Journal of Sciences, Islamic Republic of Iran 13(3): 217-223 (2002)
National Center For Scientific Research, ISSN 1016-1104

STUDY ON THE COMPLEX FORMATION BETWEEN *N*-PROPYLSALICYLIDENE BASED ON SILICA AS ION EXCHANGER AND SOME TRANSITION METAL IONS

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Abstract

N-propylsalicylidene based on silica as ion exchanger (IE) was used for the separation by complexation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+}, and UO_2^{2+} from their parent solutions. IE and its metal complexes are characterized by elemental analysis, electronic and infrared spectra, in addition to thermal analysis in atmospheric pressure. The mode of chelation and the proposed geometric structures of the metal complexes of IE are suggested by infrared and electronic spectra, respectively. Elemental and thermal analysis indicate that the percentage of the organic content increased from IE-Cr (5.409) to IE-Hg (13.5) with respect to that of IE (13.655) owing to the catalytic effect of these metal ions. Three different stages of decomposition have been accompanied by the thermal degradation of IE and IE-metal complexes. These stages were found to be affected by the presence of the investigated metal ion. By application of non-isothermal kinetic equation, the activiation energy (E_a) for the IE and its complexes was calculated. E_a follows the order, IE-Fe < IE-Co < IE < IE-Mn < IE-UO_2 < IE-Cr < IE-Ni < IE-Cu < IE-Hg. The thermodynamic parameters Ea, $\Delta H°$, $\Delta S°$ and $\Delta G°$ of the obtained complexes were found to be largely dependant on the electronegativity of the studied metal ions.

Keywords: *N*-propylsalicylidene; Ion exchanger; Transition metal ions

Introduction

The determination of trace heavy metals has attracted interest not only because of the wide spread agricultural, chemical and industrial uses of the compounds containing these ions, but also because of its hazardous effects to human health [1].

Due to the low concentration of heavy metal ions and the possible matrix interferences, the determination of these ions is difficult. Therefore, different techniques

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were used to preconcentrate and separate heavy metal ions as preliminary steps. Chelating ion exchange is the most proper technique for separation and determination of heavy metal ions [2].

Silica has been widely studied as an alternative support for the immobilization of chelating agents due to its commercial availability, high surface area and good mechanical stability [3-7]. Preconcentration and separation of Cu and Cd from their solutions were carried out by using silane-3-aminopropyltriethoxy-modified silica [8]. Koklo *et al.* [9] studied the sorption of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) on mono-, di-, tri- and tetramine based on silica gel matrix. The use of the tri- and tetramine phases was found to be better than the mono-and di-phases especially in case of Cu (II) and Ni (II).

V, Co, Ni, Ga, Y, Mo, Cd, Ce, Pr, Nd, Sm, Eu, Cd, Tb, Dy, Ho, Er, Tm, Yb, La, W and U with concentration range over six orders (10 μg - 0.01 $mg.l^{-1}$) in seawater were preconcentrated and separated by fluorinated metal alkoxide glass-immobilized-8-hydroxy quinoline [10].

In general, several trials have been done to study the preconcentration and separation of heavy metals from their solutions into modified or unmodified surface of silica [11-17].

Our previous investigations were focused on using cellulose-HYPHAN as ion-exchanger to separate Hg^{2+}, In^{3+}, Cr^{3+}, Mo^{4+} and Mn^{2+} from their aqueous solutions and studied the nature of bonding between these metal ions and the ion exchanger [18-21]. As a continuation, this work is aimed to study the nature of bonding between *N*-propylsalicylidene immobilized on controlled-pores silica, as ion exchanger, with the heavy metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+}, and UO_2^{2+} separately.

Experimental Section

Synthesis of the Ion Exchanger (IE)

N-propylsalicylidene based on silica was prepared as follows: Porous silica (PS) was prepared by acid leaching of sieved borosilicate glass (BSG), particle size < 70 μm, obtained by the sol-gel technique. The grafting with 3-aminopropyltrimethoxysilane (APMS) was achieved by refluxing 18 g PS with 36 ml APMS in xylene at 80ºC for 24 h. Eleven grams of the yield was washed with ethyl alcohol and refluxed with 15 ml salicylaldehyde in 50 ml dimethyl sulfoxide (DMSO) at 90°C for 24 h. The obtained ion IE (yellow) was washed with EtOH and dried at 80°C. A scheme of the preparation process is given in Figure 1.

Synthesis of Complexes

Complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+}, and UO_2^{2+} with IE were prepared. Equimolar amounts of IE and respective metal acetate (except for Fe and Hg where their chlorides were used) were refluxed in absolute EtOH solution for 3 h. The yield was washed thoroughly with EtOH and dried at room temperature under vacuum.

Measurements

Elemental analyses (Si, M and Cl) were performed on scanning electron microscope (SEM), model Philips XL 30 attached with EDX unit with accelerating voltage 30 kV, magnification up to 400,000x and resolution for w (3.5 mm). These samples has been coated previously with carbon. Water and organic matter content were calculated from the weight loss at 150 and 500°C, respectively obtained from TGA curves. pH-metric titration was performed to evaluate the capacity of the ion-exchanger. One hundred mg of IE was stirred with 25 ml of 0.01 M HCl and titrated against 0.0075 M NaOH.

Electronic spectra were measured with a Shimadzu UV-160 A recording spectrophotometer. The sample was grinded with nujol and a strip of Whatmann filter paper was soaked in the yielded slurry then put in the quartz cell and a strip of Whatmann filter paper wetted with nujol only, was used as blank. Infrared reflectance spectra were recorded on a Bruker IFS 48 FTIR spectrometer using a gold ball as reference. The sample in the form of fine powder was flattened on a stainless steel sheet with a drop of acetone which was allowed to vaporize then the reflectance spectrum was measured in a dry CO_2 free air atmosphere. This measurement was kindly performed in the Physikalisch Technische Bundesanstalt Braunschweig, Germany. Thermal analysis was carried out under N_2 atmosphere using a Shimadzu DTA-50 and TGA-5.

Results and Discussion

Chemical Analysis

The capacity of IE, evaluated using pH-metric titration, was found to be 0.44 m. eq./g. In view of this appreciable capacity, IE showed good efficiency of separation of different metal ions at different pH values. Table 1 shows representative examples (Fe, Co and Ni) of the distribution coefficient (K_d, cm^3 g^{-1}) and the recovery (R %) of these metal ions using the IE.

The chemical composition of the prepared ion-exchanger (IE) and its complexes with Mn^{2+}, Co^{2+}, Ni^{2+},

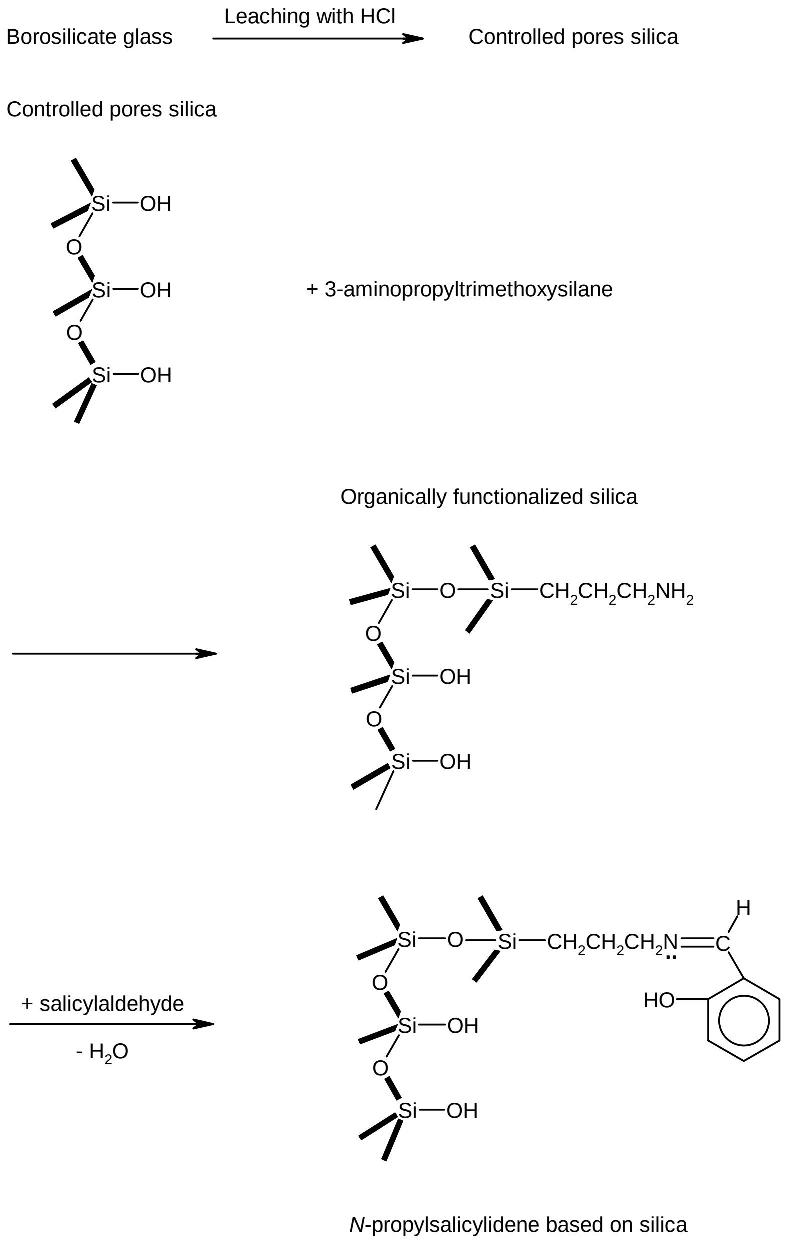

Figure 1. Immobilization of *N*-propylsalicylidene on controlled-pores silica.

Hg^{2+}, Cr^{3+}, Fe^{3+} and UO_2^{2+} using the EDX and TG data are listed in Table 2. The results indicate that the organic matter (%) increased from Cr (5.409) to Hg (13.5). This means that the organic substrates dissociate partially during the complexation process and decrease in the following order:

IE > IE-Hg > IE-Ni > IE-Co > IE-Fe > IE-UO_2 > IE-Cu > IE-Mn > IE-Cr

This sequence may be explained in view of the catalytic effect of these cations in catalyzing the hydrolysis of the Schiff base substrate, as the Cr (III) has the highest effect and Hg (II) has the lowest one.

Electronic Spectra

The band position and calculated ligand filed parameters of the IE-metal ion complexes are listed in Table 3.

Absorption spectra of IE itself show various bands below 25,000 cm^{-1} that can be assigned to intraligand transitions of the free uncomplexed IE.

The UV spectrum of the uranyl complex shows a band at 24,390 cm^{-1} assigned to the transition $^1\Sigma^+g \rightarrow {}^2\pi_4$ of the dioxouranium (VI) [22]. This band is similar to the OUO symmetric stretching frequency for the first excited state [23].

The electronic spectrum of the chromium complex shows several bands in the regions 17,953 (ν_1) and 25,907 (ν_2) cm^{-1}. The expected ν_3 band on our instrument which might be hidden below ν_2 was not observed. The three spin allowed transitions for chromium (III) in octahedral field are as follows: $^4A_{2g}$ (F) → $^4T_{2g}$ (F) (ν_1), $^4A_{2g}$ (F) → $^4T_{1g}$(F) (ν_2) and $^4A_{2g}$ (F) → $^4T_{1g}$(P) (ν_3). The ν_1 transition is a direct measurement of the ligand field parameter 10 Dq. From ν_1 and ν_2, the Racah interelectronic repulsion parameter B^- and the nenephelauxetic parameter β are computed ($\beta = B^-/B$, B for free ion is taken to be 918 cm^{-1}) [24].

Table 1. Typical values of recovery (R %) and distribution coefficient (K_d) for Fe, Co and Ni at different pH values

pH	Recovery (R %)			Log K_d		
	Fe	Co	Ni	Fe	Co	Ni
7.7	99.0	62.5	47.0	5.09	3.32	3.00
9.6	99.0	98.0	98.1	5.09	4.86	4.79
5.6	96.4	11.73	15.1	4.53	2.22	2.50

Table 2. Chemical composition of the prepared ion exchanger (IE) and its metal-complexes

Complex (color)	Constituent %	
	H_2O	Organic matter
IE (yellow)	6.096	13.655
IE-Mn(II) (yellowish-brown)	5.035	5.892
IE-Co(II) (green)	7.389	10.550
IE-Ni(II) (green)	5.573	12.110
IE-Cu(II) (green)	6.026	6.431
IE-Hg(II) (yellow)	7.500	13.500
IE-Cr(III) (green)	7.063	5.409
IE-Fe(III) (dark orange)	7.744	7.214
IE-UO_2 (yellow)	6.143	6.489

Table 3. Electronic bands and ligand field parameters of IE-metal ion complexes

Complex	Band position cm^{-1}	Dq	β	B
IE-Mn	14,409, 17,544, 25,250	660	0.63	600
IE-Co	15,670, 16,980, 20,200	–	–	–
IE-Cu	14,450, 24,000	–	–	–
IE-Cr	17,953, 25,907	1795	0.90	827
IE-Fe	14,285, 21,270, 25,250	655	–	595
IE-UO_2	24,390	–	–	–

The electronic spectrum of the Mn complex, shows three bands at 14409, 17544 and 21,505 cm^{-1} assigned to $^6A_{1g}$ → $^4T_{1g}$, $^6A_{1g}$ → $^4T_{2g}$(G) and $^6A_{1g}$ → $^4T_{2g}$(D) transitions [25], respectively. The calculated B^-, β and Dq values lie in the same range as reported for octahedrally coordinated Mn(II) ion [26]. On increasing delocalisation, β decreases less than unity in the complex.

The electronic spectrum of Fe-complex shows several bands at 14,285, 21,270 and 25,250 cm^{-1} assigned to $^4T_{1g}$ → $^6T_{1g}$ (G) and $^4T_{1g}$ → ^4E_g (G) transitions. Although d-d transitions are forbidden in high spin iron (III) complexes, the high intensity band at 25,250 cm^{-1} may be ascribed to borrowing of intensity from a low lying charge transfer ligand band [27].

The electronic spectrum of the green Co(II) complex exhibits one intense band at 15,670 cm^{-1} attributed to $^4A_2$ → $^4T_1$ (P) transition in a tetrahedral structure. The shoulder at 16,980 cm^{-1} may be due to spin coupling [28]. Another weak band at 20,200 cm^{-1} attributed to $^4A_2$ (F) → $^4T_1$(F), indicates tetrahedral stereochemistry for this complex. The green color is an additional evidence for this structure.

The spectra of Cu(II) complexes exhibit two bands, an asymmetric broad band at 14,450 cm^{-1} which is assigned to the $^2T_{2g}$ → ^2E_g transition and a more intense band at 24,000 cm^{-1} which is assigned to ligand to metal charge transfer transition [29]. Some authors have attributed the presence of this band to polymeric structures of the copper complexes [30]. The band position is in agreement with those generally observed for square-planar copper(II) complexes [31].

Infrared Spectra

IR spectra of IE show three bands at 1,100, 800 and 463 cm^{-1} assigned to ν (Si-O), ν (Si-O-Si) and δ (Si-O-Si), respectively [32].

IR bands related to the organic moiety of the ion exchanger are observed as a weak bands or shoulders in relation to that of silicate. A shoulder at 1,620 cm^{-1} assigned to azomethine group ν (C=N) and a weak band at 1,406 cm^{-1} assigned to ν (C-N) have been detected in the infrared spectra of the ion exchanger [33]. Another two bands are observed at 1,533 and 1,453 cm^{-1} assigned to ν (C=C) and the CH_2 deformation band, respectively. The weak band at 1,498 cm^{-1} is assigned to δ (N-H) in plane yielded from the tautomeric enamine. In order to confirm the presence of such bands, the IR spectra of the monomer phase were performed and the same bands were detected as separate ones.

The infrared spectra of all studied complexes show that the ion exchanger behaves as a bidentate lignad coordinating through deprotonated OH group and the nitrogen of azomethine group. This mode of complexation is confirmed by the shift of ν (C=N) and ν (C-N) to a lower wavenumbers and the disappearance of the band due to δ (N-H) in plane.

Thermal Analysis

The TG curve of the ion exchanger IE shows that the ion exchanger is thermally degraded in three steps. The first one starts from the room temperature and ending at ~150°C and it is attributed to the moisture content. The degradation of the organic part of the IE is occurred during the second step in two stages 150-480°C. The third stage occurs in the 750-850°C range, may be due to dehydration of the OH groups on the amorphous porous silica surface changing to crystoballite [34]. Representative TG curves of the ion exchanger and its complexes with Cr(III) and Hg(II) are shown in Figure 2.

The activation energy of the second stage which represents the main degradation of the IE was calculated by applying the general rate expression of the thermal degradation of the materials [35].

$$R_t = -\,(dW/dt) = (A/R_H)\, e^{-E_a/RT} \,.\, W^n \qquad (1)$$

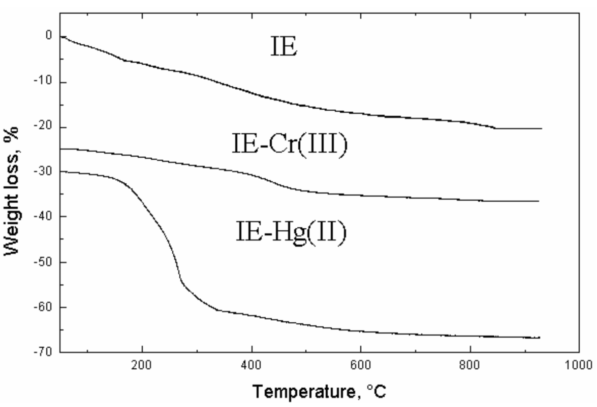

Figure 2. Thermogravimetric analysis of the Schiff-base ion exchanger IE and its complexes with Cr(III) and Hg(II).

where W is the weight of the active material remaining for a particular reaction, R_t is the rate of decomposition, R_H is the rate of heating, dW/dt is the rate of degradation, A is the frequency factor, E_a is the activation energy, R is the gas constant, and n is the reaction order.

Equation (1) can be rearranged to give,

$$\ln R_t = \ln A - E_a/RT + n \ln W \qquad (2)$$

when W is kept constant, and application of non-isothermal kinetic equation

$$\ln \alpha - 2 \ln T = \ln A - E_a/RT \qquad (3)$$

where α is the weight loss percentage.

Thus a plot of (ln α − 2 ln T) *vs.* 1/T (Fig. 3) should be linear with a slope from which the values of E_a of IE and its metal complexes are calculated (Table 4). E_a has the following order:

IE-Fe < IE-Co < IE < IE-Mn < IE-UO_2 < IE-Cr < IE–Ni < IE-Cu < IE-Hg

The high activation energy for all complexes, except for Fe and Co compared with IE itself, indicates higher stability of such chelates. Decreasing the activation energy in case of Fe and Co chelates indicates the catalytic effect of such metal ions which results in accelerating the decomposition process.

A plot of log R_t *vs.* time (Fig. 4) gives straight lines for IE decomposition and its metal complexes. This linearty confirms the suggested first-order rate constants of the thermal decomposition process.

In addition to activation energy, the thermodynamic parameters were calculated and listed in Table 4. The order of decreasing E_a was almost observed with ΔH° and ΔG° while in case of ΔS° the opposite sequence was obtained. The positive values of entropy change ΔS°, indicate that the decomposition reaction is accompained by increasing the disorder of the system. The positive sign of enthalpy change ΔH°, indicates that the decomposition processes of IE and its complexes are endothermic.

It is worthy to mention that the electronegativity and the oxidation state of the metal ions was found to affect the calculated thermodynamic parameters of the thermal degradation of the organic constitituent [36]. There was a significant relationship between E_a, ΔH°, ΔS° and ΔG° of the complexes of divalent cations with the IE and the corresponding electronegativity of the chosen metals (correlation coefficient (r)= 0.91, 0.92, −0.90 and 0.93 respectively) except for copper.

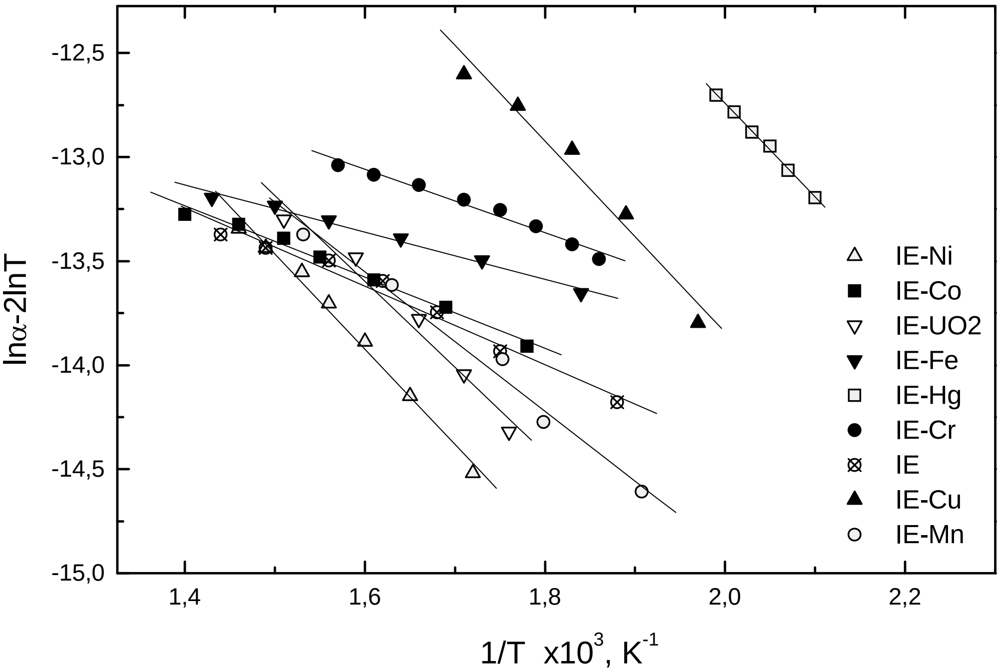

Figure 3. Plot of ln α −2 ln T for IE and its metal complexes.

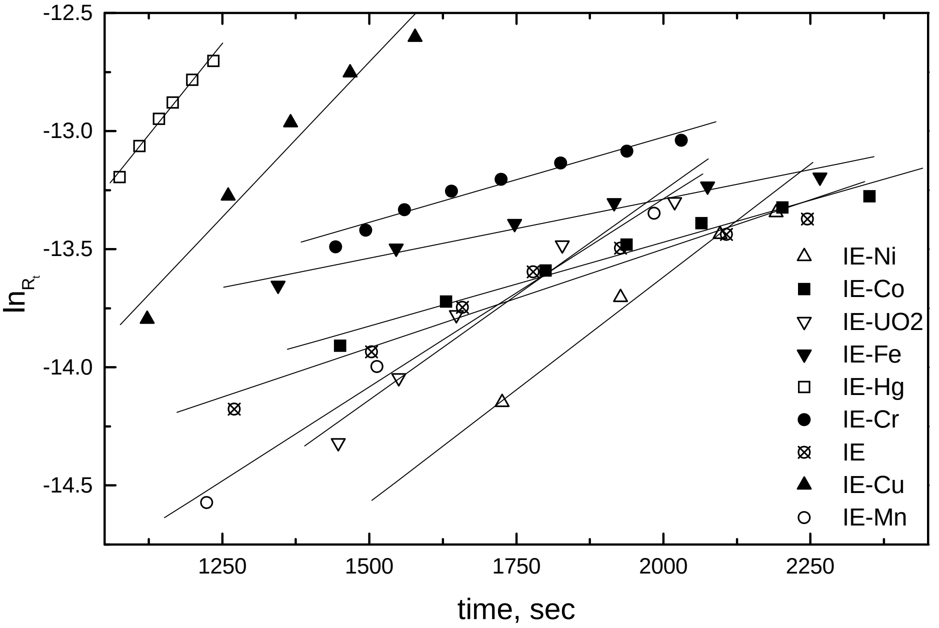

Figure 4. Variation of $\ln R_t$ with time for IE and its metal complexes.

Table 4. Values of E_a, $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the second step in the degradation process of IE and its metal complexes

Complex	**E_a (KJ mol^{-1})**	**$\Delta H°$ (KJ mol^{-1})**	**$\Delta G°$ (KJ mol^{-1})**	**$\Delta S°$ (J K^{-1} mol^{-1})**
IE	15.73	10.65	−92.07	168.84
IE-Mn	27.12	21.80	−91.85	178.17
IE-Co	14.35	9.22	−93.53	167.10
IE-Ni	38.37	32.98	−87.31	186.16
IE-Cu	39.15	33.59	−90.67	186.55
IE-Hg	49.73	45.74	−53.94	208.34
IE-Cr	37.39	33.13	−63.63	189.48
IE-Fe	9.59	4.40	−96.57	162.35
IE-UO_2	33.66	28.29	−89.45	182.81

Conclusion

N-propylsalicylidene based on silica ion exchanger was proved to form complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+}, and UO_2^{2+} elements which is an integral part in the separation process.

The structure of prepared complexes were confirmed by IR spectroscopy. The geometry of studied complexes was suggested by electronic spectra. A significant correlation between the calculated thermodynamic parameters of degradation and the electronegativity of the studied metals were confirmed.

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