

Kinetic determination of traces of Al(III) ion by its catalytic effect on oxidation of 4-hydroxycoumarin by potassium permanganate

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Oxidation of 4-hydroxycoumarin by potassium permanganate in acid media of acetate buffer is catalyzed by Al(III) ions, which is the basis of the proposed new homogenous-catalytic method for determination of Al(III) in solutions. Under the optimum conditions, Al(III) has been determined at 525 nm in solutions containing analyte at 50-1000 ng/ml with probable relative error of 15.6-5.1 % and detection limit of 20 ng/ml. Appropriate kinetic equations for both catalytic and noncatalytic processes have been derived and the mechanism of catalytic effect of Al(III) investigated. Interference studies show that most of the common cations and anions do not interfere.

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Al(III) does not exhibit classical catalyst characteristics, which may account for the fact that there are few kinetic methods for quantitative determination of Al(III) based on homogenous catalysis. However, Al(III) catalytic activity has been observed in the reaction of 4-hydroxycoumarin with permanganate. Estimation of Al(III) kinetically is based on uncatalyzed reactions and stopped-flow injection using a F⁻ ion selective electrode^{1,2}, with detection limit varying between 0 and 100 µg/ml. The reaction may be followed by spectrophotometry³, atomic absorption spectroscopy⁴, electroanalytical methods^{5,6} and adsorptive stripping voltametric methods⁷.

Experimental

4-Hydroxycoumarin was recrystallized from 3:1 water-ethanol mixture and dried at 105 °C before its 1×10^{-3} M solution was prepared. To increase its water solubility, insoluble coumarin was made into a soluble salt using equimolar quantity of NaOH. Potassium permanganate standard solution (0.02 M) was prepared from Merck ampoule. Working solutions of lower strengths were prepared immediately before start of the experiment. Acetate buffer solution was prepared from 0.2 M acetic acid and 1 M NaOH (Merck). Al(III) solution was made by dissolving 0.500 g of pure Al metal (99.999%) in 50 ml of 2 M HCl and subsequently diluted with water to 1000 ml solution. The concentration of the solution was determined gravimetrically.

The rate of the investigated reaction was followed spectrophotometrically with a Perkin-Elmer Lambda 15 spectrophotometer, connected to a thermo-circulating bath. The pH was measured by means of a Radiometer PHM 29b pH meter and a combined glass-calomel electrode (GK 2311C). The solution was thermostated at 313 K before the beginning of the reaction.

Procedure

The reactants were transferred into a 10 ml volumetric four compartment flask (Bouderin vessel) as follows: measured amount of 4-hydroxycoumarin was stored in one compartment of the flask, acetate buffer solution was placed in the second compartment of the vessel, in the third permanganate, while the fourth compartment of the vessel contained Al(III) solution. Water was added to give a total volume of 10 ml. The vessel was thermostated for 10 min and vigorously shaken. The spectrophotometer cell was rinsed well and filled with the solution. The absorbance at 525 nm was measured every 30 s over a period of 3-8 min after mixing. Instead of the reaction rate (dc/dt), the quantity dA/dt was used. The measurements were made at 313 K.

Results and discussion

A variant of the tangent method was used for the processing of kinetic data, because a linear correlation exists between the absorbance and time during the first 3-6 min after mixing. The reaction rate was followed by the change in the values of the tangent of the angle ($\text{tg}\alpha$) of the slope of the linear part of the kinetic curve to the abscissa in the coordinates $A-t$, since $\text{tg}\alpha = dA/dt$ (ref. 8).

Dependence of the reaction rate on 4-hydroxycoumarin concentration (ranging from 2.5×10^{-5} to 2×10^{-4} mol L $^{-1}$) was studied keeping all other experimental parameters constant. The order of noncatalytic reaction was found to be 0.7, while for the catalytic reaction, it was 0.6. The difference was maximum at 2×10^{-4} mol L $^{-1}$ and hence for further studies 4-hydroxycoumarin concentration of 2×10^{-4} mol L $^{-1}$ was selected.

Studies on effect of pH on reaction rates shows that the maximum difference between the reaction rates occurs at pH = 4.0, which was selected for all further work. A linear relationship between the logarithm of $\text{tg}\alpha$ and $\log c_{\text{H}^+}$ was found for both the reactions. The catalytic and noncatalytic reactions were found to be of first order.

Studies on dependence of the noncatalytic and the catalytic reaction of the permanganate concentration shows the catalytic reaction to be of first order for permanganate concentration ranging from 2.5×10^{-5} – 1.75×10^{-4} mol L $^{-1}$, and zero order for higher concentrations. Noncatalytic reaction was of zero order for $c_{\text{MnO}_4^-} > 1.75 \times 10^{-4}$ mol L $^{-1}$, and 0.8 for $c_{\text{MnO}_4^-}$ between 2.5×10^{-5} and 1.75×10^{-4} mol L $^{-1}$. For further studies permanganate concentration of 2×10^{-4} mol L $^{-1}$ was selected.

Influence of volume of acetate buffer on both the reactions was investigated. It was found that the optimal concentration of CH_3COO^- was 9.15×10^{-3} mol L $^{-1}$ and that of CH_3COOH was 5.08×10^{-2} mol L $^{-1}$.

Influence of Al(III) on the reaction rate under the optimum conditions was examined at different preset temperatures. The calibration curves for Al(III) concentration determination were constructed applying the mathematical method of the smallest quadrature on the experimentally obtained data (Fig. 1). The calibration curves were linear in the concentration range ranging of 50-1000 ng/ml. Slopes

of the linear relationships shown in Fig. 1 suggest that the calibration curve at 313 K is the most suitable for the analytic purposes. On the other hand the most convenient working temperatures are 289-298 K. Linear relationships shown in Fig. 1 can be described by Eqs 1-4 as follows:

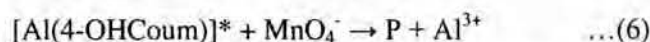
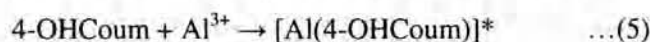
$$\text{at 289 K} \quad \text{tg}\alpha = 0.07 \times c_{\text{Al(III)}} + 0.068 \quad \dots(1)$$

$$\text{at 298 K} \quad \text{tg}\alpha = 0.083 \times c_{\text{Al(III)}} + 0.057 \quad \dots(2)$$

$$\text{at 303 K} \quad \text{tg}\alpha = 0.089 \times c_{\text{Al(III)}} + 0.053 \quad \dots(3)$$

$$\text{at 313 K} \quad \text{tg}\alpha = 0.01 \times c_{\text{Al(III)}} + 0.045 \quad \dots(4)$$

There are some oxido-reduction reactions in which the catalyst has the same oxidation number. Catalytic effect of Al(III) is based on reaction of formation of reactive intermediate complex with 4-hydroxycoumarin which then reacts with KMnO_4 . Finally, the activated complex decomposes into the products (salicyl acid, oxalatic acid) and catalyst.



where P are products of the reaction and Al^{3+} is regenerated catalyst.

The following kinetic equations were deduced on the basis of the graphic correlations obtained for the investigated processes. For the noncatalytic reaction:

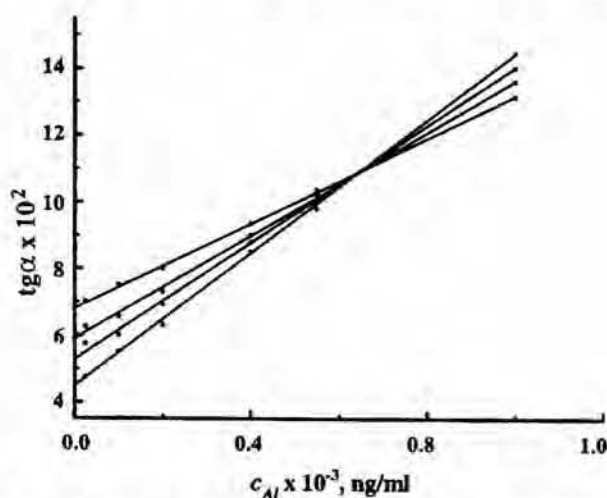


Fig. 1 — Dependence of the reaction rate on Al(III) concentration. [Initial concentrations: $c_{\text{MnO}_4^-} = 2 \times 10^{-4}$ mol L $^{-1}$, $c_{\text{coum}} = 2 \times 10^{-4}$ mol L $^{-1}$, pH = 4.00, $T = 289$ K (curve 1), $T = 298$ K (curve 2), $T = 303$ K (curve 3), $T = 313$ K (curve 4)].

Table I — Tolerance levels of interference in the kinetic determination of 1000 ng/ml Al(III) using the optimum conditions

Ion added	Tolerance level $c_{\text{ion}}/c_{\text{Al(III)}}$
Na^+ , K^+ , Cl^- , NO_3^-	10^4
NH_4^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Sn^{2+}	10^3
$\text{Cr}_2\text{O}_7^{2-}$, Pb^{2+} , SO_4^{2-} , Cu^{2+} , Cd^{2+}	10^2
Ni^{2+}	10
Mn^{2+} , SCN^- , Co^{2+} , Fe^{3+} , Zn^{2+} , PO_4^{3-} , citrates	Interfere

$$-\frac{dc}{dt} = k_0 \times c_{\text{coum}}^{0.7} \times c_{\text{H}^+} \times c_{\text{MnO}_4}^{0.8} \quad \dots(7)$$

for $2.5 \times 10^{-5} \text{ mol L}^{-1} < c_{\text{MnO}_4} < 1.75 \times 10^{-4} \text{ mol L}^{-1}$,

and for $c_{\text{MnO}_4} > 1.75 \times 10^{-4} \text{ mol L}^{-1}$

$$-\frac{dc}{dt} = k_0 \times c_{\text{coum}}^{0.7} \times c_{\text{H}^+} \quad \dots(8)$$

For the catalytic reaction:

$$-\frac{dc}{dt} = k_1 \times c_{\text{coum}}^{0.6} \times c_{\text{H}^+} \times c_{\text{Al(III)}} \quad \dots(9)$$

for c_{coum} from 1.75×10^{-4} - $2.25 \times 10^{-4} \text{ mol L}^{-1}$ and for $c_{\text{MnO}_4} > 1.75 \times 10^{-4} \text{ mol L}^{-1}$, where k_0 and k_1 stand for the conditional rate constants for the noncatalytic and the catalytic reactions, respectively.

The $-dc/dt$ at 289-313 K for the catalytic process ($\text{Al(III)} = 1 \text{ } \mu\text{g/ml}$) was in the range $9.27\text{-}9.67 \times 10^{-7} \text{ mol s}^{-1}$. For the noncatalytic process, it was in the range $4.53\text{-}3.00 \times 10^{-7} \text{ mol s}^{-1}$.

To test the reproducibility and correctness of the method used, five samples with three different Al(III) concentrations were prepared and analysed by proposed kinetic method. Probable relative error value in determination of Al(III) concentration in the proposed method for the concentration ranging 50 - 1000 ng/ml was found to 15.6-5.1 %.

Influence of the several foreign ions on the reaction rate of the 4-hydroxycoumarin oxidation with permanganate was studied. While maintaining Al(III) concentration of 1000 ng/ml as a constant, different quantities of different ions were added to the reaction mixture (Table I).

Data suggest that ions such as Co(II), Mn(II), Zn(II), Fe(III), citrates, thiocyanates and phosphates interfere in the proposed method. The other investigated ions have no influence on the determination of Al(III).

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