

ADSORPTION INDICATORS

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MECHANISM OF THE INDICATOR ACTION

As was first shown by A. Lottermoser (18, 19), the silver halides acquire a positive charge if the supernatant liquid contains an excess of silver salt, and a negative charge if the liquid contains the halide ion in excess. Silver bromide, for example, in contact with a solution containing an excess of silver nitrate fixes (adsorbs) silver ions on its surface, thus acquiring a positive charge. In the immediate neighborhood of the adsorbed silver ions an equivalent number of anions—in this case nitrate ions—must be adsorbed in order to maintain the electroneutrality of both liquid and solid phases. There is, therefore, a primary adsorption of silver ions and a secondary adsorption of foreign anions. Any anion of a dissolved silver salt when shaken with the silver bromide will be dragged to the surface by the adsorbed silver ions. According to the so-called Paneth-Fajans-Otto Hahn adsorption rule the adsorbability of the anion increases as a first approximation, with decreasing solubility of its silver salt and increasing deformability of the anions. The large organic dye ions—especially those of the fluorescein series—distinguish themselves by being easily deformable by silver ions in the adsorbed state and by the fairly slight solubility of their silver salts. These dyes, therefore, are strongly adsorbed by the silver halides, and give rise to the formation of an intensely colored adsorption layer.

The use of dyestuffs as indicators in precipitation analysis originated with K. Fajans (3, 4, 5, 6) and his collaborators. Since the color change at the end point is caused by an adsorption process, Kolthoff (9) coined the term "adsorption indicators." The principle on which the functioning of an adsorption indicator is based is clearly demonstrated by a simple experiment (2).

Take a liter of an aqueous solution of the sodium salt of eosin containing about 3 mg. of the salt. The latter is dissociated and partly hydrolyzed, and the solution shows the characteristic greenish fluorescence as well as a yellowish red color in transmitted light. Upon the addition of 2 cc. of 0.1

N silver nitrate solution, no appreciable change in the color takes place because the solubility product of the silver salt of eosin is not exceeded. If 0.5 cc. of 0.1 *N* alkali bromide solution is now added, an intense color change to red or red-violet occurs and the fluorescence decreases. The silver bromide formed is very finely divided and adsorbs silver ions which are present in excess in the solution. Simultaneously an equivalent number of eosin ions are adsorbed at the surface of the silver bromide particles, whereby the dye ions are deformed, the process being accompanied by an intense change of the color to red. On further careful addition of bromide, more silver bromide is formed and the color of the suspension deepens, until the equivalence point is passed. At this point all the adsorbed silver is removed from the surface and the adsorbed eosin ions return to the solution. The silver bromide particles are thereby decolorized, and the solution regains its yellowish red color and fluorescence. As soon as the solution contains an excess of bromide ions the latter will be primarily adsorbed and the eosin will remain in the solution. The color change is reversible.

Instead of working with an acid dye it is also possible to use a suitable dye cation as an adsorption indicator. The order of the color change is then just the reverse of that described in the above example. If a few drops of a dilute solution of the basic dye, Rhodamine 6G, are added to a silver solution, the color does not change upon careful addition of bromide. The silver ions are primarily adsorbed and prevent the adsorption of the dye cations. As soon as all the silver is precipitated and a slight excess of bromide is present, the bromide ions are adsorbed, and attract an equivalent amount of dye cations to the surface, resulting in an intense color change of the suspension to red.

The classical interpretation (3, 4, 5, 6) of the adsorption indicator mechanism therefore is as follows: A dye anion is not adsorbed by a silver halide as long as halide ions are present in excess in the supernatant liquid. With a slight excess of silver ions part of the latter are adsorbed by the silver halide, which results in an equivalent adsorption of the dye anions. The reverse is true with a dye cation as adsorption indicator. The adsorption of the dye is usually accompanied by an intense color change, which indicates the equivalence point. Although very desirable, it is not strictly necessary that a change in color shall occur at the end point. As long as the indicator is in the unadsorbed state the supernatant liquid shows the color of the dissolved dye and the precipitate is white (silver chloride) or yellowish (silver bromide and iodide); when the strong adsorption of the dye takes place the supernatant liquid is decolorized and the precipitate assumes the color of the adsorbed dye. Berry and Durrant (1) made use of this fact in the application of tartrazin as an indicator in the titration of silver with bromide or chloride. The precipitate has a yellow color as long

as there is an excess of silver in the solution; at the end point the dye is replaced by halide ions and goes into solution, imparting a yellowish green color to the latter. According to my experience the method gives satisfactory results, but one must titrate very carefully, since the color change is not strictly reversible. The use of diphenylamine blue (oxidized diphenylamine) by Lang and Messinger (17) for the titration of strongly acid chloride solutions with silver nitrate is based on the same principle. The basic dye is adsorbed with a green color in the presence of an excess of chloride and the solution is colorless; at the end point a desorption occurs and the solution becomes violet. If the titration is performed carefully, satisfactory results are obtained with 0.02 to 0.1 *N* chloride solutions; with 0.01 *N* or more dilute solutions, however, I obtained a vague end point which occurred too late.

Upon closer examination it appears that the classical interpretation of the mechanism of the adsorption indicator action is not entirely adequate to explain the experimental facts. A dye anion should not be adsorbed when there is an excess of halide in the solution, but should be dragged to the surface with silver ions when the latter are in excess. The reverse should be true for a dye cation. However, various cases are known in which an adsorption of a dye anion occurs when there is an excess of halide ion in the solution. Eosin, for example, cannot be used as an adsorption indicator in the titration of chloride; the dye ions are strongly adsorbed by the suspended particles from the very beginning of the titration, in spite of the presence of a large excess of chloride ions. Therefore no pronounced color change is noticeable at the end point, although the adsorption of the eosin increases with an excess of silver and decreases with increasing amounts of chloride. But even with indicators which are quite useful for the detection of the end point, a similar behavior is generally noticed. For example, phenosafranine—a basic dye—is quite useful in the titration of silver with bromide. Still a slight adsorption of the dye takes place when silver ions are in excess, the adsorption increasing with decreasing silver-ion concentration. At the equivalence point, and especially with a slight excess of bromide, a sudden increase of the adsorption of the dye occurs and a distinct color change is observed. The case is also clearly demonstrated by the behavior of methyl violet—a basic dye—in the titration of silver with chloride (7). In weakly acid medium with an excess of silver ions the suspension in the presence of the dye has a greenish color (in neutral medium, blue); with an excess of chloride ions all the dye is adsorbed on the particles, imparting a pink color to the latter. However, a marked adsorption of the dye occurs even when silver ions are still in excess. Hodakow titrated a mixture of 8 cc. of 0.02 *N* silver nitrate and 5 cc. of a 0.004 per cent methyl violet solution with 0.02 *N* sodium chloride

and determined the amounts of dye adsorbed at various stages during the titration. In figure 1 the percentage of dye adsorbed (ordinate) is plotted against the excess of silver and chloride respectively in the neighborhood of the equivalence point. There is a sudden increase in the amount of methyl violet adsorbed at the equivalence point, the adsorption curve resembling a potentiometric titration curve. The smaller the amount of indicator used the more pronounced is the inflection at the equivalence point.

The above phenomenon, of a dye being already markedly adsorbed in the presence of a lattice ion of the same electrical charge, is not easily

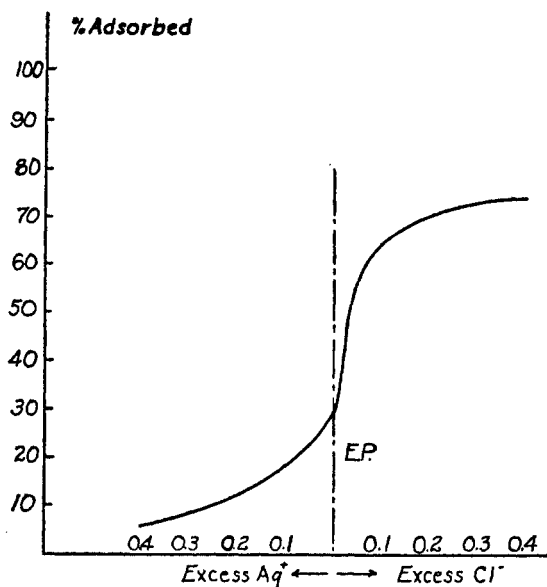
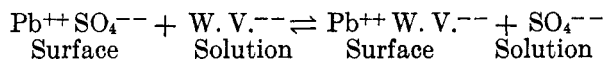


FIG. 1. Adsorption of methyl violet by silver chloride

explained on a classical basis. In the first place it should be clearly understood that the indicator action is attributed to a secondary adsorption of the dye, the lattice ion of opposite sign being primarily adsorbed. If, on the other hand, the dye is adsorbed when there is an excess of lattice ions of the same sign in solution, on the classical basis we should be forced to infer that in the latter condition a primary adsorption of dye ions occurs. A silver halide, for example, adsorbs its own ions preferentially and is thereby peptized. This adsorption is supposed to take place at active spots on the surface. It cannot be expected that the large dye ions, which do not fit in the lattice of the silver halide, can replace the halide or silver ions at the active spots. If this were true, one would expect that dye ions,

which exert such a strong replacing effect upon adsorbed lattice ions of the same electrical charge, should exert at least as strong a peptizing effect upon the particles of the precipitate as the lattice ions do. This is contrary to the behavior of colloidal solutions¹ (16).

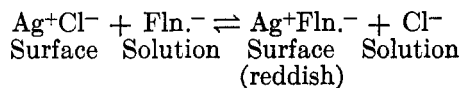
The fact that dye ions can be adsorbed although an excess of lattice ions of the same sign is in the solution, indicates that we are dealing here with an exchange adsorption, involving dye ions and lattice ions of the same sign, in the surface of the particles. Such an exchange was first described by Kolthoff and Rosenblum (12) and has been substantiated by experiments of Kolthoff and Sandell (13) and of von Fischer and Ch. Rosenblum (14). If well-aged lead sulfate, for example, is shaken with a wool violet solution, the dye ions exchange with sulfate ions on the surface of the lead sulfate:



There is a competition between wool violet and sulfate ions to be fixed on the surface of the lead sulfate. An excess of lead ions in the solution favors the adsorption of the dye, and an excess of sulfate ions naturally promotes the adsorption of the latter at the expense of the dye. The general shape of the adsorption curve of wool violet by lead sulfate therefore resembles that of an adsorption indicator which is adsorbed at both sides of the equivalence point (figure 1).

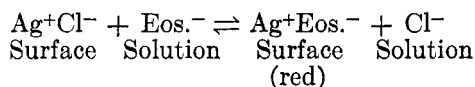
The behavior of adsorption indicators is then easily explained on the basis of an exchange adsorption between lattice ions and dye ions of the same sign at the surface of the particles.

If silver chloride which does not contain either an excess of adsorbed silver or of adsorbed chloride (equivalent body) is shaken with a solution of the sodium salt of fluorescein (Fln.⁻), a slight adsorption of the latter takes place, and an equivalent amount of chloride ions



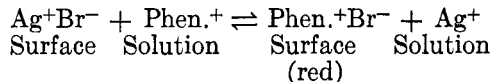
¹ Actually a positively charged sol shows very small flocculation values with suitable acid dyes, and negatively charged sols are easily flocculated by suitable basic dyes. This shows that the secondary adsorption at active spots is very pronounced and results in the destruction of a double layer. It is possible that an excess of dye will replace lattice ions of the same sign in the surface of the particles. The chemical composition of the surface layer is then entirely changed, and it is quite possible that an excess of dye may peptize the particles again, since the dye ion in the solution is identical with that fixed in the surface layer. This would explain the occurrence of the so-called "irregular series" in colloid chemistry. This point will be further tested experimentally.

are sent into solution. In this particular case there is only a slight replacement of chloride ions by fluorescein ions; in the presence of a slight excess of silver, however, the chloride-ion concentration decreases sharply, favoring a marked replacement of chloride ions in the surface by dye ions, resulting in a reddish coloration of the precipitate. Fluorescein therefore is a very suitable adsorption indicator in the titration of chloride. Eosin, on the other hand, cannot be used for this purpose, since it is adsorbed much more strongly than fluorescein ions. If an equivalent body of silver chloride is shaken with an eosin solution the precipitate is strongly colored:



The adsorption of eosin is favored by an excess of silver and is decreased by an excess of chloride. The dye is a very suitable indicator for the titration of bromide and iodide, as is easily understood by the above interpretation.

The behavior of basic dyes as adsorption indicators is similar to that of acid dyes. The basic dye competes with the silver ion in being adsorbed at the surface of the silver halide. If phenosafranine (a basic dye) is shaken with silver bromide a slight exchange takes place:



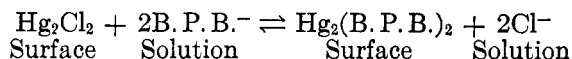
An excess of silver ions decreases this adsorption very strongly; an excess of bromide ions favors the exchange, resulting in a marked deepening of the color of the precipitate. In our interpretation, therefore, we do attribute the color change not to a secondary adsorption of the dye at active spots (Fajans et al. (3, 4, 5, 6)), but to an exchange adsorption involving lattice ions and dye ions of the same electrical sign on the entire surface of the precipitate. The secondary adsorption may be partly responsible for the color change, but does not explain why the dye is adsorbed when there is still an excess of lattice ions of the same sign as that of the indicator ions in the solution.

In the titration of chloride with fluorescein, a striking change in the appearance of the precipitate occurs at the point of distinct color change. The flocculent precipitate suddenly becomes grainy and consists of a large number of red globular particles. At this point the composition of the surface layer of the particles partly changes from silver chloride into silver fluoresceinate.

Another phenomenon in harmony with our interpretation is the fact

that the adsorption of a suitable dye by freshly formed silver chloride does not change with long periods of shaking. If the dye is added at various time intervals after the precipitation of the silver chloride, its adsorption decreases very rapidly. The adsorbed dye therefore protects the fresh precipitate from aging (agglomeration of the particles), a phenomenon similar to the inhibition of recrystallization of lead sulfate by adsorbed wool violet (14).

Experiments were performed to substantiate the above view of the mechanism of the action of adsorption indicators. In a study with W. Larson—details of which are to be published later—of the titration of chlorides and bromides with mercurous nitrate, using various adsorption indicators, it appeared that bromophenol blue was very suitable. Chloride was titrated potentiometrically with the mercurous solution exactly to the equivalence point. Then a measured volume of bromophenol blue solution was added quickly, and the change of the potential observed. It appeared that when the precipitate became colored the change in potential indicated the formation of an excess of chloride in the solution.



Experiments were also made with freshly precipitated silver chloride. The supernatant liquid, containing an excess of silver, was poured off immediately after precipitation, and the precipitate was quickly washed until no silver could be detected in the wash water. The ten-minutes old washed precipitate was suspended in a little water, and the silver-ion concentration measured potentiometrically. The potential corresponded exactly to that of a saturated solution of silver chloride in water. From this measurement and from the change of the potential upon careful addition of 0.01 *N* sodium chloride solution, it could be definitely inferred that the washed precipitate did not contain any adsorbed silver salt. Washed precipitates prepared in a similar way were shaken for 2 minutes with 10 cc. of a 0.02 per cent solution of the sodium salt of fluorescein in water. The precipitate turned orange-pink; upon washing with water it remained pink and acquired a much more intensive color upon addition of some fluorescein with a few drops of silver nitrate. The fluorescein solution with which the precipitate had been shaken was filtered and acidified with sulfuric acid, and the fluorescein removed by extraction with ether. The remaining aqueous solution was tested with silver nitrate, and the turbidity compared with a blank from an identical volume of saturated silver chloride solution containing the same amount of dye which had been treated in a similar way. The turbidity obtained with the dye solution which had been shaken with the silver chloride (0.7 g.) was much stronger than that

of the blank. The result shows very definitely that chloride ions in the surface of the silver chloride had been replaced by fluorescein ions, thus causing an excess of chloride to be present in the solution. A much stronger effect is obtained if the sodium salt of eosin is used instead of fluorescein. The former dye is much more strongly adsorbed by silver chloride and gives a much more pronounced exchange.

INFLUENCE OF VARIOUS FACTORS UPON THE SUCCESSFUL APPLICATION OF ADSORPTION INDICATORS

1. Choice of indicator

In the first place an adsorption indicator should have the property of being strongly adsorbed at the equivalence point, or with the slightest trace of excess of lattice ion of opposite electrical sign, and not at all or only very slightly adsorbed in the presence of excess of the lattice ion of the same sign. In other words, the adsorption curve during the titration should have a shape somewhat similar to a potentiometric titration curve. Preferably the indicator in the adsorbed state should show a color distinctly different from that in the liquid phase. The light sensitivity of the silver halides is greatly increased by adsorbed dye. These titrations therefore should not be carried out in direct sunlight.

2. Size of the precipitate

Since the adsorption of the indicator is limited to the surface layer, successful results can be expected only when the precipitate formed has a large surface development. This is the case with the silver halides, mercurous chloride, and mercurous bromide. In the titration of halides with silver or mercurous nitrate, the slightly soluble halide stays in colloidal solution until near the end point, when flocculation occurs. As long as the particles stay in colloidal solution they do not agglomerate and they have a large surface development. After flocculation occurs a rapid aging takes place by the formation of agglomerates, resulting in a decrease of the total surface of the precipitate. This explains why the presence of flocculating electrolytes in the solution interferes with the sharpness of the titration (20). This is especially the case in the titration of bromides with eosin as indicator. In the absence of flocculating electrolytes a beautiful color change is found at the equivalence point, especially if the titration is made in the presence of acetic acid. If by the presence of electrolytes (especially cations of higher valence exert this effect) the silver bromide flocculates long before the equivalence point is reached, it is found that the precipitate is slightly colored, thus making the color deepening at the end point less intense. The color at the surface of the precipitate in the presence of

an excess of bromide must be attributed to an exchange between bromide and eosin ions on the surface of the silver bromide. This exchange is inhibited as long as the particles remain in colloidal solution and contain the peptizing bromide ions at active spots. This view is substantiated by the following experiments. Fifty cc. of 0.02 *N* potassium bromide solution was titrated in the presence of acetic acid with eosin as indicator. The precipitate remained in colloidal suspension until 9.9 cc. of 0.1 *N* silver nitrate had been added; at 10.00 cc. the entire precipitate was flocculated and had a marked red color. The experiment was repeated, but after adding 9.6 cc. of 0.1 *N* silver nitrate, 5 cc. of 1 *N* barium nitrate were added. The silver bromide flocculated immediately and had a salmon-pink color. The deepening of the color at the equivalence point was much less pronounced.

3. Influence of the hydrogen-ion concentration

In general, hydrogen ions exert a flocculating effect and therefore an excess of acid will interfere with the detection of the end point (compare section 2). In various cases the hydrogen ions exert a specific effect upon the indicator, and the titration may be rendered impossible even in very slightly acid medium. Fluorescein, for example, is a very weak acid having an ionization constant of the same order as that of phenolphthalein. Hydrogen ions will remove the indicator ions by the formation of undissociated fluorescein. The titration therefore must be carried out in neutral medium. If the ionization constant of the indicator is increased by the introduction of chlorine, the titration can be carried out in weakly acid medium. Thus Kolthoff, Lauer, and Sunde (11) prepared dichlorofluorescein and found it very useful for titration of chloride at a pH smaller than 4. Eosin and diiodofluorescein and various other acid dyes, such as bromophenol blue, chlorophenol red, and metanil yellow, can be used in very weakly acid medium.

4. Dilution of the halide to be titrated

Bromides and iodides can be titrated with eosin as indicator in solutions even more dilute than 0.001 *N*. The silver halides separate in a very finely divided form, and the indicator is strongly adsorbed. Chlorides, on the other hand, cannot be titrated with fluorescein as indicator at dilutions greater than 0.005 *N*. Since the solubility of the silver chloride is much greater than that of the bromide or iodide, it separates in a coarser form having a smaller surface. In addition the adsorbability of the fluorescein ion is much smaller than that of eosin. Dichlorofluorescein is more strongly adsorbed than fluorescein and can, therefore, be used for the titration of more dilute chloride solutions (0.001 *N*) (11).

5. *Influence of organic solvents*

Addition of organic solvents has two pronounced effects upon the titration: (a) The solubility of most inorganic precipitates is decreased by the addition of an organic solvent. The precipitate, therefore, will separate in a much finer form as a result of an increased supersaturation. This should have a favorable effect. (b) On the other hand, the adsorbability of the indicator ions is changed—as a rule decreased—by addition of an organic solvent to the aqueous phase.

At my request Henry Yutzy in this laboratory has made several experiments in which chloride was titrated with silver nitrate in mixtures of water, alcohol, and glacial acetic acid, using eosin as an indicator. Eosin, as we have seen, cannot be used for the chloride titration in purely aqueous medium. It appeared that chloride can be titrated with this indicator, if the medium at the end point contains 10 to 25 per cent of alcohol and approximately 30 per cent of acetic acid. Although of relatively little practical importance, the results show definitely that the organic solvents favor adsorption of the chloride ions at the surface of the silver chloride at the expense of the eosin. It may be expected that alcohol and organic solvents will have a favorable effect in those cases when the primary precipitate separates in a microcrystalline form, having a small surface. If good adsorption indicators could be found for barium sulfate, calcium oxalate, lead sulfate, etc., successful titrations probably could be made in the presence of alcohol.

As a matter of record it may be mentioned that Kolthoff and Willman (15) applied eosin as an indicator in the titration of bromide with silver in glacial acetic acid as a solvent.

6. *Influence of the temperature*

Increase of the temperature quite generally will have an unfavorable effect for the following reasons: (a) Usually the solubility of the precipitate increases with the temperature, and therefore it will separate in a coarser form than at low temperature. (b) The speed of aging, resulting in a decrease of the surface of the fresh precipitate, is much greater at higher temperature. (c) The adsorbability of the indicator ions, as a rule, decreases with increasing temperature.

7. *Fractional separations*

With suitable adsorption indicators and under the proper conditions it is possible to determine an ion in the presence of another which also yields a slightly soluble salt with the reagent. According to Fajans and Wolff (5), iodide can be titrated in the presence of chloride with diiodofluorescein,

dimethyl diiodofluorescein, and rose bengal as indicators. Kolthoff (8) titrated small amounts of iodide in the presence of much chloride by adding ammonium carbonate and using eosin as an indicator.

OTHER APPLICATIONS OF ADSORPTION INDICATORS

It is beyond the scope of this paper to discuss or review all volumetric procedures with adsorption indicators.² The most important applications are in the titration of halides with silver or mercurous mercury or the reverse processes. In other cases the working conditions are very limited. G. E. Noponen in this laboratory has investigated the titration of lead with potassium ferrocyanide, using sodium alizarinsulfonate as indicator; the end point was vague.

Slightly better results were obtained in the titration of lead with potassium chromate, using orthochrome T as indicator, but the method has little practical significance. The determination of lead with oxalate, in which eight different adsorption indicators were tried, was not very successful either.

In qualitative analysis adsorption indicators are sometimes advantageously applied in the detection of traces of elements. The detection and the colorimetric determination of magnesium with titan yellow, of beryllium with curcumin and 1, 2, 5, 8-oxyanthraquinone, of aluminum with the latter reagent and with alizarin, aurintricarboxylic acid, purpurin, etc., are based on this principle.

By its behavior as an adsorption indicator it can be determined whether a dissolved dye is present as a cation or an anion. It was found, for example (10), that methyl red in neutral medium (yellow color) is adsorbed in the red form by silver thiocyanate containing an excess of silver ions. The dye therefore is present in the anion form in the solution. In 1 *N* sulfuric acid, on the other hand, the dye is strongly adsorbed by a precipitate containing an excess of thiocyanate. In strongly acid medium, therefore, the dissolved methyl red is present in the cation form. In a similar way it can be shown that various sulfonphthaleins in strongly acid medium are mainly present as cations, and in weaker acid or neutral medium as anions.

SUMMARY

1. The mechanism of the action of an adsorption indicator is to be attributed to an exchange between dye ions and lattice ions of the same electrical sign in the surface of the precipitate.

* A complete review (up to 1929) is given in I. M. Kolthoff's *Volumetric Analysis*, Vol. II, translated by N. H. Furman. John Wiley and Sons, New York (1929).

2. The various factors affecting the successful application of adsorption indicators to volumetric procedures have been discussed.

3. Applications of adsorption indicators to the qualitative detection and colorimetric determination of traces of elements have been mentioned. By examining the behavior of dyestuffs as adsorption indicators, it is possible to decide whether they are present in the form of cations or of anions.

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