TECHNICAL REPORT

COMPLEX FORMING TENDENCY OF HUMIC ACID AND SODIUM HUMATE

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The reactions of humic acid with ions like Na^+, K^+, NH_4^+ and Li^+ and the complexes of humic acid with metal ions like Ca^{+2}, Ba^{+2}, Sr^{+2}, Mg^{+2} and Zn^{+2} were studied potentiometrically. Na^+ has no effect but the depression by Li^+ ion is the highest. This is correlated to the replacing power attributable to the size of the ion. Zn^{+2} forms complexes with humic acids and the order of depression is generally found to be $Sr^{+2} > Ca^{+2} > Ba^{+2} > Mg^{+2}$.

The retention of metallic cations by soil humus is due to the formation of complexes, some of which may be chelates; although simple salt formation is also involved [1–4].

The pH titrations have been studied by Bayers[5], Mehlich[6], Puri and Sarup[7] who noted that for a wide range of addition of base, the curve of pH against ml of NaOH added, was almost a straight line. They considered this zone to be the buffering zone. Chaterjee and Bose[8], Marshall and Patnaik[9] have obtained multiple inflexions in titration curves. The distinctness of the inflexions also varies with the nature of the base used for titrations.

The replacement of H^+ ions in the functional group of humus substances is influenced both by pH of the medium and by concentration of the substance. According to Broadbent and Oat[10], the nature of cation is important. The stability of the complexes followed the order $Sr > Ba > Ca \geqslant Mg$.

Adhikari and co-workers[11] calculated the stability constants of metal complexes with organic matter at pH 4.0.

The study of the properties of humic complexes of various metal cations can be used to answer the problem of availabily of specific elements at different stages of growth in soils located in different geological formations and in different climatic zones.

EXPERIMENTAL

Potentiometric titrations of standard humic acid were carried out with 0.01N NaOH, and 0.02M $Ba(OH)_2$. Prepared sodium-humate was obtained from standard humic acid. Standard and prepared sodium humate were titrated potentiometrically with 0.05N HCl. These titrations were also carried out in presence of various metal ions. The experiments were divided into two parts. In the first part 0.1g sodium-humate was dissolved in 100 ml water and 2ml 0.02M metal ion solution was added. This mixture was titrated against 0.05N HCl without adjusting its pH to 7.0. In the other part 0.05N HCl was added to adjust the intial pH to 7.0. No attempt was made to keep ionic strength constant. The salts studied were NaCl, KCl, NH_4Cl, LiCl, $CaCl_2$, $BaCl_2$, $SrCl_2$, $MgCl_2$ and $ZnCl_2$. To study the power of complexation of sodium-humate, 0.1gm of prepared sodium-humate was dissolved in 100ml water. To this 0.5gm of metal salt was added. As mentioned earlier, they were also divided into two parts. In the first part, the pH was not adjusted to pH 7.0 and in the second part, it was adjusted to 7.0 with 0.05N HCl.

DISCUSSION

Two inflexion points have been observed from potentiometric titration curves of humic acid, and sodium humate. From potentiometric titration of standard Na-humate, the equivalent weight is estimated to be 417.

The titrations of sodium humate with 0.05N HCl in presence of various metal ions were carried out. For alkali metal and NH_4^+ ion, the depression in initial pH of sodium-humate as well as during the titration was affected by the nature

of metal ions. In the case of metal ions, sodium has obviously no effect which can be easily understood. The depression by Li^+ ion is the highest, while the depression by NH_4^+ ion and K^+ ion is to a lesser extent, which may be correlated to the replacing power attributable to the size of the ion.

In another set of experiments for the same standard and prepared sodium humate, initially pH of the solution was brought to 7.0 by addition of 0.05N HCl solution and then metal ions were added and the titrations were continued. Here also the replacing power found is to be almost the same.

For the alkaline earth metal ions, except for Sr^{+2} ion, the replacing power of all the ions are nearly the same and there is no marked depression in pH. Standard sodium humate shows uniform behaviour, while for the prepared sample, the depression by Sr^{+2} is considerable.

In all the above cases, the amount of metal ions added were 2ml of 0.02M metal salts. This may be insufficient to consume the sodium-humate available in the system. It can be seen from the graph that the initial pH of the solution after addition of metal ions was in alkaline range indicated. Metal ions were added in sufficient quantity, so that complete complex formation can take place with metal ions. In the study of the complexing power of sodium-humate prepared, sufficient amount of the metal ions were added, so that much less of the free sodium-humate may be remaining in the solution. This method leads to a better understanding of the properties of the chelate formed. In the series of Ca^{+2}, Ba^{+2} and Mg^{+2} it is found that with addition of metal ions to sodium-humate, the resulting pH is still in alkaline range and hence titrations were carried out with 0.05N HCl solution. The order of depression in pH is $Ca^{+2} > Ba^{+2} > Mg^{+2}$.

In another set after adjusting pH upto 7.0, the behaviour is observed to be nearly the same.

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