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25

The Composition and Stability of Co(II), Ni(II) and Cu(II)-o-Carboxyphenyl Azodiethylmalonate Complexes by pH metric Method in Mixed Solvents.

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Summary: o-Carboxyphenyl azodiethylmalonate was studied pH-metrically in different aqueous organic solvents. The pK_1&pK_2 were calculated to be 4.81 & 10.97, 5.60 & 12.21 and 5.15 & 11.57 in 50% and 80% aqueous ethanol and 50% aqueous dioxan respectivily. The stability constants of Co(II), Ni(II) and Cu(II) were also calculated in the same solvents. It was found that copper forms 1:2 complex in all mixed solvents, while nickel and cobalt form 1:1 complexes. There is a good relation between pK;s and dielectric constant of solvents. The pK&pK of ligand and complexes in water can be obtained graghically.

Introduction

Survey of literature reveals that ortho derivatives of azo-compounds were generally used as complexing agents for a number of metal ions such as Cu(II)[1] and Al,Ga and In[2] with o,o dihydroxy azobenzene. Also B-diketones e.g. acetylacetone or diethyl-malonate were used as complexing agents. However, the combination between these two classes of complexing compounds by diazotisation and coupling of these compounds may form new compounds which can act as good ligands, some of these compounds such as o-,m- and p- benzoic azoacetylacetone[3] were prepared and used as complexing agents for Cu^{2+}, Ni^{2+} and Co^{2+}. The spectroscopic and polarographic behaviour of such ligands were also investigated[4].

In the present work o-Carboxyphenyl-azo diethyl-malonate, (o-CPAEM) which is a product of coupling diazonium salt of anthranilic acid with diethylmalonate, has been prepared[5,6]. o determine its dissociation constant and the possibility of using it as complexing agent with some divalent metal ions namely Co^{2+}, Ni^{2+} & Cu^{2+} of electronic configurations d^7, d^8 & d^9 respectively were selected.

Methods of calculation

The potentiometric method requires the calculation of $[L^-]$ and n in order to determine the stability constant of the complex formed[7,8], where $[L^-]$ is the concentration of the free chelating species, and n is the average number of molecules of ligand bound by one atom of the metal.

The concentration of the free chelating species L^- is expressed as:

$$Log [L^-] = log$$
$$[L^0] - [KOH] - [H^+] \quad -log \quad \ldots \ldots \text{(1)}$$

where L_0 is the original concentration of the reagent H_2L and KOH is the concentration of the titrant assuming that the solvent was present in the titration vessel, and P is defind as:

$$P = \frac{[H^+]}{Ka_2} + \frac{2[H^+]^2}{Ka_1 \; Ka_2} \quad \ldots \ldots \ldots \text{(2)}$$

In equantion (1), the H^+ term usually becomes neglegible relative to other terms, above pH 4, similarly the OH^- term is seldom significant below pH = 10.0; hence in the limits of pH 4.0 to 10.0, equation (1) can be written as:

$$[L^-] = \frac{[L_0] - [KOH]}{P} \quad \ldots \ldots \ldots \ldots \text{(3)}$$

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The term n can be calculated from the potentiometric curves of both of the ligand solution and the metal-ligand solution mixture. From the horizontal sections of the two curves, the value of n can be calculated from the following equation:

$$n = \frac{[KOH]_T - [KOH]_L}{[M_o]} \qquad \ldots\ldots\ldots\ldots (4)$$

where KOH_L and $[KOH]_T$ are the concentration of KOH added to the ligand and the ligand-metal mixture at certain pH respectively, and $[M_o]$ is the total concentration of the metal ion.

In case of Cu-o-CPAEM complex, where the difference between KOH_T and KOH_L remains constant for different values of pH, another equation is used for n determination:

$$n = \frac{[L_o] - Q[L^-]}{[M_o]} \qquad \ldots\ldots\ldots\ldots (5)$$

where Q has the value given by the equation

$$Q = \frac{[H^+]}{Ka_2} + \frac{[H^+]^\dagger}{Ka_2 Ka_2} + 1 \qquad \ldots\ldots\ldots (6)$$

The correct values of K_1 & B_2 can be formed by applying the Bjerrum summation equation (10) over n=0, 1&2 for a bidentate complex of a bivalent metal, this process yields the equation (11):

$$\frac{n}{(n-1)[L^-]} = \frac{(2-n)[L^-]}{(n-1)} B_2 - K_1 \quad \ldots (7)$$

Equation (7) is an equation of straight line in which the slope is B_2 (i.e. $K_1 K_2$) and the interscept is $- K_1$ plotting this graph is difficult when it often happens, $[L^-]$ varies over several powers of ten. Therefore it is better to evaluate the constants algebraically by method of least squares. In case of Cu-o-CBAEM B_2 is the only constant obtainable and it can be easily calculated from equation 8 below[12].

$$\log B_2 = \log n - \log (2-n) - 2 \log [L^-] \quad \ldots\ldots (8)$$

In such cases, B_2 can also be calculated from the least squares equations.

Experimental

Apparatus:

pH meter: (All pH measurements were carried out using Pye-Unicam pH meter (model 290).

pH-metric titrations were carried out in double jacket cell at constant temperature of 30.±0.2 in an inert atmosphere of nitrogen, at constant ionic strength 0.05.

Reagents and Solutions

o-Carboxy phenyl Azo Diethylmalonate $C_{14}H_{16}$-O_6N_2 (o-CPAEM) solution.

A stock solution of concentration 5 x $10^{-2}M$ was prepared by dissolving 1.5400 gm of the solid reagent (prepared by Mellor and Twitcheit procedure[6] in ethanol or in dioxan and completed to 100 ml. The solution was standardized potentiometrically. The required concentrations were made by proper dilution of stock solution.

Metal-ions solution (0.1 M solution)

A stock solution of Cu^{2+}, Ni^{2+} and Co^{2+} were prepared from their nitrate hexahydrate salt (Merk) and standardized by complexmetric titration[13].

Potassium hydroxide

A concentrated solution of potassium hydroxide was prepared from the solid hydroxide (Merk) in carbon dioxide free bidistilled water. The clear solution were decanted and diluted to proper volume, stored in polyethylene bottle, and standardized by recommended procedure[14]. The required molarity 50 or 80% aqueous ethyl alcohol and 50% aqueous-dioxan were prepared through dilution.

Results

Determination of Dissociation constant of o-CPAEM.

The solvents used were 50 & 80% aqueous-ethanol as well as 50% aqueous-dioxan mediums. Each titration was repeated twice and the calculated first and second dissociation constants Ka_1 & Ka_2, in the three solvents used are given in Table 1.

Table 1.

Determination of the Dissociation constants of o-CPAEM ligand indifferent mixed solvents.

Initial concentration of o-CPAEM	Solvent	log D	pKa_1	pKa_2
3.0×10^{-3}	50% EtOH-H_2O	1.70	4.807	10.971
5.0×10^{-3}	80% EtOH-H_2O	1.65	5.6827	12.217
1.0×10^{-2}	50% Dioxan. H_2O	1.50	5.153	11.574
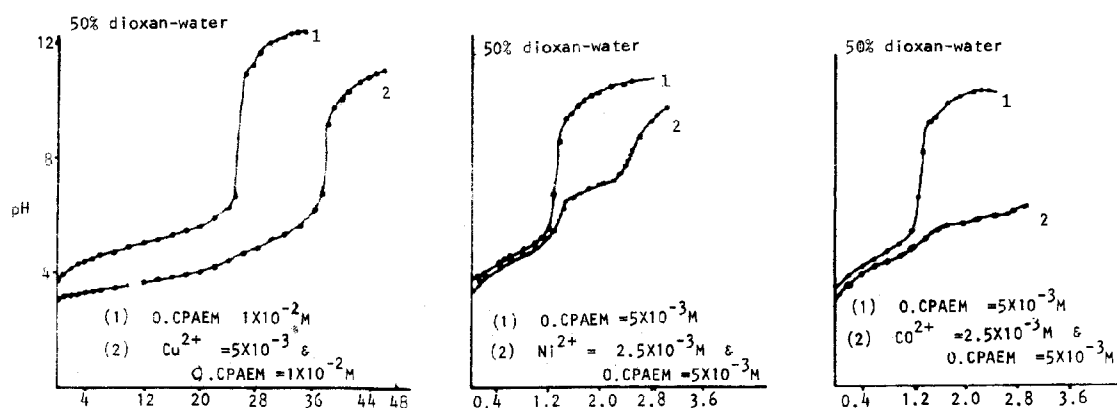
Fig. 1. Potentiometric Titration of Mixture of Metals and Ligand with KOH (1.0×10^{-1}). (μ = 0.05).

Determination of the stability constant of o-CPAEM complexes with Cu^{2+}, Ni^{2+} and Co^{2+} ions.

A mixture of metal ion and o-CPAEM solutions in the molar ratio of 1:2 were titrated using pH-metric technique under the same conditions as for the free ligand, against potassium hydroxide (0.1M) in the same solvents. Fig. 1 represent the titration curves of copper, nickel and cobalt ions respectively in aqueous dioxan solvent.

The values of the stability constants of the complexes between o-CPAEM and Cu^{2+}, Ni^{2+} and Co^{2+} are summarized in Table 2.

Discussion

Dissociation constants of o-CPAEM in different mixed solvents.

The pH metric studies on o-CPAEM in different solvents show that its dissociation constants vary with changing the dielectric constant of the solvent used. The

values of pKa_1 and pKa_2 (Table 1) show a linear relationship with the dielectric constant (expressed as log D) of the different mixed solvents used, which are equal to 1.7, 1.5, 1.65[15] respectively. The relation is represented graphically in Fig. (2) which shows that as the dielectric constant of the solvents increases). Since the ligand is insoluble in water it is not possible to determine its pKa values in pure aqueous medium. However, from Fig. (2), the values of pKa_1, pKa_2 of o-CPAEM in water could be obtained by extrapolating the resulting linear relationship to log D = 1.88 (corresponding to the dielectric constant of water at 30°C = 75.9[16]. This gives a value of pKa_1 = 4.2 and pKa_2 = 9.8 for o-CPAEM in water. The obtained results for the values of dissociation constant of the ligand in the three mentioned solvents show that the intramolecular hydrogen bonding between the carboxyl group and the nitrogen of the azo group is affected by increasing the percentage of hydroxyl solvents (i.e. the % of water). Thus increasing the percentage of water in the solvent would decrease the extent of intramolecular hydrogen bonding, which

Table 2.

Stability constants of o-CPAEM complexes with Cu(11), Ni(11) and Co(11) in different mixed solvents.

Solvent	log D*	Cu-complex log B_2	Ni-complexes log K_1	log K_2	log B_2	Co-complexes log K_1	log K_2	log B_2
50% EtOH-H$_2$O	1.70	23.60	5.31	5.04	10.35	5.53	5.54	11.07
50% dioxan-H$_2$O	1.65	25.588	6.05	4.98	11.03	6.05	6.03	12.08
80% EtOH-H$_2$O	1.50	27.46	7.21	4.74	11.96	6.99	6.15	13.14

*D is the dielectric constant of solvent at 30°C.

in turn will facilitate the removal of hydrogen ion (i.e. decrease the values of pKa of the ligand).

Stability constant of complexes in different mixed solvents.

The stability constants B$_2$ of copper complex was found to vary greatly by varying the dielectric constant of the medium. It increases with decrease of the dielectric constant, as a plot of log D *vs* log B$_2$ gave a straight line as shown in Fig. (3). This linear relationship between log B$_2$ and log D of the solvent used, can be represented mathematically as:

$$\log B_2 = a - b \log D$$

the values of a & b as obtained by the least square method, are found to be:

$$a = 29.3 \text{ and } b = 18.8$$

The stability constant of Ni^{2+} and Co^{2+} complexes were calculated from the data obtained by pH-metric methods and represented as log K$_1$, log K$_2$ and log B$_2$ as shown in table (2), where K$_1$, K$_2$ and B$_2$ are the first, the second and overall stability constants of the formed complexes. The values of such stability constants were found to vary from one solvent to another. A linear relationship was found to exist between log K$_1$ and log D as shown in Fig. (4) and this relation was found to varify the following equation:

$$\log K_1 = m - n \log D$$

where m and n are equal to 8.5 and 10.9 for nickel com complex and 7.75 & 6.6 for cobalt complex respectively.

The reason for decreasing the stability constant of the complex by increasing the percent of water (i.e. increasing D) may be due to increasing the extent of solvation of the metal ion by water molecules. In addition, the presence of water molecules will result in the formation of intramolecular hydrogen bonding between water and ligand molecules, and this in turn will lower the degree of complexation.
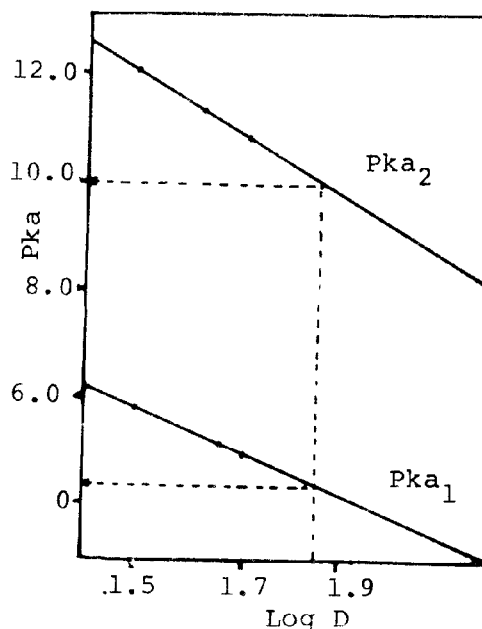

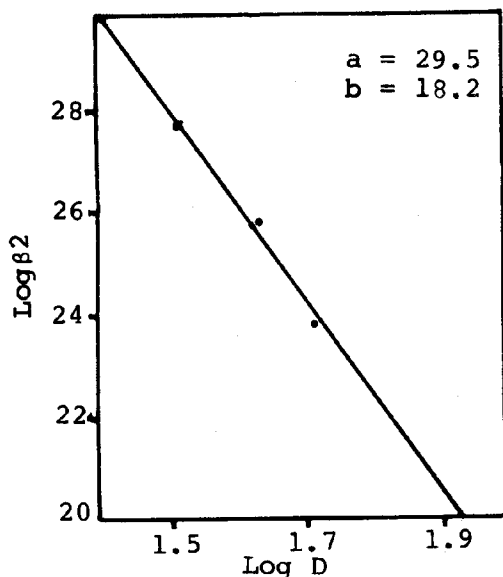Fig. 2 Relation between pka of $_o$-CPAEM and log D of different solvents.

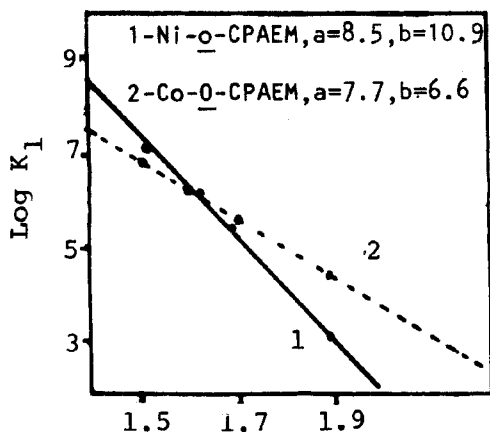Fig. 3. Relation between log B_2 of Cu-$\underline{o}$-C PAEM different solvents.

Fig. 4. Relation between log K_1 of complex and log D of different solvents.
—— spectrophotometric method
---- pH-metric method

It is clear from Table (2) that the values of overall stability constants B_2 of all complexes investigated increase with decreasing the dielectric constant D of the medium. Among these metals, Cu^{2+} was found to form a much more stable complex than that of Ni^{2+}, and Co^{2+}, and that the values of Co^{2+} in any solvent are higher than those for Ni^{2+} complexes.

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