DIFFUSION CONTROLLED THERMAL DESORPTION*

DAVID L. MILLER AND RICHARD H. WILDNAUER

Department of Skin Biology, Johnson & Johnson Research,
New Brunswick, N. J. 08903 (U.S.A.)

ABSTRACT

A special case of the non-isothermal rate equation is derived for the evaluation of thermal gravimetry data when the measured weight loss from a sheet-like specimen is governed by a diffusion process as opposed to a homogenous chemical reaction. The equation is applied to the desorption of water and propanol from a nylon film and desorption of water from a naturally occurring biopolymeric material. Satisfactory agreement with isothermal desorption is obtained. The apparent temperature dependence of the desorption is compared with results obtained by a treatment which does not take account of the diffusive mechanism.

INTRODUCTION

The desorption of small molecules from a dense polymeric film or membrane often follows the laws of diffusion. As such the desorption is a physical process governed by the rate of segregation of a mixture into its components under the influence of a concentration gradient. This is clearly distinct from the desorption of small molecules from impenetrable surfaces where they are physically or chemically attached. Often in this case diffusion can be ignored because the rate of the process depends primarily on the strength of the attachment to the substrate. Diffusion controlled desorption is primarily a property of the host matrix and its internal mobility; reversible interactions of the diffusant with the matrix are secondary.

In the case of many biological materials and experimental polymer films where the substrate is of limited supply, thermal desorption using a non-isothermal technique can in principle provide desorption or diffusion coefficients over a considerably wide range of temperatures. These results are produced by a single run on a single sample. Until recently, the problem of extracting numerical data from a thermal desorption curve of this type has not been dealt with. Ozawa[1] has given a rigorous general solution to the diffusion problem for the case of non-isothermal experiments. His approach is based on the application of the concept of reduced time. The solu-

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tion for non-isothermal desorption from a plane sheet presented in this paper was independently derived and is based on the premise that a non-isothermal process can be represented by a series of infinitely small isothermal steps, each step obeying the laws of isothermal diffusion. The validity of this approach has been shown for extending isothermal kinetics of a chemical reaction to the non-isothermal case[2].

THEORETICAL CONSIDERATIONS

The starting point for the development of a desorption equation which can be applied in the non-isothermal case is the solution of the diffusion problem for constant diffusion coefficient. The solution for a plane sheet of thickness $2l$ where the surface concentration is maintained at zero for $t > 0$ is given in the first equation in terms of the total amount of diffusant desorbed at time t, M_t, and after infinite time, M_∞:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right] \tag{1}$$

The following substitutions:

$$\theta = 1 - \frac{M_t}{M_\infty} \tag{2}$$

$$a = \frac{8}{\pi^2} \tag{3}$$

$$D' = \frac{D\pi^2}{4l^2} \tag{4}$$

are introduced into eqn (1) to arrive at eqn (5).

$$\theta = a \sum_{n=0}^{\infty} \frac{\exp\left[-(2n+1)^2 D't\right]}{(2n+1)^2} \tag{5}$$

Equation (5) describes the fractional content of diffusant in the membrane at any time, t. The rate of loss of diffusant is found by differentiating eqn (5) with respect to t:

$$-\frac{d\theta}{dt} = aD' \sum_{n=0}^{\infty} \exp\left[-(2n+1)^2 D't\right] \tag{6}$$

Requiring that θ and $-d\theta/dt$ be known and measurable at the same instant of time, the substitution $\phi = \exp\left[-D't\right]$ is made in eqns (5) and (6), respectively, to yield eqns (7) and (8):

$$\theta = a\left[\phi + \frac{1}{9}\phi^9 + \frac{1}{25}\phi^{25} \ldots\right] \tag{7}$$

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = aD'[\phi + \phi^9 + \phi^{25}\ldots] \tag{8}$$

Examination of eqn (7) reveals that at a given value of θ, a value of ϕ is uniquely defined. If the corresponding value of $-\mathrm{d}\theta/\mathrm{d}t$ is known, then D' can be calculated from eqn (9) which is a rearrangement of eqn (8):

$$D' = \frac{-\dfrac{\mathrm{d}\theta}{\mathrm{d}t}}{a[\phi + \phi^9 + \phi^{25}\ldots]} \tag{9}$$

The value of the power series in the denominator of eqn (9) corresponding to known values of θ can be calculated using simple computer techniques. A plot of the value of the power series, Φ, as a function of θ is shown in Fig. 1. The value of the series approaches θ/a as θ tends to zero and is within 0.1% of θ/a for θ less than 0.35.
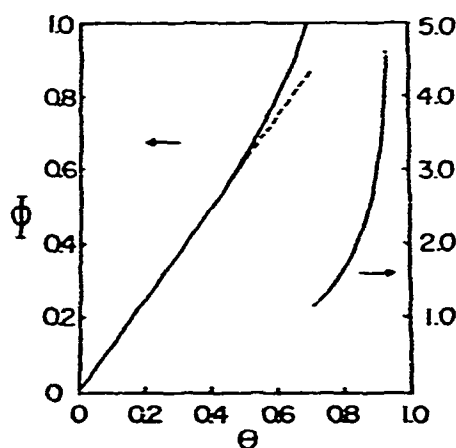

Fig. 1. Graph of theoretical dependence of the series, Φ, on the fractional content of diffusant in the membrane, θ. The broken line indicates the asymptote $\Phi = \theta/a$.

Applying eqn (9) to non-isothermal desorption involves the determination of the integral and time differential loss of diffusant while the temperature is increased at a programmed rate. The quantities θ and $-\mathrm{d}\theta/\mathrm{d}t$ are then calculated from the raw data as a function of temperature. D' is then calculated at each temperature by substitution of the appropriate terms in eqn (9). It should be obvious that eqn (9) can be applied equally well to isothermal desorption. The concentration dependence of a diffusion coefficient can be estimated by plotting D' against the mean concentration in the sheet corresponding to the values of θ and $\mathrm{d}\theta/\mathrm{d}t$ observed during the desorption process.

In this development, there are three conditions that must hold in order for the treatment to result in meaningful diffusion coefficients. The first is that the desorption measured must be diffusion controlled. The second is that non-isothermal diffusion

can be represented by a series of isothermal states each with a temperature slightly different from the previous state. Lastly, the time scale in which the measurements are made should be large compared to the time required for thermal equilibrium of the sample. The last condition is necessary because significant gradients of temperature within the sample invalidate the use of the isothermal interval concept in treating the non-isothermal case.

EXPERIMENTAL

(1) *Apparatus*

A DuPont 990 system equipped with a two-pen recorder and DuPont 951 thermogravimetric analyzer was used for carrying out the non-isothermal desorption measurements. Dry nitrogen at 50 cm^3 min^{-1} was used to purge the furnace area. The thermograms were run at either 5 or 10°C per minute programmed heating rate. The same equipment was used for isothermal desorption by preheating the furnace to the desired temperature and running in "isothermal" mode. Some isothermal desorptions were carried out using the Perkin-Elmer AR-2 auto balance equipment with a thermostated chamber.

(2) *Materials*

Stratum corneum, the upper keratinized layer of the epidermis, was obtained from the excised skin of 12 h old newborn rats. The corneum is separated from the lower layers by exposing the tissue to ammonia vapor for 10 min, then gently peeling away the upper layer. The material is stretched out on teflon sheets to dry and then desiccated until use. Footpads from guinea pigs were obtained by a process similar to that of the corneum. Commercial Nylon 6,6 film (5 mil) was obtained from the Polymer Corporation, Reading, Pa. Previous to use, the film was soaked in water for 24 h and dried. Distilled water and reagent grade chemicals were used as received.

(3) *Methods*

Five milligram corneum and 8–10 mg footpad samples were prepared for a desorption experiment by soaking the material in water for a prescribed length of time. The samples were removed from the distilled water, dabbed free of surface water, then stored in small sealed vials at least 24 h. Twenty-five milligram samples of nylon film were stored in sealed bottles containing the test liquids at least one week before use. These steps were necessary to ensure an initial equilibrium state in the membranes. A desorption experiment was carried out by placing the sample in the balance pan and programming the furnace at 5 or 10°C min^{-1} from ambient to 150°C in the case of the corneum and footpad, and ambient to 200°C in the case of the nylon film. The integral and differential weight loss were recorded simultaneously as a function of sample temperature on the 990 recorder.

RESULTS AND DISCUSSION

Examples of the desorption thermograms are shown in Figs 2 and 3. The similarity in the features of the water desorption derivative thermograms for newborn rat stratum corneum (NBRSC) and guinea pig footpad (GPFP) is surprising considering that the GPFP is 150 μm thick while the NBRSC is only 10 μm thick. The derivative thermograms of the nylon film, similar in thickness to the GPFP (125 μm thick) are quite different in character from the footpad and corneum.
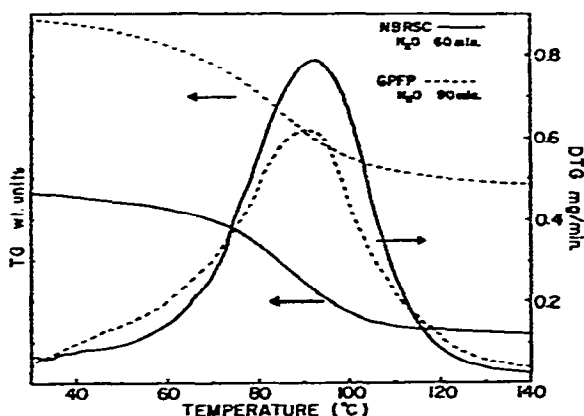

Fig. 2. Recorder traces for thermal desorption of water from newborn rat stratum corneum (NBRSC) and guinea pig footpad (GPFP).
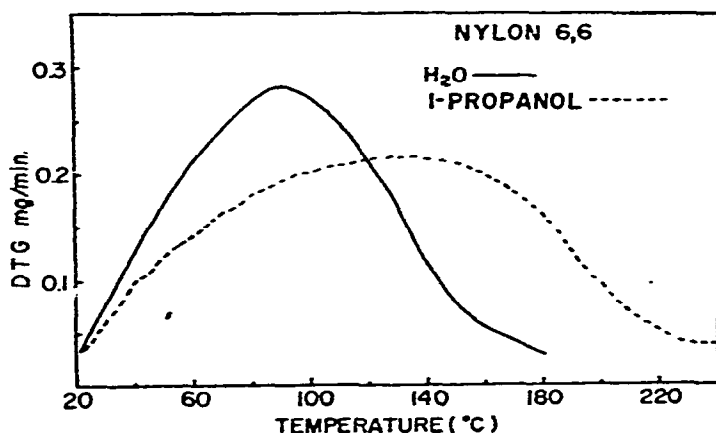

Fig. 3. Comparative recorder tracings of the differential signal from the thermal desorption of water and propanol from nylon 6,6.

The method of Broido has been used by others to evaluate the thermal desorption of solvents from nylon films[4]. This method conveniently requires only the fractional weight loss as a function of temperature to obtain a measure of the energy

of activation of the process which results in the weight loss[5]. This method, however, assumes the process is first order with an Arrhenius type temperature dependence. Its application to a diffusion controlled process could lead to spurious results. It should be considered that the Broido method provides no means of predicting the outcome of a desorption occurring under isothermal conditions.

Figures 4 and 5 illustrate the comparison of the application of the methods of Broido and thermal diffusion to the non-isothermal desorption of water and propanol from a Nylon 6,6 film. For both water and propanol, the Broido method yields data which, for nearly all of the accessible temperature range, can be represented by a straight line. According to the method of Broido, the slope of this line is proportional
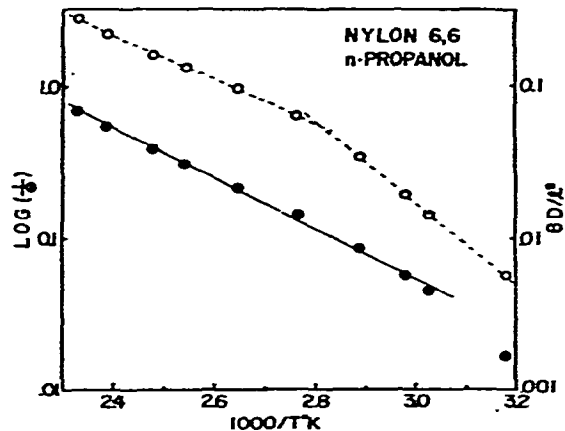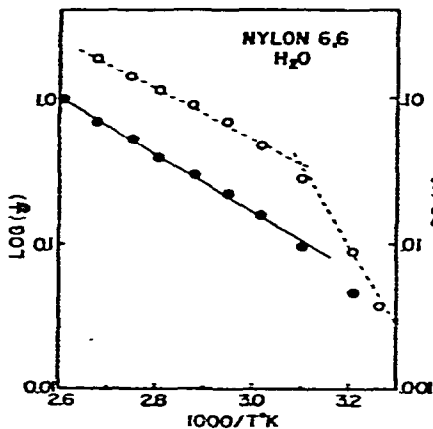
Fig. 4. Semi-logarithmic plot of desorption data for water from nylon 6,6 according to the Broido method (log $1/\theta$, ●) and the thermal diffusion method ($8D/l^2$, ○).

Fig. 5. Semi-logarithmic plot of desorption data for n-propanol from nylon 6,6 according to the Broido method (log $1/\theta$, ●) and the thermal diffusion method ($8D/l^2$, ○).
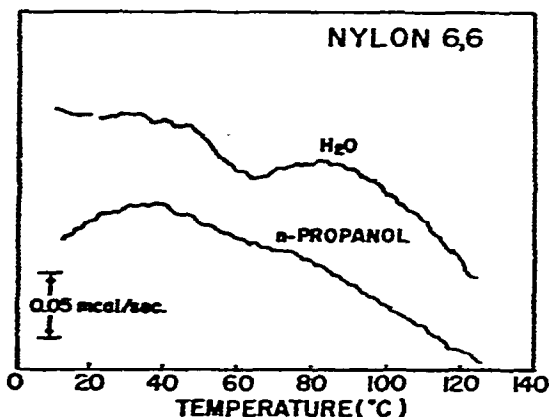
Fig. 6. Recorder traces from differential scanning calorimetry of nylon 6,6 containing sorbed water and sorbed n-propanol.

to the energy of activation of the process. The thermal diffusion method yields data which does not fit a single straight line. The observed break is not unexpected for this sytem because nylon can undergo a glass transition in the accessible temperature range. The extent or size of this transition and the temperature at which it occurs are affected by the presence of solvents which can act as plasticizers for the material. It is this effect which is detected by the thermal diffusion results for nylon. Figure 6 shows differential scanning calorimeter results which confirm the presence of a glass transition in the region of interest.

The application of the thermal diffusion method does not require the assumption of any particular mode of temperature dependence. If there are linear regions in plots of $\log D$ vs. $1/T$, the Arrhenius equation can be applied to the data. Some results are shown in Table 1. The activation energies calculated via thermal diffusion distinguish nylon from the biological material more clearly than do the values calculated via the Broido method. This difference is expected if one considers that the protein matrix contains many highly interacting polar side-chains, while the nylon has none. As discussed earlier, the footpad and corneum had similar looking desorption derivative curves. This feature reveals itself in similar activation energies. The value of the activation energy for diffusion of water in the corneum is in good agree-

TABLE 1

COMPARISON OF DESORPTION ACTIVATION ENERGIES CALCULATED VIA DIFFUSION-DESORPTION METHOD AND METHOD OF BROIDO

System	Desorption Activation Energy ($kcal\ mol^{-1}$)	
	Diffusion	Broido
Newborn rat corneum–water	23[a]	[b]
Guinea pig footpad–water	20	12
Nylon 6,6–water	8[c]	9
Nylon 6,6–propanol	6[c]	8

[a] From permeation measurements E $\sim$20 kcal mol^{-1}. [b] Too curved to calculate. [c] Above glass transition temperature.

TABLE 2

COMPARISON OF DIFFUSION COEFFICIENTS IN NYLON 6,6 CALCULATED FROM ISOTHERMAL EXPERIMENTS AND CALCULATED VIA THE THERMAL DESORPTION METHOD

Solute	D/l^2 (min)	
	Isothermal	Thermal desorption
Propanol, 120°C	1.8×10^{-2}	2.0×10^{-2}
Water, 22°C	2.7×10^{-4}	1.9×10^{-4}

ment with results obtained from water vapor permeation measurements and with water permeability measurements on human epidermis[6].

The comparison of diffusion coefficients obtained isothermally with those calculated from non-isothermal diffusion are shown in Table 2. The ability to extract estimates of isothermal desorption at a variety of temperatures adds significant practical utility to this data reduction method.

CONCLUSION

A satisfactory means of treating non-isothermal desorption data in which the process is diffusion controlled was developed using a simple line of reasoning to relate isothermal and non-isothermal processes.

In the few cases cited, the thermal diffusion method of treating non-isothermal desorption from a film represents the data realistically. It provides the possibility of meaningful reduction of the thermogram to a few constants. The application of this approach to a system can produce a rapid estimation of isothermal desorption rates over a wide range of temperatures. The method is applicable to those polymer–solute systems where diffusion is the rate controlling mechanism of desorption.

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