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Diffusion from gelatin-glycerin-water gels

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The effect of gelatin, glycerin and methylene blue concentration on the diffusion of a dye from gelatin-glycerin-water gels has been examined. The rate of diffusion depended on the pore size of the gel and on the viscosity of the interspace fluid. Except at very low concentrations of methylene blue, an aggregation factor must be added to those factors suggested by Friedman & Kraemer (1930) as controlling the rate of diffusion from gels.

THE diffusion of dyes into and from gels has been the subject of numerous investigations (Friedman & Kraemer, 1930; Calvet, 1947; Longsworth, 1954; Pontins, Kaplan & Husney, 1956; Marinin, 1958; Blyumberg & Davydkin, 1962). The direct comparison of different workers' results is not always possible because of different methods of pretreating the gels.

Although gelatin-glycerin gels have been used for many years, little systematic work has been done on their properties and the diffusion of substances from these gels has received little attention. The present work investigates the diffusion of methylene blue from gelatin-glycerin gels prepared from gelatins of varying Bloom strength.

Experimental

MATERIALS

Gelatins. The characteristics have been given in a previous paper (Nixon, Georgakopoulos & Carless, 1966). *Glycerin* was Analar grade and *methylene blue* was of B.P. quality. *Purified water* was once distilled from an all glass still (pH 5·2, specific conductivity 5 mhos cm^{-1}).

METHODS

Preparation of the gels and the *method of measuring the rigidity* were as described by Nixon & others, 1966.

Measurement of diffusion coefficient. Diffusion was measured by a method based on that of Friedman & Kraemer (1930). The dye was uniformly distributed in the molten gel (200 ml) and the container allowed to equilibrate at 25° ± 0·1° for 16 hr. A similar volume of water at the same temperature was added and the whole placed in a shaking thermostat bath (108 strokes/min; 39 mm throw). Absorptiometer readings on samples of the aqueous phase were made at intervals up to 50 hr. The samples were always returned after use to the master solution, and at the end of the experiment a check was made with a depth gauge, to be certain that no significant change in volume had occurred.

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The diffusion coefficient can be derived from the equation of March & Weaver (1928) which in its expanded form becomes

$$V = \tfrac{1}{2} - (0{\cdot}327e^{-4{\cdot}117T} + 0{\cdot}0766e^{-24{\cdot}14T} + 0{\cdot}0306e^{-73{\cdot}68T} + 0{\cdot}0160e^{-123T} + 0{\cdot}0100e^{-200T} + 0{\cdot}0067e^{-299T} \ldots) \quad \ldots \quad (1)$$

where V = the fraction of material which has diffused from the gel at a given time.

A theoretical curve was constructed from which values of T could be read using experimentally determined values of V.

The diffusion coefficient was calculated from T by means of the equation

$$T = \frac{Da^2}{t} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where D = diffusion coefficient of a solute moving into the solution above the gel; a = the thickness of the gel and also the depth of solution above the gel; t = time in sec. All values of D recorded are the mean of six readings.

Results and discussion

Gels containing 20% w/w glycerin and 10 mg% methylene blue were used to examine the effect of gelatin concentration and Bloom number on the rate of diffusion. There was a linear decrease in diffusion coefficient between 10 and 15% w/w gelatin (Fig. 1). The slope of the line depended

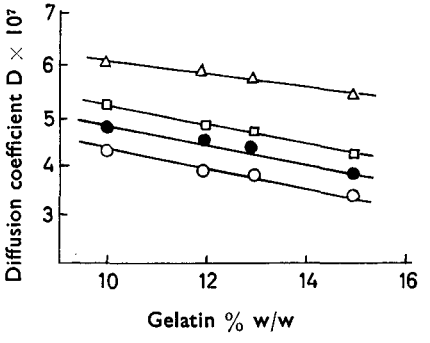

FIG. 1. Diffusion of methylene blue from gelatin-glycerin gels. Glycerin 20% w/w, methylene blue 10 mg %. Temperature 25 ±0·1°. Gelatin Bloom numbers: △ 99; □ 154; ● 200; ○ 250.

on the Bloom number of the gelatin used, the percentage fall in diffusion rate between the two concentrations of gelatin being: Bloom No. 99, 11·4; Bloom No. 154, 20; Bloom No. 200, 20·8 and Bloom No. 250, 21·1. The increase in Bloom number also resulted in a slower rate of diffusion.

Measurements were confined to this narrow range of gelatin concentrations because of experimental difficulties. At gelatin concentrations below 10% w/w, slight mechanical rupture of the gel surface after prolonged shaking of the system prevented the calculation of a true diffusion coefficient. Simple extrapolation of the curves towards low gelatin

concentrations would be incorrect, as at some point they would bend upwards towards the theoretical diffusion coefficient of methylene blue from glycerin-water mixtures into water. At high gelatin concentrations the experimental difficulty was microbial decomposition of the surface layers of the gel due to the extended experimental time necessary to calculate a diffusion coefficient. Extrapolation to zero diffusion rate gave a gelatin concentration of approximately 25% for all the gelatins except the 99 Bloom strength where the value was 40%. It is doubtful whether diffusion would cease at these concentrations as although an increase in gelatin concentration decreases the available area for diffusion due to the smaller pore size of the gel (Friedman & Kraemer, 1930) the capillaries are of different size and would allow passage of some dye molecules.

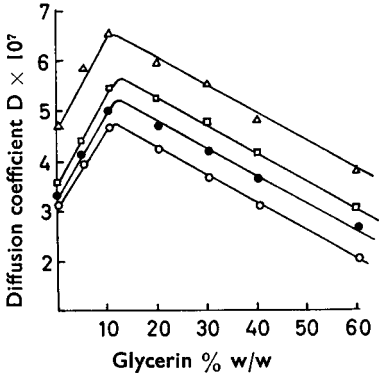

FIG. 2. Effect of glycerin concentration on the diffusion of methylene blue. Gelatin 10% w/w; methylene blue 10 mg %. Temperature 25 ±0·1°. Gelatin Bloom number: △ 99; □ 154; ● 200; ○ 250.

The effect of glycerin on the diffusion coefficient depended on its concentration (Fig. 2). The curves, which were parallel for all gelatins studied, exhibited a maximum at approximately 10% glycerin. The reduction in diffusion rate at higher glycerin concentrations was paralleled by a sharp increase in the viscosity of the glycerin-water interspace fluid. This increased viscosity was the same irrespective of the Bloom number of the gelatin and, as the concentration of the latter remained constant, the pore size of the gel network produced by a given gelatin would not vary. However, as the chain length increased the smaller pore size caused by the possibility of a greater number of linkage points along the chain led to a reduction in diffusion rate as shown in Fig. 2. The rise in diffusion rate at glycerin concentrations below 10%, where the interspace fluid viscosity remains constant, is probably due to a polarity effect of the solvent causing a decrease in the intermolecular forces of attraction between methylene blue molecules thus producing a less aggregated molecule which would more easily pass through the gel network.

The rigidity of the gels containing a given percentage of gelatin was increased by the addition of glycerin (Nixon & others, 1966) but this

increase as such played no part in determining the diffusion coefficient. Only when the pore size was decreased by an increased concentration of gelatin, resulting in an increased rigidity, did this factor affect the diffusion rate. Although there appears to be no simple relationship between rigidity and diffusion rate, the data from a large number of experiments using both different Bloom number gelatins and gelatin-glycerin ratios allow a single line to be drawn through the points (Fig. 3).

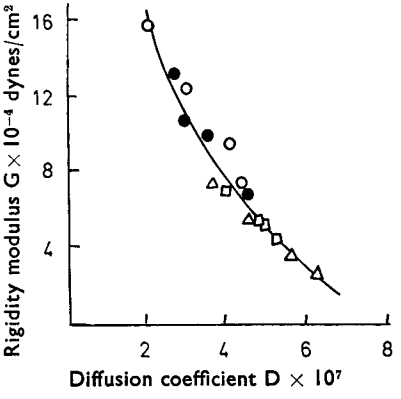

FIG. 3. Rigidity against diffusion coefficient at different % gelatin-glycerin ratios (10/10; 10/20; 10/40; 10/60). Methylene blue 10 mg %; temperature 25 ±0·1°. Gelatin Bloom numbers: △ 99; □ 154; ● 200; ○ 250.

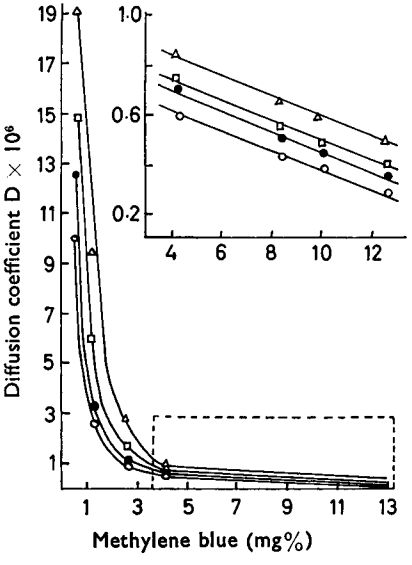

FIG. 4. Diffusion coefficient against methylene blue concentration. Gelatin concentration 12 % w/w; glycerin concentration 20% w/w; temperature 25 ±0·1°. Gelatin Bloom numbers: △ 99; □ 154; ● 200; ○ 250. Inset portion is enlargement of area within dotted lines.

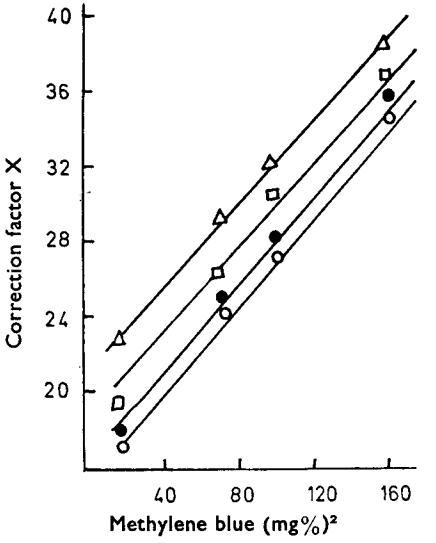

FIG. 5. Effect of concentration of methylene blue on correction factor X. Gelatin Bloom numbers: △ 99; □ 154; ● 200; ○ 250.

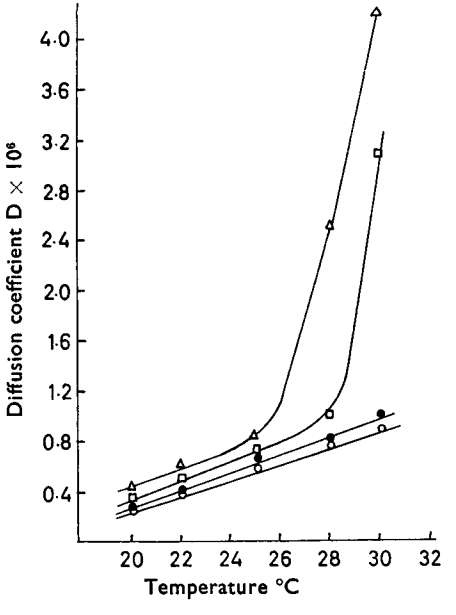

FIG. 6. Effect of temperature on the diffusion coefficient. Concentrations: gelatin 12% w/w; glycerin 20% w/w; methylene blue 4·2 mg %. Gelatin Bloom numbers: △ 99; □ 154; ● 200; ○ 250.

In these experiments, because the gelatin concentration remained constant, the increased rigidity was due to an increase in inter-chain linkage with the longer chain length gelatins.

The effect of methylene blue concentration was complicated by dissociation of the molecular aggregates at low concentrations of the dye. At concentrations above 4 mg% the diffusion coefficient was found to be a slowly decreasing linear function of the methylene blue concentration (Fig. 4 inset). The size of the molecular aggregate obviously approaches an optimum close to the pore size of the gel. When this is reached only those molecular aggregates smaller than the pores of the gel will pass through, resulting in a low diffusion rate.

At dye concentrations lower than approximately 2 mg% free movement within the gel network becomes possible as the molecular aggregates of methylene blue become small (Fig. 4) and at very low concentrations the diffusion coefficient becomes very large.

When considering the diffusion coefficient of the dye from the gels it is necessary to consider a fourth factor which affects the rate of diffusion. An aggregation factor, X, has to be included in Friedman & Kraemer's equation. The equation (3) relates the diffusion coefficient of the unaggregated molecule in water to its diffusion in the gel.

$$D_{water} = D_{gel}\,(1 + 2{\cdot}4\ r/R)(1 + a)(1 + \pi)(1 + X) \quad .. \quad (3)$$

where D = diffusion coefficient; r = radius of diffusing molecule; R = radius of gel pore; a = viscosity correction factor; π = mechanical blocking correction factor; X = aggregation factor.

At low methylene blue concentrations, aggregation has no significance and Friedman & Kraemer's equation holds and can be written

$$D_{water} = D_{gel}^{(1+X)\to 1}\,(1 + 2{\cdot}4\ r/R)(1 + a)(1 + \pi) \quad .. \quad .. \quad (4)$$

The X factor can be calculated from

$$1 + X = D_{gel}^{(1+X)\to 1}/D_{gel} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where $D_{gel}^{(1+X)\to 1}$ is the diffusion coefficient at very low concentrations of dye and D_{gel} is the diffusion coefficient at the dye concentration for which X is required.

It is necessary to know values of X in order to calculate the true diffusion coefficient of the non-aggregated dye molecules. Over the region where the factor has great significance it is proportional to the square of the dye concentration (Fig. 5), and as the curves for the different gelatins are parallel, X will depend on the pore size of the gel. Although important in calculating the diffusion coefficient of the unaggregated molecule the X factor cannot be taken as a direct measure of either pore size or degree of aggregation.

Increases in temperature caused significant increases in the rate of diffusion of methylene blue from the gel, due to both the decrease in rigidity and the increased thermal agitation of both the gelatin and methylene blue. These result in a progressively larger pore size. Up to a temperature of 25° this increased diffusion was linear and the curves for

the different gelatins were parallel (Fig. 6) suggesting that only the different pore size of the gels was causing differences between the gelatins. Above this temperature diffusion coefficient was non-linear and the temperature at which this non-linearity occurred was lower with the shorter chain length gelatins. The long chain 250 Bloom number gelatin retained its linearity up to a temperature of 30°.

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