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SPECTROPHOTOMETRIC AND PAPER ELECTROPHORETIC STUDIES OF THE COPPER (II) POLYOXOTUNGSTOBISMUTHATE COMPLEXES

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ABSTRACT. The starting point of this study is represented by the trilacunar structure of the polyoxotungstate anion $[BiW_9O_{33}]^{9-}$ having the capacity of functioning as the coordinating ligand for the cupper Cu^{2+} cation, and the formation of the complex polyoxotungstate anions of the type $[Cu_3(BiW_9O_{33})_2]^{12-}$.and $[Cu_4(BiW_9O_{33})_2]^{10-}$. The pH range of the complexes' formation was established and the stability constants were calculated by the electrophoresis method. By applying the molar ratio method to spectrophotometry, the molar ratio of polyoxometalate ligands and Cu^{2+} cations have been found to have the values of 2:3 and 2:4, respectively.

INTRODUCTION

The lacunar polyoxometalates generally react readily with any potential addenda or with a wide variety of octahedrally coordinating metal ions to refill the vacant sites. This produces complexes that are hybrids between polyoxometalate species and coordination complexes.[1] We reported a lot of works to polyoxometalate complexes containing metallic cations, especially those wherein that atoms act as a bridge connecting two lacunar units.[2-9]

This paper presents the results of our work on the formation in solution of Cu^{2+} polyoxometalates with $BiW_9O_{33}^{9-}$ as ligand by the paper electrophoresis method, which permits the identification of the formed polyoxometalates in very limited pH ranges, thus enabling them to separate in the electric field due to the various electrophoretic mobilities of the existing ionic species.[10]

One of the widely used methods in establishing the stoichiometry of the formation reactions of the complex combinations is the method of the molar ratio variation applied to the spectrophotometric study.[11,12] This method has also

been applied to the systems Cu^{2+}-$BiW_9O_{33}^{9-}$ in order to establish the values of the combination ratio between Cu^{2+} ion and the polyoxometalate ligand.

EXPERIMENTAL PART

1. Solution Preparation

The experiments were carried out on a $Na_9BiW_9O_{33}$ polyoxometalate in aqueous medium; the polyoxometalate was prepared according to Krebs [13] at the concentration of 10^{-2} - $5x10^{-2}$ mole·l^{-1} in the ligand and at pH values ranging from 1.5 to 8.5. The aqueous solutions of $Cu(SO_4)_2$ were obtained out of the $Cu(SO_4)_2 \cdot 5H_2O$ in distilled water.

2. Spectrophotometric study

A set of solutions was prepared, containing Cu^{2+} and $BiW_9O_{33}^{9-}$, and having a 10^{-2} mole·l^{-1} concentration in various molar ratios. The pHs of the solutions were adjusted to the values of 6.5 and 4 with NaOH 10^{-1} mole·l^{-1} and HCl 10^{-1} mole·l^{-1}, respectively, with the purpose of being within the optimal pH of the formation of Cu^{2+} polyoxometalates.

The absorbances of these solutions were measured with a SPECORD UV-Vis spectrophotometer, using 1 cm wide glassy cuvettes at a vawelength of 824.13 nm and 780 nm, respectively.

3. Electrophoretic Study.

This study was carried out on an ordinary electrophoresis apparatus, at usual voltage, cooled with water. The $Cu(SO_4)_2$ solution, of 10^{-4} mole·l^{-1} concentration was deposited with a microdropper in the center of a Karl-Schneider Schull chromatographic paper impregnated in the ligand solutions having 10^{-4} - 10^{-2} mole·l^{-1} concentration, with different pH values (1.5 to 8.5). The pHs were adjusted with HCl and NaOH solutions and their values were measured with a OK-102 Radelkis pH-meter. The ionic strength was maintained at constant value by a corresponding addition of $NaClO_4$ 10^{-1} mole·l^{-1}.

Experiments were performed at a difference in voltage of 360 V, at a temperature of 15±2 ^{0}C, for 3600 s. The formed polyoxometalates were identified by their green color, the Cu^{2+} ion was identified by developing with rubeanic acid and the noncomplexed ligand by reducing W^{6+} with UV rays to “blue tungsten”.

Besides the solutions containing the metallic cation, an electrically neutral glucose drop was added, towards which the shifts of the ionic species after electromigration were adjusted. The R_f values of the formed polyoxometalates were determined by the ascending paper chromatography, relating the shift of the formed chemical species to the front of the saturated NaCl as eluent.

RESULTS AND DISCUSSION

If a solution that contains Cu^{2+} ions is rapidly added to a solution of sodium salt of $[BiW_9O_{33}]^{9-}$ polyoxometalate anions, the following reactions take place, according to the following chemical equations:

$$2\ Na_9[BiW_9O_{33}] + 3\ CuSO_4 = Na_{12}[Cu_3(BiW_9O_{33})_2] + 3\ Na_2SO_4 \quad (a)$$

$Na_{12}[Cu_3(BiW_9O_{33})_2] + CuSO_4 = Na_{10}[Cu_4(BiW_9O_{33})_2] + Na_2SO_4$ (b)

We observe that the green colour of the obtained solutions appears immediately. The colour intensity doesn't change, even on standing 24 hours.

The spectrophotometric study concerned with the formation of the polyoxometalate complexes having Cu^{2+} as central ion has been carried out by the molar ratios method.

By representing graphically the absorbances of the solutions that contain the two compounds, the copper sulfate and the sodium salt of the polyoxometalate ligand, versus different molar ratios combination, we obtain three straight lines which cross each other in two points which correspond to the molar ratio of 3:2 and 4:2 respectively (Fig.1).

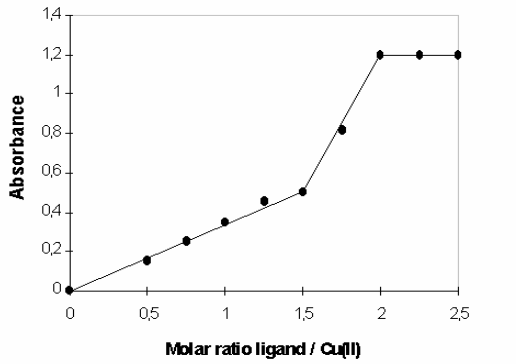

Fig. 1. Dependence of the absorbance versus various molar ratios of components: Cu^{2+}-$BiW_9O_{33}^{9-}$.

According to the reaction stoichiometry, the molar ratios Cu^{2+}:ligand=3:2 and 4:2 respectively, the values of the equivalence points that were calculed theoretically concord with the values obtained experimentally.

In order to established the pH-range of the $[Cu_3(BiW_9O_{33})_2]^{12-}$ and $[Cu_4(BiW_9O_{33})_2]^{10-}$ heteropolyanion formation, we started from the premise that the reactions (a) and (b) of the polyoxoanion species' formations may be considered as reactions with formation of complex combinations according with the following equations:

$3\ Cu^{2+} + 2\ L = Cu_3L_2$ (a`)

$Cu_3L_2 + Cu^{2+} = Cu_4L_2$ (b`)

In order to establish the optimal conditions of the formation of Cu_3L_2 and Cu_4L_2 polyoxometalates, where $L=BiW_9O_{33}^{9-}$, a study has been accomplished on their formation by the chemical reactions (a`) and (b`) in solutions of 10^{-2} mole.l^{-1} concentrations, using the electrophoresis method.

Thus, considering that the studied reactions occur according to the equations (a`) and (b`) they have the following equilibrium constants:

$$K_1 = \frac{[Cu_3L_2]}{[Cu^{2+}]^3 \cdot [L]^2} \quad (1)$$

$$K_2 = \frac{[Cu_4L_2]}{[Cu_3L_2]\cdot[Cu^{2+}]} \qquad (1')$$

The Kunkel and Tiselius [14] method has been applied to estimate the sum of the electrophoretic mobilities of the formed ions which is given by the relations:

$$M_1 = \frac{\mu_{Cu^{2+}}\cdot[Cu^{2+}] + \mu_{Cu_3L_2}\cdot[Cu_3L_2]}{[Cu^{2+}] + [Cu_3L_2]} \qquad (2)$$

$$M_2 = \frac{\mu_{Cu_3L_2}\cdot[Cu_3L_2] + \mu_{Cu_4L_2}\cdot[Cu_4L_2]}{[Cu_3L_2] + [Cu_4L_2]} \qquad (2`)$$

where: M_1, M_2=the sum of the electrophoretic mobilities;

L= $Na_9[BiW_9O_{33}]$;

$\mu_{Cu^{2+}}$, $\mu_{Cu_3L_2}$, $\mu_{Cu_4L_2}$ = the electrophoretic mobilities of Cu^{2+}, Cu_3L_2 and Cu_4L_2 ions;

$[Cu^{2+}]$, $[Cu_3L_2]$, $[Cu_4L_2]$= the mole concentrations of the Cu^{2+}, $[Cu_3L_2]$ and $[Cu_4L_2]$ ionic species.

The sum of the electrophoretic mobilities of the formed ions, which are pH-dependent, was graphically represented in order to obtain the stability range and the optimal pH of the formation of the polyoxometalates. As a result of the electrophoretic study on the formation reactions of the polyoxometalates, values ranging from to 3.5 to 5.5 for the first complex, and from to 5.5 to 7 for the second were found. Subsequently, the values of the stability constants were calculated according to the above-mentioned method in a two step chemical reaction, as follows: 3.615 and 1.879 for $Na_{12}[Cu_3(BiW_9O_{33})_2]$ and $Na_{10}[Cu_4(BiW_9O_{33})_2]$ respectively; the values of the equilibrium constants being of $0.97x10^2$ and $0.5x10^2$ respectively.

The electrophoretic study on the $Na_{12}[Cu_3(BiW_9O_{33})_2]$ and $Na_{10}[Cu_4(BiW_9O_{33})_2]$ polyoxometalates informs us about the optimum pH of formation, 4.5 and 6.25 for these compounds, about the relative stability of these compounds as well as about their purity. These compounds are unitary and not mixtures of polyoxometalates.

The displacement in centimeters of the formed polyoxometalates was observed experimentally, thus allowing the calculation of the electrophoretic mobilities (μ), the determination of the R_f values and the calculation of the real μ_d mobilities of the formed species by means of the Kunkel-Tiselius [14] relation (3):

$$\mu_d = d\cdot\frac{1}{V\cdot t\cdot R_f}\cdot\left(\frac{l'}{l}\right)^2 \qquad (3)$$

where: μ_d= the sum of the experimentally determined electrophoretic mobilities;

d= the migration of the ionic species in cm;

V= the difference of potential;

t= the time of electromigration;

l= the length of the chromatographic paper (38,5 cm);

$\frac{l'}{l}$ = 1.69; the porosity factor of the chromatographic paper ;

R_f = 0.99 for $Na_{12}[Cu_3(BiW_9O_{33})_2]$ and 0.98 for $Na_{10}[Cu_4(BiW_9O_{33})_2]$

The variation of the sum of the electrophoretic mobilities depending on the pH is plotted in Fig. 2.

It may be observed that $\mu = \mu_{Cu^{2+}}$ for the minimal μ value in case the formation of the polyoxometalate Cu_3L_2 has not proceeded yet, and $[Cu_3L_2]=0$, while $\mu = \mu_{Cu_3L_2}$ for the maximal μ value in case Cu^{2+} is partialy consumed in reaction (a`); it also be comes obvious that $\mu = \mu_{Cu_3L_2}$ for the minimal μ value in case the formation of the polyoxometalate $Cu_4L_2$ has not proceeded yet and $[Cu_4L_2]=0$, while $\mu = \mu_{Cu_3L_2}$, for the maximal μ value in case $Cu^{2+}$ is completely consumed in reaction (b`), μ being equal to $\mu_{Cu_4L_2}$.

The optimal formation ranges of the complexes were determined from the electrophoretic curves and correspond to the pH range within which the sum of the electrophoretic mobilities is: $\mu_{formation} \geq 90\%$. The optimal pH formation ranges of the formed polyoxometalates given by the $\mu_{90\%}$ values are 3.5 - 5.5 for Cu_3L_2 and 5.5 - 7 for Cu_4L_2, respectively. The values $\mu_{Cu^{2+}}$, $\mu_{Cu_3L_2}$, and $\mu_{Cu_4L_2}$ were obtained from the curves presented in Fig.2. By introducing them into relations (4) and (4'), the equilibrium constants K_1 and K_2 were determined.

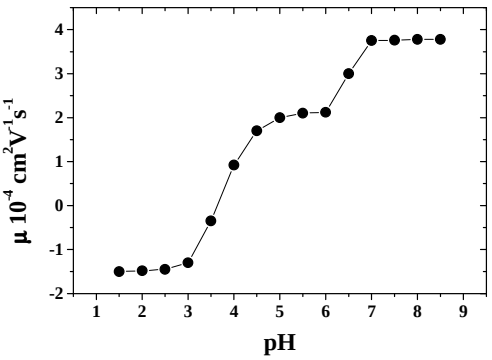

Fig.2. Dependence of μ_d electrophoretic mobilities versus pH values for the systems Cu^{2+}-$[BiW_9O_{33}]^{9-}$.

In order to study the formation (equilibrium) constants of the complexes, the Consden, Gordon and Martin equation is applied to the studied systems: [15]

$$\log \frac{M_1 - \mu_{Cu^{2+}}}{\mu_{Cu_3L_2} - M_1} = \log K_1 + \log C \qquad (4)$$

$$\log \frac{M_2 - \mu_{Cu_3L_2}}{\mu_{Cu_4L_2} - M_2} = \log K_2 + \log C \qquad (4`)$$

where: C= the concentration of the ligand solution;

K_1, K_2= the equilibrium constants.

The equilibrium constants will further be used in the determination of the β stability constants, according to relation (5).

$$\log \beta = \log K + \log c \qquad (5)$$

where: β= the stability constant;

K= the equilibrium constant;

c= the optimal concentration of the ligand solution.

Furthermore, a graphic representation of $\log [M_1 - \mu_{Cu^{2+}}/\mu_{Cu_3L_2} - M_1]$ and $\log [M_2 - \mu_{Cu_3L_2}/\mu_{Cu_4L_2} - M_2]$, respectively vs. the various ligand concentrations (Fig. 3 and 4) is presented. By extrapolating the straights presented in Fig. 3 and 4, we obtained the optimal ligand concentration which is later on introduced into relation (5) in the purpose of determining the stability constants.

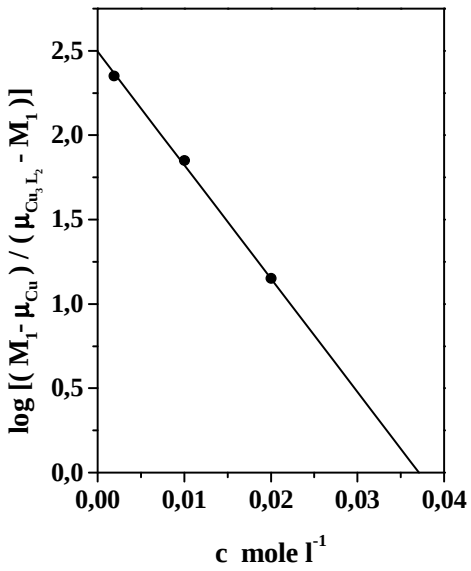

Fig. 3. Dependence of $\log M_1 - \mu_{Cu^{2+}}/\mu_{Cu_3L_2} - M_1$ vs. various ligand concentrations.

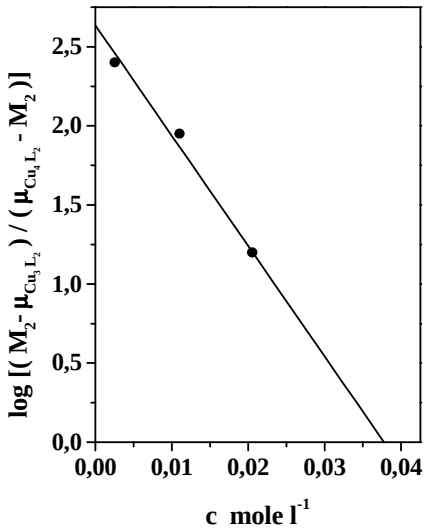

Fig. 4. Dependence of log $M_2 - \mu_{Cu_3L_2}/\mu_{Cu_4L_2} - M_2$ vs. various ligand concentrations.

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CONCLUSIONS

The spectrophotometric study and the method of molar ratios variation has established the formation, in both cases, of the complexes with the molar ratio Cu^{2+}:polyoxometalate ligands of 3:2 and 4:2 respectively.

As a result of the electrophoretic study on the Cu^{2+}-$[BiW_9O_{33}]^{9-}$ system by the paper electrophoresis method there is clear-cut evidence of the formation, in the two steps, of a single pure complex polyoxometalate species.

The formation pH range of the Cu_3L_2 and Cu_4L_2 complexes are to be found between 3.5-5.5 and 5.5-7 respectively. The optimal pH values are 4.5 and 6.25 for Cu_3L_2 and Cu_4L_2 respectively.

The similar values of the stability constants point out to the formation of some stable polyoxometalate complexes.

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