Asian Journal of Chemistry Vol. 5, No. 2 (1993), 477–480
NOTE

Binary and Ternary Complexes of Neodymium(III) with Crotonic Acid and Acrylic Acid

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Polarography between Nd(III) and crotonic acid (CA) + acrylic acid (AA) at pH 2.50 ± 0.02 and 25 ± 1°C has been used to study complexes. The methods of DeFord and Hume and of Schapp and McMaster have been successfully applied to determine the formation constants of binary and ternary complexes. $[Nd(CA)(AA)]^+$ and $[Nd(CA)_2(AA)]$ mixed complexes with formation constants values of $\log \beta_{11} = 6.02$ and $\log \beta_{21} = 8.58$, respectively have been found. Possible mechanisms of electron transfer and complex formation have been described in aqueous media.

Nd(III) gives a well defined reversible reduction wave[1] in 1.0 mol d^{-3} m KCl and 0.01% gelatin in the range of pH 2.40 to 2.75. Crotonic acid and acrylic acid have been used with In(III) for the polarographic study of mixed complexes[2,3], but no report in the literature on the mixed ligand complexes of rare earths using polarography have been reported. Hence this study has been undertaken.

All chemicals used were of AnalaR/BDH grade. A stock solution of Nd(III) was prepared by dissolving the requisite amount of a metal oxide in minimum quantity of hydrochloric acid and the solution was standardized by amperometric titration[4]. 1.0 Mol dm^{-3} KCl as supporting electrolyte and 0.01% gelatin as maximum suppressor were used while recording the polarograms.

The pH of the test solution was adjusted with dil. HCl/NaOH solution. pH Measurements were made on a Toshniwal digital pH meter, model CL–46. Polarograms were obtained on an Elico pen-recording polarograph. The DME with a characteristic of $m^{2/3}\ t^{1/6} = 2.31\ mg^{2/3}\ s^{-1/2}$ was used throughout. Pure hydrogen gas was bubbled through the test solution before recording the polarograms. All measurements were made at 25 ± 1°C.

Nd(III) and its complexes with crotonic acid and acrylic acid give a three-electron reversible and diffusion-controlled wave in 1.0 mol dm^{-3} KCl at pH 2.50 ± 0.02. The slope of linear plots of $\log \{i/(i_d - i)\}$ vs E_{de} lies in the range of 21–19 mV which attributes to the three-electron reversible reduction of Nd(III) and its complex species.

Nd(III)-Acrylate System

With the addition of increasing amounts of acrylic acid, $E_{1/2}$ of Nd(III) is shifted to more negative values, thus indicating complex formation. A plot of

$E_{1/2}$ vs. log [AA] is smooth, thereby showing the formation of successive complexes. DeFord and Hume's method[5] was applied to calculate overall stability constants of binary complexes. This revealed the formation of $[Nd(AA)]^{2+}$, $[Nd(AA)_2]^+$ and $[Nd(AA)_3]$ with stability constant values of $\log \beta_{10} = 2.55$, $\log \beta_{20} = 5.35$ and $\log \beta_{30} = 7.85$.

Nd(III)-Crotonate System

The cathodic shift in $E_{1/2}$ values along with the decrease in diffusion current with increasing concentration of crotonic acid indicated complex formation of Nd(III) with crotonic acid. The plot of $E_{1/2}$ vs. log [CA] was found to be smooth, thereby showing the formation of successive complexes. DeFord and Hume's method was applied to evaluate the stability constants. Three complex species $[Nd(CA)]^+$, $[Nd(CA)_2]^+$ and $[Nd(CA)_3]$ with $\log \beta_{01} = 2.92$, $\log \beta_{02} = 5.48$ and $\log \beta_{03} = 8.51$ were observed.

Nd(III)-Crotonate-Acrylate System

The Schapp and McMaster method[6] was applied to study mixed complexes. Two concentrations of acrylic acid, 0.2 M and 0.4 M, were chosen for the study of the mixed ligand system, where 1 : 1 and 1 : 2 complexes predominate. The concentration of crotonic acid varied form 0.0 mM to 5.0 mM. A more negative shift in $E_{1/2}$ values, as compared to shift observed in absence of acrylate ion, was observed. This indicated the formation of mixed complexes. Leden's[7] extrapolation approach was applied to calculate A, B, C and D [Table 1]. The result revealed the formation of $[Nd(CA)(AA)]^+$ and $[Nd(CA)_2(AA)]$ with formation constants $\log \beta_{11} = 6.09$ and $\log \beta_{21} = 8.62$.

The mixing constant and stability constant for the reaction

$$\tfrac{1}{2}[Nd(CA)_2]^+ + \tfrac{1}{2}[Nd(AA)]^{++} \rightleftarrows [Nd(CA)(AA)]^+$$

which is a measure of relative stability of the ternary complexes in solution as compared to the parent binary complexes have been calculated[8, 9] by the relation $K_m = \beta_{11}/\sqrt{\beta_{02}\beta_{20}}$ and $\log K_s = \log K_m - \log 2$ respectively. The low values of K_m and K_s showed that the mixed complexes are more stable than binary complexes.

ACKNOWLEDGEMENTS

Authors are grateful to Dr. K.S. Pitre of University of Sagar, Sagar for encouragement and needful discussion. Thanks are also due to Dr. S.V. Dharmadhikari, Principal, for providing laboratory facilities.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND $F_{ij}(XY)$ FUNCTIONS FOR Nd(III)-CROTONATE-ACRYLATE MIXED SYSTEM

Nd(III) = 0.1 mM, μ = 1.0 M (KCl), pH = 2.50 ± 0.02, Temperature = 25 ± 1°C, Acrylic acid = 0.02 M (Fixed), Acrylic acid = 0.104 M (Fixed)

S. No.	Concentration of crotonic acid (M) × 10	i_d (div)	$-E_{1/2}$ V vs Hg pool	$F_{00}(XY)$	$F_{10}(XY) \times 10^{-3}$	$F_{20}(XY) \times 10^{-5}$	$F_{30}(XY) \times 10^{-9}$	i_d (div)	$-E_{1/2}$ V vs. Hg pool	$F_{00}(XY)$	$F_{10}(XY) \times 10^{-4}$	$F_{20}(XY) \times 10^{-6}$	$F_{30}(XY) \times 10^{-10}$
1.	0.0	47.0	1.742	—	—	—	—	47.0	1.742	—	—	—	—
2.	1.0	38.0	1.750	4.4730	4.47	—	—	34.0	1.764	25.6715	0.57	—	—
3.	1.5	36.5	1.758	10.5527	5.70	18.00	0.47	33.5	1.772	59.0417	2.60	10.68	0.05
4.	2.0	35.0	1.764	22.1875	10.09	35.45	1.22	31.0	1.776	101.8252	4.09	15.45	0.27
5.	2.5	33.5	1.770	47.4442	18.18	60.72	1.55	30.5	1.784	267.9922	9.92	35.68	1.03
6.	3.0	32.0	1.774	69.4716	22.49	64.97	1.80	28.5	1.788	515.0530	16.50	51.67	1.39
7.	4.0	30.0	1.778	132.9237	32.73	74.33	1.58	27.0	1.796	1210.3733	29.76	71.90	1.55
8.	5.0	28.5	1.787	400.7043	81.14	156.28	2.91	26.0	1.800	2005.9633	39.72	77.44	1.35

A = 2.0, B = 3000, C = 1.11×10^6, D = 1.49×10^9, A′ = 20.0, B′ = 1.0×10^4, C′ = 1.03×10^7, D′ = 1.07×10^{10}

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(*Received:* 4 June 1992; *Accepted:* 1 August 1992) AJC–469