\Gamma}C(t)/(\hat{\Gamma}+\rho C)$
2	$k_1 \gg 1$	$k_2 \approx 1$	$\varepsilon = 1/k_1$	$\rho = k_2$	$\Gamma(t) \approx \hat{\Gamma}$
3	$k_1 \approx 1$	$k_2 \gg 1$	$\varepsilon = 1/k_2$	$\rho = k_1$	$\Gamma(t) \approx 0$
4	$k_1, k_2 \ll 1$	$k_1 \approx k_2$	$\varepsilon = 1/k_1$	$\rho = k_1/k_2$	$\Gamma(t) \approx \Gamma(0)$
5	$k_1 \ll 1$	$k_2 \approx 1$	$\varepsilon = k_1$	$\rho = k_2$	$\Gamma(t) \approx \Gamma(0)\,e^{-k_2 t}$
6	$k_1 \approx 1$	$k_2 \ll 1$	$\varepsilon = k_2$	$\rho = k_1$	$\dot{\Gamma}(t) = k_1 C(t)[1 - (\Gamma(t))/\hat{\Gamma}]$
7	$k_1 \ll 1$	$k_2 \gg 1$ $k_1 k_2 \approx 1$	$\varepsilon = k_1$	$\rho = k_1 k_2$	$\Gamma(t) \approx 0$
8	$k_1 \gg 1$	$k_2 \ll 1$ $k_1 k_2 \approx 1$	$\varepsilon = k_2$	$\rho = k_1 k_2$	$\Gamma(t) \approx \hat{\Gamma}$

Clearly from the point of view of studying adsorption kinetics only those given by cases 1, 5 and 6 are of interest. In particular case 6 may be worthy of further study.

References

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