J. Iran. Chem. Soc., Vol. 6, No. 4, December 2009, pp. 823-830.

JOURNAL OF THE
Iranian
Chemical Society

Extraction and Preconcentration Capacity of Bifunctionalized Diamine-Thiol Polysiloxane Immobilized Ligand System Towards Some Divalent Cations

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(Received 18 September 2008, Accepted 26 December 2008)

Porous solid bi-organofunctionalized diamine-thiol polysiloxane immobilized ligand system of the general formula P-$(CH_2)_3$-X, (where P represents $[Si-O]_n$ siloxane network and X represents a mixture of diamine; $-NH(CH)_2NH_2$ and thiol; -SH functional groups) has been prepared by hydrolytic polycondensation of TEOS with a mixture of 3-mercaptopropyltrimethoxysilane and 3-(2-aminoethylimino)propyltrimethoxysilane agents. The ligand system was evaluated for extraction and preconcentartion of a series of divalent metal ions from aqueous solutions including: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. Both batch and dynamic methods were used to examine maximum sorption capacity. The maximum binding capacity followed the sequence; $Cu^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ at pH 5.5. Measurement of variation of sorption of metal ions with temperature yielded negative values of $\Delta G°$ and positive values of $\Delta S°$ and $\Delta H°$ indicating a spontaneous and endothermic process of binding metal ions to the ligand system.

Keywords: Immobilized-polysiloxanes, Metal ions extraction, Thermodynamic parameters, Diamine-thiol

INTRODUCTION

Heavy metals have received special attention throughout the world due to their toxic effects even at very low concentrations [1-5]. Many technological methods have been developed for some time for removing toxic/heavy metal contaminants from different media [6-7]. Chemical precipitation, ion exchange, filtration, adsorption, electrodeposition and membrane systems are the most important methods [8-11]. Some of these approaches suffer from limitations especially the low ability to remove quantities at trace levels.

Modified inorganic solid supports are gaining importance due to their excellent thermal, mechanical and chemical stability [12-16]. Polysiloxanes functionalized by chelating ligands have been widely exploited for extraction and preconcentartion of trace metal ions from different media by batch and dynamic methods [17-31]. Consequently, there is interest in developing functionalized polysiloxanes with suitable complexing agents which have capacity for metal ions [17-31]. These immobilized ligand systems could be synthesized either directly by the sol-gel [17-22] or by chemical modification of the pre-prepared functionalized polysiloxane [23-31]. These functionalized systems have been applied in many important cases including extraction and separation of metal cations from organic solvents and aqueous solutions [24-31], chromatographic stationary phases [22,32] and heterogeneous catalysis [21,33,34].

The aim of the present work is to investigate the ability of a diamine-thiol bi-functionalized polysiloxane immobilized ligand system to extract and preconcentrate different divalent metal ions under optimal analytical conditions.

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Thermodynamic parameters standard free-energy $\Delta G°$, standard enthalpy $\Delta H°$ and standard entropy $\Delta S°$ were evaluated to examine the effect of temperature on the metal ions extraction by this functionalized ligand system.

EXPERIMENTAL

Reagents and Materials

Tetraethylorthosilicate, 3-(2-aminoethylimino)propyltrimethoxysilane, and 3-mercaptopropyltrimethoxysilane were purchased from (Merck) and used as received. Diethyl ether and methanol (analytical grade) were also used as received. Metal ion solutions of appropriate concentrations were prepared by dissolving the metal chlorides or nitrates (analytical grade) in deionized water. Buffer solutions with pH values in the range of 3.5-6.0 were prepared using acetic acid/sodium acetate mixtures.

General Techniques

Analyses for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE instrument. The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer A Analyst-100 spectrometer. The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR, spectrophotometer using KBr disk in the range 4000 to 400 cm^{-1}. All pH measurements were obtained using HM-40V pH Meter.

Preparation of Diamine-Thiol Polysiloxane Biligand System (DTP)

The diamine-thiol biligand system was prepared as reported previously for similar materials [18]. In this method, 3-(2-aminoethylimino)propyltrimethoxysilane (11.12 g, 0.05 mol) was added to a mixture of 3-mercaptopropyltrimethoxysilane, (9.82 g, 0.05 mol), tetraethylorthosilicate (20.8 g, 0.1 mol) and 4.95 ml of 0.42 M HCl as a catalyst in 35 ml methanol. Gelation occurred within 15 min. The gel was left for 12 h at room temperature and then dried in vacuum oven at 90 °C for 6 h. The material was crushed, sieved, washed with successive portions of 50 ml of water, methanol and diethyl ether. Finally, the product was dried for 12 h in vacuum oven at 90 °C. The elemental analysis for the product is given in Table 1.

Batch Experiments

A 100 mg of definite mesh size (60-80 mesh) of the diamine-thiol polysiloxane-immobilized ligand system, DTP, was shaken for 48 h with 25 ml of an aqueous solutions (0.02 M) of the appropriate metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) using 100-ml polyethylene bottles at 25 °C except where otherwise specified. Determination of the metal ion concentration was carried out by atomic absorption spectroscopy. Sample solution was prepared by allowing the insoluble complex to settle down, withdrawing an appropriate volume of the supernatant using a micropipette and then diluting to the linear range of the calibration curve for each metal ion. The maximum metal ion uptake capacity was calculated as mg or mmol of M^{2+}/g ligand. Each study was performed at least in triplicate.

Determination of Distribution Coefficients

The distribution coefficient values of the studied metal ions extracted by DTP polysiloxane ligand were determined by the batch equilibration method where 0.1 g of the ligand was immersed in 25 ml of a solution containing 0.5 mmol of metal ion at different temperatures. The metal ion remained in solution after complexation was determined by atomic absorption spectrometry. The distribution coefficients K_D were

Table 1. Elemental Analyses Data for DTP

Element	%C	%H	%N	%S	mmol N/g	mmol S/g	C/N	C/N
Expected[a]	24.0	5.0	7.0	8.0	5.0	2.5	4.0	8.0
Found	22.4	4.6	6.3	7.6	4.5	2.3	4.1	7.9

[a]Analyses of expected results for the DTP were based on complete reaction.

calculated by using the equation [35]:

$$K_D(\mathrm{cm}^3/g) = \frac{(C_i - C_f)}{C_f} \times \frac{V(cm^3)}{m(g)}$$

where C_i and C_f are the initial and final metal ion concentrations in solution, respectively, m is the mass of polysiloxane used and V is the volume of aqueous phase.

Preconcentration Experiment

A glass column (250 mm long, 10 mm diameter) was washed sequentially with 0.1 M nitric acid, water and acetone. It was then oven-dried and packed with a bed (3.0 g, 60-80 mesh) of the diamine-thiol immobilized ligand system, DTP. The packed material was activated for each run by washing with (50 ml, 0.1 M) of HNO_3, followed by deionized water. Finally, the column was preconditioned by passage of 25 ml of the buffered aqueous solution at pH 5.5 to equilibrate the column as that of the working solution. Solutions (50 ml) of different concentrations (50-12,000 ppm) buffered at pH 5.5 were passed through the column with a flow rate of 1.0-1.5 ml min^{-1}. The adsorbed metal ions were eluted by passing (50 ml, 0.1 M) HNO_3 and diluted by deionized water; then measured by atomic absorption spectroscopy.

RESULTS AND DISCUSSIONS

Preparation of Diamine-Thiol Polysiloxane Bi-ligand System (DTP)

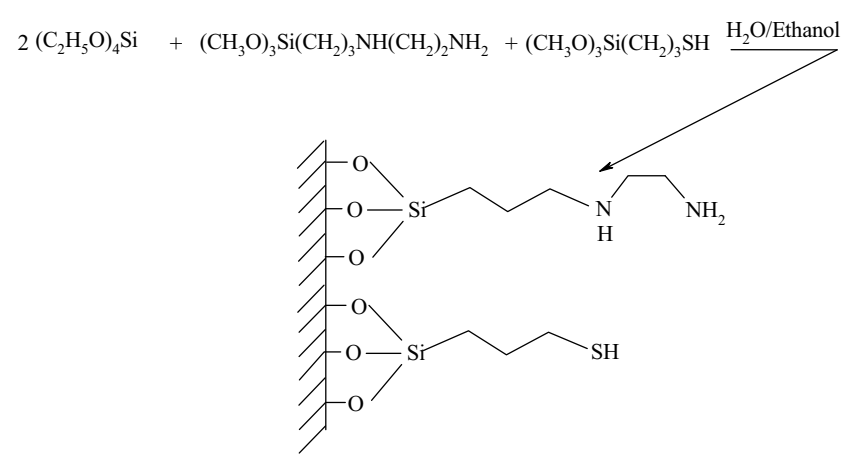
The diamine-thiol polysiloxane ligand system (DTP) was made by hydrolytic polycondensation between tetraethylorthosilicate and a mixture of 3-(2-aminoethylimino) propyltrimethoxysilane and 3-mercaptopropyltrimethoxy-silane, (Scheme 1). The elemental analysis results of the prepared polysiloxane bi-ligand system are given in Table 1. It is found that percentages of C, N and S are slightly lower than expected due to formation of small oligomers which leached during the washing process [36-38]. Formation of soluble non-cross linked oligomers is enhanced by the presence of self base catalyzed amino groups which leads to rapid gelation [36-38]. The equal C/N or C/S ratios of both expected and found results confirm that complete functionalized ligands were leached.

FTIR Spectrum

The FTIR spectrum of the immobilized diamine-thiol polysiloxane ligand system (DTP) is given in Fig. 1. The spectrum shows three characteristic absorption regions at 3500-3000 cm^{-1} due to ν(OH) and/or ν(NH_2), 1649 cm^{-1} due to δ(OH) and/or δ(NH_2) and 1200-900 cm^{-1} due to ν(Si-O). The characteristic band at 2555 cm^{-1} is due to ν(SH). The bands at 2971 cm^{-1} and 2941 are due to symmetric and asymmetric ν(C-H) aliphatic stretching vibrations. These absorption bands confirm that both the diamine and thiol functional groups are chemically bonded to the polysiloxane matrix.

Metal Uptake Capacity of DTP

The extraction capacity of DTP for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions was determined by batch method.



Scheme 1. Preparation of diamine-thiol polysiloxane ligand system (DTP)

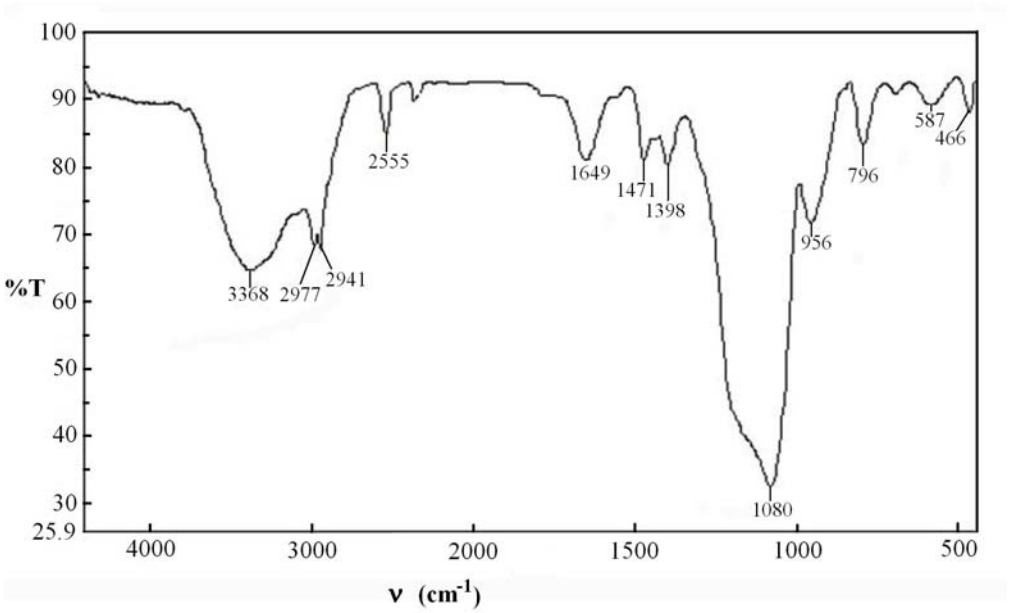


Fig. 1. FTIR spectrum of diamine-thiol polysiloxane immobilized ligand system (DTP).

Table 2. Maximum Metal Uptake by DTP

Maximum uptake[a]	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
mg M^{2+}/g Ligand	91.9 ± 0.045	107.4 ± 0.033	140.4 ± 0.034	113.1 ± 0.021	225.6 ± 0.044	437.2 ± 0.048
mmol M^{2+}/g Ligand	1.56 ± 0.045	1.83 ± 0.033	2.21 ± 0.034	1.73 ± 0.021	1.98 ± 0.044	2.11 ± 0.048

The functionalized ligand system was shaken with buffered metal ions solutions at the optimum conditions, where pH = 5.5 and shaking time was 48 h. The results are given in Table 2. The elemental analyses of nitrogen or sulfur of the immobilized ligand (DTP), as given in Table 1, show that about 2.25-2.30 mmol of functionalized bi-ligand is present in each gram of the ligand system. Comparing this range with the maximum uptake of the different metal ions, make it possible to suggest that 1:1 metal to ligand is assumed for copper, lead and cadmium metal ions. However, not all of the functional groups are accessible to binding with the nickel, zinc and cobalt metal ions, assuming that ligand to metal complexation ratio is 1:1. It is obvious that uptake of metal ions increases in the order:

$$Cu^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$$

It is clear that the amine-thiol bi-functionalized immobilized ligand system has two characteristic soft and hard basic centers which have an advantage to bind soft and hard metal ions with equal efficiency. This property enables the modified ligand system to be used in extraction of trace metals from natural water supplies [3].

Effect of pH on Preconcentration of Metal Ions

The effect of the pH on the preconcentration of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions by DTP was studied using the column technique. Uptake percentages were plotted against pH as shown in Fig. 2. The results show an increase of

metal ion preconcentration with increasing pH value reaching its maximum at pH 5.5. Minor uptake capacity occurs at low pH values (pH = 3.5) due to protonation of amine groups. This reduces the ability to form metal complexes. It is clear that the metal uptake starts to decrease after reaching the maximum value. This is probably due to the formation of hydrolyzed species of metal ions [39].

Effect of Metal ion Concentration

The ability of DTP to preconcentrate metal ions from aqueous solutions was studied at different concentrations (50-12,000 ppm) of metal ions using the column technique. The results are given in Fig. 3. The amount of metal ion recovered (mg) by the ligand system increases with increasing concentration up to the maximum value. The maximum chemisorption values were obtained at concentration range 500-12,000 ppm of the eluted metal ions using 3.0 g bed material. The amounts of metal ions preconcentrated were: 156.4 mg Co, 203.1 mg Ni, 239.2 mg Cu, 222.0 mg Zn, 384 mg Cd and 450 mg Pb. According to the elemental analysis of DTP, the functionalized bi-ligand found to be 2.25-2.3 mmol g^{-1} ligand system, thus, the corresponding loading efficiency of the column in percentages were 39.3%, 46.1% 55.8%, 50.2%, 50.6% and 32.1% for cobalt, nickel, copper, zinc, cadmium and lead, respectively. These results showed that binding capacity for these metal ions depends on ionic size, structure of the complexing agent and steric hindrance. At lower concentrations (50-2000 ppm) about 80-100% extractions were achieved. This promises the column to extract these metal ions at low or trace levels effectively, but at high concentrations multistep preconcentrations or large amounts of bed material should be used.

Effect of Solution Flow Rate

Preconcentration of metal ions by DTP was studied at different flow rates of Cu^{2+} metal ion solutions as an example. Solutions of Cu^{2+} (50 ml, 100 ppm), buffered at pH 5.5, were eluted through the column of 3.0 g bed material at flow rate range of 0.5-50 ml min^{-1}. The chemisorbed ions were then desorbed with (50 ml, 0.1 M) HNO_3. The percentage amounts of Cu^{2+} extracted *vs*. flow rate are given in Fig. 4. It was found that the optimum flow rate was in the range of 0.5-1.5 ml min^{-1}. The amount of Cu^{2+} extracted decreased after a flow rate of 2 ml min^{-1}.

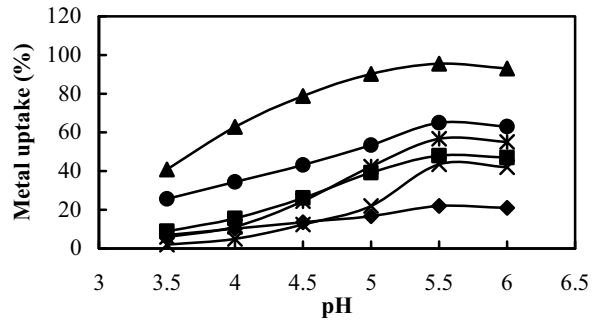


Fig. 2. Uptake (%) of metal ions by diamine-thiol polysiloxane immobilized ligand system (DTP) *vs*. pH using column method (bed material = 3 g, mesh size = 60-80, flow rate = 1.0-1.5 ml min^{-1}): (◆) %Co(II), (■) %Ni(II), (▲) %Cu(II), (×) %Zn(II), (✶) %Cd(II) and (●) %Pb(II).

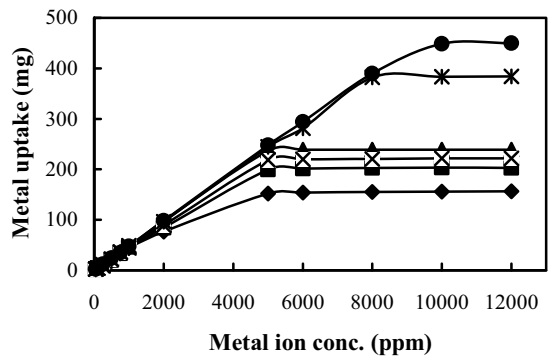


Fig. 3. Metal uptake by diamine-thiol polysiloxane immobilized ligand system (DTP) *vs*. concentration of metal ions using column method (bed material = 3 g, mesh size = 60-80, flow rate = 1.0-1.5 ml min^{-1}, pH = 5.5): (◆) Co(II), (■) Ni(II), (▲) Cu(II), (×) Zn(II), (✶) Cd(II) and (●) Pb(II).

Effect of Temperature

The influence of temperature on metal ions chemisorption by DTP from aqueous solutions was investigated at different temperatures (298-333 K) at pH 5.5 by batch method. The results are presented in Fig. 5. It is observed that the amount of

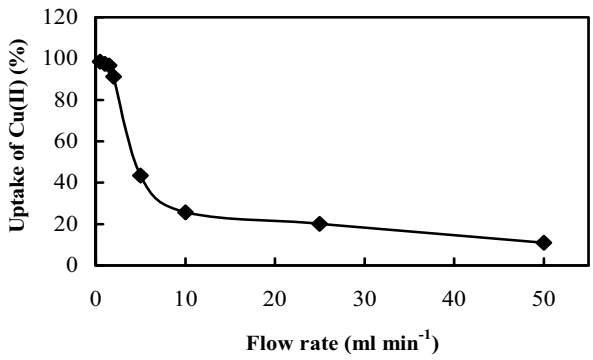


Fig. 4. Uptake (%) of Cu^{2+} ions by diamine-thiol polysiloxane immobilized ligand system (DTP) *vs*. flow rate in ml min^{-1} (bed material = 3 g, mesh size = 60-80, pH = 5.5).

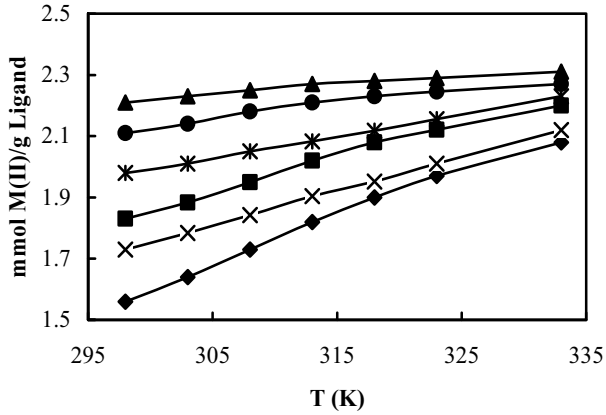


Fig. 5. Uptake of metal ions by diamine-thiol polysiloxane immobilized ligand system (DTP) *vs*. temperature in Kelvin (bed material = 3 g, mesh size = 60-80, flow rate = 1.0-1.5 ml min^{-1}, pH = 5.5): (◆) Co(II), (■) Ni(II), (▲) Cu(II), (×) Zn(II), (✶) Cd(II) and (●) Pb(II).

metal ions extracted increases with increasing of temperature. The shapes of curves in the case of Co^{2+}, Ni^{2+} and Zn^{2+} (Fig. 5) indicate higher affinity of the sorbent toward these metal ions than Cu^{2+}, Cd^{2+} and Pb^{2+}, suggesting higher endothermic effect and increase in mobility and diffusion rates of these metal ions within the polysiloxane particles.

Thermodynamic Investigations

The distribution coefficients, K_D for the extraction of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions from solutions by DTP was studied at different temperatures (Table 3). The results show that the distribution coefficients K_D increased with increasing temperature. Thermodynamic parameters were evaluated using the equation $\Delta G° = -RTlnK_D$ and $\Delta G° = \Delta H° - T\Delta S°$, where $\Delta G°$, $\Delta H°$, $\Delta S°$ and T are Gibbs free energy, enthalpy, entropy, and absolute temperature, respectively. R is the gas constant (8.314 J mol^{-1} K^{-1}) and K_D is the equilibrium constant. Plots of log K_D against $1/T$ give the numerical values of $\Delta H°$ and $\Delta S°$ from slope and intercept, respectively. The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are given in Table 3. The negative values of the free energy changes $\Delta G°$ for all temperatures show a reasonable affinity of DTP towards Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} (spontaneous process of sorption). The positive values of $\Delta H°$ (variation of enthalpy accompanying sorption of metal ions on the DTP) indicate an endothermic process, which is facilitated by higher temperatures. The positive entropy changes $\Delta S°$ characterize an increase in the disordering of the system on metal ions sorption by the DTP (probably due to the release of hydration water molecules, previously bound to the metal ions). The computed thermodynamic data showed that, chemisorption process is favored at higher temperatures.

CONCLUSIONS

The immobilized diamine-thiol bi-ligand system was prepared by the sol-gel process. This functionalized ligand system exhibits high potential for extraction of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions. The optimum conditions for preconcentartion of these metal ions by dynamic method were at pH = 5.5 and a flow rate of 1.0-1.5 ml min^{-1}. The equilibrium distribution coefficients of various metal ions between the sorbent and solution phases are temperature dependent. The thermodynamic parameters suggest a spontaneous and an endothermic affinity of the chelating ligand system towards metal ions.

ACKNOWLEDGMENTS

The author is thankful to the Islamic University of Gaza

Table 3. Thermodynamic Parameters of Metal Ions Chemisorbed by Diamine-thiol Polysiloxane Immobilized Ligand System (DTP)

Metal ion	*T(K)*	Lnk_D	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})
Co^{2+}	298	4.73 ± 0.04	-11.72 ± 1.24	10.79 ± 1.54	75.60 ± 3.10
	303	4.80 ± 0.03	-12.10 ± 1.36		
	308	4.88 ± 0.02	-12.51 ± 1.61		
	313	4.96 ± 0.05	-12.92 ± 1.74		
	318	5.03 ± 0.04	-13.30 ± 1.56		
	323	5.09 ± 0.02	-13.67 ± 1.34		
	333	5.18 ± 0.03	-14.35 ± 1.36		
Ni^{2+}	298	4.97 ± 0.06	-12.32 ± 1.11	7.56 ± 1.68	66.72 ± 4.65
	303	5.01 ± 0.03	-12.63 ± 1.15		
	308	5.07 ± 0.02	-12.99 ± 1.85		
	313	5.13 ± 0.04	-13.36 ± 1.25		
	318	5.18 ± 0.04	-13.70 ± 1.87		
	323	5.22 ± 0.05	-14.00 ± 1.58		
	333	5.28 ± 0.04	-14.62 ± 1.33		
Cu^{2+}	298	5.29 ± 0.03	-13.10 ± 1.21	1.92 ± 0.36	50.46 ± 4.54
	303	5.30 ± 0.02	-13.36 ± 1.32		
	308	5.32 ± 0.06	-13.63 ± 1.35		
	313	5.34 ± 0.05	-13.89 ± 1.32		
	318	5.35 ± 0.03	-14.13 ± 1.65		
	323	5.35 ± 0.02	-14.38 ± 1.37		
	333	5.37 ± 0.01	-14.86 ± 1.94		
Zn^{2+}	298	4.88 ± 0.04	-12.10 ± 1.63	7.86 ± 1.78	66.93 ± 5.13
	303	4.93 ± 0.05	-12.42 ± 1.86		
	308	4.98 ± 0.03	-12.76 ± 1.56		
	313	5.04 ± 0.02	-13.10 ± 1.68		
	318	5.08 ± 0.03	-13.42 ± 1.56		
	323	5.12 ± 0.05	-13.76 ± 1.87		
	333	5.22 ± 0.04	-14.44 ± 1.68		
Cd^{2+}	298	5.10 ± 0.01	-12.63 ± 1.43	4.66 ± 1.43	58.0 ± 3.1
	303	5.12 ± 0.03	-12.91 ± 1.54		
	308	5.16 ± 0.07	-13.21 ± 1.65		
	313	5.18 ± 0.03	-13.49 ± 1.61		
	318	5.21 ± 0.04	-13.78 ± 1.23		
	323	5.24 ± 0.02	-14.08 ± 1.44		
	333	5.30 ± 0.02	-14.69 ± 1.68		
Pb^{2+}	298	5.21 ± 0.04	-12.90 ± 1.34	3.15 ± 1.57	53.94 ± 4.78
	303	5.23 ± 0.05	-13.18 ± 0.45		
	308	5.26 ± 0.02	-13.48 ± 1.56		
	313	5.29 ± 0.04	-13.76 ± 1.77		
	318	5.30 ± 0.01	-14.02 ± 1.66		
	323	5.32 ± 0.03	-14.28 ± 1.68		
	333	5.34 ± 0.07	-14.78 ± 1.55		

for financial assistance. The author also acknowledges the technical guidance he received from Miss Doaa' Al-Swarki and Mrs. Alaa' Al-Kharrobi.

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