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Kinematics of Calcium Chloride Aggregation Reaction Nephelometrically

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Abstract
The process of aggregate formation of calcium chloride and oxalic acid reaction is studied nephelometrically and kinetically. It has been observed that reaction proceeds with the time which is indicated by the nephelometry turbidity unit (NTU) which shows dependence on the concentration of calcium chloride. This reaction also studied at different temperature which shows increase in reaction with the increase of temperature. Effect of ionic strength is also carried out showing negligible effect. With this study different thermodynamic parameters were calculated such as entropy change, enthalpy change, energy of activation etc.

Keywords
Calcium chloride, oxalic acid, precipitation reaction, aggregate formation, kinetics, Nephelometer.

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INTRODUCTION:
The scientist Nernst in the year 1899 showed that there exist an equilibrium between solid ion and salt and its solutions in water is directed by the solubility product expression the solubility of salt in pure water depends upon solubility product, when two solutions are mixed and a salt precipitates. Unless the two solutions are exactly in the stoichiometric ratio, the common ion effect will decrease the solubility of the salt and make the precipitation more complete. There are number of cases in which the solubility of an ionic salt can be calculated from its solubility product alone. A number of other factors also influence the solubility and must be taken into account. The solubility also depends on ionic strength of the solution.

Kabiruddin [1] had studied role of manganese (III) micelles and inorganic salts on the kinetics of redox reaction of L-Sorbore and chromium (VI). Steel. M.B. Bellakki [2] and others have given kinetic study of oxidative decarboxylation and de-amination of L-glutamine by Di-periodatonickelate (IV) in aqueous alkaline medium. Schneider and G. Inden [3] have studied the Simulation of kinetics of precipitation reaction in ferric steel. Precipitation reactions are important, from environmental point of view also [4]. The important uses of nephelometry are the determination of Barium Sulphate, Carbonate as Barium carbonate, and Chloride as Barium chloride. The determination of Sulphate is of particular importance and serves for the routine determination of total Sulphur in coke, coal, oils, rubbers, plastics and other organic substance. Precipitation removes

gases pollutants from the atmosphere, A H Mahvi & M Razvi used is application of poly electrolyte in turbidity removal from surface water. Here the most important process is the formation of precipitate and coagulation of different types of elements in our previous research we have different compounds present in water followed by sedimentation. [5-7]. Earlier we have reported, kinetics of precipitation of sodium thiosulphate [8] also precipitation of cerium chloride and silver nitrate in aqueous medium by nephelometric study [9].

The salts such as Nickel Sulphate, Cobalt Chloride, and Cadmium Sulphate were also studied [10, 11 and 12] Nephelometrically. Study of water containing different types of inorganic salts shows the importance of $CaCO_3$ as the invertebrates contains calcium carbonates as the inorganic component of their exoskeleton [13] the study of precipitation of calcium in different salt form is essential particularly in scale deposition with water, precipitation of minerals like siderite, calcite or aragonite, magnetite etc [14, 15] Nephelometry follows the principle of the Rayleigh scattering. This technique is usually used to measure the content of suspended solids in water. Nephelometry is highly sensitive and selective technique of measurements.

Experimental

The chemicals used for the present investigations were of S.D. Fine Chemicals Ltd and used without further purification. Double distilled water was used as solvent. A (CL 52D) Elico make Nephelometer was calibrated using farmazine solution, which was prepared by using Hydrazine Sulphate and Hexamethylenetetramines. Equal volume of these solution was mixed and kept for 48 hours, this solution was used for calibration of Nephelometer. A known amount of Calcium Chloride was mixed with known concentration of Oxalic acid and the of the reactant mixture was determined Nephelometrically at different time intervals and constant temperature, the experiment was repeated by varying the amount of Calcium chloride, amount of Oxalic acid, amount of different salts. Similarly, experiments were carried out at different temperature keeping concentration of both oxalic acid and calcium chloride constant. These studies were measured by using Nephelometer.

RESULTS AND DISCUSSION:

Part-IReaction between Calcium chloride and $C_2 H_2 O_4$

Nephelometry follows the principle of Rayleigh scattering. This technique is usually used to measure the content of suspended solids in water when a light beam is passed through an aqueous solution. It is subjected to scatter due to the presence of particle in suspension in Nephelometry, the light is also allowed to pass directly through the sample solution having suspended particles. The amount of radiation scattered by the particles is measured at any angle (usually 90^0) to the incident beam. Raleigh scattering is fitted well to particles smaller than 50nm.The simplified Rayleigh scattering formula is [16-17]

$$I = kCMI_0$$

Where I is the intensity of light scattered, I_0 the intensity of incident light, C is the concentration of scattering particles k is ratio and M is the molecular weight of scattering particles, therefore, when the intensity of incident light and molecular weight of scattering particles are certain, the intensity of scattered light is directly proportional to the concentration of scattering particles.

For the present study, we have taken a definite amount of solid calcium chloride, which is treated with Oxalic acid solution. The solution becomes turbid, due to the formation of calcium Oxalate. The reaction takes sufficient times; therefore, it can be successfully studied by using Nephelometry.

It is possible that calcium chloride gets dissociate in solution.

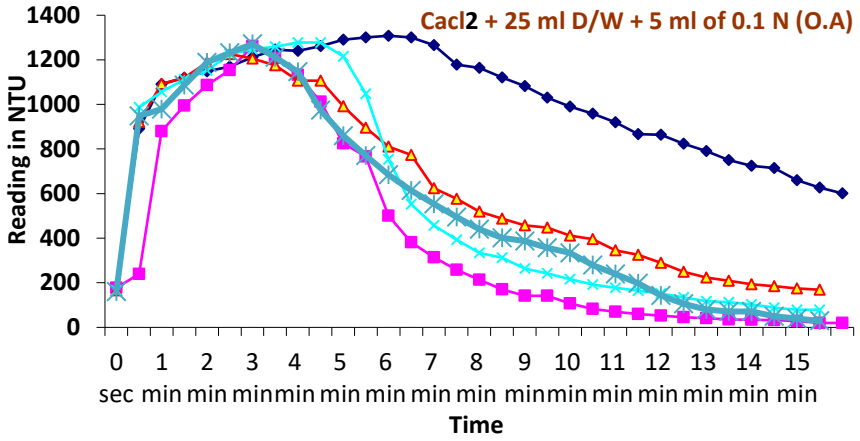
$$CaCl_2 \longrightarrow Ca^{+2} + Cl^{-2}$$

$$C_2H_2O_4 \longrightarrow C_2O_4^{-2} + H^{+2}$$

$$Ca^{+2} + C_2O_4^{-2} \longrightarrow CaC_2O_4$$

In the present investigation, we monitored the turbidity obtained due to product formation. Although reaction order is different, we maintained pseudo first order conditions. So the different order reactions exhibit different

Functional forms for the time dependence of reactant concentrations.



It was observed that initially NTU reading is slow for few seconds than increases up to 2 to 3 min and then slightly decreases for two to three readings and smoothly decreases, for lower concentration of calcium chloride. The curve shows sudden increase in NTU reading for 1 to 3min then slightly towards constant than smooth decrease in reading is shown for higher concentration of calcium chloride, when 500 mg of calcium chloride was dissolved in Oxalic Acid. A smooth curve was observed.

Rate constants were determined (Table 1). It is observed that with the increasing the concentration of calcium chloride the rate constant increases but decreasing the concentration Oxalic acid increases the rate constant. This increase in rate constant with the increase in concentration can be explained on the basis of collision theory of reaction rate, which says increase in collision with the increase in concentration there by increasing the rate of precipitation. [18]

Table No.1 Rate constant change with [$CaCl_2$] (k Sec-1)

[$H_2C_2O_4$] M	[$CaCl_2$]		
	0.0013 M	**2.702×10^{-3}M**	**4.053×10^{-3}M**
0.1	0.00382	0.0086	0.0095
0.05	0.023	0.0508	0.306
0.025	0.0081	0.029	0.11

To check the effect of added salt on precipitation, we added KCl, The result reveals that at [$C_2H_2O_4$] = 0.1 M and [CaCl2] =13.51 x 10^{-2} M, 27.02 x 10^{-2} M and 40.53. It has been observed that there is increase in rate constant with increasing concentration of potassium chloride. [19] Variation in rate constant with KCl is shown in (Table No. 2)

Table No. 2 Effect of Salt [KCl] On Rate Constant (k sec-1), [$C_2H_2O_4$] = 0.1 M

[KCl] M	[$CaCl_2$]		
	1.351×10^{-3} M	**2.702×10^{-3}M**	**4.053×10^{-3}M**
0.0	3.82×10^{-3}	8.6×10^{-3}	9.5×10^{-3}
0.1	1.3×10^{-2}	9.6×10^{-3}	1.26×10^{-2}
0.2	1.28×10^{-2}	1.7×10^{-2}	1.47×10^{-2}
0.3	2.98×10^{-2}	4.49×10^{-2}	1.50×10^{-2}

Table No. 2 Effect of Temperature On Rate Constant (k sec-1), [$C_2H_2O_4$] = 0.1 M

Temp	[$CaCl_2$]		
	1.351x10^{-3} M	**2.702x10^{-3}M**	**4.053x10^{-3}M**
293^0	1.7 x 10^{-2}	3.8 x 10^{-2}	2.81x 10^{-2}
299^0	1.55x 10^{-2}	3.47 x 10^{-2}	1.65 x 10^{-1}
303^0	2.9 x 10^{-2}	4.9 x 10^{-2}	8.5x 10^{-2}

From the values it has been observed that there is rate constant with the increase in temperature. [20]

From the values of rate constant activation energy values were calculated by using

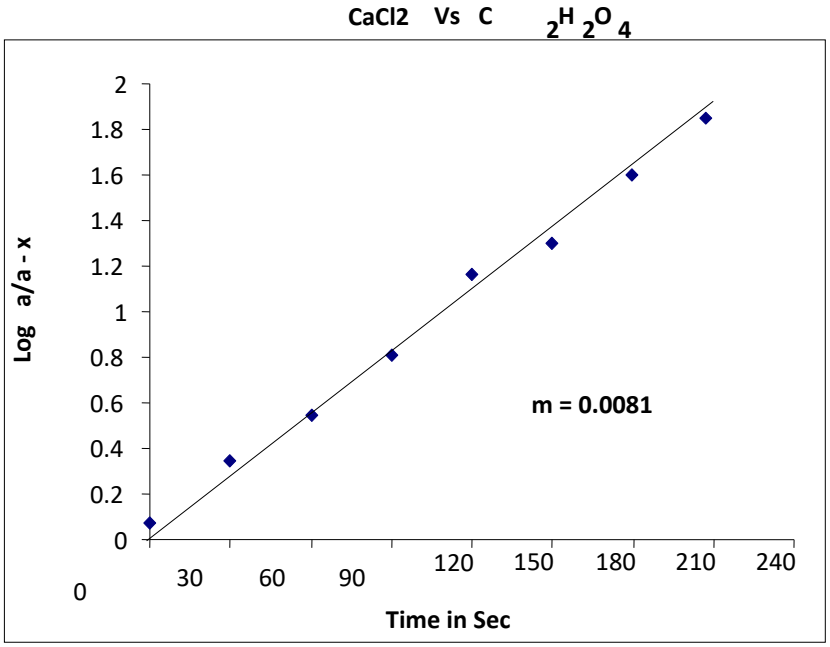
Arrhenius equation $k = Ae^{-E/RT}$

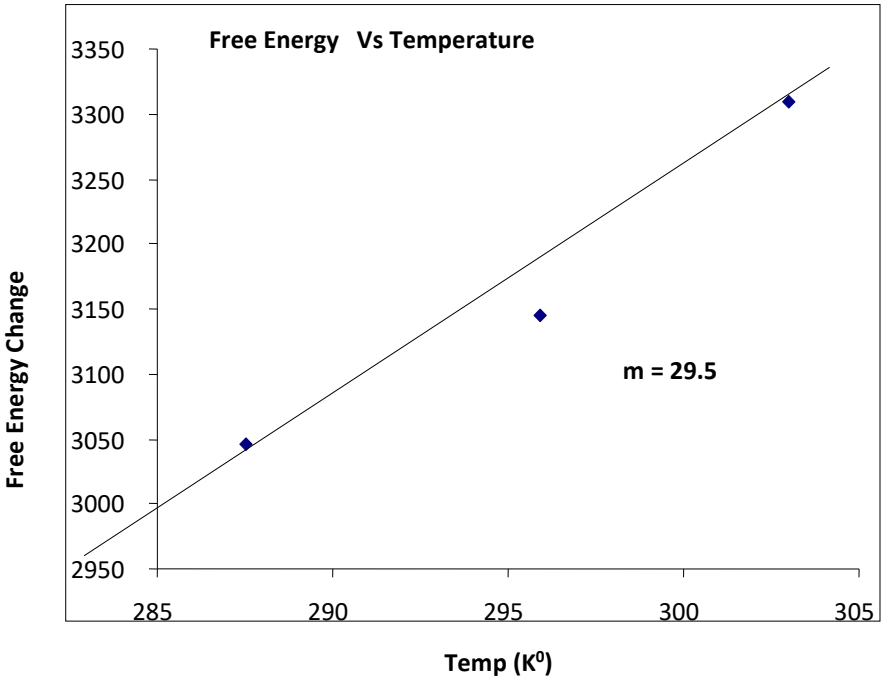
Free energy value, ΔG* is calculated by using an equation. R.L Yadav and Verma have reported Ceric-Cerium oxidation of Catchechol and said that Arrhenius law was found to be valid [21].

$$\Delta G^* = -RT\ln K$$

Free energy at different temperature were calculated and graph of ΔG* Vs temperature was plotted which gives straight line, slope of this line is used to calculate ΔS* values i.e. entropy change, intercept of this line gives values of ΔH*.the of different thermodynamic parameters which are calculated are, Ea*= 33.622x10^{2}KJ mol^{-1}

ΔG=30.1x10^{2}KJmol^{-1}, ΔH=30.00x10^{2}KJ mol^{-1}, ΔS= 29.5KJ mol^{-1}





CONCLUSION:

From the above discussion it is concluded that Rate of reaction is depends on concentration of reactants, reaction also show increase in rate constant with addition of salt. Effect of temperature also increases the rate of reaction thereby increasing rate of precipitation. Different thermodynamic parameter calculated for the reaction, in this value of ΔG positive value of enthalpy is also positive indicates that the reaction is endothermic and the product is having higher energy than the reactants.

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