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Malate Complex of Al(III)

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Malate complex of aluminium has been studied pH-metrically in the pH range 2·8-8·0. Al^{3+} reacts with malic acid in the pH range 2·8-3·4 to form a neutral complex (C) with simultaneous liberation of 3 protons. At higher pH, the neutral complex (C) undergoes step-wise dissociation to form anionic complexes (C_1^-) and (C_2^{2-}). The equilibrium constants of the three reactions,

$$Al^{3+} + H_2ML \rightleftharpoons C + 3H^+$$
$$C \rightleftharpoons C_1^- + H^+$$
$$C_1^- \rightleftharpoons C_2^{2-} + H^+$$
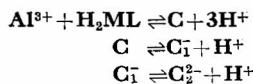
are found to be $4·12 \times 10^{-6}$, $1·91 \times 10^{-5}$ and $2·58 \times 10^{-8}$ respectively.

PAVLINOVA and Vysotskaya[1] have studied the complex formation between Al^{3+} and malic acid by potentiometric and conductometric titrations. This note reports the pH-metric determination of stability constants of malate complexes of Al(III) in the pH range 2·8-8·0.

Aluminium perchlorate was prepared by dissolving a known amount of aluminium hydroxide (prepared from a known amount of aluminium sulphate) in a known weight of standardized 70% perchloric acid. The solution was diluted to one litre and then aluminium estimated as Al_2O_3 (ref. 2) and as $Al(C_9H_6ON)_3$ (ref. 3). The excess perchloric acid present in the solution was neutralized by standard sodium hydroxide solution after the addition of known amount of malic acid.

The following solutions (total volume 200 ml) were titrated against 0·1M NaOH:

(i) $6·063 \times 10^{-4}M$ malic acid $+0·01M$ NaClO$_4$

(ii) $4·997 \times 10^{-4}M$ Al(ClO$_4$)$_3 + 6·063 \times 10^{-4}M$ malic acid $+0·01M$ NaClO$_4$

(iii) $2·425 \times 10^{-3}M$ malic acid $+0·01M$ NaClO$_4$

(iv) $4·997 \times 10^{-4}M$ Al(ClO$_4$)$^3 + 2·425 \times 10^{-3}M$ malic acid $+0·01M$ NaClO$_4$

(v) $6·25 \times 10^{-4}M$ sodium malate $+0·01M$ NaClO$_4$

(vi) $4·997 \times 10^{-4}M$ Al(ClO$_4$)$_3 + 6·25 \times 10^{-4}M$ sodium malate $+0·01M$ NaClO$_4$

(vii) $2·5 \times 10^{-3}M$ sodium malate $+0·01M$ NaClO$_4$

(viii) $4·997 \times 10^{-4}M$ Al(ClO$_4$)$_3 + 2·5 \times 10^{-3}M$ sodium malate $+0·01M$ NaClO$_4$.

As observed in the case of cadmium citrate[4], manganese tartrate[5] and other systems[6,7], the amount of acid liberated during the complex formation between Al^{3+} and malic acid remains the same even though the metal-ligand ratio is increased from 1:1·25 to 1:5 indicating the formation of a 1:1 complex. The reaction between malic acid and aluminium perchlorate [titrations (i)-(iv)] may be represented by Eq. 1.

$$Al^{3+} + H_2ML \rightleftharpoons C + nH^+ \qquad ...(1)$$

$$K = \frac{[C] \times [H^+]^n}{[Al^{3+}][H_2ML]} \qquad ...(2)$$

By proceeding in the same manner as described in the case of cadmium citrate[4] system, it can be shown that,

$$\frac{\Delta[NaOH] - a/b\,\Delta[ML]}{[C]} = n - a/b \qquad ...(3)$$

where $\Delta[NaOH] = [NaOH]_B - [NaOH]_A$
$$\Delta[ML] = [ML]_B - [ML]_A$$
$$a = \frac{k_1}{[H^+]} + \frac{2k_1k_2}{[H^+]^2}, \; b = 1 + \frac{k_1}{[H^+]} + \frac{k_1k_2}{[H^+]^2}.$$

k_1 and k_2, the dissociation constants of malic acid[8] are $5·5 \times 10^{-4}$ and $2·1 \times 10^{-5}$ respectively.

When the formation of the complex is complete, it can be shown that,

$$\frac{\Delta[NaOH] - a/b\,\Delta[ML]}{[Al(ClO_4)_3]} = n - a/b \qquad ...(4)$$

Using Eq. 4, the n values at different pH can be calculated from the titration curves (i) and (ii) and the values are found to be higher than 3 and 4 at pH $\geqslant 3·6$ and 6·2 respectively. Below pH 3·6, a neutral complex C is formed and assuming the n value to be 3, below pH 3·6, K values were calculated and found to be $4·68 \times 10^{-6}$, $4·22 \times 10^{-6}$, $4·24 \times 10^{-6}$, $3·94 \times 10^{-6}$ and $3·52 \times 10^{-6}$ at pH 2·8, 2·9, 3·0, 3·1 and 3·3 respectively. The mean value of K is $4·12 \times 10^{-6}$.

In the pH range 3·6-6·2, the n values are greater than 3, but less than 4. This indicates the dissociation of neutral complex (C) according to Eq. 5.

$$C \rightleftharpoons C_1^- + H^+ \qquad ...(5)$$

and

$$K_1 = \frac{[C_1^-][H^+]}{[C]} \qquad ...(6)$$

It can be shown as in the case of cadmium citrate complex[4] that,

$$K_1 = \frac{(n-3)[H^+]}{(4-n)} \qquad ...(7)$$

The values of K_1 were calculated using Eq. 7 and found to be $1·56 \times 10^{-5}$, $2·62 \times 10^{-5}$, $2·33 \times 10^{-5}$,

1.69×10^{-5}, and 1.35×10^{-5} at pH 3·6, 4·2, 4·4, 4·6 and 4·8 respectively; the mean being 1.91×10^{-5}.

The anionic complex C_1^- dissociates in the pH range 6·2-8·4 as: $C_1^- \rightleftharpoons C^{2-} + H^+$. The dissociation constant will then be given by Eq. 8.

$$K_2 = \frac{[C_2^{2-}][H^+]}{[C_1^-]} \qquad \ldots(8)$$

It can be shown as before that,

$$K_2 = \frac{(n-4)[H^+]}{(5-n)} \qquad \ldots(9)$$

K_2 values were calculated using Eq. 9. These are 1.72×10^{-8}, 2.83×10^{-8}, 3.26×10^{-8} and 2.51×10^{-8} at pH 6·6, 7·0, 7·4 and 8·0 respectively. The mean value is 2.58×10^{-8}.

The values of K, K_1, and K_2 obtained from titrations (iii) and (iv) are very similar.

The nature of the curves in titrations (v-viii) are similar. As the ratio of metal to ligand is 1 : 5 in the case of titrations (vii-viii), the formation of the complex is complete. As observed in the titrations (i) and (ii) in the pH range 3·6-6·2, where both the complexes C and C_1^- exist, similar species are likely to be present in titrations (vii-viii).

It can be shown as before[5-7] that,

$$[M] = [C] + [C_1^-] \qquad \ldots(10)$$

$$[HML^-] = \frac{[TML] - [M]}{1 + \dfrac{k_2}{[H^+]} + \dfrac{[H^+]}{k_1}} \qquad \ldots(11)$$

$$[C_1^-] = [H^+] + [NaOH] - [M] + [HML^-]\left(1 + \frac{2[H^+]}{k_1}\right) \qquad \ldots(12)$$

$$[C] = [M] - [C_1^-] \qquad \ldots(13)$$

K_1 values were calculated using Eq. 6 and are 3.03×10^{-5}, 2.32×10^{-5} and 1.26×10^{-5} at pH 5·5, 5·6 and 5·7 respectively. The mean values of K_1 is 2.20×10^{-5} which is in close agreement with that obtained from titrations (i) and (ii).

Since in the pH range 6·6-8·4 [titrations (i) and (ii)] both C_1^- and C_2^{2-} exist, it can be shown in the case of titrations (vii) and (viii) that

$$[C_2^{2-}] = [H^+] + [NaOH] + [HML^-]\left(1 + \frac{k_2}{[H^+]} + \frac{[H^+]}{k_1}\right) - 2[M] \qquad \ldots(14)$$

$$[C_1^-] = [M] - [C_2^{2-}]$$

K_2 values were calculated using Eq. 8 at different pH and are found to be 1.19×10^{-8}, 1.63×10^{-8}, 1.78×10^{-8}, 1.96×10^{-8} and 2.47×10^{-8} at pH 7·5, 7·6, 7·7, 7·8 and 8·0 respectively. The mean value of K_2 is 1.81×10^{-8} which is also similar to that obtained from titrations (i) and (ii).

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Spectrophotometric Studies of Some Nitrosonaphthols

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The electronic absorption spectra of some nitrosonaphthols are recorded in organic solvents and discussed in relation to medium effects and molecular structure.

IN view of the interesting chelating properties of nitrosonaphthols it was considered of interest to study the electronic spectra of α-nitroso-β-naphthol (I) and some of its derivatives, viz. 3-chloro(II), 3-bromo-(III), 3-iodo-(IV) and 3-carboxy (V) in organic solvents of varying polarities. For sake of comparison β-nitroso-α-naphthol (VI) is also included in the study.

The parent compounds I and VI were of BDH quality. II and III were obtained by the halogenation[1,2] of I and IV was obtained from III[3]. The 3-carboxy derivative (V) was obtained by the nitrosation of the corresponding hydroxy naphthoic acid[4]. The products were purified by crystallization from the appropriate solvent.

The procedure and apparatus employed were the same as described previously[5].

The electronic spectra of the compounds show mainly three bands. The bands below 300 nm are due to π-π* transitions within the naphthyl moiety. The band in the region 335-380 nm can be assigned to an intramolecular charge transfer from the naphthyl ring as donor to the nitroso group as acceptor[6]. Such a charge transfer would be enhanced by charge migration from the OH-group. Such a mesomeric shift finally leads to the ketoxime (VII) tautomer, the existence of which has been confirmed by the IR spectrum.

The results given in Table 1 show that the values of λ_{max} and ϵ_{max} are dependent on both solvent
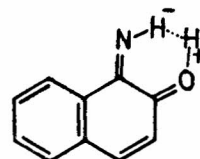
(VII)

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