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Complexation and thermodynamic studies of polysiloxane iminobis (N-diethylenediamineacetamide) ligand system with some transition metal ions

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ABSTRACT

Complexation and thermodynamic studies of insoluble porous solid polysiloxane immobilized ligand system bearing chelating ligand group of the general formula $P-(CH_2)_3-N[CH_2CONH(CH_2)_2NH(CH_2)_2NH_2]_2$, (Where P represents $[Si-O]_n$ polysiloxane network) were studied. The Batch equilibration method has been performed to calculate the distribution coefficient (K_D) and the thermodynamic parameters (ΔG^o , ΔH^o , and $T\Delta S^o$) for the stoichiometric 1:1 complexation of Co^{2+}, Ni^{2+}, and Cu^{2+} ions with iminobis(diethylenediamineacetamide) polysiloxane. The complexation behavior at pH 5 in aqueous media is discussed from the thermodynamic point of view.

KEYWORDS

Thermodynamic parameters;
Thermal stability;
Metal uptake;
Iminodiacetic acid;
Diethylenetriamine;
Polysiloxane-immobilized ligand systems.

INTRODUCTION

Many research concerning the synthesis of insoluble polysiloxane immobilized ligand systems, have been reported[1-21]. These functionalized polysiloxanes have been prepared by two methods. The first method; using the sol-gel process by hydrolytic polycondensation of tetraethylorthosilicate (TEOS) and the appropriate silane coupling agent $(RO)_3SiX$, where X=ligand group)[1,2]. The second method is by modification of a pre-prepared polysiloxane with a silane coupling agent containing the appropriate functional group[13-21]. These hybrid materials show high thermal, hydrolytic and mechanical stability over the organic polymers[5,6]. These polysiloxane immobilized ligand systems have several applications such as extraction, recovery and separation of metal ions[13-21]. They also used as supports for heterogeneous catalysis and chromatography[2,11,22]. These materials have been characterized recently by many techniques including high-resolution solid state NMR[23-26], XPS analysis and thermal analysis[27-35]. In this work iminobis(N-diethylenediamineacetamide) polysiloxane-immobilized ligand system was prepared as previously reported[36] and complexed with Co^{2+}, Ni^{2+} and Cu^{2+} metal ions from aqueous solutions. This study may be useful because the selection and separation of the chelating functionalized ligand system closely related to the stability of the complexes formed.

EXPERIMENTAL

Reagents and materials

Tetraethylorthosilicate, 3-chloro propyl trimethoxysilane, iminodiacetic acid and diethylenetriamine were purchased from (MERCK) and used as received. Acetone, diethyl ether and methanol (spectroscopic grade) were used as received. Metal(II) solutions of the appropriate concentrations were prepared by dissolving the metal(II) chloride (analar grade) in deionized water. pH values were controlled by using acetic acid/sodium acetate buffer solutions.

General techniques

Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. XP spectra were obtained using a Kratos Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). ^{13}C CP-MAS Solid State NMR experiments were carried out at room temperature on Bruker MSL-400 MHz spectrometer at frequency of 100. 6 MHz (^{13}C) using a bruker CP/MAS probe. Thermogravemetric analysis TGA and DTG was carried out using METZSCH Simultaneous Thermal Analyzer STA 409 in the range of 293-873 K under nitrogen. The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer AAnalyst-100, spectrometer. The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR, spectrometer using KBr disk in the range 4000 to 400cm^{-1}. All pH measurements were obtained using HM-40V pH Meter. All ligand samples were shaken in aqueous metal ion solutions using an ELEIA-Multi Shaker.

Preparations

Preparation of 3-iodopropyltrimethoxysilane (L-I)

The 3-iodopropyltrimethoxysilane was prepared as previously described[7], where 3-chloropropyltrimethoxysilane was added dropwise with stirring to a solution of sodium iodide in dry acetone, at room temperature.

Preparation of 3-iodopropylpolysiloxane (P-I)

3-Iodopropylpolysiloxane was prepared as previously reported[7] by adding 3-iodopropyl trimethoxysilane to stirred solution of tetraethylorthosilicate in the presence of HCl as a catalyst.

Preparation of polysiloxane-immobilized diethyliminodiacetate ligand system (P-DIDA)

Diethyliminodiacetate polysiloxane was prepared as reported before[13] by adding diethyliminodiacetate to the iodopolysiloxane in toluene. The elemental analysis for the diethyliminodiacetate polysiloxane is given in TABLE 1.

Preparation of iminobis (diethylenediamineacetamide) Polysiloxane (P-IDEA)

Diethyliminodiacetate polysiloxane (10.0g) was added to an excess of 10.0g diethylenetriamine, in 50cm^3 toluene. The mixture was refluxed at 383 K for 48 h under nitrogen. The mixture was cooled, and the solid product was filtered, washed with successive portions of 50 cm^3 water, methanol and diethyl ether. The final product was dried at 363 K in vacuum oven (0. 1 torr) for 10 h[36], (Scheme 1).

Determination of distribution coefficients

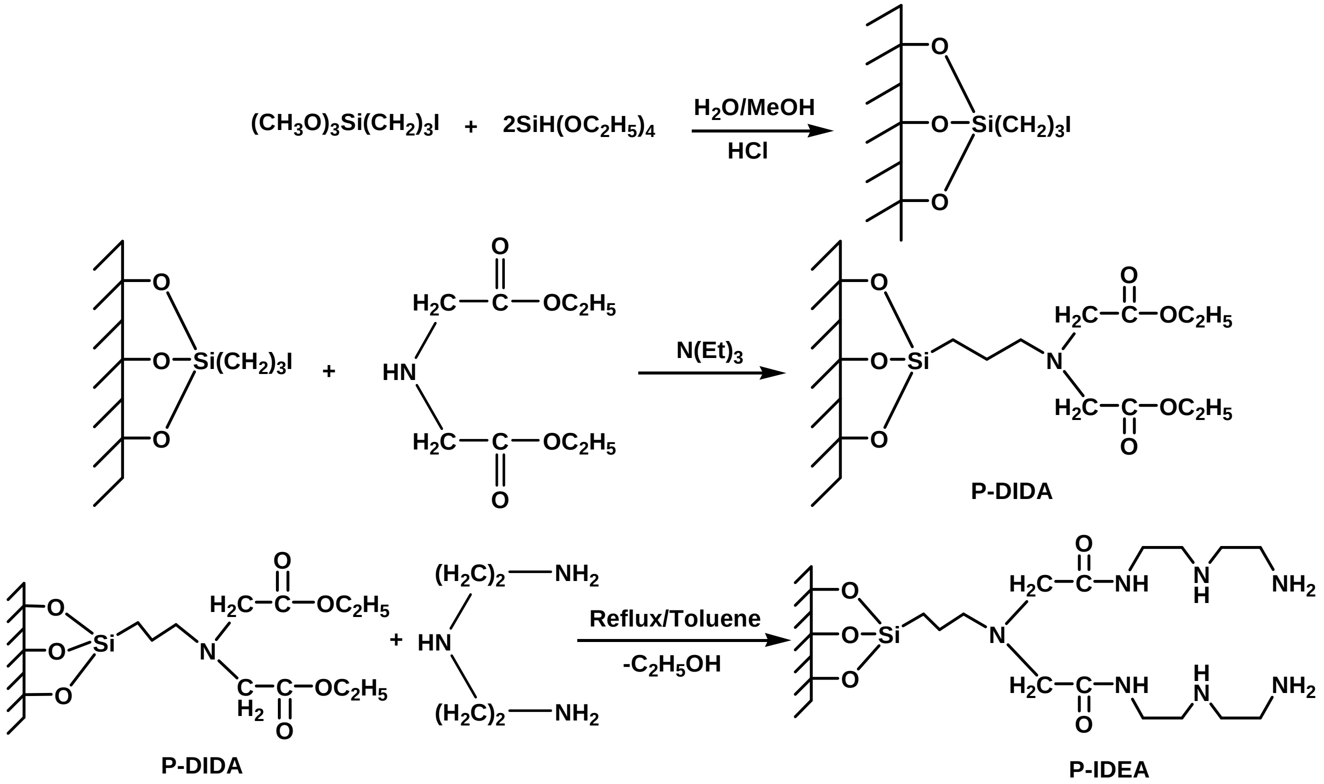
The distribution coefficient values of the studied metal ions by P-IDEA polysiloxane ligand were determined by the batch equilibration method where 0.15 g of the ligand were immersed in 50cm^3 of a solution containing 400 ppm each of Cu^{2+}, Ni^{2+}, and Co^{2+} at different temperatures. The metal ion retained in solution after complexation was determined by atomic absorption spectrometry. The distribution coefficient K_D values is related to the amount of metal ion taken up, the volume of solution and the amount of polysiloxane matrix and is defined according to the equation[37]:

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

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.

Effect of temperature

The effect of temperature on the amount of metal ion uptake by polysiloxane-immobilized P-IDEA in aqueous medium was studied. In each experiment, 0.10g of polysiloxane resin was suspended in 100cm^3



Scheme 1

of aqueous solution containing 400 ppm of each metal ion solution studied. The solution was shaken in ELEIA-Multi-Shaker for 48 h thermostated at the intended temperature in the range of 298-333 K. The pH was controlled at pH 5 using acetate buffer solution. After the equilibrium was attained at 72 h shaking time as reported for such systems[15-21], the amount of metal ion remained in the solution was estimated by atomic absorption spectrometry.

RESULTS AND DISCUSSIONS

Preparation of the immobilized ligand system (P-IDEA)

The iminobis(diethylenediamineacetamide) polysiloxane immobilized ligand system was prepared as previously reported[37] *via* three-steps sequence of reactions which summarized in Scheme 1. The elemental analysis results of both P-DIDA and P-IDEA are given in TABLE 1.

It is obvious from TA 1 that there is an increase in nitrogen percentage from 1.73 to 11.0 by treatment of the immobilized diethyliminodiacetate ligand system with diethylenetriamine. A slightly higher values of carbon, hydrogen and nitrogen percentages for P-IDEA, compared with the expected values are observed. This is probably due to the reaction between the diethylenetriamine molecules with the unreacted iodide atoms.

The immobilized iminobis (diethylene diamineacetamide) ligand system (P-IDEA) was well characterized in our previous work[37] using ^{13}C CP-MAS NMR, FTIR, photo electron spectroscopy (XPS) and thermogravimetric analysis (TGA) methods. This characterization is discussed briefly below.

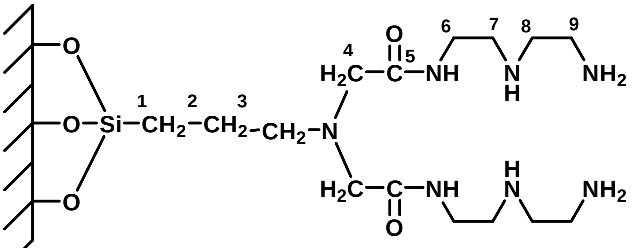
FTIR spectra

The FTIR spectra of the diethyliminodiacetate; P-DIDA and iminobis (diethylenediamineacetamide); P-IDEA, ligand systems show three regions of absorptions at 3500-3000cm^{-1}, 1750-1650cm^{-1} and 1200-900cm^{-1} due to ν(OH), ν(C=O) and ν(Si-O) respectively[32-33].

The FTIR spectrum of P-IDEA shows a strong absorption band at 1658cm^{-1} and no bands at 1740cm^{-1} which provide a strong evidence for a complete reaction between P-DIDA and diethylenetriamine[36].

^{13}C CP-MAS NMR spectra

The ^{13}C CP-MAS NMR spectrum for P-IDEA (Scheme 2) is shows signals at 11.1, 21.2 and 40.6ppm, corresponding to three methylene carbon atoms C1, C2 and C3. The spectrum shows the carbonyl carbon, C5 at 173.7ppm and the methylene carbon C4 at 59 ppm. An intense signal at 49.5ppm was observed which involve the four methylene carbons C6, C7, C8 and C9[36]. These assignments were based on spectral data of similar systems[23-26].



Scheme 2

Thermal analysis

Thermogravimetric analysis suggested that this immobilized ligand system is thermally stable at ambient temperature and only about 17% weight lost at temperature range 323-475K which attributed to evaporation of volatile physisorbed species such as water and alcohols and solvent from the polysiloxane pores without changing the polysiloxane matrix. While about 34 % of the initial weight lost up to 716K with some modification in the surface and bulk of the immobilized ligand system. Further lost in weight (about 5 %) occurred in the range of 673-873K leading to formation of silica like network[36].

XPS results

The XPS survey spectra for P-IDEA displayed the main peaks for Si2p, C1s, N1s and O1s centred at 103, 285, 400 and 532eV, respectively. It is interesting to note the intense N1s peak due to the seven nitrogen atoms per ligand[36].

Thermodynamic parameters

To elucidate the thermodynamic origins of immobilized ligand complexation with the examined metal ions, the thermodynamic quantities upon complexation were determined. TABLE 2 summarizes the temperature dependence of the thermodynamic parameters for the complexation of P-IDEA immobilized ligand with Cu^{2+}, Co^{2+}, and Ni^{2+} metal ions. As can be recognized readily from TABLE 2, the values of enthalpic and entropic contributions are positive which indicates that the complexation is driven predominantly by favorable entropic change, showing larger entropic contribution ($T\Delta S°$ ranging from 18. 5 to 31. 7kJ/mol) and somewhat smaller positive enthalpic contribution ($\Delta H°$ ranged from 2. 0 to 12. 5kJ/mol). This behavior can be explained by the extensive desolvation of both ligand and the examined divalent metal ions during the complexation, affording the highly positive entropy change upon complexation.

The thermodynamic study of complexation reactions of P-IDEA ligand 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 298-333K in aqueous medium.

The thermodynamic functions of the studied polysiloxane complexes were evaluated using the standard relationship:

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T}$$

Where T is the absolute temperature and $\Delta G°$ is evaluated from the distribution coefficient, K_D, as

$$\Delta G° = -2.303 \log K_D$$

The distribution coefficient values and the thermo-

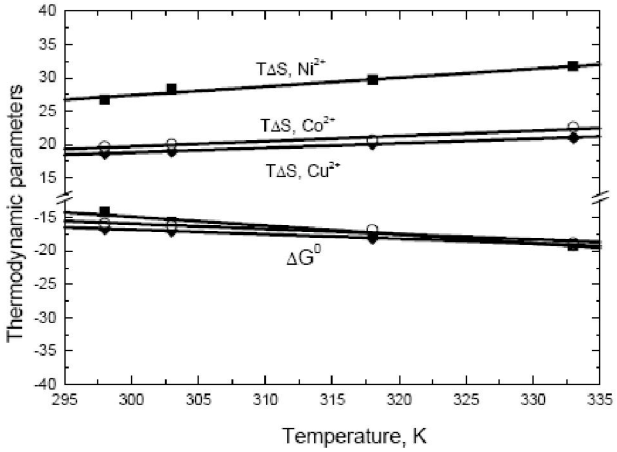


Figure 1 : Dependence of thermodynamic parameters ($T\Delta S°$ and $\Delta G°$) for the immobilized ligand P-IDEA with Cu^{2+} (◆), Co^{2+} (○) and Ni^{2+} (■) metal ions in aqueous solutions at pH 5. The lines represent the linear regression analysis of the experimental data for the divalent metal ions studied.

TABLE 1 : Elemental analysis data for the polysiloxane immobilized; 3-iodopropylpolysiloxane(P-I), diethyliminodiacetate (P-DIDA) and iminobis (diethylenediamineacetamide) (P-IDEA)

Polysiloxane	Element	C%	H%	I%	C/I
P-I	Found	9.0	2.2	32.3	3.0
Polysiloxane	**Element**	**%C**	**%H**	**%N**	**C/N**
P-DIDA	Expected*	22.6	3.4	2.4	11. 0
	Found	18.8	4.1	1.73	12.7
P-IDEA	Expected*	19.5	3.7	10.6	2.2
	Found	23.5	5.9	11.0	2.5

***The expected values in case of P-DIDA is based on the found results of P-I, While in case of P- P-IDEA is based on the found results of P-DIDA assuming 100% reactions.**

TABLE 2 : Thermodynamic parameters of metal ions chemisorbed by P-IDEA at pH 5

Metal ion	T (K)	Log K_D	ΔG^o (kJmol^{-1})	ΔS^o (Jmol^{-1}K^{-1})	ΔH^{VH} (kJmol^{-1})
Cu^{2+}	298	3. 37	-19.23	79. 66	4.51±0.77
	308	3. 37	-19.87	79. 16	
	318	3. 43	-20.88	79.84	
	333	3. 45	-21.99	79.60	
Co^{2+}	298	3. 21	-18.32	90.60	8.67±5.81
	308	3. 23	-19.05	90.00	
	318	3. 19	-19.42	91.20	
	333	3. 40	-21. 68	91.14	
Ni^{2+}	298	2.87	-16. 37	151.21	28.69±6.18
	308	3.13	-18.46	153.10	
	318	3.26	-19.84	152.61	
	333	3.47	-22.12	152.60	

dynamic parameters computed are listed in TABLE 2. The standard Gibbs energies of reaction, ΔG°, and the standard entropies of complexation, ΔS°, were calculated directly from the calculated distribution coefficient.

It is obvious that, in all cases studied, the complex formation process is favored 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-IDEA ligand system accompanied by an absorption of heat and enthalpically unfavorable under the studied conditions, so more stable complex is obtained at higher temperature.

Figure (1) shows the temperature dependence of thermodynamic parameters ΔG° and TΔS° for ligand complexation with Cu^{2+}, Ni^{2+}, and Co^{2+} with temperature. The signs of enthalpic and entropic changes may provide some clues to the kind of interaction involved through the complexation process. 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 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. As can be recognized readily from figure (1) and TABLE (2), the values of enthalpy changes and entropy changes of complexation are positive in the range of temperature studied. These results indicate that the complexation of polysiloxane P-IDEA ligand with the divalent ions examined is driven predominantly by the favorable entropic change, typically showing large positive entropy change (TΔS° ranging between 18.66 and 32.70kJ/mol) and somewhat smaller positive enthalpy changes (ΔH° ranging between 1.96 and 12.45kJ/mol). The positive entropic contributions can be explained by the dehydration of metal ions upon complexation with P-IDEA ligand and therefore is accompanied by an entropic gain from the transfer of water molecules into the bulk solvent. These larger positive entropic contributions and somewhat smaller positive enthalpic ones can be explained by the enthalpy-entropy compensation process.

CONCLUSION

The immobilized iminobis(N-aminoethylacetamide) ligand system was prepared by step-wise modification of the prepared 3-iodopropylpolysiloxane. On the other hand, the complexation of the immobilized ligand with the studied divalent metal ions is entropically driven over the temperature studied.

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