

*Studies on Fluorescence and Photosensitization in Aqueous Solution.*II.—*Fluorescence in Aqueous Solution.*

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In the present work we have attempted to make a general systematic survey of the effect of the addition of salts to fluorescent solutions. The effect of the presence of salts on fluorescent solutions was noticed by the earliest workers on the subject; Stokes,\* for instance, reports that while solutions of quinine in sulphuric, nitric, tartaric, succinic and phosphoric acid were fluorescent, the addition of the halogen hydracids and of sodium chloride extinguished the fluorescence. Similar observations were made by Buckingham† and recently by Desha, Sherrill and Harrison.‡

*Apparatus.*—We chose as measuring instrument the photoelectric cell. After preliminary experiments had shown that the inconstancy of the light source made it troublesome and inaccurate to measure the current from a single photo-cell illuminated directly by the fluorescent light, we finally adopted a differential method, the essentials of which are sketched below.

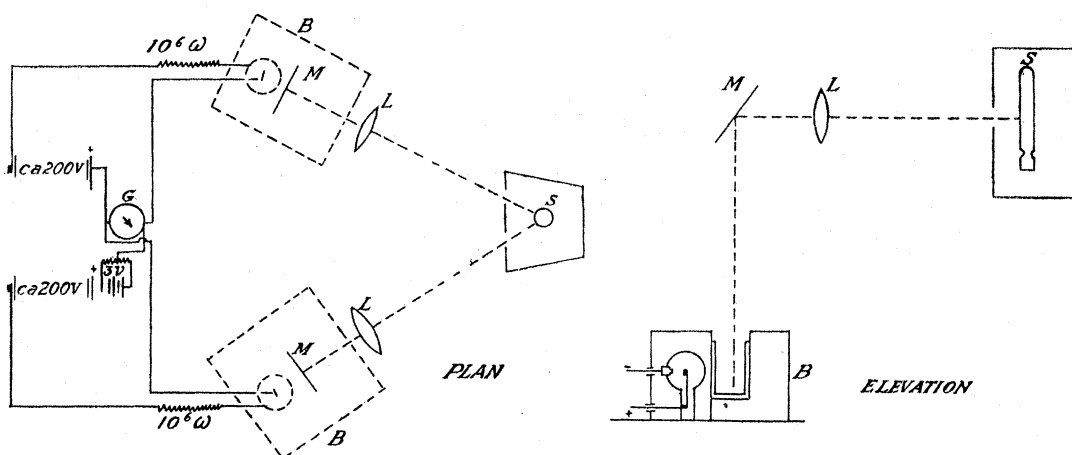


FIG. 1.—Apparatus.

\* 'Phil. Trans.,' vol. 142, p. 541 (1852).

† 'Z. Phys. Chem.,' vol. 14, p. 129 (1894).

‡ 'J. Amer. Chem. Soc.,' vol. 48, p. 1493 (1926).

Two gas-filled potassium surface photo-cells, with characteristics as similar as possible, were connected in opposite ways through the same galvanometer. In front of each cell was a rectangular glass vessel containing the fluorescent solutions, illuminated by equal beams from an upright mercury vapour lamp in a manner made sufficiently obvious by the diagrams. One solution, the "standard," was kept unchanged during an experiment; the other, the "working solution," was varied in the desired way. The lenses (L) and the mirrors (M) were of glass, so that the shortest wave-length reaching the fluorescent solution would be about 3300 Å. The glass vessels, which were as nearly as possible identical, fitted snugly into blackened brass containers enclosing them on three sides and fashioned so as to be placed readily and accurately in position in front of the photo-cells through a slit in the lid of the blackened wooden box (B). The current and voltage of the lamp were read by the necessary instruments, as were also the potentials applied to the photo-cell. The whole of the optical train and the measuring instruments were rigidly mounted on a board so as to prevent displacement of the parts.

This arrangement, although not a null method, and though still showing the effects of fluctuations in the intensity of the source when there is a considerable difference in the intensities of fluorescence in the standard and working solutions, is a great improvement on the direct use of a single cell in that it is most precise in the region where greatest precision is required, *i.e.*, for small differences in intensity between the standard and the working solution. The simpler method, on the other hand, is subject to greatest error in this region. We assured ourselves by preliminary measurements that the photo-currents yielded by the cells were linear functions of the intensity of illumination within the range with which we were concerned.

The procedure was as follows: The mercury lamp having become constant, the standard and working vessels, containing 25 c.c. of pure fluorescent solution and 25 c.c. of distilled water, were placed in front of the photo-cells and the potentials on the latter adjusted until the galvanometer reading was zero. The working vessel was then withdrawn and filled with 25 c.c. of fluorescent solution and 25 c.c. of the salt solution whose effect was being examined. When the working cell was replaced, if the salt had any effect the photo-currents no longer compensated, and the galvanometer showed a deflection. This was repeated for various concentrations.

The effects of the salt are expressed as percentage extinctions of the fluorescence due to the pure fluorescent solution. To obtain the value for the pure fluorescent substance we placed in the standard vessel 25 c.c. of fluorescent

material plus 25 c.c. of distilled water. In the working vessel was placed 25 c.c. of fluorescent solution to which was added 25 c.c. of salt solution of sufficient concentration to extinguish the fluorescence. Since the light reflected from the glass walls of the vessel and from the surface of the liquid would be the same in both cases, their effects would compensate, and, the presence of the salt not adding to the absorption in the wave-length region used in these experiments, the observed galvanometer deflection must then be a measure of the fluorescent light alone.

The salts used were chemically pure preparations which were submitted to at least one crystallization. The fluorescent substances were also purified, where possible by recrystallization, but in some cases the contamination of the commercial samples by inorganic salts was so great that only by preparing and isolating the substances by methods excluding the use of inorganic salts was a satisfactory product obtained.

As the work of Desha, Sherrill and Harrison (*loc. cit.*) has shown the importance of the hydrogen ion concentration in determining the fluorescence of certain solutions, we exercised due precautions to prevent changes in this factor. Stock solutions of the fluorescent materials were kept in waxed bottles protected against carbon dioxide from the air, and the salt solutions were also kept in waxed bottles.

### *Results.*

*Quinine Bisulphate.*—A 0.0025 molar aqueous solution of quinine bisulphate was used. The results are shown in Table I and fig. 2, in which the percentage extinction of the fluorescence is plotted against the concentration of the salt present in the solution; the concentrations are expressed in milli-equivalents per litre. In this series the positive ion, the potassium ion, was constant and the negative ion varied. It will be observed that the effect varies enormously with the salt; iodide, thiocyanate, bromide and chloride have a very great power of diminishing the fluorescence; sulphate, nitrate and fluoride have scarcely any effect, and oxalate and acetate occupy intermediate positions.

We now performed a series of experiments in order to determine whether any difference could be detected in the behaviour of various positive ions. The effects of the chlorides of Li, Na, K, Rb and La were examined. The result was rather surprising; within the limits of error, equivalent concentrations of three different salts produced identical extinctions in the fluorescence of quinine bisulphate solution. (*Cf.* fig. 2.)

According to all modern conceptions of the constitution of salt solutions,

Table I.—Extinction of the Fluorescence of Quinine Acid Sulphate by the Addition of Salts.

Salt concentration in milli-equivalents per litre.	Percentage extinction.										
	KNO <sub>3</sub> .	K <sub>2</sub> SO <sub>4</sub> .	KAc.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	KCl.*	KBr.	KCNS.	KI.	HgCl <sub>2</sub> .	AgNO <sub>3</sub> .	AgAc.
2.5	—	0.7	7.5	10.5	23.5	27.5	30.0	35.0	<0.5	4.5	8.0
5.0	—	1.2	14.0	19.5	38.0	42.5	45.0	53.0	0.8	6.5	15.5
10	—	2.2	24.5	35.0	55.5	61.5	63.5	72.0	1.5	8.5	22.0
15	—	3.1	33.5	46.5	66.0	71.0	72.5	81.0	2.2	10.0	36.5
25	0.5	4.8	45.0	59.5	76.5	81.5	83.5	89.5	3.5	12.0	51.0
50	1.0	8.5	56.5	75.0	84.0	90.5	91.5	96.0	5.7	13.5	72.0
100	—	10.8	62.0	81.0	92.5	95.0	96.0	100	10.1	22.5	—
500	<2.0	17.0	65.0	—	97.5	99.0	100	—	25.0†	—	—
1000	—	20.2	65.0	—	99.0	100	—	—	—	—	—

\* Same curve for LaCl<sub>3</sub>, LiCl, NaCl, RbCl.

† Concentration 400 milli-equivalents.

we must attribute the extinguishing of the fluorescence to the ions from the added salt. Since it is much more likely that the positive ions mentioned above

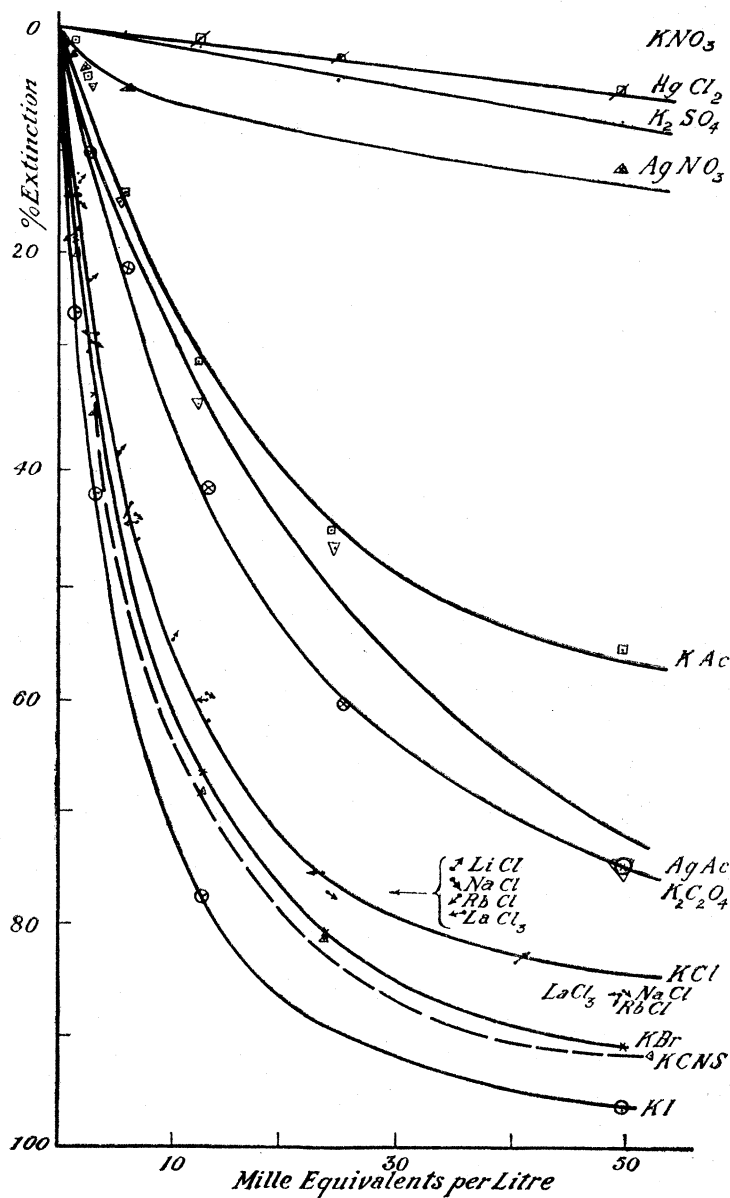


Fig. 2.—Effect of Salts on the Fluorescence of Quinine Bisulphate.

are almost entirely without effect on the fluorescence than that particles which differ so much in size and charge should have identical effects, we are led to

conclude that only the negative ion is effective. As will be mentioned later, other cases, of at first sight quite a different nature from this studied here, are known in which negative ions exert large influences and positive ions are nearly without effect.

In order to verify if the presence of ions was essential for the extinguishing of the fluorescence, we observed the effect of the addition of mercuric chloride, a "salt" which is known to be very slightly ionized in solution at concentrations at which the chlorides previously used are practically completely ionized. The curve is shown in fig. 2, from which it is evident that, under comparable conditions, the effect of mercuric chloride is much smaller than that of the other chlorides. The apparent degree of electrolytic dissociation of  $\text{HgCl}_2$  at 0.1 normal concentration is less than 1 per cent. A solution of KCl at 0.1 normal concentration diminished the fluorescence intensity by 92.5 per while the same concentration of  $\text{HgCl}_2$  diminished it only by approximately 10 per cent.\* Since the concentration of  $\text{Cl}^-$  ions in the latter solution was less than 0.001 normal, inspection of the curve shows that this was approximately the diminution to be expected, if the effect is due essentially to the chloride ions. Mercuric nitrate and acetate each react with quinine bisulphate with the formation of a yellow precipitate, hence it was impossible to observe the effect of mercuric ion from a highly ionized mercuric salt. The ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{La}^{+++}$ , each possess the rare gas structure of the outer electronic shell. The silver ion, however, has an outer shell of 18 electrons, and in order to find if this type of electronic configuration has a different effect on fluorescence, the light emitted by the quinine bisulphate in the presence of silver nitrate was measured. This substance was found to cause a distinctly greater diminution of fluorescence than potassium nitrate (see fig. 2). The effect of silver ion was confirmed on experiment with silver acetate, the curve for which was found to fall below that of potassium acetate.

Zinc and cadmium ions (from the nitrates) while possessing the same outer electronic configuration as silver ion, have no measurable effect on the fluorescence, which shows that this particular configuration is not in itself sufficient to account for the effect; magnesium nitrate also had no extinguishing effect.

A comparison of the curves for potassium acetate, silver nitrate and silver acetate suggests that the ionic effects may be approximately additive in those cases where both ions of a salt extinguish the fluorescence.

\* The difference between the effects of  $\text{HgCl}_2$  and KCl on the fluorescence of quinine bisulphate has also been noted by Buckingham.

Finally, as examples of non-electrolytes, solutions of cane sugar and of urea were added. The effect of both substances was very slight; a 0.95 normal solution of cane sugar diminished the fluorescence 2.86 per cent. and a 1.89 normal solution by 5.72 per cent. It was found, moreover, in a qualitative experiment that the inhibiting effect of potassium bromide on the fluorescence of quinine bisulphate was distinctly less when the solvent for the substances was a very concentrated, viscous solution of cane sugar, than when water was the solvent. These effects may perhaps be accounted for by the high viscosity of these solutions.

*Uranine.*—The substance was prepared in a pure condition by hydrolysis of purified fluorescein diacetate,\* which was in turn prepared from a good commercial sample of fluorescein. A solution of the disodium salt was used in the experiments, obtained by dissolving the acid in the necessary amount of sodium hydroxide solution. The concentration of the solution used was 0.00025 molar. The effects on this substance were much the same as on quinine bisulphate, but much higher concentrations were required to produce the same percentage of extinction. Solutions of potassium nitrate, sulphate, oxalate and chloride at concentrations as high as 1.00 normal had no measurable effect. The silver ion, again, had an unusually large effect in concentrations less than N/10, above which silver ion causes precipitation of the fluorescein. The results are given in Table II and fig. 3; the units used are the same as in the preceding table and figure.

Table II.—Extinction of the Fluorescence of Disodium Fluorescein by the Addition of Salts.

Salt concentration in milli-equivalents per litre.	Percentage extinction.			
	KBr.	KCNS.	KI.	AgNO <sub>3</sub> .
25	1.5	22.0	29.0	50.0
50	3.5	38.0	44.0	62.5
100	6.0	57.5	65.0	—
250	12.5	80.0	83.0	—
500	19.0	90.5	94.5	+
1000	27.0	93.0	98.9	—

\* Orndorff and Hemmer, 'J. Amer. Chem. Soc.,' vol. 49, p. 1272 (1927).

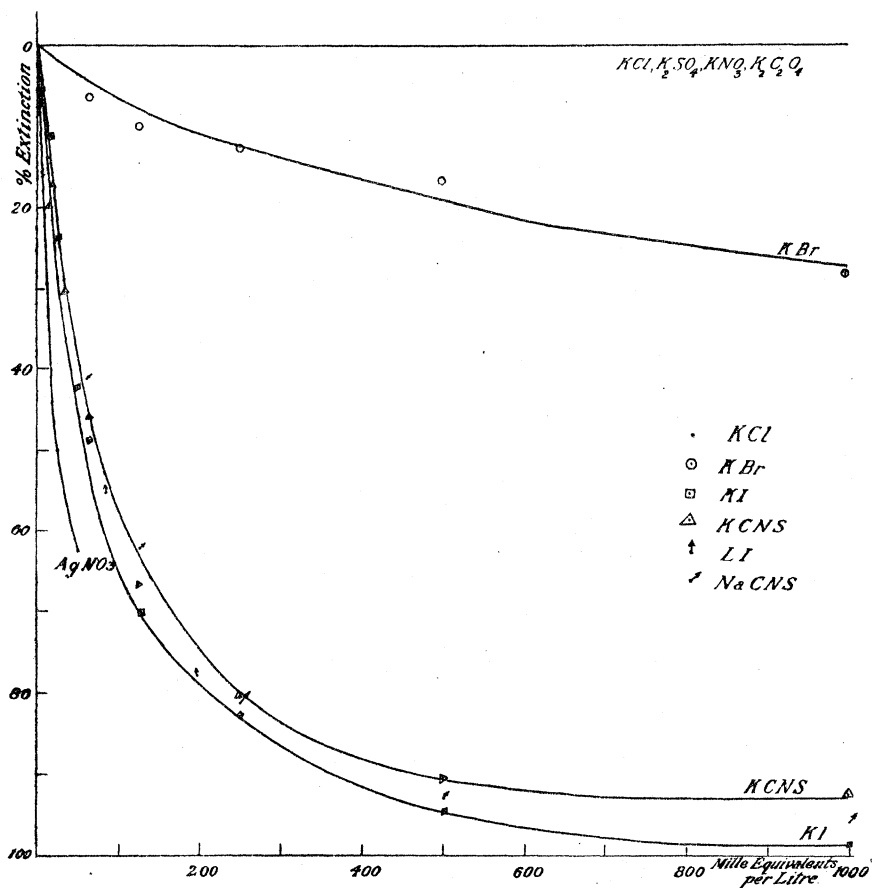


FIG. 3.—Effect of Addition of Salts on Fluorescence of Disodium Fluorescein.

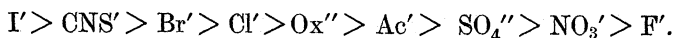
*Uranyl Salts.*—The uranyl salts are particularly interesting owing to their known photo-catalytic properties. A survey of some common orange salts showed that the sulphate and nitrate fluoresced quite brightly, with a green colour, the acetate less, and, significant from our point of view, the chloride very feebly. But the intensity of fluorescence even of the sulphate, which was chosen for investigation, is considerably feebler than that of uranine and is in a wave-length region to which the potassium surface photo-cell is not very sensitive. Accordingly, we made no effort in this case to determine the course of the extinction curve, but contented ourselves with ascertaining the order of the effect of various salts by noting the volume of salt solution which had to be added in order to diminish the fluorescence nearly to zero. A cell containing N/10 uranyl sulphate was placed in a box and illuminated by an intense beam of light from a carbon arc, which was passed through a condensing lens,



a water cell, and a blue glass filter. Salt solution was added from a burette until the fluorescence, observed perpendicularly to the exciting beam, practically disappeared. The results are collected below :—

<i>Salt added.</i>	<i>Volume required to reduce fluorescence to zero.</i>
Sodium fluoride N .....	Addition of a few cubic centimetres markedly increased the fluorescence. Further addition weakened it somewhat from the increased value, but the fluorescence was still bright after addition of 25 c.c.
Potassium sulphate N/1 .....	Addition of 25 c.c. had little effect.
Potassium nitrate N/10 .....	" "
Potassium acetate N/10 .....	" "
Potassium oxalate N/10 .....	28 c.c. reduced fluorescence to zero.
Potassium chloride N/10 .....	11 c.c. " "
Potassium bromide N/10 .....	1 c.c. " "
Potassium thiocyanate N/10 ..	0.5 c.c. " "
Potassium iodide N/10 .....	0.30 c.c. " "
Mercuric chloride .....	Addition of 30 c.c. 0.4 normal HgCl <sub>2</sub> diminished the fluorescence only by about 2/3.

In all these fluorescent substances there is a well-defined order in which negative ions exert an inhibiting effect on the fluorescence. Beginning with the most powerful inhibitor, the series is



There are, however, a number of fluorescent substances which are quite unaffected by some of the most powerful inhibitors of the above series, and largely influenced by the nitrate ion which has little effect on the three substances mentioned above. On investigating the effect of salts on the fluorescence of the sodium salts of beta-naphthol and 1-4 naphthalene disulphonic acid and on anthranilic acid, we found that potassium chloride, bromide and thiocyanate were without effect even to concentrations as high as 4 normal, iodide at high concentrations had in all cases a well-marked inhibiting effect, while potassium nitrate, one of the most inert ions for the former substances, was the most powerful inhibitant for these. In these compounds it is practically certain that the fluorescence originates in the aromatic nucleus. The

fluorescence of benzene vapour has been found to be little influenced by the addition of foreign gases,\* and evidently the stability of the fluorescent centre indicated by this fact persists in solution. The effect of the nitrate ion, however, is still unexplained.

*Discussion.*—In seeking for an explanation of the inhibiting effect of certain ions on fluorescence, we find that the most obvious possibility is that the added salt prevents the *excitation* of the fluorescent molecule to a condition in which it can re-emit its energy as radiation. This could happen in two ways: (1) If the salt possessed an absorption band in the neighbourhood of that of the fluorescent substance, it could act as an internal screen and prevent the excitation of the fluorescent molecules; or (2) some kind of “compound” could be formed between the added salt and the fluorescent substance which has not the properties, whatever they may be, which permit an energy-rich molecule to regain its normal state by the emission of radiation. We examined the absorption spectra of the salts at concentrations up to the greatest used in the fluorescence experiments and found that in no case did the absorption band extend into the region of the spectrum to which the fluorescent substance was exposed. The first possibility therefore falls to the ground. Information on the second was sought by examining the absorption spectrum of the fluorescent substance in the presence of the salt. For quinine, the small Hilger quartz spectograph E 31 was used, while for the visibly coloured substances the Hilger constant deviation glass spectograph was used. No material change in the absorption was observed, whence we conclude that the addition of the salt has produced no fundamental change in the constitution of the molecule of the fluorescent substance, and, further, that this molecule is still capable of undergoing, in the presence of the added salt, the transition from the normal to the excited state, the return from which, in the absence of the salt, is accompanied by the emission of radiation. The return to the normal condition must then take place through a radiationless transfer of energy to some other molecule in the system in the course of a “collision of the second kind.”

The diminished inhibiting power of ions in very viscous solutions is in complete accord with the interpretation in terms of collisions. Frances Perrin† has shown that with increased viscosity of the solvent, the concentration of fluorescent substance at which maximum fluorescence occurs will increase.

\* Pringsheim, in Geiger and Scheel's "Handbuch der Physik," vol. 23, "Quanten," chap. 5, p. 529.

† 'C. R.,' vol. 178, p. 2252 (1924).

Now we must ascribe the diminishing fluorescent power of a substance with increasing concentration to collisions of the second kind between the fluorescent molecules themselves, and evidently, with an increase in viscosity of the medium, the frequency of collision between fluorescent molecules is diminished. The same is true for collisions with other molecules. The effect of increased viscosity in diminishing the inhibiting powers of ions is thus of exactly the same nature as its effect in increasing the concentration at which maximum fluorescence of the pure fluorescent substance occurs.

For the three fluorescent substances under discussion the fluorescence must be ascribed mainly to fluorescent ions in solution. Quinine bisulphate, the sodium salt of fluorescein, and uranyl sulphate are typical salts and as such must be nearly completely ionized at the concentrations employed. It was therefore possible that the effect of the added salt might be immediately explicable in terms of the modern thermodynamic theory of ionic solutions, and, in particular, as an effect of the salt on the thermodynamic activity of the fluorescent ion. The absence, however, of differences in the effects of positive ions (except in the case of silver ion) is strongly against there being any direct effect of this kind; the trivalent lanthanum ion, for instance, ought to have had a markedly different effect from the monovalent rubidium ion, which is contrary to experience. In short, the evidence is against there being any direct relation between the different effects of ions on fluorescence and the following concepts in the theory of solution: (1) Differences in ionic size, whether in the hydrated condition or not; (2) difference in the activity coefficients of the individual ions of the salt added; (3) differences in the changes in the activity coefficients of the fluorescent ions produced by the added salts; (4) differences produced by the added salts in the degree of hydrolysis of the fluorescent salts.

The order in which ions suppress the fluorescence of the substances discussed in this report is very similar to the well-known lyotropic series of ions which appear in many diverse fields of physical chemistry. These salt series further resemble that which we have found to hold for fluorescence in that the differences between positive ions are frequently much less marked than those between negative ions.

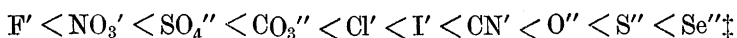
The parallelism between the lyotropic series as usually found and that observed in fluorescence is, however, not exact. Thiocyanate in the lyotropic series usually comes beyond iodide, while we have consistently found its effect on fluorescence to be between that of bromide and iodide; and nitrate, which in the lyotropic series occurs between bromide and iodide, is in ours at the

opposite end of the series from iodide. As we shall indicate, we believe these differences to be significant.

Heydweiler\* in 1913 pointed out that the order of the optical dispersions of negative ions for visible light was parallel to that of their precipitating power in colloid chemistry, *except that thiocyanate, instead of being beyond iodide, was intermediate between iodide and bromide.* The molecular refraction is expressed by the Lorenz-Lorentz equation

$$R = (n^2 - 1)/(n^2 + 2) \cdot M/\rho$$

in which  $n$  is a value of the refractive index for infinitely long wave-length found by extrapolation of the dispersion curve in the visible.  $R$  is a measure, in the first place, of the polarization produced in the atoms by the displacement of the electrons under the influence of the electro-magnetic field, and hence, in general, of the ease with which the electrons are displaced by electrical forces. The greater the refraction the greater the deformation produced in an atom or ion by the displacement of its outer electrons, or the looser the binding of the electrons. In recent years the work, particularly of Fajans and Joos, of Smyth, of Born and Heisenberg† and others, has emphasized the importance of the information to be obtained about the forces concerned in atomic and molecular structure from the study of atomic and ionic deformabilities. The order of the deformability of negative ions on the basis of these considerations is



In the following table is arranged the order in which the ions extinguish fluorescence; under each ion is a number which is a measure of its deformability. For simple ions this is the refraction for the D line; for the nitrate and sulphate, the ionic refraction per oxygen atom has been used, the electrons of the central N and S atoms respectively being so tightly bound as to contribute practically nothing to the refraction for visible light (Fajans and Joos, *loc. cit.*). The interatomic bindings in the acetate, oxalate and thiocyanate are too uncertain to allow an average value of the refraction per atom to have much significance as a measure of the binding of the electrons; but the

\* 'Ann. Physik,' vol. 41, p. 499 (1913).

† Fajans, 'Naturwiss,' vol. 2, p. 165 (1923); Fajans and Joos, 'Zeit. f. Physik,' vol. 23, p. 1 (1924); Smyth, 'Phil. Mag.,' vol. 50, p. 361 (1924); Born and Heisenberg, 'Z. Physik,' vol. 23, p. 388 (1924).

‡ Fajans, 'Naturwiss,' vol. 2, p. 165 (1923).

position of thiocyanate between bromide and iodide is indisputably given by the dispersion constants of these ions:—

F'	NO <sub>3</sub> '	SO <sub>4</sub> ''	Ac''	Ox''	Cl'	Br'	CNS'	I'
2.5	3.66	3.65			8.7	12.2		18.5

Dispersion constant =  $(\Delta n_\gamma - \Delta n_a)10^3$  for Br', 73; CNS', 100; I', 175.

$\Delta n_\gamma$  is a measure of the difference in refractive index between solution and solvent for the hydrogen line H<sub>γ</sub>, and  $\Delta n_a$  this quantity for H<sub>α</sub>. The value of the ionic refractions for some positive ions is also given for comparison.

Li•	Na•	K•	Rb•	La***	Zn**	Ag•
0.2	0.5	2.23	3.6	4	0.29	4.79

The high deformability of silver ion in comparison with the others is evident. It may also be mentioned that the absence of an effect of the positive ion in fluorescence is paralleled by a similar lack of contribution of positive ions to the dispersion in visible light; the dispersion for visible light of different salts with a common anion is with some exceptions practically independent of the cation.\*

A comparison of the deformability series and of the fluorescence series shows a parallelism too close to be accidental. We can state with certainty that the ions which exert the greatest inhibiting effect on fluorescence are those which are most deformable, *i.e.*, those in which the binding of the outer electrons is loosest.

It will be noticed that nitrate and thiocyanate ions are displaced in the Hofmeister and related series from the positions which they occupy in the deformability and fluorescence series. It is generally agreed that the action of the ions in the salting-out effect and in the related phenomena most probably takes place through their effect on the water dipoles in the solution. Now the nitrate and thiocyanate ions are likely to possess, in addition to the electric moment induced in the individual atoms by displacement of the electrons, a permanent dipole moment due to unsymmetrical distribution of charge over the ion as a whole. This would not contribute to the dispersion in the visible and hence would not appear in the deformability series which refers to the induced moment produced by electronic as distinct from atomic displacements; but might be an important factor in determining the effect of an ion on other permanent dipoles like water molecules. The identity of the ionic deformability series and the fluorescent series must be taken to indicate a type of interaction between the extinguishing ion and the fluorescent substance in which the outer

\* Heydweiler and Grube, 'Ann. Physik,' vol. 49, p. 653 (1916).

electrons of the former are primarily concerned; any nuclear vibration in the extinguishing ion is not affected by the fluorescent substance except in so far as it may be coupled with an electronic charge.

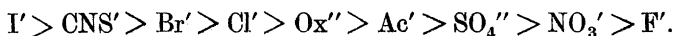
The fate of the energy transferred from the fluorescent molecule to the extinguishing particle in a collision of the second kind is a question still unanswered. Since, however, we find that the most deformable ions are most effective in extinguishing fluorescence, our first hypothesis would naturally be that the energy goes to produce a deformation in the ion, or, more precisely, that an outer electron is displaced from its normal position to a position in which the force binding it to the core is weakened. The chemical activity of the ion will therefore be increased, and we can see how fluorescent substances might photo-catalyse actions depending on the presence of an "acceptor" for the electron (*i.e.*, oxidation-reduction reactions); for instance, how quinine illuminated by light might catalyze the oxidation of the iodide ion.\* If the ions are really in some condition of strain such as we have imagined, their optical properties might be influenced by the addition of the fluorescent substance, and we have accordingly undertaken an examination of the refractive indices of mixture of salts and fluorescent substances in order to test the hypothesis.

*Summary.*

The effects of various salts on the fluorescence of aqueous solutions of three representative fluorescent substances, quinine bisulphate, sodium salt of fluorescein and uranyl sulphate have been quantitatively examined.

It has been found that:—

1. The extinguishing effect is associated practically entirely with the anion, silver ion being the only positive ion whose effect was noticeable.
2. The order of the extinguishing effect of the anions is



This series is identical with the deformability series of the ions.

The effects are interpreted in terms of the conception of collisions of the second kind, and the main result of the investigation may be summarised in the statement that the more deformable the electron orbits of the colliding particles, the more probable is a collision in which energy is transferred to it from particles in a higher quantum state than the normal.

\* Pinnow, 'Ber. D. Chem. Ges.,' vol. 34, p. 2528 (1901).

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