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Thermodynamic Study of Complexation of Iminobis(N-2-aminoethylacetamide) Polysiloxane Immobilized Ligand System with Co^{2+}, Ni^{2+} and Cu^{2+} Ions

NIZAM M. EL-ASHGAR and ZEYAD J. YASSEEN*
Department of Chemistry, The Islamic University of Gaza, PO Box 108, Gaza, Palestine
E-mail: zyasseen@mail.iugaza.edu.ps; nashgar@mail.iugaza.edu.ps

The thermodynamic parameters characterizing the complexation of Co(II), Ni(II) and Cu(II) metal ions with porous solid iminobis(N-2-aminoethylacetamide) polysiloxane-immobilized ligand system of the general formula $P\text{-}(CH_2)_3\text{-}N(CH_2CONHCH_2CH_2NH_2)_2$, where P represents $[Si\text{-}O]_n$ siloxane network, were investigated. The complexations were achieved at pH 5. The negative values of ΔG and the positive values of ΔH indicate that the complex formation proceeds spontaneously and endothermically. The positive changes of both enthalpy and entropy during the complexation clearly indicate that the driving force for complexation is enthalpically unfavoured but entropically favoured resulting from the dehydration during the complex formation. The plots of log K_D *vs.* the reciprocal of absolute temperature were linear for all studied cases and were utilized to calculate the enthalpies of complexation reactions.

Key Words: Polysiloxanes, Immobilized-polysiloxane ligand systems, Thermodynamic parameters, Thermal stability of complexes, Transition metals.

INTRODUCTION

Polysiloxane immobilized with organic chelating ligands has been widely used in extraction, separation and preconcentration of metal ions[1–9]. These hybrid polymeric supports can be synthesized either by the low temperature sol-gel process or by the modification of pre-prepared polysiloxanes[1–9]. The sol-gel process involves hydrolysis and polycondensation of tetraethylorthosilicate and the appropriate silane coupling agent $(RO)_3SiL$ where L is an organo-functionalized group. Few appropriate silane agents are available, so the modification method was used to introduce many organofunctionalized groups[1–9]. Iminodiacetate derivatives bearing multidentate chelating ligands[7, 8] have been prepared and well characterized. These solid polymeric materials have many advantages over organic polymers due to their high thermal, hydrolytic and mechanical stability in addition to lack of swelling in solvents[10, 11]. In addition to their high capacity to chemisorb many metal ions[1–9] they are also used as stationary phases in chromatography[4] and as supported ligands for heterogeneous catalysis[3, 12]. Many spectroscopic techniques such as solid-state nuclear magnetic resonance (NMR) and photoelectron spectroscopy (XPS) and other spectroscopic methods have been employed to study the ligand-modified polysiloxane systems[13–21]. In this work iminobis(N-2-aminoethylacetamide) polysiloxane-immobilized ligand system was prepared as previously reported and complexed with. Co^{2+}, Ni^{2+} and Cu^{2+} metal ions from aqueous solutions. Evaluation of the thermodynamic parameters for the complexation of polysiloxane immobilized ligand systems with transition metal ions has not been studied before. This study may be useful because of the selection and separation of the chelating functionalized groups closely related to the stability of the complexes formed.

EXPERIMENTAL

Tetraethylorthosilicate, 3-chloropropyl trimethoxystlane, iminodiacetic acid and ethylene diamine were purchased from Merck and used as received. Acetone, diethyl ether and methanol (spectroscopic grade) were used as received. Metal-ion solutions of Cu(II), Ni(II) and Co(II) of the appropriate concentration were prepared by dissolving the metal chloride (analytical grade) in deionized water. pH 5 was controlled by using acetic acid/sodium acetate buffer solutions.

Elemental analyses of carbon, hydrogen and nitrogen were carried out using an EA 11106 CHNS CE elemental analyzer. Concentrations of metal ions in aqueous solutions were measured using a Perkin-Elmer AAnalyst-100 spectrometer. Infrared spectra for the materials were recorded on a Perkin-Elmer FTIR spectrometer using KBr disk in the range 4000–400 cm^{-1}. All pH measurements were obtained using an HM-40V pH-meter. All ligand samples were shaken in aqueous metal ion solutions using an Ultronic OR multi shaker.

Preparation of 3-iodopropyl trimethoxysilane: 3-Iodopropyl trimethoxysilane was prepared as previously described[2, 9], where 3-chloroprdpyl trimethoxysilane was added dropwise with stirring to a solution of sodium iodide in dry acetone, at room temperature.

Preparation of 3-iodopropyl potysiloxane (P-I): Iodopropyl polysiloxane was prepared as previously reported[2, 9] by hydrolysis and polycondensation of 3-iodopropyl trimethoxysilane with tetraethyl orthosilicate in methanol, in the presence of HCl as a catalyst.

Preparation of polysiloxane-immobilized diethyliminodiacetate ligand system (P-DIDA): The immobilized diethyliminodiacetate polysiloxane ligand system (P-DIDA) was first prepared as described before[5] by the reaction of 3-iodoperpylpolysiloxane with diethyliminodiacetate.

Preparation of polysiloxane-immobilized iminobis(N-2-aminoethyl acetamide) ligand system (P-IAEA): The polysiloxane-immobilized iminobis(N-2-aminoethyl acetamide) ligand system was prepared as described previously[22] by the reaction of the immobilized diethyliminodiacetate with an excess of ethytenediamine. The final product was dried at 90°C in a vacuum oven (0.1 torr) for 10 h. The elemental analyses are given in Table-1.

Determination of distribution coefficient: The distribution coefficient of the studied metal ions by polysiloxane-immobilized iminobis(N-2-aminoethyl acetamide) P-IAEA ligand was determined by the batch equilibration method. The metal ion retained in solution after complexation was obtained by atomic absorption spectrometry. The distribution coefficient K_D value is related to the amount of metal ion taken up, the volume of solution and the amount of polysiloxane matrix is defined according to the equation[23]:

$$K_d = \frac{(C_i - C_f)}{C_f} \times \frac{V}{m}$$

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

TABLE-1
ELEMENTAL ANALYSIS DATA FOR THE POLYSILOXANE IMMOBILIZED IODOPOLYSILOXANE (P-I), DIETHYLIMINODIACETATE (P-DIDA) AND THE MODIFIED FORM P-IAEA

Polysiloxane	Element	C (%)	H (%)	I (%)	C/I
P-I	Found	9.2	2.2	32.3	3.0
P-DIDA	Expected*	23.60	3.4	2.40	11.5
	Found	20.80	3.6	1.98	12.3
P-IAEA	Expected*	15.70	2.9	8.40	2.20
	Found	17.10	3.3	9.10	2.20

*The expected values in case of P-DIDA are based on the found results of P-I. In case of P-IAEA they are based on the results found for P-DIDA assuming 100% reactions.

Effect of temperature: The effect of temperature on the amount of metal ion uptake by polysiloxane-immobilized iminobis(N-2-aminoethylacetamide), P-IAEA in aqueous medium was studied by shaking 50 mL of 400 ppm metal ion solutions at various temperatures in the range of 25–60°C. The pH was controlled at pH 5 using acetate buffer solution. In each experiment, 0.1 g of polysiloxane was immersed in a 100 mL conical flask containing 25 mL of acetate buffer solution. The metal ion solution/polysiloxane was then shaken for 48 h (which was found to be sufficient to attain equilibrium). The amount of metal ion remaining in the solution was then estimated by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Synthesis of the iminobis(N-2-aminoethyl acetamide) ligand system (P-IAEA) was achieved as described before[22] *via* three-steps sequence of reactions which are summarized in **Scheme-1.**

The elemental analyses of P-I, P-DIDA and P-IAEA are given in Table-1. From elemental analysis it is clear that there is an increase in nitrogen percentage from 1.98 to 9.1 upon treatment of the immobilized diethyliminodiacetate ligand system with ethylenediamine. The higher values of carbon, hydrogen and nitrogen percentages than those expected for P-IAEA are probably due to the reaction of ethylenediamine with unreacted iodide present in excess in the P-DIDA precursor.

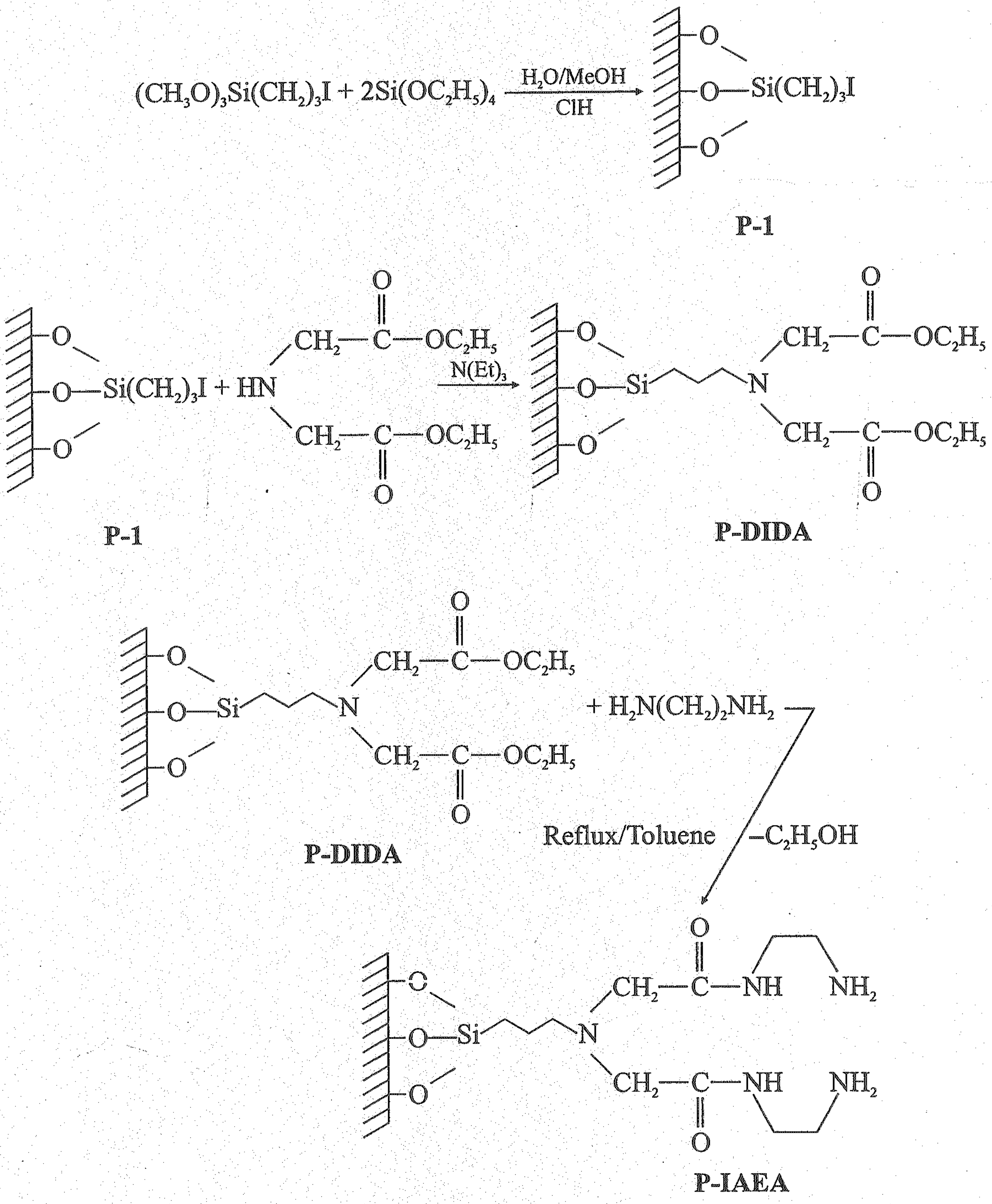
The immobilized iminobis(N-2-aminoethyl acetamide) ligand system (P-IAEA) was well characterized in our previous work[22] using ^{13}C CP-MAS NMR, FTIR, photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) methods.

Thermodynamic studies

The thermodynamic study of complexation reactions of P-IAEA with Co^{2+}, Ni^{2+} and Cu^{2+} metal ions can be achieved by considering the enthalpic and entropic contributions to these reactions. The Van't Hoff enthalpic contributions during the complexation process were determined on the basis of distribution constants (K_d) of each metal ion as a function of temperature in the range of 25-60°C in aqueous medium.

The thermodynamic functions of the studied polysiloxane complexes were evaluated using the well-known relations:

$$\Delta G = -2.303RT \log K_d, \quad \Delta G = \Delta H - T\Delta S \quad \text{and} \quad \Delta S = \frac{\Delta H - \Delta G}{T}$$



Scheme-1

The computed thermodynamic data are represented in Table-2 which showed that, in all cases studied, the complex formation process is favoured at higher temperatures. The distribution coefficient values increased with increasing temperature indicating that the complex formation process of metal ions Cu^{2+}, Ni^{2+} and Co^{2+} with P-IAEA ligand system accompanied by an absorption of heat and enthalpically unfavourable under the studied conditions; so more stable complex is obtained at higher temperature. Comparison of the K_d values collected in Table-2 follows the overall sequence Cu(II) > Ni(II) > Co (II).

TABLE-2
THERMODYNAMIC PARAMETERS OF METAL ION COMPLEXES WITH POLYSILOXANE P-IAEA

Metal ion	T (K)	log K_d	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	$ΔH^{VH}$ (kJ mol^{-1})
Cu^{2+}	298	3.35	−16.62	68.74	3.86 ± 0.45
	308	3.38	−17.03	68.94	
	318	3.47	−18.37	69.91	
	333	3.51	−19.45	70.00	
Co^{2+}	298	3.21	−15.90	71.21	5.33 ± 0.71
	308	3.23	−16.26	71.26	
	318	3.37	−17.81	72.77	
	333	3.42	−18.92	72.84	
Ni^{2+}	298	2.95	−14.64	64.06	4.45 ± 0.23
	308	3.13	−15.79	66.79	
	318	3.16	−16.68	66.46	
	333	3.19	−17.68	66.46	

The negative values of ΔG indicate the high ability of the studied polysiloxane as immobilized ligand to form stable complexes with the studied metal ions and the process tends to proceed spontaneously. However, the obtained positive

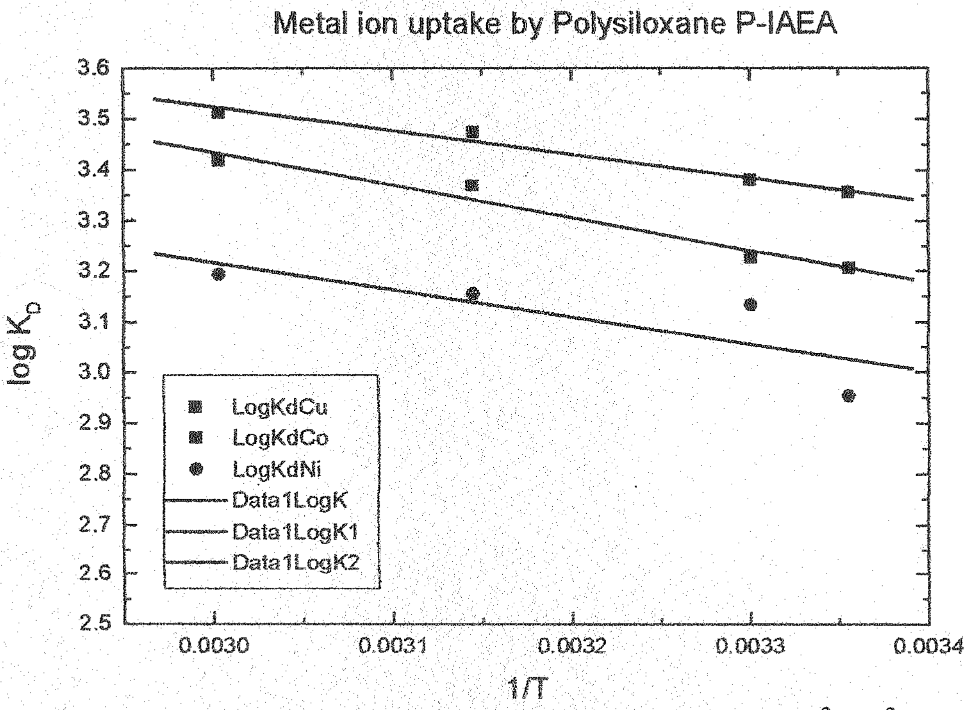


Fig. 1. Distribution coefficient (log K_d) *vs.* 1/T for P-IAEA complexes with Cu^{2+}, Co^{2+} and Ni^{2+} metal ions in aqueous solutions at pH 5

enthalpies reveal that the complexation process is achieved by absorption of heat and is endothermic; so the enthalpic contributions are not the driving force for the complex formation. On the other hand, the positive values of entropy changes are responsible for the complexing process, *i.e.*, the complex formation is entropically favoured under the studied conditions. It has been reasonably assumed that the increase in entropy upon complexation is due to dehydration during the complexation process.

In conclusion, the immobilized iminobis(N-aminoethylacetamide) ligand system was prepared by stepwise modification of the prepared 3-iodopropylpolysiloxane. Thermodynamic studies showed that the immobilized ligand forms quite stable complexes with the divalent Cu^{2+}, Ni^{2+} and Co^{2+} metal ions and the driving force for the complexation reaction is the entropy.

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