# Metal Chelates of Diacetylacetanilide

BARSOUM N BARSOUM, MAGDI M NAOUM* & GAMAL R SAAD

Department of Chemistry, Faculty of Science,
University of Cairo, Giza, Egypt

Chelation of iron(III), copper(II), cobalt(II), and nickel(II) with diacetylacetanilide (DAA) has been studied spectrophotometrically in 50% ethanol-water mixture. The results indicate the formation of 1:1 (metal:ligand) complex of iron(III) at pH 4, and 1:2 complexes of Fe(III), Cu(II), Co(II) and Ni(II) at pH 6.5, 5.5, 6.5, and 5.5, respectively. Use of the anilide as an analytical reagent for the volumetric and spectrophotometric determination of these metals has also been investigated.

$\beta$-Diketones are well known ligands capable of formation of stable complexes with various metal ions[1,2]. Acetoacetanilide, on the other hand, has been found to be a very selective reagent for metals with hard acid properties as defined by Pearson[3]. In the present study we have investigated the applicability of a new reagent containing both these groups, namely, diacetylacetanilide [(DAA), $(CH_3CO)_2CHCONHC_6H_5)$] for the determination of Fe(III), Cu(II), Co(II), and Ni(II) in solution. Methods for the spectrophotometric and volumetric estimation of the metals have been studied.

Diacetylacetanilide (DAA) was prepared according to the method described by Micheal[4]. All other chemicals used were of AR (BDH or Merck) grade.

Fresh anilide solutions (0.1 $M$) were prepared by dissolving the exact weights of DAA in ethanol. Aqueous solutions of the metal ions ($10^{-2}$ $M$) were prepared and standardized against EDTA[5].

Measurements of pH were made on an Orion pH-meter fitted with SCE-Glass electrode assembly. Electronic absorption spectra were measured on a Pye-Unicam SP800 spectrophotometer.

Determination of the acid dissociation constant, $pK_a$, of the anilide was made in 50% (v/v) ethanol-water at 30°C and ionic strength = 0.1 $M$. The pH-dependence of the absorbance ($A$) of DAA at 300 nm, was studied and the $pK_a$ was calculated using the relation,

$$pK_a = pH + \log \frac{A_{max} - A}{A - A_{min}} \qquad \ldots (1)$$

where $A_{max}$ and $A_{min}$ are the absorbances in the basic and acidic media, respectively. The observed value

(6.82) agrees well with that determined before[6].

The stability constants, $\log \beta_n$, for the chelates of the metals investigated were determined spectrophotometrically, at the appropriate pH values, applying the molar ratio[7] and Job's[8] methods.

Studies on the effect of pH on the formation of metal chelates using solutions with molar ratio 1:10 (metal:ligand), indicated that optimum pH values for the formation of Cu(II), Co(II), and Ni(II) chelates are 5.5, 6.5, and 5.5, respectively. The complexes of Cu(II) and Ni(II) seem to decompose when the pH increases beyond these values, while for Co(II), the complex formed is stable up to pH 9. In case of iron(III), two steps were observed in the pH-dependence curve indicating probable formation of two complex species in the pH ranges, 4-5 and 6.5-8.

The absorption maxima of the complexes formed in solution, at constant metal ion concentration, increase with increasing ligand concentration and attain a limiting value. This behaviour is indicative of the formation of one type of complex under the conditions of experiment.

The stoichiometries of the complexes formed in solution were investigated applying the molar ratio[7] and Job's[8] methods. Both methods indicated the formation of 1:1 and 1:2 (metal:ligand) complexes with iron(III) at pH 4 and 6.5, respectively. However, only one type of complex, namely 1:2 is formed by the remaining metal ions. It seems that two molecules of the water coordinated to the metal ion are substituted by each of the bidentate ligand molecule, resulting in a complex formation in which coordination number of the metal remains six. The probable octahedral structure of the 1:2 complex may be represented by structure (I).



(I)
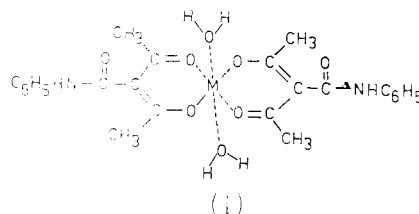
The stability constants of the complexes studied were determined in 50% (v/v) aqueous ethanol, applying the molar ratio[7] and Job's[8] methods (Table 1). Ionic strength was kept constant at 0.1 $M$ using sodium perchlorate. The data in Table 1 reveal that the stability constants ($\log \beta_n$) of the metal chelates

Table 1—Spectrophotometric Data, Stability Constants and Optimum pH Values for Metal Chelates of DAA (Stability Constants for Chelates of AAA are Included for Comparison)

| Metal | M:L | DAA | | | AAA | | |
|---|---|---|---|---|---|---|---|
| | | $pH$ | $\lambda_{max}$ | $\varepsilon_{max}$ | $\log \beta_n$ | $\log \beta_n$ | Ref. |
| Fe(III) | 1:1 | 4.0 | 485 | 4600 | 7.01 | 10.29 | 11 |
| Fe(III) | 1:2 | 6.5 | 510 | 4300 | 11.88 | 18.17 | 11 |
| Cu(II) | 1:2 | 5.5 | 480 | 11300 | 11.41 | 14.68 | 12 |
| Ni(II) | 1:2 | 5.5 | 420 | 9800 | 11.01 | | |
| Co(II) | 1:2 | 6.5 | 490 | 6300 | 10.74 | | |

investigated agree well with the Irving-Williams[9] order of stabilities for a given ligand: Fe(III) > Cu(II) > Ni(III) > Co(III). On the other hand, comparison of $pK_a$ values of DAA (6.81) with that of the parent compound acetoacetanilide (AAA, 11.39)[10], indicates that DAA behaves as a stronger acid than AAA. Consequently, the stabilities of metal chelates of DAA are expected to be less than those of AAA[11,12]. This is found to be true (see Table 1).

*Analytical studies*

In order to test the applicability of DAA as a spectrophotometric reagent for the quantitative determination of Cu(II), Co(II), and Ni(II) in solution, absorbance of solutions covering the concentration ranges $0.3\text{-}10 \times 10^{-4}$ $M$, $0.6\text{-}10 \times 10^{-3}$ $M$, and $0.2\text{-}5 \times 10^{-3}$ $M$, were recorded at 30°C. The $pH$ of solutions were adjusted to the appropriate values using acetic/acetate buffer. In all cases, Beer's law was obeyed at the appropriate $\lambda_{max}$, with ligand concentration being always in excess of the metal ion. Co(II) can be determined at $pH$ 8 in presence of Ni(II) and Cu(II) cations since their complexes seem to decompose at $pH$ greater than 6.

Also, DAA was tested as a reagent for the determination of Fe(III) ions in three different ways. In the first, absorbances at 30°C were recorded for Fe(III) solutions $(3\text{-}10 \times 10^{-2}$ $M)$ in the presence of sufficient excess of the ligand at the wavelength 485 nm. The $pH$ of solution was adjusted at 4 with the aid of acetic/acetate buffer. The results obeyed Beer's law with a standard deviation of 0.002. Alternatively, the violet coloured Fe(III)-DAA (1:1, $pH$ 4) mixture was titrated spectrophotometrically at 485 nm using standard EDTA solution as a titrant. Thirdly, when a few drops of 0.1% ethanolic solution of DAA were added to an aqueous solution of Fe(III), a violet colour developed which faded to give a colourless solution at the equivalent point when titrated with standard EDTA solution. In the latter case, DAA serves as a metalochromic indicator. The results obtained were in agreement within $\pm 1\%$ of those determined by standard procedures. Fe(III) could be determined at $pH$ 4, in presence of the other three cations.

Solutions containing about 10 $\mu$g of Fe(III) and varying amounts of foreign ions were prepared at $pH$ 4. The following ions (amounts given in parentheses) did not interfere with more than $\pm 3\%$ error in absorbance: $Al^{3+}$ (480 $\mu$g); $Zn^{2+}$ (520 $\mu$g); $Ba^{2+}$ (450 $\mu$g); $Ca^{2+}$ (400 $\mu$g); $Pb^{2+}$ (180 $\mu$g); Mo(IV) (380 $\mu$g); $C_2O_4^{2-}$ (1500 $\mu$g); $NO_3^-$ (1000 $\mu$g); $Br^-$ (500 $\mu$g); and $PO_4^{3-}$ (280 $\mu$g).

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