INTRODUCTION

In recent years lots of investigations about complex formation between metal cations and different ligands in binary solvents have been done for industrial purposes. 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 5,5′-(2E, 2′E)-2,2′-(ethane-1,2-diylidene)bis(4-amino-4H-1,2,4-triazole-3-thiol) (HYT) [1–8]. This is shown in Fig. 1 complex with Cd²⁺ metal cation in some binary mixtures of methanol (MeOH), n-propanol (PrOH) and dimethylformamide (DMF) at different temperatures using the conductometry and spectrophotometry. The stability constants of the complex was determined using a GENPLOT computer program. The conductance data and absorbance-mole ratio plots show that in all solvent systems, the stoichiometry of the complex formed between (HYT) and Cd²⁺ cation is 1 : 1. The obtained results show that the stability of (HYT)—Cd complex is sensitive to the mixed solvents composition. The values of thermodynamic parameters (ΔG°, ΔH°, and ΔS°) for formation of (HYT)—Cd 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 pH, time, temperature and the nature of the solvent.

Keywords: macrocyclic ligand, Cd²⁺ cation, spectrophotometric, conductometric

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Study of Complex Formation of 5,5′-(2E, 2′E)-2,2′-(Ethane-1,2-diyldene)bis(hydrazine-1-yl-2-ylidene)bis(4-amino-4H-1,2,4-triazole-3-thiol) (HYT) Macrocyclic Ligand with Cd²⁺ Cation in Non-aqueous Solution by Spectroscopic and Conductometric Methods¹

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Abstract—In this paper the complexation reaction of the 5,5′-(2E,2′E)-2,2′-(ethane-1,2-diyldene)bis(hydrazine-1-yl-2-ylidene)bis(4-amino-4H-1,2,4-triazole-3-thiol) ligand (HYT) with Cd²⁺ education was studied in some binary mixtures of methanol (MeOH), n-propanol (PrOH) and dimethylformamide (DMF) at different temperatures using the conductometry and spectrophotometry. The stability constants of the complex was determined using a GENPLOT computer program. The conductance data and absorbance-mole ratio plots show that in all solvent systems, the stoichiometry of the complex formed between (HYT) and Cd²⁺ cation is 1 : 1. The obtained results show that the stability of (HYT)—Cd complex is sensitive to the mixed solvents composition. The values of thermodynamic parameters (ΔG°, ΔH°, and ΔS°) for formation of (HYT)—Cd 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 pH, time, temperature and the nature of the solvent.

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In the present paper, we report the results which are obtained in conductometric and spectrophotometric study of complexation Cd\(^{2+}\) cation by (HYT) in some binary mixtures of methanol (MeOH), \(n\)-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. The results show that the newly synthesized compound (HYT) is suitable ligand for complexation with Cd\(^{2+}\) cation and these tests can be a gateway for new works to improve the detection limits measured Cd\(^{2+}\) cation.

**EXPERIMENTAL**

**Materials and Methods**

**Materials.** Cd(NO\(_3\))\(_2\) (Merck) was used without further purification. The solvents: methanol (MeOH), \(n\)-propanol (PrOH) and dimethylformamide (DMF) all from Merck were of the highest purity.

**Conductometric Method**

The experimental procedure to obtain the formation constants of complex was as follows: a solution of metal salt (5 \(\times\) 10\(^{-5}\) mol L\(^{-1}\)) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step addition of the (HYT) solution prepared in the same solvent (5 \(\times\) 10\(^{-4}\) mol L\(^{-1}\)) 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 maintained within \(\pm 0.1^\circ\)C. 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 cation molar ratio for complexation of (HYT) and Cd\(^{2+}\) cation in some binary mixtures of methanol (MeOH), \(n\)-propanol (PrOH) and dimethylformamide (DMF) at different temperatures were studied. The value of log \(K_f\) calculated from the (HYT)–Cd complex calculated from the conductivity measurements in non-aqueous solvent at different temperatures [19]. The value of thermodynamic parameters (\(\Delta H^o\), \(\Delta S^o\)) for formations of (HYT)–Cd complex was obtained from temperature depended of stability constant.

**Spectrophotometric Method**

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

In this method to obtain the maximum absorbance of ligand and complex, the stock solutions of ligand 0.005 mol L\(^{-1}\) and Cd \(^{2+}\) cation with 0.001 mol L\(^{-1}\) concentration was prepared. Ligand absorbance spectra were taken and the maximum absorbance of ligand was found at 315 nm. At least, 10 times fold of ligand 2 mL were added to cation 1 mL. Then complex solution was placed at room temperature for 2 h 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 450 nm. The maximum absorbance is shown in Fig. 2.

To draw calibration curve, standard solution with equal concentration of Cd\(^{2+}\) cations and different concentration of ligand (HYT) was prepared. After dissolving it in 5 mL methanol, it was treated sonication, and then was transferred to a 25 mL flask after filtering. As much as 1 mL of 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 \(\lambda_{\text{max}} = 450\) nm for (HYT)–Cd was measured.

**RESULTS AND DISCUSSION**

**Conductometric Method**

It is shown that molar conductivity in methanol system increases with the ligand to cation molar ratio. The slope of molar conductance mole-ratio curves change at the point (=1) which indicates the formation of complex 1 : 1 (ligand : cation). This is shown in Fig. 3.

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 qualitative criterion of complex stability.