Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 723–736

THERMAL DECOMPOSITION OF CHLOROMETHYLATED POLY(STYRENE)-PAN RESIN AND ITS COMPLEXES WITH SOME TRANSITION METAL IONS

I. M. M. Kenawy[*], *M. A. H. Hafez and R. R. Lashein*

Department of Chemistry, Faculty of Science, University of Mansoura, Mansoura, Egypt

(Received July 6, 2000; in revised form February 18, 2001)

Abstract

The complexes formed by the chemically modified chloromethylated poly(styrene)-PAN (CMPS-PAN) as a resin chelating ion exchanger were characterized by infrared and potentiometry. The thermal degradation of pure CMPS-PAN resin and its complexes with Au^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Pt^{4+} in air atmosphere has been studied using thermal gravimetry (TG) and derivative thermal gravimetry (DTG). The results showed that four different steps accompany the decomposition of CMPS-PAN resin and its complexes with the metal ions. These stages were affected by the presence of the investigated metal ions. The thermal degradation of CMPS-PAN resin in the presence of the ions showed different stability of the resin in the following decreasing order: $Au^{3+}>Pt^{4+}>Mn^{2+}>Cu^{2+}>Cr^{3+}>Fe^{3+}$. On the basis of the applicability of a non-isothermal kinetic equation, the decomposition process was a first-order reaction. The activation energy, E_a, the entropy change, ΔS^*, the enthalpy change, ΔH^* and the Gibbs free energy of activation, ΔG^* were calculated by applying the theory of the reaction rates. The effect of the different central metal ions on the calculated thermodynamic activation parameters was discussed.

Keywords: chloromethylated poly(styrene)-PAN resin, DTG, TG, transition metal complexes

Introduction

Polymer-supported organic compounds play an important role in many applications. Some of them, especially those serving as chelating agents, can be used as polymer-supported materials in waste water treatment as well as selective sensing and separation of some harmful heavy metal ions. On the other hand, α-pyridylazo-β-naphthol (PAN) is well known to have a strong ability to a complex with many metal ions [1–6]. Chloromethylated poly(styrene)-PAN resin was previously used successfully for the preconcentration of multi-element and mercury in environmental water and biological samples and some ores [7, 8]. Thermogravimetric analysis (TG) has

---

[*] Author for correspondence: E-mail: sinfac@mum.mans.eun.eg

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

been widely used to investigate the thermal analysis of polymers and cellulose and to determine the kinetic and thermodynamic parameters [9–11]. The study of organometallic compounds in the solid state by qualitative and quantitative thermochemical analysis has attracted considerable attention [12]. The majority of compounds including complexes undergo physical and chemical changes when subject to heat energy. In spite of the fact that some authors studied TG and DTA of some covalent organometallic compounds [13, 14], there is a relatively moderate work in literature concerning the thermal analysis of coordinate metal complexes [15–24].

Heavy metal ions have important industrial applications and using of them often causes environmental contaminations. Several heavy metals have serious biochemical roles and are toxic even at low concentrations. The presence of heavy metal ions in the aquatic habitats creates potential threat to aquatic food webs.

Due to the importance of the present ion-exchanger for the preconcentration and separation of the investigated metals, our aim was the preparation, isolation and thermal stability study of chloromethylated poly(styrene)-PAN (ion-exchanger), and its chelates with Au^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Pt^{4+}.

The kinetic and thermodynamic parameters of these chelates were determined and, in addition, the effect of the different central metal ions on the chelates stability and the calculated thermodynamic activation parameters of the thermal decomposition reactions are discussed.

Experimental

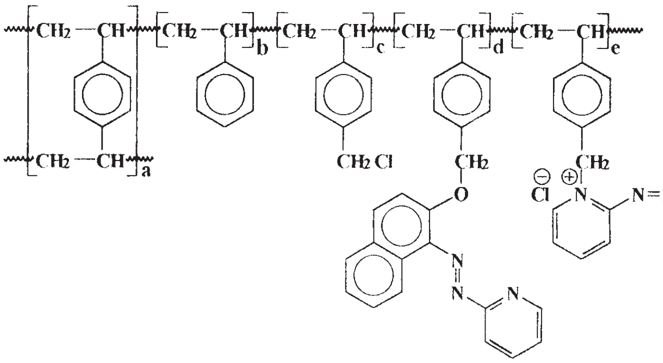
Preparation of chloromethylated poly(styrene)-PAN (ion-exchanger)

Commercial chloromethyl poly(styrene)-copolymer with divinyl benzene (A) (MP-500A; Bayer Co., Germany); 2% DVB; specific surface area (BET) is 66 $m^2 g^{-1}$ and 46 meq Cl g^{-1} resin was used. Pyridylazo-β-naphthol (PAN), cetyltrimethyl ammonium bromide (CTAB) and the salts of the metal ions (Aldrich) were used. The reaction was followed up in all experiments with the aid of FT-IR spectroscopic analysis.

Reaction of (A) with PAN under PTC-condition

In a 50 cm^3 round bottom flask, 200 mg (0.92 meq Cl) chloromethylated poly(styrene) (A) was soaked for three days in 20 cm^3 of chloroform as swelling medium. To the swollen polymer 650 mg (2–5 mmol) PAN, 70 mg (0.2 mmol), CTAB and 15 cm^3 of 30% aqueous solution of sodium carbonate were added.

The reaction mixture was refluxed on a water bath and stirred magnetically for 96 h. On cooling, the modified polymeric product was filtered off, washed thoroughly with acetic acid, methanol, distilled water, acetone and finally diethyl ether. The polymeric product (B) was dried at 40°C overnight and characterized by means of FT-IR spectroscopic, thermal and potentiometric measurements. The suggested structure of the prepared CMPS-PAN ion-exchanger is shown in Scheme 1.



Scheme 1 Chloromethylated poly(styrene)-PAN (ion-exchanger)

where *a* is the crosslinking reagent (DVB), *b* is the remaining styrene units after chloromethylation, *c* is the remaining chloromethylated styrene units after reaction with pyridylazo-β-naphtanol (PAN), *d* is the O-alkylated PAN units and *e* is the N-alkylated PAN units.

Preparation of the CMPS-PAN-metal chelates

5 cm^3 of each investigated heavy metal ion (10 μg cm^{-3}) in solution was transferred to a 100 cm^3 capacity beaker. The pH was adjusted in the range of 2–9 using 0.5 mol dm^{-3} NaOH and/or 0.1 mol dm^{-3} HCl. The contents were transferred to a 100 cm^3 conical flask and 20 mg ion-exchanger, CMPS-PAN was added to each solution. These solutions were stirred for 20 min with a mechanical shaker. The loaded resin was filtered through sintered glass (0.45 μm membrane), washed with doubly distilled water, absolute ethanol, ether and dried for 48 h in a vacuum desiccator.

Infrared spectra

The IR spectra of the ion-exchanger and its chelates were measured using Mattson 5000 FT-IR spectrophotometer (England).

Thermal analysis

Thermal studies were carried out using a Shimadzu Thermogravimetric Analyzer (Japan) DTA-50, TGA-50, with a heating rate of 10°C min^{-1} using a crucible fitted with Pt–Pt, Rh(10%) thermocouple. The mass of the samples varied from 2–4.5 mg.

Adjustment of pH

The pH’s of sample solutions were adjusted using a Tacussel Electronic Digital pH meter (France), with a glass – saturated calomel electrode calibrated on the operational state with standard buffer solutions.

Potentiometric measurements

Potentiometric measurements were performed using a Metrohm E536 potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). All titrations were carried out at 25°C. It was adjusted to ±0.05°C by circulating water from an ultra-thermostat (Kollermann 4130, Germany) through the annular space of a double-walled Pyrex titration cell of 100 cm^3 capacity. Alkali was added from the Dosimat and the content of the titration vessel was titrated magnetically. The following solution mixtures (1–3) were prepared and titrated potentiometrically with standardized NaOH solution (0.013 M) at constant ionic strength (0.05 KCl):

1. 5.0 cm^3 HCl (0.003 M)+2.5 cm^3 KCl (0.5M).
2. Solution (1)+CMPS-PAN (100 mg).
3. Solution (2)+1 cm^3 metal ion (5·10^{-3} M).

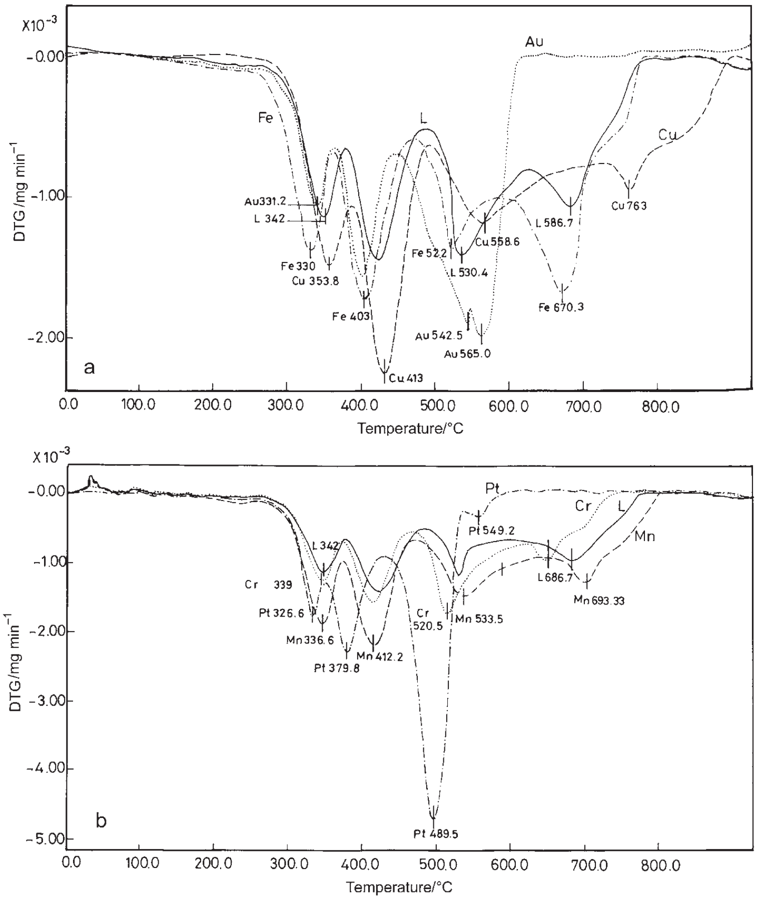


Fig. 1 DTG curves of CMPS-PAN and its complexes: Au–L, Cr–L, Cu–L, Fe–L, Mn–L and Pt–L

All the above solutions mixtures were made up to 25 cm^3 with doubly distilled water. The capacity of the present ion-exchanger was found to be 0.2 meq g^{-1} which is comparable to other previous ion-exchange resins [19].

Results and discussion

IR absorption spectra measurements were used to characterize the complexes formed between CMPS-PAN and Au^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Pt^{4+} ions. The spectrum of CMPS-PAN resin exhibited a medium band at 1425 cm^{-1} due to the ν(N=N) vibration [25]. This band exhibits a blue shift by 15–20 cm^{-1} in the complexes. The resin also showed a broad band at 3420 cm^{-1}, which was attributed to different vibrational modes of OH group [25]. Such breadth was due to the presence of intramolecular hydrogen bonding between the azo group and the ortho hydroxy groups of PAN (I). The increase in the stretching vibration of the –OH by 10–15 cm^{-1} and also the formation of the more intense band at 3430–3435 cm^{-1} in the spectra of investigated complexes confirmed the increase in bond order in presence of metal ions due to complex formation. Also, the absence of broadening of the band at 3430–3435 cm^{-1} in the IR spectra of metal complexes proves the absence of hydrogen bonding with the participation of –OH group in the coordination process. This indicates that both the –N=N– and the –OH groups take part in the complexation with all of the studied metal ions.

The thermal decomposition of CMPS-PAN resin and its complexes with the investigated metal ions is represented in Figs 1a and 1b respectively. During heating the CMPS-PAN resin, DTG curves undergo a series of thermal changes associated with a mass loss. These curves show that the resin has a series of decomposition steps starting at 200 and finishing at 780°C. The first midpoint located at 342°C is accompanied with 4.97% mass loss. As the temperature increases, the DTA curve shows three endothermic peaks corresponding to three midpoints at 421.79, 530.4 and 686.7°C respectively, accompanied with a total mass loss of 23.9% or (28.87% from the start of decomposition), and may correspond to three stages suggested by Chatterjee [26] to represent the thermal degradation of the resin as follows:

First stage

$A\rightarrow B_1$ initiation (volatile product).

Second step, propagation (thermal degradation):

$B_1\rightarrow B_2+V$
$B_2\rightarrow B_3+V$
$B_n\rightarrow B_{n+1}+V$
$\Sigma B_n\rightarrow B_{n+1}+V$

Third step

$\Sigma B_{n+1}\rightarrow$carbonisation

Table 1 Analysis of TG curves of thermal decomposition of chloromethylated poly(styrene) (CMPS) modified with α-pyridylazo-β-naphthol (PAN) (CMPS-PAN) and its complexes

Comp.	Stage (1)			Stage (2)			Stage (3)			Stage (4)			Total mass loss from start
	range/°C	mid-point/°C	mass loss/%	range/°C	mid-point/°C	mass loss/%	range/°C	mid-point/°C	mass loss/%	range/°C	mid-point/°C	mass loss/%	
CMPS–PAN (*L*)	199.85–375.22	341.95	4.97	375.22–467.7	421.79	7.13	467.7–592.82	530.4	8.88	592.82–780.29	686.7	7.89	28.87
Au–L	244.59–358.59	331.23	4.46	359.9–432.59	399.96	7.66	432.59–532.03	542.5	14.54	532.03–609.02	565.0	5.59	32.25
Cr–L	218.36–369.08	339.04	4.72	369.08–450.43	413.11	6.64	450.43–570.58	520.59	9.04	570.58–735.79	647.06	6.75	27.15
Cu–L	292.29–389.03	353.78	5.04	389.03–471.41	431.05	8.0	471.41–642.66	558.62	10.36	642.66–885.07	763.79	11.71	35.11
Fe–L	185.15–348.26	319.93	6.16	348.26–449.60	402.94	10.31	449.6–578.13	521.88	14.11	578.13–775.5	670.31	10.58	41.16
Mn–L	166.4–367.66	336.59	6.85	367.66–453.99	412.21	8.88	453.99–600	533.33	11.08	600–793.37	693.33	8.95	35.96
Pt–L	174.32–349.58	326.63	5.43	349.58–410.83	379.81	8.15	410.83–528.82	489.49	20.5	529.82–583.67	549.16	1.04	35.12

where A denotes the initial molecules of resin, $B_1 \ldots B_n$ are fragmented molecules and V denotes volatile products.

The broad endothemric peak at 467.7–592.82°C accompanied by 8.88% mass loss (Table 1) may be due to the decomposition of the stable intermediate fragment (carbonized product). The thermal decomposition of the complexes of CMPS-PAN resin with Au, Cr, Cu, Fe, Mn and Pt has been carried out following the same described experimental conditions used for the resin alone. DTG results, Fig. 1, are compared with the original resin. The temperature ranges for different degradation steps are shown in Table 1. Some trends and conclusions may be suggested:

i) The decomposition of the resin and its complexes start at 160–292°C with a range of mass loss of 4.5–6.9%.

ii) The process of decomposition of the resin and its complexes finished at 529.8–642.6°C with a mass loss of 1.04–11.71%.

iii) The total mass loss (%) from the start is 41.16 (Fe–L), 35.96 (Mn–L), 35.12 (for both Pt–L and Cu–L), 32.25 (Au–L) and 27.15 (Cr–L), respectively. (CMPS-PAN (*L*)).

iv) The investigated elements stabilize the resin and decrease its rate of decomposition.

v) In case of Cr, a stabilization for the resin was done as indicated by the increase of $t_{1/2}$, min of all decomposition steps compared to the resin itself (Table 1) and increase in the B residue of the decomposed Cr–L complex (72.85%). The residue of the resin alone was 71.13%.

The specific rate of degradation, *k*, of the samples was taken in terms of the rate of the mass loss ($\mathrm{d}w/\mathrm{d}t$). The thermal degradation of the polymer can be represented by the following equation:

$$R_t = -\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{A}{R_H} \mathrm{e}^{-E_a/RT} W^n \tag{1}$$

where W is the mass of the active material remaining for a particular reaction, R_H is the rate of heating, R_t is the rate of decomposition, $s^{-1}=(\mathrm{d}w/\mathrm{d}t)$, T is absolute temperature, K. A is frequency factor, E_a is activation energy, kJ mol^{-1}, R, 8.314 J mol^{-1} K^{-1} is universal gas constant and n is reaction order.

The above equation can be arranged to give:

$$\ln R_t = \ln A/R_H - E_a/RT + n \ln W \tag{2}$$

when W is kept constant and application of non-isothermal kinetic equation [26],

$$\ln\alpha - 2\ln T = \ln A - E_a/RT \tag{3}$$

where α is mass loss percentage.

Equation (3) requires the plotting of $\ln\alpha - 2\ln T$ *vs.* $1/T$ for the second step to be linear as it is experimentally observed (Fig. 2). A good linear regression with a linear correlation coefficient (r) between 0.94 to 0.98 associated with breaks of straight lines was observed for other steps. The calculated values of activation energies of each stage together with the total activation energies of the whole stages for

CMPS-PAN (*L*) alone and its complexes with the studied metals are shown in Table 2.

Table 2 Evaluated values of the activation energy of the thermal decomposition of CMPS-PAN and its complexes

Compound	E_a/kJ mol^{-1}				
	E_{a_1} Stage (1)	E_{a_2} Stage (2)	E_{a_3} Stage (3)	E_{a_4} Stage (4)	E_a (total)
CMPS-PAN (*L*)	26.60	93.55	85.61	81.84	287.60
Au–L	118.14	242.79	244.44	416.34	1021.71
Cr–L	78.09	201.35	222.59	170.21	672.32
Cu–L	152.46	261.50	163.75	174.24	751.75
Fe–L	65.81	189.61	201.21	129.63	606.56
Mn–L	45.25	375.88	183.38	127.92	802.48
Pt–L	59.03	312.20	197.50	269.72	838.45

The magnitude of the activation energy measured for solid phase decomposition reaction has often been explained by the energy barrier in the limiting step e.g. bond rupture, electron or proton transfer or enthalpy of decomposition. The values of E_a were in good agreement with that of the thermolysis processes. Higher activation energy in case of CMPS-PAN (*L*) with Au and Pt complexes than Cr, Cu, Mn and Fe

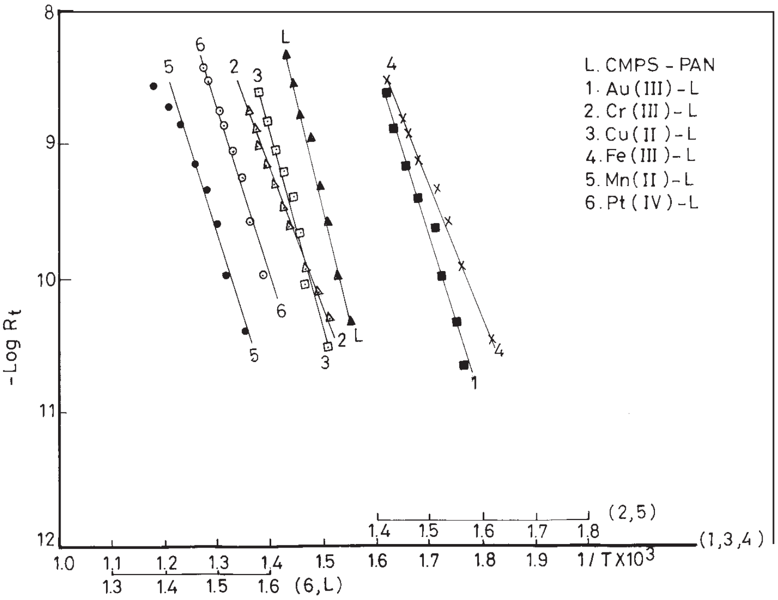


Fig. 2 Graphical determination of the activation energy by thermal decomposition process of second step by the Chatterjee's method of CMPS-PAN and its complexes

complexes indicates the high stability of such chelates due to their covalent bond character [27]. These trends in case of Au^{3+} and Pt^{4+} are in a good agreement with their higher values of effective electrical field strength, F (Table 3). The lowest activation energy in case of Cr–L is in a good agreement with its lowest value of F (Table 3). Also, the total activation energy of decomposition of (L) resin is lower than that of resin-metal chelates, Table 4, where the investigated metal ions increased the stability to decomposition of the resins and do not act as catalysts for thermolysis.

Table 3 Summary for the total activation energy, ionic radius, effective nuclear charge (z) and effective electrical field strength (F) of the studied metal ions

Metal ions	Atomic no.	r/pm	$1/r\cdot 10^2$	$F=Z/r^2$ (Slater)	I.P./ kJ mol^{-1}	$E_{a,total}$/ kJ mol^{-1}
Au^{3+}	79	91	1.098	4.20	5770.1	1027.71
Cr^{3+}	24	64	1.563	3.45	5231.7	671.32
Cu^{2+}	29	72	1.390	4.20	2703.4	751.95
Fe^{3+}	26	67	1.490	3.75	5277.3	606.56
Mn^{2+}	25	91	1.098	3.60	2226.4	802.48
Pt^{4+}	78	70	1.430	4.05	9361.0	838.72

Note: The activation energy of CMPS-PAN resin=287.6 kJ mol^{-1}

Straight lines are obtained for a plot of $-\log R_t$ *vs.* time for all the four decomposition steps of the CMPS-PAN resin and its complexes. Figure 3 is recorded as a representative example. Such linearity confirms the suggested first-order rate constants of the thermal decomposition process. The values of the specific rate of reaction, k, min^{-1} and consequently $t_{1/2}$, min could be calculated from the slope of the obtained figure (Table 4).

Table 4 The kinetic parameters of CMPS-PAN and its complexes

Comp.	Stage (1)		Stage (2)		Stage (3)		Stage (4)		$t_{1/2}$ total/ min
	$k\cdot 10^2$/ min^{-1}	$t_{1/2}$/ min	$k\cdot 10^2$/ min^{-1}	$t_{1/2}$/ min	$k\cdot 10^2$/ min^{-1}	$t_{1/2}$/ min	$k\cdot 10^2$/ min^{-1}	$t_{1/2}$/ min	
CMPS-PAN (L)	9.87	7.00	22.98	3.0	15.39	4.5	10.46	6.6	21.10
Au–L	26.34	2.63	35.95	1.78	27.93	2.48	37.19	1.86	8.75
Cr–L	5.40	12.83	24.33	2.84	16.43	4.22	8.58	8.08	27.97
Cu–L	28.36	2.45	24.30	2.84	11.87	5.84	7.00	9.48	20.61
Fe–L	11.69	5.93	21.77	3.18	16.80	4.12	8.97	7.72	20.96
Mn–L	9.85	7.03	26.61	2.60	16.55	4.19	13.62	5.08	18.90
Pt–L	7.85	8.82	32.95	2.10	16.20	4.27	16.50	4.20	19.39

The thermodynamic activation parameters were calculated from the rate theory (Table 5). The positive values of entropy change, ΔS^*, shown in Table 5 may suggest that the disorder of the decomposed fragments increases much more rapidly than that of the undecomposed ones. Also, higher $\Delta S^*_{\text{total}}$ values of the investigated metal complexes compared with that of the free resin, suggest that these metal ions play a role in increasing the disordering of the decomposed fragments. The positive sign of the enthalpy change, $\Delta H^*_{\text{total}}$ of the whole four decomposition steps for CMPS-PAN resin and its complexes indicates that the decomposition stages are endothermic processes (Table 5). Higher $\Delta H^*_{\text{total}}$ values of Au–L and Pt–L confirm the higher stability of such chelates due to the covalent bond characters compared to the other chelates [27].

Table 5 Values of the enthalpy change ΔH^*, entropy change ΔS^* and free energy change ΔG^* of various thermal decomposition steps of CMPS-PAN and its complexes

Compound	1st step ΔH_1^*	2nd step ΔH_2^*	3rd step ΔH_3^*	4th step ΔH_4^*	$\Delta H^*_{\text{total}}$/ kJ mol^{-1}
CMPS-PAN (*L*)	23.75	90.04	81.20	76.13	271.12
Au–L	115.39	239.46	239.93	411.64	1006.42
Cr–L	75.27	197.92	218.26	164.83	656.28
Cu–L	149.52	257.92	159.11	167.94	734.48
Fe–L	63.15	186.26	196.78	144.36	590.55
Mn–L	42.45	372.45	178.95	122.20	716.06
Pt–L	56.31	309.04	193.43	265.15	823.93
	ΔS_1^*	ΔS_2^*	ΔS_3^*	ΔS_4^*	$\Delta S^*_{\text{total}}$ / J mol^{-1} K^{-1}
CMPS-PAN (*L*)	43.24	134.63	106.56	85.27	360.70
Au–L	356.67	607.04	450.58	736.28	2150.57
Cr–L	230.33	487.40	427.57	236.05	1408.34
Cu–L	430.95	606.66	293.13	228.13	1558.87
Fe–L	205.70	470.57	385.55	223.67	1285.49
Mn–L	134.44	911.85	343.84	184.57	1574.70
Pt–L	180.72	821.99	403.48	491.15	1897.34
	$-\Delta G_1^*$	$-\Delta G_2^*$	$-\Delta G_3^*$	$-\Delta G_4^*$	$-\Delta G^*_{\text{total}}$/ kJ mol^{-1}
CMPS-PAN (*L*)	5.11	5.77	6.68	7.97	25.53
Au–L	2.75	3.33	4.51	4.36	14.95
Cr–L	2.82	2.94	4.33	5.38	15.50
Cu–L	2.94	3.58	4.64	6.30	17.46
Fe–L	2.66	3.35	4.43	5.57	16.01
Mn–L	2.80	3.42	4.43	5.77	16.42
Pt–L	2.72	3.16	4.07	4.57	14.52

The negative sign of $\Delta G^*_{\text{total}}$ indicates that the free energy of the final residue is lower than that of the initial compound, and hence, all the decomposition steps are

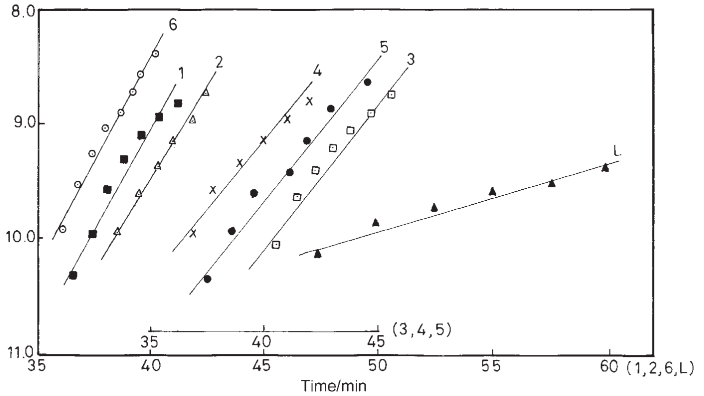


Fig. 3 The variation of logR_t with time of second step for CMPS-PAN (L) and its complexes: 1 – Au–L, 2 – Cr–L, 3 – Cu–L, 4 – Fe–L, 5 – Mn–L and 6 – Pt–L

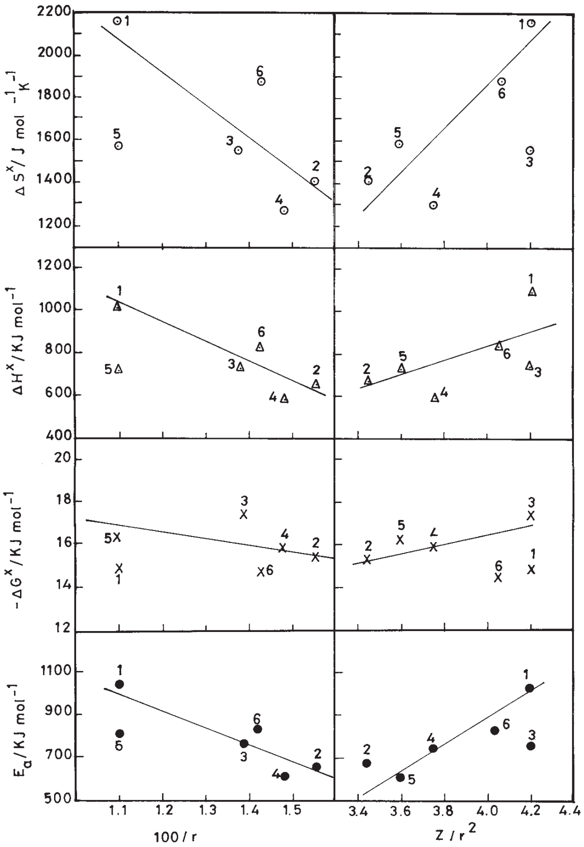


Fig. 4 The relation between the activation energy and thermodynamic parameters of complexes of 1– Au, 2 – Cr, 3 – Cu, 4 – Fe, 5 – Mn and 6 – Pt with CMPS-PAN and the reciprocal of ionic radius and electric field strength

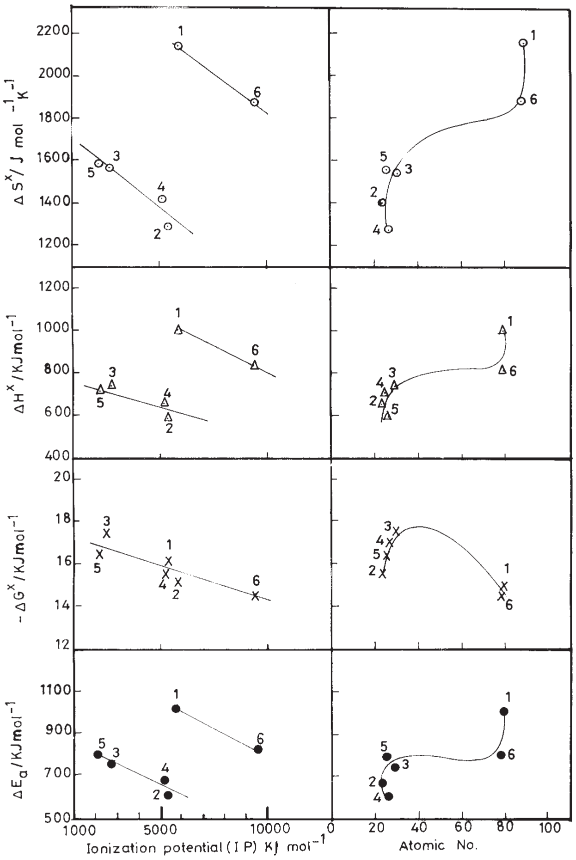


Fig. 5 The relation between the activation energy and thermodynamic parameters of complexes of 1– Au, 2 – Cr, 3 – Cu, 4 – Fe, 5 – Mn and 6 – Pt with CMPS-PAN and the ionization potential and atomic no.

spontaneous processes. Au–L and Pt–L chelates have the least ΔG^* values compared to the other investigated chelates of Cr^{3+}, Cu^{2+}, Fe^{3+} and Mn^{2+} indicating there low rate of decomposition (their high stability). One can arrange the stability of the CMPS-PAN resin (*L*) and its chelates in the following increasing order (Table 5):

L<Cu<Mn<Fe<Cr<Au< Pt

A relation between the activation energy and the thermodynamic parameters of complexes of Au, Cr, Cu, Fe, Mn and Pt with CMPS-PAN and the reciprocal of ionic radius and electrical field strength is shown in Fig. 4. The relations between ΔS^*, ΔH^*, E_a and $1/r$ are reversible ones and both Au and Pt has the largest values for ΔS^*_{total}, ΔH^*_{total} and $E_{a,total}$ respectively. The relation between the thermodynamic parameters and the electrical field strength (Z/r^2) is irreversible. ΔG^*_{total} for Au and Pt has the lowest value compared with the other investigated metal chelates. All these correlations confirm the high stability of Au and Pt chelates due to the covalent bond character [27].

Concordant conclusions were achieved by plotting a relation between the activation energy and thermodynamic parameters of the complexes of the investigated metal ions with CMPS-PAN resin and the ionization potential and atomic number (Fig. 5).

A potentiometric titration was done for HCl alone, HCl+CMPS-PAN (resin) and HCl+resin+studied metal ions. The values of pK_1^H=1.89 and pK_2^H= 12.2 for the loaded PAN on the resin refer to the stepwise dissociation of two protons. When the same titration was done in the presence of the studied metal ions, the inflection on the titration curves shifted to the right, due to the complex formation between the metal ions and the resin. The number of millimoles of protons liberated in case of Au^{3+} and Pt^{4+} is lower than that of Cr^{3+}, Cu^{2+}, Fe^{3+}, and Mn^{2+} indicating the covalent character of the former ions.

Conclusions

The success of CMPS-PAN resin as an ion-exchanger for the preconcentration of different metal ions and mercury [7, 8] in our laboratory, encourage us to study the stability such resin in more details.

1. The IR, potentiometry and thermal analysis confirm the chelation and high stability of the present resin and its complexes.

2. The calculated thermodynamic parameters and activation energy confirm that the chelation of the present resin and both Au^{3+} and Pt^{4+} is carried through a covalent bond with the resin. In case of Cr^{3+}, Cu^{2+}, Fe^{3+} and Mn^{2+} the chelation is done through the liberation of protons with some ionic bond characters.

3. Both Au^{3+} and Pt^{4+} complexes have the same thermal degradation character, because they have large atomic number and ionization potential. The higher values of thermodynamic and stability of CMPS-PAN resin lead to expect its successful use in the analytical preconcentration of other metal ions.

4. The negative values of $\Delta G^*_{\text{total}}$ indicate that the decomposition process of the resin and its complexes is a spontaneous reaction.

5. Au–L and Pt–L chelates have the least ΔG^* values indicating there low rate of decomposition (high stability) compared to the other investigated chelates.

References

1 A. Jha and R. K. Mishra, J. Ind. Chem. Soc., 73 (1996) 704.
2 E. Pramauro, A. B. Prevot, V. Zelano, M. Gulmini and G. Viscardi, Analyst, 121 (1996) 1401.
3 E. M. Basova, T. A. Bolshova and V. I. Ivanov, Anal. Chem., 51 (1996) 406.
4 Z. Zhou and Z. Liang, Hangzhou Daxue Xuebao, Ziran Kexueban, 15 (1988) 327; C. A., 108 (1988), 118554k.
5 S. B. Khoo, M. K. Soh, Q. T. Cai, M. R. Khan and S. X. Guo, Electroanal., 9 (1997) 45.

6 M. Kan, M. D. Guiver, G. P. Robertson, S. N. Willie and R. E. Sturgeon, React. and Funct. Polymers, 31 (1996) 207, C. A., 125 (1996), 338473, p. 681.
7 I. M. M. Kenawy, M. A. H. Hafez, M. A. Akl and R. R. Lashein, Anal. Sci. (Japan), 16 (2000) 493.
8 M. A. H. Hafez, I. M. M. Kenawy, M. A. Akl and R. R. Lashein, Talanta, 53 (2001) 749.
9 H. Niskizaki, K. Yoshida and J. H. Wang, J. Appl. Polym. Sci., 25 (1980) 2869.
10 S. Boutros and A. A. Hanna, Polym. Sci., 16 (1979) 89.
11 A. A. Hanna, A. Abd El-Wahid and M. H. Abbas. Thermochim. Acta, 71 (1983) 119.
12 I. Horvath, E. Jona, L. Galikova and M. Jamnicky, J. Thermal Anal., 28 (1983) 435.
13 C. E. Carraher, J. Am. Chem. Soc., Div., Org. Cont. Plast. Paper, 35 (1975) 380, C. A., 83 (1975), 10900w, p. 375A.
14 H. S. O. Chan, T. S. A. Hor, C. S. M. Chaim and T. C. Chong, J. Thermal Anal., 32 (1987) 1115.
15 M. E. M. Emam, M. A. H. Hafez and M. N. H. Moussa, J. Thermal Anal., 32 (1987) 945.
16 M. E. M. Emam, M. A. H. Hafez and M. N. H. Moussa, J. Thermal Anal., 37 (1991) 1005.
17 M. E. M. Emam, I. M. M. Kenawy and M. A. H. Hafez, Thermochim. Acta, 249 (1995).
18 A. A. Said and I. M. M. Kenawy, J. Thermal Anal., 36 (1990) 1257.
19 P. Burba and P. G. Willmer, Fresenius' Z. Anal. Chem., 321 (1987) 109.
20 M. Sikorska-Iwan, R. Mrozek and Z. Rzaczynska, J. Therm. Anal. Cal., 60 (2000) 139.
21 D. Czakis-Sulikowska, J. Radwanska-Doczekalska and M. Markiewicz, J. Therm. Anal. Cal., 60 (2000) 145.
22 S. H. Tarulli, O. V. Quinzani, J. Dristas and E. J. Baran, J. Therm. Anal. Cal., 60 (2000) 505.
23 Y. Masuda, Y. Seto, X. Wang, Y. Yukawa and T. Arii, J. Therm. Anal. Cal., 60 (2000) 1033.
24 W. Brzyska and W. Ozga, J. Therm. Anal. Cal., 61 (2000) 135.
25 Bellamy, The Infrared Spectra of Complex Molecules, 2nd Ed., Chapman and Hall, London 1966, p. 354.
26 P. K. Chatterjee, J. Polym. Sci., 6 (1968) 3217.
27 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 4th Edn., John Wiley and Sons, UK, 1980, p. 900, 959, 969, 979 and 1229.