

Thermogravimetric evaluation of decomposition kinetics of metal surfactant complexes

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Abstract Thermal behavior of various synthesized transition metal surfactant complexes of the type $[M(\text{CH}_3\text{COO})_4]^{2-}[\text{C}_{12}\text{H}_{25}\text{NH}_3^+]_2$ where M: Cu(II), Ni(II), Co(II) has been investigated using Thermogravimetric Analysis (TGA). It was found that pyrolytic decomposition occurs with melting in metal complexes, and that metal oxides remain as final products. The activation energy order obtained, $E_{\text{Cu}} > E_{\text{Ni}} > E_{\text{Co}}$, could be explained on the basis of size of transition metal ion and metal ligand bond strength. In the course of our investigation on the decomposition of complexes, we carried out a comparative study of different measurement and calculation procedures for the thermal decomposition. A critical examination was made of the kinetic parameters of non-isothermal thermoanalytic rate measurement by means of several methods such as Coats–Redfern (CR), Horowitz–Metzger (HM), van Krevelen (vK), Madhusudanan–Krishnan–Ninan (MKN), and Wanjun–Yuwen–Hen–Cunxin (WYHC). The most appropriate method among these was determined for each decomposition step according to the least-squares linear regression. It was found that the results obtained using CR method differ considerably from HM method, as the former method involves a lot of approximations and is not much reliable. The application of thermoanalytic techniques to the investigation of rate processes has also been discussed.

Keywords Activation energy · Transition metal surfactant complexes · Thermal behavior · TG/DTG · DSC · Thermal decomposition kinetics

Introduction

The ever-increasing demand for new materials and technology [1, 2] has encouraged the development and study of a new class of amphiphiles, i.e., metallosurfactants. The molecular design of metallosurfactants can be created as desired. The facility to synthesize complexes with various hydrophobic chains and head group (metal ions) provides great flexibility in tailoring the amphiphiles to have specific physical architecture and chemical functionalities. It finds numerous potential applications in various areas including templating of mesoporous materials [3, 4], thin-film devices [5], interfacial photophysics, and both homogeneous as well as heterogeneous catalysis [6–10]. While their aggregation properties have been examined extensively, thermal properties of such metal complexes have not been reported in the literature, till date. There clearly remains a great amount to be investigated in this area as thermal properties have crucial importance in materials science.

The study of reaction kinetics dates back to as early as 1889 when the much celebrated formula for the temperature dependence was proposed by Arrhenius. Research in the field of reaction rates led to the award of the first Nobel Prize in chemistry (1901) to J. H. van't Hoff. Kinetic studies do not only predict thermal decomposition mechanisms, but also the data obtained are extremely important in designing such devices where thermal decomposition takes place. The postulation of kinetic equations is based on the knowledge of the mechanism, and kinetics is the starting point to postulate mechanisms for the thermal decomposition.

A simple parameter such as value of the activation energy can give an idea about the optimum reaction conditions in process chemistry, thermal stability, and the

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expected lifetime of a compound to be kept at a certain temperature. The activation energy of the thermal decomposition reaction is an indication of the relative bond strengths within the molecules studied and can be related to vibrational frequencies determined from IR and Raman spectroscopy. Therefore, this area has gained much attention of the researchers in the recent past. Takahashi et al. [11] have investigated the thermal stabilities of the Ni(II)-complexes with 4-iodopyrazole. Kinetic analysis of thermal decomposition of some Cobalt complexes of unsymmetrical *vic*-dioximes ligands have been carried out by Sahin et al. [12] using various thermoanalytical methods.

Thermogravimetry (TG) is the most commonly used technique for thermal analysis. Thermogravimetric analysis (TGA) measures mass or weight loss as a function of time and temperature to determine kinetic parameters which involves both thermal and isothermal techniques [13]. Isothermal techniques involve introducing the sample into a furnace held at constant temperature and observing mass change with time. Non-isothermal studies involve heating a sample in an apparatus, at a constant heating rate, and continually weighing it to develop a mass versus time curve. Once a mass (or conversion) versus time curve has been generated using the TGA, the particular method of determining the activation energy can lead to differing results. Data from isothermal experiments are traditionally plotted in the form of the natural log of the reaction coefficient against the inverse of temperature. This method linearizes the data, and the kinetic parameters can then be determined from the slope and intercept of the resulting linearized equation. Traditional non-isothermal experiments also involve linearizing an equation in some manner and fitting the resulting straight line. In addition, it enables one to determine the apparent kinetic parameters of reactions (the reaction order n , the activation energy E , and the frequency factor A). Considerable attention is paid to the kinetic parameters' calculation from TG curves. New calculation methods are still being published [14, 15]. We tested several determination methods for the activation energy on the transition metal complexes.

The present communication describes the thermal decomposition studies (TG, DTG, and DSC) of surfactant metal complexes and its comparison with the conventional organic surfactant. Various kinetic parameters of the thermal decomposition have also been determined by means of five different non-isothermal methods, namely, Horowitz–Metzger, Coats–Redfern, Madhusudanan–Krishnan–Ninan, Wanjun–Yuwen–Hen–Cunxin, and van Krevelen. A plausible decomposition mechanism for the metal surfactant complexes has also been proposed based on the TG/DTG curves obtained.

Experimental

All materials were commercially available and of analytic grade unless stated otherwise.

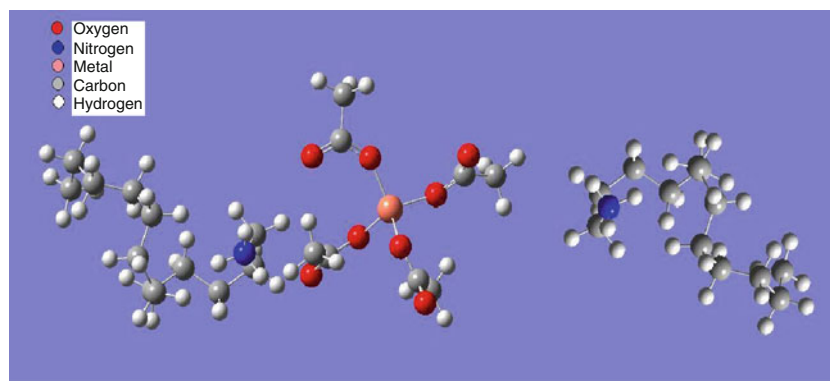
Sample preparation

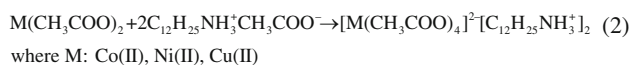
Metallosurfactants of the type, $[M(\text{CH}_3\text{COO})_4]^{2-}[\text{C}_{12}\text{H}_{25}\text{NH}_3^+]_2$, where M: metal ion (Fig. 1) were synthesized by the literature procedure [16]. The synthesis was carried out in two steps. The reaction scheme involved the preparation of dodecylamine acetate by reacting equimolar quantities of dodecylamine and acetic acid with continuous stirring. In the subsequent step, dodecylamine acetate and metal acetate were refluxed in ethanol in desirable amount for approximately 2 h to get the required metal–surfactant complex. The reactions taking place are as shown in Scheme 1. The complexes were further recrystallized in dichloromethane–ethyl acetate mixture and stored in vacuum desiccators till further use. The full characterization of compounds will be described elsewhere.

Instrumentation

Simultaneous TG–DTG–DSC curves were obtained with thermal analysis system; model SDT Q-600, from TA Instruments. The purge gas was nitrogen flow of

Fig. 1 Graphical representation of metallosurfactant





Scheme 1 Synthesis of metal–surfactant complexes

100.0 mL min⁻¹. A heating rate of 10 °C min⁻¹ was adopted, with samples weighing about 10.0 mg. This technique consists of heating the sample to a given temperature at a fixed heating rate (β). So, in a TG experiment, the instrument typically registers hundreds or thousands of experimental points that can be used for kinetic analysis of the reaction. Alumina crucibles were used for recording the curves.

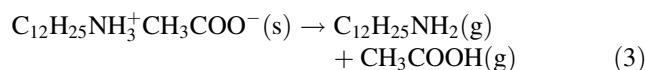
Results and discussion

TGA was employed to monitor the thermal behavior of the metal surfactant complexes and to determine various kinetic parameters of thermal decomposition, such as activation energy (E), frequency factor (A), enthalpy (ΔH), Gibbs free energy (ΔG), entropy (ΔS) etc.

Thermal behavior

Dodecylammonium acetate

The thermal behavior of the dodecylammonium acetate surfactant as synthesized in the first step of metallosurfactant preparation (Scheme 1) has been summarized in Eq. 3. The TG/DTG/DSC superimposed curves for (Fig. 2) $\text{C}_{12}\text{H}_{25}\text{NH}_3^+\text{CH}_3\text{COO}^-$ indicate that the decomposition process took place in a single step, which can be reduced to



The entire surfactant gets decomposed to gaseous state by 190 °C, in a single step without leaving any residue. Dialkylammonium salts investigated by Ouriques et al. [17] show decomposition behavior similar to that observed with dodecylammonium acetate (Fig. 2).

Surfactant metal complexes

The TG traces of the surfactant metal complexes show high thermal stability. The Co(II), Ni(II), and Cu(II) complexes of surfactant show transition temperatures at 201, 230, and 224 °C, respectively. The decomposition of all the transition metal complexes is almost similar.

Primarily, two major mass loss regions have been observed: the first region between room temperature and approximately 250 °C is associated with the breakdown of complex and the decomposition of quaternary ammonium structure. The second mass loss step involved the decomposition of metal acetate to metal oxide which formed the composition of the final product. However, the TG trace of nickel surfactant complex (Fig. 3a) indicates the presence of multiple decomposition steps suggesting the formation of quite stable intermediates. TG results obtained experimentally are in excellent agreement with the calculated values as summarized in Table 1.

The DSC curves for the complexes prepared exhibit an endothermic process initially. The area of endothermic peak corresponds to heat of fusion and the peak temperature corresponds to melting point. Multiple peaks have been observed after melting point transition, an exothermic peak followed by an endothermic. These peaks relate to complex solid–gas–solid reactions involving probably the

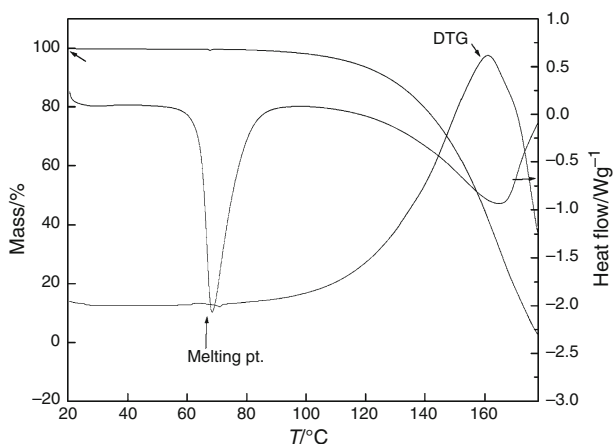


Fig. 2 TG/DTG/DSC superimposed curves of $\text{C}_{12}\text{H}_{25}\text{NH}_3^+\text{CH}_3\text{COO}^-$ at 10 °C min⁻¹

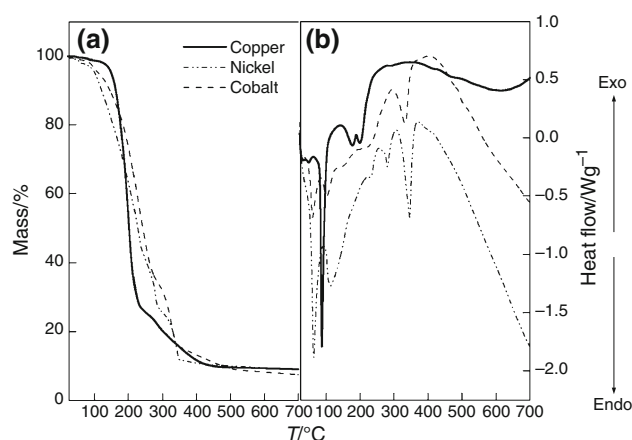


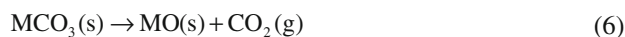
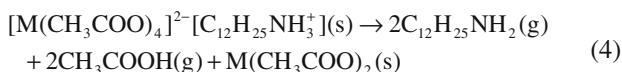
Fig. 3 a) TG traces and b) DSC curves for the metal surfactant complexes

Table 1 TGA analysis for different decomposition steps of all the metal surfactant complexes

Complex	Transition temperature/°C	Mass loss/%	
		Calculated	observed
Copper	201	72.3	72.7
	285	88.2	90.9
Nickel	230	55.5	56.5
	278	73.5	74.4
	347	88.2	90.9
Cobalt	224	66.0	66.2
	327	88.8	90.6

production of volatile or gaseous products depicted in Scheme 2.

Plausible Mechanism for the thermal decomposition is as follows:

**Scheme 2** Thermal decomposition mechanism for metal–surfactant complexes

Kinetic consideration and calculation procedure: In general, the rate constant, k of a solid-state reaction is given by the formal kinetic equation:

$$\frac{d\alpha}{dt} = kf(\alpha) = Ae^{-\frac{E}{RT}}f(\alpha) \quad (7)$$

where α is the fractional reaction; t , is time; A is the pre-exponential factor; E is the activation energy; R is the gas constant; T is temperature in Kelvin, and $f(\alpha)$ is the kinetic function, which takes different forms depending on the reaction rate equation [18]. In isothermal kinetic studies, the rate equation used to calculate the rate constant has the form:

$$g(\alpha) = kt \quad (8)$$

where $g(\alpha) = \int \frac{d\alpha}{f(\alpha)}$ is obtained by the integration of $f(\alpha)$. However, non-isothermal methods are becoming more widely used because they are more convenient [19].

In non-isothermal kinetics, the time dependence on the left side of Eq. 7 is eliminated using a constant heating rate $\beta = dT/dt$, so that $T = T_0 + \beta t$, where T_0 is the starting temperature, and t is the time of heating. With the use of integral methods of analysis, Eq. 7 may be written as

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dt \quad (9)$$

Considering that reaction rate is negligible at low temperatures, integration of this equation leads to Doyle's equation [20]:

$$g(\alpha) = \frac{AE}{R\beta} \int_{T_0}^T \frac{e^{-x}}{x} - \int_0^\infty \frac{e^{-u}}{u} du = \frac{AE}{R\beta} P(x) \quad (10)$$

where $u = E/RT$, and x is the corresponding value of u at which a fraction of material has decomposed. This equation has been reformulated as

$$\ln g(\alpha) - \ln P(x) = \frac{AE}{R\beta} = B \quad (11)$$

where B is a constant for a particular reaction at a constant heating rate. The integral function $P(x)$ is not definite; it may be written in an expanded form and estimated using a procedure of trial-and-error type involving iteration.

In this study, analysis of non-isothermal data has been performed using the approximate computational approaches due to Coats–Redfern [21], Horowitz–Metzger [22], Madhusudanan–Krishnan–Ninan [23], van Krevelen [24] and Wanjun–Yuwen–Hen–Cunxin [25]. Integral methods are often more reliable and generally preferred than imprecise differential methods of kinetic analysis.

In the Coats–Redfern method [21], the function $g(\alpha)$ is approximated to the form

$$g(\alpha) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-E/RT} \quad (12)$$

The equation has been written in the form:

$$-\ln \frac{g(\alpha)}{T^2} = -\ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] + \frac{E}{RT} \quad (13)$$

The quantity $\ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right]$ is reasonably constant for most values of E and over the temperature range in which most reactions occur. However, both E and A could vary with the experimental heating rate.

$$-\log \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (14)$$

for $n \neq 1$

$$-\log \frac{-\log(1 - \alpha)}{T^2} = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (15)$$

for $n = 1$

A graphical representation of the left-hand side of the above equations against $1/T$ gives a straight line with inclination $-2.303E/R$ and the intercept yields value of A .

In the Madhusudanan method [23], the equation used has the form:

$$-\ln \frac{g(\alpha)}{T^{1.9206}} = -\ln \frac{AR}{\beta E} + 3.7678 - 1.9206 \ln E - 0.12040 \frac{E}{RT} \quad (16)$$

where the symbols have their usual significance. Similar equations were obtained using methods of Wanjun–Yuwen–Hen–Cunxin and the van Krevelen with different approximations: Wanjun–Yuwen–Hen–Cunxin method [25]

$$-\ln \frac{g(\alpha)}{T^{1.8946}} = -\ln \frac{AR}{\beta E} + 3.6350 - 1.8946 \ln E - 1.0014 \frac{E}{RT} \quad (17)$$

van Krevelen method [24]

$$\ln g(\alpha) = \ln \left(\frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta \left(\frac{E_a}{RT_m} + 1 \right)} \right) + \left(\frac{E_a}{RT_m} + 1 \right) \ln T \quad (18)$$

Horowitz–Metzger [22], introduced a parameter such that, $T = T_m + \theta$. If the reaction order is 1, then T_m is defined as the temperature at which $(1 - \alpha)_m = 1/e = 0.368$ and the final expression takes the form:

$$\ln \ln g(\alpha) = \frac{E\theta}{RT_m^2} \quad (19)$$

A plot of $\ln g(\alpha)$ versus θ can yield activation energy. In the equations above, α , $g(\alpha)$, β , T_m , E , A , and R are the degree of reaction, integral function of conversion, heating rate, DTG peak temperature, activation energy (kJ mol^{-1}), pre-exponential factor (min^{-1}), and gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations (Eqs. 14–17) versus $1/T$. For van Krevelen equation (Eq. 18), the left-hand side is plotted versus $\ln T$. The values E and A were calculated from the slope and intercept of the straight lines, respectively. In this study, the above several methods based on a single heating rate were used in the thermal analysis.

Analysis for dodecylammonium acetate

The representative linearization curve of the decomposition step obtained using the least squares method by Coats–Redfern method has been presented in Fig. 4. From the TG/DTG curves, the activation energy, E , of the decomposition for dodecylammonium acetate has been elucidated and compared with metal surfactant complexes (Table 2). The kinetic data obtained by different methods agree with each other.

Analysis for surfactant metal complexes

The kinetic result of TG and DTG evaluations by employing different methods for all the complexes

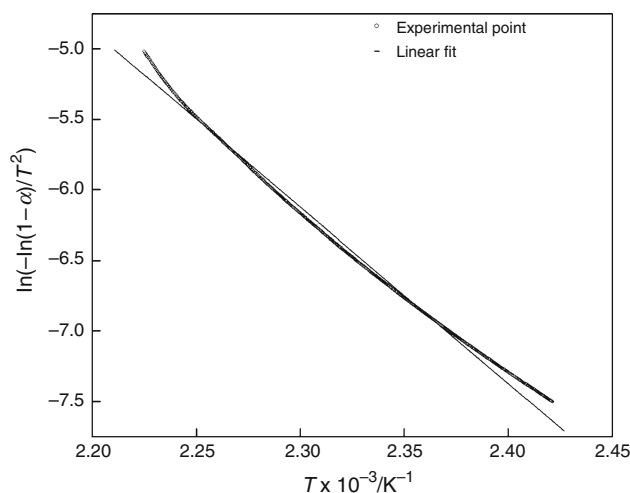


Fig. 4 Representative linearization curve for dodecylammonium acetate by Coats–Redfern method

synthesized has been presented in Table 2. The representative linearization curves for the nickel surfactant complex obtained by all the five methods have been shown in Fig. 5. The best linearity, corresponding to the maximum value of the correlation coefficient has been chosen for all the models. The results indicate that the values of all the methods are comparable.

The various kinetic parameters ΔH , ΔS , and ΔG of the complexes can be calculated using Eqs. 20–22, once E has been determined [26].

$$\Delta S = 2.303 \log \left[\frac{Ah}{kT} \right] R \quad (20)$$

$$\Delta H = E - RT \quad (21)$$

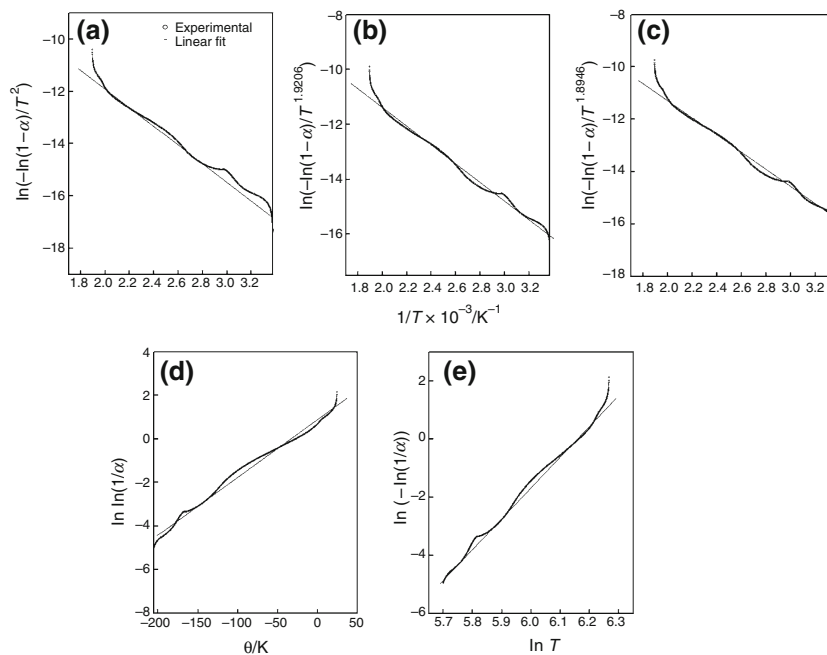
$$\Delta G = \Delta H - T\Delta S \quad (22)$$

where h is Planck constant, T is temperature in K, A is Arrhenius constant or frequency factor, and k represents Boltzmann constant. The results of TG and DTG evaluations for kinetic parameters have been presented in Table 3.

The value of reaction order, n , is around 1 for decomposition of all the complexes synthesized. Based on the TG traces, it can be elucidated that nickel complex is thermally the least stable out of all the complexes, which is in accordance with the studies observed previously in the literature [27]. The kinetic parameters thus calculated, are also helpful in assigning the bonding strength of the ligand moieties with the metal ion. In general, the smaller the metal ion, the greater is the metal–ligand bond energy. The activation energy of transition metal complexes is expected to increase proportional to the decrease in their radii. A smaller size of Cu(II) ($r_{\text{Cu}^{2+}} = 70 \text{ pm}$) permits a closer approach of ligands as compared to Ni(II) ($r_{\text{Ni}^{2+}} = 72 \text{ pm}$)

Table 2 Calculation of activation energy and regression coefficients using different methods

Surfactant complex	Horowitz–Metzger		Coats–Redfern		Madhusudanan– Krishnan–Ninan		Wanjun–Yuwen–Hen– Cunxin		van Krevelen	
	$E/\text{kJ mol}^{-1}$	R	$E/\text{kJ mol}^{-1}$	R	$E/\text{kJ mol}^{-1}$	R	$E/\text{kJ mol}^{-1}$	R	$E/\text{kJ mol}^{-1}$	R
Dodecyl ammonium acetate	101.0	0.9971	105.6	0.9892	102.2	0.9985	104.2	0.9996	106.2	0.9993
Copper	94.06	0.9988	76.88	0.9969	77.77	0.9974	77.83	0.9974	87.36	0.9992
Nickel	57.57	0.9817	29.42	0.9946	29.65	0.9929	29.72	0.9846	41.94	0.9880
Cobalt	50.68	0.9984	33.37	0.9863	33.75	0.9866	33.72	0.9866	40.32	0.9954

Fig. 5 Linearization curves obtained by (a) Coats–Redfern (CR), (b) Madhusudanan–Krishnan–Ninan (MKN), (c) Wanjun–Yuwen–Hen–Cunxin (WYHC), (d) Horowitz–Metzger (HM), and (e) van Krevelen (vK) methods**Table 3** Thermodynamic decomposition parameters for the metal surfactant complexes

Complex	$E/\text{kJ mol}^{-1}$	A/min^{-1}	$\Delta G/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$
Dodecylammonium acetate	105.6	1.33×10^{12}	109.55	101.97	-16.02
Copper	76.88	1.28×10^8	117.31	72.94	-93.61
Nickel	29.42	3.10×10^2	126.64	25.24	-201.6
Cobalt	33.37	5.37×10^2	131.26	29.24	-196.96

and Co(II) ($r_{\text{Co}^{2+}} = 74 \text{ pm}$) [28]. Hence, the E value for the Cu(II) complex is higher than that of Ni(II) and Co(II), and can be placed in descending order as

$$E_{\text{Cu}} = 94.06 \text{ kJ mol}^{-1} > E_{\text{Ni}} = 57.57 \text{ kJ mol}^{-1} > E_{\text{Co}} = 50.68 \text{ mol}^{-1}$$

From the above, we could infer that thermal decomposition of metal surfactant complexes to metal oxides proceeds via the breaking of metal ligand bond. The complexes show negative entropy values which indicate that the complexes under study have more ordered structures

than the reactants and the reaction rates are slower than normal.

Another interesting feature observed was that the activation energy of thermal decomposition decreased considerably on complexation of dodecylammonium acetate to the metal ion. This may be attributed to the fact that the metal ligand coordinate bond present in metal surfactant complex responsible for thermal decomposition is weaker than the ionic bond existing in dodecylammonium acetate. Hence, lesser energy is required by surfactant metal complexes for bond breakage and decomposition.

Conclusions

The surfactant metal complexes synthesized $[M(\text{CH}_3\text{COO})_4]^{2-}[\text{C}_{12}\text{H}_{25}\text{NH}_3^+]_2$ with different transition metals, Cu(II), Ni(II), Co(II) decompose by a two-step process to yield metal oxide as residue. Thermal stabilities of the complexes follow the order Ni(II) < Co(II) < Cu(II) with Cu(II) complex displaying the highest stability. Five different methods have been utilized to calculate the thermal behavior and the kinetic parameters of thermal decomposition in non-isothermal conditions. Thermodynamic parameters have been estimated, and the activation energy follows the order: Cu(II) > Ni(II) > Co(II). Another important finding is that the metal counterpart of organic surfactant (dodecyl ammonium acetate) possesses lower activation energy, which may be due to the weakening of bond strength upon changing from ionic bond to coordinate bond due to complexation. Consequently, it is concluded that the relationship between radius of the metal ion and the coordination of the metal ion to ligand is responsible for thermal stabilities of the metal complexes. This study provides key insights into the chemical decomposition pathways that are important during decomposition of transition metal complexes and provides data critical for refining existing and developing new applications.

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