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J. A. Leermakers, B. H. Carroll, and C. J. Staud

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Surface-Dye Concentration Relationships in Sensitized Photographic Emulsions*

J. A. LEERMAKERS, B. H. CARROLL AND C. J. STAUD

Eastman Kodak Company, Rochester, New York

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A study has been made of the relationship between the total surface of silver halide in a photographic emulsion and the concentration of sensitizing dye necessary to produce maximum sensitizing. It was found that the amount of dye producing maximum sensitizing is directly proportional to the silver halide surface. Approximate calculations indicate that at optimum sensitizing concentration, the sensitizing dye is adsorbed to the silver halide grains in a mono-molecular layer.

I N the optical sensitizing of photographic emulsions by dyes, the photographic sensitivity conferred is dependent among other factors upon the dye concentration in the emulsion. The sensitivity increases with increasing dye concentration until a point is reached, beyond which definite decreases in sensitivity result. One important variable in the relation between dye concentration and photographic sensitivity is the total surface of the silver halide.

There are in the literature reports of two adsorption studies for two cyanine dyes[1, 2] and some acid dyes,[3] but no definite correlation is shown between the grain surface area and the dye concentration necessary to produce a given sensitizing effect, which the dyes in question are capable of producing.

This communication presents the results of a study of the surface-dye concentration relationships for seven emulsions and for three dyes. For all of the emulsions used, size frequency measurements were available. From these measurements, the total surface per cubic centimeter of emulsion was readily obtained.

The dyes used in the present investigation were cyanines.

To determine the effect of dye concentration upon photographic sensitivity as a function of the total surface of the silver halide grains, an extended series of emulsion coatings was made for each dye in each emulsion. Each series included coatings of the same emulsion sensitized with varying amounts of dye, in some cases a 250-fold range of dye concentration being investigated. The coated plates were exposed on an Eastman IIb sensitometer supplied with strips of standard Wratten tricolor filters, Nos. 25, 58, and 49, and processed according to the conditions most suitable for the particular emulsion. H and D curves were plotted for the sensitivities in the blue, green, and red spectral regions, and from these curves the inertia speeds and the contrasts (γ) were obtained.

In Figs. 1 and 2 are presented the results of a typical concentration study. The H and D speed and gamma for the three spectral regions are plotted against the logarithm of the dye concentration. It is seen in Fig. 1 that the sensitivities in the red and green spectral regions increase with increasing quantity of dye added to the emulsion until a definite maximum speed is reached. Greater quantities of dye result in marked decreases in sensitivity. The blue speed remains practically constant until the optimum dye concentration is exceeded, after which marked decreases in sensitivity result. The contrast changes are parallel to those of the speed changes, as seen in Fig. 2. For some dyes the concentrations giving maximum speed are almost the same as those for maximum contrast. For other dyes, or other emulsions, it is sometimes found that the contrasts decrease at a concentration of dye slightly lower than that which produces maximum sensitivity.

Curves similar to those of Figs. 1 and 2 have been constructed, and the concentration of dye producing maximum sensitivity has been determined for each combination of dye and

* Communication No. 644 from the Kodak Research Laboratories.

[1] S. E. Sheppard and H. Crouch, J. Phys. Chem. 32, 751 (1928).

[2] S. E. Sheppard, R. H. Lambert and R. L. Keenan, J. Phys. Chem. 36, 174 (1932).

[3] A. J. Rabinovitch and K. C. Bagdassarjan, Kino-Photo Res. Inst. Moscow 3, 5 (1935).
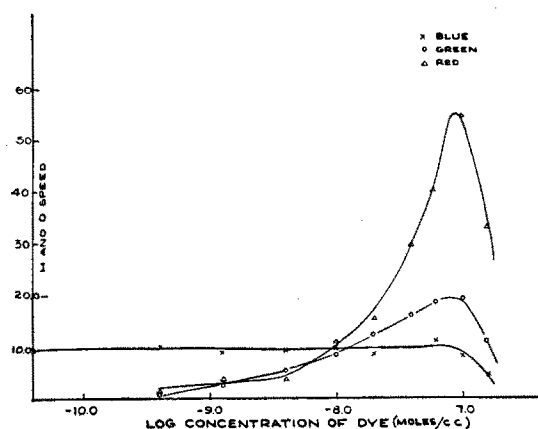
FIG. 1.

FIG. 2.

emulsion used. This concentration has been taken as a significant constant in the determination of the relationship between sensitizing and grain surface. The second significant figure is the total surface of the silver halide in the emulsion.

The surface area for each emulsion was determined from the projective area of the average grain, the number of grains per cubic centimeter, the silver content of the emulsion, and the density of the silver bromide. For the present purpose, since the experimental errors are fairly large, it is not critical how the projective area per cubic centimeter of emulsion is calculated. The total projective area has been obtained by multiplying the area of the average grain by the total number of grains, rather than by integrating the size frequency curve. The thickness of the average grain was calculated, assuming various projective shapes, e.g., an equilateral triangle, a circle, and a square. From these the thickness and total surface of a grain of each shape were calculated. It was found that with the assumption of different shapes, the surface area did not vary more than 15 percent, and the average of the three was taken as a measure of the total surface. An example of the calculations is as follows:

An emulsion was found by count to have 2.24×10^{10} grains per cubic centimeter. The projective area of the average grain was 8.6×10^{-9} cm^2. From the silver content and the density of silver bromide, the total volume of the average grain was calculated to be 25.4×10^{-14} cc, and the thickness 2.96×10^{-5} cm. For a square, the
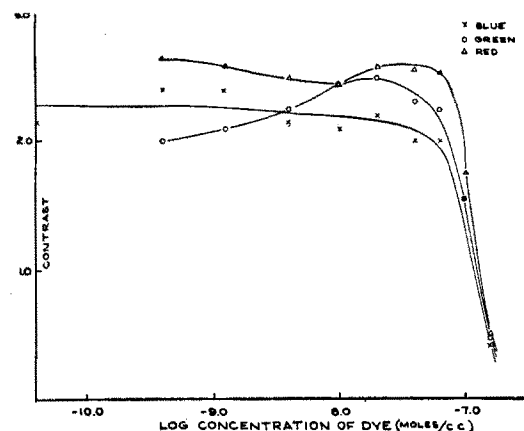
ratio of length of side to thickness is 3.1. For an equilateral triangle, the ratio of length of side to thickness is 4.8, and for a circle, the ratio of radius to thickness is 1.8. From these values, the total surface is found to be:

Triangle: 3.4 times projective area
Square: 3.3 " " "
Circle: 3.1 " " "

The average of these values, 3.3, was used to calculate the total surface of the emulsion.

In Table I are collected the results of the concentration studies.

It is seen immediately from the fifth column that the dye necessary for optimum sensitizing is directly proportional to the surface. The constancy of the ratio (dye/surface) for different emulsions is perhaps better than the size frequency data warrant, but since these were determined in a systematic manner by the same workers, errors should be uniform and reasonably constant. It is felt that, although the absolute values of the surface areas may be in error by as much as 50 percent, the relative values are much more accurate than this.

The emulsions used in this investigation were prepared, both from neutral silver nitrate and ammoniacal silver oxide solutions. These two types of emulsion were used, because it has been pointed out by Carroll and Hubbard[4] that the external habits of the silver bromide crystals are somewhat different in the two cases. The fact that these two types of emulsion show the

[4] B. H. Carroll and D. Hubbard, J. Phys. Chem. **31**, 917 (1927).

same (dye/surface) ratio indicates that their surface characteristics are similar as regards sensitizing properties.

The constancy of the (dye/surface) ratio for emulsions of different types and of varying average grain size leads to the conclusion that the important factor in determining the concentration of dye necessary for optimum sensitizing is the degree of saturation of the surface of the halide with the dye. From these experiments it appears that the orientation or state of the adsorbed dye is the same with all of the emulsions studied, and hence that accidental irregularities in the crystals are not of major importance in determining concentration effects.

The question naturally arises as to what percentage of the sensitizer added to an emulsion is adsorbed to the silver halide. Experiments have shown that at least 99 percent of each of the sensitizing dyes used in the present experiments is adsorbed to the grain at the optimum sensitizing concentration. At concentrations of the dyes greater than optimal, the amounts of unadsorbed dye increase rapidly.

If it be arbitrarily assumed that the dye molecules lie flat on the surface of the halide, the data in Table I afford basis for estimation of the degree of surface saturation of the silver halide at the optimum sensitizing concentration. Dye II will serve as an example.

Dye II is an 8-alkylthiacarbocyanine. Estimates of the projective area of this molecule can be made by using the atomic radii values of Pauling and Huggins,[5] and assuming complete ionization of the halide. The estimate for dye II is 150A^2. Using this figure, together with the data of Table I, it is found that the projective area of the dye molecules adsorbed to one square centimeter of silver halide surface is nearly one square centimeter. This calculation is consistent with the view that at optimum sensitizing concentration, the surface of the silver halide grains in the emulsion is covered with a monolayer of dye molecules.

Sheppard and Crouch[1] and Sheppard, Lambert and Keenan[2] have calculated the numbers of surface bromide ions per dye molecule adsorbed at saturation for two cyanine dyes, Orthochrom

[5] L. Pauling and M. Huggins, Zeits. f. Krist. 87, 205 (1934).

T and Pinacyanol. The figure is 2.3 for Orthochrom T, and 1.7 for Pinacyanol. Bokinik[6] has reported a value of 10.0 for Pinacyanol. Similar calculations for the present experiments yield the figures: dye I, 10; dye II, 10; dye III, 20. The agreement with the result of Bokinik is good. The difference between the latter figures and those of Sheppard et al. may be explainable on the basis that saturation of the silver halide surface, as measured by effects on photographic sensitivity, is not the same as saturation obtained from a study of adsorption isotherms. This would be in confirmation of the results with Orthochrom T.[1] No direct comparisons can be made with the present data.

That the size of the dye molecule has a definite influence upon the concentration of dye at "sensitizing" saturation may be seen from the data of Table I. Dye II is a thiacarbocyanine, and dye III a thiadicarbocyanine. The number of moles of dye III which saturate the surface of the silver halide is about one-half that required of dye II. Since dye III is the larger molecule, this effect is in the right direction. In magnitude, however, the change in concentration is too large to be explained on a simple basis.

Evidence has been given[7] that cyanine dyes

TABLE I.

EMULSION	SURFACE cm²/cm³	DYE	OPTIMUM CONCENTRATION moles/cc emul. ×10⁸	$\frac{\text{Moles Dye}}{\text{cm}^2 \text{ surface}} \times 10^{11}$
1	400	I	3.6	9.0
2	480		3.8	7.9
3	580		5.2	9.0
4	660		6.0	9.1
5	840		7.2	8.6
6	950		9.0	9.4
7	1080		12.0	11.1
1	400	II	4.4	11.0
3	580		6.3	10.9
4	660		8.0	12.1
6	950		11.2	11.8
7	1080		12.6	11.6
1	400	III	1.9	4.8
3	580		2.3	4.0
4	660		2.9	4.4
6	950		4.8	5.0
7	1080		4.8	4.4

[6] J. I. Bokinik, Kino-Photo Res. Inst. Moscow 3, 14 (1935).
[7] J. A. Leermakers, B. H. Carroll and C. J. Staud, Communication No. 642 from the Kodak Research Laboratories this issue, p. 878.

adsorbed to silver halides are in an aggregated state. No strict definition of the term "aggregated" has been given, but, in general, the term is used to include those cases where two or more molecules interact with each other in such a way that the light absorption characteristics of the system are fundamentally different from those of the unassociated or simple dye molecule or ion. The sensitizing dyes used in this investigation have been found to be adsorbed in an aggregated state. Any statement concerning the orientation of the molecules at the surface of the halide must take cognizance of this phenomenon.

The fact that the calculations just described are in accord with the idea of a uniform, monomolecular layer of dye at the surface of the halide may result from coincidence. A second explanation is that the dye is adsorbed in multilayer patches, with a portion of the silver halide surface bare. A third possible structure of the system is that of a uniformly adsorbed layer, one molecule thick, with the dye molecules so oriented with respect to each other that definite interaction may take place, resulting in a shift of the absorption curve. The strict proportionality between concentration and surface is most easily explained on the basis of a uniform layer. To reconcile this with the evidence for aggregated adsorption is difficult, unless the structure is the third postulated above.

A Theory of Liquid Structure

JOSEPH HIRSCHFELDER, DAVID STEVENSON AND HENRY EYRING
Frick Chemical Laboratory, Princeton, New Jersey
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A simple model of the liquid is used to extend the equation of state previously obtained and to treat the process of fusion, viscous flow, and binary liquid systems. Our equation of state which applies to dense liquids has been fitted on to Happel's modification of van der Waals equation to give a single equation applicable over the entire range from gas to liquid. A liquid differs from a solid in that the surplus volume in one part of the liquid becomes available in another part without an activation energy appreciable as compared to kT. This communal sharing of volume gives rise to an entropy of fusion R modified, of course, if there are other structural changes. Other entropy changes arise from expansion, changes of librations into free rotations and from polymerization. Double molecules held together by van der Waals forces are considered quantitatively and used in the explanation of viscous flow and deviations of the equation of state at the critical point. An explicit expression is given for the osmotic pressure of a binary liquid mixture. "Holes" are used to complete the analogy between critical phenomena for a one component system and critical solution phenomena of binary liquids. In binary liquids the presence of a lower critical solution temperature above which two phases exist results from hydrogen (or analogous) bonds or bridges between unlike molecules which prevent free rotation. The critical mixing point coincides with the onset of free rotations which disrupt these bonds.

INTRODUCTION

IN this paper, we extend the theory of liquids developed in previous papers.[1-3] By using a simple model it is possible to compute the physical properties and to examine in detail the processes of melting and of vaporization. In developing a theory for the structure of liquids it is sufficient to focus our attention on the free energy or on the partition function since all of the thermodynamical properties can be readily computed

[1] Henry Eyring, J. Chem. Phys. **4**, 283 (1936).
[2] Roy Newton and Henry Eyring, Trans. Faraday Soc. **33**, 73 (1936).
[3] H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).