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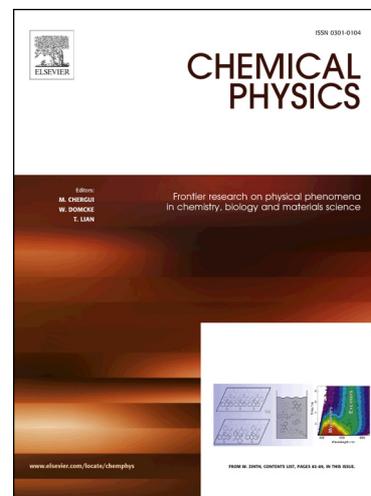
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1 **Comment on “Re-evaluation of the century-old Langmuir isotherm for**
2 **modeling adsorption phenomena in solution”, published by Azizian et al.**
3 **[Chemical Physics 513 (2018) 99-104]**

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12 *Keywords:* Langmuir isotherm, adsorption and desorption rates, modified Langmuir
13 model

14 Azizian et al. [1] question the appropriateness of the well-known Langmuir model for
15 adsorption processes from liquid phases. Considering the history and the wide
16 application of this model, this is certainly a challenging approach. Briefly, Azizian et
17 al. [1] propose a modification of the rate equation for the desorption step in the
18 Langmuir model for a reversible adsorption/desorption process from

19 $r_d = k_d \cdot \theta$ (1) in the conventional Langmuir model to

20 $r_d = k_d^* \cdot (C_s - C) \cdot \theta$ (2) in the modified version

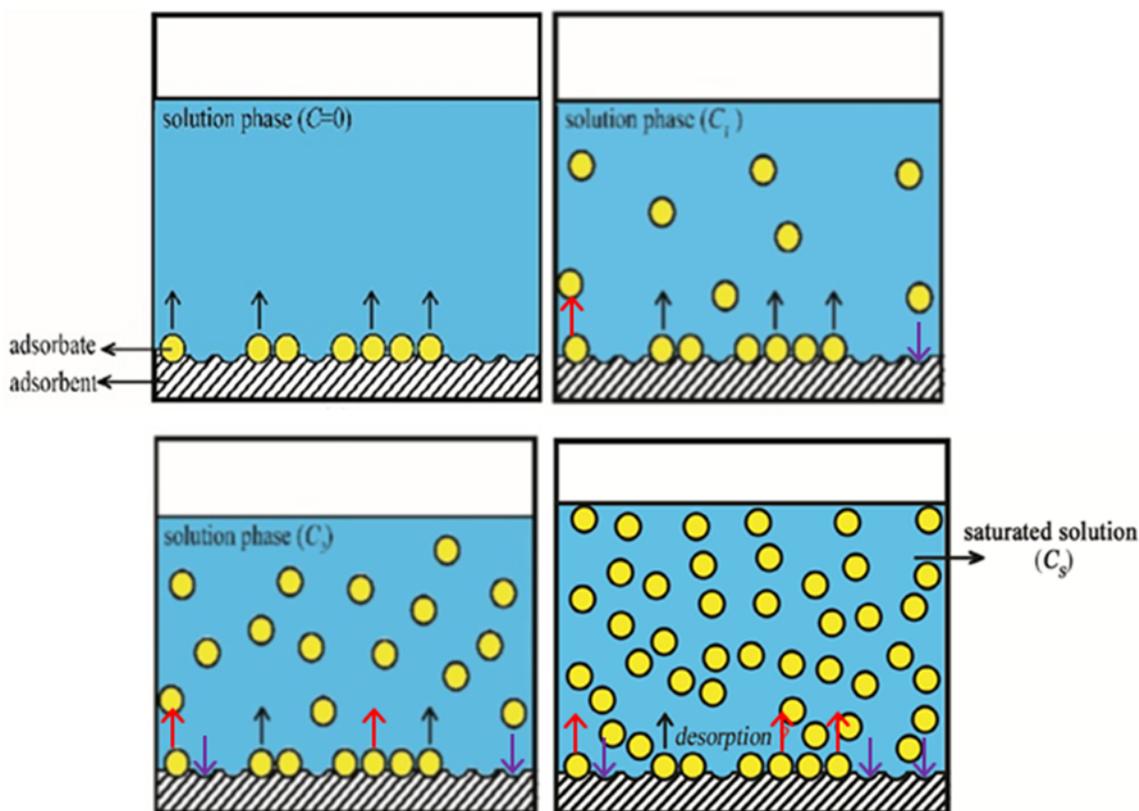
21 with r_d and k_d or k_d^* as desorption rate and desorption rate constants, respectively, θ
22 as dimensionless degree of site coverage ($\theta = 0 \dots 1$), C_s as the solute saturation
23 concentration in the fluid medium, and C as the actual concentration of dissolved

24 solute. Note that eqs. (1) and (2) are identical to eqs. (6) and (11) in the commented
25 article with the exception that we use different symbols (k_d and k_d^*) for the two
26 desorption rate constants; this is necessary because they have different meanings
27 and units. Using identical symbols in this case may give rise to misunderstandings.

28 We point out that the proposed modification of the Langmuir model has significant
29 consequences. First of all, one should be aware that in the frame of the Langmuir
30 model, r_d and r_a are microscopic rates at the molecular level, not macroscopic net
31 rates of desorption and adsorption. According to eq. (2), the desorption rate r_d
32 approaches zero when the solute concentration approaches its saturation value. The
33 adsorption/desorption equilibrium becomes static. This consequence follows
34 inevitably from the formulas, but it is incorrect. Therefore, we cannot accept the
35 proposed modification of the Langmuir isotherm model.

36 In the following, we will consider the approach of Azizian et al. [1] in more detail. The
37 Langmuir model is based on the assumption of a dynamic equilibrium between
38 adsorbed and free (gas-phase or dissolved state) molecules. At equilibrium the two
39 rates (adsorption and desorption rate) are equal, but not zero ($r_a = r_d \neq 0$). So far
40 there is consensus about the model frame. Azizian et al. [1] challenge the fact that
41 the solute concentration C is not taken into account for the desorption rate in the
42 conventional Langmuir model (eq. 1). They stress the different properties of gases
43 and liquids as fluid phases in adsorption systems, which - in their argumentation -
44 make it necessary to introduce C explicitly in the desorption term of the Langmuir
45 model. They do so by introducing the distance between the saturation concentration
46 C_s and the actual solute concentration C . The authors present no exact derivation of
47 this modification. A plausible understanding of the term $C_s - C$ may be a limited
48 capacity of the solvent phase to hold the solute. At the saturation point, its holding

49 capacity is exhausted. Consequently, the desorption rate r_d approaches zero.
50 However, one has to be aware of the meaning of the two rates r_a and r_d in the frame
51 of the Langmuir model: they are microscopic rates rather than observable net rates.
52 Thus, $r_d \rightarrow 0$ means that the equilibrium would become static, which cannot be true.
53 Azizian et al. [1] justified their model modification by referring to the chemical
54 potential of the dissolved solute μ_b , which increases with increasing solute
55 concentration. In our view and after checking the cited literature sources, this is an
56 improper blending of kinetic and thermodynamic categories. The thermodynamics
57 (chemical potentials) controls the state of the equilibrium. The adsorption/desorption
58 equilibrium keeps its dynamic character, even at the saturation point. This could be
59 easily demonstrated by tracing the exchange between isotopologues of an adsorbate
60 in contact with its saturated solution. Figures 1 and 2 in Azizian's article [1] are
61 misleading and falsely interpreted. We present here a slightly modified version (Fig.
62 1).



63

64 Figure 1: Schematic representation of the effects of solute concentration on the
 65 desorption profile for systems with the same adsorbate surface concentration and
 66 variable bulk concentrations according to [1]. The colored arrows are introduced by
 67 these authors.

68 The differences to the original figures are some red and violet arrows indicating the
 69 microscopic desorption and adsorption steps, respectively. They illustrate no loss in
 70 desorption rate but some increase in adsorption rate due to increased solute
 71 concentrations. This is in line with the basic understanding that adsorption is a
 72 second-order process for which solute and empty site concentration are rate-
 73 determining, whereas desorption is a unimolecular process.

74 Let us check now the hypothesis of dissimilarity of gases and liquids as fluid phases,
75 which makes the proposed model modification necessary according to Azizian et al.
76 [1]. Examining the two phases more closely, we see that the addressed saturation
77 phenomena are similar. A maximum holding capacity for adsorptive molecules does
78 exist in the gas phase as well as in solution: it is given by the saturation vapor
79 pressure of the adsorbate (p_s). At concentrations above C_s or p_s an additional phase
80 is formed in both systems. This phase formation would not stop the adsorbate
81 desorption process (provided that there is still a thermodynamic driving force). The
82 excess of desorbing molecules would be deposited as a separate phase (liquid or
83 solid). It is interesting to note how the original and the modified Langmuir model
84 predict the approach to surface saturation ($\theta \rightarrow 1$): in the frame of the conventional
85 model this occurs for $C \rightarrow \infty$. According to the modified model this already occurs at
86 the point $C = C_s$ (according to eq. 17i in the original article). We suggest that the point
87 of saturation of the adsorbent is an implausible image. What actually happens at the
88 saturation point of the aqueous phase? The solute starts to form another phase, e.g.
89 a crystalline phase, which may be thermodynamically beneficial, over the adsorbed
90 state. Clearly, the experimenter is not able to increase the solute concentration
91 beyond this point, but the adsorbent is not necessarily in a saturated state already.
92 Instead, the adsorption isotherm has not yet reached its plateau, and the
93 experimenter is simply not able to trace the isotherm further. To illustrate our
94 consideration by a practical example, let us consider the pair of phenanthrene and
95 anthracene as adsorbates. They are both three-ring polycyclic aromatic
96 hydrocarbons (PAHs) which may be expected to behave similarly as adsorbates from
97 an aqueous solution onto graphite as adsorbent. This assumption is supported by
98 their similar octanol-water partition coefficients ($\log K_{ow,anthracene} = 4.68$ and \log
99 $K_{ow,phenanthrene} = 4.57$ [4]). Their aqueous solubilities, however, differ widely ($S_{w,anthracene}$

100 = 45 $\mu\text{g L}^{-1}$, $S_{w,\text{phenanthrene}} = 1100 \mu\text{g L}^{-1}$ [4]) due to a more favorable crystallization of
101 anthracene. According to the modified Langmuir model, the monolayer capacity for
102 adsorption of PAHs onto the same graphite sample would be quite different from
103 adsorption experiments with phenanthrene and anthracene, because of the condition
104 $\theta = 1$ at $C = C_s$. However, the actual monolayer capacity should be similar for the two
105 similar adsorbates.

106 Another questionable aspect of [1] regards the units of rate constants. The
107 desorption rate constants in the conventional and in the modified Langmuir model
108 have different units, e.g. $\text{mol L}^{-1} \text{s}^{-1}$ for k_d and s^{-1} for k_d^* respectively. In the first
109 model, k_d quantifies a first-order desorption kinetics, whereas in the modified
110 Langmuir model k_d^* describes a second-order kinetics. The reader should not be
111 confused by the unfamiliar k units, e.g. s^{-1} for a second-order rate constant. This is
112 due to the definition of rates in the Langmuir terminology as change of dimensionless
113 surface coverages (θ) as in $r_{a/d} = d\theta/dt$. Using a second-order rate constant k_d^* for a
114 unimolecular dissociation process (Surface-Adsorbate \rightarrow Surface-site + Solute), as
115 it is applied in the modified Langmuir model, is hard to accept. Unfortunately, the
116 authors avoid throughout the entire article the assignment of units to any of the
117 applied kinetic parameters, such as rates r and rate constants k .

118 Furthermore, Azizian et al. [1] point to the difficulty resulting from the dimensional
119 nature of the Langmuir isotherm constant $K_L = k_a/k_d$ in L mol^{-1} which is the quotient of
120 adsorption (k_a in s^{-1}) and desorption rate constants (k_d in $\text{mol L}^{-1} \text{s}^{-1}$). According to the
121 mathematical rules, a dimensional constant cannot be used as an argument to the
122 logarithm, e.g. for calculating the free energy of adsorption as $\Delta G_{\text{ads}}^\circ = -RT \cdot \text{LN}(K_L)$.
123 This issue and possible solutions to the problem have been extensively discussed in
124 several publications (e.g. [2], [3] and refs. therein) and will not be reconsidered here.

125 Admittedly, the proposed modification of the Langmuir model delivers an isotherm
126 constant K_L which is dimensionless, because the two rate constants have the same
127 units. This 'advantage', however, cannot justify inconsistencies in the model
128 assumptions and predictions.

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