[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE USE OF DICHLOROFLUORESCEIN AS AN ADSORPTION INDICATOR FOR THE ARGENTOMETRIC TITRATION OF CHLORIDES

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Introduction

K. Fajans and his collaborators[1] have recently described a new type of indicator for the argentometric titration of halides to which the name of adsorption indicator was given. The substances used as indicators are not sensitive to dissolved silver or halide ions, but change their color at the equivalence point where colored compounds are formed on the precipitate due to adsorption phenomena. Other investigators[2] have confirmed the results of Fajans and his collaborators and obtained accurate results with the new type of indicator. Fluorescein has been used as the indicator in the titration of chlorides but its application is limited. Good results are obtained only if the chloride concentration is greater than 0.005 N and if the solution has a neutral or weakly alkaline reaction. Other indicators which were applicable in weakly acid solutions have been found, but the color changes are less distinct than is the case with fluorescein.[3]

When chloride ions are titrated with silver nitrate, the silver chloride adsorbs silver ions at the equivalence point or better slightly beyond. The "silver body" then adsorbs fluorescein ions from the solution and dark red silver fluoresceinate is formed on the surface of the precipitate. Fluorescein possesses a weak acidic character; in weak acid solution the concentration of fluorescein ions is so small that the color change no longer takes place. The introduction of halogen atoms into the fluorescein molecule has two effects: the dissociation constant is increased and the adsorbability of the dye anions by the silver halide increases. It would therefore be expected that substances with a stronger acid character than fluorescein could be used as indicators in weak acid solutions. On the other hand, the stronger adsorbability might either interfere or be favorable. During the titration of chloride ions with silver nitrate the silver chloride formed at the beginning of the titration adsorbs chloride ions. In the presence of the anions of the indicator, the latter also have a tendency to be adsorbed and if their adsorption is larger than that of the chloride ions, the color change will take place during the early stages of the titra-

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[1] (a) Fajans and Hassel, *Z. Elektrochem.*, **29**, 495 (1923); (b) Fajans and Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

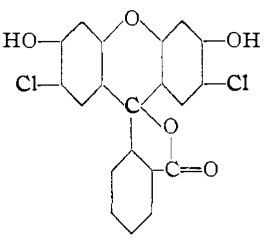
[2] W. Böttger and K. O. Schmidt, *ibid.*, **137**, 246 (1924); I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **70**, 369 (1927).

[3] Kolthoff, *ibid.*, **71**, 235 (1927).

tion. Such is the case when eosin is used. Therefore this indicator cannot be used in the argentometric determination of chlorides, even though it gives highly accurate results when bromides, iodides and thiocyanates are titrated even in weak acid solutions. On the other hand, stronger adsorbability may exert a favorable influence in that it might make possible the titration of very dilute chloride solutions. In this case, the absorption of fluorescein ions is too small and no color change is observed.

The indicator in order to be better than fluorescein must have a larger dissociation constant and greater adsorbability than fluorescein. The adsorbability, however, must not be so great that it replaces the chloride ions from silver chloride. It was expected that dichlorofluorescein would serve the purpose, and as is shown in the following part of this paper it proved to be an excellent indicator for the titration of chlorides under different conditions. That dichlorofluorescein is a stronger acid than fluorescein can easily be shown by the fact that its color change interval from green-yellow (without fluorescence) to a strongly fluorescent yellow-green lies between *P*H 3 to 5; so that the dissociation constant is of the order of 10^{-4}.

Dichlorofluorescein.—Dichlorofluorescein was prepared by condensing monochlororesorcinol with phthalic anhydride. It was purified by converting it into the diacetate and then saponifying the diacetate with alcoholic potassium hydroxide, in accordance with the procedure used by Orndorff and his collaborators.[4] Dichlorofluorescein prepared from dichlorophthalic anhydride and resorcinol has been known for some time, but dichlorofluorescein containing two chlorine atoms in the "resorcinol part" of the molecule has not been described hitherto. The most probable formula for the dichlorofluorescein here described is that indicated. All attempts to prepare a dichlorofluorescein by the direct chlorination of fluorescein failed.



Experimental

The Preparation of Dichlorofluorescein

Monochlororesorcinol was first prepared by the action of sulfuryl chloride on resorcinol: 100 g. of resorcinol was dissolved in 360 g. of absolute ether. This solution, placed in a 2-liter round-bottomed flask fitted with an efficient reflux condenser, was then treated with 120 g. of sulfuryl chloride (added dropwise). This operation was carried out in a well-ventilated hood. After the addition of the sulfuryl chloride the ether was distilled off on a steam-bath. After the low-boiling material had been removed completely, the residue was subjected to vacuum distillation. Since monochlororesorcinol has a lower boiling point than resorcinol, the unchanged resorcinol was separated by vacuum frac-

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[4] Orndorff and Hemmer, This Journal, 49, 1275 (1927), and various other studies by Orndorff and co-workers.

tional distillation. The monochlororesorcinol distilled at 131° under a pressure of 6–7 mm. It was analyzed for chlorine by the method of Carius.

Anal. Calcd.: Cl, 24.54. Found: Cl, 24.50, 24.72.

Dichlorofluorescein.—Ten grams of phthalic anhydride mixed intimately with 19.7 g. of monochlororesorcinol was heated to 160° in an iron crucible by means of an oil-bath. Five grams of anhydrous zinc chloride, finely ground, was then added with stirring during a period of about ten minutes. The temperature was then raised to 175–180° and maintained for about two and one-half hours. After cooling, the reaction product was ground and then boiled for fifteen to twenty minutes in dilute hydrochloric acid (10 cc. of concd. acid to 200 cc. of water) and filtered.

The precipitate was dissolved at room temperature in a saturated aqueous solution of sodium bicarbonate, filtered, heated to boiling and then acidified with hydrochloric acid (approx. 4 *N*). After cooling and filtering, the precipitate was refluxed with acetic anhydride for several hours (2 g. of crude dichlorofluorescein to 10–12 cc. of acetic anhydride). The diacetate crystallized out upon cooling. It was filtered off and the above process repeated four or five times. The diacetate (almost colorless) was then digested with a small amount of alcohol, cooled and filtered. After drying for several hours at 100° it was analyzed for chlorine.

Anal. (Carius). Calcd.: Cl, 14.64. Found: Cl, 14.49, 14.98.

The diacetate was then saponified by refluxing 2–3 g. with alcoholic potassium hydroxide (6–7 g. of base in 40 cc. of alcohol) for two hours. Water was then added, the solution transferred to a distilling flask and the alcohol removed by distillation. The solution was then filtered (if necessary), heated to boiling and acidified with hydrochloric acid. An ochre-colored product was obtained.

Application to Halide Titrations

Indicator Solution.—One-tenth gram of the indicator was dissolved in 60 cc. of alcohol, 2.5 cc. of 0.1 *N* sodium hydroxide was added and the volume of the solution was then made up to 100 cc. with distilled water. An aqueous alcoholic solution (60–70%) of approximately the same concentration of unneutralized indicator may also be used.

Procedure.—For every 10 cc. of chloride solution 2 drops of indicator are added and the titration is started with silver nitrate. The silver chloride remains in colloidal solution which, near the end-point, has a yellowish-orange appearance. About 0.5% before the equivalence point the silver chloride flocculates in voluminous flocks; the titration is then conducted carefully. At the end-point the silver chloride suddenly turns dark red.

Note 1.—Concentrated chloride solutions should be diluted to a salt-concentration of about 0.025 *N*. In this case the color change is extremely sharp. In six titrations 100 cc. of 0.025 *N* sodium chloride required 25.00 to 25.03 cc. of 0.1 *N* silver nitrate.

Note 2.—Even very dilute chloride solutions can be determined satisfactorily. In these cases it is recommended not to add more than 2 to 4 drops of indicator to 50 cc. of solution.

A 0.01 *N* chloride solution can be titrated with an accuracy of 0.5%. Near the end-point the liquid appears more brownish; the titration is finished when the color changes to distinct orange. One or two drops of 0.01 *N* silver nitrate in excess deepens the color to pink or reddish.

If the end-point is passed the excess of silver nitrate can be titrated back with a chloride solution of known constant. This reverse titration should be made immediately after the addition of silver nitrate. After longer standing the adsorbed indicator reacts slowly.

The following data show that the method gives satisfactory results.

TABLE I

TITRATION OF DILUTE CHLORIDE SOLUTIONS

Sodium chloride, cc.	10 of 0.01 N	50 of 0.002 N	100 of 0.001 N
0.01 N $AgNO_3$, cc.	10.02 to 10.05[a]	10.05 to 10.15	10.10 to 10.15[b]
0.01 N $AgNO_3$ calcd., cc.	10.00	10.00	10.00

[a] End-point of an orange color which turned pink after addition of 10.07 to 10.09 cc. of 0.01 N silver nitrate solution.

[b] With a larger excess of silver nitrate the color became more intense.

Especially in these very dilute solutions the back titration with chloride gives a sharp end-point.

Solutions containing as little as 15 to 20 mg. of chloride in a liter can be titrated with an accuracy of 1 to 2%. Therefore the method is superior to the ordinary Mohr procedure, as the latter has an appreciable titration error (at those dilutions). It might be expected that the indicator can be used advantageously in the titration of chloride in tap water. Special tests were run in order to see if calcium bicarbonate, magnesium bicarbonate and other salts had an interfering action. Though larger amounts of salts, especially those containing higher valence cations affect the color change a little, the results were still accurate to about 2% in 0.002 N chloride solution.

The tap water of Minneapolis contains only 2.6 mg. of chloride in a liter, which is too small to be titrated. Moreover, it seems that the tap water of this city contains some interfering substance. If a 0.001 N chloride solution prepared in tap water was titrated, no color change at all was observed. With artificial water of the same chemical composition as the tap water of Minneapolis and containing 1 milliequivalent of chloride in a liter a good end-point was observed. Even in the titration of 0.01 N chloride solution the tap water had a distinct retarding action on the formation of the color change. In all these cases it was observed that in the presence of tap water the silver chloride did not flocculate at all or very slowly with an excess of silver nitrate. Therefore it was thought that protecting colloids in the tap water might interfere with the observation of the end-point. The influence of different hydrophyllic colloids was tested. Some of them, especially gelatin even in small concentration, make the color change much less distinct and the end-point appears late. The presence of traces of colloidal material may explain the peculiar behavior of the Minneapolis tap water. On the other hand, it was shown that a dilute solution of silicon dioxide (from sodium silicate and acid) did not affect the color change of the indicator.

Another advantage of the new indicator over potassium chromate is that the titration can be carried out in weakly acid solution. If the acidity is regulated by some buffer in such a way that the P_H is larger than about

4.0, the color change is still very distinct. In the titration of 0.025 N sodium chloride solution in the presence of an acetate buffer with a P_{H} equal to or greater than about 4.4, the first color change to orange occurred after overstepping the end-point 0.1 to 0.2%. An advantageous application of the method is a direct chloride titration of those salts of heavy metals which are slightly hydrolyzed. Mohr's method gives unsatisfactory results in the above cases. In the titration of 0.025 N (to chloride) solutions of copper, zinc, manganese, nickel, aluminum, calcium, strontium, barium and magnesium chloride, the end-point was very sharp and appeared at the right place. In most cases the silver chloride flocculated 50 to 20% before the end-point was reached. Near the equivalence point the precipitate was slightly colored. At the equivalence point the sudden increase of the color to intense red could be observed with an accuracy of 0.05 cc. of 0.1 N silver nitrate. In the titration of very dilute solutions it is better to work at neutral reaction.

Bromides and iodides can be titrated in the same way as chlorides, even in very dilute solutions. In the application of fluorescein as an indicator, K. Fajans and H. Wolff[1] found that a mixture of iodide and chloride required an excess of silver nitrate, the error being +1 to 1.5%. Therefore, the use of the dichlorofluorescein for this purpose was tested. During the titration the same phenomena are observed that Fajans and Wolff described; about 2% before the end-point the silver iodide and chloride flocculate, the precipitate has a yellowish-brown color which turns brown-orange at the equivalence point and changes to orange-pink with an excess of about 0.5% silver nitrate. Though the color change is not as sharp as in the titration of both halides separately, the end-point still can be detected with an accuracy of 0.5%, if the mixture is so far diluted that its concentration is no more than 0.01 N to halide. The change in color in this case is much sharper than with fluorescein as an indicator.

Summary

Dichlorofluorescein is a very suitable indicator for the argentometric titration of chlorides in very dilute as well as in weakly acid solutions.

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