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POTENTIOMETRIC STUDIES OF NICKEL (II) AND COPPER (II) ACETYL ACETONATO COMPLEXES

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ABSTRACT
The dissociation constant pKa of acetylacetone has been determined potentiometrically. The pKa value obtained is 9.40, indicating a weak acid. The stability constants of the complex compounds formed from the reaction of nickel (II) and copper (II) with acetylacetone determined using potentiometer are $6.32x10^{15}$ and $2.82x10^{14}$, respectively. Similarly, the number of acetylacetonato ligands coordinated to each metal ion determined potentiometrically is 3.

Key words: Potentiometry, Acetylacetone, Dissociation and Stability Constants.

INTRODUCTION

Acetylacetone was, prepared by claisen condensation between ethyl acetate and acetone (Finar, 1973) and reacts with metal ions to form the (*O, O'*) chelates of $[M(\beta\text{-dik})_n]$, soluble in organic solvents, and are used as analytical reagents(Yukio, *et al.*, 1981). The complexes are also useful for comparative studies of metal ions, as starting materials in the preparation of organometallic compounds and as catalyst for organic synthesis (Calvin, 1950; Mark, 1954; Bernal and Reiger, 1963; Chung-Ling, 1969; Mehrotra *et al.*, 1978).

Previously we have reported (Aliyu and Mustapha, 2005) potentiometric studies on manganese (II) and cobalt (II) acetylacetonate complexes, where the two metal complexes have been found to show high formation constant of 9.52×10^{13} and 7.89×10^{13} for the Mn(II) and Co(II) complexes, respectively. In that paper we reported that when exposed to air, the coordination number of the metal ions was in favour of the preferred oxidation number of these metals which is three. In this paper we report some Potentiometric studies on acetylacetonate complexes of Nickel (II) and Copper (II) ions, as extensive literature search shows that no such work has been previously reported. As such we investigated these metal complexes with the view of comparing their stability constant against those reported for manganese(II) and cobalt(II), and to investigate their preferred coordination number with acetylacetonate ligand in solution.

MATERIALS AND METHOD

In the preparation of reagents, chemicals of analytical grade purity and distilled water were used. All weighings were carried out on electric metler balance model AB54, pH measurements were carried out using Jenway pH metre model 3320.

Determination of Dissociation Constant of Acetylacetone

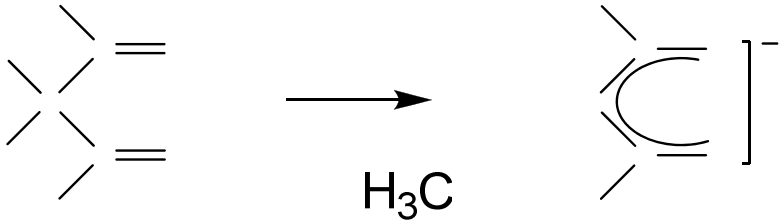
Into a 500 cm^3 beaker containing a bar magnetic stirrer, 90 cm^3 distilled water, 10 cm^3 of 0.1 M nitric acid, 100 cm^3 of 0.2 M potassium nitrate was added 10 cm^3 of 0.4 M acetylacetone. The electrodes of a standardized pH meter were introduced into the mixture. Standardized NaOH solution was added to the mixture with constant stirring to a total volume of $10cm^3$. After each $0.5cm^3$ aliquot addition, the corresponding pH of the solution was recoded. The dissociation constant of acetylacetone was calculated from the pH values obtained as reported by Gregory *et al.*, (1978).

Determination of Stability Constants of Nickel (II) and Copper (II) Acetylacetonato Complexes

To a 500 cm^3 beaker containing a bar magnetic stirrer were added 90 cm^3 distilled water, 10 cm^3 of 0.1 M nitric acid, 100 cm^3 0.2 M potassium nitrate and one mmole of the corresponding metal salt. A solution of the sodium salt of acetylacetone, prepared by neutralizing a known quantity of the acetylacetone with calculated amount of standardized NaOH solution was added gradually. After each $0.2cm^3$ aliquot addition, the corresponding pH of the stirred reaction mixture was recorded. From the results obtained, the stability constant of each metal complex compound and the average number of ligands per metal ion were calculated as reported Gregory et al., (1978).

RESULTS AND DISCUSSION

The acid dissociation constant, pKa, of acetylacetone was determined by measuring the $[H^+]$ in 0.4M solution of acetylacetone according to the reaction below (Norman 1978; Finar, 1990).



The activity, a_{H^+}, determined was converted to [H^+] using the equations:

$a_{H^+} = \gamma_{\pm}[H^+]$ .....(i)

pH = -log a_{H^+} .....(ii)

Rearranging and substituting into equation (ii) gives,

Log[H^+] = -pH - log $\gamma_{\pm}$ .....(iii)

The constant, log $\gamma_{\pm}$, can be obtained from the expression,

$$-\log \gamma_{\pm} = \left(\frac{0.5 Z_1 Z_2 \mu^{1/2}}{1 + \mu^{1/2}} \right) - 0.1\mu \quad \text{.....(iv)}$$

Where Z_1 and Z_2 are the charges +1 or -1 which are H^+ and NO_3^{-1}, respectively. The ionic strength, μ, of the solution may be calculated from;

$\mu = \frac{1}{2} \sum M_i Z_i^2$ .....(v)

Where M_i is the molar concentration of i and Z_i is its charge, while the expression for the acid dissociation constant for the reaction,

$$HA \rightleftharpoons H^+ + A^-$$

is given by, $Ka = \frac{[H^+][A^-]}{[HA]}$ ..... (vi)

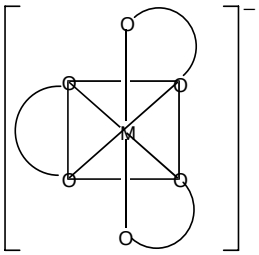
Where [H^+] is from equation (iii), while [A^-] and [HA] are known concentrations of dissociated and undissociated acetylacetone (Gregory *et al.*, 1978).

The dissociation constant, pKa of acetylacetone determined (Table 1) is 9.40, which is in agreement with literature value of 9.45, reported by Perrin (1981). The average number of acetylacetonato ligands coordinated to each metal (Tables 2 and 3) is 3, indicating the formation of 1:3 metal to ligand ratio, resulting in octahedral complex compounds, a feature common with the first row transition metals (Fernelius and Blanch, 1957; Nakamoto *et al*, 1961; Charle, 1963; Holm and Oconnon, 1971; Cotton and Wilkinson, 1988; ClarK, 1988). The stability constants of nickel (II) and copper (II) complexes of acetylacetone determined (Table 4) are 6.32×10^{15} and 2.82×10^{14}, respectively. These high values of stability constants suggest good stable complex compounds, a usual trend of divalent transition metal complexes with ligands such as acetylacetone (Calvin and Wilkinson, 1945; Calvin, 1950; Irvin, 1953; Goldberg, 1962; Guenther, 1967)

From the analysis of the potentiometric results, the following molecular structure is proposed for nickel (II) and copper (II) complex ions formed with acetylacetonato ligand.

Conclusion

The potentiometric studies carried out on acetylacetone established a pKa value of 9.40. The stability constant values of 6.32×10^{15} and 2.82×10^{14} for nickel (II) and copper (II) complexes, respectively were also determined. Similarly, the number of coordinated acetylacetonato ligands to a metal ion is 3.



Where M is nickel or copper and  is acetylacetonato ligand.

Table 1: Determination of Dissociation Constant (pKa) of Acetylacetone

Vol NaOH (cm^3)	pH	$[H^+]x10^{-12}$	$[OH^-]x10^{-3}$	$[NaOH]x10^{-4}$	pKa
2.00	11.34	3.06	5.30	9.60	9.12
2.50	11.37	2.85	5.68	14.00	9.15
3.00	11.41	2.60	6.23	14.40	9.19
3.50	11.46	2.32	6.99	16.80	9.23
4.00	11.50	2.12	7.66	19.20	9.27
4.50	11.56	1.84	8.80	21.60	9.33
5.00	11.61	1.64	9.87	24.00	9.38
5.50	11.66	1.46	11.07	26.40	9.43
6.00	11.73	1.25	13.01	28.80	9.51
6.50	11.79	1.09	14.94	31.20	9.56
7.00	11.86	0.92	17.56	33.60	9.63
7.50	11.93	0.77	20.63	36.00	9.70
8.00	12.01	0.65	24.80	38.40	9.78

Average pKa of acetylacetone is 9.40

Table 2: Determination of Number of Acetylacetonato Ligands in the Complex Compound Formed Between Nickel (II) and Acetylacetone

Vol Sodium acac (cm^3)	pH	$[H^+]x10^{-5}$	$[OH^-]x10^{-12}$	$Log[A^-]$	ň
2.00	2.33	313.00	5.18	-9.57	1.87
2.20	2.35	298.90	5.43	-9.58	2.01
2.40	2.37	285.40	5.68	-9.59	2.14
2.60	2.40	266.10	6.09	-9.60	2.34
2.80	2.42	254.40	6.38	-9.62	2.45
3.00	2.45	237.40	6.83	-9.63	2.62
3.20	2.47	220.67	7.15	-9.65	2.73
3.40	2.51	206.80	7.84	-9.69	2.93
3.60	2.54	193.00	8.40	-9.71	3.06
3.80	2.58	176.00	9.22	-9.76	3.24
4.00	2.62	160.50	10.10	-9.82	3.39
4.20	2.67	143.10	11.34	-9.92	3.57
4.40	2.72	127.50	12.72	-10.07	3.72
4.60	2.76	116.30	13.95	-10.25	3.84
4.80	2.85	99.00	16.39	-11.39	3.99
5.00	2.91	82.00	19.70	-10.06	3.82
5.20	3.00	66.90	24.23	-9.71	3.67
5.40	3.12	50.80	31.95	-9.41	3.51
5.60	3.27	38.50	45.13	-8.20	3.38
5.80	3.43	24.80	65.24	-8.92	3.25
6.00	3.66	14.60	110.79	-8.63	3.14
6.20	3.99	6.80	236.86	-7.26	3.06
6.40	4.30	3.30	483.62	-7.93	3.03
6.60	4.49	2.20	749.03	-7.75	3.02
6.80	4.69	1.40	1185.13	-7.55	3.01
7.00	4.89	1.10	1529.32	-7.45	3.01
7.20	4.91	0.82	1970.15	-7.32	3.00
7.40	5.04	0.61	2657.66	-7.19	3.00
7.60	5.13	0.49	3269.64	-7.09	3.00
7.80	5.22	0.40	4022.54	-7.00	3.00
8.00	5.29	0.34	4726.07	-6.93	3.00

The average number of coordinated ligands (ň) is 3

Table 3: Determination of Number of Acetylacetonato Ligands in the Complex Compound Formed Between Copper (II) and Acetylacetone

Vol Sodium acac (cm^3)	pH	$[H^+]x10^{-5}$	$[OH^-]x10^{-12}$	$Log[A^-]$	ň
2.00	2.36	292.07	5.55	-9.58	2.08
2.20	2.39	272.60	5.95	-9.59	2.27
2.40	2.40	266.40	6.09	-9.60	2.34
2.60	2.43	248.60	6.52	-9.62	2.51
2.80	2.45	237.40	6.83	-9.64	2.62
3.00	2.47	226.70	7.15	-9.65	2.73
3.20	2.50	211.60	7.66	-9.68	2.88
3.40	2.53	197.50	8.21	-9.71	3.02
3.60	2.55	188.60	8.60	-9.73	3.11
3.80	2.58	176.00	9.22	-9.76	3.24
4.00	2.60	168.10	9.65	-9.79	3.32
4.20	2.63	156.90	10.34	-9.84	3.43
4.40	2.66	146.40	11.08	-9.90	3.54
4.60	2.69	136.60	11.87	-9.97	3.63
4.80	2.73	124.60	13.02	-10.10	3.75
5.00	2.76	116.30	13.95	-10.25	3.84
5.20	2.80	106.00	15.29	-10.65	3.94
5.40	2.84	96.70	16.77	-10.87	3.97
5.60	2.88	88.20	18.39	-10.27	3.88
5.80	2.92	80.40	20.16	-10.01	3.80
6.00	2.95	75.10	21.60	-9.88	3.75
6.20	3.00	66.90	24.24	-9.71	3.67
6.40	3.05	59.60	27.19	-9.57	3.60
6.60	3.08	55.70	29.14	-9.50	3.56
6.80	3.13	49.60	32.70	-9.39	3.49
7.00	3.17	45.20	35.85	-9.32	3.45
7.20	3.22	40.30	40.23	-9.23	3.40
7.40	3.27	35.90	45.13	-9.15	3.35
7.60	3.32	32.00	50.64	-9.07	3.32
7.80	3.35	29.90	54.26	-9.03	3.30
8.00	4.41	26.00	62.30	-8.95	3.20

The average number of coordinated ligands (ň) is 3.

Table 4: Determination of Stability Constants

Complex Compound	Stability Constant
Ni (II) Complex Compound	$6.32x10^{15}$
Co (II) Complex Compound	$2.82x10^{14}$

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