Spectrophotometric Determination of Cu²⁺ with Quinolinyl Derivative in Organic and Aqueous Solutions

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A spectrophotometric study of complex formation of 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene)]amino}phenol (4-Cl-2-QMAP)with copper (II) in aprotic acetonitrile and in protic ethanol and *n*-butanol has been carried out. The stability constants and stoichiometry of the complexes have been estimated. The stability constant of copper (II)-ligand complex formation grows with growth of solvent polarity/polarizability and is the greatest in polar aprotic acetonitrile, whereas spectral characteristics of the metal-ligand complex (long-wavelength shift of absorbance maximum, extinction coefficient) grow in H-bond donating solvents-in protic ethanol and *n*-butanol. 4-Cl-2-QMAP on dioctyl phthalate plasticized PVC film has shown efficient selectivity and sensitivity towards Cu²⁺ in aqueous solution. *ortho*-Hydroxy-phenol quinolinyl derivative on PVC film is found to have higher photostability with respect to same quinolinyl in water and methanol solutions. Embedding of 4-Cl-2-QMAP on PVC is shown to be useful for the spectroscopic determination of Cu²⁺ trace amounts ($< 10^{-4}$ M) in aqueous solutions.

Key Words: Cu²⁺-ligand complex, Stability constants, Solvent effect, Complex formation, PVC film, Quinolinyl.

INTRODUCTION

It is known that azo compounds (arylazoheterocycles), containing the fragments -N=N-C=N-, -C=N-C-N=N-, -C=N-C=N-C-, -C-N=C-C=N-C-, and, according to Hata and Uno[1], especially azo compounds containing hydroxy group in *ortho*-position of phenylic ring, give coloured chelates with Cu²⁺ or Cu⁺ ions. Thus they are used for spectroscopic copper determination[1-10]. The interest in 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol (4-Cl-2-QMAP) (Fig. 1) is based not only on its bio-

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medical application[11] but also its detected sensitivity and selectivity towards Cu^{2+} in methanol solutions[12].
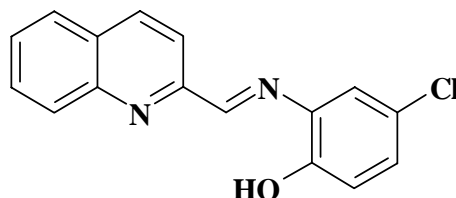

Fig. 1. 4-Chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol (4-Cl-2-QMAP)

The application of 4-Cl-2-QMAP for spectroscopic determination of Cu^{2+} in various solvents, one should know the influence of solvent effects on the complex formation parameters. The influence of solvent effects on the stability constant and on spectral properties of 4-Cl-2-QMAP-Cu complex has not been studied yet. Thus the present paper represents the results of the study of 4-Cl-2-QMAP complex formation with Cu^{2+} in organic solvents of aprotic acetonitrile and in protic *n*-butanol and ethanol. An aqueous phase study was employed by embedding the 4-Cl-2-QMAP on PVC film.

Spectroscopic determination methods by the employment of thin films are preferred for practical widespread applications, for re-use and for not disposing the hazardous and expensive organic dye. These factors bring immense economical and environmental advantages[13].

The present study deals with the possibility to determine low concentrations of Cu^{2+} ions in aquatic solution using 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol (4-Cl-2-QMAP), embedded on dioctyl phthalate (DOP) plasticized PVC film by means of UV/vis spectroscopy. Determination of Cu^{2+} ions in aquatic solution in trace amounts ($< 10^{-4}$ M) by the employment of a heterogenous phase method, would present a simple and practical method for wide spread applications.

EXPERIMENTAL

Organic solvents used were all of spectrophotometric grade and were used as supplied from Fluka. The membrane components, PVC (high molecular weight) and the plasticizer *bis*(2-ethylhexyl)phthalate (DOP), were supplied from Fluka. The organic solvents used were all of spectro-photometric grade and were used as supplied from Fluka or Aldrich. The CuCl$_2$.2H$_2$O and FeSO$_4$, AlCl$_3$.6H$_2$O, FeCl$_3$, MgCl$_2$.6H$_2$O, MnCl$_2$.4H$_2$O used in complexation experiments were purchased from Merck.

The compound (4-Cl-2-QMAP) was synthesized by condensation of quinoline-2-carboxaldehyde with 2-amino-4-chlorophenol[14,15].

4-Chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol (4-Cl-2-QMAP) was obtained as yellow needles (77%); mp 159ºC; IR (KBr, ν_{max}): 3381, 3080, 3029, 2897, 1612, 1594, 1488, 1364, 1232, 1162, 906, 874, 821 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ (ppm) 6.97-8.31 (m, aromatic and CH, 10H), 8.98 (s, OH, 1H) ppm ; MS: m/z 284 (M + 2), 283 (M + 1), 282 (M+), 281 (M - 1), 265, 253, 221, 155, 129, 109, 101.

Polymer film preparation

Polymer films were prepared from a mixture of 360 mg PVC, 720 mg DOP and 4.5 mL of 4-Cl-2-QMAP (6.6×10^{-5} M) in dry tetrahydrofuran. The resulting polymer solution was spread onto a 125 µm polyester support (Mylar Type) having a width of 120 mm, by the use of a manual spreading device. Thicknesses of the films were determined as 10-15 µm by using a Leitz ortopcan polarise microscope. PVC films were placed diagonally into sample cuvette, in order to improve the reproducibility of the measurements[13].

Spectroscopic measurements

The electronic absorption spectra were recorded using Jasco UV/vis double-beam spectrophotometer, model V-530, with quartz cell of 1 cm path length. All the measurements were made at 25ºC. Fluorescence emission spectra were recorded on PTI-QM1 fluorescence spectrophotometer. In order to determine the stoichiometry and stability constants of 4-Cl-2-QMAP-Cu^{2+} complex, photometric titrations were performed. The concentration of ligand was kept fixed at 2×10^{-4} mol L^{-1}, while the concentration of copper(II) was changed in the range $2 \times 10^{-5} - 3.4 \times 10^{-4}$ mol L^{-1}.

Determination of Stoichiometry and Stability Constant of Metal Complexes from Spectrophotometric Titrations

Information on the stoichiometry of the complexes was obtained from the method of Adamovich[15]. According to the method of Adamovich, spectrophotometric titration curves (*i.e.*, plots of Absorbance (abs) at chosen wavelength *vs.* metal ion concentration [M]) is hyperbola. As the ligand concentration was always kept higher than this of metal cation, the possibility of formation of polynuclear complexes has been neglected. Let us consider a complex ML$_n$ (where ligand denoted L and the metal ion M) formed according to the equation:

$$M + nL \rightleftharpoons ML_n \tag{2}$$

with stability constant:

$$K_S = [ML_n]/(([M] - [ML_n])(L_0 - n[ML_n]^n)) \tag{3}$$

where [ML$_n$] = equilibrium concentration of complex ML$_n$, [M] = cation concentration, L$_0$ = initial concentration of ligand.

The stoichiometry of the complex was calculated by equation:

$$L_0/b = n \tag{4}$$

where b = abscissa of the point where tangent to hyperbola (going through point abs = 0, [M] = 0) and horizontal line abs = abs$_{max}$ are crossed. abs$_{max}$ = absorbance at given wavelength in the presence of excess of cation such that the ligand is fully complexed. In other words, b is equal to metal cation concentration, corresponding by stoichiometry to L$_0$.

The equation (4) is valid when it follows condition $K_S \leq 50/(L_0)^n$.

Coefficients of molar extinction of the complex was calculated by equation:

$$\varepsilon_{MLn} = n(abs_{max} - abs_0)/(l\,L_0) \tag{5}$$

where abs$_0$ = absorbance of the free ligand at given wavelength before addition of the cation, l = the thickness of absorbing layer (cm).

Knowing ε_{MLn}, one could calculate concentration of metal-ligand complex [ML$_n$] for every value [M] of the experimental series. Then, K$_S$ values were calculated for each pair of concentrations [ML$_n$] and [M] by use of eqn. 3.

RESULTS AND DISCUSSION

UV-vis, fluorescence and photostability studies of 4-Cl-2-QMAP

Organic solutions

Drastic changes in absorption spectrum of 4-Cl-2-QMAP have been observed by addition of Cu^{2+} ions to solutions of 4-Cl-2-QMAP. A new band in long-wavelength region appears (Figs. 1 and 2). The observed long-wavelength band is attributed to the formation of donor-acceptor complexes of Cu^{2+} ion with the participation of lone electrone pairs of the quinoline and of the azomethine nitrogen atoms of 4-Cl-2-QMAP.

The absorption wavelengths of 4-Cl-2-QMAP-Cu^{2+} complex in various solvents are presented in Table 1. Figs. 1 and 2 show the absorption spectra of 4-Cl-2-QMAP-Cu^{2+} complex in protic (Fig. 1) and in aprotic solvent (Fig. 2). Long-wavelength shift of the absorption spectrum of 4-Cl-2-QMAP-Cu^{2+} complex is observed in polar proton-donating solvents in comparison with the absorption spectrum of the complex in polar non-hydrogen-bonding acetonitrile (Table-1). Taking into account that lone electron pairs of quinoline and azomethine nitrogens participate in complex formation with Cu^{2+} ions. It is expected that electronic density redistributes from periphery of 4-Cl-2-QMAP molecule to quinoline and azomethine nitrogens on excitation. Hydrogen bond donor solvents interact with unshared valence electron pairs of the nitrogen atoms, thus, enhance charge-transfer by introducing a partial positive charge into the nitrogen atoms. Such interaction stabilizes the charge-transfer excited state relative to the ground state, so that the absorption spectrum of 4-Cl-2-QMAP-Cu^{2+} complex is shifted to the lower energies in protic solvents.
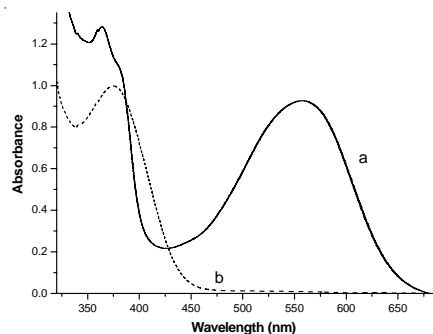
Fig. 1. Electronic absorption spectra of 4-Cl-2-QMAP-Cu^{2+} complex (a) ([4-Cl-2-QMAP-Cu^{2+}] = 1 × 10^{-4} mol L^{-1}) and 4-Cl-2-QMAP (b) ([4-Cl-2-QMAP] = 2 × 10^{-4} mol L^{-1}) in *n*-butanol
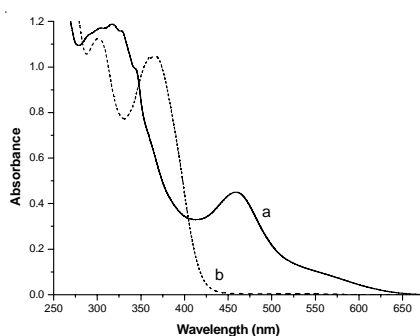
Fig. 2. Electronic absorption spectra of 4-Cl-2-QMAP-Cu^{2+} complex (a) ([4-Cl-2-QMAP-Cu^{2+}] =1 × 10^{-4} mol L^{-1}) and 4-Cl-2-QMAP (b) ([4-Cl-2-QMAP] = 2 × 10^{-4} mol L^{-1}) in acetonitrile

TABLE-1

SPECTRAL CHARACTERISTICS AND STABILITY CONSTANTS (K$_S$) OF
4-Cl-2-QMAP-Cu^{2+} COMPLEX IN VARIOUS SOLVENTS

Solvent	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})	Stoichiometry of 4-Cl-2-QMAP-Cu^{2+}	K$_s$ (L mol^{-1})	Kamlet-Taft solvent parameters		
					π^*	α	β
n-Butanol	555	9300	2:1	$(2.6 \pm 1.1) \times 10^8$	0.47	0.79	0.88
Ethanol	550	11400	2:1	$(5.1 \pm 2.1) \times 10^8$	0.54	0.83	0.77
Methanol*	540*	11600[a]	2:1[a]	$[(2.2 \pm 1.1) \times 10^9]$[a]	0.6	0.93	0.62
Acetonitrile	460	4500	2:1	$[(1.6 \pm 1.2) \times 10^{10}]$	0.75	0.19	0.31

Here λ_{max} and ε_{max} are the position (nm) and molar extinction coefficient of the long-wavelength maximum in the absorption spectra of Cu^{2+} complex; * data taken from Posokhov *et al.*[12], a = recalculated using data from Posokhov *et al.*[12], because calculation method in Posokhov work gave more rough estimate for the stoichiometry and for the formation constant; in parantheses [ ] = values of K$_s$, calculated with greater uncertainty (*i.e.* when K$_s \geq (50/L_o^2)$, where L$_o$ = ligand concentration).

The influence of solvent on absorption maximum and molecular extinction of 4-Cl-2-QMAP-Cu^{2+} complex was evaluated quantitatively by means of Kamlet-Taft solvent parameters[16-18].

The advantage of the Kamlet-Taft treatment is to sort out the quantitative role of solvent properties on physical (positions and intensities of maximal absorption in IR, NMR, ESR and UV/vis absorption and fluorescence spectra, *etc.*) and chemical (reaction rate, equilibrium constant, *etc.*) arameters[16-18].

Linear regression equation with the use of Kamlet-Taft solvent parameters for absorption maximum (expressed in 10^3 cm^{-1}) and for extinction coefficients of 4-Cl-2-QMAP-Cu^{2+} complex are:

$$\nu_{max} = (19.244 \pm 0.94) + (4.330 \pm 0.945)\pi^* - (3.985 \pm 0.336)\alpha \qquad (6)$$
with n = 4, R = 0.9986, SD = 0.115 kK;
$$\varepsilon_{max} = (-1587 \pm 6749) + (5336 \pm 8418)\pi^* + (11152 \pm 2992)\alpha \qquad (7)$$

with n = 4, R = 0.9677, SD = 1028 L mol^{-1} cm^{-1}

where π^* = solvent polarity/polarizability, α = solvent acidity (solvent hydrogen bond donor), β = solvent basicity (solvent hydrogen bond acceptor).

The contribution of solvent hydrogen bond accepting ability (solvent basicity, β) is considered to be negligible: the nonlinear regression equations, which included solvent basicity β, have much worse correlation coefficient, than the equations, where parameter β is omitted.

Negative value of coefficient for solvent acidity α in equation 6 means that grows of solvent acidity (*i.e.* H-bond donating ability) tend to shift the absorption maximum to long-wavelength region, whereas the opposite is true for solvent polarity/polarizability π^*, having positive value of coefficient in equation 6. The position of absorption maximum has approximately the same sensitivity to each solvent parameter, because the absolute values of the coefficients for π^* and α are rather close.

In case of eqn. 7, both solvent parameters (π^* and α) have positive values of the coefficients and, thus, the growth of each parameter tend to increase the molar extinction value.

4-Cl-2-QMAP on PVC film

Absorption and fluorescence emission of 4-Cl-2-QMAP both in methanol solution and on plasticized PVC film had shown similar spectra (Fig. 3, Table 2). Wavelength of absorption, λ_{max}, in film is shifted to higher wavelength about 15 nm compared to absorption λ_{max} in methanol solution. Red shift of absorption of 4-Cl-2-QMAP may be either due to enhanced conjugation in immobilized polymer phase by hindrance of vibrational rotational motions or aggregate formation. The fluorescence quantum yield (φ_f) of 4-Cl-2-QMAP in methanol was stated as 1.4×10^{-3} in our previous study[12]. This value of θ_f has decreased approximately 25 % on PVC film, which strengthens the possibility of aggregate formation in the film.

TABLE-2

UV–VIS SPECTROSCOPY DATA (λ AND ε), STOKES' SHIFTS ($\Delta\lambda$), RATE CONSTANTS (k_p) AND HALF-LIVES $t_{1/2}$ (h) FOR PHOTODEGRADATION OF 4-Cl-2-QMAP

Media	λ_{max}^{abs} (nm)	λ_{max}^{emis} (nm)	$\Delta\lambda$ (nm)	k_p (s^{-1})	$t_{1/2}$ (h)
Methanol	371	431	60	3×10^{-5}	6.41
On PVC	384	465	81	5×10^{-6}	38.5

Placing the films into aqueous solutions of CuCl$_2$.2H$_2$O salt induced drastic changes in absorption spectra of 4-Cl-2-QMAP: with the increase in Cu^{2+} concentration in the cuvette, the appearance of a new band in 500 nm region was observed (Fig. 4). The spectroscopic measurements were
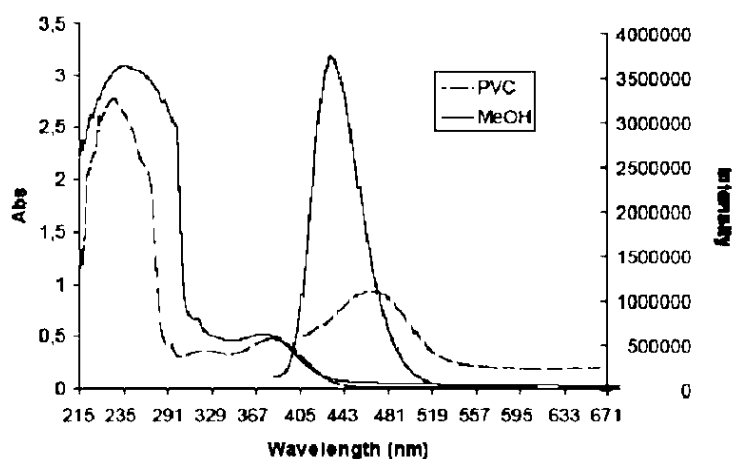
Fig. 3.   Absorption and emission spectra of 4-Cl-2-QMAP in methanol solution
           $(1.3 \times 10^{-4}$ M) and on DOP plasticized PVC film

done *ca.* 2 min of contact time between the ligand film and Cu^{2+} aqueous
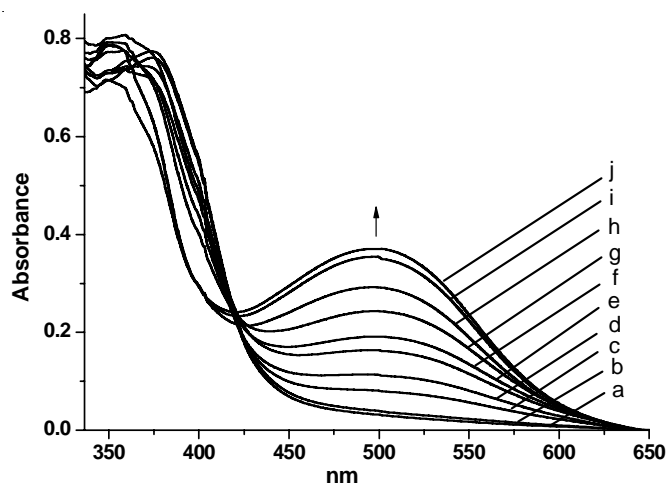solution (with agitation of the solution).

Fig. 4.   Changes in the absorption spectra during the complex formation of 4-chloro-2-
           {[(1*E*)-quinolin-2-yl-methylene]amino}phenol (4-Cl-2-QMAP) embedded on
           PVC film, with the Cu^{2+} ions in water. Arrow indicate a change in the absorbance
           with the increase in the concentration of Cu^{2+}/mol L^{-1}: (a) 0 (b) 3.3×10^{-5}
           (c) 6.6×10^{-5} (d) 9.6×10^{-5} (e) 1.6×10^{-4} (f) 1.9×10^{-4} (g) 2.5×10^{-4} (h) 2.8×10^{-4} (i) 3.1×10^{-4} (j) 3.4×10^{-4}

    The observed changes in absorption spectra of 4-Cl-2-QMAP can be
attributed to the formation of donor-acceptor complex of Cu^{2+} ion with the
participation of lone electron pairs of the quinoline and the azomethine
nitrogen atoms of 4-Cl-2-QMAP.

Photodecomposition of 4-Cl-2-QMAP is studied both in methanol solution and on PVC film with a steady-state spectrofluorimeter in time based mode (Xe lamp irradiation). The excitation is performed at 371 and 384 nm, for the methanol solution and PVC film, respectively, that correspond to the maximum wavelength of absorption in two different media (Table 2). The photodecompotion data were acquired at the emission wavelength maximum of the compound, *i.e.* 431 and 465 nm, for the methanol solution and PVC film, respectively.

The rate constants for photodegradation of 4-Cl-2-QMAP are obtained from the relation

$$-\ln(I/I_0) = k_p t \qquad (3)$$

where I_0 and I are the emission intensity of the compound at times zero and t, respectively k_p is the first-order rate constant (s^{-1}). Half-lives $t_{1/2}$ (s) were also calculated by replacing I with I/2,

$$t_{1/2} = 0.693/k_p \qquad (4)$$

First-order rate constants estimated from the regression $-\ln(I/I_0)$ *vs.* time (s), shown in Fig. 5, and the half-lives for photodegradation together with rate constants are given in Table 1. The stability of the compound has increased approximately 6 times on PVC film which brings an application advantage to the compound.
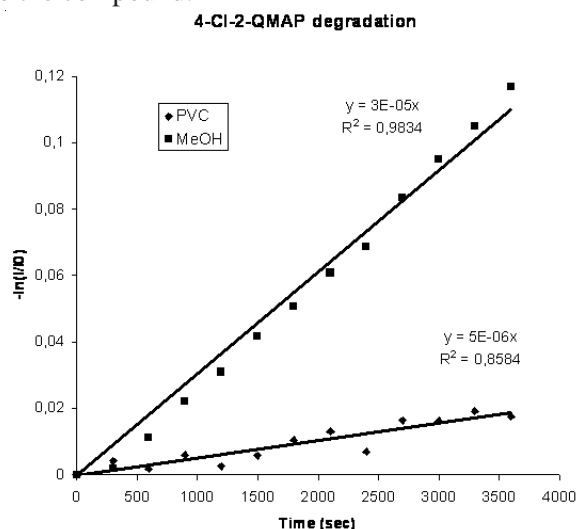

Fig. 5.   First-order relations for photodegradation of 4-Cl-2-QMAP in methanol solution and on PVC film under Xe-lamp irradiation for 1 h

Structure and Stability of 4-Cl-2-QMAP-Cu^{2+} Complexes

Organic solutions

On the base of spectrophotometric titration curves (*i.e.* plots of 4-Cl-2-QMAP-Cu^{2+} absorbance *vs.* total Cu^{2+} concentration) the stoichiometry of

metal-ligand complex and the stability constants of the complex were calculated for all the solvents used (Figs. 6-7 and Table-1).
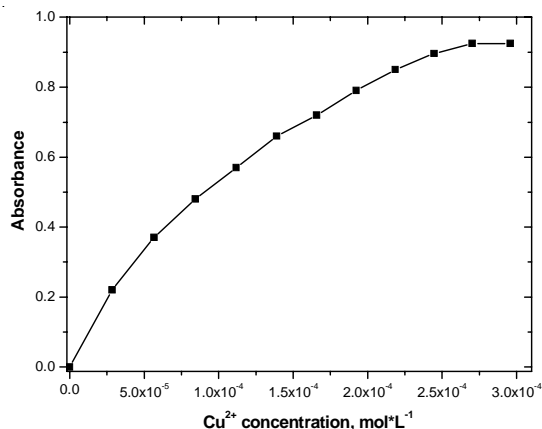
Fig. 6.   Photometric titration curve for 4-Cl-2-QMAP-Cu^{2+} complex formation in *n*-butanol based on the 550 nm absorption
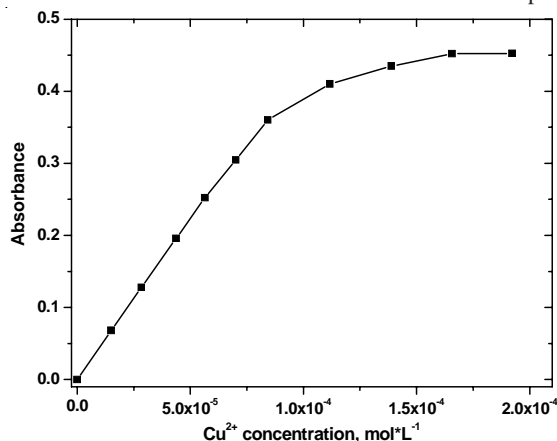
Fig. 7. Photometric titration curve for 4-Cl-2-QMAP-Cu^{2+} complex formation in acetonitrile based on the 460 nm absorption

The stoichiometry of 4-Cl-2-QMAP-Cu^{2+} complex was found to be 2:1 at used concentration of the ligand (2×10^{-4} mol L^{-1}) in all the solvents used for the study.

The computed formation constant (K_s) values of 4-Cl-2-QMAP-Cu^{2+} complex in various solvents presented in Table-1. It is evident that the formation constant of the complex increases with growth of solvent polarity/polarizability π^*. Taking into account that the delocalization of the negative charge over the conjugated system during the Cu^{2+} complex formation takes place, this trend can be interpreted on the basis that the complex would be more stabilized in a polar solvent with high polarity/polarizability owing to increasing dipole-dipole or dipole-induced dipole interactions.

It should be noted that stability constant K_s for 4-Cl-2-QMAP-Cu^{2+} complex in aprotic acetonitrile is the greatest among the corresponding values for the complex in protic solvents.

This could be explained by the fact that lower hydrogen bonding in acetonitrile should promote the substitution of the solvent molecules around the metal; consequently, greater stabilization of 4-Cl-2-QMAP-Cu^{2+} complexes will occur in aprotic acetonitrile compared to that in protic solvents[19,20].

Linear regression equation with the use of Kamlet-Taft solvent parameters for stability constant is:

$$K_s = (-3.66 \times 10^9 \pm 6.72 \times 10^9) + (2.95 \times 10^{10} \pm 8.41 \times 10^9)\pi^* - $$
$$(1.31 \times 10^{10} \pm 2.99 \times 10^9)\alpha \quad (8)$$

with n = 4, R = 0.9938, SD = 1.02×10^9 L mol^{-1}

The contribution of solvent hydrogen bond accepting ability (solvent basicity, β) is considered to be negligible: the nonlinear regression equations, which included solvent basicity β, have much worse correlation coefficient, than the equations, where parameter β is omitted.

The coefficients describe the sensitivity of complex formation process to each of the individual contributions: the absolute value of the coefficient for solvent polarity/polarizability π^* is more than two times greater than the absolute value of the coefficient for solvent acidity α. This means that K_s value depends mainly on solvent polarity/polarizability π^*: the value of the stability constant K_s of 4-Cl-2-QMAP-Cu^{2+} complex grows with growth of π^*-value.

Negative value of the coefficient for solvent acidity parameter α is in good accordance with the fact that K_s are lower in protic solvents in comparison with aprotic acetonitrile.

4-Cl-2-QMAP on PVC film in aqueous solutions of Cu^{2+}

In case of 4-Cl-2-QMAP embedded on PVC film, an additional process appears in order to make complex with Cu^{2+}, some amount of the ligand on PVC must dissolve into water:

$$(L)_{PVC} \rightleftharpoons (L)_{Water} \quad (9)$$

The concentration of saturated solution of 4-Cl-2-QMAP in water is low and could not be estimated by UV/vis spectroscopy.

Because the concentration of saturated solution of 4-Cl-2-QMAP in water is unknown, we could not use formula 4 for stoichiometry determination. For this reason, taking into account that the stochiometry of Cu^{2+}-ligand complex for 4-chloro-2-{[(1E)-quinolin-2-ylmethylene]amino}-phenol (2×10^{-4} mol L^{-4}) have been found to be 2:1 in all the organic solvents used, we have made an assumption that the same stochiometry of metal-ligand complex is true also for the complex formation in water. Thus,

the apparent stability constant K_s^{app} could be calculated by the equation:

$$K_s^{app} = [Cu^{2+}L_2]_{Water}/(([Cu^{2+}]_{Water} - [Cu^{2+}L_2]_{Water}) ((L_0)_{pvc} - 2[Cu^{2+}L_n]^2_{Water})) \quad (10)$$

On the basis of the spectrophotometric titration curve (Fig. 8), the apparent stability constant K_s^{app} was calculated (Table-3). The value of the apparent stability constant K_s^{app} was found to be considerable (Table-3), but lower than all the stability constants for all organic solvents used (Table-1).
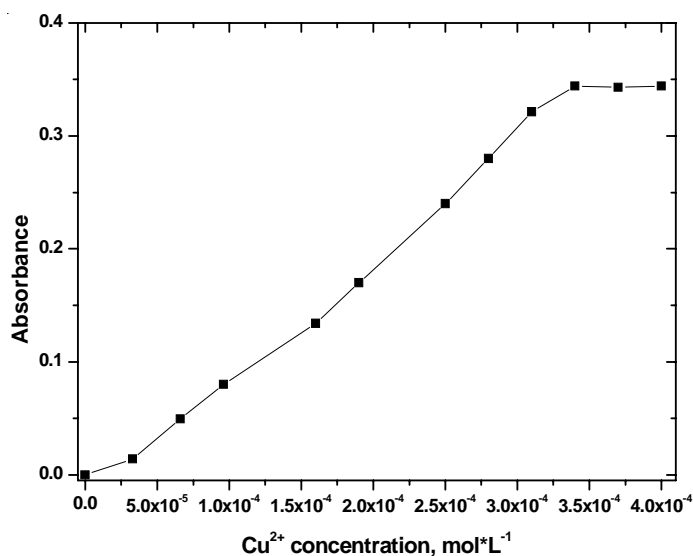

Fig. 8. Photometric titration curve for 4-Cl-2-QMAP-Cu^{2+} complex
formation in aqueous solutions based on the 500 nm absorption

TABLE-3
COMPLEX FORMATION OF 4-Cl-2-QMAP, EMBEDDED ON PVC FILM
WITH THE Cu^{2+} IONS

Complex	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})	K_s^{app} (L mol^{-1})
4-Cl-2-QMAP-Cu^{2+}	500	1012	$(3.7 \pm 1.4) \times 10^7$

λ_{max} = position of the long-wavelength maximum in the absorption spectra of Cu^{2+} complex; ε_{max} = molar extinction coefficient of the long-wavelength maximum in the absorption spectra of Cu^{2+} complex in water; K_s^{app} = apparent stability constant of the Cu^{2+} complex in water.

None of the following ions affected the direct determination of 1×10^{-4} mol L^{-1} of Cu^{2+}: Al^{3+} (1×10^{-1} mol L^{-1}), Mg^{2+} (2×10^{-1} mol L^{-1}), Mn^{2+} (2×10^{-1} mol L^{-1}), Zn^{2+} (3×10^{-3} mol L^{-1}), Ni^{2+} (2×10^{-2} mol L^{-1}), Ti^{2+} (2×10^{-2} mol L^{-1}), . The ions were considered as non-interfering when they caused a change in the absorbance of the Cu^{2+}-4-Cl-2-QMAP complex (abs = 0.22) less than 5 %. The detection limit for Cu^{2+} ion determination in water solution was found to be 1.6×10^{-5} mol L^{-1}.

Conclusion

The stoichiometry of copper(II)-ligand complex was found to be 1:2 in all the studied organic solvents. The stability constants of copper(II)-ligand complex were calculated to be 2.5×10^8, 5.1×10^8, 2.2×10^9, 1.6×10^{10} L mol^{-1} in *n*-butanol, ethanol, methanol and acetonitrile, respectively.

It was found, that the stability constant of copper (II)-ligand complex formation grows with growth of solvent polarity/polarizability and is the greatest in polar and aprotic acetonitrile, whereas spectral characteristics of the metal-ligand complex (long-wavelength shift of absorbance maximum, extinction coefficient) grow in H-bond donating solvents.

The influence of solvent parameters on stability constant values, on absorption maximum and on molecular extinction coefficient of 4-Cl-2-QMAP-Cu^{2+} complex was evaluated quantitatively by means of Kamlet-Taft solvent parameters.

4-Chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol, embedded on PVC film, has shown good properties as colorimetric chemosensor. Indeed, 4-Cl-2-QMAP, embedded on PVC film, form complex with Cu^{2+} in water with rather high constant K_s^{app}. The association causes changes in the absorption properties, *i.e.* the appearance of the long-wavelength absorption band (500 nm) of Cu^{2+} complex. Taking into account rather good selectivity, high affinity and sensitivity of 4-Cl-2-QMAP, embedded on PVC film, for Cu^{2+} ions in water solution, the studied 4-Cl-2-QMAP could be proposed as reagent for spectroscopic determination of trace amounts of Cu^{2+} (1×10^{-4} mol L^{-1}, detection limit 1.6×10^{-5} mol L^{-1}).

Overall results prove that one can determine the presence of Cu^{2+} ions $\geq 10^{-5}$ mol L^{-1} concentrations with 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol, both in organic and in aqueous solutions. Embedding of 4-Cl-2-QMAP on PVC is shown to be useful for the determination of trace Cu^{2+} ions in water.

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