

«Note»

The Adsorption of Hydrogen and Hydroxyl Ions During Precipitation Titration

During the course of investigations on the halide determination by means of potentiometry using reverse-hydrolysable anions as an indicator¹⁾, an interesting response of the glass electrode to the purely precipitation system was observed. The pH of the titrating solution varies with titration in a manner that can be associated with colloidal properties of the precipitate. Thus the dynamic effect of adsorption or desorption of the hydrogen and/or hydroxyl ion has not been studied in the literature. Analytically, hydrolytic precipitation and the titration that based upon precipitation of hydroxides are the sole mode which adopted the glass electrode (as hydrogen ion sensing) for electrometric investigations of the precipitation systems²⁾. Meanwhile, the adsorption phenomena of the lattice ions, as potential-determining ions were studied thoroughly³⁾. The effects and roles of the counter ions, however, have been under-estimated, because of their triviality and difficulty to investigate in their effects.

In this note, qualitative explanation of the observed phenomena involved is attempted, it may be attributed by the participation of the hydrogen and hydroxyl ions, as adsorbates.

EXPERIMENTALS

Metrohm combined glass electrode and Metrohm Potentiograph E 336 (Metrohm AG Herisau, Switzerland) recording titrator were used for pH measurements and recordings of the titration curves, for most of the works. Microburet, 10-ml in capacity, motor driven and attached to the titrator was used. 0.1M stock solution of silver nitrate was prepared from extra pure reagent and was standardized against sodium chloride as usual. Halide solutions were prepared directly from reagent grade potassium salts. The pH of the silver nitrate solution was 5.9. The

titrating rate was kept always less than 0.4-ml per minute and the stirring rate was kept constant at the maximum of the used magnetic stirrer. The starting pH of the titrate was adjusted using dilute nitric acid and sodium hydroxide solution, if it was necessary.

RESULTS

Fig. 1 show the pH changes during the titration of various halide solutions, in 0.01M, as a function of the volume of the titrant, 0.1M silver nitrate solution. The starting pH's were the natural pH of the

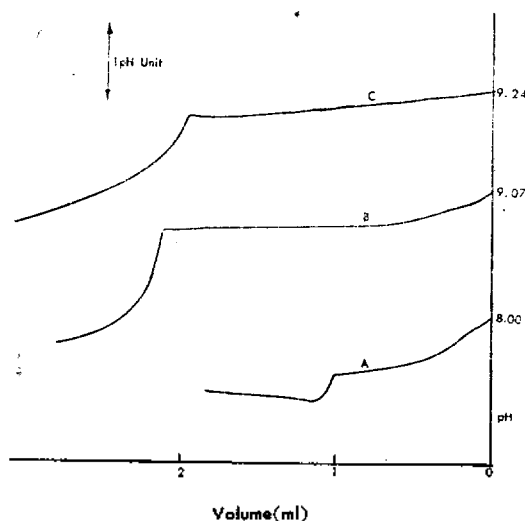


Fig. 1. Glass electrode responses during precipitation titrations of halides with 0.1018M silver nitrate.

- A. Distilled water, 10ml.
- B. 0.01M Chloride solution, 10ml.
- C. 0.01M Bromide solution, 20ml.
- D. 0.01M Iodide solution, 20ml.

prepared solution, that is, no pH adjustments were made prior to the titrations. In Fig. 2, titrations were started from some higher pH, after adjustment.

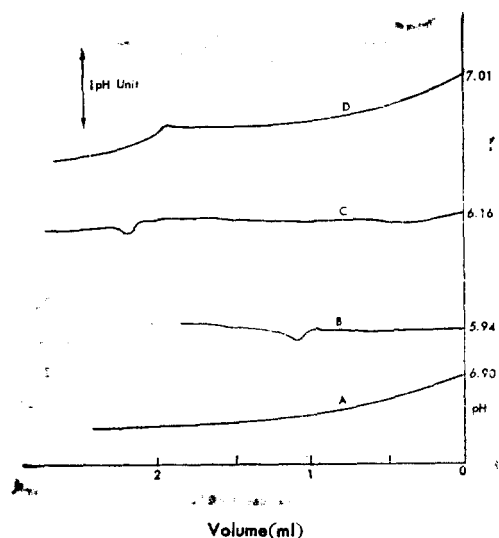


Fig. 2. Potentiograms of the halide titrations at some adjusted initial pH. The titrant and the volumes of the titrates are same as in Fig. 1.

A. Chloride; B. Bromide; C. Iodide.

In most instances, a change in pH occurs concomitantly, yielding a marked decrease in pH near the equivalence point in precipitation titration. A typical titration curve, exaggerated in pH scale arbitrarily for illustration, is re-drawn in Fig. 3. Curve I, a blank curve, illustrates the mixed result of two solutions slightly differ in pH (note that the titrant is more acidic than titrate) as is the curve A in Fig. 1. On the curve I (Fig. 3), descending portion AB rep-

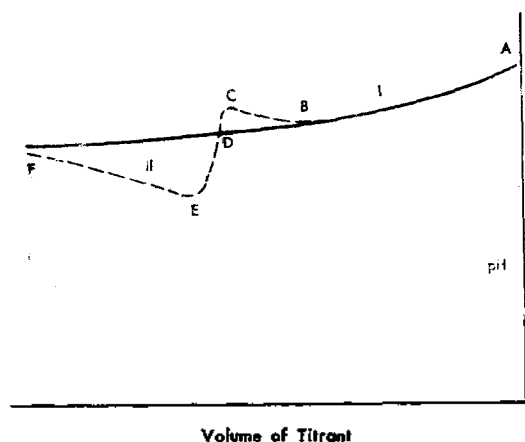


Fig. 3. Illustration of the pH variation of the pure precipitating system (in acidic side). I; solid II; dotted.

resents simply, the base line, the dilution or neutralization effect of hydrogen ion. The slope and shape of this line are determined by the difference and strength of the pH between the titrant and titrate. Ascending portion BC of the line, corresponds to the consumption of hydrogen ion from or supply of hydroxyl ion to the solution, by the titrant or titrated precipitate. Difference in pH between the maximum and that of the blank, h_1 , varies with the kind of halide ions titrated. Thus, denoting the potentiogram as in Fig. 3, the observed results can be summarized as follows;

a. Visual observations indicate that the break point C (max. pH) corresponds to the "clear point" in the titration to the clear point.

b. The quantities, h_1 , increase in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$ with varying the kind of halide titrates. Generally, h_1 is minute in magnitude for silver halide systems, in instances, hardly detectable for chloride; 0.017 for bromide; 0.023 for iodide in pH unit respectively (significant effect was observed for barium sulfate system; a few pH⁴⁾.

c. i) Increased starting pH results increased $h_1 + h_2$, the total amounts of breaks after the equivalence point. At extremely alkaline solutions (above pH 10), however, no breaks are observed at all.

ii) After the point E, pH of the system increases gradually again, approaches the blank line asymptotically. h_2 decreases in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The iodide solution fails again to give such phenomena, regardless of the starting pH.

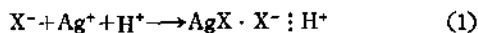
DISCUSSION

In order to explain the process that occurs and will give the exhibited results, it is desirable to note the colloidal properties of the silver halide precipitates formed during the titration. Noting the solution composition of the system, it is evident that the whole phenomena involved are governed predominately by the surface chemical properties of the precipitates. Otherwise, some alternative explanations can be thought. The irregular response of the glass electrode, for instance, by coating and disclosing of the electrode surface by the precipitate during the titration. Experimental conditions oppose this approach. Secondly,

the reverse-hydrolyzable anion such as HCO_3^- , from dissolved carbon dioxide, can affect the shape of the curve, due to the formation of the insoluble silver carbonate and releasing the hydrogen ion at the region of the equivalence point. Simple calculation shows that the concentration of the bicarbonate ion is so low that be able to hardly affect such a profound pH changes in effects. Result c, i), stated above, support this argument, from the fact that at higher pH, the fraction of HCO_3^- of the total dissolved carbon dioxide is decreased. As with all precipitation reaction, an important consideration is adsorption effect. In the case at hand, hydrogen and/or hydroxyl ion do participate in adsorption, as counter ions mainly, in addition to the conventional ions, in such a degree to be observable.

It is well known that the lattice ion is preferentially adsorbed according to the rule that is stated by Paneth and Fajans⁹⁾ as the potential-determining ions throughout the entire course of the titration except the equivalence point region. Portion of the curve (Fig. 3) BC, indicating the supply of hydroxyl ion to or consumption of hydrogen ion from the solution, whatever the mechanism may be, can be attributed by the increasing adsorption of hydrogen ion, as counter ions, by increased adsorbent as titration proceeds.

Thus by the following reaction



hydrogen ion is eliminated from the supernatant solution, in turn, the pH increased correspondingly, and

$$\text{H} = f(\text{H}^+) \cdot m \quad (2)$$

where H; adsorbed amount of hydrogen ion, m; weight of precipitate, $f(\text{H}^+)$ a type of the adsorption isotherm.

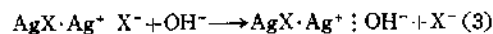
Although Paneth-Fajans-Hahn adsorption rule⁹⁾ does not predict the preference of adsorption as counter ions quantitatively when the concentration, charge and bond character are different respectively, the greater covalency of the hydrogen halides than the alkali halides and the order of polarizability of the halides and the polarizing character of the proton justify the proposed assumption.

In this respect, the greater and profound h_1 is expected for the barium sulfate system, remembering

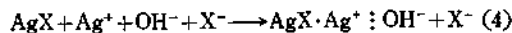
the profound strength of the interionic attraction between the proton and sulfate ion than that of between alkaline metal ion and sulfate.

Under this assumption, the sharp and significant decrease in pH immediately after the isoelectric point, line CD, is attributed by the destroying of the double layer structure, $\text{AgX} \cdot \text{X}^- : \text{H}^+$, as is well known in the titration to the clear point⁷⁾. Thus the h_1 may correspond to the released (therefore adsorbed by the formed precipitate) amount of hydrogen ion accompanied by the destruction of the double layer. But the greater change in pH is observed as is shown by the portion DE, in Fig. 3.

After the isoelectric point, the system rebuild the double layer, for example, $\text{AgX} \cdot \text{Ag}^+ : \text{X}^-$, as is usual. The consumption of hydroxyl ion, resulting the exchange of counter ions, as in the equation



may begin around the point D, as the further silver ion is added. Considering the hydrogen and hydroxyl ions as one of the adsorbates, detailed mechanism at the immediate vicinity of the isoelectric point is complicated and ambiguous owing to the concentrations of the lattice ions are comparable with that of the hydrogen or hydroxyl ions. Direct adsorption of hydroxyl ions as counter ions, compatible with reaction (3), as in the equation



can be considered. Equilibrium of the reaction (3) or (4) is reached at the point E, where after the reverse reaction or another exchange reaction of the hydroxyl ion by the ions, such as nitrate, will cause the increase in pH, again, corresponding to EF, Fig. 3. The excess halide ions, which appear at the right hand side of the reaction (3) or (4), correspond to the difference between the theoretical and actual concentrations observed in many cases^{3,9)} due to the adsorption of the silver ion and this distortion increases in magnitude in the order of chloride, bromide and iodide corresponding to the increased hydroxyl ion consumption, the result c, i) and ii) are meant.

At high pH, another reaction, the formation of silver oxide (mixed with AgOH) may be incorporated and continuous decrease in pH will be resulted.

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