Thermochimica Acta, 88 (1985) 363–368
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

NON-ISOTHERMAL KINETICS OF DYEING

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(Received 10 December 1984)

ABSTRACT

This paper aims to present an essay to use the non-isothermal kinetic method in order to obtain the kinetic parameters of dyeing in a certain dye–fibre system. Some limitations of the model are discussed.

INTRODUCTION

Dyeing processes are considered to be the processes of colouring textile fibres with either natural or synthetic dyes. In most cases the material to be dyed is brought into contact with a transfer medium containing the dye. The most common medium is water in which the dye may be dissolved or dispersed; during dyeing the dye molecules pass from this medium into the fibre.

The whole dyeing process can be divided into three stages [1]:

(a) the transfer of dye from the bulk of solution to the fibre surface;
(b) the sorption of dye at the fibre surface;
(c) the diffusion of dye into the fibre.

Any one of these processes may control or influence the rate of dyeing, e.g., in commercial dyeings at low rates of flow, the diffusion through a static boundary layer, whose thickness varies inversely with the velocity of flow past the fibre, determines the rate of dyeing. The laboratory conditions are usually adjusted so that stage (c) becomes the rate-determining step.

The diffusion of dye in a fibre is governed by Fick's law

$$ds/dt = -D dc/dx \qquad (1)$$

where ds/dt is the mass of dye diffusing across a unit area during the time dt (the diffusion flux), c is the concentration of dye at a point x from the surface, and D is the diffusion coefficient which is usually considered to be only temperature dependent. This dependence is written as an Arrhenius-type equation, i.e.

$$D = D_0 \exp(-E/RT) \tag{2}$$

where D_0 is a constant, $R = 1.987$ cal mol^{-1} K^{-1} is the gas constant, T is the temperature (K), and E is the activation energy of the diffusion (cal mol^{-1}). The whole dyeing process can be schematically written as follows

$$\text{dye} + \text{fibre} \rightleftharpoons \text{dyed fibre} \tag{3}$$

Equation (3) describes a quasi-chemical reaction and, therefore, its kinetics can be analysed by chemical kinetic methods.

The study of the kinetics of reaction (3) should take into account that the reaction is heterogeneous and, thus, it is described by the kinetics of heterogeneous processes.

The dyeing process is usually represented in the (t, T) plane as shown in Fig. 1. Actually, the regions AB, BC and CD are not straight lines [2] but they can be well approximated. According to Fig. 1 the whole process is composed of two isothermal regions (AB and CD) and two non-isothermal regions (BC and DE). Within the region AB the material to be dyed is wetted and reaches a thermodynamic equilibrium with the bath. Across the region BC the temperature is raised to a so-called "dyeing temperature", T_d. CD represents the boiling region and region DE is the cooling one. Actually, only regions BC and CD are of practical meaning for dyeing processes; during the former the dye molecules are picked up by the fibre and during the latter the dye molecules migrate and become fixed into the fibre. This description is scarcely correct since dye molecules are picked up and fixed by the fibre in both regions. Thus, we cannot discriminate the three stages (a, b and c) of dyeing on a diagram such as that given in Fig. 1 where they occur simultaneously within the regions A–D.

For a kinetic description of the whole dyeing process (represented by eqn. 3), involving all the three stages, one has to take into account at least one

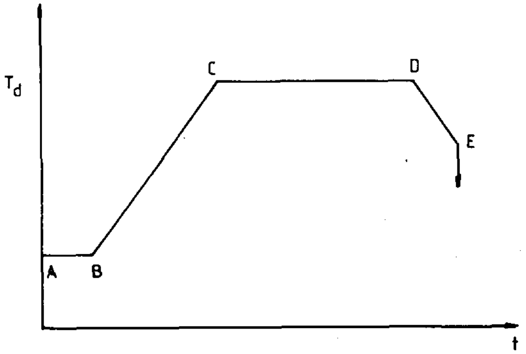

Fig. 1. The dyeing diagram.

non-isothermal region and one isothermal region (region AB can be bypassed by using a wetted material) and to work the BC region by means of the non-isothermal and the CD region by the isothermal kinetic methods. To overcome the difficulties due to the use of two different descriptions, the whole dyeing process can be considered as taking place within one of the two regions: BC or CD. In this paper we shall try to point out the utility of the non-isothermal kinetic description. The kinetic formalism we shall use, as follows, will be the heterogeneous non-isothermal one.

A common variable for describing the dyeing processes is defined by the next equation

$$\alpha = Q_t/Q_\infty \tag{4}$$

where Q_t is the amount of dye in fibre at time t and Q_∞ is the amount of dye in the fibre at the end of dyeing. Equation (4) defines a varaible which is similar to the conversion degree. Some observations referring to it should, however, be made:

(1) the value of Q_∞ is dependent, for a given dye–fibre system, on the amount of dye in the bath at the beginning of the process. The dependence curve is given in Fig. 2. It is thus evident, from a certain amount of dye at the beginning of the dyeing, Q_s, an increase in the initial quantity, Q_i, does not influence the value of Q_∞;

(2) the magnitude of Q_∞ is influenced by temperature; generally, increasing temperature decreases its value, as Fig. 3 shows [3]. This decrease is noticeable for some dye–fibre systems but can be easily neglected for the others.

Summing up, the variable defined by eqn. (4) can only be considered as a conversion degree for dye–fibre systems for which Q_∞ is not greatly affected by temperature and for initial concentrations of the dye which do not exceed the saturation value, Q_s. These considerations lead to the following equation

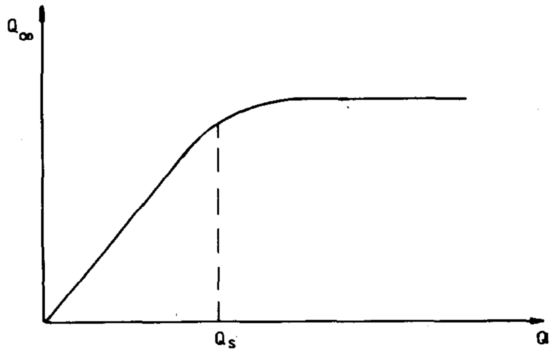

Fig. 2. Influence of the initial amount of dye in the bath on the final amount of dye in the fibre.

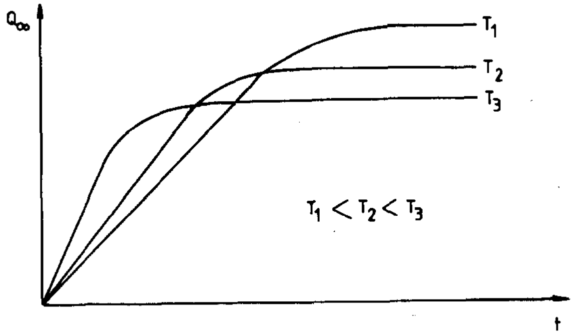

Fig. 3. Influence of temperature on the final amount of dye in the fibre.

for all dyeing systems which fulfil the conditions mentioned above

$$r = d\alpha/dt = f(\alpha)g(T) \tag{5}$$

Assuming that $g(T)$ obeys an Arrhenius-type equation and changing the variable time into temperature, eqn. (5) becomes

$$d\alpha/dT = \frac{1}{b} f(\alpha) A \exp(-E/RT) \tag{6}$$

which is a typical non-isothermal kinetic rate eqn. [4] where $b = dT/dt$ stands for the heating rate, A for the pre-exponential factor and E for the activation energy of the dyeing.

According to above discussion, eqn. (6) describes the region BC of the dyeing diagram and all the three dyeing stages occur within it. Therefore, the activation energy of dyeing from eqn. (6) should be almost equal to the activation energy of diffusion from eqn. (2). In order to apply this eqn. to the study of dyes, the exhaustion curves under non-isothermal conditions should to be recorded. They will represent the amount of dye lost from the bath and will be similar to the thermogravimetric curves, so we shall refer to them as thermoconcentration curves (TC).

EXPERIMENTAL

We choose an acid dye, CI Acid Blue 62, to dye wool fibre in a loose form (fineness of 23 μm). The dye was previously purified by extraction. The dyeing apparatus was an Ahiba type with 12 glasses for dyeing, each containing 3.0000 g wool and 1% (w/w) dye solution with a liquor ratio equal to 40/1. The heating rate was choosen to be 1.5 K/min^{-1} and the temperature ranged from 20 to 100°C. TC curves were drawn through the 12 points given by spectrophotometric measurements of the solutions from each dyeing glass available after certain periods of time (necessary for certain

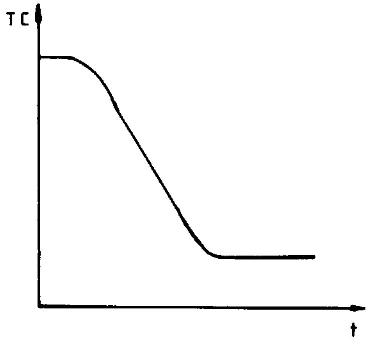

Fig. 4. TC curve of CI Acid Blue 62 ($b = 1.5$ K min^{-1}).

TABLE 1

Values of the Q_t/Q_∞ ratio

T (K)	Extinction	$\alpha = Q_t/Q_\infty$
323	0.62	0
328	0.60	0.057
333	0.58	0.114
338	0.51	0.314
343	0.43	0.543
348	0.38	0.686
353	0.29	0.943
358	0.28	0.971
363	0.27	1

temperature increase) and are given in Fig. 4. The measurements of Q_t/Q_∞ are given in Table 1.

The data obtained from the TC curve have been worked with the help of the Coats and Redfern method [5] within the framework of the reaction order model. This model has been used for reasons of simplicity, but some future work has to be done concerning this point. With these considerations an analysis of the data from the TC curve given in Table 1 leads to the following results: $A = 2 \times 10^{19}$ s^{-1}; $E = 32$ kcal mol^{-1}; $n = 1$. The value of the activation energy, E, is within the range of activation energies for acid dyes on wool fibres [3]. It appears, therefore, that the results obtained offer a real characterization of dyeing systems.

CONCLUSION

The use of the non-isothermal kinetic method to analyse a dyeing system leads to kinetic parameter values in close agreement with those obtained through isothermal methods, but with some simplications in the experiment.

Moreover, the use of non-isothermal methods offers the opportunity for an investigation of the kinetic equation which is followed by the dyeing system through recording three or four TC curves at different heating rates, and successive application of Ozawa's method [6]. A paper on this topic will soon be submitted for publication.

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