STUDIES OF o-CRESOL PHTHALEIN COMPLEXONE AND ITS METAL COMPLEXES:
Part I. Spectroscopic Studies of o-Cresol Phthalein Complexone with Special Reference to Medium Effects on its Ionisation Constants

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The electronic absorption spectra of o-cresol phthalein complexone (o-CPC) were studied in water-organic solvent mixtures at different pH. The absorption bands were assigned and the effect of solvent polarity on their position has been discussed. The pK_a of the acid-base equilibria set were determined and discussed in relation to the nature and proportion of the organic solvent added. The main bands of their spectra and signals of the 1_{HNMR} spectra are as well discussed. The mixing of o-CPC with some transition and rare earth metal ions leads to drastic changes in colour and hence the visible absorption spectra of both organic compounds and metal ions.

INTRODUCTION

Alizarin complexone (AC) is chiefly used as its La^{3+} or Ce^{3+} chelate for photometric determination of fluoride [1-3], or in analytical applications involving colour formation with metal ions [4-9]. O-Cresol phthalein complexone (o-CPC) can be used also as a chelating agent and in analytical applications involving colour formation with metal ions. Despite the fact that a large number of organic molecules of the complexone type have been the subject of some interesting studies, yet the absorption spectrum of o-cresol phthalein complexone, its ionization and ability to form chelate compounds have not been adequately investigated.

The present paper is devoted to the spectral study of o-CPC essentially medium effect on the position of its absorption bands and ionization constants using spectrophotometric techniques and potentiometric titration. The effect of some transition and rare earth metal ions on the o-CPC visible spectrum has also been investigated, revealing that this compound could function as a chelating agent and can be used in analytical applications. In this connection, ir and 4.NMR assignments have been done.

EXPERIMENTAL

All compounds used in the present work were pure laboratory grade BDH chemicals.

10^{-3} M o-CPC solutions were prepared by dissolving the appropriate quantity of the solid in the 10^{-3} M solutions of NaOH. More dilute solutions used for spectral measurements were obtained by accurate dilution.

For pH control the modified universal buffer series of Britton and Robinson [10] was used. In order to account for difference in pk values in water-organic solvent mixtures relative to pure aqueous media, the pH values in the former case were corrected making use of the attempt made by Douheret [11, 12].

The electronic absorption spectra were measured on a Unicam SP 1800 Ultraviolet spectrophotometer within the range 200-750 nm using 1.0 cm matched silica cells. The potentiometric titration was performed at 250 in the same way as described previously [9] using a Beckmann expanded scale pH-meter. The ir-spectra were recorded on the SP 1200 infrared spectrophotometer using the KBr wafer technique, whereas the 1_{HNMR} spectra were recorded in d_6-DMSO with a Varian EM-360 spectrometer.

RESULTS AND DISCUSSION

The spectral measurements in buffer solutions are confined to bands in the uv and visible regions since those in the visible side do not appear below pH $\leqslant$ 8.0, Representative spectra are given in Fig. (1a, b).

The uv absorption spectra of o-CPC in solutions of pH $\leqslant$ 1.2 display a single band with λ_{max} at 282 nm which correspond to absorption by the neutral molecule. With increase in pH, the band shifts gradually to longer wave-

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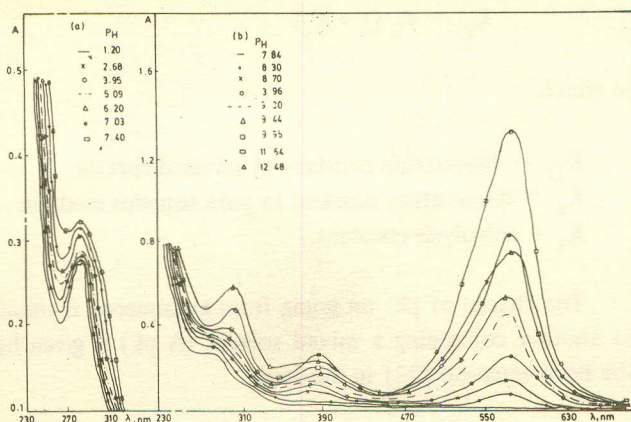** Faculty of Science, Tanta University.

Fig. 1. Effect of pH on the absorption spectra at 3×10^{-3} M o-CPC in universal buffer solution.

length and its extinction increases. This shift can be explained by a gradual ionization of the carboxyl groups to mono-and dianionic molecules which exhibit λ_{max} at 286 nm.

In solutions of pH 5-7.5, the original band is slightly shifted to longer wavelength with λmax at 290 nm. The change in the spectrum can be ascribed to the ionization of the two—OH groups. This is based on the data obtained for the ionization of similar ligands e.g., calcein [13, 14], Methyl Thymol Blue (15) and Xylenol orange [16-19] as shown in Table 1.

The magnitude of changes in the extinction of the band and its λ_{max} position varies with the nature and proportion of the organic solvents. At pH $\geqslant 8.0$, the ionization of the imino groups takes place where a new band appears in the visible region with λ_{max} at 570 nm; the intensity of the band increases with increasing pH and also exhibits a further minor shift to longer wavelength. At pH $\leqslant 11.0$ the intensity of the band decreases again.

The absorbance-pH curves (Fig. 2) obtained at some selected wavelengths display more or less identical characteristics. All curves are characterised by a gradual decrease of absorbence within the lower pH range, gradual

increase in the middle pH range followed by a rapid decrease in the higher range. The fact that no isosbestic points are observed during the ionization of o-CPC can be ascribed to the overlap between the different equilibria set. The dissociation steps can be represented as follows:
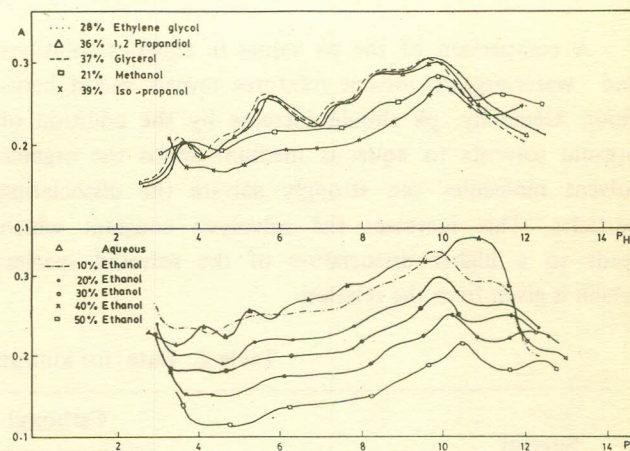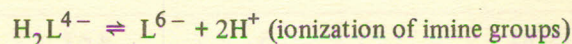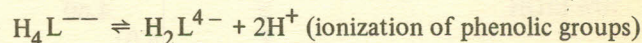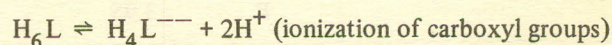

Fig. 2. Absorption — pH curve for o-CPC in different water organic solvent mixtures.

$$H_6L \rightleftharpoons H_4L^{--} + 2H^+ \text{ (ionization of carboxyl groups)}$$

$$H_4L^{--} \rightleftharpoons H_2L^{4-} + 2H^+ \text{ (ionization of phenolic groups)}$$

$$H_2L^{4-} \rightleftharpoons L^{6-} + 2H^+ \text{ (ionization of imine groups)}$$

The values of the dissociation constants for the three ionization steps are determined using the limiting absorbence method [20] as modified for acid-base equilibria [21]. The mean values obtained are collected in Table 2 from which it is evident that the ionization constant depends largely on the nature and proportion of the organic solvent added to the buffer mixture.

Due to the symmetry present in the molecule the separation betweek K_1 and K_2, K_3 and K_4 is difficult from spectral data, while when the ionization of the fifth H$^+$ begins to start the molecule probably loses its symmetry

Table 1

Compound	Carboxy - groups		Phenol groups	Imino groups		
	pk_{a1}	pk_{a2}	pk_{a3}	pk_{a4}	pk_{a5}	pk_{a6}
Calcein (Wallach)	< 4.0		5.4	9.0	10.5	12
Calcein (Iritani)	2.1	2.9	4.2	5.5	10.8	11.7
Methyl Thymol Blue	1.8	2.0	3.04	6.9	11.14	12.94
Xylenol Orange	0.76	2.58	4.09	6.4	10.46	11.0

and the spectral data obtained enable us to separate the K_5 and K_6 values.

Attempts were made by applying potentiometric titration in order to determine the different pK_a values of o-CPC. The results of the potentiometric titrations are also presented in Table 2.

A comparison of the pk values in aqueous solutions and water-organic solvent mixtures reveals varied behaviour. Generally, pk should increase by the addition of organic solvents to aqueous medium unless the organic solvent molecules can strongly solvate the dissociating particles. This increases the solvolysis constant which leads to a higher dissociation of the solvated species, which is given from the relation

$$K_D = K_a (1 + K_s)$$

in which

K_D = dissociation constant of solvated species
K_a = dissociation constant in pure aqueous medium
K_s = solvolysis constant.

The change of pk on going from an aqueous medium to another containing a mixed solvent (Δ pk) is given by the Born equation [22] in the form

$$\Delta pk = \frac{Ne^2}{4.6\,RT}\left(\frac{1}{r_{HA^+}} - \frac{1}{r_{H_3^+O}}\right)\left(\frac{1}{D_{mix}} - \frac{1}{D_{H_2O}}\right)$$

Table 2. Data for ionization of o-CPC in different media.

Solvent		Carboxyl		Phenol		Imino	
		pk_1	pk_2	pk_3	pk_4	pk_5	pk_6
Aqueous	S	4.35		7.94		8.85	9.95
	P	3.95	6.85	7.64	8.50	9.10	10.30
10% EtOH	S	4.60		8.03		0.30	10.20
	P	4.01	6.90	7.82	8.60	9.48	10.55
20% EtOH	S	4.67		8.08		9.48	10.25
	P	4.13	6.95	7.91	8.74	9.75	10.65
30% EtOH	S	4.74		8.20		9.55	10.45
	P	4.20	7.02	7.98	9.05	9.95	10.72
40% EtOH	S	4.81		8.38		9.80	10.65
	P	4.40	7.09	8.02	9.32	10.06	10.85
50% EtOH	S	4.94		8.50		9.95	10.95
	P	4.60	7.20	8.13	9.44	10.15	11.20
21% EtOH	S	4.63		8.01		9.28	10.23
39% Isopropanol	S	4.87		8.41		9.84	10.72
28% Ethyleneglycol	S	4.21		6.35		8.26	9.90
36% 1,2-propandiol	S	3.80		6.10		8.05	9.85
37% glycerol	S	3.76		6.04		8.02	9.82

S = Spectrophotometry P_{27} = Potentiometry
    Values of similar ligands
    i) EDTA pk_1 = 2.0, pk_2 = 2.7
          pk_3 = 6.8 and pk_4 = 10.3
    ii) NTA pk_1 = 1.9 pk_2 = 2.5 and pk_3 = 9.7

where

  N = Avogadro's number

  e = charge of electron

r_{HA}^+ = radius in a medium of dielectric constant D_{mix}

and

$r_{H_3^+O}$ = radius in water

At constant mole fraction of the organic solvents and based on the above relation, it can be concluded that hydrogen bonding, solvent basicity, dispersion factors and proton-solvent interaction effects are to be considered as factors influencing the ionization of *o*-CPC in aqueous media containing organic solvents. The pk values decrease in the case of glycerol, 1,2-propandiol and ethylene glycol. This behaviour is commonly observed with weak organic acids, i.e. the higher proton acceptor property of polyhydric alcohols compared to monohydric ones. This deprotonation of the weak acid is favoured in the presence of polyhydric alcohols, though these solvents are less basic than water [23]. Nevertheless, they can solvate *o*-CPC and its ions strongly than water and hence lower the pk values. The rise of pk with increased ethanol proportion can be presumably attributed to decrease in solvent basicity with a rise in ethanol content since water molecules have a high tendency to donate hydrogen bond as compared to ethanol [24]. Thus, the change in the behaviour of the various organic solvents in the buffer mixture could be ascribed to the difference in their structures, polarities and their ability to function as proton acceptors from *o*-CPC.

If the mole fraction of the organic solvents is kept constant according to the relation given by Charlot and Termillon [23], pk_a would be a linear function of $\frac{1}{D}$. This is however not the case with the ionization of *o*-CPC. Therefore, besides the change of pk with the medium (in spite of being influenced by the solvent dielectric constant) there are other factors contributing to solvent effect and playing a major role [25, 26], essentially with regard to change of the radius and solvation effects. Accordingly, it seems that the role contributed by any factor to the total effect governing the change of pk_a in water-organic solvent mixtures will largely depend on the properties of both organic solvent used and its mode of interaction with *o*-CPC.

The IR-spectrum. The ir spectrum of *o*-CPC in the solid state as KBr disc displays a series of intense broad bands within the 3450-2400 cm^{-1} range with some broad and sharp peaks. The broad peaks at 3430 and 3250 cm^{-1} can be assigned to ν_{OH} of the carboxylic and phenolic-OH groups. The shrap peaks at 3100 and 3050 or 2950 and 2880 cm^{-1} are assigned to assymetric ν_{CH} of aromatic or aliphatic C-H groups. The group of bands within the

2800-2400 cm^{-1} can be assigned to a proton attached to a positive quaternary nitrogen atom resulting from the Zwitterion formed through a proton transfer from acetic and rests to the imino nitrogen.
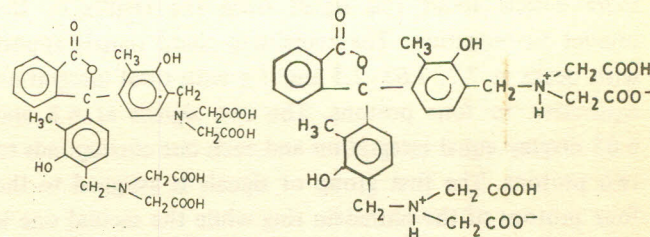
The intense band at 1750 cm^{-1} is assigned to the stretching mode of the carbonyl group in the phthalein part, while the two medium intensity bands at 1660 cm^{-1} are assigned to the carboxy carbonyls.

The broad bands at 1390 and 1230 cm^{-1} can be ascribed to δ_{OH} while those at 1250 and 1165 cm^{-1} are due to ν_{C-OH} vibrations. The four adjacent hydrogens of the phthalein ring yields the two medium and strong bands at 755 and 710 cm^{-1} whereas the isolated hydrogens of the cresol ring lead to the medium doubled band with the peaks at 895 and 885 cm^{-1}

Besides the bands due to the OH and C=O groups, the C-N bands would be of interest in the chemistry of chelate compounds with the ligand since chelation to metal ions, in comparison with ligands having identical structure, would take place as follows:
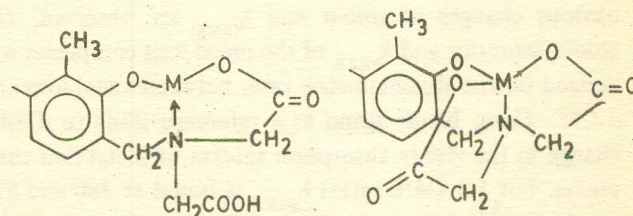
Divalent metal ions   Trivalent metal ions

The C-N band for aliphatic amines is usually observed within the 1100-900 cm^{-1} range and usually exhibits medium or low intensity. In the spectrum of *o*-CPC there exists a group of seven low intensity bands within this region. The assignment of these bands based on simple comparison is however rather difficult.

The ^{1}HNMR spectrum. An approach concerning the assignment of the ^{1}HNMR signals for *o*-CPC would be of help in studying its metal chelates by this method. The ^{1}HNMR spectrum of *o*-cresol phthalein complexone in d$_6$-DMSO exhibits a broad signal within the 8-7 ppm range with small peaks near 7.6 and 6.8-6.65 ppm. The

broad signal vanishes on treatment with D_2O. The broad signal concerns thus the protons of the various OH groups. It is however, not possible to get resolved signals for these groups and accordingly it is rather difficult to give more details about this signal from the results of the present investigation. The remaining sharp signals appear with peaks at 7.7, 7.63, 7.5 and 7.4 with total integration equivalent to four protons. The two signals at 6.8 and 6.65 display equal integration and each one corresponds to two protons. The first group of signals is assigned to the four protons of the phthalein ring while the second one is due to the protons of the *o*-cresol ring. The multiple signal within the 2.6-2.3 ppm. range exhibit four sharp peaks at 2.53, 2.47, 2.41 and 2.38 with an integration equivalent to 14 protons and a singlet at 2.30 with an integration equivalent to four protons. The first signal can be ascribed to the protons of the two CH_3 group and the protons of the four CH_2 groups of the acetic acid rests. The other signals are due to the four protons of the two methylene groups falling between the cresol ring and the imino diacetic acid parts.

Effect of metal ions in the absorption spectra of o-CPC' The formation of a complex compound is usually accompanied by the appearance of its corresponding absorption spectrum. Because of this, the shift in the spectrum may be accompanied by a change in the colour of the solution, which can be observed visually. On mixing *o*-CPC solutions with those fo some transition and rare earth metal ions obvious changes of colour and λ_{max} are observed. The colour intensity and λ_{max} of the metal ions complexes will depend on the stoichiometric ratio between metal ions and *o*-CPC. Using blank ligand as a reference leads to drastic change in the visible absorption spectra of metal ions complexes. For 1:1 (M:L ratio) λ_{max} is found at 380 and 570 nm for Mn^{2+}, 525 nm for Co^{2+}; 375 and 575 nm for Ni^{2+}, 385 and 585 nm for Cu^{2+}, 500 nm for Zn^{2+}, 465 nm for Cr^{3+} and 460 nm for Ce^{3+} while for 2:1 (M:L ratio) λ_{max} lies at 370 and 580 nm for Mn^{2+}, 550 nm for Co^{2+}, 390 and 580 nm for Ni^{2+}, 410 and 520 nm for Cu^{2+}, 430 and 500 nm for Zn^{2+}, 380-420 nm for Cr^{3+} and 410-480 nm for Ce^{3+}. The difference in the λ_{max} in the case of the metal ions refers to the difference of the perturbing influence of metal ions. The shift of the bands together with the change in colour of the solution denotes complex formation. The metal complex formed between *o*-CPC and these metal ions require a more detailed study which is being carried out in our laboratory.

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