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Spectrophotometric and conductometric investigation of 5,5$^{/}$-(2E,2$^{/}$E)-2,2$^{/}$-(ethane-1,2-diylidene)bis (hydrazine-1-yl-2-ylidene) bis (4-amino-4H-1,2,4-triazole-3-thiol) (HYT) macrocyclic ligand with Cu^{2+} cation

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ABSTRACT

The complexation reaction of macrocyclic ligand, 5,5$^{/}$-(2E,2$^{/}$E)-2,2$^{/}$-(ethane-1,2-diylidene) bis (hydrazine-1-yl-2-ylidene)bis (4-amino-4H-1,2,4-triazole-3-thiol) (HYT)[1-8] with Cu^{2+} cation was studied in some binary mixtures of methanol (MeOH), propanol (PrOH) and dimethylformamide (DMF) at different temperatures using the conductometric method[9-14]. In additions the interaction of (HYT) with Cu^{2+} cation in non-aqueous solvent was studied by spectroscopic method. The stability constants of the complex was determined using a GENPLOT computer program[15]. The conductance data and Absorbance–mole ratio plots show that in all solvent systems, the stochiometric of the complex formed between (HYT) and Cu^{2+} cation is 1:1 (ML). The obtained results show that the stability of (HYT)-Cu complex is sensitive to the mixed solvents composition. The values of thermodynamic parameters (ΔGÏ, ΔHÏ and ΔSÏ) for formation of (HYT)-Cu complex were obtained from temperature dependence of the stability constant using the Van't Hoff plots. The results show that in most cases the complex are enthalpy destabilized but entropy stabilized and the complex formation is affected by the pH, time, temperature and nature of solvent.

KEYWORDS

Macrocyclic ligand;
Cu^{2+} cation;
Spectrophotometric;
Conductometric.

INTRODUCTION

In this study, we investigated the effect of the nature of the cation and the solvent properties on the stability, selectivity, and thermodynamic parameters of (HYT) complex with Cu^{2+} metal cation in some binary mixtures of methanol (MeOH), propanol (PrOH), and dimethylformamide (DMF) at different temperatures using the conductometric method. The process of complex formation depends on the cavity size of (HYT), cation size, and the salvation capability of solvent system[16-19]. In order to achieve appropriate solvent properties, we often use mixtures of two or more solvents (mixed solvents). Although mixtures of water and organic solvents are most frequently used, mixtures of two organic solvents are also used in many applications, such as electrochemistry, separations, and organic synthesis. A variety of physicochemical techniques, such as calorimetry, polarography, potentiometry, NMR spectrometry, UV spectrophotometry and conductometry, have been used to study the complex formation between various ligand and metal ions in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

In the present paper, we report the results which are obtained in conductometric and spectrophotometric study of complexation Cu^{2+} cation by (HYT) in some binary mixtures of methanol (MeOH), propanol (PrOH) and dimethylformamide (DMF) at different temperatures using the conductometric method and the complex formation, effect of pH, time and temperature in pure DMF using the spectroscopic method.

MATERIALS AND METHODS

Materials

Cu $(NO_3)_2$ (Merck) was used without further purification. The solvents: methanol (MeOH), propanol (PrOH) and dimethylformamide (DMF) all from Merck were used with the highest purity.

Conductometric method

The experimental procedure to obtain the formation constants of complex was as follows: a solution of metal salt (5×10^{-5} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase of the (HYT) solution prepared in the same solvent (5×10^{-4} M) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed on a digital Metrohm conductivity apparatus, model 712, in a water bath thermostated at a constant temperature which maintained within ±0.1ÚC. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 1.06 cm^{-1} was used throughout the studies.

The variations of molar conductance versus the ligand to the cation molar ratio for complexation of (HYT) and Cu^{2+} cation in some binary mixtures of methanol (MeOH), propanol (PrOH) and dimethylformamide (DMF) at different temperatures were studied and is shown in [Figure 2]. The value of log k_f calculated from the (HYT)-Cu complex calculated from the conductivity measurements in non-aqueous solvent at different temperatures[19]. the value of thermodynamic parameters (ΔHÏ,ΔSÏ) for formations of (HYT)-Cu complex was obtained from temperature depended of stability constant.

Spectrophotometric method

All spectrophotometric measurements were performed on a Cary 50 Bio spectrophotometer equipped with Cary Win UV software and using a 1 cm quartz cell. The pH was checked by Metrohm 780. All measurements were carried out at room temperature.

In this method to obtain the maximum absorbance of complex, the stock solutions of ligand (0.005 M) and Cu^{2+} cation with (0.001M) concentration was prepared. At least, 10 times fold of ligand were added to cation. Then complex solution was placed at room temperature for 2 hours so that complex formation reaction can be completed. Complex absorbance spectra were taken and the maximum absorbance of complex came from by spectrophotometer set at 430 nm, The maximum absorbance is shown in [Figuru 1].

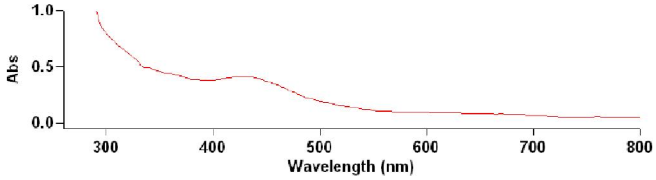

Figure 1 : The calculated absorption spectra of (HYT)-Cu complex

To draw calibration curve, standard solution with equal concentration from Cu^{2+} cations and different concentration from ligand (HYT) was prepared. After dissolving it in 5 ml methanol, it was evened by sonication, and then was transported to a 25 ml flask after filtering by whatman. As much as 1 ml from HCl was added to the whole solution to get optimum pH equal 8. After wards, they were diluted by deionized water. If HCl increases, the rate of absorption will go up. After adjusting pH, the rate of absorption at λ_{max}=430 nm for (HYT)-Cu was measured. Absorption variation is drawn on the basis of concentration one.

RESULTS AND DISCUSION

Conductometric method

It is shown that molar conductivity in methanol system increases with the molar ratio increase of the ligand to cation. The slope of molar conductance mole ratio curves change at the point (=1) which indicates the formation of complex 1:1 (ligand: cation). [Figure 2].

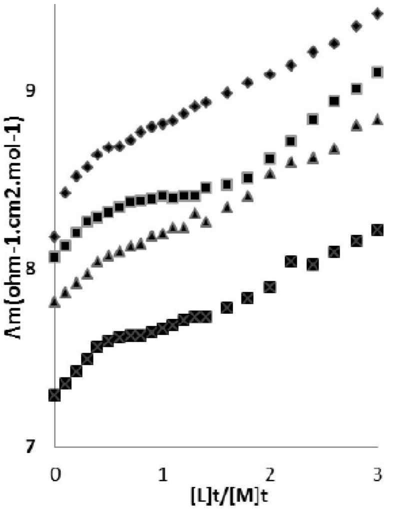

Figure 2 : Molar conductance–mole ratio plots for (HYT)-Cu complex in PrOH–DMF, (mol% PrOH =25) at different temperatures

The investigations of the curves show that raising (HYT) concentration will cause the increase of molar conductivity so the alterative slope will depend on solvent. The relevant curve slope can be a criterion of stable complex qualitatively.

The value of log K_f calculated form the (HYT)-Cu complex calculated conductivity measurements in some binary mixtures of methanol (MeOH), propanol (PrOH), and dimethylformamide (DMF) at different temperatures [TABLE 1].

TABLE 1 : log K_f values of complex in binary mixtures at different temperatures

cation	Medium	$\log K_f \pm SD^a$			
		15?C	25?C	35?C	45?C
Cu^{2+}					
	Pure MeOH	b	b	b	b
	75.00%DMF -25.00% MeOH	7.46±0.03	7.19±0.05	6.88±0.1	6.76±0.15
	Pure DMF	6.55±0.2	5.38±0.2	4.25±0.4	c
	75.00%DMF -25.00% PrOH	7.20±0.06	6.18±0.2	5.97±0.22	4.96±0.21
	Pure PrOH	b	b	b	b

[a]SD = standard deviation; [b]The ligand is not dissolved; [c]With high uncertainty

The Van't Hoff plots of log K_f versus 1000/T for all of investigated systems were constructed [Figures 3 and 4]. The changes in standard enthalpy ($\Delta H_c^{Ú}$) were obtained from the slope of the Van't Hoff plots and the changes in standard entropy ($\Delta S_c^{Ú}$) were calculated from the relationship (1):

$$\Delta GÏ_{c,298.15}=\Delta H_c^{Ú}-298.15\Delta S_c^{Ú} \qquad (1)$$

The thermodynamic data are summarized in [TABLE 2].

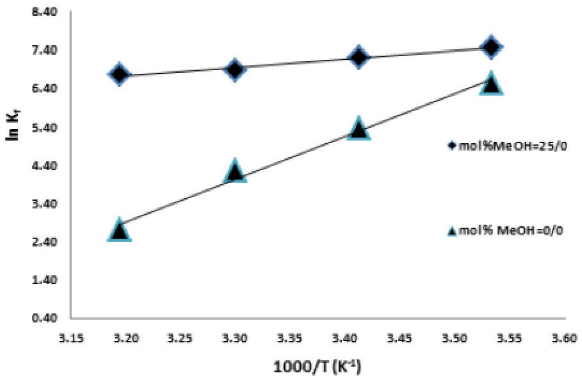

Figure 3 : Van't Hoff plots of (HYT)-Cu complex in MeOH–DMF binary systems

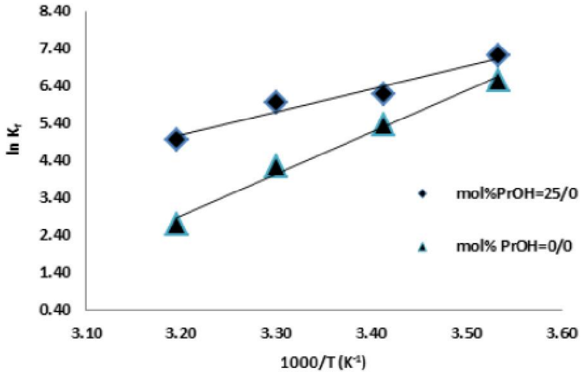

Figure 4 : Van't Hoff plots of (HYT)-Cu complex in PrOH–DMF binary systems

The variations of log K_f versus the mole fraction of PrOH–DMF and MeOH–DMF for (HYT)-Cu complex in binary systems at different temperatures are shown in [Figures 5 and 7]. Enthalpy and entropy of complexation were determinated from temperature dependence of complexation Constance [TABLE 2]. The thermodynamic data given in [TABLE 2] show that, depending on the solvent composition, the sign of the enthalpy values for formation of (HYT)-Cu complex can be negative or positive, but in the case of the (HYT)-Cu complex the values of enthalpies are negative. These results reveal that the complexation processes between Cu^{2+} and (HYT) is exothermic (favorable) at all solvent compositions. The results in [TABLE 1] show that in some of the solvent system compositions, the formation constant of (HYT)-Cu complex increases with increasing the temperature at all solvent compositions and, therefore, there is an endothermic reaction between Cu^{2+} cation with (HYT) in these binary mixed solvents, The positive values of ΔS [TABLE 2] show that the complexation processes between Cu^{2+} cation with (HYT) are entropy stabilized.

TABLE 2 : Thermodynamic parameters for (HYT)-Cu complex in binary mixture

Cation	Medium	ΔG_c° ±SD^a (25 ?C) (Kj/mol)	ΔH_c° ±SD^a (kJ/mol)	ΔS_c° ±SD^a (kJ/mol)
Cu^{2+}				
	Pure MeOH	B	b	b
	75.00%DMF -25.00% MeOH	2.25±0.5	-17.71±1.9	7.48±2
	Pure DMF	71.27±0.2	-83.06±1.2	238.7±1
	75.00%DMF -25.00% PrOH	36.09±0.7	-51.05±7	120.8±2
	Pure PrOH	B	b	b

[a]SD = standard deviation; [b]The ligand is not dissolved; [c]Composition of binary mixtures is expressed in mol%for each solvent system

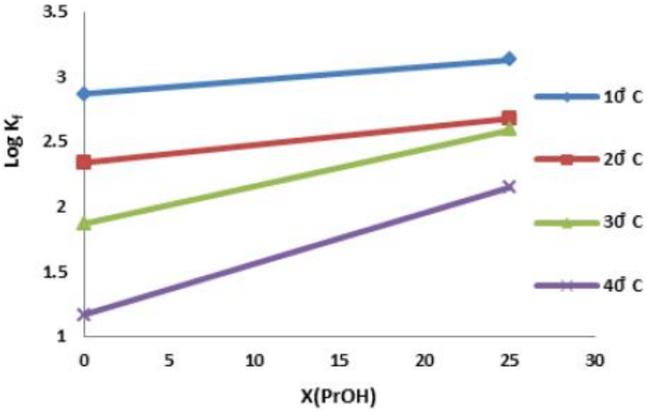

Figure 5 : Changes of the stability constant (log K_f) of (HYT)-Cu complex with the composition of PrOH–DMF binary systems at different temperatures

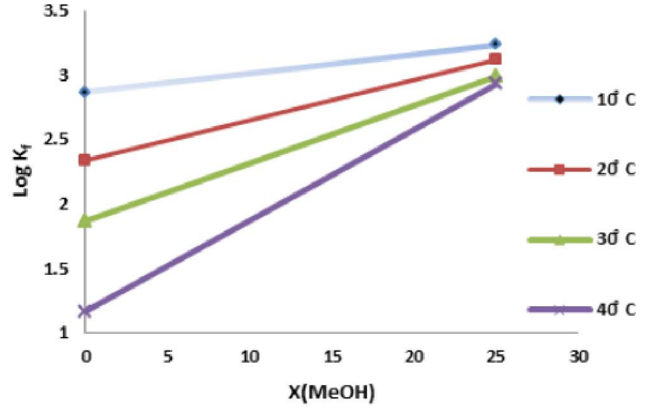

Figure 6 : Changes of the stability constant (log K_f) of (HYT)-Cu complex with the composition of MeOH–DMF binary systems at different temperatures

Spectrophotometric method

The maximum absorbance of complex cames from by spectrophotometer set at 430 nm using constant variations solutions with (0.001 M) concentration in DMF solution were prepared from dense ligand and cation solution. Then they were mixed with different volumetric ratio so that the final volume could be equal to 5 ml. After adjusting the optimum pH the absorption of solutions were measured at λ=430 nm. The resulting Absorbance-mole ratio plots at 25ÚC are shown in [Figuru 7]. As seen, the absorbance versus (HYT) -to- Cu^{2+} mole ratio plots show one distinct breaks at (HYT) -to- cation mole ratios of about 1, emphasizing the successive formation of 1:1 ((HYT) -to- cation) species in DMF solution.

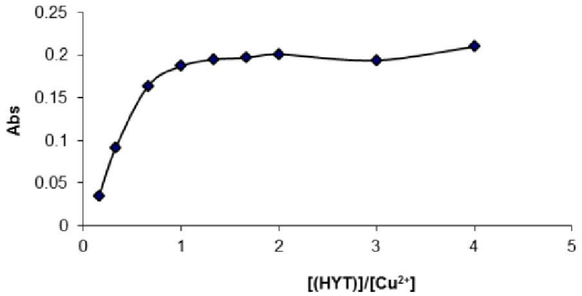

Figure 7 : The variation of absorbanse of [(HYT)]/[Cu^{2+}] at selected wavelength at room temperature

The stoichiometries of the resulting molecular complex was further examined by the method of Jobs plot[20, 21]. the resulting plots are shown in [Figure 8].

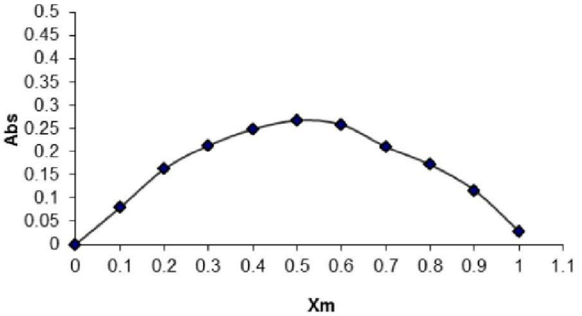

Figure 8 : Jobs plot for the reactions of compelex at selected wavelength

As seen, the plots possess one distinct inflection points at the X_{Cation} of 0.5, which emphasize the formation of 1:1 (HYT) -to- cation species in DMF solution.

Complex absorbance spectra are considerably under the influence of acid media. To investigate the effect of pH, cations and (HYT) ligand with concentration of ligand (0.005M) and cation with (0.001M) concentration in DMF solution was prepared. Ligand was added ten times more than cation concentration so that the complex with any stochiometric ratio could be completely formed and finally complex absorbance on the basic of pH variation at λ= 430 was measured. In [Figure 9] the diagram of maximum absorption variations on the basic of pH at λ= 430 nm is shown. As it illustrated, the optimum pH equals 8. To find out the effect of temperature on forming complex, a series of solutions with 0.005 M from ligand and 0.001M from cation at 10 to 1 volumetric ratio was prepared and the absorbance of complex in various temperatures was measured. The results showed raising temperatures don't have effect on the absorption. The results are shown in [Figure 10]. Also, to measure the necessary time to conduct complex production reaction a series of solvents with 0.005 M from ligand and 0.001M from cation were prepared. After that, the absorbance of complex at optimum pH was calculated. It was observed that the formed complex absorption remained stable with the passing of time. The results are shown in [Figure 11].

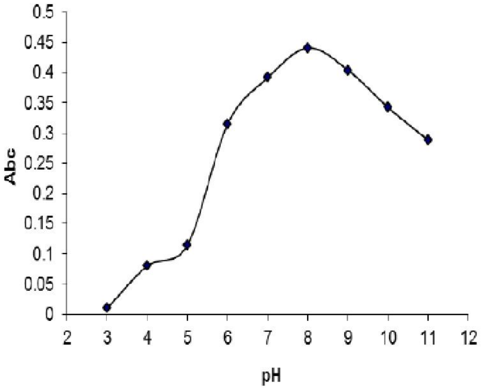

Figure 9 : The variation of absorbanse vs pH of compelex at selected wavelength at room temperature

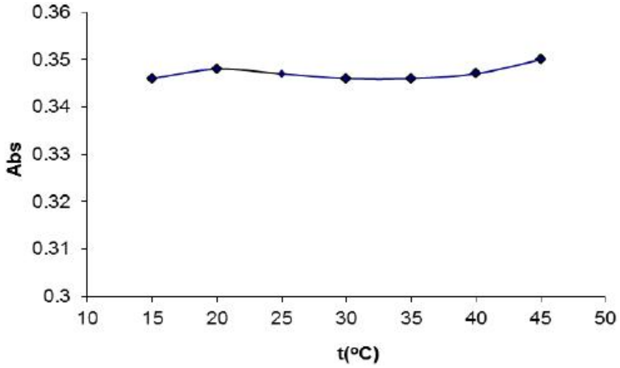

Figure 10 : The variation of absorbanse vs. temperature of compelex at selected wavelength

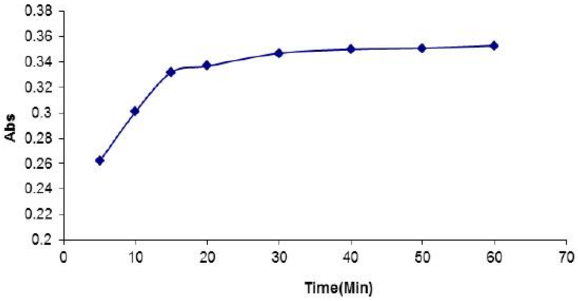

Figure 11 : The variation of absorbanse vs. time of compelex at selected wavelength

To investigate the effect of the interfering ions, solutions of Co^{2+}, Cd^{2+}, Ag^{+}, Fe^{2+},Ni^{2+}, Zn^{2+}, Mn^{2+} and Cr^{2+} were prepared. These cations were added 100 times concentration to Cu^{2+} ion having 10^{-3} M concentration. The complex absorption equaled 0.29 at the absorbance of interfering ion. [TABLE 3].

TABLE 3 : The effect of interfering ions

interfering ions	Concentration ratio of interfering ions to Cu^{2+}	Abs	RSD%
Ag^{+}	100	0.507	5<
Cd^{2+}	100	0.568	5<
Co^{2+}	100	0.559	5<
Cr^{2+}	100	0.501	5<
Fe^{2+}	100	2<	5<
Mn^{2+}	100	0.322	5?
Ni^{2+}	100	0.482	5<
Zn^{2+}	100	0.310	5>

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