

Potential Errors in Determining Freundlich and Langmuir Constants from Adsorption Isotherms

Keyphrases □ Adsorbents—determination of Freundlich and Langmuir constants, potential errors □ Freundlich constants—potential errors in determination □ Langmuir constants—potential errors in determination

To the Editor:

Numerous pharmaceuticals have been shown to be adsorbed on various adsorbents such as charcoal and kaolin (1–4). Adsorption data are generally presented as Freundlich constants (Eq. 1) and/or Langmuir constants (Eq. 2):

$$\frac{x}{m} = kC^n \quad (\text{Eq. 1})$$

$$\frac{x}{m} = \frac{\alpha C}{1 + \beta C} \quad (\text{Eq. 2})$$

where x/m is the amount of drug (grams) adsorbed per gram of adsorbent, C is the equilibrium concentration of unbound drug, k and n are Freundlich constants, and α and β are Langmuir constants.

Freundlich constants are obtained from the logarithmic form of Eq. 1:

$$\log \frac{x}{m} = \log k + n \log C \quad (\text{Eq. 3})$$

Equation 3 is a straight line equation. When experimental data are plotted as $\log x/m$ versus $\log C$, the slope equals n and the intercept yields $\log k$. The use of log–log graph paper is popular in plotting such data. Ganjian *et al.* (5) recently utilized log–log graphs to evaluate Freundlich constants for cimetidine adsorption on charcoal, talc, kaolin, and magnesium trisilicate. The intercept was evaluated by directly reading values on the y -axis (*i.e.*, $\log x/m$) where the x -axis shows a value of 1.0. According to Eq. 3, this is correct when the value of C equals 1.0 ($\log C = 0$). Hence, Eq. 3 reduces to

$$\log \frac{x}{m} = \log k \quad (\text{Eq. 4})$$

and since log–log paper is used, the intercept values read are k values.

Although the x -axis shows the printed value of 1.0 on log–log graph paper, any exponent value of concentration must be considered. In this plot (Fig. 1, Ref. 5), the value of C at the printed value of 1.0 equals $1.0 \times 10^{-5} M$. Ganjian *et al.* read the intercept value at the $1.0 \times 10^{-5} M$ value of C . This is incorrect. To read intercept values graphically, the authors need at least 6-cycle logarithmic graph paper to obtain a value of $C = 1.0$. The value of an

Table I—Corrected Freundlich Constants for Adsorption of Cimetidine onto Various Adsorbents

Adsorbent	n^a	$k \times 10^4$, g(adsorbed)/g(adsorbent)	Corrected Value ^b , $k \times 10^1$
Kaolin	0.621	4.02	5.12
Magnesium trisilicate	0.943	3.43	178
Talc	0.384	2.91	0.24
Charcoal	0.347	256	13.91

^a Reported values (Table I, Ref. 5). ^b The value k evaluated at $C = 1.0 M$.

Table II—Effect of Equilibrium Concentration Units on the Freundlich Constant

Adsorbent	Freundlich Constant k , g(adsorbed)/g(adsorbent)		
	C , moles/liter	C , g/liter	C , mg %
Kaolin	5.12×10^{-1}	1.65×10^{-2}	9.45×10^{-4}
Magnesium trisilicate	1.78×10^1	9.67×10^{-2}	1.26×10^{-3}
Talc	2.42×10^{-2}	2.89×10^{-3}	4.94×10^{-4}
Charcoal	1.39	2.04×10^{-1}	4.13×10^{-2}

intercept could also be obtained by solving Eq. 3 for $\log k$. Using values obtained by these authors (Table I, Ref. 5) and citing kaolin as an example:

$$\begin{aligned} \log (4.02 \times 10^{-4}) &= \log k + n \log (1 \times 10^{-5}) \\ &= 5.12 \times 10^{-1} \end{aligned}$$

The values so obtained are listed in Table I. The value of n remains unaffected. The order of adsorbents according to k value and the value of k are dramatically changed.

The second potential error lies with the usage of proper units. Although concentration is generally expressed in molar or molal quantities, Freundlich isotherms are generally obtained by expressing C values as milligrams percent or grams percent. Since k is an adsorbent capacity when $C = 1$, the choice of units is particularly important. Using a unit molar concentration when the experimental range is $\sim 1 \times 10^{-5} M$ yields an order of adsorbents that does not coincide with the experimental results of evaluation using other techniques, *e.g.*, Langmuir's equation.

The Freundlich constant k can be readily calculated at any unit concentration. If C is converted into another concentration, C' , using a factor f , then Eq. 1 is rewritten as:

$$\frac{x}{m} = \frac{k}{f^n} C'^n f^n \quad (\text{Eq. 5})$$

where $k/f^n = k'$, a Freundlich constant using another unit concentration. For kaolin, the difference between Freundlich constants calculated using moles/liter and g/liter is $252.34^{0.621}$ (molecular weight of cimetidine = 252.34 g). Similarly, other values can be calculated.

Table II shows the effect of units on the Freundlich constant k . The order of adsorbents according to adsorption capacity (k) can be visually observed from Freundlich isotherms. The order of adsorbents according to the corrected value is magnesium trisilicate > charcoal > kaolin > talc. If isotherm slopes can be visually imagined extending 6 cycles to the right, this order is correct, at least theoretically. However, this order does not reflect its proper order within the experimental range. This result is best achieved by use of other appropriate units such that a unit equilibrium concentration falls reasonably within the experimental range. An equilibrium concentration of 1 mg % ($3.962 \times 10^{-5} M$) falls well within the range of experimental data. The order obtained is charcoal > magnesium trisilicate > kaolin > talc. This order coincides well with the experimental data.

The Langmuir equation (Eq. 2) can be rearranged to yield the following linear equation.

$$\frac{C}{x} = \frac{1}{\alpha} + \frac{\beta}{\alpha} C \quad (\text{Eq. 6})$$

The plot of $C/(x/m)$ versus C yields the value of α from

the reciprocal of an intercept and β can be evaluated from the slope.

A visual observation of the intercepts of a Langmuir isotherm (Fig. 2, Ref. 5) shows the order of adsorbents according to α to be charcoal > talc > kaolin > magnesium trisilicate. The calculated values (Table II, Ref. 5) show the order to be charcoal > kaolin > talc > magnesium trisilicate. The discrepancy arises because the calculated value of α for talc is in error¹ and should be ~ 71.4 (based on an estimated $1/\alpha$ value of 1.4×10^{-2} from Fig. 2, Ref. 5). The corrected values will show that the order coincides well with visually observed intercept values.

It should be noted that, for Langmuir plots, the use of units other than moles/liter for C will not change the order of adsorbents according to α values, since α is evaluated when C equals zero. However, numerical values of α will change.

It is to be expected that the order of adsorbents would be retained regardless of the equation utilized. This would be true if the adsorption isotherms did not cross over, as in this case. The difference in order is due to the fact that the Freundlich constant k is evaluated at unit equilibrium concentration and the Langmuir constant α is evaluated at zero equilibrium concentration. If the isotherms crossed over between zero and a unit concentration, the order of adsorbents would be different.

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(4) B. C. Walker, W. H. Thomas, and B. R. Hajratwala, *Proc. Univ. Otago Med. Sch.*, **57**, 77 (1979).

(5) F. Ganjian, A. J. Cutie, and T. Jochsberger, *J. Pharm. Sci.*, **69**, 352 (1980).

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¹ There is also a typographical error in Table II, Ref. 5. Units of α should be given (adsorbed) per gram (adsorbent) and not gram (adsorbed) per milligram (adsorbent).

Potential Errors in Determining Freundlich and Langmuir Constants from Adsorption Isotherms: A Response

Keyphrases □ Adsorbents—determination of Freundlich and Langmuir constants, potential errors, reply □ Freundlich constants—potential errors in determination, reply □ Langmuir constants—potential errors in determination, reply

To The Editor:

In a recent publication (1) we calculated Freundlich and Langmuir constants for the adsorption of cimetidine on various adsorbents. A number of points in this article have been criticized by Hajratwala (2) and we wish to respond to some of these criticisms.

We believe the author has incorrectly assumed that the

intercepts on which our values were based were read directly from the graph. Actually, both intercepts and slopes were calculated using standard linear regression methods. We also fail to see why 6-cycle paper would be necessary in any case. In addition, we feel that the calculation of the parameters based on a single point, as the author has done, is inappropriate. The accuracy of the values obtained is questionable given the closeness of the logarithmic values employed.

With respect to the use of units, we wish to point out that physical chemistry texts (3, 4) employ molarity as the unit for concentration in determining Freundlich parameters, not milligrams percent or grams percent as suggested by Hajratwala. Indeed, we are puzzled as to why this should make a difference in any case. We agree that utilizing different units will yield different values for the constants. However, one need only state which units are used and this should not affect the relative order of constants.

Finally, we acknowledge the error in Table II as pointed out by the author. The value for α is indeed 70.4 (the intercept being 1.42×10^{-2}) and the correct value of β is $15.2 \times 10^4 M^{-1}$. We regret the miscalculation. There is a typographical error in Table II as Hajratwala notes; however, we feel that this was a misreading. The correct units are neither g(adsorbed)/mg(adsorbent) as printed nor g(adsorbed)/g (adsorbent) as stated by Hajratwala, but g(adsorbed)/M-g(adsorbent). The capital "M" (for molarity) was obviously misread as a lower case "m."

(1) F. Ganjian, A. J. Cutie, and T. Jochsberger, *J. Pharm. Sci.*, **69**, 352 (1980).

(2) B. R. Hajratwala, *ibid.*, **71**, 125 (1982).

(3) S. H. Maron and J. B. Lando, "Fundamentals of Physical Chemistry," Macmillan, New York, N.Y., 1974, p. 762.

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1-Aryl-3,3-dialkyltriazenes with Antitrypanosomal Activity

Keyphrases □ Antitrypanosomal agents—1-aryl-3,3-dialkyltriazenes □ Antitumor agents—1-alkyl-3,3-dialkyltriazenes □ Triazenes, substituted—antitrypanosomal and antitumor activity

To the Editor:

We recently reported the activity of 1-(*p*-tolyl)-3-acetyl-3-methyltriazene (I), against *Trypanosoma rhodensiense* in the mouse (1). We now wish to report that a number of 1-aryl-3-alkyl-3-methyltriazenes (II) have shown significant activity against these parasites in the mouse model.

The synthesis and characterization of the 1-aryl-3-