ISSN 2321-807X
Volume 12 Number11
Journal of Advances in Chemistry

SPECTROPHOTOMETRİC STUDY of the Complex fORMATİON OF COPPER (II) WİTH 1-Phenyl-2- [2-Hydroxy-3-sulfo-5-nİtrophenylazo] 1,3-butadİONE İn the presence OF CATİONİC SURFACTANTS.

R. A. Aliyeva, A. V. Ayvazova, F. M. Chiragov, S. R. Lahicova
Department of Chemistry, Baku State University, Z.Khalilova st. 23, Baku, Azerbaijan, AZ1148,
ayvazova_89@mail.ru

ABSTRACT

Based on benzoylacetone synthesized 1-phenyl-2- [2-hydroxy-3-sulfo-5-nitrophenylazo] 1,3-butadione (PHSNPAB). Studied complex formation of copper (II) with 1-phenyl-2- [2-hydroxy-3-sulfo-5-nitrophenylazo] 1,3-butadione (PHSNPAB) in the presence and absence of the third component such as cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr). Single ligand complexes are formed at pH = 3, λ = 444nm, and mixed ligand complexes at pH = 2 λ = 456, 454, and 461 nm, respectively (CPCl, and CPBr, CTMABr). İdentified the relations of the reacting components in homogeneous composition of Cu-R (1: 2) and mixed ligand Cu-R-CPCl (1: 2: 2), Cu-R-CPBr (1: 2: 2) and Cu-R-CTMABr (1 2: 1) complexes, which concentration interval subordinated to Beer's law. The influence of external ions and masking substances on complex formation was studied. Method for the photometric determination of copper in the rocks was established.

Keywords

Synthesis, complex formation, CPCl, CPBr, CTMABr, stability constant.

Academic Discipline And Sub-Disciplines

Chemistry and analytical chemistry

SUBJECT CLASSİFİCATİON

Analytical chemistry; Inorganic Chemistry; Organic Chemistry; General chemistry

TYPE (METHOD/APPROACH)

Types of research: experiments; Approach: quantitative research

1. İntroduction

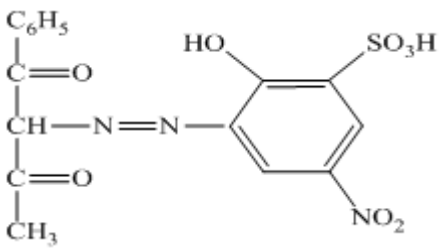
Azo compounds are important, well-known and commonly used compounds in textile, paper industries and as dying agent in food and cosmetic industries. Azo compounds possess important analytic features, by providing a strong chromophore label-the quantity of which is determined by a colorimetric, spectrophotometric or spectrofluorometric methods. Additionally, azo compounds as have been reported show various biological activities, including antibacterial, antifungal, pesticides, antiviral and anti-inflammatory activities [1-5].

It is known from literature that, azo derivatives of benzoylacetone are widely used in photometric determination of elements [6-8]. Therefore, the study of analytical capabilities of azo derivative of benzoylacetone-1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] butadiene-1,3 (PHSNPAB) and application for photometric define of copper in itself represents analytical interests.

The purpose of the following work is the development of photometric determination method for identifying copper (II) with PHSNPAB in the presence and in the absence of the third component.

2. Experimental part

PHSNPAB synthesized as a result of azocoupling reaction of diazotized 2-amino-4-nitro-6-sulphophenol-1 with benzoylacetone in a weakly alkaline medium [9], and its composition and structure were established by IR and NMR-spectroscopy.



Obtained reagent is water-soluble. İn work used $1 \cdot 10^{-3}$ M water solution of PHSNPAB, $1 \cdot 10^{-3}$ M water solution of CPCl, CPBr, CTMABr and $1 \cdot 10^{-3}$ M solution of copper (II) which were prepared from metallic copper (99,9%) on the base of methodology [10].

İn order to create the necessary pH, used fixanal HCl (pH 1-2) and ammonium acetate buffer solution (pH 3-11). The pH of the solution was monitored by using an ionomer PHS-25 with a glass electrode. Absorbance of solutions was measured on a spectrophotometer Lambda 40 (Perkin Elmer) and CPK-2 photocolorimeter in a cuvette with 1 cm layer thickness.

3. RESULTS AND İTS DİSCUSSİON

The investigated complex compounds are formed immediately after mixing solutions. The ratio of the reactants in the complexes was found by method of isomolar series, the relative yield of Starika-Barbanel, equilibrium shift [11]. All methods showed that the ratio of Cu (II) -R in binary complexes is 1: 2, and in mixed-ligand complexes Cu (II)-R-CPCl = 1: 2: 2, Cu (II) -R-CPBr = 1 : 2: 2, Cu(II)-R-CTMABr = 1: 2: 1. The molar absorption coefficients of complexes were calculated from the saturation curves [11]. Established concentration ranges where Beer's law is observed (Table 1).

Table1. Main photometric characteristics of copper (II) complexes

Complexe	pH	λ_{max} nm	εx10^4	lg β	Ratio of components	linearity interval grad.graf mcg / ml
CuR	3	444	1,40	6,04±0,12	1:1	0,25-3,07
CuR-CPCl	2	456	2,3	11,24±0,12	1:2:2	0,12-2,56
CuR- CPBr	2	454	2,2	10,82±0,10	1:2:2	0,12-2,56
CuR-CTMABr	2	461	2,5	12,04±0,09	1:2:1	0,12-2,56

3.1. Absorption spectra.

The study of complex formation depending on the acidity of the medium, showed that the maximum output of the complex CuR observed at pH 3 (λ_{max} = 444nm), respectively. However, reagent in itself has a maximum absorbance at pH 2 (λ_{max} = 461 nm) (Figure 2).

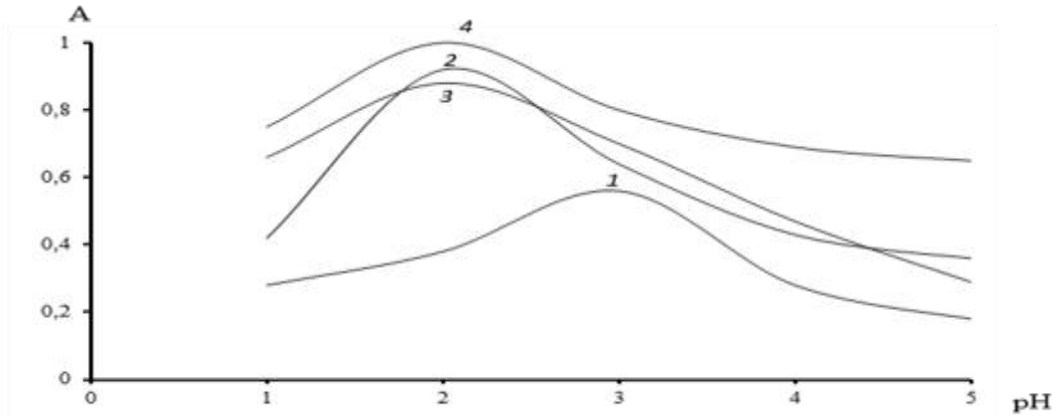


Fig.1. The dependence of the optical density of solutions of copper(II) complex from pH in the presence and absence of surfactants at λ_{opt} on the background of control experiment.
***1* – CuR; 2 – CuR-CPCl; *3* – CuR-CPBr; *4* - CuR-CTMABr.**

Note: [$C_{Cu} = 1 \cdot 10^{-3}$ M; $C_R = 1 \cdot 10^{-3}$ M ; $C_X = 1 \cdot 10^{-3}$ M. (X= CPCl, CPBr and CTMABr)

Figure 2 shows the absorption spectrum of the reagent.

ISSN 2321-807X
Volume 12 Number11
Journal of Advances in Chemistry

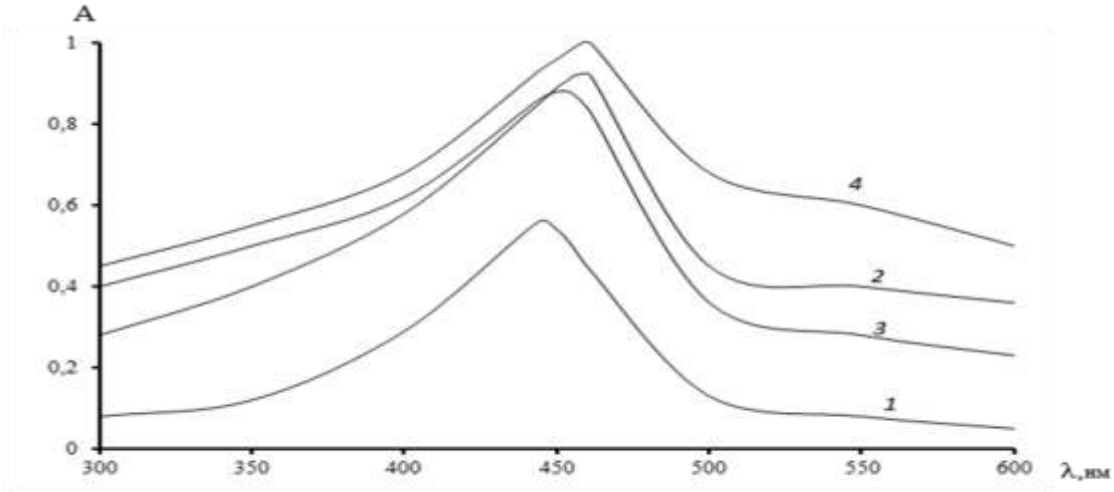


Fig.2.The absorption spectra of solutions of complexes with copper(II).
***1*-CuR; *2*-CuR-CPCl; *3*-CuR- CPBr; *4*-CuR – CTMABr.**

İn the presence of the third component-cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr) optimum pH complex formation shifted to pH = 2 (CuR-CPCl), pH = 2 (CuR-CPBr) and pH= 2 (CuR-CTMABr). The absorption maximum of complexes (Figure 2.) is equal to: λ = 444nm (CuR), λ = 456nm (CuR-CPCl), λ = 454nm (CuR-CPBr), λ = 461nm (CuR-CTMABr) respectively. It is found that in the presence of the third component-cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr) ternary complexes are formed, which are observed to form a bathochromic shift in compare with the spectrum of the binary complex and the optimum pH in complex formation shifted to more acidic environment pH = 2 (CuR-CPCl), pH = 2 (CuR-CPBr) and pH = 2 (CuR-CTMABr).

The effect of external ions and masking substances on the photometric determination of copper (II) in the form of binary and mixed-ligand complexes was studied. Relative selectivity of systems is shown in Table. 2.

Table 2. Acceptable ratios of external substances to the copper (II) when it is defined as the homo- CuR and mixed-ligand CuR -CPCl; CuR -CPBr and CuR -CTMABr complexes (5% error).

İon or substance	**R**	**R-CPCl**	**R-CPBr**	**R-CTMABr**	**N,N-Di-(2-carboxy-ethyl) -3,4-xylidine [13]**
Na	*	*	*	*	1000
K	*	*	*	*	1000
Ca	*	*	*	*	250
Zn	*	*	*	*	1000
Cd	*	*	*	*	200
Mn	*	*	*	*	1000
Ni	46	118	115	115	500
Co	277	364	340	345	500
Al	*	*	*	*	750
Sm	*	*	*	*	1
Fe(III)	9	60	55	55	
Ga(III)	547	647	610	600	0,01
In(III)	539	645	620	620	
Bi(III)	33	124	110	110	
Sn(IV)	186	280	255	250	
Hf(IV)	351	460	430	415	

Ti(IV)	375	520	490	495	
Zr(IV)	711	830	795	805	
Mo(VI)	150	244	220	220	
W(VI)	287	415	380	380	
$C_2O_4^{2-}$	104	190	160	170	
EDTA	10	57	54	55	
Thiourea	59	113	104	100	
Lemon acid	985	1170	1160	1055	
$Na_2HPO_4 \cdot 12H_2O$	703	790	760	770	
Wineacid	279	350	345	340	
F^-	281	355	350	350	

Study of the effect of external ions and masking agents for photometric determination of copper (II) in the form of binary complexes and mixed-ligand showed that in the presence of cetylpyridinium chloride, cetylpyridinium bromide, and cetyltrimethylammonium bromide the selectivity of the reaction increases. The data on selectivity make it possible to apply the developed methodology for the photometric determination of copper (II) in the form of mixed-ligand complexes for the determination of trace amounts of its facilities in the complex.

3.2. The effect of pH and concentration of reactant.

The study of complex formation depending on pH (1-8) showed that the yield of binary Cu-R complex is maximal at pH = 3. In the presence of a third component - CPCl, CPBr and CTMABr form intensely colored ternary compound CuR - CPCl, CuR – CPBr and CuR – CTMABr, that have the maximum yield at pH = 2. The influence of reactants concentrations on the complex formation was studied. It was established that the yield of the complex Cu-R was maximum at $8 \cdot 10^{-5}$ M R, Cu(II)-R-CPCl $8 \cdot 10^{-5}$ M (R) and$4 \cdot 10^{-5}$ M(CPCl), Cu(II)-R- CPBr $8 \cdot 10^{-5}$ M (R) and $4{,}8 \cdot 10^{-5}$ M (CPBr), Cu(II)-R- CTMABr $8 \cdot 10^{-5}$ M (R) and $3{,}2 \cdot 10^{-5}$ M (CTMABr).

3.3. The calibration graph.

Prepared a series of solutions containing 0,25-3,07mcg / ml (homo-ligand), 0,12-2,56 mcg / ml (mixed-ligand) Cu (II) complexes and their absorption measured at λ_{opt}=490 nm relative to a control experiment solution. Established concentration ranges where Beer's law is observed and the molar absorption coefficients of the complexes from saturation curves (11) (Tabl 1). From Table 1 it is clear that using our proposed mixed-ligand complexes, it is possible to determine very small microgram amounts of copper.

3.4. Calculation of the stability constants of complexes.

Calculated stability constants one and mixed-ligand complexes of copper (II). İn order to calculate the complex stability constants used method of intersection of curves [12].
The concentration of the complex was calculated from the expression

$$C_K = C_{Cu}\left(\frac{\Delta A_x}{\Delta A_i}\right)$$

$$\beta_n = \frac{C_K}{(C_{Cu} - C_K)(C_R - nC_K)^n}$$

Where, A_X and A_0 optical densities of solutions of complex at current value of C_R and at saturation respectively. Then, according to the equation

$$C_K = C_{CuR}\left(\frac{\Delta A_x}{\Delta A_i}\right)$$

$$\beta_n = \frac{C_K}{(C_{CuR} - C_K)(C_x - nC_K)^n}$$

At the molar ratio of the components Cu:R=1:2; Cu:R:CPCl=1:2:2; Cu:R:CPBr=1:2:2; Cu:R :CTMABr =1:2:1; calculated stability constant (x= CPCl; CPBr; CTMABr). According to calculations lgβ(Cu(II)R)=6,04±0,12; lgβ(Cu(II)RCPCl)=11,24±0,12; lgβ(Cu(II)R CPBr)=10,82±0,10; lgβ (Cu(II)RCTMABr)=12,04±0,09.

3.5. Determination of copper(II) in the rocks.

For the analysis, was taken three different mountain-pyrite rock samples containing altered quartz diorite. The content of copper (II) in the samples was determined by the photometric and atomic absorption methods (Table. 3).

3.6. The progress of analysis.

5g of sample in a glassy carbon plate is dissolved in a mixture of 10 ml of 9 mL HF + HCl + 3 ml HNO_3. The resulting paste is treated with 5-6 ml of HNO_3 at 50-60° C till the complete distillation of HF. The resulting precipitate was dissolved in water, filtered to the flask 50 ml and diluted to the mark with water. By determining the copper (II) with photometric method aliquot part of the resulting solution is placed in 25 ml flask, added 2 ml of 1×10^{-3} M R solution, 1 mL 1×10^{-3} CTMABr solution and diluted with a solution till the mark pH 2. The absorption of the solutions was measured at 490 nm in a cuvette with l = 1 cm KFK- 2 with respect to the blank test solution. The results of analysis are shown in Table 3.

Table 3. The results of determination of copper in the rocks (%) (n = 5, P = 0.95)

Samples	By photometric method found , %	By atomic - absorption method found %
1	0,61±0,10	0,600±0,006
2	0,93±0,13	0,937±0,003
3	4,15±0,12	4,17±0,004

CONCLUSİON

It has been studied a complexs formation of Cu(II) with 1-phenyl-2- [2-hydroxy-3-sulfo-5-nitrophenylazo] -1,3 butadiene in the presence sulface-active substances by spectrophotometric method. Molar light absorption coefficients of complexes CuR, CuR – CPCl, CuR - CPBr and CuR - CTMABr equal 1400, 2300, 2200 and 2500. It was determined the stabilitiy constant of complexes. lgβ(Cu(II)R)=6,04±0,12; lgβ(Cu(II)-CPCl)=11,24±0,12; lgβ(Cu(II)R-CPBr)=10,82±0,10; lgβ(Cu(II)R-CTMABr)=12,04±0,09. Ber′s law is obeyed observes in region 0,25-3,07 mcg/ml for CuR, 0,12-2,56 mcg/ml for CuR – SPCl, CuR - CPBr and CuR - CTMABr. The fotometric determination of copper (II) has been developed on the mountain rock.

REFERENCES

1. *Pathak P., Jolly V.S. & Sharma K.P.* Synthesis and biological activities of some new substituted arylazo Schiff bases.//Orient.J.Chem., 16, 2000, 161-162.
2. *Xu H.& Zeng X.* Synthesis of diaryl-azo derivatives as potential antifungal agents. //Bioorg. Med. Chem. Lett., 20, 2000, 4193-4195.
3. *Samadhiya S.& Halve A.* Synthetic utility of Schiff bases as potential herbicidal agents. //Orient. J.Chem., 17, 2001, 119-122.
4. *Tonelli M.,Vazzana I.,Tasso B.,Boido V., Sparatore F., Fermeglia M.,Paneni M.S., Posocco P.,Pricl S., Colla P., Ibba C., Secci B., Collu G. & Loddo R.* Antiviral and cytotoxic activities of aminoarylazo compounds and aryltriazene derivatives. //Bioorg. Med. Chem., 17, 2009, 4425-4440.
5. *Rani P.,Srivastava V.K.& Kumar A.* Synthesis and anti-inflammatory activity of heterocylic indole derivatives. //Eur. J. Med. Chem., 39, 2004, 449-452.
6. Aliyeva R.A, Basargin N.N, Sulhnedzhad R.G, Chiragov F.M and others. Novaya metodika opredeleniya medi v vulkanoqennoy porode i splava.(A new method for determination of copper in the volcanic rock and fusion).// Journal of Analytical chemistry. 2011., № 9. T. 66, p. 871-875.
7. *Espandi F, Aliyeva R.A, Alieva F.S, Chiragov F.M, İzucenie kompleksobrazovaniya jeleza (III) s 3-(2- qidroksi 3-sulfo-nitrofenilazo)-pentan -2,4-diona v prisutstvii diantipiril metana i eqo qomoloqov. (Study of chelation of iron (III) with 3-(2-hydroxy-3-sulfo nitrophenylazo) -pentane-2,4-dione presence of diantipiril methane and its homologues). // Herald BU.Estestvennye science.* 2012. №3.p 30-37.
8. Hajiyev S.R, Chiragov F.M, Mahmudov K.T. Kompleksobrazvanie medi (II) s azoproizvodnim benzoilasetona. (Complexing of copper (II) with azoderivatives benzoilasetona.). // Journal of Analytical Chemistry, 2007. T. 62. №11. p.1-4
9. Dedkov Y.M. Metodi poluceniya ximiceskix reaktivov i preparatov (Methods for producing chemicals and drugs) M.IREA 1970. в. 22.56p
10. Korostelev P.P. *Priqotovlenie rastvorov dlya ximiko – analiticeskix rabot*. (Preparation of solutions for chemical analysis). M:. Chemistry, 964. 386p.
11. Bulatov M.I., Kalinkin I.P. *Prakticeskoe rukovodstvo po fotometriceskim i spektofotometriceskim metodam analiza.*.(A practical guide to photometric and spectrophotometric methods). analiza.L:. Chemistry,1972. 407 p.
12. Shevchenko F.D // Ukr. Chem.journal. 1965. T. 31., №1, P. 229
13. Neudachina L.K ., Osintseva E.V., Skorik Y.A., Vshivkova A.A .// Journal. Analit.chemistry. 2005. T. 60. № 3. P. 271.

Aliyeva Rafiqa Alirza qizi – professor of sub department “Analytical chemistry”, doctor of chemical sciences, member of Academy of sciences, Academic. İn 1956 she graduated the chemical department of BSU, in 1970 she defended PhD. Dissertation on thesis «Spectrophotometric investigation of compounds of germanium with some organic reagents and determination of it by photometric method», in 1999 she defended doctor dissertation on thesis «Different ligand complexes d-, f-elements and germanium with N-, S- and O- contained ligands and application of these complexes». From 2001 she lead scientific-research laboratory «Ecological chemistry and protect of environment». She is assistant of head of council under Dissertation dependences of BSU on specialties 02.00.02, 02.00.03., 02.00.04., and also she is member of scientific Council of BSU and chemical department.

Chiragov Famil Musa oglu in 1984 year he graduated chemical department, BSU. 1987- Ph.D1 on thesis ‘Synthesis, properties and structure of complexes of Mn(II), Co(II) and Ni(II) with paraderivatives of benzoic acid“. 1999- Ph.D2 on thesis “complex compounds with azoderivatives of β-diketonos: synthesis, structure, properties and analytical application». Since 2004 year Dr. Chiragov is professor of sub department “Analytical chemistry”. Since 2006 he is the Head of sub deportment “Analytical chemistry”. He is a member of expert commission of chemical department, of Scientific Council, and also the member of Dissertation Council on specialties D.02.001, 02.00.02, 02.00.03., 02.00.04.

Ayvazova A. V - graduate student of faculty of analytical chemistry, Baku State University. Research interests: analytical chemistry.

Lahicova S. R - teacher, Kazakh branch of BSU. Research interests: analytical chemistry.