

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

METHYL RED AS AN ADSORPTION INDICATOR

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The discovery of adsorption indicators by Fajans and Hassel¹ and the application of these indicators to the volumetric estimation of halides is well known. Although this work has been repeatedly verified and the number of available indicators increased, attempts to extend the principles involved to the quantitative determination of other ions have been comparatively rare. Investigations of this nature include the titration of lead with ferrocyanide² and the titration of mercurous ion with bromides³ by Burstein, the estimation of phosphates and magnesium by Hahn and Meyer,⁴ and more recently the titration of fluoride with cerous nitrate by the authors.^{5,6}

In the titration of fluoride by means of cerous nitrate, either amphoteric magenta or methyl red was used and both were described as adsorption indicators. Subsequent experiments have demonstrated that the use of methyl red depends upon a principle which is different from the one usually ascribed to adsorption indicators. It is our purpose in the present paper to present evidence which will demonstrate that in precipitation titrations of fluoride and sulfate hydrolytic adsorption may take place with a resulting change of P_H , the function of the methyl red being that of an acid indicator.

The Titration of Sulfate with Barium Chloride.—In the titration of

¹ Fajans and Hassel, *Z. Elektrochem.*, **29**, 495–500 (1923).

² Burstein, *Z. anorg. allgem. Chem.*, **164**, 219–222 (1927).

³ Burstein, *ibid.*, **168**, 325–326 (1928).

⁴ Hahn and Meyer, *Ber.*, **60**, 975–977 (1927).

⁵ Batchelder and Meloche, *THIS JOURNAL*, **53**, 2131–2136 (1931).

⁶ For a review of the work on adsorption indicators the following bibliography may be consulted: K. Fajans and O. Hassel, *Z. Elektrochem.*, **29**, 495–500 (1923); R. Burstein, *Z. anorg. allgem. Chem.*, **164**, 219–222 (1927); R. Burstein, *ibid.*, **168**, 325–326 (1928); F. Hahn and H. Meyer, *Ber.*, **60**, 975–977 (1927); G. Batchelder and V. Meloche, *THIS JOURNAL*, **53**, 2131–2136 (1931); H. A. J. Pieters, *Chem. Weekblad*, **26**, 6–9 (1929); A. Frumkin, *Ber.*, **60**, 1816–1820 (1927); K. Fajans and K. von Beckerath, *Z. physik. Chem.*, **97**, 478–502 (1921); K. Fajans, *Naturwiss.*, **11**, 165 (1923); K. Fajans and W. Frankenburger, *Z. physik. Chem.*, **105**, 255–272 (1923); K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 221–245 (1924); O. Hassel, *Kolloid-Z.*, **34**, 304–307 (1924); W. Bottger and K. O. Schmitt, *Z. anorg. allgem. Chem.*, **137**, 246–248 (1924); O. Tomiček, *Časopis Českoslov. Lékárnictva*, **5**, 1–3 and 15–16 [*Chem. Zentr.*, **97**, 269–270 (1926)]; I. Kolthoff and L. van Berk, *Z. anal. Chem.*, **70**, 369–394 (1927); I. Kolthoff, *ibid.*, 395–397 (1927); I. Kolthoff, *ibid.*, **71**, 235–294 (1927); J. Hodakow, *Z. physik. Chem.*, **127**, 43–50 (1927); I. Kolthoff, W. Lauer and C. Sunde, *THIS JOURNAL*, **51**, 3273–3277 (1929); N. Rudenko, *J. Russ. Phys.-Chem. Soc.*, **62**, 505–548 (1930) (*Chem. Abst.*, **24**, 4233 (1930)); W. Hok, *Svensk. Farm. Tids.*, **34**, 161–167 and 185–190 (1930) (*Chem. Abst.*, **24**, 4899 (1930)).

fluoride with cerous nitrate, there was an unexpected interference of the sulfate ion. The nature of this interference led us to believe that adsorption principles might be used as the basis of a titration of sulfate by barium chloride. Stock solutions of barium chloride and sodium sulfate were prepared from c. p. reagents which had been purified by recrystallization and the strength of the solutions was determined by the customary gravimetric methods. Portions of the standard sodium sulfate solution were titrated according to the general procedure which follows.

Procedure.—An aliquot of the stock sulfate solution was placed in a beaker, heated to boiling⁷ and titrated with standard barium chloride solution. Three to five drops of methyl red, 0.1% in alcohol, were used as indicator. At the end-point the solution changed from its initial yellow color to the red color corresponding to the acid range of the indicator. The visible particles of precipitate are not perceptibly colored. A few characteristic results are given in Table I.

TABLE I

STANDARD SOLUTION OF BaCl ₂ : 1 Cc. ≈ 0.01786 G. OF Na ₂ SO ₄			
BaCl ₂ , cc	Na ₂ SO ₄ added, g.	Na ₂ SO ₄ found, g.	Initial vol., cc
0.83	0.0150	0.0149	15
.84	.0150	.0154	15
.86	.0150	.0150	15
.86	.0150	.0154	15
1.43	.0250	.0255	25
1.41	.0250	.0252	25
1.43	.0250	.0255	25
8.20	.1500	.1462	150
8.15	.1500	.1455	150

As will be noted from these results, the precision of this method proved to be only about 3%. The optimum conditions for the titration demanded the use of a relatively concentrated solution of barium chloride and this in turn necessitated the use of a microburet. The only conclusion to be drawn is that as a volumetric method for the estimation of sulfate, the above procedure has as yet little significance. However, the method is important in that it represents together with the previously mentioned more precise fluoride titration an example of a different application of adsorption principles to titrations.

The Behavior of Methyl Red.—The color change of adsorption indicators is usually described as being due to the deformation of the molecular structure of a dye ion when adsorbed upon an oppositely charged micelle. Thus, when silver ion is added to chloride ion in the presence of a small quantity of eosin, the halide is adsorbed upon the surface of the silver

⁷ It has become evident that the advantage of boiling is mainly due to the adjustment of the P_H by the removal of carbon dioxide. The same result is accomplished by passing hydrogen into the solution as was done in making potentiometric measurements.

chloride sol as soon as the latter develops, and particles of the type $(\text{AgCl})_n\text{-Cl}^-$ are produced. However, when sufficient silver has been added to precipitate the last of the halide, the first excess of the silver is adsorbed to form particles of the type $(\text{AgCl})_n\text{Ag}^+$, and these particles in turn take up the negative eosin ion with a concomitant change of color. The reaction is reversible so that if enough chloride is now added to exceed the concentration of the silver, the latter (together with the eosin) is again removed from the micelle and the color change is reversed.

When neutral solutions of sodium fluoride were titrated with cerous nitrate using amphi magenta as the indicator, at the equivalence point the precipitate was colored and it seemed probable that the mechanism of the color change was quite similar to that described for the chloride titration. However, when methyl red was used as the indicator in the fluoride or sulfate titrations, the precipitated cerous fluoride or barium sulfate was not perceptibly colored at the equivalence point. The color change appeared in solution. Furthermore, the color change appeared to be quite similar to the usual acid color of methyl red.

The fact that with methyl red as the indicator the precipitate was not colored was further verified by use of the centrifuge. Standard barium chloride was added to an aliquot of sodium sulfate solution to which methyl red had been added. When the barium chloride was in excess and the color of the solution had changed from yellow to red, the mixture was centrifuged until the precipitated barium sulfate had thoroughly settled. In all cases the supernatant liquid was red and the precipitate was not colored. Finally, standard barium chloride was added to sodium sulfate solution in the absence of indicator. When the precipitate had been completely settled by means of the centrifuge, a few drops of methyl red were added to the surface of the supernatant liquid. A red color immediately appeared. These experiments were duplicated in the precipitation of cerium fluoride. When cerous nitrate was added in slight excess to a solution of sodium fluoride in the presence of methyl red and the resulting cerous fluoride separated by means of the centrifuge, the supernatant liquid was red and the precipitate was not colored.

From these experiments and the additional fact that the red color in the supernatant liquid could be discharged by the addition of alkali, it seemed evident that a change of P_{H} occurred during the precipitation titrations mentioned. For this reason subsequent sulfate titrations were studied by means of the potentiometer, using the hydrogen electrode with the calomel half cell as reference electrode. The following curve is typical.

Attempts to make potentiometric studies of the fluoride titration were not successful. This was supposedly due to the formation of a coating of gelatinous cerous fluoride on the hydrogen electrode. Due to the conditions of the above sulfate titration good absolute P_{H} values were not expected.

An examination of the curve suggests that, if a change of P_H actually occurs as indicated, it should be possible to corroborate these results by means of properly selected indicators. The sulfate titration was therefore repeated using a variety of dyes. Of these dyes *p*-nitrophenol (P_H 5.6 colorless–7.6 yellow), brom cresol purple (5.2 yellow–6.8 purple), and brom thymol blue (6.0 yellow to 7.6 blue) exhibited characteristic color changes in their respective ranges along the curve. Other indicators, whose color changes did not fall within the P_H limits of the curve, did not give a change of color. This may be considered to indicate further a change of P_H during titration.

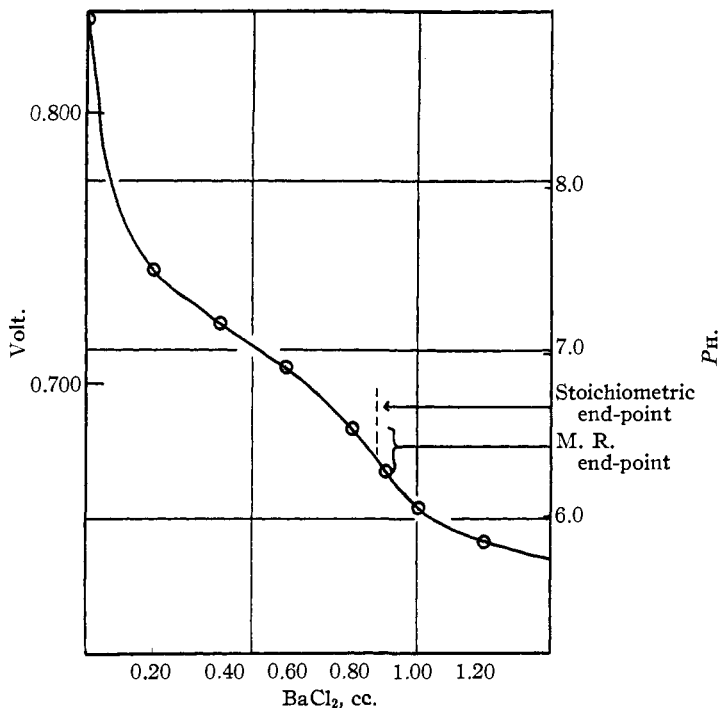


Fig. 1.—Titration of Na_2SO_4 with BaCl_2 . Hydrogen electrode vs. satd. calomel.

Hydrolytic Adsorption.—It is difficult to explain the results given on any basis other than that of a change of the P_H of the solution during titration. Similar phenomena have been known to colloid chemists for some time. Under proper conditions very appreciable quantities of acid may be produced in neutral solutions through the addition of activated charcoal. Some of the more recent studies of this phenomenon have been made by Bartell and Miller,⁸ Frumkin⁹ and Kolthoff and Kameda.¹⁰

⁸ Bartell and Miller, *THIS JOURNAL*, **44**, 1866–1880 (1922).

⁹ Frumkin, *Ber.*, **60**, 1816–1820 (1927).

¹⁰ Kolthoff and Kameda, *THIS JOURNAL*, **51**, 2888–2900 (1929).

Earlier examinations of barium chloride and cerous nitrate solutions indicated that the results of the above titrations could not be due to ordinary hydrolysis but were probably due to hydrolytic adsorption. Assuming this to be the case, the following explanation seems reasonable. At the beginning of the sulfate titration particles of the type $(\text{BaSO}_4)_n\text{SO}_4^-$ are formed. When enough barium chloride has been added just to exceed the stoichiometric point the particle type becomes $(\text{BaSO}_4)_n\text{Ba}^+$. Then, unlike the micelle of the chloride titration, the micelle in the sulfate titration adsorbs hydroxyl in preference to the negative dye ion. Likewise in the fluoride titration, at the beginning of the titration particles of the type $(\text{CeF}_3)_n\text{F}^-$ are formed and when the stoichiometric point is just exceeded the particle type becomes $(\text{CeF}_3)_n\text{Ce}^+$. This latter micelle adsorbs hydroxyl rather than negative dye ion.

Whether this adsorption be preferential or the hydroxyl ion together with other negative ions is involved in a dynamic relationship between the micelles and the solution, the observed effect is the same as if hydroxyl ions had been removed from the solution.

The methyl red, then, in both the fluoride and the sulfate titration acts not in the usual capacity of adsorption indicators but rather as an indicator which detects the change of P_H which takes place as a result of adsorption during the titrations.

It seems likely that the phenomenon described may be characteristic of other precipitation reactions. Further investigations along these lines are being undertaken at the present time.

Summary

A precipitation titration of sulfate by means of barium chloride is described. Although this procedure is not satisfactory for the quantitative determination of sulfate, it has been used, together with a more precise fluoride titration, to illustrate a different application of methyl red to adsorption titrations.

Methyl red is described as an acid indicator which detects the change of P_H at the end-point of two precipitation titrations. This change of P_H was attributed to adsorption during the titrations.

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