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SUMMARY

The kinetics of complex formation between Al^{3+} and 5-nitrosalicylic acid and acetylacetone have been measured by the spectrophotometric method at 25°C , ionic strength of 0.30 M. The measurements were carried out in acidic aqueous solutions (pH 0.8-3.1) in order to avoid precipitation and to minimise polymerization. An ionic strength of 0.30 M was maintained with NaCl and the pH of solutions were buffered with sodium chloroacetate-chloroacetic acid.

The results of the reaction between Al^{3+} and 5-nitrosalicylate ion are interpreted according to a reaction mechanism consisting of two parallel paths involving the species Al^{3+} and AlOH^{2+} reacting with 5-nitrosalicylate ion, respectively; giving rise to a 1:1 complex $[\text{Al}(\text{NSA})]^+$. The forward rate constant for Al^{3+} is $2.66 \text{ M}^{-1}\text{s}^{-1}$, and $2.95 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$ for AlOH^{2+} . These results can be interpreted in terms of the interchange dissociative mechanism proposed by Eigen. The pathway via AlOH^{2+} and 5-nitrosalicylate ion has the much higher rate constant confirming the enhanced reactivity of the hydrolyzed species. The stability constant of Al^{3+} and 5-nitrosalicylate ion has been measured at 25°C and 0.30 M ionic strength by spectrophotometric method. The value ($K_1 = 5.48$) agrees fairly well with that derived from kinetics.

The results of Al^{3+} and acetylacetone are also interpreted in terms of two reaction paths, the Al^{3+} and AlOH^{2+} reacting with the undissociated form of acetylacetone (HA), giving a 1:1 complex $[\text{Al}(\text{acac})]^{2+}$. The formation rate constant for Al^{3+} and AlOH^{2+} ions

with HA are $2.68 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, $4.37 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$, respectively. The rate constant for the hydrolyzed species is again much larger than for the aluminium ion. The reaction between Al^{3+} ion and HA is much slower than the normal substitution reaction of Al^{3+} ion. The value of the formation constant, for the reaction of $\text{Al}^{3+} + \text{HA} \rightleftharpoons \text{AlA}^{2+} + \text{H}^+$, was found to be 1.42 at ionic strength medium 0.30 M and 25°C by spectrophotometric method.

The effect of the buffer concentration on the observed rate constant have been considered. The buffer dependence of k_{obsd} is curvilinear reaching an asymptotic value.