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Evaluation of Complex Formation during Polymerisation of Acrylamide Initiated by Ce(IV) Aminopolycarboxylate Ligands

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The aqueous polymerisation of acrylamide initiated by Ce(IV)-aminopolycarboxylate ligands (APCL) like glycine (GLY), iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), 1,2-diamino-cyclohexanetetraacetic acid (CDTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriamine pentaacetic acid (DTPA) are investigated. These APC ligands form stable complexes with Ce(IV). In the presence of monomer acrylamide these complexes get decomposed to form ligand radicals (R) which initiated the polymerisation reaction. Such a type of system is characterised by the formation constant 'K' and decomposition (disproportionation) constant k_d. K and k_d values are evaluated for the above six systems, by determining the rate of disappearance of Ce(IV) in the polymerisation experiment in which the concentration of the ligand is varied keeping [Ce(IV)] as constant. The complex formation is supported by the absorption spectra.

INTRODUCTION

The aminopolycarboxylate ions are well known chelating ligands which form stable complexes with many metal ions.[1] It is expected that these ligands form stable complexes with Ce(IV) in the polymerisation reaction mixture. In the presence of monomer, this complex gets decomposed by transfer of electron from the ligand to metal ion in which process the ligand radical (R) is formed and polymerisation is initiated. Such a type of system is characterised by the formation constant K and decomposition constant k_d (also called as disproportionation constant).

$$\mathrm{Ce(IV)} + \mathrm{Ligand} \overset{K}{\rightleftharpoons} \underset{\text{Complex C}}{(\mathrm{Ce(IV)\text{-}Ligand})}$$

$$\underset{\text{Complex C}}{(\mathrm{Ce(IV)} + \mathrm{Ligand})} \xrightarrow{K_d} \underset{R^{\bullet}}{(\mathrm{Ce(IV)\text{-}Ligand}^{\bullet})} + H^+$$

EXPERIMENT

From Eq. (10), (see Page 772) it is evident that the constants K and k_d can be evaluated by determining rate of disappearance of Ce(IV) in the polymerisation experiment in which the concentration of the ligand is varied keeping [Ce(IV)] as constant. In practice the reaction mixture containing 0.15 mol dm^{-3} of monomer acrylamide and 2.0×10^{-3} mol dm^{-3} of Ce(IV) and the ligand concentration is varied from 0.5×10^{-4} to 1.9×10^{-3} for NTA, CDTA, EDTA and DTPA systems and for GLY and IDA systems [L] is varied from 0.5×10^{-3} to 1.9×10^{-3} mol dm^{-3}. Some of the results are shown in Tables 1 and 2 and plots are drawn taking 1/[APCL] on x-axis and $\frac{[Ce(IV)]}{-d([Ce(IV)]/dt}$ in y-axis and straight lines are obtained (Fig. 1). From the values of slopes and intercepts, the values of K and k_d are shown in Table 2.

TABLE-1

EVALUATION OF FORMATION CONSTANT (K) AND DISPROPORTIONATION CONSTANT (k_d)

Ce(IV)-Nitrilotriacetic acid-Acrylamide System

[M] = 0.15 mol dm^{-3}, [Ce(IV)] = 2.0×10^{-3} mol dm^{-3}
(H^+) = 0.1 mol dm^{-3}, Temp. 40°C

[NTA] $\times 10^4$ mol dm^{-3}	$\frac{1}{[NTA]} \times 10^3$	$\frac{-d[Ce(IV)]}{dt} \times 10^6$ mol dm^{-3} s^{-1}	$\frac{[Ce(IV)]}{-d[Ce(IV)]/dt}$
0.5	20.00	3.1900	626.9
0.7	14.28	3.4900	573.0
0.9	11.11	3.8800	519.4
1.1	9.09	3.9900	501.2
1.3	7.69	4.1600	480.7
1.5	6.66	4.2600	469.5
1.7	5.88	4.3400	460.8
1.9	5.26	4.3750	457.0

Plot: $\frac{1}{[NTA]}$ *vs.* $\frac{[Ce(IV)]}{-d[Ce(IV)]/dt}$ (Fig. 1)

$K = 3.267 \times 10^4$, $K_d = 2.557 \times 10^{-3}$

TABLE-2

FORMATION CONSTANTS (K) AND DISPROPORTIONATION CONSTANT (k_d)

Ce(IV)-Aminopolycarboxylate ligand (L)-Acrylamide Systems

Ligand (L)	Formation constant K	Disproportionation constant k_d
GLY	8.780×10^2	1.779×10^3
IDA	9.043×10^2	2.096×10^3
NTA	3.267×10^4	2.557×10^3
CDTA	4.656×10^4	3.748×10^3
EDTA	7.670×10^4	6.150×10^3
DTPA	7.898×10^5	1.223×10^2

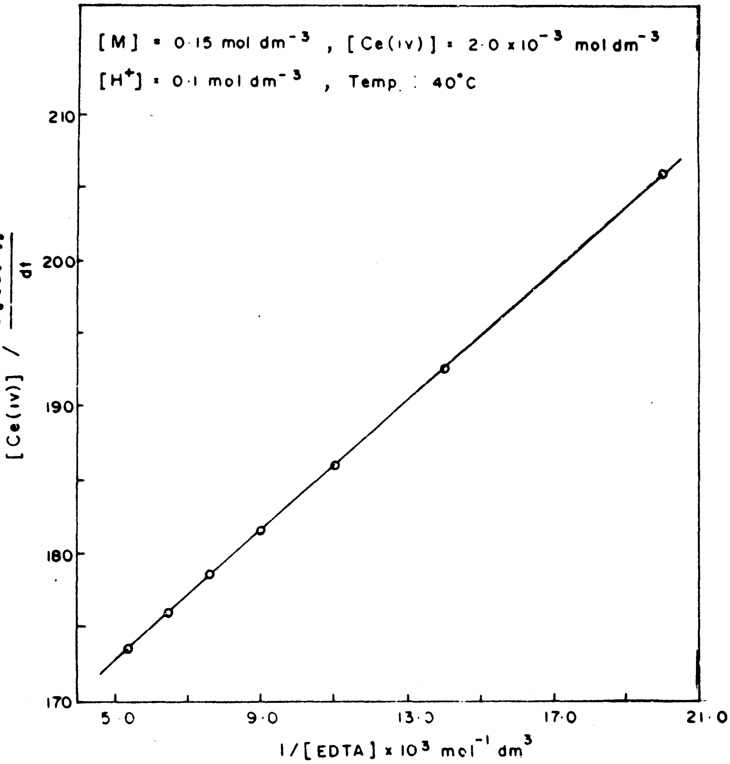

Fig. 1 Evaluation of formation cnstant (K) and disproportionation constant (k_d) Ce(IV)—Ethylenediaminetetracetic acid-acrylamide system

$$\text{Plot: } \frac{1}{[\text{EDTA}]} \text{ vs. } \frac{[\text{Ce(IV)}]}{-d[\text{Ce(IV)}]/dt}$$

RESULTS AND DISCUSSION

In the polymerisation of vinyl monomers using Ce(IV) and L (L = triethanolamine, diethanolamine, triethylamine and diethylamine series). Saha *et al.*[2] have evaluated k_d and K values. Nayak *et al.*[3] and Samal *et al.*[4] assume the constants K and k_d in the initiating systems Mn(III)-G (G = 1-propanol, glycerols and cyclo alcohols) and Mn(III)-A (A = formamide, acetamide, succinamide and thioacetamide) respectively, but the values have not been reported. However, in the vinyl polymerisation by Ce(IV) and EDTA Wen-Cheng *et al.*[5] have evaluated K and k_d values. We have also evaluated the K and k_d values for the series of aminopolycarboxylate ligands (APCL) like GLY, IDA, NTA, CDTA, EDTA and DTPA in the present study, following the method of Wen-Cheng.

$$\text{Ce(IV)} + \text{APCL} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Complex C}}{\text{(Ce(IV)-APCL)}} \tag{1}$$

$$\underset{\text{Complex C}}{(\text{Ce(IV)-APCL})} \xrightarrow{K} \text{R}^{\bullet} + \text{Ce(III)} + \text{H}^{+} \tag{2}$$

$$\frac{-\,d[\text{Ce(IV)}]}{dt} = k_d[C] \tag{3}$$

$$k_1[\text{Ce(IV)}][\text{APCL}] = k_{-1}[C]$$

$$\frac{k_1}{k_{-1}}[\text{Ce(IV)}][\text{APCL}] = [C] \qquad \text{since } k_1/k_{-1} = K$$

Using Eq. (1) as well as the material balance on the [Ce(IV)], *i.e.*

$$K[\text{Ce(IV)}]_f[\text{APCL}] = [C] \tag{4}$$

and

$$[\text{Ce(IV)}] = [C] + [\text{Ce(IV)}]_f \tag{5}$$

where [C] and $[\text{Ce(IV)}]_f$ represent the concentrations of the chelated complex and of the unchelated cerium ions, respectively.

Substituting the value of [C] from Eq. (4),

$$[\text{Ce(IV)}] = K[\text{Ce(IV)}]_f[\text{APCL}] + [\text{Ce(IV)}]_f \tag{6}$$

$$[\text{Ce(IV)}] = [\text{Ce(IV)}]_f(K[\text{APCL}] + 1)$$

$$\frac{[\text{Ce(IV)}]}{1 + k[\text{APCL}]} = [\text{Ce(IV)}] \tag{7}$$

Substituing Eq. (7) in Eq. (4)

$$\frac{[C] = K[\text{Ce(IV)}][\text{APCL}]}{1 + K[\text{APCL}]} \tag{8}$$

Substituting Eq. (8) in Eq. (3)

$$\frac{-\,d[\text{Ce(IV)}]}{dt} = \frac{k_dK[\text{Ce(IV)}] + [\text{APCL}]}{1 + k[\text{APCL}]}$$

$$\frac{1 + K[\text{APCL}]}{k_dK[\text{APCL}]} = \frac{[\text{Ce(IV)}]}{-\,d[\text{Ce(IV)}]]/dt}$$

$$\frac{1}{k_dK[\text{APCL}]} + \frac{1}{k_d} = \frac{[\text{Ce(IV)}]}{-\,d[\text{Ce(IV)}]/dt} \tag{9}$$

$$\frac{1}{k_dK} + \frac{1}{[\text{APCL}]} + \frac{1}{dt} = \frac{[\text{Ce(IV)}]}{-\,d[\text{Ce(IV)}]/dt} \tag{10}$$

where k = formation constant and k_d = disproportionation constant.

It can be seen from the Table-2 that K value for DTPA is about 1000 times higher than that of GLY. The DTPA is a polydentate chelating ligand capable of forming complexes with higher stability constant, while GLY being monodentate forms labile complexes. This is in accordance with our observations. In IDA, one would expect coordination by the —NH group and —COO⁻ group. However, in the case of DTPA, the five carboxylate groups and three tertiary nitrogen atoms easily chelate with the metal ions. It has been known that more stable complexes initiate vinyl polymerisation effectively in the Ce(IV) aminopolycarboxylate ligand systems and the reactivity is shown to be primary < secondary < tertiary amines.[2] The ease of complex formation is also in the same order: tertiary > secondary > primary amines. In the above study +I groups substituted on nitrogen have been shown to accelerate the polymerisation due to increased electron density on nitrogen, thereby increased ease of complex formation. The groups with –I effect retard the polymerisation, since the complex formed is weaker comparatively. The statistical number of —OH groups on the reducing ligand has been reported to increase the rate of polymerisation.[3]

Thus, the initiation of polymerisation occurs by free radicals which are produced by the decomposition of complex and the easiness of the decomposition is characterised by the constant k_d. Higher the k_d value, the higher is reactivity of complex for initiation. The k_d value for DTPA is higher and for GLY, it is lower. It is reasonable to assume that the electron transfer reaction from ligand to metal is faster in the case of DTPA and is lower in the case of GLY. Thus among the six APC ligands the order of reactivity is found out as DTPA > EDTA > CTDA > NTA > IDA > GLY.

The reactivity may depend upon the combined result of complex formation, inductive effect of adjacent groups and the statistical effect of reactive centres. The above facts may act collectively or individually in influencing the formation of the complex and subsequent decomposition to form ligand radicals.

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