

Conversion of Freundlich Adsorption K Values to the Mole Fraction Format and the Use of S_γ Values to Express Relative Adsorption of Pesticides¹

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ABSTRACT

Anomalies in the Freundlich isotherm equation prevent the simple conversion of K values to a common set of units for assessment of relative adsorption. Although there is a straightforward way to properly convert the units of K values, serious extrapolation errors can result because, in the new set of units, the K value may be evaluated considerably outside the concentration data range. In the mole fraction format, concentration is reported as a mole fraction, and adsorption as mol g^{-1} , giving units of mol g^{-1} for K . In this format, K loses any practical meaning since it is evaluated at $\log Z = 0$, $Z = 1$. An improved and more flexible method of reporting relative adsorption using S_γ values is presented as well as a procedure to convert existing data to this format.

Additional Index Words: isotherm, units of K .

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THE USE of K values has considerably increased as a result of the requirement by regulatory agencies for quantitation of relative pesticide adsorption in soil water systems (13). A recent paper (2) showed that some inherent anomalies present in the Freundlich isotherm equation prohibit the simple conversion of the various units for Freundlich K values, found in the literature, to a common set of units to permit comparison of relative adsorption.

These anomalies (2) can be eliminated by converting the concentration term in the Freundlich equation to mole fraction (Z) and reporting the adsorption in mol g^{-1} . However, this does not solve the problem of comparing existing K values in the literature which were derived in the traditional fashion.

The two principal purposes of this report are: (i) to demonstrate the advantages of reporting adsorption data in the mole fraction format with increased flexibility for making relative adsorption comparisons, and (ii) to demonstrate how to convert existing K values in the literature to the mole fraction format so that they can continue to be useful.

THEORY AND DISCUSSION

The Freundlich equation can be represented as follows:

$$S = KC^N, \quad [1]$$

where S = amount of solute adsorbed/unit amount of adsorbent, C = equilibrium concentration of solute, and K , N = empirical constants which can be related to adsorption phenomena. The $1/n$ value traditionally shown as the exponent for C has been replaced by N to avoid confusion. In a recent paper (1), the authors defined the exponent to be $1/n$, but showed values for the reciprocal, n , in a table which, although technically correct, could easily lead to a misinterpretation of the data. Likewise, S replaces x/m as a measure of adsorption for reasons of clarity.

The units of K follow directly from a dimensional analysis of rearranged Eq. [1]:

$$K = S/C^N. \quad [2]$$

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For example, if the units of S are $\mu\text{g g}^{-1}$ and for C are $\mu\text{g ml}^{-1}$, then the units of K will be:

$$K \text{ (units)} \equiv \frac{\mu\text{g g}^{-1}}{(\mu\text{g ml}^{-1})^N} = \mu\text{g}^{1-N} \text{g}^{-1} \text{ml}^N \quad [3]$$

It can be seen that the units of K are not the units of S alone, as is commonly shown in the literature (5, 8), but also include the units of C with its appropriate exponent (N). All too often, authors do not indicate that K has units (2, 4, 6, 10, 12), thereby possibly resulting in the mistaken belief by some that K is a unitless constant. In a brief survey of the adsorption literature, summarized in Table 1, a great variety of units was found for the two adsorption variables, S and C, which in turn determine the units of K. In Table 1, the first unit shown for S is the amount of solute, and the second is the amount of adsorbent; i.e., for item 4, the units of S are mg solute/mg carbon. In two of the references in Table 1 (5, 6), the authors expressed the concentration only in terms of ppm or ppb, which can imply $\mu\text{g ml}^{-1}$ or mg L^{-1} , and ng ml^{-1} or $\mu\text{g L}^{-1}$, respectively. In both cases, units consistent with those for S were chosen for use in Table 1. As an example of the errors that could be created by the traditional use of K (where units of K = units of S), units of K would be $\mu\text{g g}^{-1}$ for both items 1 and 2 in Table 1, despite the fact that there was a 1,000-fold difference in the equilibrium concentrations reported ($\mu\text{g ml}^{-1}$ vs. $\mu\text{g L}^{-1}$). To correctly convert K in item 2 to that in item 1 would require K to be multiplied by 10^{3N} .

Although it is a fairly straightforward task to convert the "correct" units of K values to a common set of units for comparison purposes (by multiplying by "equivalent fractions," i.e., 1,000 ml/L, or 1 mg/1,000 μg), there could be serious extrapolation errors introduced as a result of this process. The K values are traditionally obtained from a plot of $\log S$ vs. $\log C$, evaluated at $\log C = 0$. The units of C should be chosen such that the range of observations includes or is close to $\log C = 0$ so that K can be evaluated with a minimum of extrapolation. The conversion of the units of K (for comparison purposes) can often place the evaluation point of K well away from the concentration data range. Although theoret-

Table 1—Units of Freundlich K compiled from literature citations using Eq. [2].

Item	S	C	K	Reference
1	$\mu\text{g g}^{-1}$	$\mu\text{g ml}^{-1}$ (ppm)	$\mu\text{g}^{1-N} \text{g}^{-1} \text{ml}^N$	5
2	$\mu\text{g g}^{-1}$	$\mu\text{g L}^{-1}$ (ppb)	$\mu\text{g}^{1-N} \text{g}^{-1} \text{L}^N$	6, 9
3	ng mg^{-1}	ng ml^{-1} (ppb)	$\text{ng}^{1-N} \text{mg}^{-1} \text{ml}^N$	8
4	mg mg^{-1}	mg L^{-1} (ppm)	$\text{mg}^{1-N} \text{mg}^{-1} \text{L}^N$	11
5	pmol g^{-1}	pmol ml^{-1}	$\text{pmol}^{1-N} \text{g}^{-1} \text{ml}^N$	12
6	nmol g^{-1}	nmol ml^{-1}	$\text{nmol}^{1-N} \text{g}^{-1} \text{ml}^N$	2
7	$\mu\text{mol g}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol}^{1-N} \text{g}^{-1} \text{L}^N$	1
8	$\mu\text{mol kg}^{-1}$	$\mu\text{mol L}^{-1}$	$\mu\text{mol}^{1-N} \text{kg}^{-1} \text{L}^N$	7
9	mol g^{-1}	Z - unitless	$\text{mol g}^{-1} (K_{MF})$	3

ically K values can be changed to values in any equivalent set of units for comparison purposes, care must be taken that the new values have a practical meaning.

The conversion of K to larger units (extrapolation to higher concentrations) appears to be much more risky than the conversion to smaller units because of (i) the limited solubility of many materials in water, and (ii) the likelihood of departure of the adsorption isotherms from the Freundlich equation at higher concentrations. When extrapolating from higher to lower concentrations it is the usual case that the experimental isotherms being compared will at least converge at or near the origin, and since the Freundlich equation also predicts this, the magnitude of the extrapolation errors should be fairly minimal. An example of a large extrapolation error, when the units of S and C were converted to larger units, is shown in some data from an earlier paper (3). When changing the units of S and C from nmol g^{-1} and nmol ml^{-1} to $\mu\text{mol g}^{-1}$ and $\mu\text{mol ml}^{-1}$, respectively, K changed from $741.3 \text{ nmol}^{-0.772} \text{ g}^{-1} \text{ ml}^{1.772}$ to $1.535 \times 10^5 \mu\text{mol}^{-0.772} \text{ g}^{-1} \text{ ml}^{1.772}$. The concentration at which K would have been evaluated in the new units ($1.0 \mu\text{mol ml}^{-1}$) was 11-fold greater than the water solubility of fenitrothion ($9.09 \times 10^{-2} \text{ mol ml}^{-1}$), thereby rendering K to a meaningless value in these units.

Obviously the technique using equivalent fractions for converting K values to a common set of units for comparison purposes does not solve the problems associated with making relative adsorption comparisons. Perhaps since the N value, unique to each isotherm, also appears in units of K (Eq. [3]), comparison of K values from isotherms having different slope values may be impossible since the units would be different.

The method of plotting $S(\text{mol g}^{-1})$ vs. mole fraction (Z) instead of concentration, C, introduced earlier (2), circumvents all the problems associated with units and, in addition, provides a more flexible means of making relative adsorption comparisons. The Freundlich equation in the mole fraction format becomes:

$$S = K_{MF} Z^N, \quad [4]$$

or in the log transformation form:

$$\log S = \log K_{MF} + N \log Z, \quad [5]$$

where $K_{MF} = S$ at $Z = 1.0$ and is designated in this fashion to avoid confusion with the K value in the traditional Freundlich isotherm. The K_{MF} value is only an empirical regression constant and has no real value as a means of comparing adsorption since it is evaluated at $Z = 1.0$ (pure insecticide). Instead of using K values as a measure of relative adsorption, adsorption values (S_Y) for each compound to be compared (obtained from Eq. [5]) are determined at a common Z value within the range of the data, where $Y = \log Z$. This subscript, Y, is a simple way of quickly identifying the log concentration (log mole fraction) at which the relative adsorption comparisons were made. Using this format, all adsorption data can now be plotted in the same units, with S being mol g^{-1} , and concentration being represented by mole fraction, a unitless number ratio.

An example of this evaluation procedure using adsorption data from an earlier study (2) (reproduced in Fig. 1A) is shown in the mole fraction format in Fig. 1B. The Z range common to all three isotherms occurs between $\log Z = -7.5$ and -7.2 , with -7.4 being arbitrarily chosen as the reference point. Thus the $S_{-7.4}$ values for the three isotherms are a measure of relative adsorption, in a fashion analogous to K values in the traditional Freundlich isotherm, except that K values always had to be evaluated at $\log C = 0$ in whatever units that particular adsorption system was plotted.

Values of K from the literature can be converted to K_{MF} values in the mole fraction format, thereby removing the problems associated with units. Once the K_{MF} value has been obtained (and already having the N value) the isotherm can be replotted in the mole fraction format and an appropriate S_y value can be calculated in or near the range of the data. The following three steps are involved in converting K values to the mole fraction format and subsequently using these values in making relative adsorption comparisons.

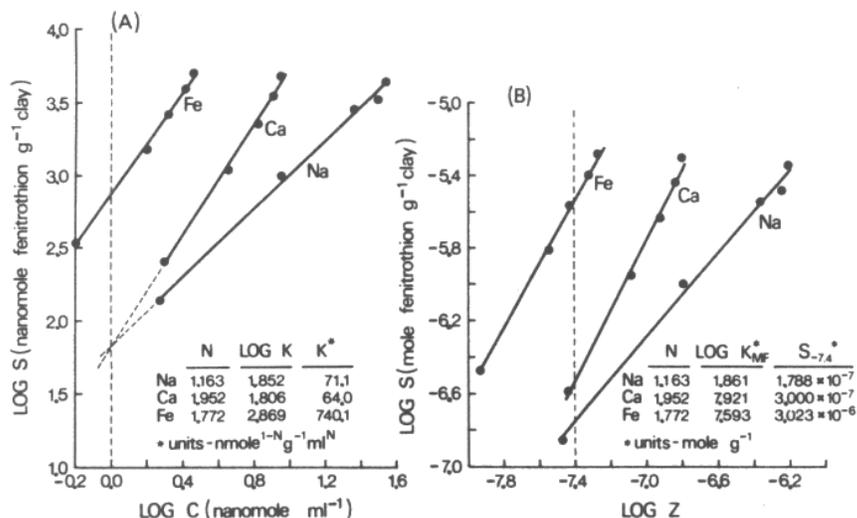


Fig.1- Adsorption isotherms for fenitrothion in Na-, Ca-, and Fe-montmorillonite systems expressed in the traditional Freundlich and mole fraction formats.

Step 1

The conversion of K values from a set of units in the literature (i.e., Table 1) to mol g⁻¹ (the units of K_{MF} in the mole fraction format) using the "dimensional analysis-equivalent fraction technique" involves a two-step procedure:

- convert units of K to mol^{1-N} g⁻¹ L^N, and
- convert units of mol^{1-N} g⁻¹ L^N to mol g⁻¹.

The factor for step (a) is obtained by multiplying the appropriate terms which must be converted in the units of K by "equivalent fractions". As an example, the units of K in Table 1, item 1, will be converted as follows:

$$\mu\text{g}^{1-N} \text{g}^{-1} \text{ml}^N \times \left[\frac{1\text{g}}{10^6 \mu\text{g}} \right]^{1-N} \times \left[\frac{1 \text{mol}}{M \text{g}} \right]^{1-N} \times \left[\frac{1 \text{L}}{10^3 \text{ml}} \right]^N \rightarrow \text{mol}^{1-N} \text{g}^{-1} \text{L}^N.$$

Thus, $K(\mu\text{g}^{1-N} \text{g}^{-1} \text{ml}^N) \times (M^{N-1}) \times (10)^{3N-6} = K(\text{mol}^{1-N} \text{g}^{-1} \text{L}^N)$, [6]
 where M = molecular weight of compound in grams.

If the units of K are already in molar quantities, as in Table 1, item 6, the conversion becomes:

$$\text{nmol}^{1-N} \text{g}^{-1} \text{ml}^N \times \left[\frac{1 \text{mol}}{10^9 \text{nmol}} \right]^{1-N} \times \left[\frac{1 \text{L}}{10^3 \text{ml}} \right]^N \rightarrow \text{mol}^{1-N} \text{g}^{-1} \text{L}^N.$$

Thus, $K(\text{nmol}^{1-N} \text{g}^{-1} \text{ml}^N) \times (10)^{6N-9} = K(\text{mol}^{1-N} \text{g}^{-1} \text{L}^N)$. [7]

The factor for step (b) is obtained as follows:

By definition, $Z = C/\text{mol solvent L}^{-1}$ (for dilute solutions), [8]

where C is expressed in mol solute L⁻¹. For water at 20°C, the denominator of Eq. [8] is 55.457 mol L⁻¹. Solving for C in Eq. [8] and substituting into Eq. [1]:

$$S = K(55.457 Z)^N \quad \text{or} \quad S = K(55.457)^N Z^N. \quad [9]$$

From Eq. [4],

$$S = K_{MF} Z^N; \quad \text{Thus,} \quad K_{MF} = K(55.457)^N, \quad [10]$$

where K is expressed in mol^{1-N} g⁻¹ L^N and K_{MF} is expressed in mol g⁻¹. The factor for step (b), $(55.457)^N$, is multiplied by the factor for step (a) and by the numerical value of K expressed in the original set of units to arrive at K_{MF} expressed in mol g⁻¹.

As an example, the complete conversion of the units of K in Table 1, item 6, to K_{MF} would be:

$$\text{nmol}^{1-N} \text{g}^{-1} \text{ml}^N \times \left[\frac{\text{mol}}{10^9 \text{nmol}} \right]^{1-N} \times \left[\frac{\text{L}}{10^3 \text{ml}} \right]^N \times \left[\frac{\text{mol}}{\text{L}} \right]_{\text{water}}^N \rightarrow \text{mol g}^{-1}.$$

The conversion factor becomes

$$[10^{9(N-1)}][10^{-3N}][55.457]^N = [10^{6N-9}][55.457]^N.$$

Thus, $K(\text{nmol}^{1-N}\text{g}^{-1}\text{ml}^N) \times (10^{6N-9})(55.457)^N = \text{KMF} (\text{mol g}^{-1})$ [11]

This K_{MF} value, along with N (which remains constant in all systems of units), would only be used as regression coefficients in Eq. [5], not for purposes of assessing relative adsorption.

Step 2

Determine the range of the data from which K was originally obtained. Usually isotherms are shown in papers, or initial concentrations ranges are given so that an estimate of the data range for C can be made. These concentration limits can then be expressed in terms of mole fraction.

Step 3

Choose a $\log Z$ value, for comparison purposes, which is common to all adsorption systems being examined, or is the best compromise possible, should some data ranges fall slightly to one side or the other of $\log Z$. Substitute this $\log Z$ value into each of the log regression equations (Eq. [5]) and determine an S_γ value for each system, as shown above in Fig. 1B. In situations where the lowest Z values of some isotherms are considerably above the highest Z values of other isotherms, for comparison purposes, it is less risky to extrapolate the isotherm at higher Z values down to the lower isotherm, as was discussed earlier, recognizing the fact that there will be some minor extrapolation errors.

One attractive advantage of the S_γ comparison is that relative adsorption can be assessed at various $\log Z$ values, as opposed to K which had to be evaluated at one concentration, $\log C = 0$. An example of this is shown in Fig. A where the Na- and Ca isotherms crossed just above $\log C = 0$. The K values show that fenitrothion adsorbs more on Na montmorillonite than on Ca^{2+} montmorillonite, which is true below the crossover point of the isotherms. Using the K value there is no way of showing that at higher concentrations the Ca system adsorbs considerably more fenitrothion. In the mole fraction format, S_γ values could be obtained both below and above the crossover points of the isotherms, thereby giving a more complete picture of the adsorption processes. In Fig.1B, the $S_{-7.4}$ values show that the Ca^{2+} montmorillonite adsorbed 68% more fenitrothion than the Na montmorillonite.

When quoting S_γ values for pesticides, researchers should include the range of mole fraction values for each isotherm in terms of $\log Z$ values which for most pesticides occurs between -10 and -5. This information would be most helpful when comparing S_γ values from different sources.

Although at first the mole fraction concept may seem complex, it is as straightforward to use as the traditional Freundlich equation once one is familiar with the magnitudes and ranges of data generated by this system. The greatest benefit is that the units used for reporting adsorption data are simple and universally consistent. Consequently, the values used to measure relative adsorption (S_γ) never have to be changed to another set of units, thereby avoiding the large changes in the magnitude that K values sometimes undergo when making relative adsorption comparisons. Furthermore, the flexibility in making relative adsorption comparisons using S_γ values allows isotherms to be extrapolated to lower concentrations (rather than to higher concentrations) if necessary, a feature that was not possible with K values because of their singular point of evaluation ($\log C = 0$). These features of the mole fraction format and S_γ values become important considerations when making judgments as to the environmental suitability and safety of pesticides.

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