Electronic Supplementary Material (ESI) for RSC Advances.

Transition metal based surfactants: synthesis, aggregation behavior and enhanced photoluminescence properties of fluorescein

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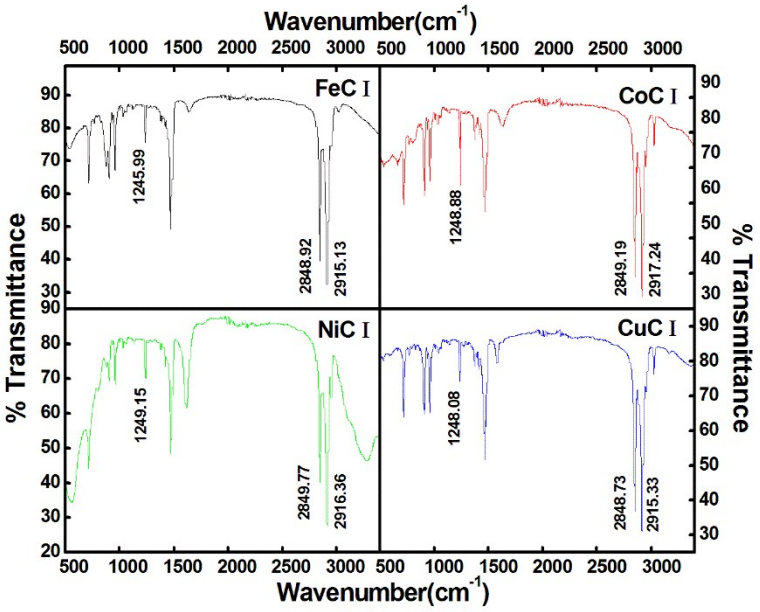
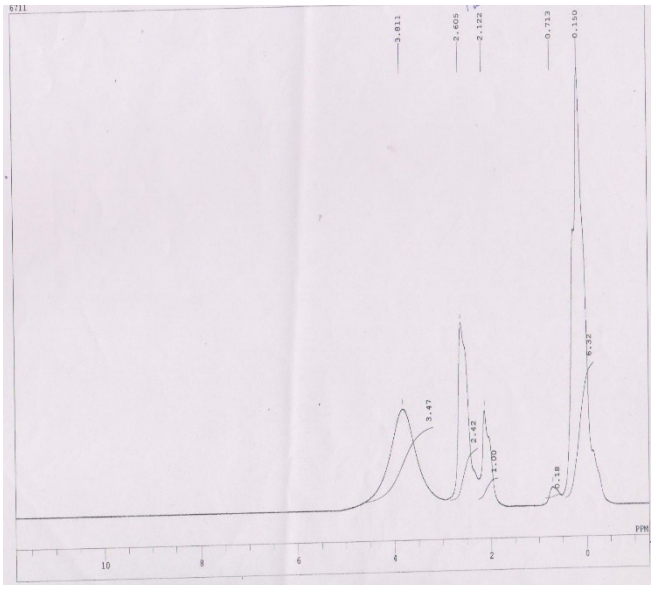


Fig. ES1. FTIR spectra of Metal complexes.

(a)



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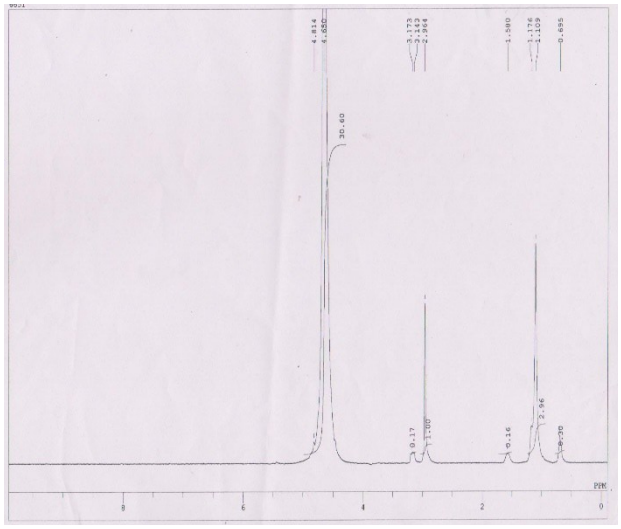

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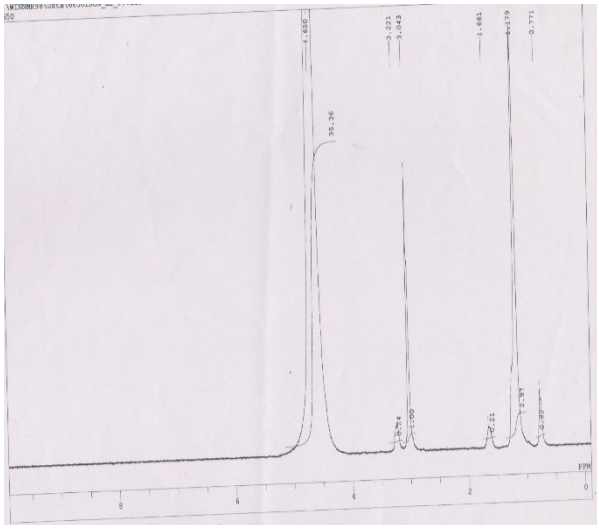

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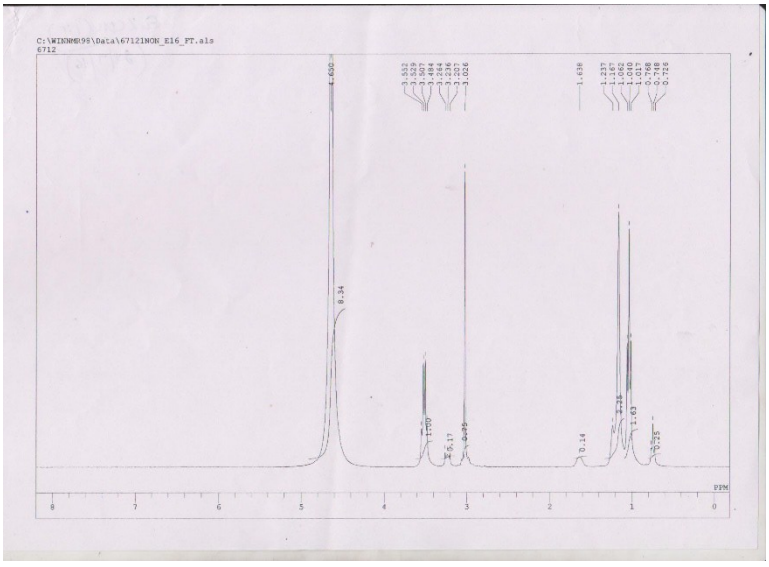


(e)

Fig. ES2. ^{1}H- NMR spectra of (a) CTAC (b) FeCI (c) CoC I (d) NiC I (e) CuC I.

THERMOGRAVIMETRIC METHODS AND THEIR EQUATIONS

The five different methods were applied for evaluation the kinetic and thermodynamic parameters of metal complexes for the decomposition of step-1.

(i) CR method

$$g(\alpha) = \frac{ART^2}{\beta E}\left[1 - \frac{2RT}{E}\right]e^{-E/RT} \qquad \text{(S1)}$$

Taking natural log

$$-\ln\frac{g(\alpha)}{T^2} = -\ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] + \frac{E}{RT} \qquad \text{(S2)}$$

The fraction mass loss (α) and corresponding $(1-\alpha)^n$ are calculated from TG curves, where *n* depends upon the reaction model.

$$-\log\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.303RT} \text{ for } n \neq 1 \qquad \text{(S3)}$$

$$-\log\frac{-\log(1-\alpha)}{T^2} = \log\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.303RT} \text{ for } n=1 \qquad \text{(S4)}$$

A straight plot between the left hand side of the above equations against 1/T gives the slope (-2.303E/R) and the intercept (A).

(ii)MKN method

$$-\ln\frac{g(\alpha)}{T^{1.9206}} = -\ln\frac{AR}{\beta E} + 3.7678 - 1.9206\ln E - 0.12040\frac{E}{RT} \qquad \text{(S5)}$$

(iii) WYHC method

$$-\ln\frac{g(\alpha)}{T^{1.8946}} = -\ln\frac{AR}{\beta E} + 3.6350 - 1.8946\ln E - 1.0014\frac{E}{RT} \qquad \text{(S6)}$$

(iv) VK method

$$\ln g(\alpha) = \ln\left(\frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta(\frac{E_a}{RT_m}+1)}\right) + \left(\frac{E_a}{RT_m}+1\right)\ln T \qquad \text{(S7)}$$

(v) HM method

Parameter $T = T_m + \theta$ is used here. If the order of reaction is 1, T_m is defined as the temperatureat which $(1-\alpha)_m = 1/e = 0.368$ and therefore

$$\ln\ln(\alpha) = \frac{E\theta}{RT_m^2} \qquad \text{(S8)}$$

Here, symbols β, T_m, E, A, $R$are heating rate, DTG peak temperature, activation energy (kJmol^{-1}), pre-exponential factor (min^{-1}) and gas constant (8.314 Jmol^{-1}K^{-1}), respectively. Other parametersΔH, ΔS and ΔG were calculated using following equations.

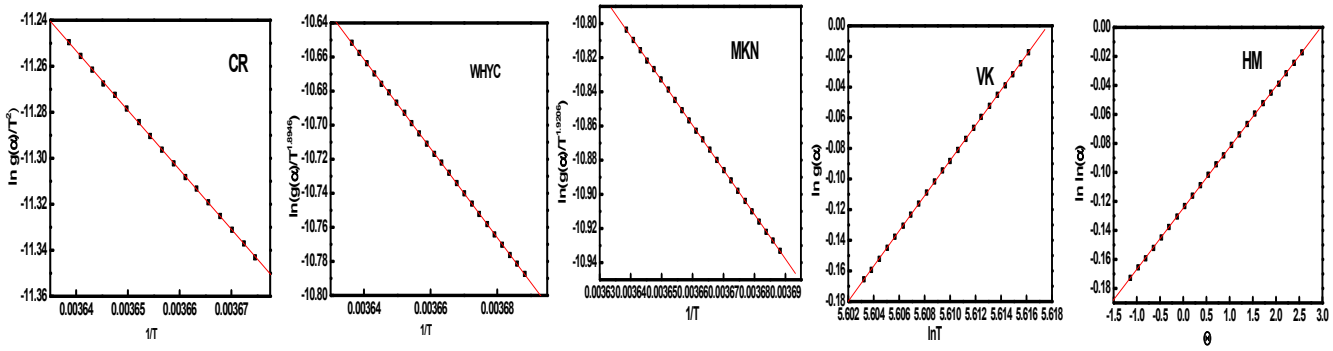
$$\Delta S = 2.303\log[Ah/kT]R \qquad \text{(S9)}$$

$$\Delta H = E - RT \qquad \text{(S10)}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{(S11)}$$

where, h, T, A and k is Planck constant, temperature in K, Arrhenius constant or frequency factor and Boltzmann constant respectively.

(a)



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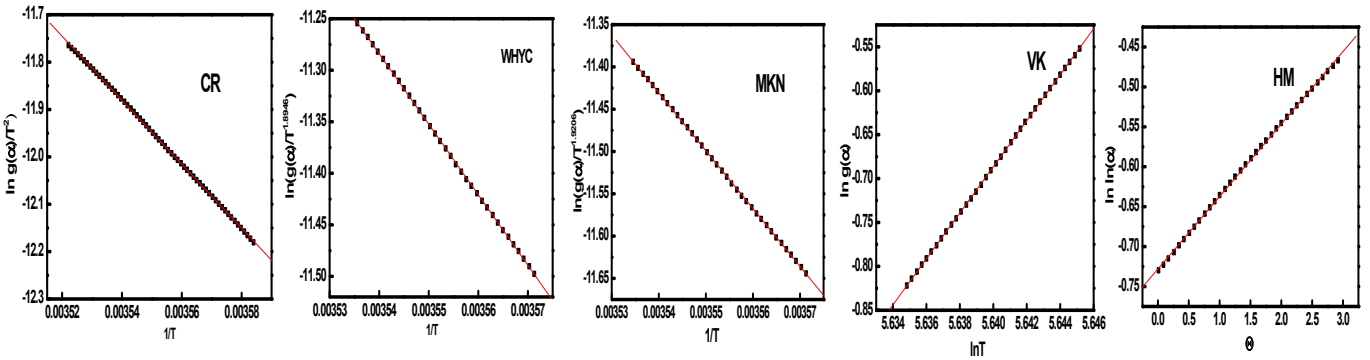

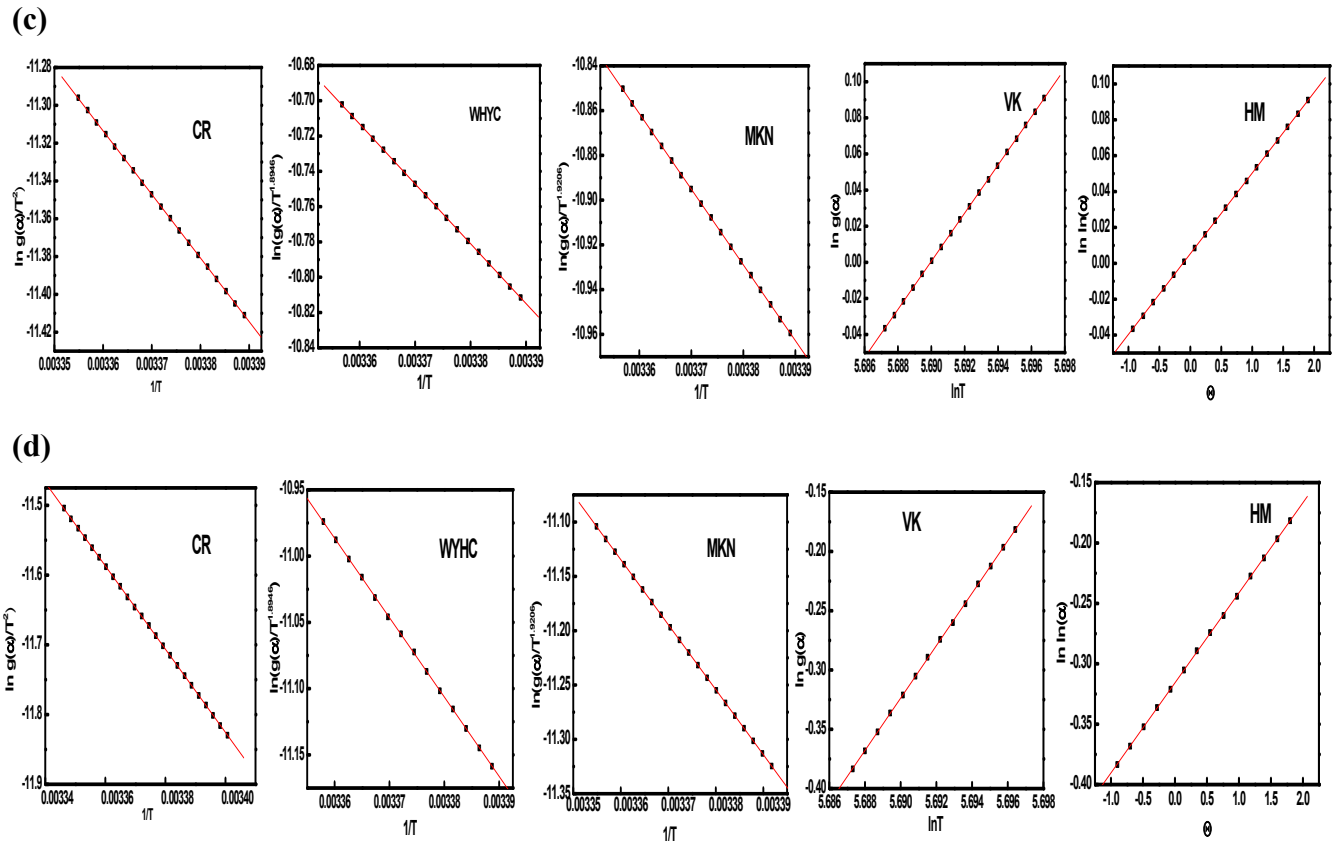

Fig. ES3. Linearization curves obtained by different methods for (a) FeCI (b) CoC I (c) NiC I (d) CuC I.

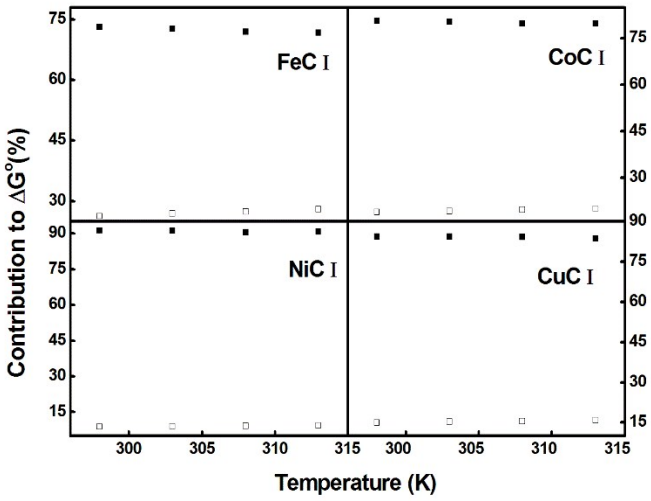

Fig. ES4. Enthalpic (□) and Entropic (■) contributions to ΔG^{O} for metal complexes

Table ES1.C, H and N value of metal complexes with metal content.

Metal complexes	Experimental (%)	Calculated (%)	Metal content(ppm)
FeCI	C=49.94, H=9.657,N=2.701	C=51.03,H=9.40, N=3.31	2.34
CoCI	C=50.16,H=9.467,N=3.161	C=50.68,H=9.337,N=3.110	2.01
NiCI	C=41.19,H=8.690,N=2.422	C=40.88,H=7.539,N=2.510	3.11
CuCI	C=47.12,H=8.947,N=2.974	C=46.48,H=8.563,N=2.854	4.15

Table ES2. Vibrational peaks of CTAC and metal complexes

Modes of Vibration	pure CTAC (cm^{-1})	FeC I	CoC I	NiC I	CuC I
-CH_2- asym stretching	2915.26	2915.13	2917.24	2916.36	2915.33
-CH_3- sym stretching	2848.41	2848.92	2849.19	2849.77	2848.73
-CH_2-CH_2- stretching	1470.16	1470.15	1471.26	1471.67	1470.30
N-$(CH_3)_3$-sym stretching	1260.25	1245.99	1248.88	1249.15	1248.08
Terminal Cl	325	362.29	341.76	358.67	324.87
Bridging Cl	-	281.06	279.87	282.20	283.85

Table ES3. ^{1}H NMR chemical shifts (ppm)of CTAC and metal complexesexcept FeC I in D_2O.

Complex	$\nu_{Terminal\ CH_3}$	$\nu_{N(CH_3)_3}$	ν_{CH_2}	$\nu_{\alpha\text{-}CH_2}$	$\nu_{\beta\text{-}CH_2}$
CTAC	0.74	3.04	1.174	1.64	3.20
CoC I	0.69	2.96	1.176	1.58	3.14
NiC I	0.77	3.04	1.179	1.66	3.22
CuC I	0.72	3.02	1.167	1.63	3.23

Table ES4. Thermodynamic decomposition parameters for the metal complexes using TGA.

Complex	A/min^{-1}	ΔG /$kJmol^{-1}$	ΔH/$kJmol^{-1}$	ΔS/$JK^{-1}mol^{-1}$
FeC I	5.060×10^6	22.443	19.217	-11.83

CoC I	1.318×10^{6}	37.541	33.835	-13.19
NiC I	0.974×10^{6}	29.847	25.547	-13.54
CuC I	1.688×10^{6}	51.237	47.395	-12.98

Table ES5. Values of Tc, σ and ΔC_p° for metal complexes using conductivity measurement.

Complex	T_c (K)	σ	(-) ΔC_p^{o}(kJmol^{-1} K^{-1})
FeC I	102.2	0.2036	0.028
CoC I	100.4	0.1449	0.029
NiC I	97.8	0.0821	0.082
CuC I	96.1	0.0383	0.077