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Potentiometric Studies on Binary complexes of La (III) ion with Quinaldic Acid

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ABSTRACT
The binary solid complex of La(III) ion with Quinaldic Acid was isolated from the mixture of equimolar solutions of metal nitrates and ligand. The pH of the solution was adjusted to 7.0. The equimolar solution was refluxed in ethyl alcohol for about 3-4 hours on water bath. On refluxing, the solid mass is obtained on cooling. This solid mass was filtered, washed, recrystallized and dried at 60-70°C. The complex was subjected to elemental analysis. The metal content present in complex was estimated by conventional standard methods. The probable formula of complex was assigned on the basis of elemental analysis, which was well supported by TG curves.
The kinetic parameters like activation energy (Ea), Order of reaction (n), frequency factor (log Z) and activation Entropy (S°) were calculated by applying Doyle's method modified by Zsako [(2)] and Coat's and Redfern methods. [(3)]
[Key words: - Patentiometry, mixed ligand complexes, stability constant, frequency factor activation energy, Order of reaction, activation entropy],

INTRODUCTION
The thermal decomposition of complexes has attracted the attention of several workers [(4-9)]. Till now various methods were developed for deriving kinetic data from TG curves. But It is difficult to find a suitable equation to describe the kinetics of all reactions. Particularly in the case when kinetics varies during the process.
The thermal decomposition rate of a complex is determined by the rate at one or more of the states.
The method proposed by Coats and Redfern's determines the order of the reaction and energy of activation from thermogravimetric data. By using standard deviation instead of curve fitting, the trial and error method of Doyle, which was modified by J. Zsako for the calculations. The TG data obtained for the second step of decomposition process of copper lucine complex was used for kinetic studies. The first step contributes to the loss of crystallization of water in the complex.

METHOD
Derivatograph (MOM – Budapest Paulik Frdey) with a basic sensitivity of 20±0.2 mg full scale detection a working mass range of 10mg to 10gm was used to record the weight loss of the sample with rising temperature. Ar was used as the furnace atmosphere at atmospheric pressure and 94.8°C /minute heating rate was employed.

Preparation of Sample
Solid complexes of La (III) with Quinaldic Acid was prepared by mixing a equimolar (0.1M) solutions of metal perchlorates and ligand solutions. The pH of the mixture was raised with NaOH and the precipate obtained was filtered, washed and dried.

The Elemental analysis of the complexes: -
La (III) - Quinaldic Acid Complex
C = 38.60%. H=1.93%, O = 10.29%, N = 4·50%., La = 44.68% (calculated)
C = 38.54% H = 1.18% O=10.25%. N=4·43%, La=44.61 %. (Experimental)
which correspond to probable formula La (III) - Quinaldic acid having 1:1 metal to ligand complex ratio respectively.

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Result and Discussion

The thermogravimetric curve was obtained (using 4.8°C / minute heating rate) up to a temperature of 890°. Coats and Redfern determine the order of the reaction on the basis of thermogravimetric data based on a plot of

$\log\left[\left[1-(1-\alpha)^{1-n}\right]/T^2(1-n)\right] = A \text{ vs } \frac{1}{T}\times 10^3$, where "$\alpha$" is the thermal decomposition rate calculated from thermogravimetric data of the sample

The value of α can be calculated as;

$$\alpha = \frac{W_o - W}{W_0 - W_t} \qquad \ldots\ldots\ldots \text{(i)}$$

where Wo, W and Wt are initial, actual and final weights of the sample respectively. 'n' is the order of reaction. For assumed value of "n" a number of relationships are plotted and correct value of 'n' gives a straight line.

The activation energy can be calculated by using this equation.

E = 2.303 mR

where "m' is the slope of the straight line and 'R' is gas constant

By using this equation method the value of energy of activation and the order of the reaction can be calculated. The obtained values were compared with the method of Doyle as modified by Zsako.

The equation for themogravimetric curves given by Doyle is:

$$g(\alpha) = \frac{ZEa}{Rq}P(x) \qquad \ldots\ldots\ldots\ldots \text{(ii)}$$

Where

$g(\alpha)$ =A certain function of α where α stands for the fraction of initial compound reacted.

Z = Frequency factor, Ea = Activation energy

R = Gas constant

q = Heating Rate

P(x) is the value of integral.

$$P_{(x)} = \frac{e^{-x}}{x} - x\frac{e^{-x}}{u}du$$

Where, $u = \frac{Ea}{RT}$

But the value of P(x) depends both on Temperature and Activation energy.

Doyle has suggested a trial and error curve Fitting Method for activation energy which was modified by Zsako.

The value of α can be calculated by equation '1'

The values of $g(\alpha)$ may be calculated for various values of b (order of decomposition) in a general equation,

$$\frac{d\alpha}{dt} = K(1-\alpha)^b \qquad \ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

Where values of 'b' are considered as 0, 1 and 2.

B = 0; $g_0 = (\alpha)$

B= 1; $g_1 (\alpha) = \ln(1-\alpha)$

B = 2; $g_2 (\alpha) = \frac{\alpha}{1-\alpha}$

if we take the logarithm equations (2) then,

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$$\log \frac{ZEa}{Rq} = \log g(\alpha) - \log Px = B.....(iv)$$

The Values of the integral

$$P(x) = \frac{e^{-x}}{x} - x\frac{e^{-x}}{u}du.....(v)$$

were calculated by Doyle for x, values covering a range from 10 to 50 and these values were used in calculating "B" then,

$$B_0 = \log g_0(\alpha) - \log P(x).....(vi)$$

$$B_1 = \log g_1(\alpha) - \log P(x).....(vii)$$

$$B_2 = \log g_2(\alpha) - \log P(x).....(viii)$$

The -log P(x) values were taken corresponding to over a range of 10 to 20 Ea value (As Ea value according to graphical method is Near 14 kcal/mol) and cover a temperature range 160° to 250° (Corresponding to temperature prior to decomposition and the formation of oxide from the complex). The average 'B' values are calculated at different temperatures and the values of standard deviations are Calculated as –

$$\delta = \sqrt{\frac{\left(B_1 - \overline{B}\right)^2}{r}}.....(ix)$$

Where B_1 is any individual value,

$\overline{B}$ is arithmetical mean

r is number of values.

δ values for B_0, B_1 and B_2 are similarly calculated and given in tables

Table-1- Sample weight and log(α) data of [La (III) – Quinaldic acid] complex at different temperature Wo = 19.0mg Wt = 9.8992 mg

Temp. (^{0}C)	W (mg)	α	Log (α)	$\log\left(\ln\frac{1}{1-\alpha}\right)$	$\log\left(\frac{\alpha}{1-\alpha}\right)$
300	17.08423	0.21370	-0.67495	-0.62441	-0.57183
310	17.02004	0.21842	-0.66071	-0.60829	-0.55368
320	16.95585	0.22546	-0.64692	-0.59263	-0.53597
330	16.89166	0.23251	-0.63356	-0.57736	-0.51863
340	16.82746	0.23956	-0.62059	-0.56247	-0.50165
350	16.76327	0.24660	-0.60801	-0.54797	-0.48503
360	16.69908	0.25365	-0.59577	-0.53378	-0.46871
370	16.20885	0.30745	-0.51222	-0.43489	-0.35268
380	16.13314	0.31576	-0.50064	-0.42085	-0.33585
390	15.57940	0.37654	-0.42419	-0.32563	-0.21899
400	15.03944	0.43581	-0.36070	-0.24233	-0.11213
410	14.94018	0.44670	-0.34998	-0.22778	-0.09294

Table 2 – Activation Energy and order of reaction of [La (III)- Quinaldic Acid] complex.

Ea	B=0	B=1	B=2
14	0.008393	0.009328	0.004024
16	0.007695	0.011751	0.008764
18	0.008080	0.002292	0.006983

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20	0.004639	0.008714	0.013406

The value of 'δ' is minimum, if the apparent order of the reaction is taken as one i.e. first order of reaction so from the tested δ value, B=1 is the best, δ has minimum value for Ea=18kcal/mole and $\bar{B}$ is 8.15197 for the Corresponding Ea.

The apparent frequency factor log Z can be calculated by the equation –

Log Z = $\bar{B}$ + log Rq – log Ea

The calculated value of log Z for [La(III) – Quinaldic acid] Complex is 8.193801.

The apparent activation entropy is calculated by using the equation

S° = 2.303 log Zh/KT

Where T is taken as temperature ($T^{1/2}$) at which the weight loss is half of the total weight loss. "h" is planck's constant and 'K' is boltzmann's constant. For complex [La(III) – Quinaldic acid] the value of S° is -10.934kcal/mole.

The values of apparent activation energy and reaction order calculated by Coats and Redfern and Zsako's modified by Doyle method was given as –

	Ea (kcal/mol)	Order of Sceaction
Coats and Redfern.	18.00	01
Zsako	18.39	01

The above given values are in good agreement with one another,

The other kinetic parameters for the complex La (III) Quinaldic Acid is as follow –

	Activation Energy (kcal/mol)	Order of reaction	Frequency factor (log Z)	Activation Energy (S^0)
Coats and Redfern	18.00	01	8.193801	-10.935
Zsako's method	18.39	01	8.32160	-10.945

References

1. Doyle. J Appl. Polym Sci (1961), 2, 285
2. Wendiandt, W.W. and EL Simmons, Thermochim Acta (1971), 2,217.
3. Coats AW. And JP Redfern, Nature (London), (1964), 68, 20).
4. Simmons, E.L and W.W. Wandlandt., J. Inoag Nucl. Chem. (1965), 27, 2325
5. Wendlandtg W. W. and E. L. Simmons, J Inog Nucl. Chem. (1965), 27, 2317
6. Evaluation of reliability of coats – Redfern method for kinetic analysis of non-isothermal TGA of nonferrous metals, society of China vol 18, issue 1 (2008), 217-221
7. Bayaty, S.A. Jubier N. J. and quaily R.A.H. "Study of thermal decomposition Behaviour and kinetics of epoxy / polystyrene composites by using TGA and DSC". "Journal of Xian University of Architecture and Technology" (2020), 12(3) PP-1331-1341.
8. Mahoud. Sharare, Samy Sadaka (2014) 'Thermogravimetric analysis of swine manure solids obtained from farrowing and growing finishing farms". "Journal of sustainable Bioenergy Sysem." Vol No. (1)
9. Dariga Altynbaeva, Alexander Astafer and Roman Tabakaev (2018), 'Kinetics of biomass low-temperature pyrolysis by Coats - Redfern Method', "MATEC web, of conferences" 194,01058, https://doi.org/10.1051/mate conf/ 2018, 19401058.
10. Ansari A., Lisheng Liu and Linfeng Rao (2015), "Binary lantuonide (III)/nitrate and. tomary lanthaoude C)/nitrate chloride complexes in an ionic liquid. Containing water: optical abreption and luminescence studies. Dalton transaction 44, 2907-2914
11. B. Varshney, K. C. Gupty (2003), studies on the stabilities of some mixed ligand complexes of lanthanide (III) ions. "Asian Journal of Chemistry. 1598-1602

DOI:10.46647/ijetms.2022.v06i06.105 ISSN: 2581-4621

12. M.S. kaurar, Grajendra Grour (2008), Potentiometric study of the biligand 1:1:1 Ln (III) - CPTA-valine/lucin serine complexes and evaluation of thermodynamic Asian Journal of Chemistry", 18(4), 3027-3032
13. Omar M. El-Roudi, Elham M. Mbd Alla and Said A. Ibrahim, (1997), 'Patentiometre studies on the Binary complexes of N-[Tire (hydroxyouthyl)methyl] glycine with Th^{4+}, Ce^{3+}, La^{3+} and UO^{2+}_2 and Medium Effects on a th- trieme Bimary complex, J. Chem. 1 ang. Data, 42, 3, 609-613.
14. Toraishi T, Farkas, I., Szabo, Zoltan (2005) (Complexation of Th (IV) and various lanthanides (III) by glycolic acid, patentionetree, C-13-NMR and EXAFS studies, " Journal of the chemical society, Dalton Transactions, no. 20, P-3805-38/2
15. Kaczmarek MIT. Jastrzab R., Rade cka –Paryzek W. Pa (2013),' Potentiometric study of lanthanide Salicylaldimine schiff base complexes, J. Solut. Chem', 4218-26, doi – 10.1007/S10953-012 9946-9