The History and Use of the Freundlich Adsorption Isotherm

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The history of the log–log plot of adsorption of a gas or solute against the concentration in the external phase, usually known as the Freundlich isotherm, is traced, from its first use by Boedeker in 1859, in studying adsorption of inorganic compounds by soil, and its applicability to dye–fibre systems is described.

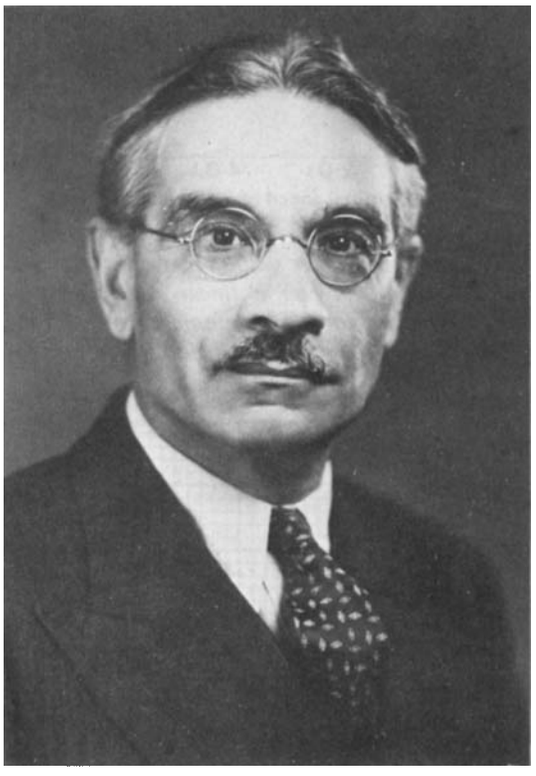
Introduction

All colour chemists are acquainted with the Freundlich isotherm, a graph sometimes used to show the extent to which dye in a dyebath is taken up by a fibre. It seems to be particularly used for dyeings on cellulose, for a reason which will become apparent below. Probably few, if any, who use or quote it know of its long and varied history. This note is intended to bring this history to the attention of colour chemists in the hope that they will then find a little more of interest in their quantitative studies of dyeing processes. A more detailed history of the early development of the quantitative treatment of adsorption and of the experiments on base exchange outlined below is given elsewhere [1a].

History

The log–log plot of pressure against volume of gas adsorbed by a solid, usually known as the Freundlich isotherm (see, e.g., ref. 2, at pp. 14, 54, 82, 121), is familiar to all adsorption chemists, though it is now less used than the Langmuir [3a] or the BET [3b] methods of plotting the same data. The log–log isotherm has lost favour partly because it has usually been assumed that it was purely an empirical method of expressing the adsorption data, and that it did not arise from any basic theory. This is, however, not strictly true. Moreover, it should have a special place in the history of chemistry because in one form it was the earliest attempt – as far back as 1859 – to formulate a mathematical expression of the adsorption process; likewise, it is of special interest to the colour chemist in that it was used in probably the first mathematical treatment of dyeing processes.

In the mid 19th century the nature of inorganic reactions in soil [1a, b] began to attract the attention of several chemists in Britain and on the Continent. This interest, in fact, began as a result of experiments made independently in about 1845 by Huxtable and Thompson. These two practical agriculturists became interested in the ability of soil to clarify the liquid manure from their farmyards and particularly its ability to take up ammonia [1a*]. Their observations communicated to Way led to his classic experiments on the base-exchange properties of soil. Way's experiments were mainly qualitative. A little later, Henneberg and Stohmann [4] described the amounts of calcium displaced from soil or pure calcium carbonate by ammonia in various ammonium salt solutions. In 1859 Boedeker published an analysis [5] of Henneberg and Stohmann's results, from which he established a simple law, viz. that, to increase the amount of lime released by ammonia by a factor of f, the ammonia solution had to be increased in concentration by f^2 times. This relation seemed to hold over a wide range of concentrations. A plot of some of the data as analysed by Boedeker is shown in Figure 1. Thus a log–log representation of the respective concentrations is seen to be linear.



Professor H. M. Freundlich (1880–1941) (by courtesy of the photographic laboratories, University of Minnesota)

Boedeker based his calculations on the *initial* concentrations of the ammonia solutions (see Appendix). It was Van Bemmelen nearly 30 years later who first pointed out that in theory the *final* and not the initial concentration† should have been used, but at the same time he deprecated attempts to discover fixed relations of this type [1a]. Indeed, since the mechanism of the adsorption process was unknown, and the

*Huxtable's experiments created considerable interest and were discussed in various papers, including Spooner's 'The Adventures and Transformations of Nitrogen and Ammonia, or the Rev. A. Huxtable's Great Pig Secret Analysed' (1850).

†It can however be shown theoretically that the use of initial concentrations should also give linear plots [1a].

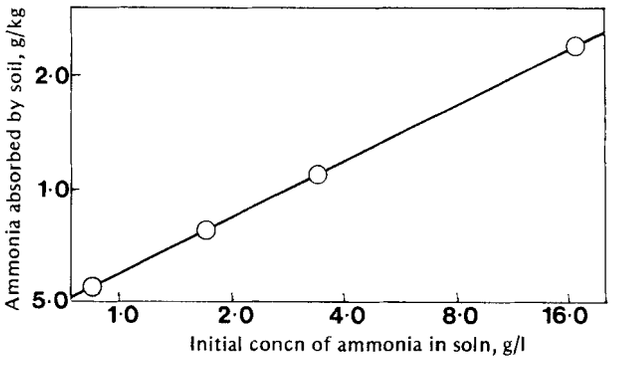


Figure 1 – Plot of Boedeker's data taken from Henneberg and Stohmann's results, showing a linear relation between the logarithms of the amount of ammonia adsorbed by soil and the initial amount in the applied solution [from ref. 1b]

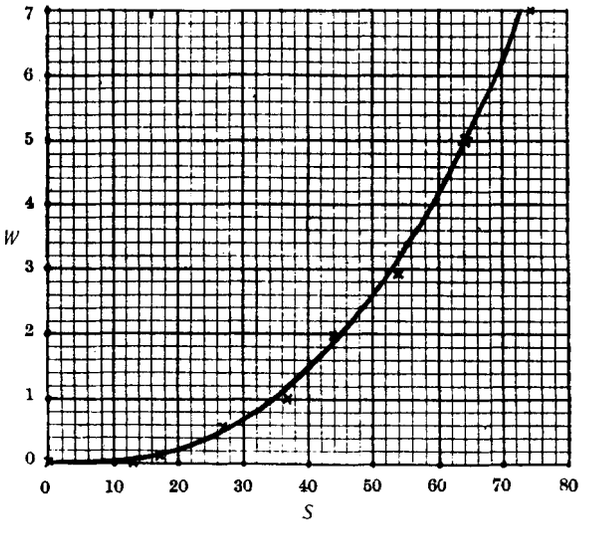
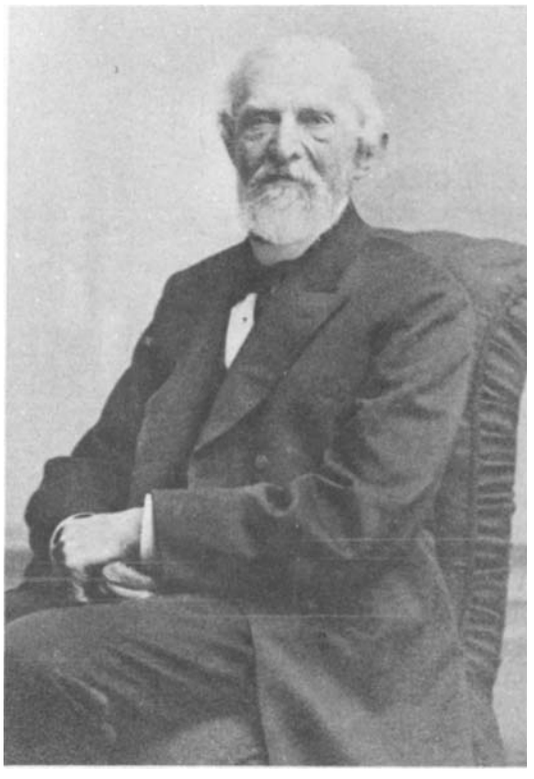


Figure 2 – Walker and Appleyard's [9] curve relating the equilibrium concentrations of picric acid in solution and on silk. Possibly the first published solute adsorption isotherm (1896), giving quantitative data. An earlier sketch of the general shape was published by van Bemmelen in 1888 [1a]. s, w = mg picric acid in 1 g silk and 1 ml solution respectively. Conditions: 2 g silk (regain, 8.4%) in 100 ml solution at 60°C for 40 h

ionic theory had only recently been formulated and was not yet taken seriously, no significant theoretical advance was possible. Nevertheless, this log–log relation soon received fresh impetus from a different direction.

The law of constant partition of a solute between two immiscible solvents, first described by Berthelot [6a–d] in 1869–72, had been extended by Nernst [6e,f] (and Aulich [6g]) in 1890–91 to cover cases where the solute is associated in one phase, which introduces a power term into the distribution fraction. Thus if the solute is monodisperse in both phases the ratio of its concentrations (strictly, activities) in two liquids A and B, i.e. C_A/C_B, is constant, but, if it is completely associated into units of n molecules in say B, while remaining monodisperse in A, then $C_A/C_B^{1/n}$ rather than



Professor Carl H. D. Boedeker (1815–1895) (by courtesy of Staats-und-Universitatsbibliothek, Göttingen)

C_A/C_B is constant. Perhaps this development by Nernst stimulated Witt [7], also in 1890, to propose the 'solution theory' of dyeing, in which the fibre and the dyebath are considered to be the two solvent phases between which the dye is partitioned.

Witt's theory could clearly have been tested by a logarithmic plot of the dye concentration in the two phases, but Witt himself does not seem to have made this test – his paper is entirely descriptive and has no quantitative data. As far as can be traced, the first author to apply the Nernst concept to adsorption was Von Georgevics [8], who in 1894–95 found a constant value of $1/n$ for adsorption of dyes. He refers to Nernst, but not to Witt's hypothesis. In 1896 Walker and Appleyard [9]** studied the adsorption of picric acid by silk and found that their results obeyed a log–log relation, although it is clear from the *arithmetric* plot of their results (Figure 2) that they did not obtain saturation of the fibre. Figure 2 is especially interesting as being apparently the first published adsorption isotherm for a dyeing.

These early authors were more interested in calculating a value for $1/n$, and determining its constancy, than in plotting the results. They show no log–log plots. Biltz [10] in 1904–5 also applied the log–log relation in studying the adsorption of dyes by inorganic solids. The name of Freundlich probably became associated with the isotherm after he had discussed it in two lengthy papers [11] in 1907, describing the adsorption of dyes and simpler organic solutes by charcoal and other solids.

**Walker and Appleyard were respectively professor of chemistry and lecturer in dyeing, University College, Dundee. Walker had been a student under Arrhenius, formulator of the ionic theory.

The Nernst treatment certainly was in the minds of these early authors, who took great pains to determine the value of $1/n$ in the partition ratio. We may say therefore that in its early days the Freundlich isotherm was used as a test of a fundamental theory [12, 13].

In the absence of clear ideas either of the actual mechanism of adsorption or of the molecular structure of many of the solids used, especially of fibres, no more than this could be attempted to give a rational quantitative explanation of solute-adsorption phenomena. As an example of the limitations set by the knowledge of the time, we may take Walker and Appleyard's conclusion [9]. The value they obtained from the exponent $1/n$ in the picric acid–silk system in water implied, on the solution theory, that the picric acid was highly associated in water, and yet it was known not to be so. The fallacy in this argument, as we now know, lies in the assumption that the fibre can be considered a single phase in which the picric acid is uniformly dissolved. In fact, it is a porous solid with a limited amount of internal surface on which adsorption can take place.

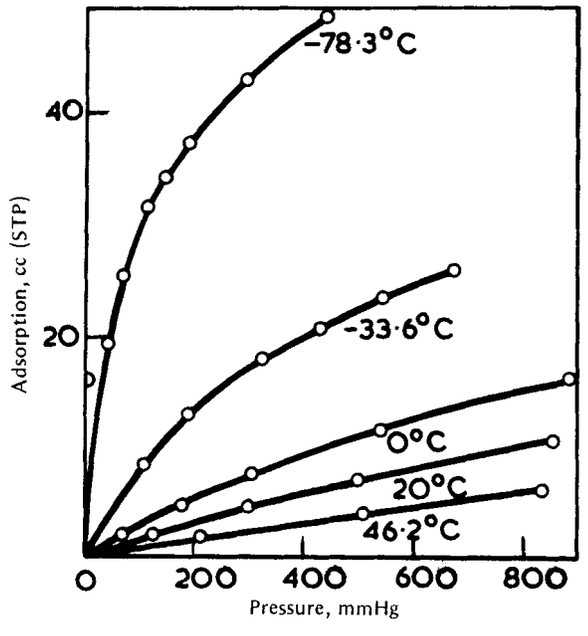


Figure 3 – Vapour-phase isotherms of carbon monoxide adsorption on charcoal (ref. 2 at p. 56)

Applicability

If we describe the relation between equilibrium pressure p and volume v of gas adsorbed, as $v=kpq$, where k is a constant, then q falls from unity at low pressures to zero at pressures where the surface has become saturated and no more adsorption can occur. Over the intermediate range q is a positive fraction, and in many cases its value is constant over a fairly wide range of the isotherm. When this is so, then $\log v = \log k + q\log p$, and the Freundlich isotherm is obtained (Figures 3 and 4). This can also be obtained with many dye and other solute adsorptions using appropriate concentration values (Figures 5–7). The equation is a parabolic function and therefore the isotherm plotted thereby cannot become asymptotic to the pressure axis, which an isotherm plotted with the Langmuir equation, being hyperbolic, can do. It has been

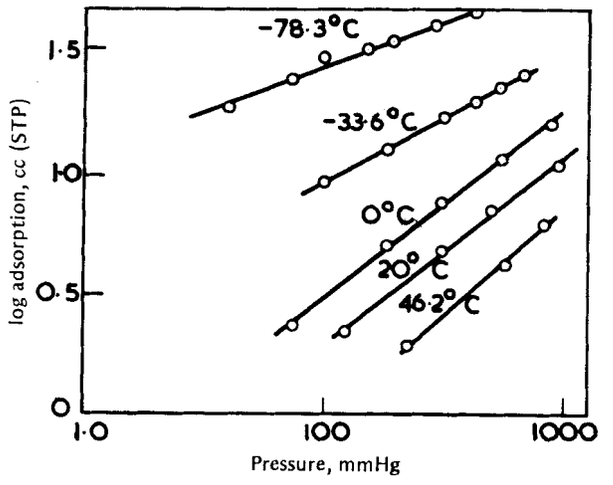


Figure 4 – 'Freundlich' isotherms plotted from the data of Figure 3

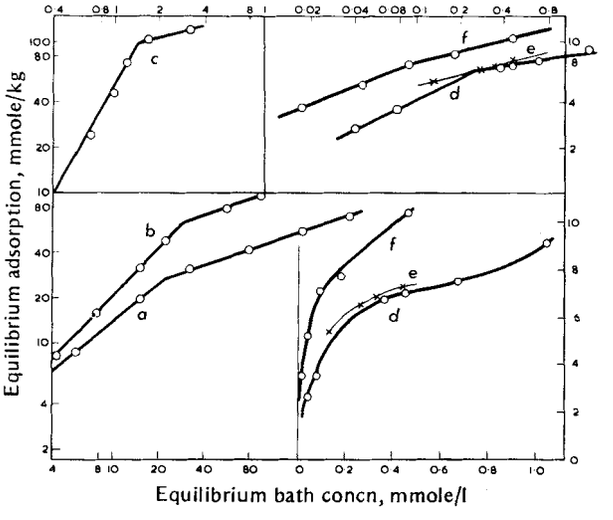


Figure 5 – Isotherms for dye adsorption: (a) Solway Blue BS (C.I. 63010) on nylon [14] at pH 1.35 and 85°C; (b) As (a), on wool [14]; (c) p-n-Dodecylaniline→1-acetamido-8-hydroxynaphthalene-3,6-disulphonic acid on chromatographic alumina [15] at 60°C; (d) Chrysophenine G (C.I. 24895) on cotton from 0.02-N NaCl solution [16] at 60°C; (e) Sky Blue FF (C.I. 24410) as (d) [16]; and (f) Congo Red (C.I. 22120) on cotton [16] from 0.01-N NaCl at 90°C. (The lower and upper curves respectively (d–f) show arithmetic and log–log ('Freundlich') plots of the same data)

shown [19] that, in theory, a constant value of q implies that the number of adsorption sites having a heat of adsorption ΔH rises exponentially with fall in ΔH.

If points in the middle regions of an adsorption isotherm are required to be obtained by interpolation, or if experimental accuracy is to be checked, the Freundlich plot is still a convenient method of setting out the data, which can be plotted directly on to logarithmic graph paper.

In particular, in the literature of dyeing mechanisms Freundlich isotherms are often mentioned, especially in adsorption tests of direct dyes on cellulose (cf. Figure 5d–f)

and it is sometimes implied that systems conforming to this isotherm differ from those conforming to the Langmuir isotherm, which is obtained for most dye adsorptions. They do not necessarily differ (cf. Figure 5); conformity with the Freundlich plot is an indication that saturation of the fibre has not been reached, probably because of experimental difficulties, e.g. limited solubility of the dye. The plot is chiefly used with cellulose-dyeing experiments probably because these are not usually taken to near saturation of fibre, in the region where the relation would fail.

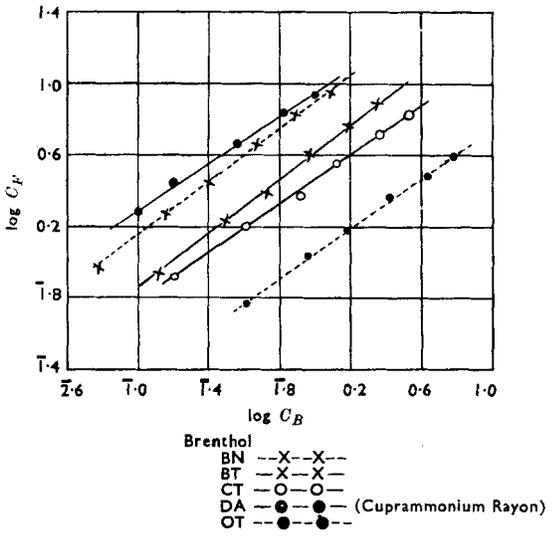


Figure 6 – Log–log ('Freundlich') plots of Brenthol adsorption by cellulose fibres [17]. In these tests, made under normal technical conditions, i.e. at room temperature for 30 min, the systems had probably not reached equilibrium, thus, like Boedeker's results, illustrating the applicability of the relation under these conditions

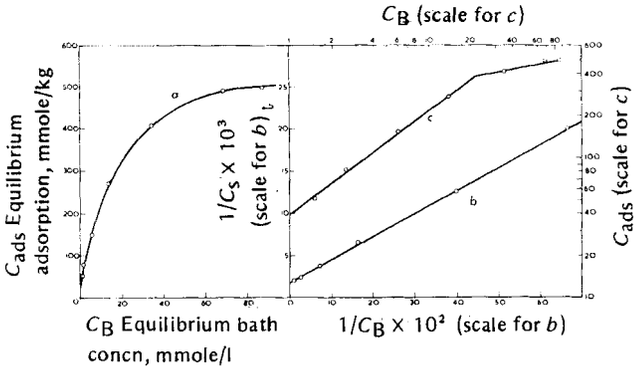


Figure 7 – Isotherm for adsorption of methanol in benzene on intensively dried cellulose: (a) plotted on arithmetic scale [18]; (b) plotted on reciprocal scales, according to the Langmuir equation; and (c) plotted on log–log scales ('Freundlich' plot)

For other typical examples of this plot see, e.g., ref. 2, p. 59, Figure 32 (vapour phase), and ref. 20, p. 211, Figure 74 (dye adsorption).

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Appendix

Although the final (equilibrium) solute concentration should be used, as abscissa, it can readily be shown that under normal circumstances a linear curve will be obtained with an abscissa of initial solute concentration, as in fact Boedeker showed. Thus, let the initial solution concentration be C_O, and C_S be the proportion of this which is taken up by the solid. Then the final solution concentration is $C_O - C_S$, and the Freundlich curve will be given by the relation:

$$C_s = k(C_o - C_s)^{1/n} \tag{1}$$

Where k is a constant; expanding the right-hand side of this equation, we obtain:

$$C_s = kC_o^{\,1/n}\left[1 - \left(\frac{C_s}{C_o}\right)\right]^{1/n} \tag{2}$$

$$C_s = kC_o^{\,1/n}\left[1 - \frac{1}{n}\left(\frac{C_s}{C_o}\right) + \frac{1}{2}\left(\frac{1}{n}\right)\left(\frac{1}{n} - 1\right)\left(\frac{C_s}{C_o}\right)\right]^2 \tag{3}$$

The right-hand side of Eqn 3 is a converging series, and if n is $>$ ca 2, as it normally is, and was in Boedeker's test, the third term is very small and can be eliminated. Thus, approximating:

$$C_s = kC_o^{\,1/n}\left[1 - \frac{1}{n}\left(\frac{C_s}{C_o}\right)\right] \tag{4}$$

and Eqn 4 reduces to

$$C_s = kC_o^{\,1/n}$$

over all but the early part of the isotherm, since excepting over this part:

$$C_s < C_o \text{ and } \left[1 - \frac{1}{n}\left(\frac{C_s}{C_o}\right)\right] \sim 1$$