JOURNAL OF MATERIALS SCIENCE 22 (1987) 2058–2062

Rate equation for photochromic glasses considering both thermal and optical regeneration

THOMAS FLOHR, REINHARD HELBIG
Institut für Angewandte Physik, Glückstrasse 9, 8520 Erlangen, FRG
H. J. HOFFMANN
Schott Glaswerke, Hattenbergstrasse 10, 6500 Mainz 1, FRG

The problems of describing the behaviour of photochromic glasses by a rate equation are discussed. A rate equation considering both thermal and optical regeneration is derived from optical measurements. The stationary-state absorptivity of the glasses under the influence of optical bleaching of various strengths is measured and compared to theoretical predictions from the rate equation.

1. Introduction

A photochromic substance shows different absorptivity when it is illuminated with different light intensities.

Although a variety of organic and inorganic substances exhibit photochromic properties [1], only glasses doped with silver halide have technological interest (e.g. application as spectacles). Commercial photochromic silver halide glasses consist of a borosilicate matrix with an admixture of silver halides and some copper oxide. To induce photochromism, the glasses have to be heated to a temperature of 500 to 700° C [2, 3]. In this process precipitates containing Ag^+, Hal^-, Cu^+ etc. (where Hal = halide) are formed, which are responsible for the photochromic properties. Exposure to UV light causes an increase of the absorbance in the wavelength range of 350 to 900 nm. When the UV light is switched off, the glasses return to their initial transparent state. Regeneration may be accelerated by additional exposure to red light (600 to 800 nm) (e.g. [4]).

By the absorption of ultraviolet light, electron-hole pairs are produced in the silver halide precipitates [2, 5]. As in the photographic process, electrons are trapped by Ag^+ ions and metallic silver is produced.

The situation of the holes in a photochromic material is different from that in a photographic material. In photographic emulsions the holes are trapped by halide ions to form halide atoms. The halide atoms diffuse and react with the gelatine. They are no longer available for regeneration: the photographic process is irreversible.

In photochromic glasses, the trapped holes remain within a precipitate and do not react: regeneration is possible. The holes may be trapped by Hal^- as well as by Cu^+ ions. The photochromic reaction therefore may be written as

$$Ag^+ + Hal^- \xrightarrow{h\nu} Ag^0 + Hal^0 \qquad (1)$$

$$Ag^+ + Cu^+ \xrightarrow{h\nu} Ag^0 + Cu^{++} \qquad (2)$$

Equation 1 describes the process in a hypothetical precipitate of pure silver halide. Small additions of copper cause a considerable strengthening and acceleration of the photochromic reaction (for the rôle of copper in the photochromic process see [6–8]). The photolytically formed silver atoms are assumed to form clusters at the surface of the silver halide precipitates. These clusters may be spherical or elliptical and are separated from each other, or the silver atoms may form a thin surface layer [9]. A random distribution of spherical silver clusters of sufficient sizes causes a broad absorption band with a maximum at about 500 nm. If the clusters are elliptical, this absorption band splits up into two sub-bands [1]. A similarly split absorption band has to be expected with quasi-two-dimensional structures [9]. This is true energy dissipation, as the clusters are much too small for resonant scattering (for this case particle sizes of the order of a wavelength of light are necessary).

Marquardt *et al.* [7] point out that in addition to the absorption by metallic silver clusters an absorption by colour centres in the precipitates (e.g. Cu^{++} ions) has to be taken into account.

In a recent investigation, Hoffmann and Krämer [10] surprisingly observed almost no dependence of the induced absorption coefficient on wavelength in the range 400 to 750 nm. According to Hoffmann and Krämer, the silver clusters in the investigated glasses were too small, so that the critical size for resonant colloid absorption was not reached.

Regeneration of the glasses is due to two mechanisms: thermal regeneration and optical regeneration by exposure to red light.

In the thermal regeneration process a random motion of the trapped holes in a precipitate is assumed. The trapped holes diffuse towards the silver clusters and a recapture of electrons occurs. A microscopic model

0022–2461/87 $03.00 + .12

for thermal regeneration is given by Araujo *et al.* [11, 12].

In the optical regeneration process, electrons from the metallic silver clusters are activated by the red light into the conduction band of the silver halide. Up to now, optical regeneration has scarcely been examined.

A quantitative treatment of the physical properties of photochromic glasses on a microscopic scale has proved to be very difficult. Therefore most approaches are confined to a phenomenological description.

In Section 2 we will give the concept of a rate equation for the phenomenological description of photochromic behaviour. In order to determine the introduced parameters experimentally, we will discuss some simple cases.

In Section 3, the experimental situation will be described, and in Section 4 we will discuss the results.

2. The concept, problems and experimental derivation of a rate equation for photochromic glasses

2.1. Concept

In a rate equation for the description of processes in photochromic glasses, the rate of change $\mathrm{d}Z/\mathrm{d}t$ of the concentration of photolytically induced centres of absorption is equated with a rate of generation G' describing the formation of absorbing centres minus a rate of recombination R' describing the return of the centres into the initial state by thermal and by optical regeneration:

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = G' - R'_{\mathrm{therm}} - R'_{\mathrm{opt}} \tag{3}$$

G' and R' will be connected to parameters determined by experiments, e.g. the absorption coefficient k.

2.2. Problems

A rate equation like Equation 3 only makes sense if the photochromic reaction is caused by one-particle processes which lead to an absorption coefficient proportional to the number of absorbing centres (e.g. $k \propto Z$, Beer's law). This is certainly true for absorption by colour centres and for quasi-metallic, non-resonant absorption by small silver clusters. In these cases the absorption coefficient k is proportional to the number of absorbing particles Z: $k = \alpha(\lambda)Z$, with $\alpha(\lambda)$ as an optical cross-section which may be a function of the wavelength.

In the case of resonant absorption by silver clusters, we have to proceed with caution.

After Born [13], the resonant part of the optical cross section α_{R} of a spherical silver cluster on the basis of Rayleigh theory is given by

$$\alpha_{\mathrm{R}} = 24\pi^3 \left(\frac{\eta^2 - 1}{\eta^2 + 2}\right)^2 \frac{V^2}{\lambda^4} \tag{4}$$

V is the volume of the cluster and η the complex index of refraction of the cluster; $\eta = (n/n_0)(1 + \mathrm{i}n_{\mathrm{i}})$ where n_0 is the real part of the index of refraction of the surrounding medium, n the real part of the index of refraction of the cluster and $\mathrm{i}k$ is the imaginary part of the index of refraction of the cluster. For $\eta^2 + 2 = 0$, α_{R} has a resonance. In this case, even with small silver particles a sharp maximum of absorption has to be expected which hardly depends on the number of silver atoms in a cluster as soon as the critical size for resonant absorption is reached.

Such a reaction can no longer be treated in terms of Beer's law, and the simple description by a rate equation is not possible.

Typical absorption spectra of photochromic glasses, however, do not exhibit a sharp resonance, but a relatively broad maximum at a wavelength of about 500 nm; the denominator of Equation 4 is here only smaller than for other wavelengths.

In this case the absorption coefficient depends again on the number of silver atoms in a cluster, which get there by one-particle processes: V is a measure of this number. The dependence is rather complicated, as the imaginary part of the index of refraction n_{i} depends on V.

Furthermore, the above formula is valid only for spherical silver clusters; it cannot be applied to thin surface layers.

The conditions of one-particle processes and Beer's Law and therefore the possibility to use a rate equation are not given for the case of weakly resonant colloid absorption, it is no longer possible to set $k \propto Z$.

The glasses studied in this work did not show any evidence for resonant absorption. We therefore assume that the above-mentioned problems did not arise.

2.3. Relation to simple experimental situations

If the induced absorption coefficient $k(\lambda)$ is proportional to the concentration of photolytically induced centres of absorption, as we assume, we may set $k(\lambda) = \alpha(\lambda)Z$. For a fixed wavelength (in this case 632 nm), Equation 3 can be written as

$$\frac{\mathrm{d}k}{\mathrm{d}t} = G - R_{\mathrm{therm}} - R_{\mathrm{opt}} \tag{5}$$

In order to trace G, R_{therm} and R_{opt} back to parameters determined by experiments, simple cases will be examined.

2.3.1. Onset of darkening

For $t = 0$ (the onset of darkening), $Z \approx 0$ and R_{therm} as well as R_{opt} are nearly zero, as they are assumed to be proportional to Z. We obtain

$$\frac{\mathrm{d}k}{\mathrm{d}t} = G \tag{6}$$

2.3.2. Switching off the exciting UV light

After switching off the exciting UV light, we have $G = 0$, so that

$$\frac{\mathrm{d}k}{\mathrm{d}t} = -R_{\mathrm{therm}} - R_{\mathrm{opt}} \tag{7}$$

Without red light, or with small intensities of red light, $R_{\mathrm{opt}} \approx 0$ and $\mathrm{d}k/\mathrm{d}t = -R_{\mathrm{therm}}$.

With large intensities of red light, optical bleaching dominates ($R_{\mathrm{opt}} \gg R_{\mathrm{therm}}$), and we obtain $\mathrm{d}k/\mathrm{d}t = -R_{\mathrm{opt}}$.

2.3.3. Stationary state

In the stationary state we have

$$G = R_{\text{therm}} + R_{\text{opt}} \qquad (8)$$

because $\mathrm{d}k/\mathrm{d}t = 0$. In order to determine the corresponding parameters experimentally, we have to measure $\mathrm{d}k/\mathrm{d}t$ at the beginning of darkening and regeneration, and the stationary induced absorption as a function of the exciting UV intensity.

3. Experimental situation

3.1. Experimental set-up

The experimental set-up is shown schematically in Fig. 1. The photochromic glasses were darkened by light from a 200 W mercury lamp. The exciting intensity was varied by a variable aperture and measured by a photomultiplier. The transmission of the glasses was measured by a photodiode at a fixed wavelength of $\lambda = 632\,\text{nm}$ (He–Ne laser, maximum power 5 mW). The laser intensity was variable, and the laser could simultaneously serve to bleach the glasses optically in a controlled way.

3.2. Problems of optical measurements on photochromic glasses

For the interpretation of optical measurements on photochromic glasses, the spatial inhomogeneity of the induced absorption has to be taken into account. As the exciting UV light is absorbed in the sample, its intensity decreases with increasing depth, and fewer absorption centres are induced. For the probing beam, the Lambert–Beer law

$$I(d) = I_0\,\mathrm{e}^{-kd} \qquad (9)$$

(d = sample thickness, k = absorption coefficient) is no longer valid, but it has to be replaced by the integral form

$$I(d) = I_0\,\mathrm{e}^{-k_0 d} \exp\left[-\int_0^d k(x)\,\mathrm{d}x\right] \qquad (10)$$

k_0 is the absorption coefficient of the undarkened glass, which is very small at 632 nm and was not taken into account. The photodiode, however, measures the transmitted intensity. Therefore, only an averaged $k = (1/d)\ln(I/I_0)$ may be determined. In order to obtain k or $\mathrm{d}k/\mathrm{d}t$ from optical measurements, only thin samples should be used to avoid difficulties arising from the spatially inhomogenous absorption (in this work we used 0.2 mm thick samples). The photoacoustic method is another way to avoid these difficulties [14].

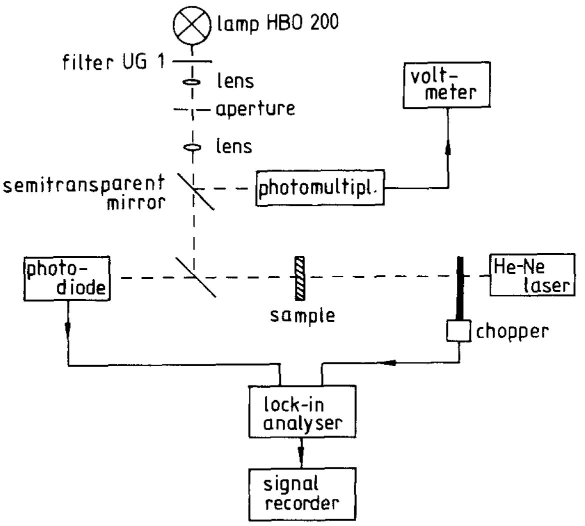

Figure 1 Schema of the experimental set-up.

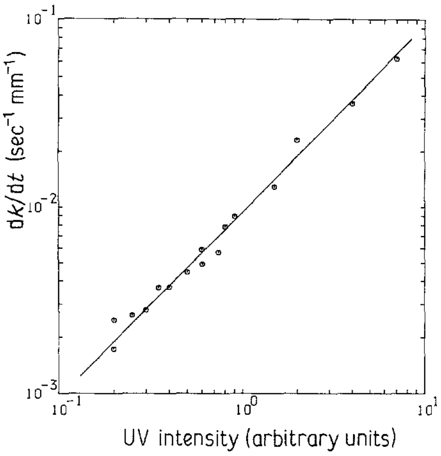

Figure 2 Rate of change of the averaged induced absorption coefficient $\mathrm{d}k/\mathrm{d}t$ immediately after switching on the exciting UV light, as a function of the exciting UV intensity (sample thickness 0.2 mm).

4. Results and discussion: the rate equation

4.1. Onset of darkening

Fig. 2 shows the rate of change of the averaged induced absorption coefficient $\mathrm{d}k/\mathrm{d}t$ of a 0.2 mm thick sample immediately after switching on the exciting UV light as a function of the exciting UV intensity. In practice this is done by observing k as a function of t and extrapolating the rate $\mathrm{d}k/\mathrm{d}t$ for $t \to 0$. Fig. 2 demonstrates that $\mathrm{d}k/\mathrm{d}t$ is proportional to I_{UV}.

Since $\mathrm{d}k/\mathrm{d}t$ should decrease with increasing k, as otherwise stationary absorption would never be reached, we set

$$G = g(k_{\max} - k)I_{\text{UV}} \qquad (11)$$

where $k_{\max}$ is the maximum absorption coefficient and g is the generation coefficient.

4.2. Switching off the exciting UV light

The value of $\mathrm{d}k/\mathrm{d}t$ immediately after switching off the exciting UV light as a function of k is shown in Figs 3 and 4.

For the measurements shown in Fig. 3, the laser intensity was strongly reduced so that we have negligible optical bleaching. Here we obtain $\mathrm{d}k/\mathrm{d}t \propto k^2$.

For the measurements shown in Fig. 4, full laser intensity (5 mW) was used (= prevailing optical bleaching) and $\mathrm{d}k/\mathrm{d}t \propto k$.

While optical bleaching is a first-order process, thermal regeneration is a second-order process. We may write

$$R_{\text{therm}} = rk^2 \qquad (12)$$

or

$$R_{\text{opt}} = dkI_{\text{Red}} \qquad (13)$$

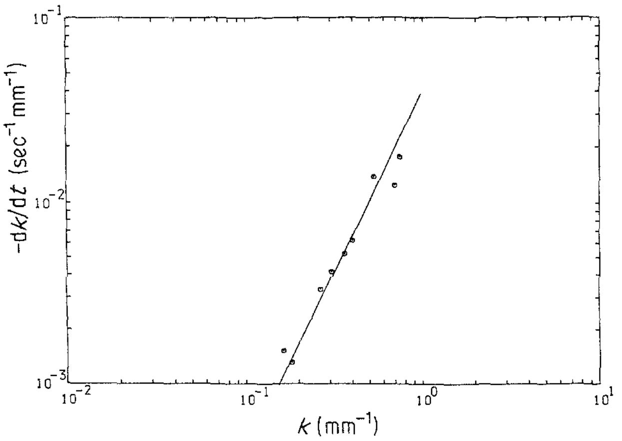

Figure 3 Rate of change of the averaged induced absorption coefficient $\mathrm{d}k/\mathrm{d}t$ immediately after switching off the exciting UV light as a function of k, with negligible optical bleaching, $I_{\mathrm{Red}} = 0.01 I_{\mathrm{Red,0}}$.

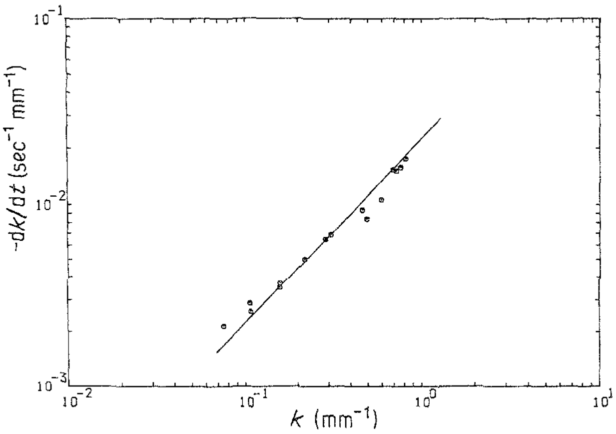

Figure 4 Rate of change of the averaged induced absorption coefficient $\mathrm{d}k/\mathrm{d}t$ immediately after switching off the exciting UV light as a function of k, with prevailing optical bleaching, $I_{\mathrm{Red}} = I_{\mathrm{Red,0}}$.

The linear dependence of the optical bleaching on I_{Red}, which is assumed here, will be verified later.

Now G, R_{therm} and R_{opt} are determined, and the following differential equation for the change of the induced absorption coefficient as a function of time is obtained:

$$\begin{aligned}\frac{\mathrm{d}k}{\mathrm{d}t} &= G - R_{\mathrm{therm}} - R_{\mathrm{opt}} \\ &= g(k_{\mathrm{max}} - k)I_{\mathrm{UV}} - rk^2 - dI_{\mathrm{Red}}k \qquad (14)\end{aligned}$$

4.3. Stationary-state absorption

In order to prove the dependence described by this equation, the induced absorption coefficient in the stationary state k_{stat} may be measured as a function of the exciting UV intensity for various intensities of the bleaching light (laser). This will also give information about the dependence of k_{stat} as a function of I_{Red}. A stationary state means $\mathrm{d}k/\mathrm{d}t = 0$ (see Section 2.3.3).

In the case of prevailing optical bleaching, that means for $dI_{\mathrm{Red}}k \gg rk^2$, we neglect rk^2, and we obtain

$$k_{\mathrm{stat}} = k_{\mathrm{max}} \frac{I_{\mathrm{UV}}}{I_{\mathrm{UV}} + (d/g)I_{\mathrm{Red}}} \qquad (15)$$

For small UV intensities, k_{stat} should be proportional to I_{UV}, but for increasing UV intensities, a limiting value should be reached.

In the case of prevailing thermal regeneration, that means for $dI_{\mathrm{Red}}k \ll rk^2$, we neglect $dI_{\mathrm{Red}}k$, and we write

$$k_{\mathrm{stat}} = -\frac{g}{2r} I_{\mathrm{UV}} + \left[\left(\frac{-g}{2r} I_{\mathrm{UV}}\right)^2 + \frac{gk_{\mathrm{max}}}{r} I_{\mathrm{UV}}\right]^{1/2} \qquad (16)$$

For small values of I_{UV}, k_{stat} should be proportional to $I_{\mathrm{UV}}^{1/2}$. With increasing UV intensity, a limiting value should be reached again.

By variation of I_{Red}, any case between these two cases should be adjustable.

We obtain for the general case

$$\begin{aligned}k_{\mathrm{stat}} = {}& \frac{-g}{2r} I_{\mathrm{UV}} - \frac{d}{2r} I_{\mathrm{Red}} \\ &+ \left[\left(\frac{g}{2r} I_{\mathrm{UV}} + \frac{d}{2r} I_{\mathrm{Red}}\right)^2 + \frac{gk_{\mathrm{max}}}{r} I_{\mathrm{UV}}\right]^{1/2} \qquad (17)\end{aligned}$$

In Fig. 5, k_{stat} is shown as a function of I_{UV} for different values of I_{Red}. Only the curve $I_{\mathrm{Red}} = 0.04 I_{\mathrm{Red,0}}$ is fitted by adjusting g/r, d/r and k_{max}. The other curves were obtained from the fitted one by variation of I_{Red} alone. The theoretical values of I_{Red} were consistent with the experimentally determined values, so that the linear dependence on I_{Red} is confirmed.

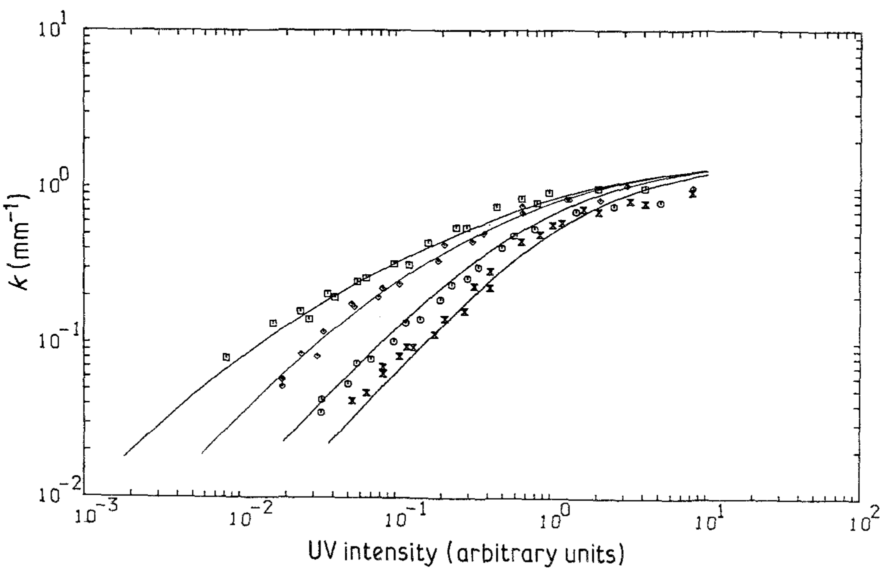

Figure 5 Induced absorption coefficient k in the stationary state as a function of the exciting UV intensity I_{UV} for different values of I_{Red}: (⧖) $I_{\mathrm{Red}} = I_{\mathrm{Red,0}}$, (⊙) $I_{\mathrm{Red}} = 0.48 I_{\mathrm{Red,0}}$, (◇) $I_{\mathrm{Red}} = 0.15 I_{\mathrm{Red,0}}$, (⊡) $I_{\mathrm{Red}} = 0.04 I_{\mathrm{Red,0}}$.

5. Conclusion

The kinetics of the photochromic process for silver chloride glasses were described by a rate equation. Thermal and optical regeneration could be separated by different experimental situations. We have shown that thermal regeneration can be described as a second-order process, whereas optical regeneration is a first-order process that depends linearly on the intensity of the bleaching light.

The satisfactory agreement between theory and experimental results for the dependance of the stationary-state induced absorption on the exciting UV intensity with different intensities of the bleaching light leads to the conclusion that our rate equation describes the basic features correctly. This means that the photochromic process for silver chloride glasses may be described in terms of Beer's law and that the definition of an optical cross-section $\alpha(\lambda)$ per absorption centre is possible.

References

1. R. J. ARAUJO, in "Treatise on Materials Science", Vol. 12, edited by M. Tomazawa and R. H. Doremus (Academic Press, New York, 1977) p. 91.
2. G. GLIEMEROTH and K. H. MADER, *Ang. Chemie* **82** (1970) 421.
3. H. BACH and G. GLIEMEROTH, *Glastechn. Ber.* **44** (1971) 305.
4. R. J. ARAUJO, *Contemp. Phys.* **21** (1980) 77.
5. G. P. SMITH, *J. Mater. Sci.* **2** (1967) 139.
6. C. L. MARQUARDT, *Appl. Phys. Lett.* **28** (1976) 209.
7. C. L. MARQUARDT, J. F. GIULIANI and R. T. WILLIAMS, *J. Appl. Phys.* **47** (1976) 4915.
8. C. L. MARQUARDT, J. F. GIULIANI and G. GLIEMEROTH, *ibid.* **48** (1977) 3669.
9. C. L. MARQUARDT and G. GLIEMEROTH, *ibid.* **50** (1979) 4584.
10. H. J. HOFFMANN and G. KRÄMER, DGPh Intern, Sonderausgabe zum 2, Münchener Symposium über wissenschaftl. Photographie, 27–28. Oktober 1983, G. Haase (Ed.), p. 78–91.
11. R. J. ARAUJO, N. F. BORELLI and D. A. NOLAN, *Phil. Mag.* **B40** (1979) 279.
12. *Idem, ibid.* **B44** (1981) 453.
13. MAX BORN, "Optik", (Springer, Berlin, 1933) Ch. 7.
14. T. FLOHR and R. HELBIG, *Appl. Optics* **25** (1986) 2008.

Received 6 December 1985
and accepted 22 September 1986