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Optical spectroscopy studies of the complexation of bis(azophenol)calix[4]arene possessing chromogenic donors with Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+}

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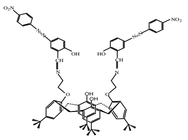
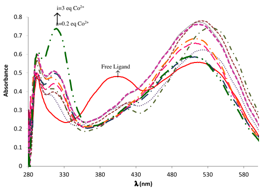
HIGHLIGHTS

- ▶ We explored interaction between some M^{2+} metal ions and bis(azophenol)calix[4]arene H_2L in DMSO.
- ▶ The absorption spectra of calix[4]arene with cations show marked changes, especially for Co^{2+} ion.
- ▶ Job's plot indicated 1:1 binding-stoichiometry for calix[4]arene with Co^{2+} ion.
- ▶ 1:1 association constant of H_2L with Co^{2+} is determined on the base of Bensi-Hilderbrand plot at $\lambda = 317$ nm.
- ▶ It is revealed that the stability constant of calix[4]arene H_2L with cobalt is $K_a = 2.40 \times 10^4\ M^{-1}$.

GRAPHICAL ABSTRACT



H_2L



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ABSTRACT

Due to their potential applicability as selective receptors in electrochemical or optical sensors, a bis(azophenol)calix[4]arene derivative H_2L has been investigated. The complexation properties of this molecule towards Ni^{2+} and Co^{2+} metal ions has been studied. It is revealed that this ligand exhibits tetradentate with N_2O_2 core when bound to Ni (II) or Co (II) metal ion. The optical response of azo groups of H_2L towards Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+} metal ions has been investigated in DMSO by UV–vis spectroscopy. The absorption spectra of calix[4]arene with cations show marked changes, especially for Co^{2+} ion. Furthermore, Job's plot indicate 1:1 binding-stiochiometry for calix[4]arene with Co^{2+} ion and Benson-Hilderbrand plot is used for the determination of its association constant. The investigation of UV–vis spectra of chromogenic calix[4]arene in different solvents shows that cis–trans isomerization of azo groups probably depends on kind of solvent. Also the different between the polarity and viscosity of organic solvents used is likely responsible for the changes of the band shape of the spectra.

Introduction

Calixarenes are the third generation of supramolecular receptors after cyclodextrines and crown ethers [1]. It is possible to prepare various calixarene derivatives by functionally modifying either the upper and/or lower rims. The modification of calixarenes has been the subject of numerous studies, due to their potential applicability as active ligands in electrochemical and/or optical sensors [2–8] with different selectivities for various guest ions and small molecules.

Among calix[4]arene receptors, various types chromogenic calix[4]arene derivatives have recently been synthesized, which have shown selective complexation with metal ions [9,10]. McKervy and

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Table 1
IR spectra data (cm^{-1} in KBr) for H_2L, NiL and CoL.

Compound	$\nu_{C=N}$	ν_{O-H}	$\nu_{C-O\ phenolic}$
H_2L	1633	3443	1197
NiL	1611	3432	1195
CoL	1615	3433	1195

Diamond [11,12] have demonstrated that novel chromogenic calixarene-based ligands can be used for the optical recognition of alkali ions. Bodenant et al. [13] have reported a bipyryl calix[4]arene-based receptor designed for the optical detection of Cu(II) and Ni(II) metal ions in solution. Bitter et al. [14] have studied the complex forming behavior and selectivity of a calix[4]arene derivative with alkali and alkali earth ions. Lang and co-workers [15] have reported on the comparative study of alkali metal receptors based on the calix[4]arene or thiacalix[4]arene scaffolds. Recently, Bingol and co-workers [16] have synthesized a novel calix[4]arene derivative containing benzothiazole azo groups at the upper rim and investigated sensing properties with some heavy metal ions.

In this paper, we report solvent effect on optical behavior of calix[4]arene derivative containing two nitrophenylazo groups at the lower rim and its complexation properties towards some heavy metal ions such as Ni^{2+},Co^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+} by UV–vis spectrophotometery. We found marked changes in the absorption spectra of calixarene ligand with studied heavy metal ions, especially for Co^{2+} ion.

Material and methods

General

5,11,17,23-Tetra-tert-butyl-25,27-bis[2-[(2-hydroxy-5-(4-nitroazo)benzylidene)amino]ethoxy]-26,28-dihydroxycalix[4]arene H_2L was prepared according to literature method [17]. Starting materials were all purchased commercially and used without further purifications. Elemental analyses were performed on Elementar Vario EL III. IR spectra were recorded on a FT-IR Spectrometer Bruker Tensor 27 in the region 4000–400 cm^{-1} using KBr pellets. Electronic absorption spectra in the UV–vis region were recorded with T 60 UV/vis Spectrometer PG Instruments Ltd. Melting points were obtained with an Electrothermal 9100 and are uncorrected.

Synthesis of Ni(II)complex (NiL)

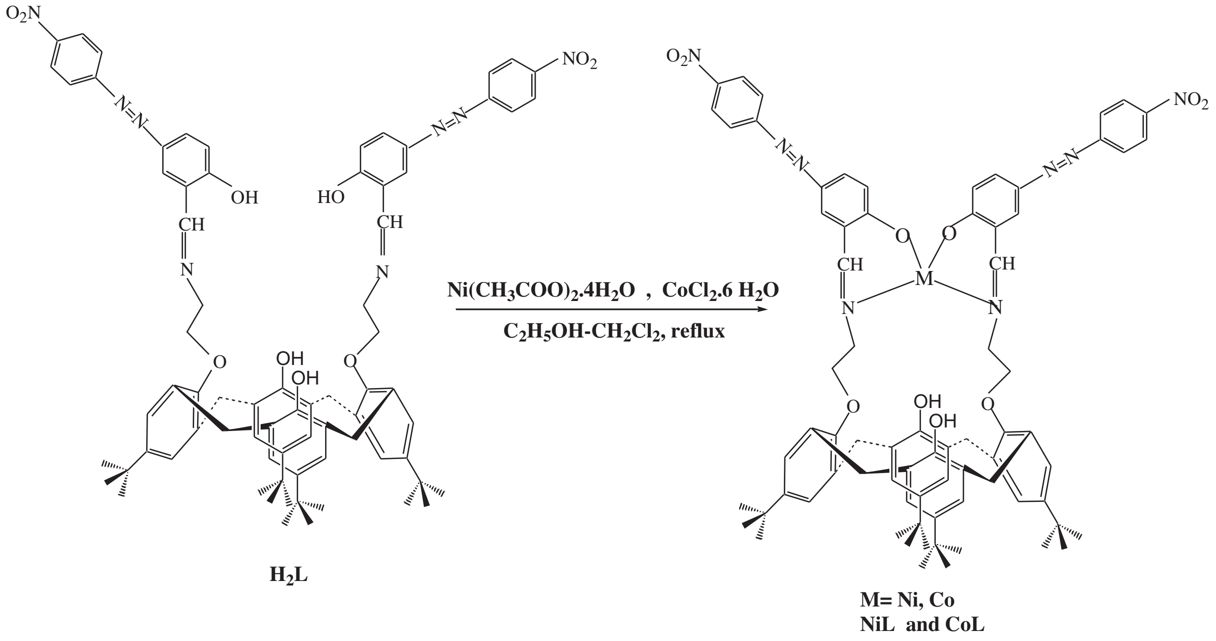
Ni(II)acetate.tetrahydrate (0.081 mmol, 0.020 g) in ethanol (5 ml) was added drop wise, over 15 min, to an ethanol-dichloromethane solution (15 ml) of calix[4]arene derivative H_2L (0.0081 mmol, 0.100 g). The mixture was refluxed for 4 h, then it was filtrated and the obtained solid was purified by crystallization using the same solvents ($C_2H_5OH–CH_2Cl_2$) and a red-brown powder was obtained. Yield: 0.060 g, 55.0%. IR (KBr, cm^{-1}) 3432(O–H groups), 2955(C–H aliphatic), 1611 (–C=N– imine), 1524 and 1474 (–N=N– cis and trans), 1383, 1334 (NO_2 group), 1197(C-O phenolic), 1150, 1107, 1035, 856, 749. Elem. Anal. Calcd for Ni $C_{74}H_{80}N_8O_{10}$: C, 68.48; H, 6.31; N, 8.63. Found: C, 68.18; H, 5.99; N, 8.30. Decomp: 340 °C.

Synthesis of Co(II) complex (CoL)

Co(II)chloride.hexahydrate (0.081 mmol, 0.019 g) in ethanol (5 ml) was added drop wise, over 15 min, to an ethanol-dichloromethane solution (15 ml) of calix[4]arene derivative H_2L (0.081 mmol, 0.100 g). The solution was refluxed for 24 h, then the solution was evaporated under reduce pressure. The oil residue was washed n-hexane and then purified by crystallization by using the same solvents ($C_2H_5OH–CH_2Cl_2$) and a brown powder was obtained. Yield: 0.070 g, 63.0%. IR (KBr, cm^{-1}) 3433(O–H groups), 2957(C–H aliphatic), 1615 (–C=N– imine), 1521 and 1476 (–N=N– cis and trans), 1386, 1335 (NO_2 group), 1197(C–O phenolic), 1154, 1107, 1043, 859, 749. Elem. Anal. Calcd for $CoC_{74}H_{80}N_8O_{10}.4CH_2Cl_2$: C, 57.17; H, 5.13; N, 6.84. Found: C, 56.99; H, 5.27; N, 7.45. Decomp: 245 °C.

Stability constant of cobalt complex

The stability constant K_a of 1:1 complex of H_2L with Co^{2+} transition metal ion was determined from the following Benesi-Hildebrand equation [8]:



Scheme 1. Synthesis of NiL and CoL complexes (azo groups have been shown without consideration to trans–cis izomerization).

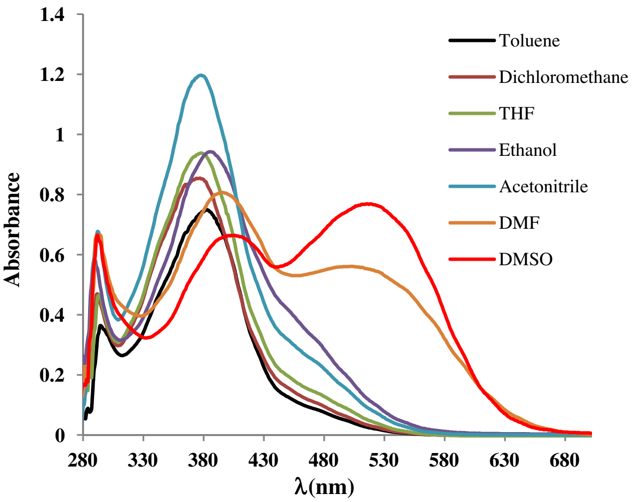


Fig. 1. UV–vis spectra of H_2L (~10^{-4} M) in different solvents.

$$1/\Delta A = 1/\Delta A_{sat} + 1/(\Delta A_{sat} K_a[\text{guest}])$$

Where ΔA is the absorption difference between the apparent metal complex and the free ligand and ΔA_{sat} is the absorption difference at saturation. The association constant value K_a was evaluated graphically by plotting $1/\Delta A$ against 1/[metal ion]. In this study, the concentration of the ligand was kept constant (10^{-4} M), and the concentration of metal ions was kept in the range ([metal ion]/[ionophore]) = 0.2–3.0 eq. Plot gave a straight line, and the K_a value was obtained from the slop and intercept of this line.

Results and discussion

IR Spectra

The major difference in the IR spectra of NiL or CoL compared to H_2L is the shift of the imine peak at 1633 cm^{-1} in H_2L to 1611 and 1615 cm^{-1} at complexes, respectively. This shows nitrogen electron pairs coordinate to empty orbital's of Ni(II) or Co(II) metal ion. Also, shifts in C–O phenolic and O–H peaks for complexes compared to H_2L indicate that H_2L acts as a tetradendate ligand with N and O donors (Table 1 and Scheme 1).

Molar conductivity

The molar conductivity of NiL and CoL complexes in DMSO are, 0.007 and 0.074 $Cm^2\,\Omega^{-1}mol^{-1}$, respectively. These values show that these complexes are non-electrolyte. Therefore, Schiff-base ligand H_2L exhibits dianionic, tetradentate with N_2O_2 core when bound to Ni (II) or Co (II) metal ion.

Table 2
UV–vis data for H_2L (~10^{-4} M) in different solvents.

Solvent	λ_{max} (nm)		
	$\pi \to \pi^*$ (aromatic)	$\pi \to \pi^*$(azo groups)	$n \to \pi^*$ (azo groups)
Toluene	294	381	487 (weak)
Dichloromethane	292	377	487 (weak)
THF	293	383	489 (weak)
Ethanol	291	385	482 (weak)
Acetonitrile	292	378	482 (weak)
DMF	293	389	495 (strong)
DMSO	292	399	518 (strong)

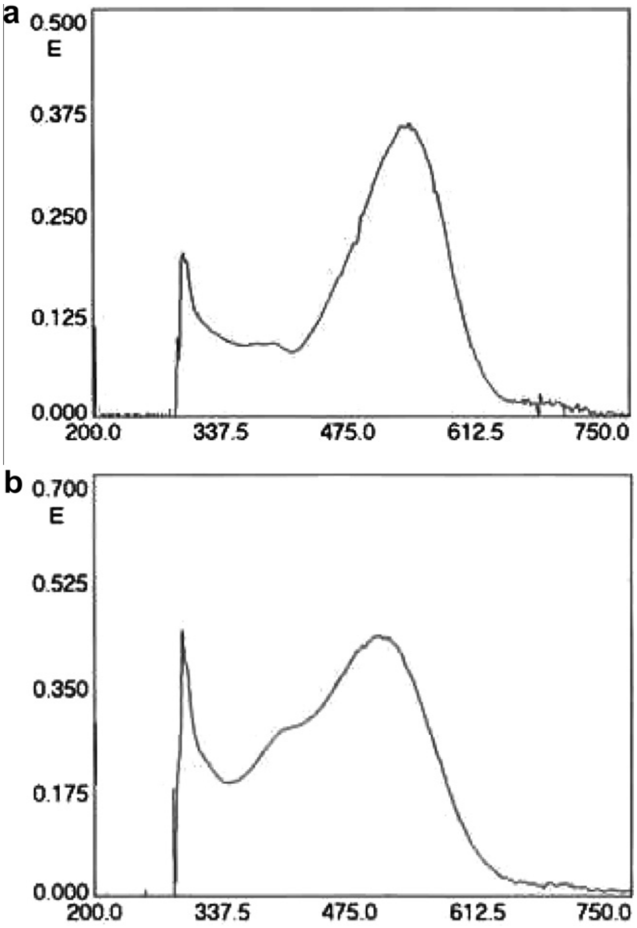


Fig. 2. UV–vis spectra of NiL (a) and CoL (b) in DMSO (~10^{-4} M).

UV–vis experiments

Effect of the solvent

The absorption bands of azo compounds in UV–vis spectra are usually revealed at 300–500 nm [18]. Azobenzene-containing molecules have two cis and trans isomers [19]. These compounds show two broad absorption peaks, depending on $\pi \to \pi^*$ and $n \to \pi^*$ transitions of azo groups (–N=N–). In general, $n \to \pi^*$ ($S_o \to S_1$) transition of trans-isomer is symmetrically-forbidden, whereas $\pi \to \pi^*$ ($S_o \to S_2$) is symmetrically-allowed transition [20]. Trans-azobenzene can be transformed into cis-azobenzene by rotating or inverting a phenyl ring upon photo-excitation with ultraviolet light; the reverse transformation from cis-azobenzene to trans-azobenzene can be obtained through photo-irradiation with visible light or thermal isomerization. Also, it is demonstrated that visible light source can be utilized in studying the photo-conversion of azobenzene-containing compounds in an appropriate solution without using any UV light sources [20]. The effects of solvent viscosity and polarity on the isomerization have been recently reported by Serra and Terentjev [21]. Different dipole moments or dielectric constants of different solvents may result in the dissimilar trans–cis isomerization depending on the solvent.

The UV–vis spectra of Schiff-base ligand H_2L have been recorded in solutions with different solvents: tetrahydrofuran, dichloromethane, toluene, ethanol, acetonitrile, dimethylformamide (DMF) and DMSO (Fig. 1). Ligand H_2L shows two broad and strong absorption bands at λ = 389 and 495 nm in DMF and λ = 399 and 518 nm in DMSO, apparently corresponding to the

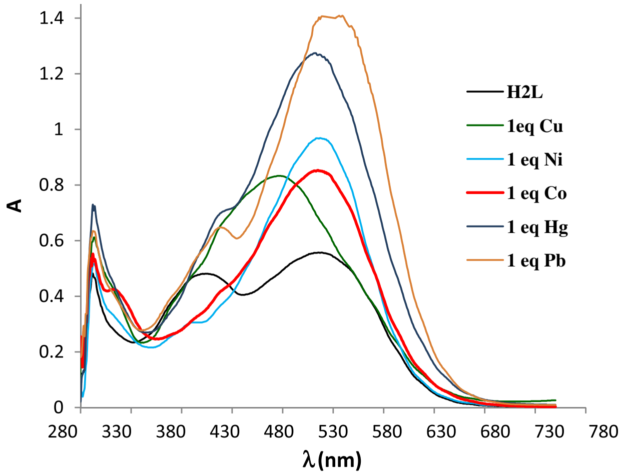


Fig. 3. UV–vis spectra of H_2L (0.1 Mm) before and after adding a 0.1 Mm concentration of various metal acetates in a DMSO solution.

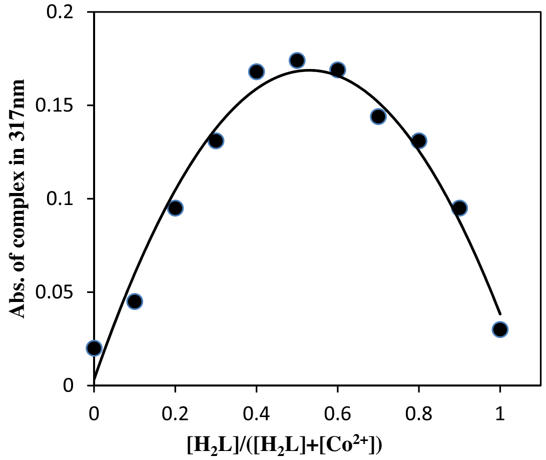


Fig. 5. Jop plot for H_2L and Co^{2+}, where the absorption at 317 nm was plotted against the mole fraction of H_2L at an invariant total concentration of 10^{-4} M in DMSO.

$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azo groups of calix[4]arene molecule, respectively [15,16,22]. While, in other studied solvents, $\pi \rightarrow \pi^*$ transitions are observed as strong bands in the range of 377–388 nm (Table 2). In these solvents, dissimilar to DMF and especially DMSO, $n \rightarrow \pi^*$ transitions are appeared as weak bands in the range of 482–487 nm ($\pi \rightarrow \pi^*$ transitions are a lot stronger than of $n \rightarrow \pi^*$ transitions in intensity, so that $n \rightarrow \pi^*$ transitions are negligible). It seems these results probably correspond to the existence of azo groups of calix[4]arene molecule as trans configuration in studied solvents exception DMSO and DMF (because $n \rightarrow \pi^*$ transition is strong in intensity in DMSO and DMF, while, this transition is symmetrically forbidden and weak for trans-isomer).

Also, the different between the polarity [7] and viscosity [21] of organic solvents used is likely responsible for the changes of the band shape of the spectra.

The UV–vis spectra of NiL and CoL complexes

The UV–vis spectra for NiL and CoL complexes in DMSO in 200–750 nm are shown in Fig. 2. Both compounds were determined to show a strong absorption peak at 293 nm apparently corresponding to $\pi \rightarrow \pi^*$ transition of aromatic rings. There are broad and strong bands in the absorbance spectra of NiL and CoL at $\lambda = 521$ nm and 485 nm (a blue shit to shorter wavelength), corresponding to $n \rightarrow \pi^*$ transition of azo groups respectively. The major difference in the UV–vis spectra of NiL and CoL compared to H_2L is more decreasing of $\pi \rightarrow \pi^*$ transition in intensity upon complexation.

Complexes formed in solution

The binding ability of compound H_2L for some heavy metal cations is investigated by UV–vis absorbance method. Absorption spectra of 0.1 mM H_2L in the presence 0.1 mM of metal ions (Ni^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+}) are shown in Fig. 3. In fact, the absorbance spectra show remarkable changes after addition of metal ions. In all cases, $n \rightarrow \pi^*$transition increases in intensity (Generally, absorbance intensity for Pb^{2+} and Hg^{2+} is more than Ni^{2+}, Co^{2+} and Cu^{2+}) and the band at around 399 nm, assigned to the $\pi \rightarrow \pi^*$ transition of azo groups of calixarene, decreases in intensity. Complexation of these metal ions for compound H_2L probably affects the equilibrium of tautomeric forms and there is likely a subtle balance between metal complexation-induced release of protons from the azophenols to the quinone–hydrazone in DMSO solution [10,23,24]. When H_2L treats with Pb^{2+}, a small red shift from $n \rightarrow \pi^*$ transition at 518 nm to 538 nm (+20 nm) is observed. Whereas, adding one equivalent of Cu^{2+} ion results a blue shift (40 nm). It can be seen as color change of solution from red to orange-yellow. In addition to aforementioned changes, an especial behavior is seen after adding Co^{2+} cation. A new absorption band appears at wavelength at around 317 nm, indicating significant selectivity towards Co^{2+} ion. This band increases in intensity with the addition of concentration of cation.

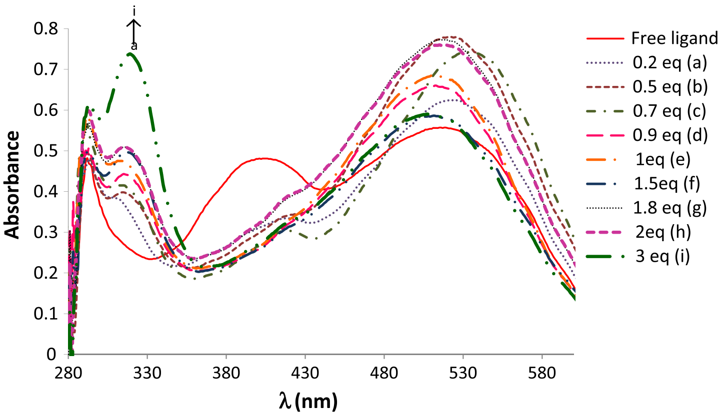


Fig. 4. Changes in the UV–vis spectra of H_2L (0.1 Mm) upon titration by $Co(CH_3COO)_2$ in a DMSO solution, where the concentration of $Co(CH_3COO)_2$ varies from 0.02–0.3 mM.

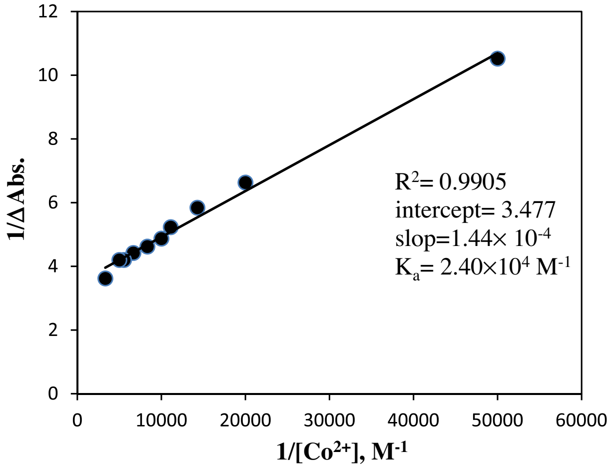


Fig. 6. Benesi-Hilderbrand plot of H_2L with $Co(CH_3COO)_2$.

UV–vis titrations

UV–vis spectra, obtained upon the addition of cobalt ions to the solution of calix[4]arene H_2L, have been presented in Fig. 4. It can be seen that the absorbance band at $\lambda = 518$ nm increases in intensity with the addition of concentration of cation. While the continuous decreasing of the band at $\lambda = 399$ nm, assigned to the π–π^* transition of the azo groups of calixarene and appearance a new absorption band at $\lambda = 317$ nm can be attributed to the formation of complexes with cobalt ions. The band at $\lambda = 317$ nm gradually increases in intensity and vice versa the band at $\lambda = 399$ nm disappears with the extra addition of $Co^{2+}$to the solution of ligand. The spectra features in Fig. 4 are consistent with a 1:1 ratio between calix[4]arene H_2L and Co^{2+} ion. Further support of the 1:1 binding ratio comes from Job's plot experiment, where the absorptions of the complex at 317 nm is plotted against molar fractions of H_2L under the conditions of an invariant total concentration. As a result, the concentration of $H_2L{\cdot}Co^{2+}$ complex approaches a maximum when the molar fraction of $[H_2L]/([H_2L] + [Co^{2+}])$ is about 0.5 (Fig. 5).

Among studied cations, especial remarkable changes are only observed in the absorbance spectra of ligand with different equivalents of Co^{2+} ion (disappearing of $\pi \rightarrow \pi^*$ transition at $\lambda = 399$ nm and appearance a new band at 317 nm ($\Delta\lambda = 82$ nm)). Therefore, 1:1 association constant of H_2L with $Co^{2+}$is determined on the base of Bensi-Hilderbrand plot at $\lambda = 317$ nm. A typical plot for ligand and Co^{2+} is shown in Fig. 6. It is revealed that the stability constant of calix[4]arene H_2L with cobalt is $K_a = 2.40 \times 10^4\ M^{-1}$.

Conclusions

The investigation of UV–vis spectra of azo calix[4]arene derivative in different solvents indicated two strong and broad bands, corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azo groups in DMF and DMSO, while in the other solvents, $n \rightarrow \pi^*$ transitions were very law in intensity. It showed that cis–trans isomerization of azo groups of calix[4]arene molecule probably depends on solvent. Also, the different between the polarity and viscosity of organic solvents used is likely responsible for the changes of the band shape of the spectra. The study of absorbance spectra of calix[4]arene ligand with Ni(II), Co(II),Cu(II), Pb(II) and Hg(II) cations showed remarkable changes in the intensity of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Dissimilar to the spectra of ligand with studied cations, especial changes were observed in the absorption spectra of calix[4]arene with Co^{2+}. A new absorption band at $\lambda = 317$ nm was appeared. Upon the appearance of new absorption band and increasing of this band in intensity with the addition of concentration of Co^{2+}, 1:1 binding-stiochiometry was determined from Job plot. Finally, association constant H_2L with Co^{2+} obtained on the base of Bensi-Hilderbrand plot.

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