Chapter 3

RESULTS AND DISCUSSION

III-RESULTS AND DISCUSSION

Polyesters [polyhexamethylene asparate (PHMA), polydiethylene asparate (PDEA), poly propylene asparate (PPA) and polydipropylene asparate (PDPA) based on aspartic acid were prepared by the reactions of aspartic acid with 1,6 hexamethylene, diethylene, propylene and dipropylene glycols, respectively.

III-A-Chemoselective polycondensation:

Aspartic acid, being an acidic amino acid, can exist in two Zwitter ionic forms, I and II[59].

$$HOOC - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \rightleftharpoons \bar{O}OC - CH_2 - \underset{\displaystyle N^+H_3}{\underset{|}{CH}} - COOH$$

(I) (II)

It has a greater contribution from the weakly acidic-N^+H_3 group rather from the basic-NH_2 group[97].

So under the experimental conditions and the type of reacting substances the formation of polyamides is not expected[59]. This is because to attack the carboxylic carbon atom of aspartic acid, two competing nucleophiles are present: the hydroxyl groups of glycols, and the amino group of aspartic acid itself. However, the hydroxyl groups of hexamethylene, diethylen, propylen or dipropylen glycols are better nucleophiles than the amino group of aspartic acid[59].

Actually, in the neutral condition, the basic group in amino acids is - COO^-, not – NH_2.

Also the excluding of the formation of polyamide is confirmed form the absence of the strong absorption band near 1550 cm^{-1} which is very characteristic of N-mono substituted amide, (see below).

III-B-Composition of prepared compounds:

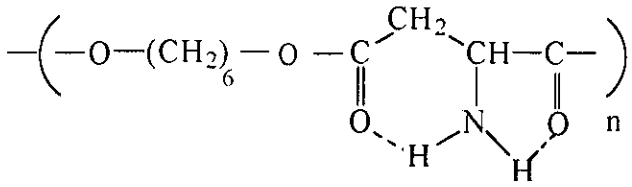
III-B-1- Elemental analysis studies

The elemental analysis of the polymers and their complexes are summarized with the theoretical compositions based on assumed structures in Tables (1-5). Although the results of elemental analysis do not have much significance, but we can get some information about the number of metal atoms attached to the polymeric chains. The observed analytical values are found to be in the best agreement with the ones calculated for the six metal ions per oligomer. The deviation of the observed analysis data from the theoretical values may be attributed to the polymeric nature. The complexes may have a broad molecular weight distribution including low molecular weight oligomers bound to metal ions. Further, in one case, a metal ion may be complexed to only one polymer molecule, and in another, two or three polymers (oligomers) may be attached as ligands to the metal.

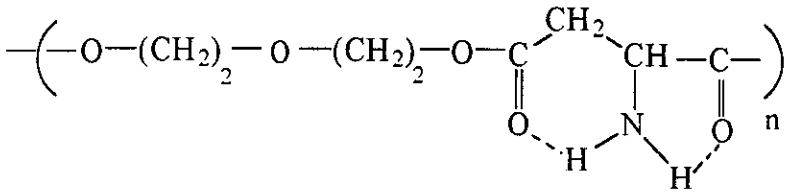
III-B-2-IR spectral studies:

IR spectra of investigated compounds are shown in Figs. (1-11) and the main IR bands are listed in Tables (6-10). The IR spectra of polyesters, showed very broad and strong bands in the region 3500-3400 cm^{-1}. The broad band observed for the polyesters PHMA, PDEA, PPA and PDPA in this region suggests the merger of asym (NH) and sym (NH)[98] and may be attributed also to the OH of the terminal hydroxyl groups of the polyesters, as glycols has been taken in excess during the polyesters synthesis. Further, the lowering of the frequencies and the

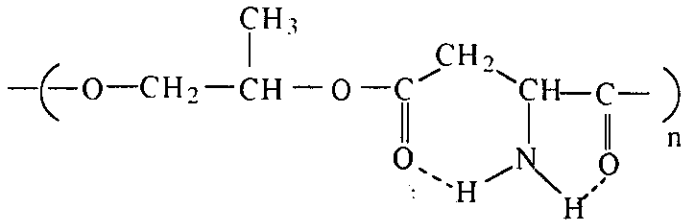
broadening of the band in this region suggests intermolecular hydrogen bonding[99]. Which is possible between carbonyl oxygen and amine hydrogens as shown below:



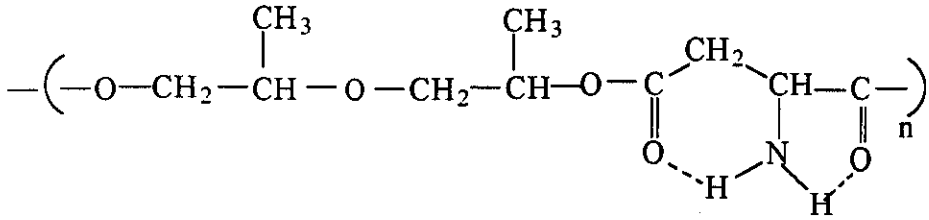
Intramolecular hydrogen bonding in PHMA



Intramolecular hydrogen bonding in PDEA



Intramolecular hydrogen bonding in PPA



Intramolecular hydrogen bonding in PDPA

IR spectra show also two strong bands at (2923-2979 cm^{-1}) and (2853-2861 cm^{-1}) due to the CH asymmetric and symmetric stretching modes of the – CH_2- group [100].

In the C = O region, the IR-spectra show a split band with peaks at 1725 cm^{-1} and 1715 cm^{-1}. The splitting of this band suggests the different environment around C = O groups of the polyesters chain as mentioned above. The slight lowering of the C = O frequency from the normal predicted wave number may be the results of hydrogen bonding as mentioned before. The order of characteristic absorptions arising from the C– O group[99] appear at 1220 and 1170 cm^{-1}.

A weak bands observed at 1640 cm^{-1} are ascribed to the δNH vibration of the amino groups [98]. The bands observed at ~ 1420 cm^{-1} and ~ 1470 cm^{-1} are assigned to the CH deformation of CH and CH_2 groups adjacent to the carbonyl group, respectively[101].

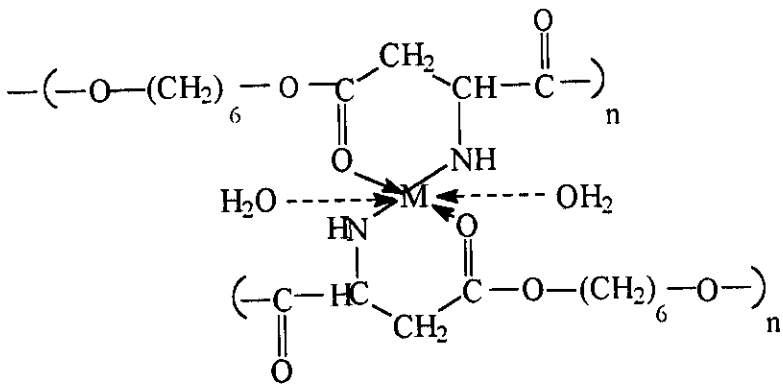
A weak and broad band observed at ~ 740 cm^{-1} are assigned to $-(CH_2)_n-$ of the polyesters chain[98].

The spectra of polyesters – metal complexes show a hump or a very broad band in the region ~650-450 cm^{1}. The greater broadness of this band than that of the ligand polyesters is attributed to the merger of NH (metal – coordinated)[102], the OH of the polyester terminal, and metal-coordinated water molecules. The presence of the coordinated water in complexes is further confirmed by the bands in the region ~ 1600 – 1570 cm^{-1} for HOH deformation and ~ 670 – 650cm^{-1} for the rocking mode of the coordinated water[103-104]. The band due to the C = O of the ligand is shifted to a lower frequency region in the spectra of the complexes and indicates to the involving of the C = O group in the complexation.

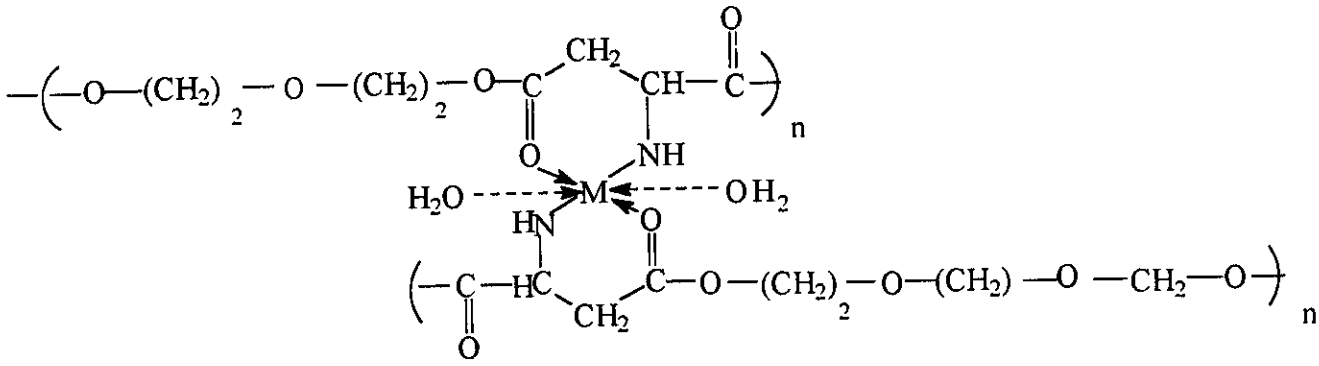
The band of δNH at ~ 1640 cm^{-1} in the polyesters spectra shifts to a lower frequency in the metal complexes and appears as a broad band,

which accounts for the participation of the amino group in the coordination. The participation of nitrogen and oxygen in the coordination in all the complexes is further supported by the appearance of M-O and M-N modes in the regions ~ 690 – 620 and ~ 560 – 410 cm^{-1}, respectively.

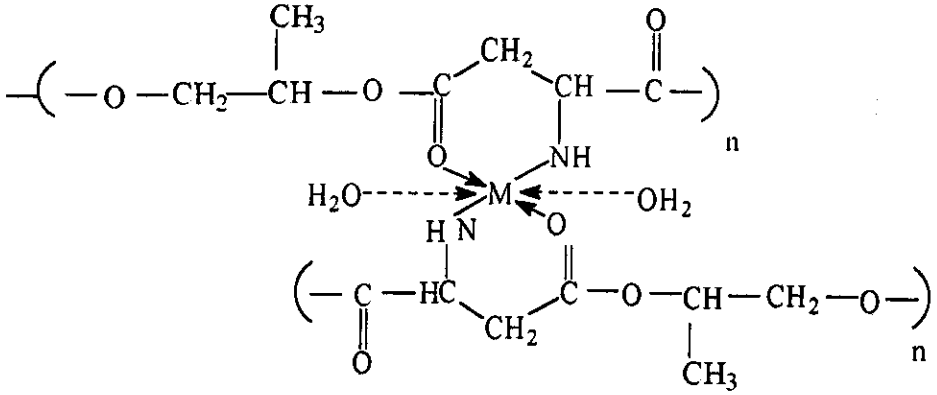
So, from the analytical results, the metal-oxygen and metal-nitrogen bonding concluded from the IR studies, the structure proposed for the polyester-metal complexes is a mixed coordination between two liqand units and one metal ion as well as one ligand and one metal ions inside the polymer chain. The coordinated bonds formed between two ligand units and one metal ion is represented below:



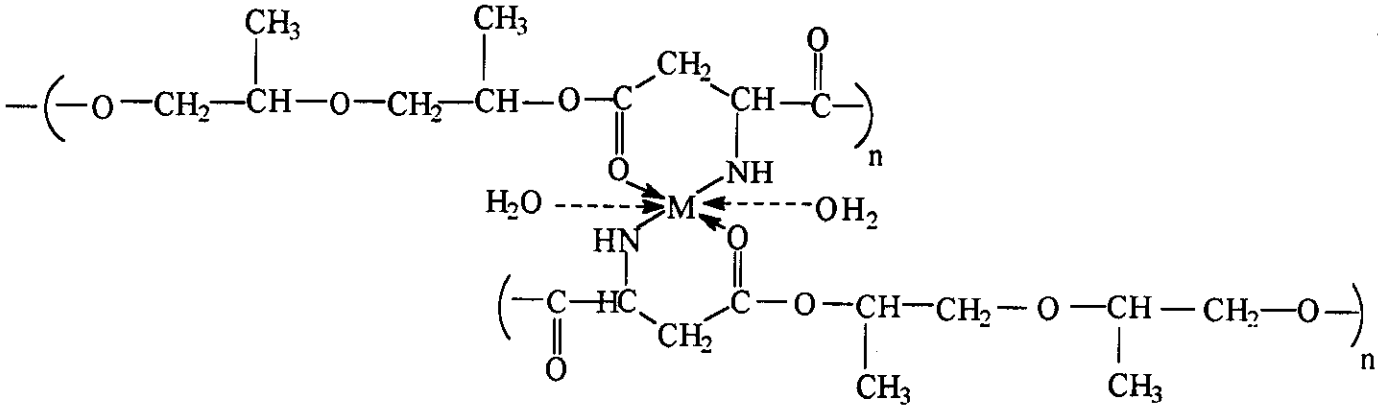
Structure of PHMA – metal complex



Structure of PDEA- metal complex



Structure of PPA- metal complex



Structure of PDPA-metal complex

In order to show the effect of ion type on the covalent strength of the bond forming by complexation, the shift in frequency ν for both NH_2 and OH groups have been ploted against the ionic radius of the ions used, Figs (12, 13). The results obtained show non-systematic behaviour referring to that the bonding strength between NH_2 group and M^{2+} ion is independent upon the size of metal ion.

III-B-3- ^{1}H-NMR spectral studies:

^{1}H-NMR spectrum Fig. (14 a, b) of polyhexa methylene aspartate (PHMA) illustrate the following peaks:

(i) 0.9 – 1.8 δ (broad, 10 H) due to methyene protones.

(ii) 3.7-4.1 δ (multiplet, 1 H) due to methyene protone.

(iii) 4.2 – 5.2 δ (broad, 4 H).

These peaks confirmed the proposed structure for (PHMA) as follow:

H- [-O- $(CH_2)_6$ –OCO – CH_2 – CH (NH_2) – CO- $]_n$ – O- $(CH_2)_6$ – OH

Table (1): Analytical Data of PHMA and its Metal Complexes

Compounds	Elemental Analysis							
	% C		% H		% N		% M	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PHMA $C_{96}H_{167}N_9O_{36}$	57.0	55.5	8.3	7.7	6.2	5.8	0.0	0.0
PHMA-Pb(II) $C_{96}H_{167}N_9O_{36}.Pb_6.12H_2O$	33.1	30.7	4.8	4.6	3.6	3.6	35.7	[33.7] (36.1)
PHMA-Ni(II) $C_{96}H_{167}N_9O_{36}.Ni_6.12H_2O$	44.5	42.8	6.4	5.8	4.9	4.1	13.6	[12.8] (14.6)
PHMA-Cd(II) $C_{96}H_{167}N_9O_{36}.Cd_6.12H_2O$	39.6	37.4	5.7	5.2	4.3	4.1	23.2	[21.3] (22.7)
PHMA-Cu(II) $C_{96}H_{167}N_9O_{36}.Cu_6.12H_2O$	44.0	41.6	6.4	5.7	4.8	3.8	14.6	[12.6] (14.9)
PHMA-Co(II) $C_{96}H_{167}N_9O_{36}.Co_6.12H_2O$	44.5	42.3	6.4	5.8	4.9	3.5	13.6	[12.9] (14.4)

[ ] Results by using atomic absorption, ( ) Results by using EDTA analysis

Table (2): Analytical Data of PDEA and its Metal Complexes

Compounds	Elemental Analysis							
	% C		% H		% N		% M	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PDEA $C_{76}H_{127}N_9O_{48}$	47.2	42.8	6.6	4.2	6.5	5.8	0.0	0.0
PDEA-Pb(II) $C_{76}H_{127}N_9O_{48}.Pb_6.12H_2O$	26.9	23.9	3.7	3.2	3.7	3.4	36.6	[35.0] (37.5)
PDEA-Ni(II) $C_{76}H_{127}N_9O_{48}.Ni_6.12H_2O$	36.5	34.6	5.1	4.7	5.0	4.9	14.1	[13.0] (13.7)
PDEA-Cd(II) $C_{76}H_{127}N_9O_{48}.Cd_6.12H_2O$	32.3	30.8	4.5	3.65	4.5	3.8	23.9	[21.6] (24.7)
PDEA-Cu(II) $C_{76}H_{127}N_9O_{48}.Cu_6.12H_2O$	36.0	35.6	5.0	4.5	5.0	4.2	15.1	[12.5] (16.2)
PDEA-Co(II) $C_{76}H_{127}N_9O_{48}.Co_6.12H_2O$	36.4	34.6	5.1	4.8	5.0	4.9	14.1	[13.6] (14.6)

[ ] Results by using atomic absorption, ( ) Results by using EDTA analysis

Table (3): Analytical Data of PPA and its Metal Complexes.

Compounds	Elemental Analysis							
	% C		% H		% N		% M	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PPA $C_{66}H_{107}N_9O_{38}$	48.5	46.9	6.6	5.8	7.7	7.0	0.0	0.0
PPA-Pb(II) $C_{66}H_{107}N_9O_{38}.Pb_6.12H_2O$	25.6	23.8	3.5	2.9	4.1	3.9	40.2	[38.6] (41.1)
PPA-Ni(II) $C_{66}H_{107}N_9O_{38}.Ni_6.\ 12H_2O$	36.0	34.4	4.9	4.2	5.7	4.9	16.0	[13.4] (16.5)
PPA-Cd(II) $C_{66}H_{107}N_9O_{38}.Cd_6.12H_2O$	31.9	29.8	4.2	4.5	5.0	3.8	26.7	[24.6] (25.4)
PPA-Cu(II) $C_{66}H_{107}N_9O_{38}.Cu_6.12H_2O$	35.5	33.6	4.8	4.5	5.6	4.9	17.1	[16.8] (18.0)
PPA-Co(II) $C_{66}H_{107}N_9O_{38}.Co_6.12H_2O$	36.0	34.9	4.9	4.2	5.7	5.2	16.1	[13.6] (16.4)

[ ] Results by using atomic absorption, ( ) Results by using EDTA analysis

Table (4): Analytical Data of PDPA and its Metal Complexes.

Compounds	Elemental Analysis							
	% C		% H		% N		% M	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PDPA $C_{96}H_{167}N_9O_{48}$	52.1	48.6	7.5	6.8	5.7	5.9	0.0	0.0
PDPA-Pb(II) $C_{96}H_{167}N_9O_{48}.Pb_6.12H_2O$	31.4	30.6	4.5	4.3	3.4	3.2	33.9	[28.8] (33.7)
PDPA-Ni(II) $C_{96}H_{167}N_9O_{48}.Ni_6.\ 12H_2O$	41.4	37.5	6.0	4.0	4.5	3.7	12.7	[11.6] (13.1)
PDPA-Cd(II) $C_{96}H_{167}N_9O_{48}.Cd_6.12H_2O$	37.1	35.1	5.4	4.9	4.1	4.0	21.7	[19.3] (22.2)
PDPA-Cu(II) $C_{96}H_{167}N_9O_{48}.Cu_6.12H_2O$	41.0	38.7	5.9	4.9	4.5	3.7	13.6	[12.4] (13.9)
PDPA-Co(II) $C_{96}H_{167}N_9O_{48}.Co_6.12H_2O$	41.4	40.8	6.0	4.8	4.5	4.3	12.7	[11.8] (13.0)

[ ] Results by using atomic absorption, ( ) Results by using EDTA analysis

Table (5): Analytical Data of PDPA and its Double Metals Complexes.

Compounds	Elemental Analysis											
	%C		%H		%N		% Metal					
							%Ni		%Co		%Cu	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PDPA $C_{96}H_{167}N_9O_{48}$	52.1	51.0	7.5	6.6	5.7	4.9	0.0	0.0	0.0	0.0	0.0	0.0
PDPA-Ni(II),Co(II) $C_{96}H_{167}N_9O_{48}.Ni_3Co_3.12H_2O$	41.4	40.5	6.0	5.9	4.5	4.2	6.3	5.8	6.4	5.5	0.0	0.0
PDPA-Ni(II),Cu(II) $C_{96}H_{167}N_9O_{48}.Ni_3Cu_3.12H_2O$	41.2	40.9	6.0	4.8	4.5	3.9	6.3	5.6	0.0	0.0	6.8	[5.3]
PDPA-Cu(II),Co(II) $C_{96}H_{167}N_9O_{48}.Cu_3Co_3.12H_2O$	41.2	39.8	6.0	4.6	4.5	4.3	0.0	0.0	6.3	5.7	6.8	[5.4]

[ ] Results by using atomic absorption

Table (6): Important IR spectral Assignments of PHMA and its Metal Complexes.

Compound	OH	O ‖ -C-	C – O	CH_2	CH	NH_2	NH	M-N
PHMA	3426	1724	1058 1117	1462	2937 2861	853 895	-	-
PHMA-Cd(II)	3433	1725	1057 1175	1465	2934 2861	-	3786	409 422
PHMA-Ni(II)	3432	1726	1057 1173	1464	2932 2860	-	3787	409 433
PHMA-Pb(II)	3445	1724	1056 1170	1458	2925 2856	-	3783	418 457
PHMA-Mn(II)	3445	1715 1650	1054	1459	2943 2855	-	3802	417
PHMA-Cu(II)	3441	1632	1135	1454	2926 2855	-	3797	428
PHMA-Fe(III)	3446	1734	1120	1458	2924 2854	-	3790	420
PHMA-Hg(II)	3447	1643	1160	1460	2925	-	3775	380
PHMA-Co(II)	3447	1716 1650	1056 1166	1460	2926 2856	-	3810	390
PHMA-Mg(II)	3444	1645	1049	1456	2924 2854	-	3764	375

All data are given in cm^{-1} unit

Table (7): Important IR Spectral Assigments of PDEA and its Metal Complexes.

Compound	OH	O ‖ -C-	C – O	CH_2	CH	NH_2	NH	M-N
PDEA	3487	1717	1169	1539	2955	814	-	-
PDEA-Pb(II)	3364	1715	1175	1559	2949	-	3510	410
PDEA-Ni(II)	3436	1717	1168	1542	2956	-	3540	416
PDEA-Cd(II)	3448	1719	1169	1560	2957	-	3568	418
PDEA-Cu(II)	3448	1719	1169	1560	2957	-	3568	415
PDEA-Co(II)	3435	1718	1168	1542	2956	-	3525	413

All data are given in cm^{-1} unit

Table (8): Important IR Spectral Assignments of PPA and its Metal Complexes.

Compound	OH	O ‖ -C-	C – O	CH_2	CH	NH_2	NH	M-N
PPA	3495	1718	1168	1537	2949	817	-	-
PAP-Pb(II)	3434	1718	1167	1543	2957	-	3500	417
PPA-Ni(II)	3429	1717	1166	1540	2947	-	3520	419
PPA-Cd(II)	3423	1719	1166	1561	2949	-	3569	409
PPA-Cu(II)	3447	1719	1165	1525	2949	-	3515	407
PPA-Co(II)	3447	1719	1166	1530	2940	-	3560	409

All data are given in cm^{-1} unit

Table (9): Important IR Spectral Assignments of PDPA and its Metal Complexes.

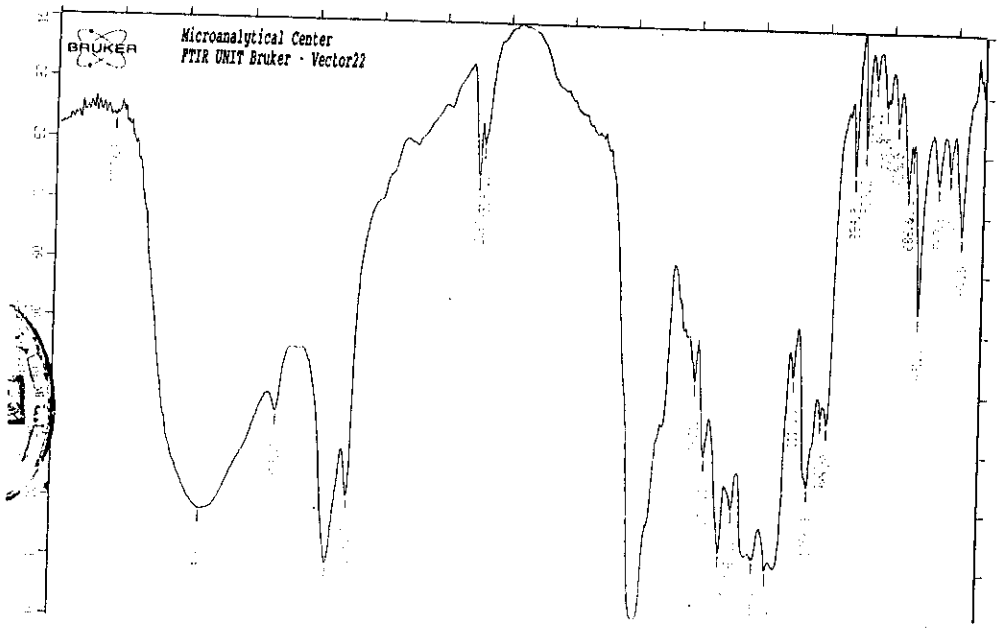
Compound	OH	O ‖ -C-	C – O	CH_2	CH	NH_2	NH	M-N
PDPA	3488	1721	1167	1503	2978	812	-	-
PDPA-Pb(II)	3448	1719	1166	1543	2939	-	3649	405
PDPA-Ni(II)	3376	1718	1169	1559	2975	-	3610	423
PDPA-Cd(II)	3481	1719	1166	1542	2978	-	3630	406
PDPA-Cu(II)	3482	1719	1166	1542	2978	-	3625	407
PDPA-Co(II)	3448	1719	1163	1544	2926	-	3652	415

All data are given in cm^{-1} unit

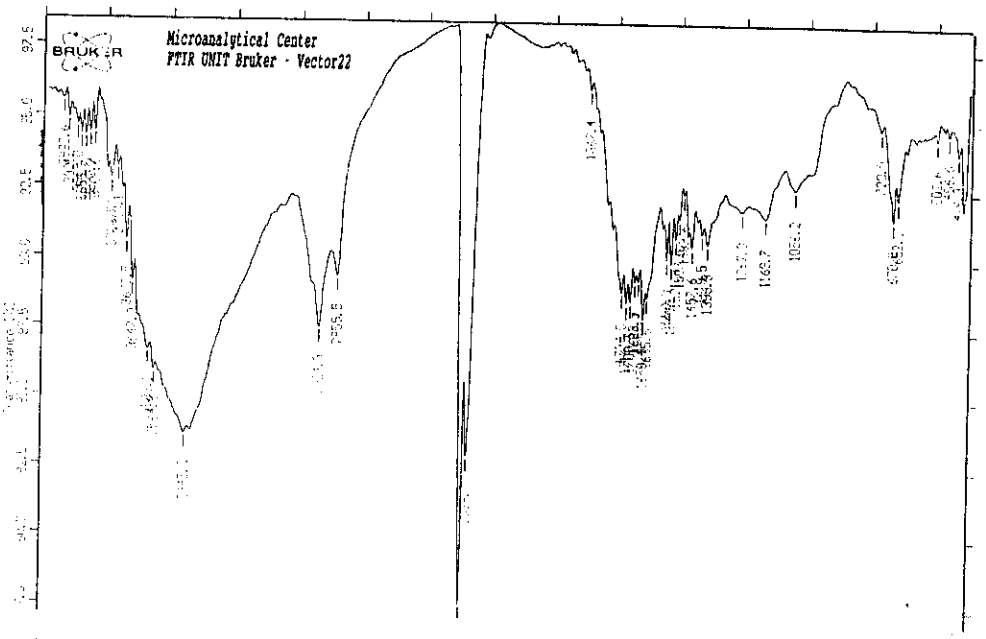
Table (10): Important IR Spectral Assignments of PDPA and its Double Metal Complexes.

Compound	OH	O ‖ -C-	C – O	CH_2	CH	NH_2	NH	M-N
PDPA	3464	1721	1167	1394	2979	818	3751	-
PDPA-Ni(II), Co(II)	3461	1719	1217	1393	2978	-	3510	697
PDPA-Ni(II), Cu(II)	3446	1721	1258	1393	2940	-	3535	405
PDPA -Cu(II), Co(II)	3448	1722	1168	1393	2976	-	3752	436 404

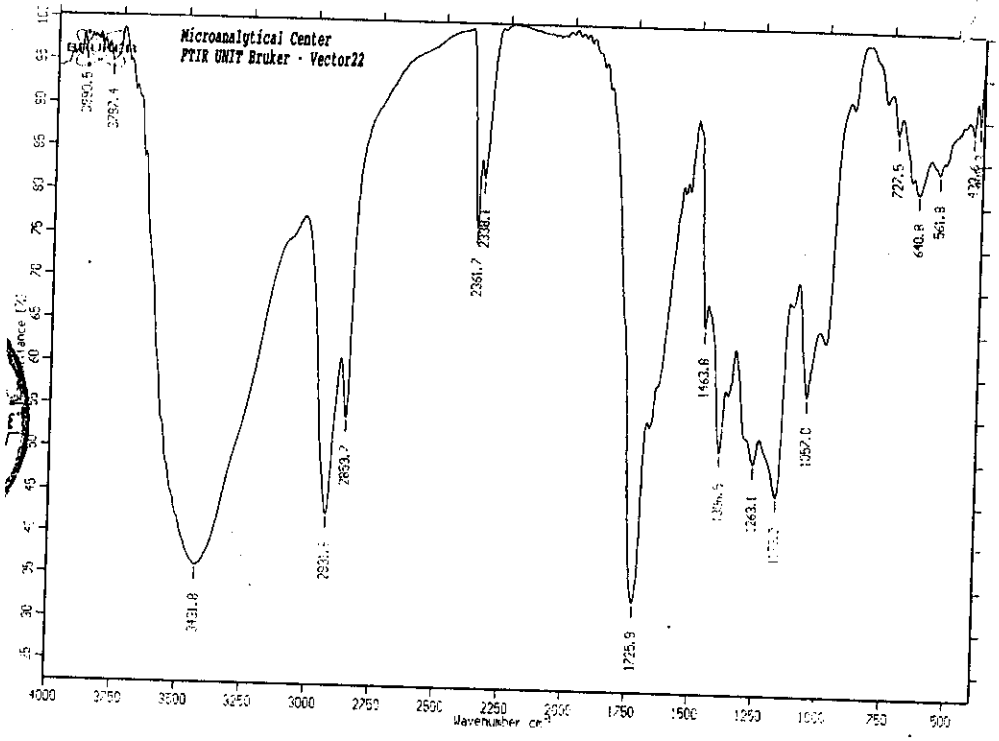
All data are given in cm^{-1} unit



PHMA polyester



PHMA-Pb(II) Complex



PHMA-Ni(II) Complex

Fig. (1): IR Spectra of PHMA, PHMA-Pb(II) and PHMA-Ni(II) complexes.

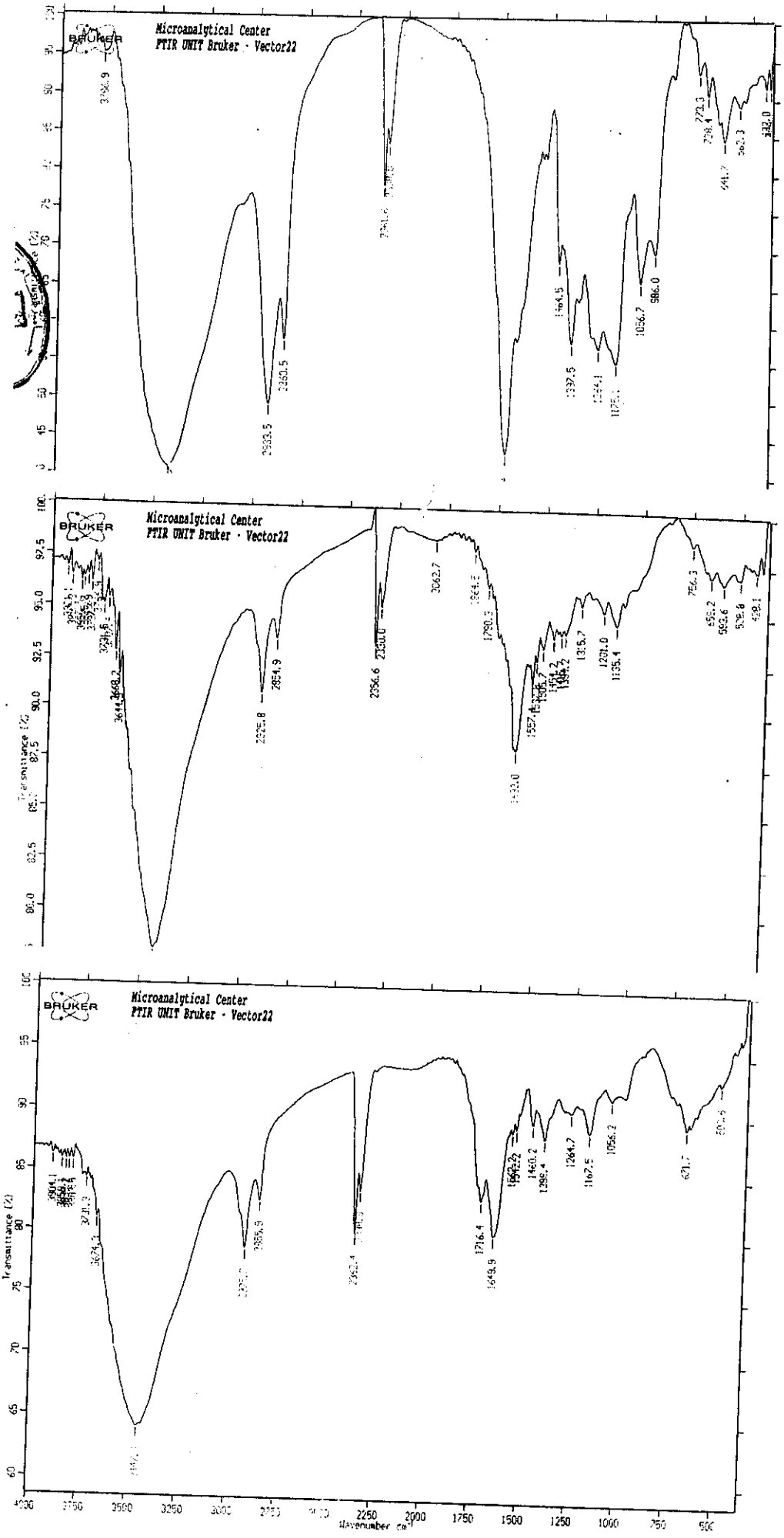
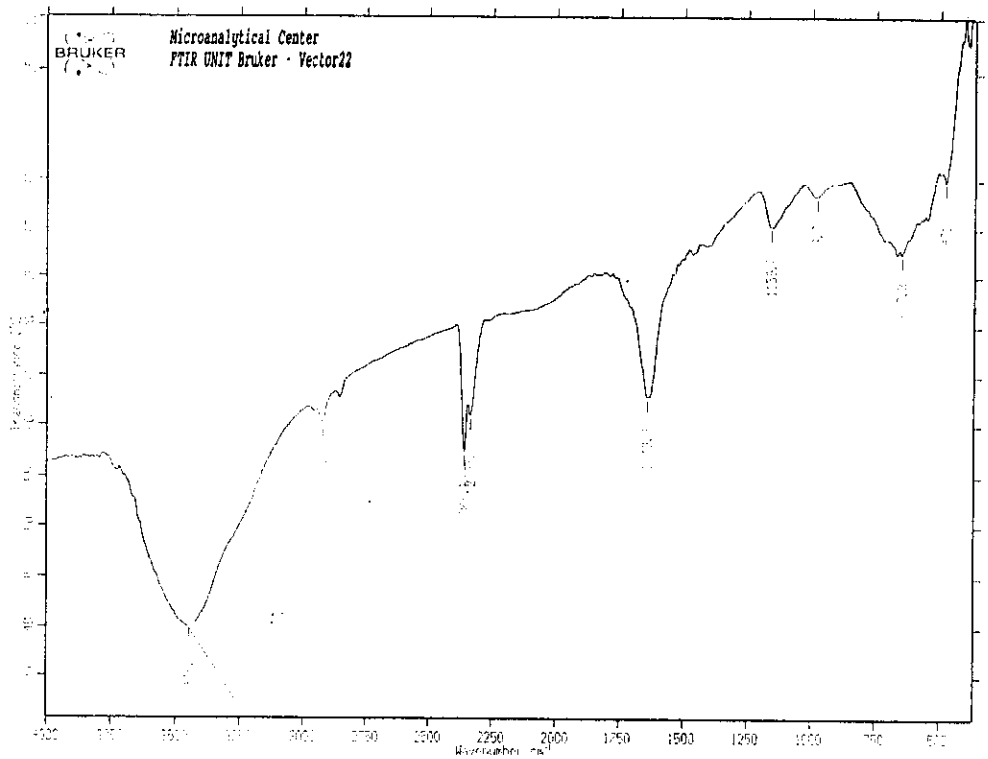
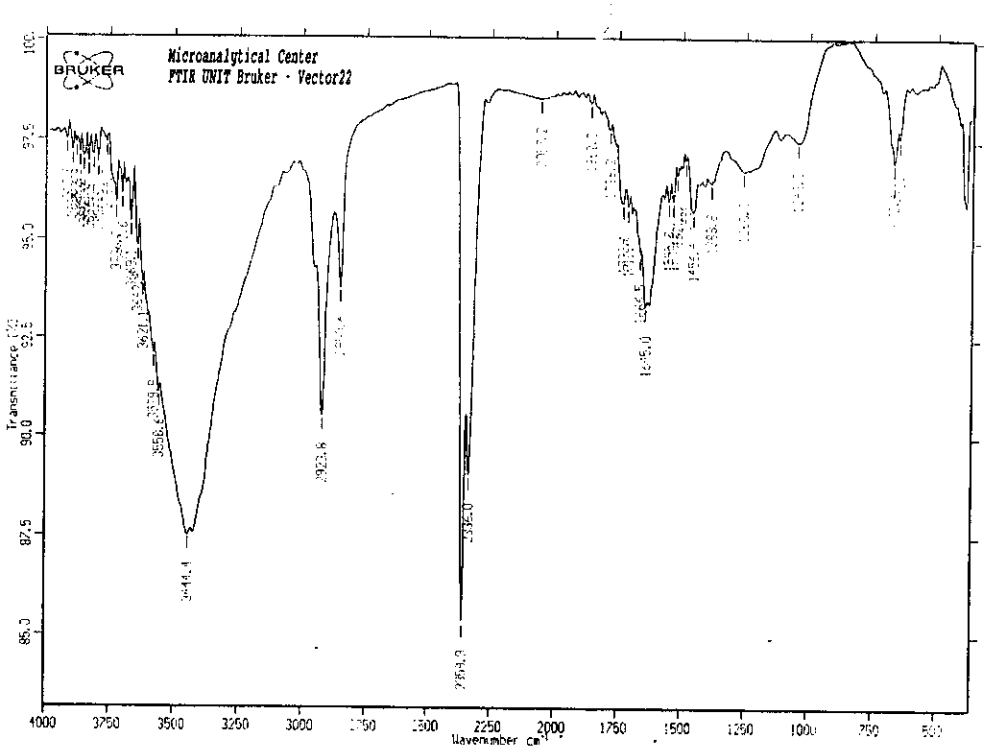


Fig. (2): IR Spectra of PHMA-Cd(II), PHMA-Cu(II) and PHMA-Co(II) complexes.

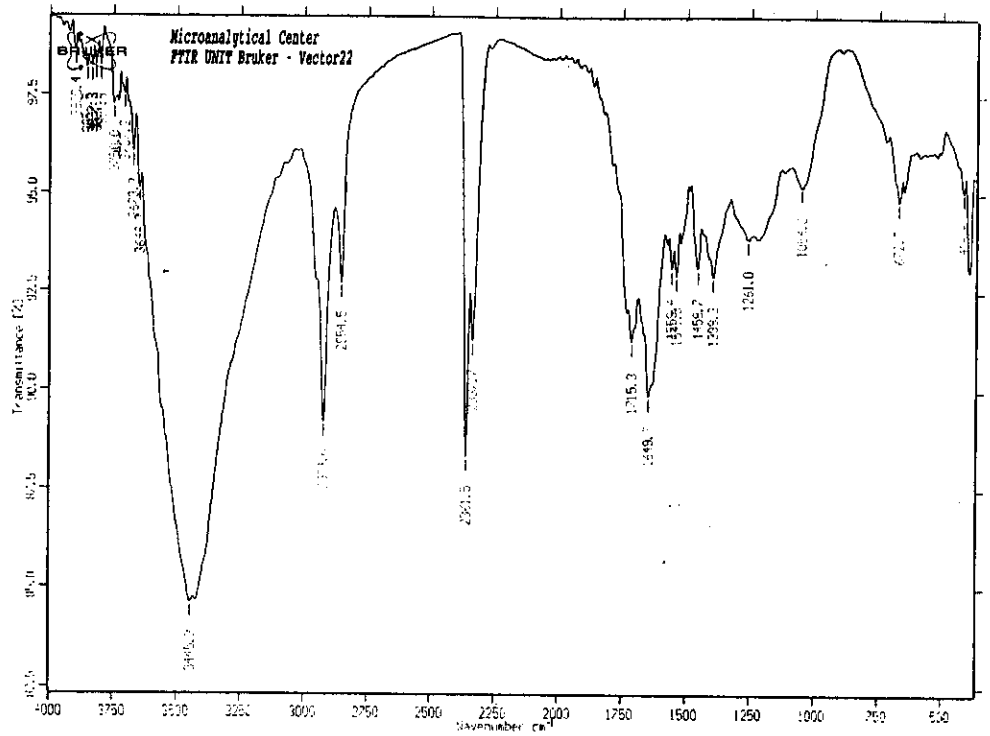


PHMA-Hg(II) Compl

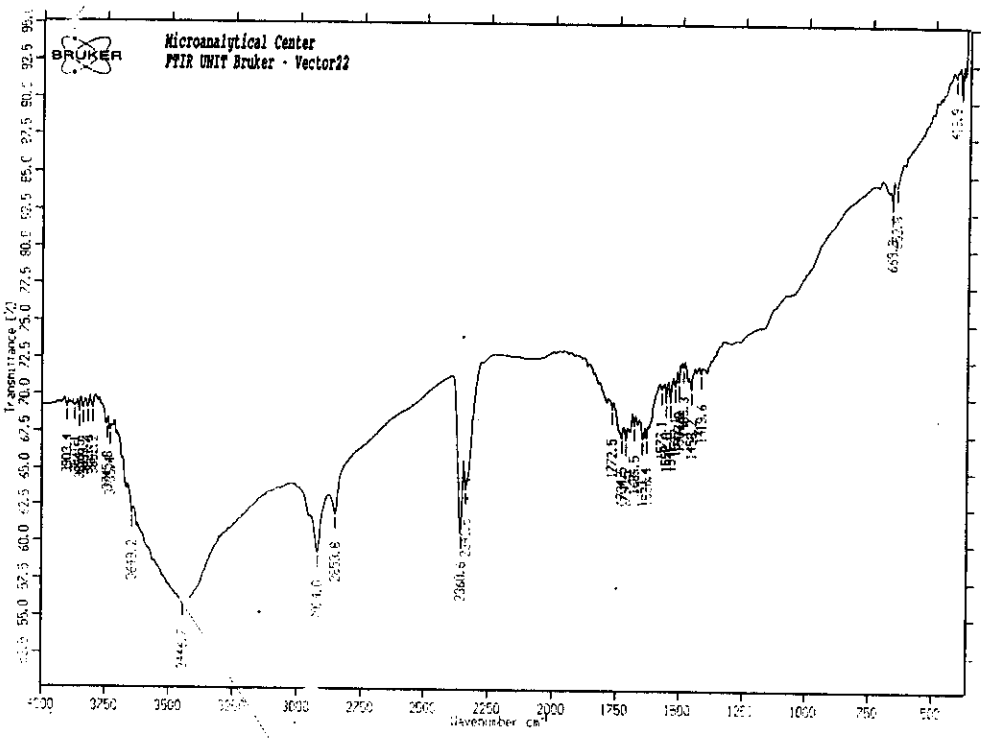


PHMA-Mg(II) Compl

Fig. (3): IR Spectra of PHMA-Hg(II) and PHMA-Mg(II) complexes.

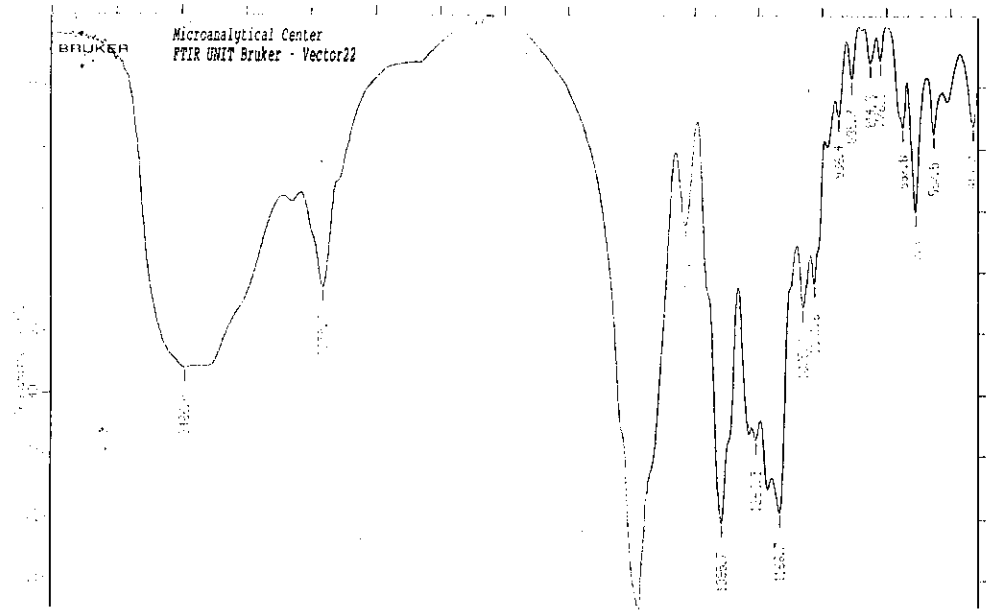


PHMA-Mn(II)

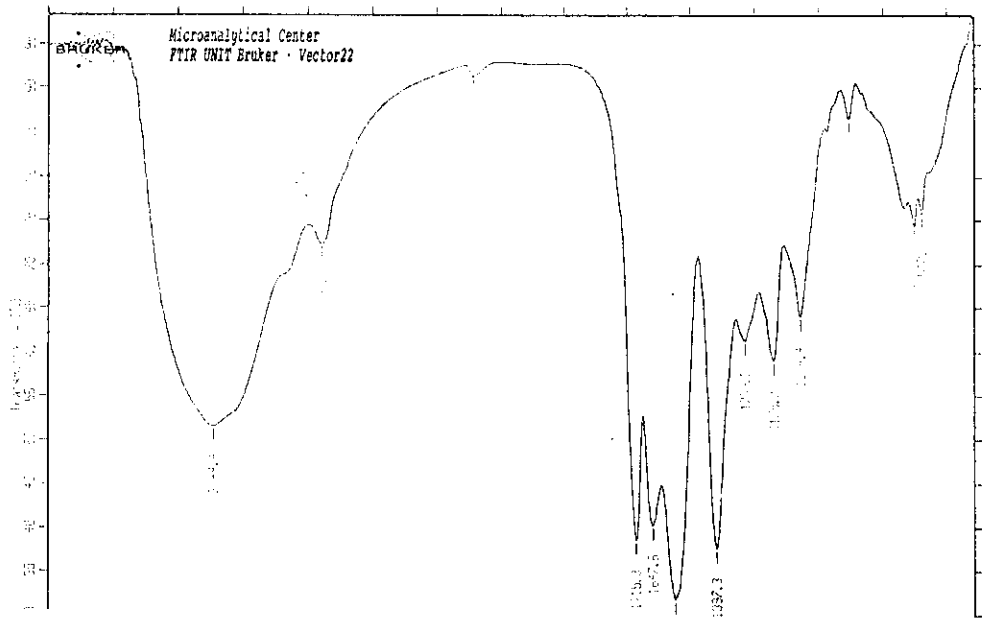


PHMA-Fe(III) complex

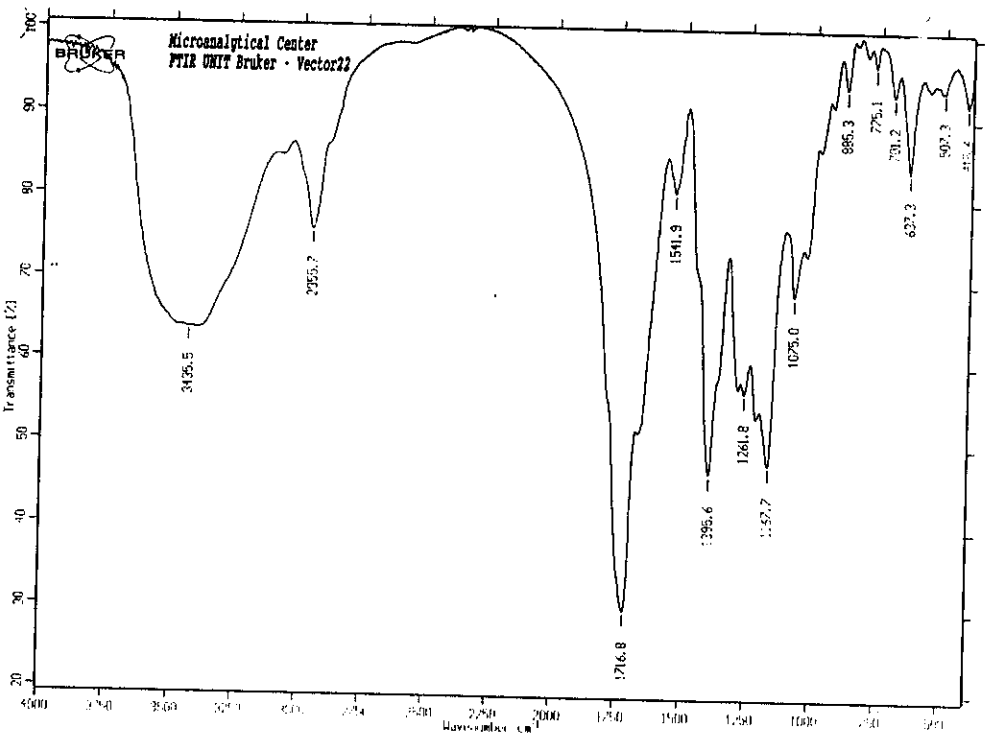
Fig. (4): IR Spectra of PHMA-Mn(II) and PHMA-Fe(III) complexes.



PDEA polyester

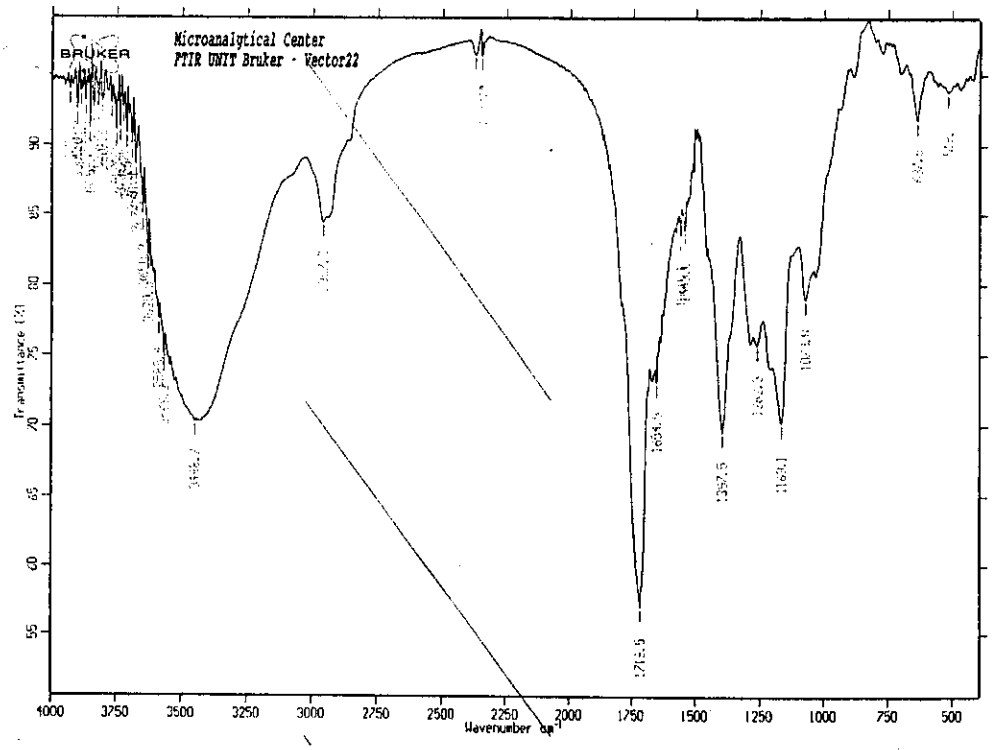


PDEA-Pb(II) Complex

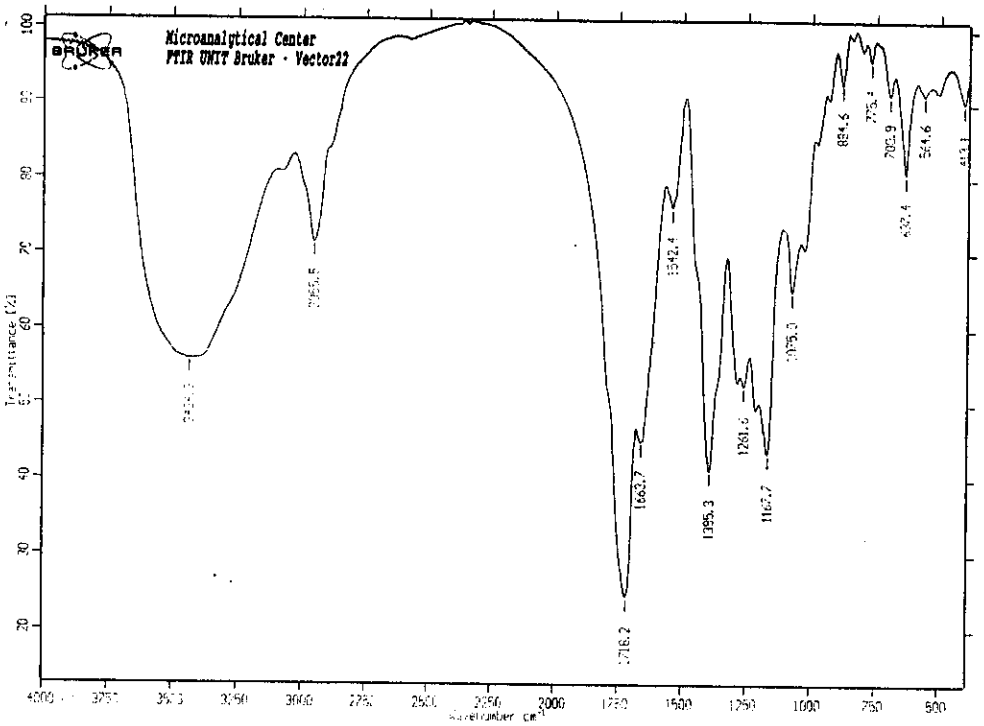


PDEA-Ni(II) Complex

Fig.(5): IR Spectra of PDEA, PDEA-Pb(II) and PDEA-Ni(II) complexes.

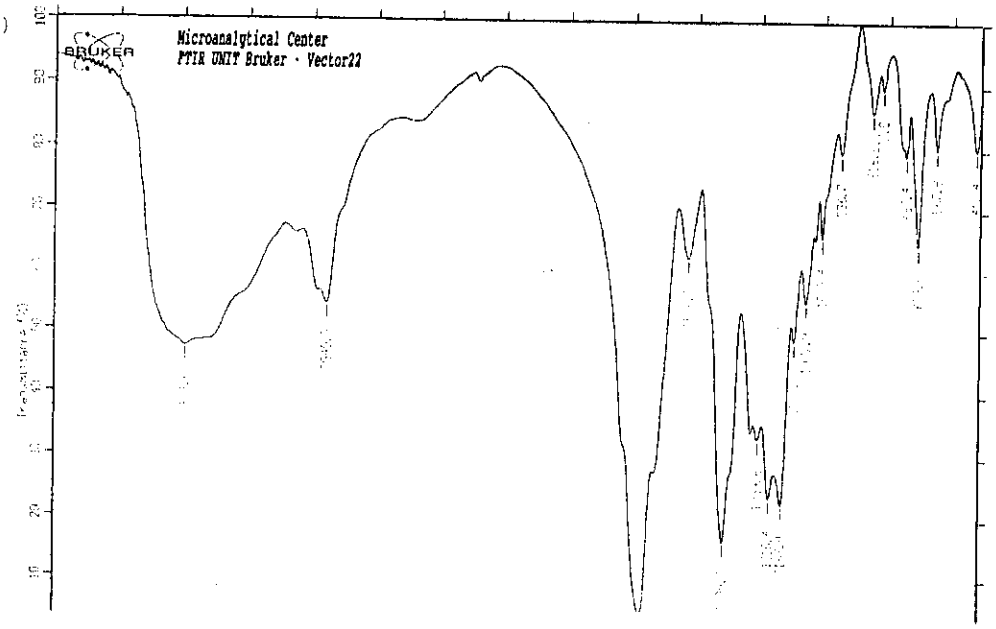


PDEA-Cu(II) Complex

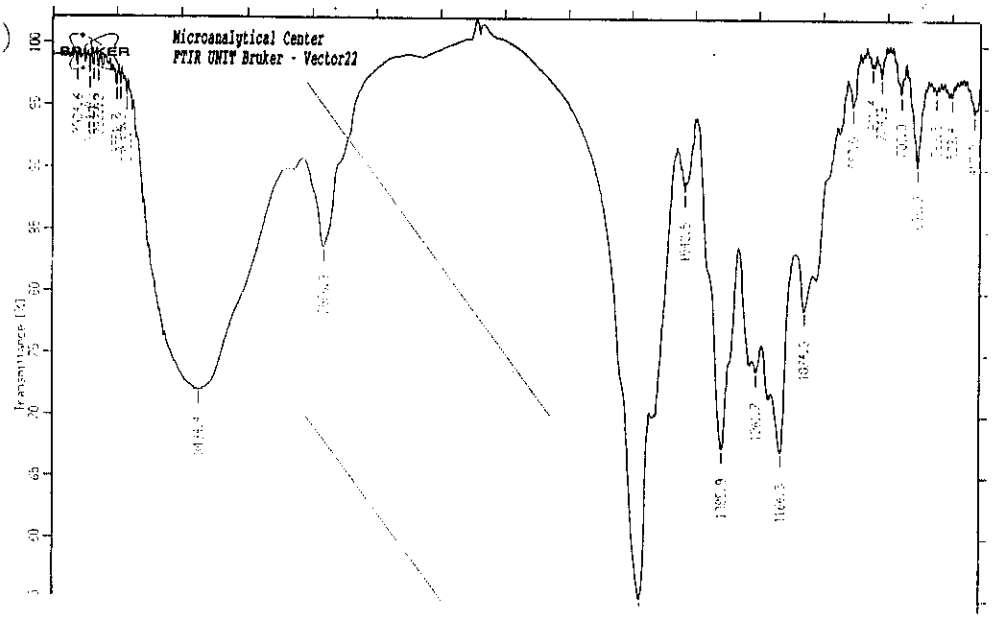


PDEA-Co(II) Complex

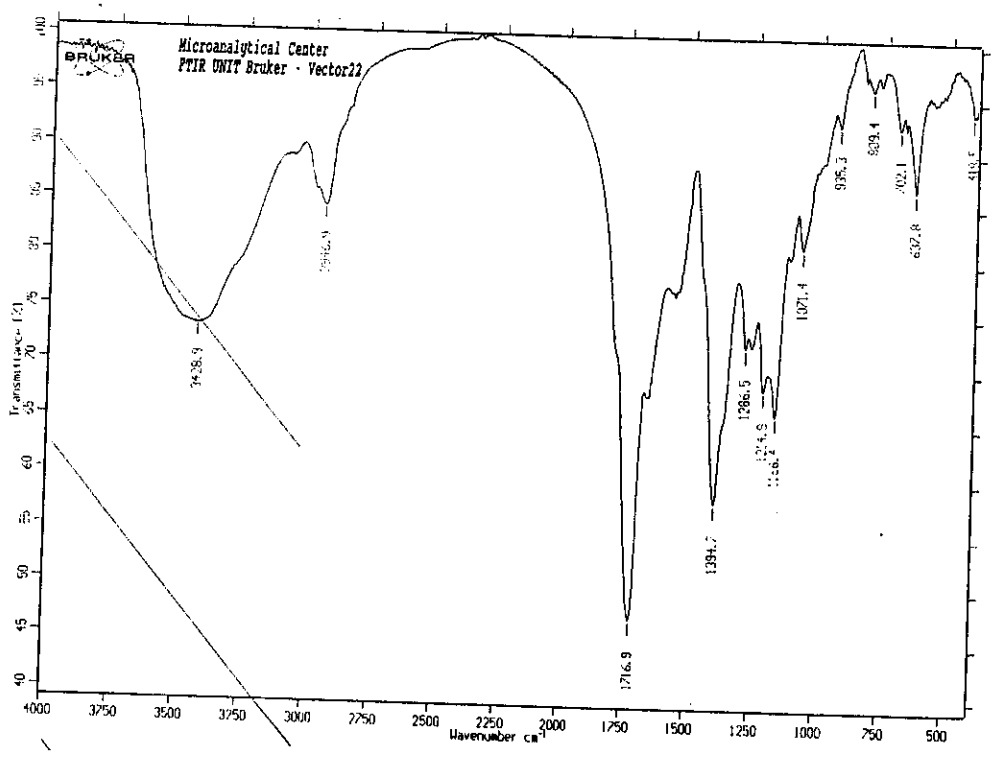
Fig.(6): IR Spectra of PDEA-Cu(II) and PDEA-Co(II).



PPA polyester

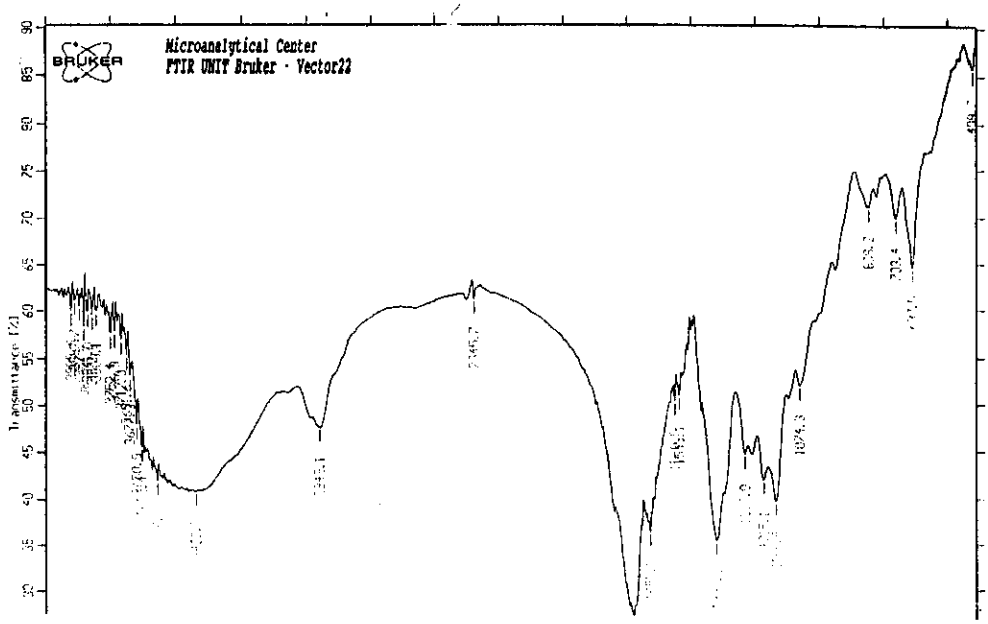


PPA-Pb(II) Complex

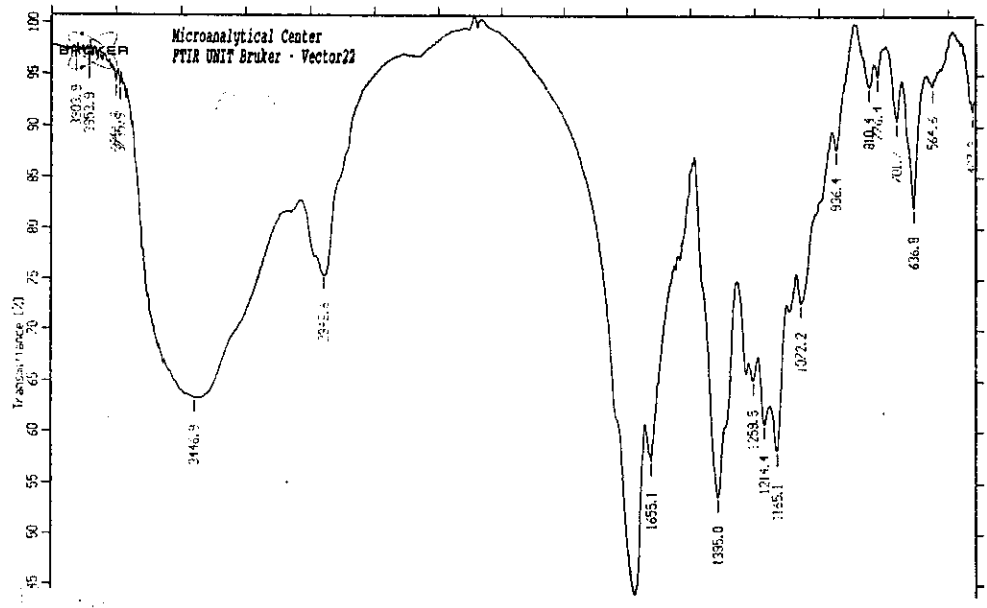


PPA-Ni(II) Complex

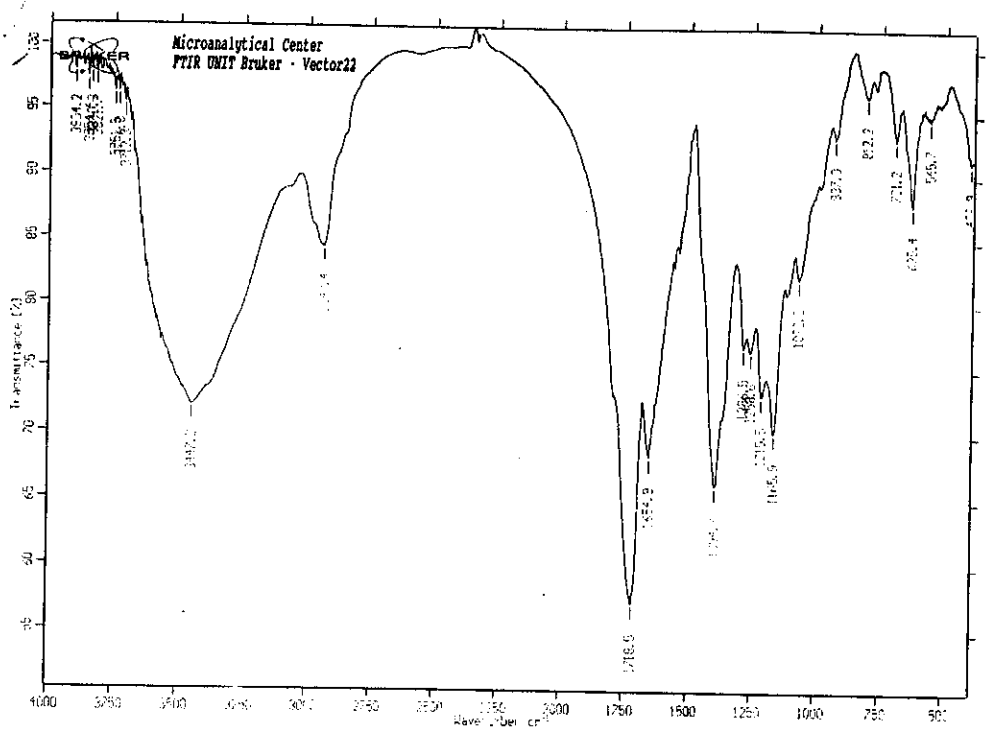
Fig. (7): IR Spectra of PPA, PPA-Pb(II) and PPA-Ni(II) complexes.



PPA-Cd(II)

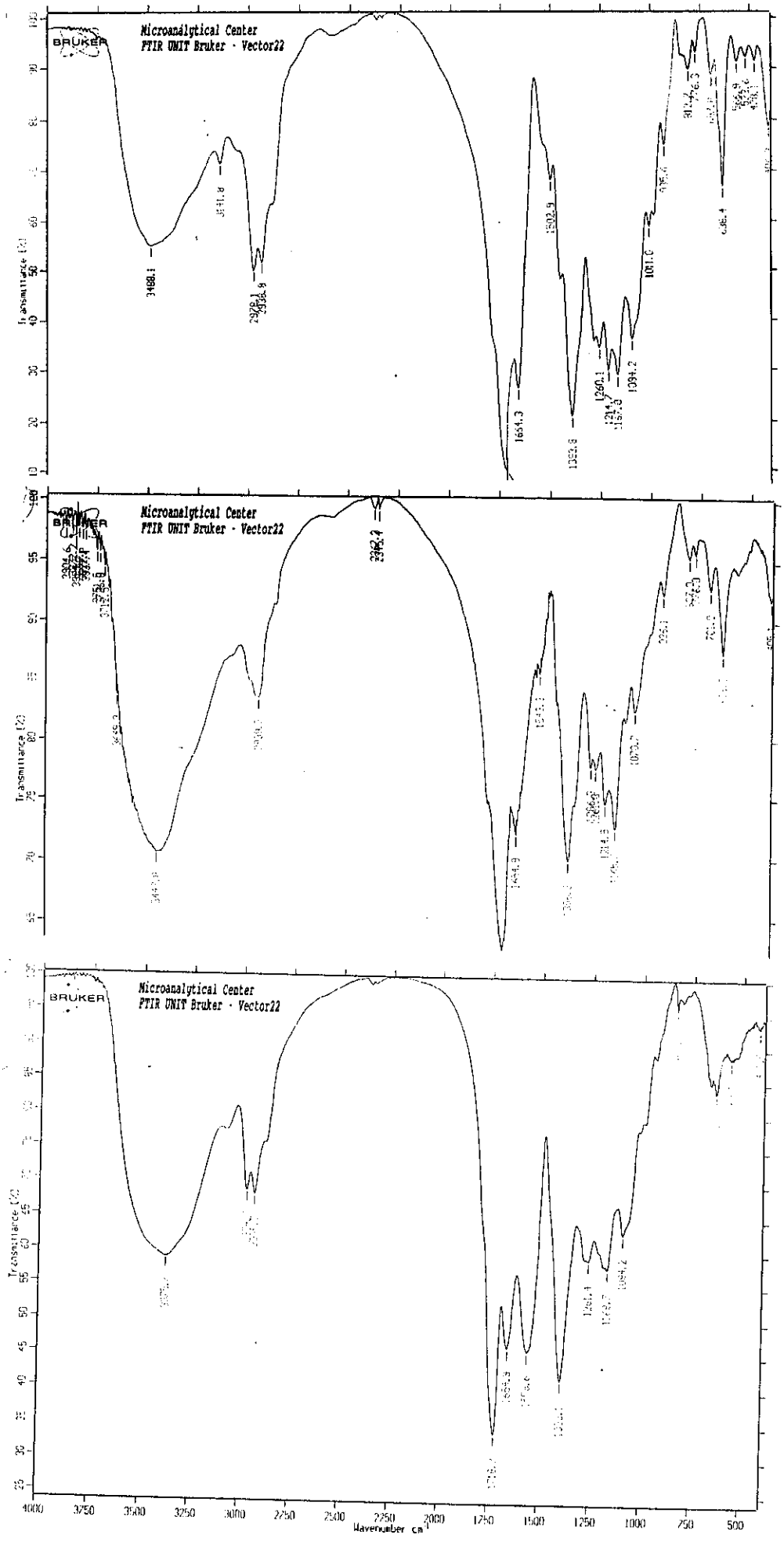


PPA-Cu(II) Complex



PPA-Co(II) Complex

Fig. (8): IR Spectra of PPA-Cd(II), PPA-Cu(II) and PPA-Co(II) complexes.

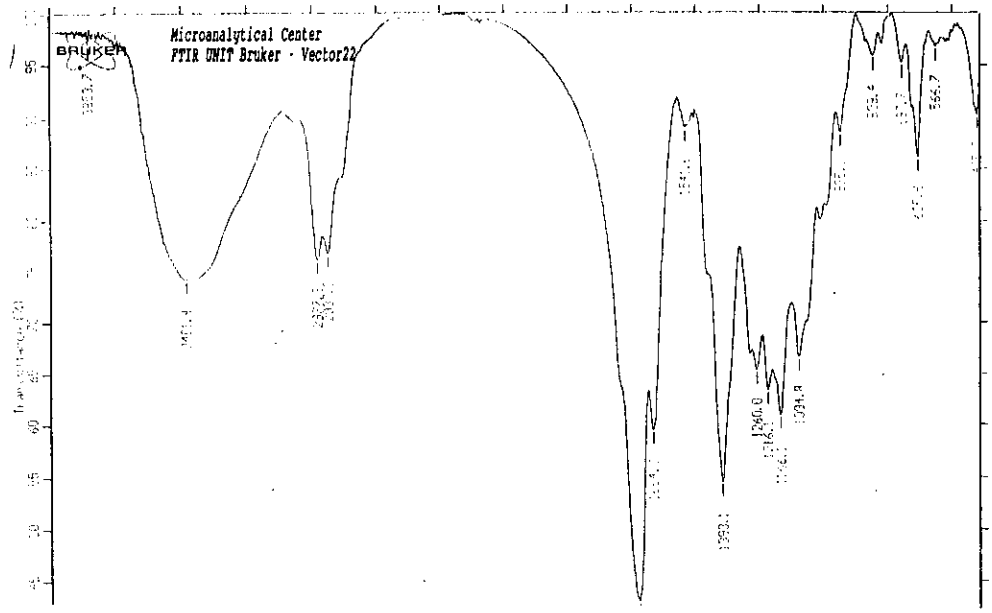


PDPA polyester

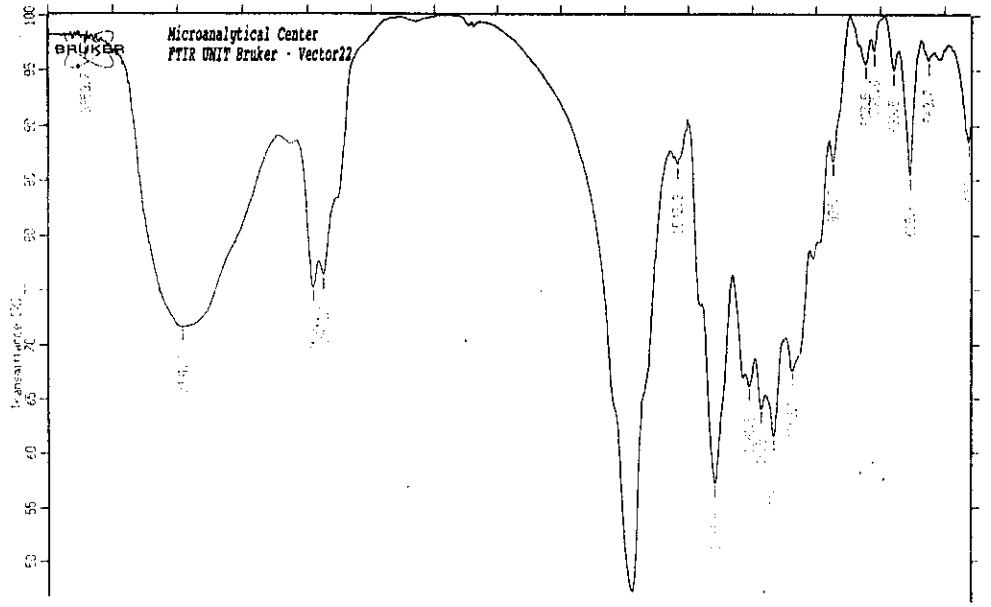
PDPA-Pb(II) Complex

PDPA-Ni(II) Complex

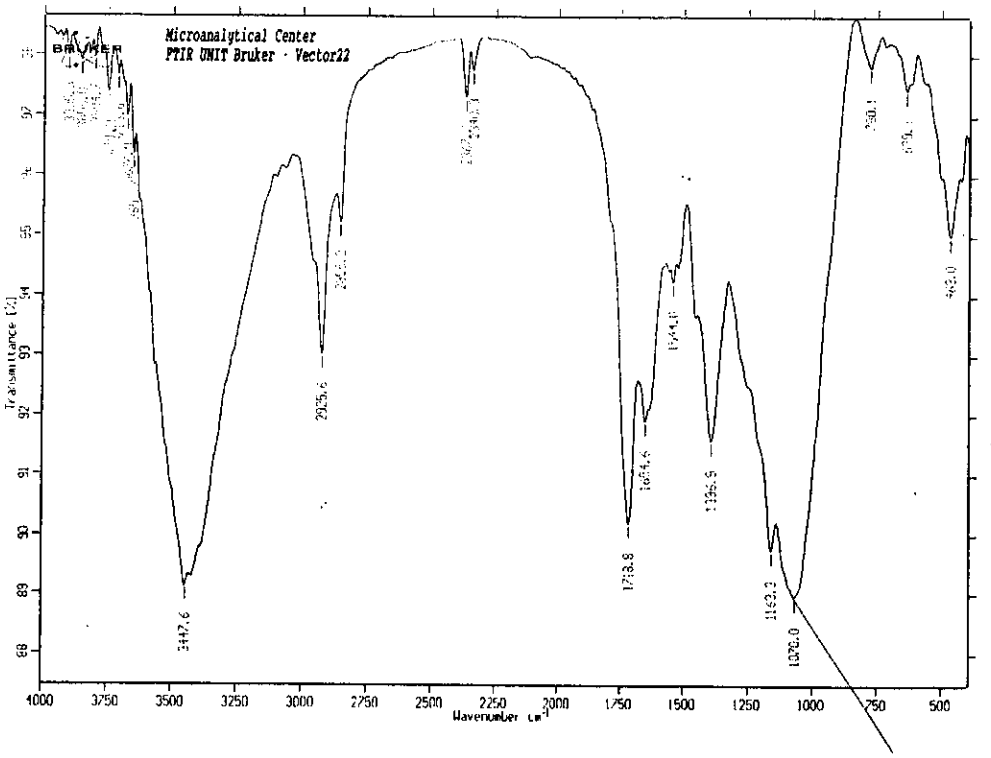
Fig. (9): IR Spectra of PDPA, PDPA-Pb(II) and PDPA-Ni(II)complexes.



PDPA-Cd(II) Complex



PDPA-Cu(II)



PDPA-Co(II) Complex

Fig. (10): IR Spectra of PDPA-Cd(II), PDPA-Cu(II) and PDPA-Co(II) complexes.

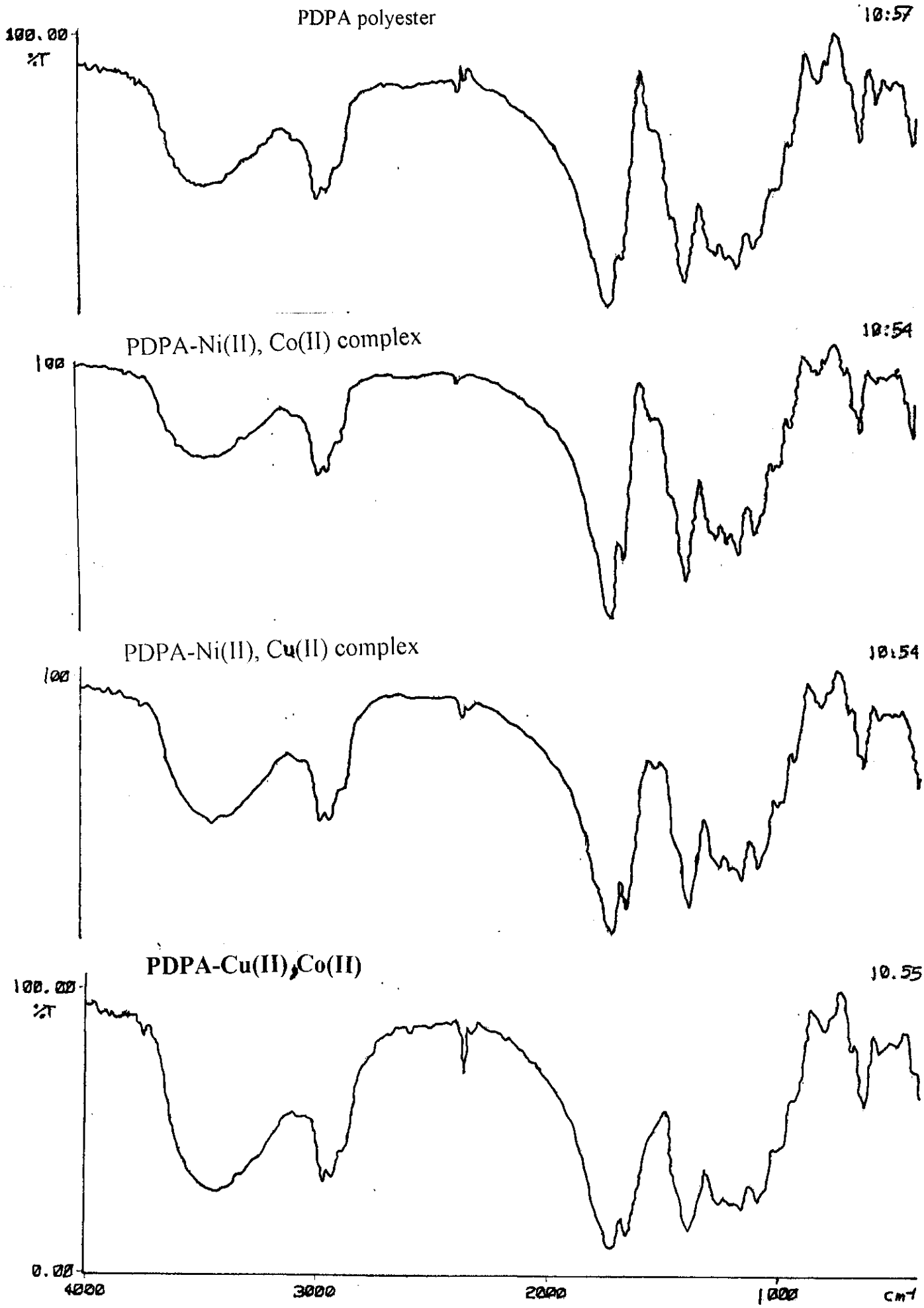
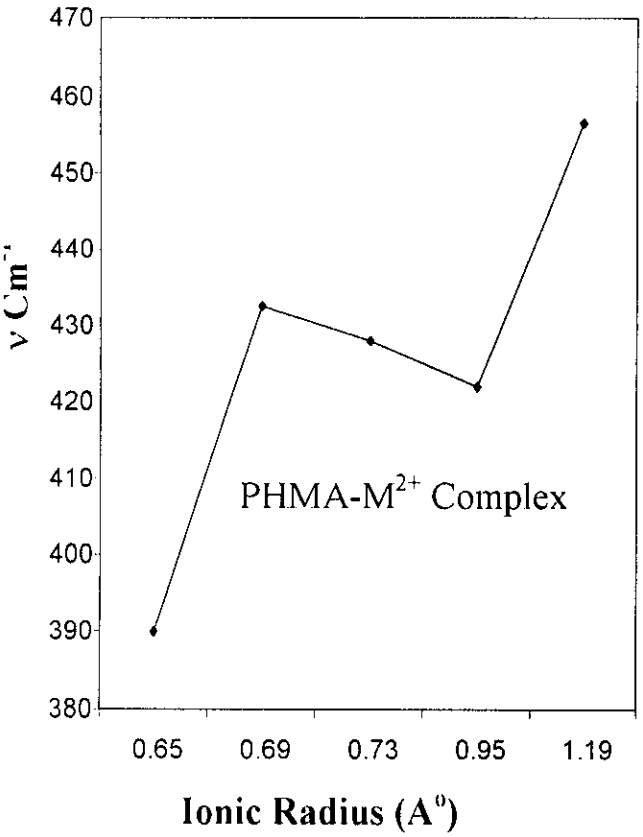
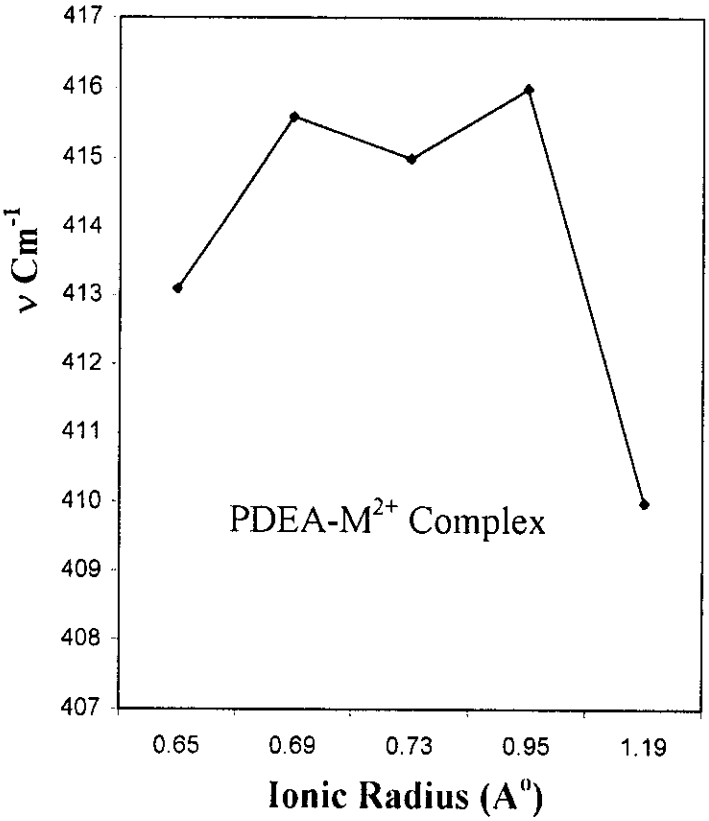
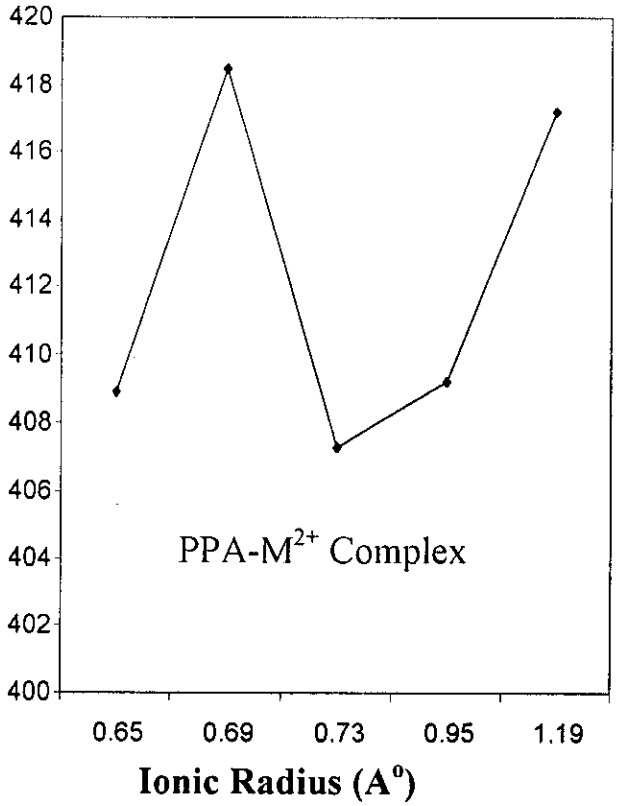


Fig. (11): IR Spectra of PDPA and Its Double Metals Complexes.







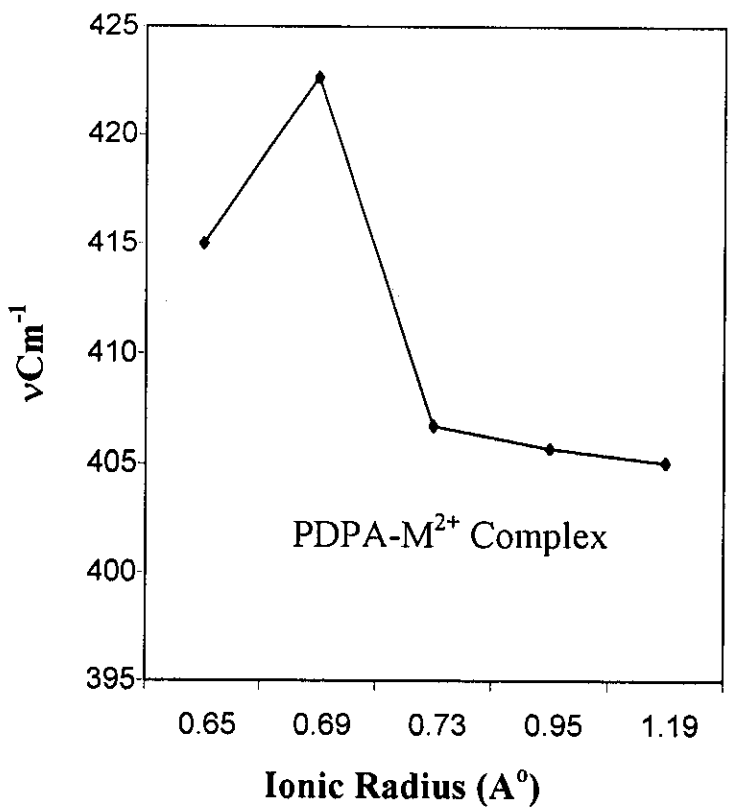
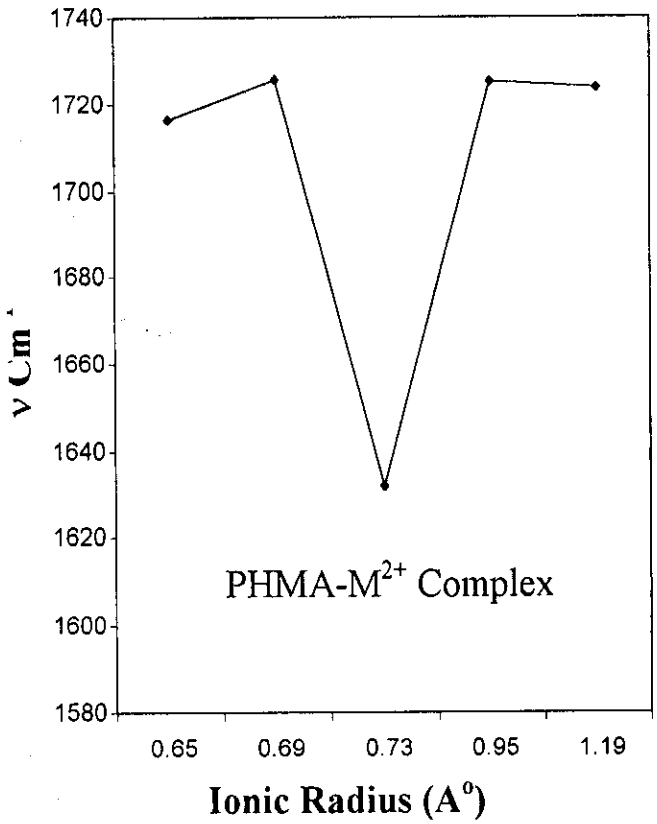
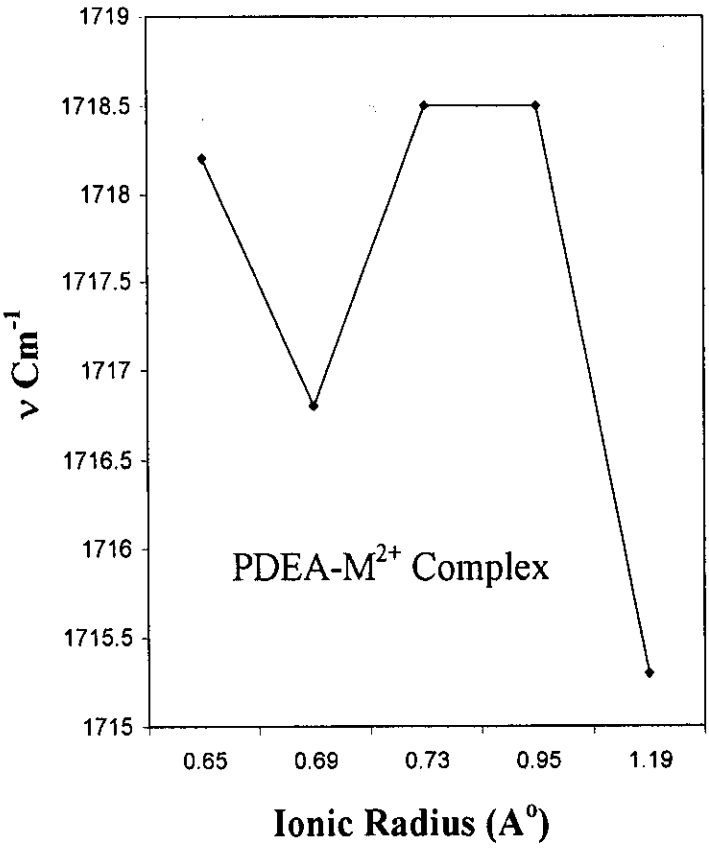
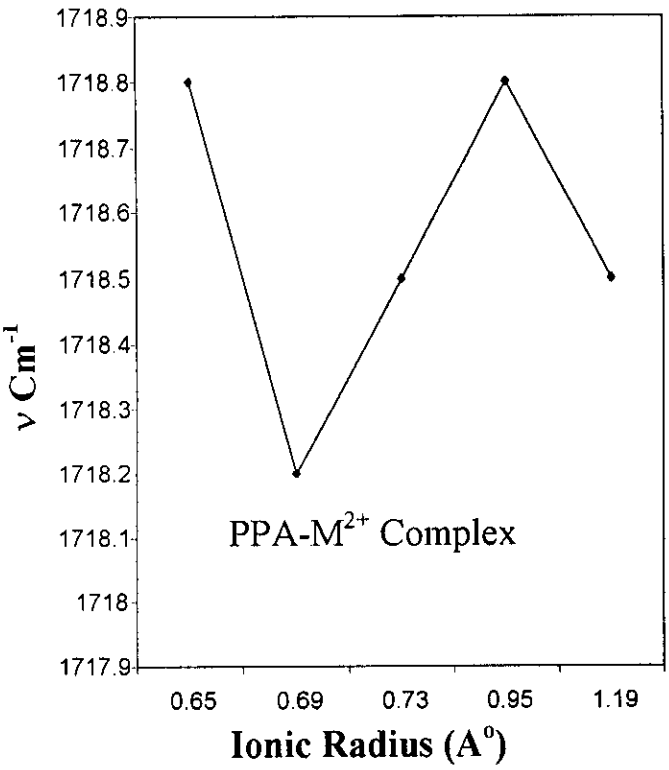


Figure (12): Relation between ν cm^{-1} of M^{2+} - N and Ionic Radius (A°) for Investigated Compounds.







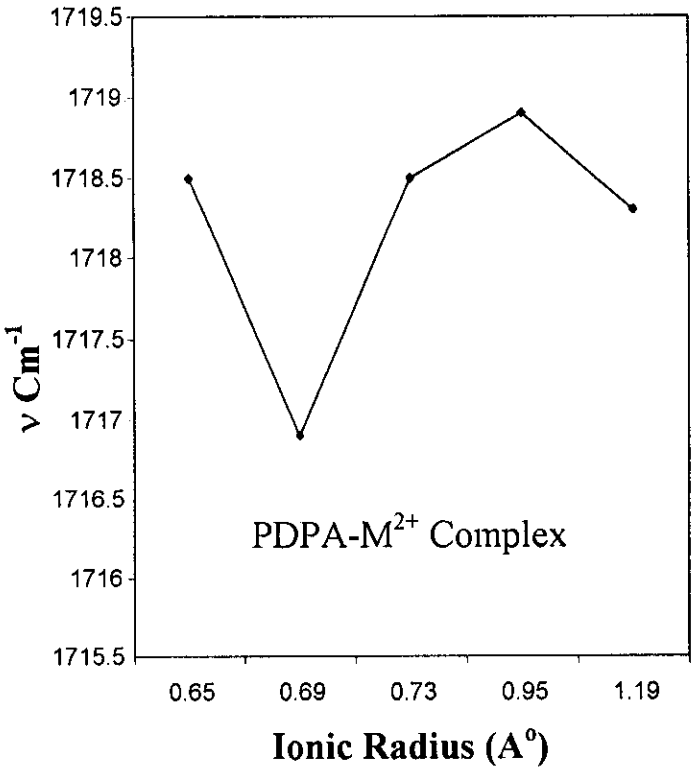


Figure (13): Relation between ν cm^{-1} of C = O and Ionic Radius (A^o) for Investigated Compounds.

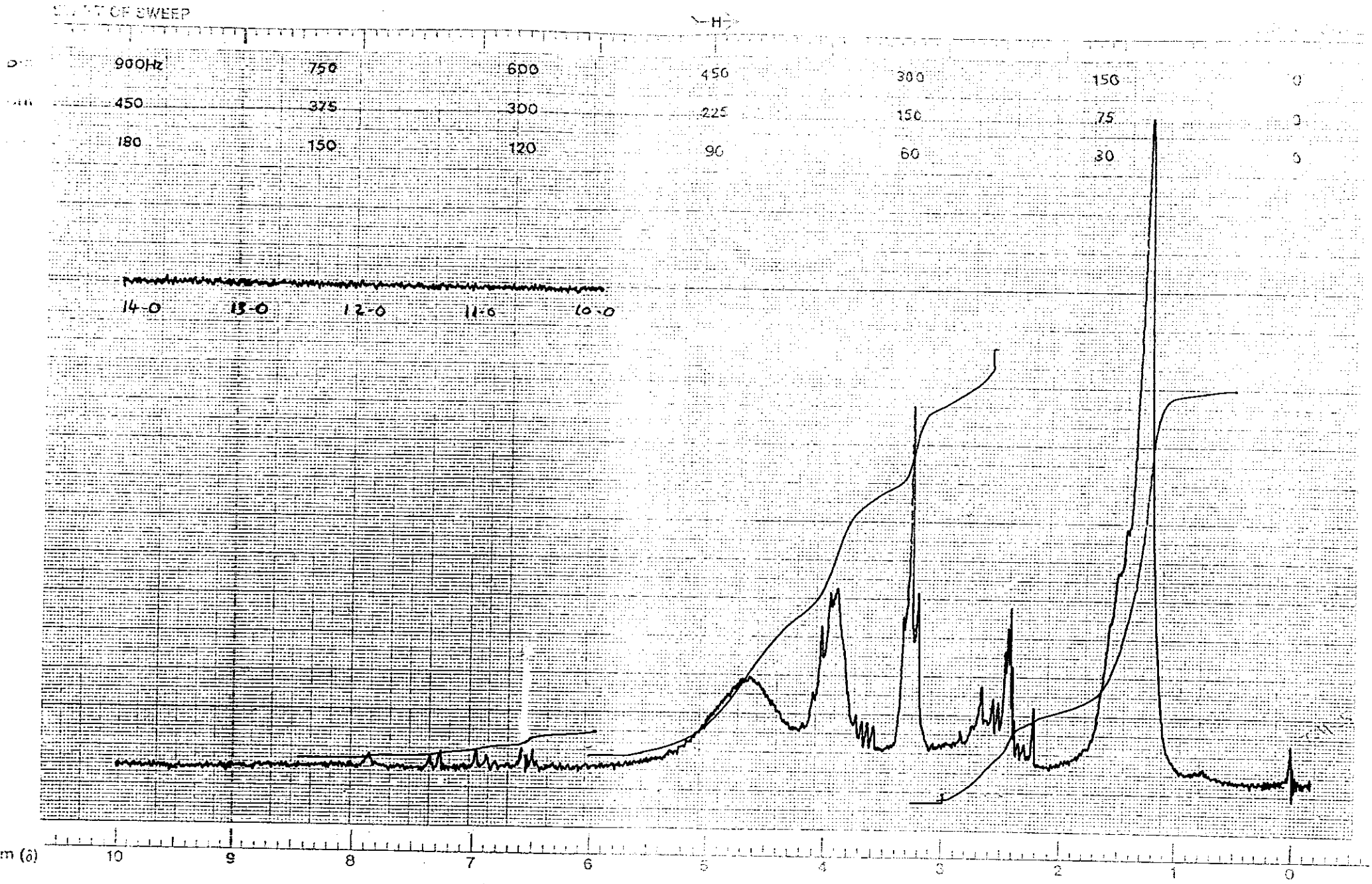


Fig. (14 a): ^{1}H-NMR Spectrum of PHMA polyester.

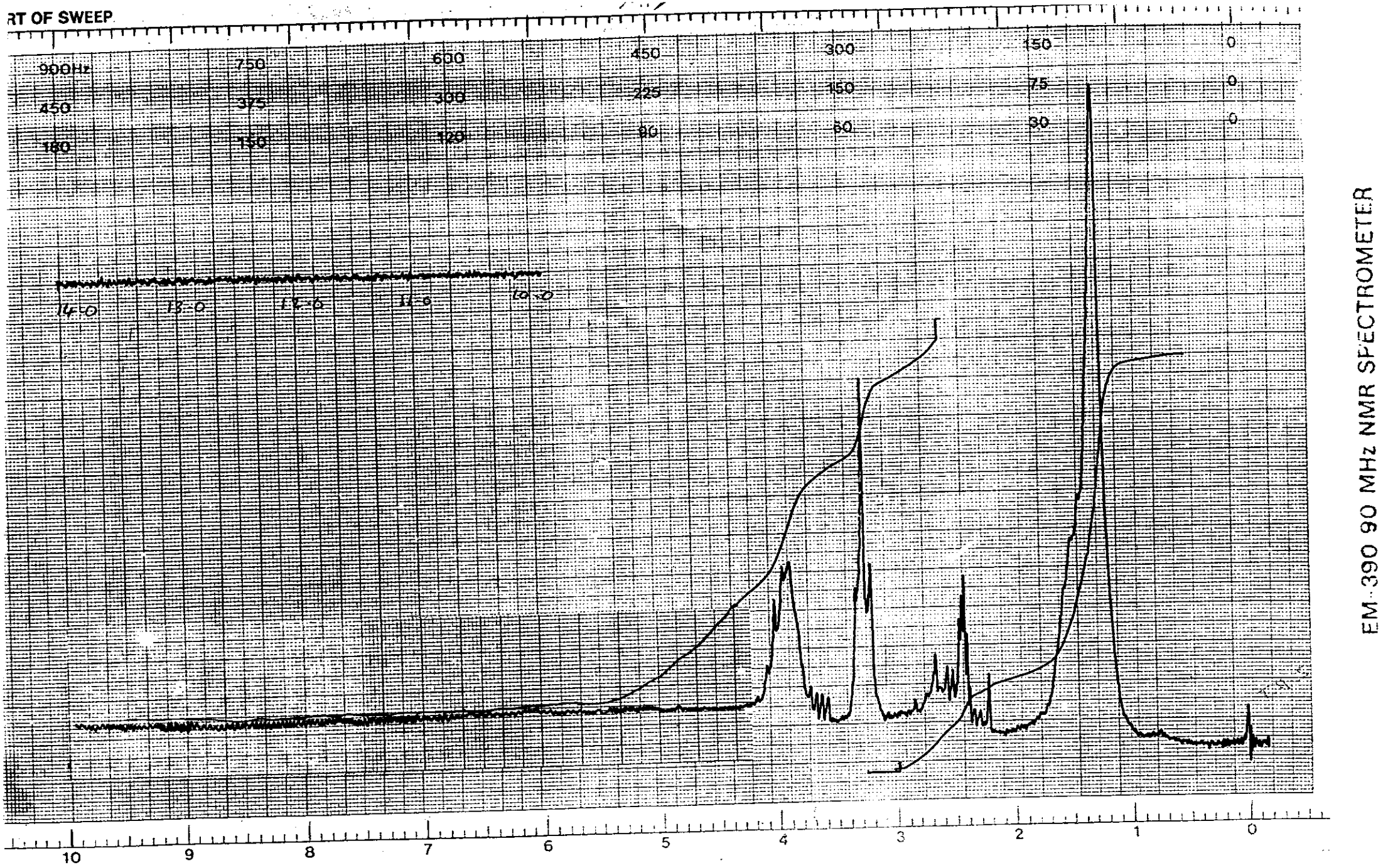


Fig. (14 b): ^{1}H-NMR Spectrum of PHMA polyester.

Solvent DTO

III-C-Thermal Analysis of Investigated Polyesters and its Metal Complexes

III-C-1-Thermal gravimetry TG and differential thermal analysis DTA.

Thermal studies, DTA and TG, for the polyesters and their metal complexes were carried out in static air and at a temperature range of 298-973 K. This is mainly done to determine the temperatures at which the investigated compounds starting to decompose and to investigate the presence of any phase changes and the number of water molecules present in the compounds before their dissociations.

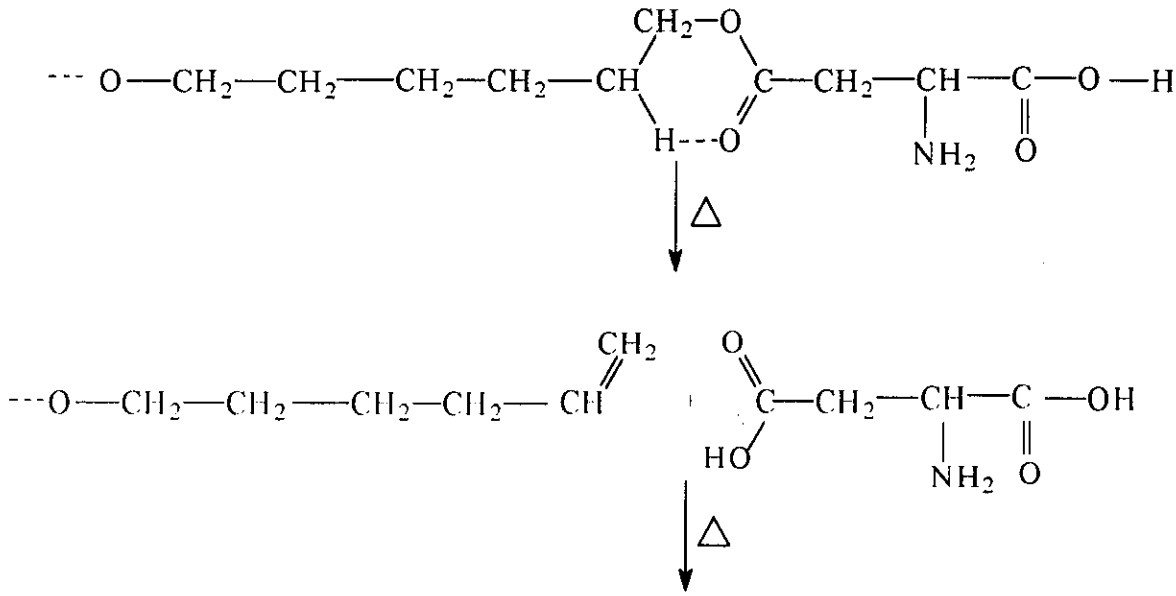
Thermogravimetry (TG) is a technique for measuring the change in weight of a substance as a function of increasing temperature under controlled atmosphere. While the differential thermal analysis (DTA) is the technique for measuring the change occurring in the phase or in the weight of the sample as a function of temperature.

The results of thermal analysis of investigated compounds are shown in Figs (15-18) and Summarized in Tables (11-15). Many decomposition steps depending on the composition of the investigated materials are detected.

III-C-1-a-Thermal analysis of PHMA and its metal-complexes:

The ligand PHMA exhibits thermal dissociations in many steps, Fig. (15). The first one corresponding to 1.8% weight loss at 383 K, which may be due to the loss of absorbed water. The observed percentage weight loss in the range 383-513 K is 7% which corresponds to the

dissociation of the-O-CO-CH_2-CH(NH_2)-COOH unit. This has been formed as a first decomposition stage of the polymer. This unit is dissociated into volatile gases of CO_2, H_2O and nitrogen derivatives. The thermal degradation of the terminal fragments can also occur through the formation of the six membered chelate ring as follows:



Further degradation

Above 513 K a rapid weight loss is observed and 79% weight loss is obtained at 863 K due to the greatly decomposition of the ligand into volatile products, and above this temperature no more volatile compounds, is formed. The dissociated residues are formed from many dissociated units of the parent polymer.

The perusal of Figure (15) clearly indicates that the metal complexes of the polyester ligand PHMA exhibit superior thermal stabilities to those of the ligand. For Co(II), Ni(II) and Cu(II) complexes, the initial weight loss up to 388-398 K corresponds to the elimination of

two water molecules. Therefore, it is suggested that coordinated water molecules are lost up at this temperature range.

In case of Cd(II) and Pb(II) complexes, the weight loss corresponding to two water molecules is occurred at 403 and 418 K respectively.

Below 398 K, the order of the stability of the complexes with respect to metal ions is :

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

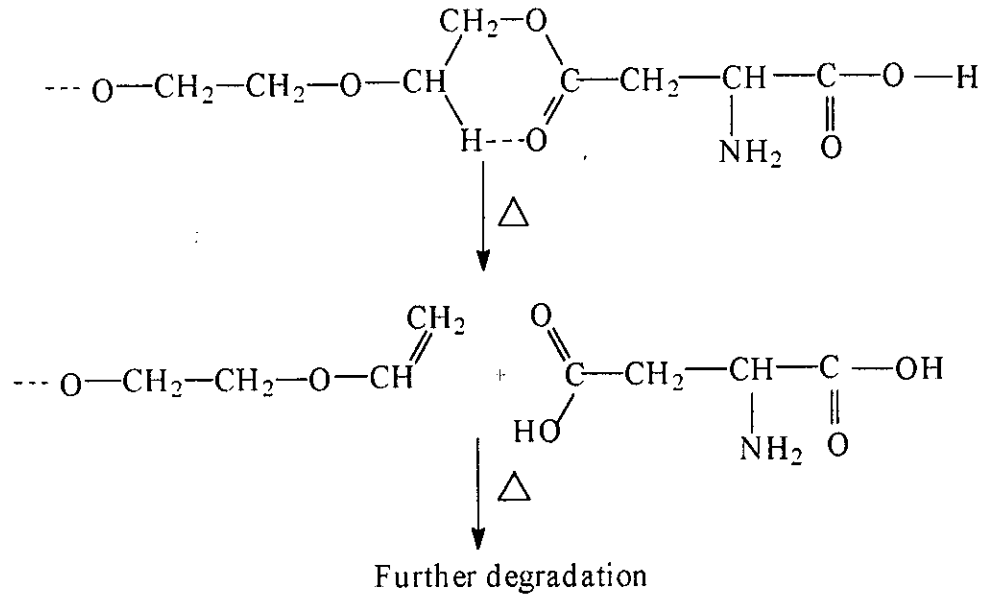
This stability order is the same as that of the familiar order of the stability of hydration for the first transition series[105]. The highest stability of the Pb(II) complex may be due to the large radius and molecular weight of Pb[105].

A steeper decrease in the weight of the complexes is observed at temperatures depending on the composition of the complex see Fig. (15) and Table (11). The residual weight in all the complexes is more than that of the metal content. It indicates that the metal complexes are not decomposed into their free metals by heating at the investigated temperature range. But the final product depends on the type of complex, where PbO, CdO, $CoCO_3$, $NiCO_3$ and Cu oxalates are the main end products formed in the investigated complex Table (11).

III-C-1-b-Thermal analysis of PDEA and its metal-complexes:

The ligand PDEA dissociates also in many steps Fig. (16). The first one exhibit 1.9% weight loss at 363 K, which may be due to the loss of adsorbed water. The observed percentage weight loss in the range 363-473 K is 8% which corresponds to the dissociation of the $-O-CO-CH_2-CH(NH_2)-COOH$ unit. This has been formed as a first decomposition

stage of the polymer. This unit is dissociated into volatile gases of CO_2, H_2O and nitrogen derivatives. In the case of PDEA the thermal degradation of the terminal fragments can also occur through the formation of the six membered chelate ring as follows:



Above 473 K a rapid weight loss is observed in the ligand PDEA and 67% of weight loss obtained at 873 K due to the highly decomposition of the ligand into volatile products, and above this temperature no more volatile compounds, is formed. The dissociated residues are formed from many dissociated units of the parent polymer.

The perusal of Figure (16) clearly indicates that the metal complexes of the polyester ligand PDEA exhibit superior thermal stabilities to those of the ligand. For Cu(II) and Ni(II) complexes, the initial weight loss up to 378-383K corresponds to the elimination of two water molecules. Therefore, it is suggested that coordinated water molecules are lost at this temperature range. But they may be decomposed into metal oxalate, metal carbonate or metal oxide as illustrated in Table (11).

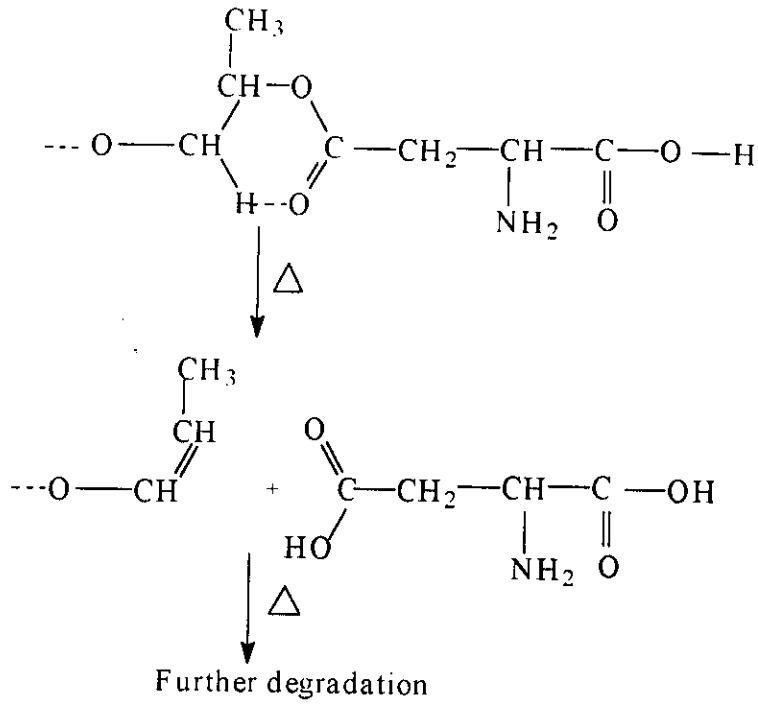
In case of Pb(II) complex, the weight loss corresponding to two water molecules is occurred at 388 K.

Below 383 K, the order of the stability of the complexes with respect to metal ions is : $-Pb-^{2+} > -Cu-^{2+} > -Ni-^{2+}$. This stability order is the same as that of the familiar order of the stability of hydration for the first transition series[105]. The highest stability of the Pb(II) complex may be due to the large radius and molecular weight of Pb[105] as mentioned above.

A steeper decrease in the weight of the complexes is observed at higher temperatures, its value depends on the composition of the polymer complex. The residual weight in all the complexes is more than that of the metal content. It indicates that the metal complexes are not decomposed into their metals by heating at the investigated temperature range, but may be decomposed into metal oxalate, metal carbonate or metal oxide as illustrated in Table (12).

III-C-1-c-Thermal analysis of PPA and its metal-complexes:

The thermal dissociation of ligand PPA occurred also in many steps, Fig (17). The first one exhibit 2.4% weight loss at 353 K, which may be due to the loss of adsorbed water. The weight loss in the range 353-563K is 9% which corresponds to the dissociation of the –O-CO-CH_2-$CH(NH_2)$-COOH unit. This has been formed as a first decomposition stage of the polymer. This unit is dissociated into volatile gases of CO_2, H_2O and nitrogen derivatives. The thermal degradation of the terminal fragments can also occur through the formation of the six membered chelate ring as follows:



Above 563 K a rapid weight loss is observed and 47% of weight loss is obtained at 853 K due to the greatly decomposition of the ligand into volatile products, and above this temperature no more volatile compounds, is formed. The dissociated residues are formed from many dissociated units of the parent polymer.

The perusal of Figure (17) clearly indicates that the metal complexes of the polyester ligand PPA exhibit superior thermal stabilities to those of the ligand. For Ni(II) and Co(II) complexes, the initial weight loss at 373K corresponds to the elimination of two water molecules. Therefore, it is suggested that coordinated water molecules are lost at this temperature.

In case of Cu(II) complex, the weight loss corresponding to two water molecules is occurred at 378 K.

Below 373 K, the order of the stability of the complexes with respect to metal ions is:

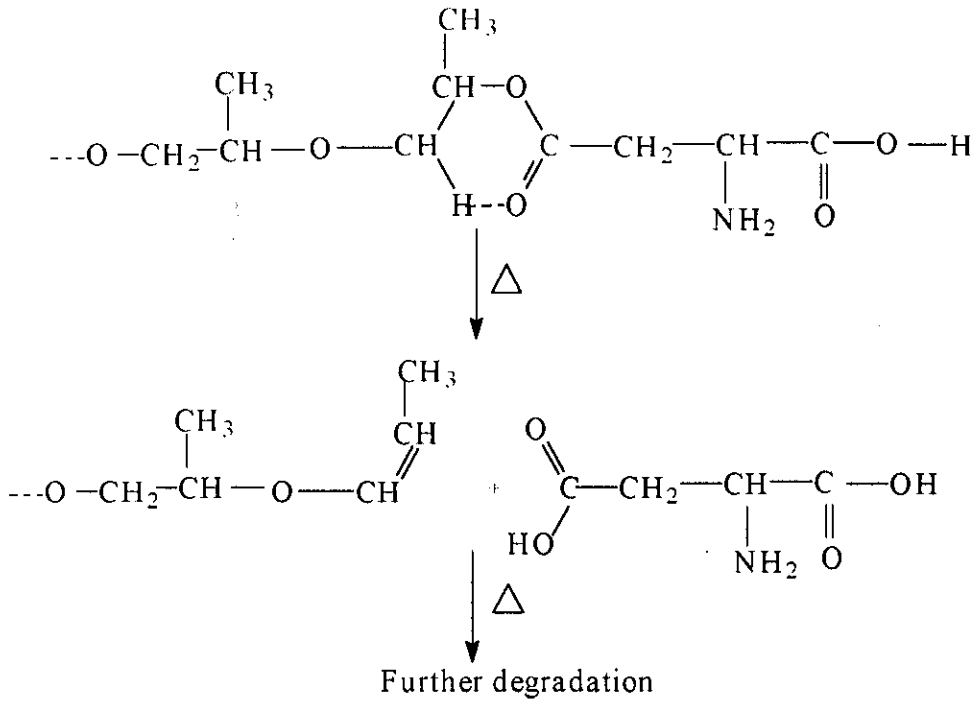
$$-Cu-^{2+} > -Ni-^{2+} > -Co-^{2+}.$$

This stability order is the same as that of the familiar order of the stability of hydration for the first transition series[105]. The highest stability of the Cu(II) complex may be due to the large radius and molecular weight of Cu(II)[105].

A steeper decrease in the weight of the complexes is observed at higher temperatures depending on the composition of the polymer complex. The residual weight in all the complexes is more than that of the metal content. It indicates that the metal complexes are not decomposed into their metals by heating at the investigated temperature range but may be decomposed into metal oxalate, metal carbonate or metal oxide as illustrated in Table (13).

III-C-1-d-Thermal analysis of PDPA and its "metal-complexes and double-metals complexes":

The thermal dissociation of ligand PDPA occurred also in many steps Fig (18). The first one exhibit 1.6% weight loss at 403 K, which may be due to the loss of adsorbed water. The observed weight loss at 563 K is 6% which corresponds to the percentage weight of the dissociation of $-O-CO-CH_2-CH(NH_2)-COOH$ unit into its volatile compounds as mentioned above. This has been formed as a first decomposition stage of the polymer. The thermal degradation of the terminal fragments can also occur through the formation of the six membered chelate ring as follows:



Above 563 K a rapid weight loss is observed in the ligand PDPA and 51% of weight loss is obtained at 853 K due to greatly decomposition of the ligand into volatile products, and above this temperature no more volatile compounds, is formed. The dissociated residues are formed from many dissociated units of the parent polymer.

The perusal of Figure (18) clearly indicates that the metal complexes and double metals complex of the polyester ligand PDPA exhibit superior thermal stabilities to those of the ligand. For Ni(II) complex, the initial weight loss at 408 K corresponds to the elimination of two water molecules. Therefore, it is suggested that coordinated water molecules are lost at this temperature range.

In case of double metal complexes as [Co(II) + Cu(II)], [Cu(II) + Ni(II)] and [Ni(II) + Co(II)] complexes, the weight corresponding to tow water molecules is lost at 433 K.

Below 433 K, the order of the thermal stability of the complexes with respect to metal ions is:

[Co(II) + Cu(II)] > [Cu(II) + Ni(II)] > [Ni(II) + Co(II)]> Ni(II).

A steeper decrease in the weight of the double metal complexes is observed at temperatures depending on the composition of the complex, Fig. (18). The residual weight in all the complexes is more than that of the metal content. It indicates that the metal complexes are not decomposed into their metals by heating at the investigated temperature range, but may be decomposed into metal oxalate, metal carbonate or metal oxide as illustrated in Table (13).

In order to determine the effect of molecular weight on the thermal stability of the investigated compounds, Tg (the temperature at which the polyester and its complex start to decompose) was plotted against molecular weight of the sample. The plots are shown in Fig. (19) from which it can be seen that Tg value increases in non linear manner with increasing the molecular weight, which refers to that the formation of three-dimentional or network structure due to the complexation causes an increase in the thermal stability of the polymeric complex.

By using the initial temperature of decomposition as a measure of the thermal stability, it can be seen also that the thermal stability of investigated polyesters increases in the order:

PDPA > PHMA > PDEA> PPA

And the thermal stability of metal-complexes increases in the order:

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

The effect of ionic radius upon Tg value of the polymeric complex has been also investigated, Figure (20). It shows an increase in Tg value with increasing the ionic radius.

The relation between Tg value and ionization potential of the ion are also investigated and represented in Figure (21). No common behaviour has been observed. It means that, the ionization potential does not play the important role in determining the thermal stability of the investigated complexes such as that of molecular weight of the compound or ionic radius of metal ion.

From the above results of thermal analysis of PHMA, PDEA, PPA, PDPA and their metal complexes it can be concluded that the enhancement in the thermal stability of polyester-metal complexes and polyester-double metals complexes in comparison to the ligands may be due to the following facts:

1- Increase in the molecular weight due to the linking of different polyester chains on account of the coordination.

2- Formation of a three-dimensional or network structure due to complexation.

3- Formation of the six-membered ring in the backbone of the polyester chain which increases the stiffness of the polyester chain.

4- The mechanism of the decomposition of the polyester has been suggested here on the bases of the decomposition of simple esters[93]. In the first step, a carboxyl compound and a vinyl ester is formed as a result of cis-elimination in the presence of β-H atoms preceded by the formation of a six-membered chelate ring through H-bonding.

III-C-2-Thermal mechanical analysis (TMA):

By applying pressure upon a solid sample by pushing rod can be accurately controlled, the deformation of the sample on heating under a known applied load may be measured and various mechanical properties of the sample may be monitored as a function of temperature.

The compression mode of TMA is particularly useful for studying the softening and melting phenomena of materials. The compression curves for the investigated polymers are shown in Figure (22).

The temperatures at which the softness of the sample appears are given in Table (16), From which it can be seen that the mechanical stability of the investigated polymers increases in the order:

PPA > PHMA> PDPA> PDEA

It seems that the thermal mechanical stability almost increases with decreasing the chain length of monomer and with increasing its branching.

The observed sudden change on the TMA curves my be used to indicate the melting of some units in the polymer. The increase in displacement values at the temperature range of 570-595, 570-600, 480-580 K for PPA, PDPA and PDEA respectively may be attribute to the dissociation of the polymers and the formation of new compounds as shown in DTA and TG.

The higher changes observed in the slope of TMA curve of PDEA is attributed to many degradation steps of the polymer and its less mechanical stability even at lower temperature.

This may be attributed to the probability of the easily rotation of O-$(CH_2)_2$-O unit in the monomer.

Table (11): Thermal Stability of PHMA and its Metal Complexes

Compound	M.wt	DTA (K) type	TG (K) From	TG (K) To	Exp. wt. loss%	MC_2O_4 Th. wt loss%	MCO_3 Th. wt Loss%	MO Th. wt loss%	% H_2O Th. wt loss%
PHMA $C_{96}H_{167}N_9O_{36}$	2237	382 (endo) 448(endo) 558(endo) 733(endo)	381 383 513 603	383 513 603 863	1.8 7 27 79	0.0	0.0	0.0	* 1.8 - - -
PHMA-Pb(II) $C_{96}H_{167}N_9O_{36}.Pb_6.12H_2O$	3480.1	- 618 (exo) 673 (exo) 743 (exo)	418 573 663 783	573 663 783 803	6 33 47 63	- - 49 -	- - - -	- - - 62	6.2 - - -
PHMA-Ni(II) $C_{96}H_{167}N_9O_{36}.Ni_6.12H_2O$	2589.1	433(endo) 493 (exo) 648(endo) 813(endo)	393 473 513 783	473 513 783 843	8 48 57 73	- - - -	- - - 72	- - - -	8.3 - - -
PHMA-Cd(II) $C_{96}H_{167}N_9O_{36}.Cd_6.12H_2O$	2912.4	- - 803(exo)	403 483 763	483 763 843	7 54 70	- 57 -	- - -	- - 71	7.4 - -
PHMA-Cu(II) $C_{96}H_{167}N_9O_{36}.Cu_6.12H_2O$	2618.2	408(endo) 455(exo) 548(exo) 673(exo)	398 418 493 603	418 493 603 743	8 45 52 64	- - - 65	- - - -	- - - -	8.2 - - -
PHMA-Co(II) $C_{96}H_{167}N_9O_{36}.Co_6.12H_2O$	2590.6	- 563(endo) 728(exo) -	388 443 683 773	443 683 773 813	8 47 63 72	- - 66 -	- - - 72	- - - -	8.3 - - -

*** Adsorbed water molecules, Th. wt loss % = Theoretical weight loss according to the present molecular formula**

Table (12): Thermal Stability of PDEA and its Metal Complexes.

Compound	M.wt	DTA (K) type	TG (K) From	TG (K) To	Exp. wt. loss%	MC_2O_4 Th. wt loss%	MCO_3 Th. wt loss%	MO Th. wt loss%	% H_2O Th. wt. loss%
PDEA $C_{76}H_{127}N_9O_{48}$	2149	362 (exo)	361	363	1.9	0.0	0.0	0.0	*1.94
		418(endo)	363	473	8				-
		588 (exo)	473	713	38				-
		793(exo)	713	873	67				-
PDEA-Pb(II) $C_{76}H_{127}N_9O_{48}.Pb_6.12H_2O$	3392.1	-	388	413	6	-	-	-	6.3
		-	413	513	14	-	-	-	-
		613 (exo)	513	713	32	-	-	-	-
		-	713	753	47	48	53	-	-
PDEA-Ni(II) $C_{76}H_{127}N_9O_{48}.Ni_6.12H_2O$	2501.1	410(exo)	378	443	8	-	-	-	8.6
		473(exo)	443	503	13	-	-	-	-
		638(exo)	503	773	36	-	-	-	-
		808(exo)	773	843	49	-	-	-	-
PDEA-Cu(II) $C_{76}H_{127}N_9O_{48}.Cu_6.12H_2O$	2530.2	423(exo)	383	463	8	-	-	-	8.5
		603(exo)	463	743	42	-	-	-	-
		768(endo)	743	793	63	64	-	-	-

*** Adsorbed water molecules, Th. wt loss %= Theoretical weight loss according to the present molecular formula**

Table (13): Thermal Stability of PPA and its Metal Complexes.

Compound	M.wt	DTA type	TG (K)		Exp. wt. loss%	MC_2O_4	MCO_3	MO	% H_2O
			From	To		Th. wt loss%	Th. wt loss%	Th. wt loss%	Th. wt loss%
PPA $C_{66}H_{107}N_9O_{38}$	1849	352 (exo)	351	353	2.4	0.0	0.0	0.0	*2.4
		358(exo)	353	563	9				-
		663(endo)	563	763	35				-
		808(exo)	763	853	47				-
PPA-Ni(II) $C_{66}H_{107}N_9O_{38}.Ni_6.12H_2O$	2201.1	413(exo)	373	453	11	-	-	-	9.8
		603(exo)	453	753	45	-	-	-	-
PPA-Cu(II) $C_{66}H_{107}N_9O_{38}.Cu_6.12H_2O$	2230.2	400(exo)	378	423	9	-	-	-	9.6
		453(exo)	423	483	14	-	-	-	-
		608(exo)	483	733	56	59	-	-	-
PPA-Co(II) $C_{66}H_{107}N_9O_{38}.Co_6.12H_2O$	2202.6	415(exo)	368	463	9	-	-	-	9.8
		508(exo)	463	553	13	-	-	-	-
		673(exo)	553	793	49	-	-	-	-

*** Adsorbed water molecules, Th. wt loss %= Theoretical weight loss according to the present molecular formula**

Table (14): Thermal Stability of PDPA and "its Metal and Double Metals Complexes".

Compound	M.wt	DTA type	TG (K) From	TG (K) To	Exp. wt. loss%	MC_2O_4 Th. wt loss%	MCO_3 Th. wt loss%	MO Th. wt loss%	% H_2O The. wt loss5
PDPA $C_{96}H_{167}N_9O_{48}$	2429	402(exo)	401	403	1.6	0.0	0.0	0.0	*1.6
		483(exo)	403	563	6				-
		638(exo)	563	713	37				-
		783(exo)	713	853	51				-
PDPA-Ni(II) $C_{96}H_{167}N_9O_{48}.Ni_6.12H_2O$	2781.1	420(exo)	408	433	7	-	-	-	7.8
		498(exo)	433	563	15	-	-	-	-
		628(exo)	563	693	41	-	-	-	-
		738(exo)	693	783	55	-	-	-	-
PDPA-Ni(II),Cu(II) $C_{96}H_{167}N_9O_{48}.Ni_3.Cu_3.12H2O$	2795.6	428(exo)	423	433	7	-	-	-	7.7
		488(exo)	433	543	16	-	-	-	-
		603(exo)	543	663	34	-	-	-	-
		698(exo)	663	733	41	-	-	-	-
		748(endo)	733	763	58	-	-	-	-
PDPA-Cu(II),Co(II) $C_{96}H_{167}N_9O_{48}.Cu_3.Co_3.12H_2O$	2796.4	-	433	463	7	-	-	-	7.7
		-	463	503	17	-	-	-	-
		603(exo)	503	703	57	-	-	-	-
		-	703	773	78	-	74	83	-
PDPA- Ni(II),Co(II) $C_{96}H_{167}N_9O_{48}.Ni_3\,Co_3.12H_2O$	2781.8	-	418	433	7	-	-	-	7.8
		-	433	583	17	-	-	-	-
		-	583	693	46	-	-	-	-
		743(exo)	693	793	66	68	-	-	-

* Adsorbed water molecules, Th. wt loss %= Theoretical weight loss according to the present molecular formula

Table (15): Molecular weight, Ionic radius, Ionization potential and dissociation temperature T_g for some Investigated Compounds.

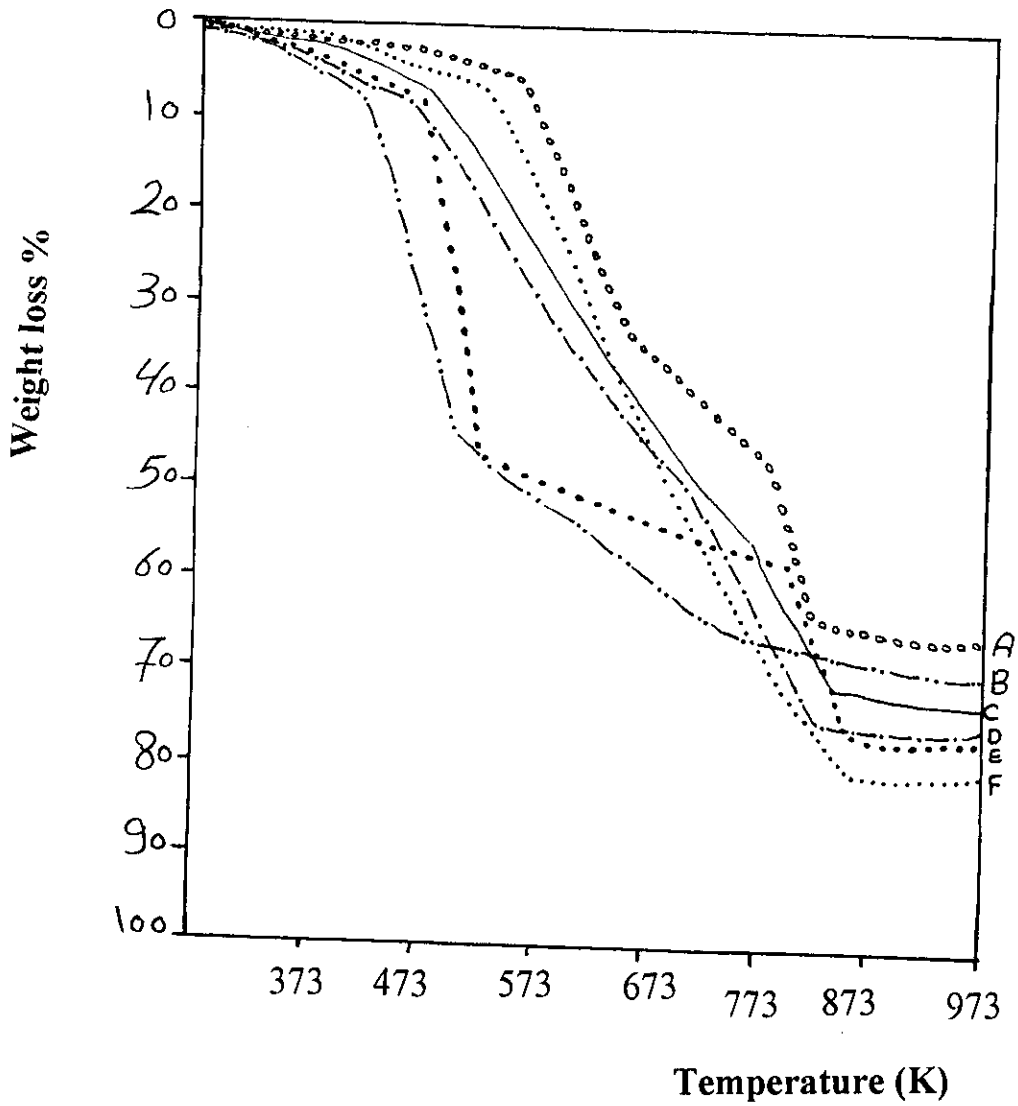
Compound	M.wt "by unit"	Ionic radius (A^0)	Ionization potential (volts)	T_g (k)
PHMA	333.0	0.0	0.0	383
PDEA	309.0	0.0	0.0	363
PPA	249.0	0.0	0.0	353
PDPA	365.0	0.0	0.0	403
PHMA –Pb(II)	909.2	1.19	15.3	418
PHMA-Ni(II)	760.7	0.69	18.5	393
PHMA-Cd(II)	814.4	0.95	12.0	403
PHMA-Cu(II)	765.5	0.73	20.3	398
PHMA-Co(II)	760.9	0.65	17.1	388
PDEA-Pb(II)	861.2	1.19	15.3	388
PDEA-Ni(II)	712.7	0.69	18.5	378
PDEA-Cu(II)	717.5	0.73	20.3	383
PPA-Ni(II)	592.7	0.69	18.5	373
PPA-Cu(II)	597.5	0.73	20.3	378
PPA-Co(II)	592.9	0.65	17.1	368
PDPA-Ni(II)	824.7	0.69	18.5	408
PDPA-Ni(II),Co(II)	824.9	0.65	17.1	418
PDPA-Cu(II),Co(II)	829.5	0.73	20.3	433
PDPA-Ni(II),Cu(II)	824.7	0.69	18.5	423

Table (16): TMA data of investigated polymers:

Polymer	T_s* (K)
Polyhexamethylene asparate (PHMA)	325
Poly diethylene asparate (PDEA)	290
Poly propylene asparate (PPA)	360
Poly dipropylene asparate (PDPA)	315

* Softening temperature

Figure (15): TGA of PHMA and Its Metal Complex.



(A) PHMA-Pb(II) Complex

(B) PHMA-Cu(II) Complex

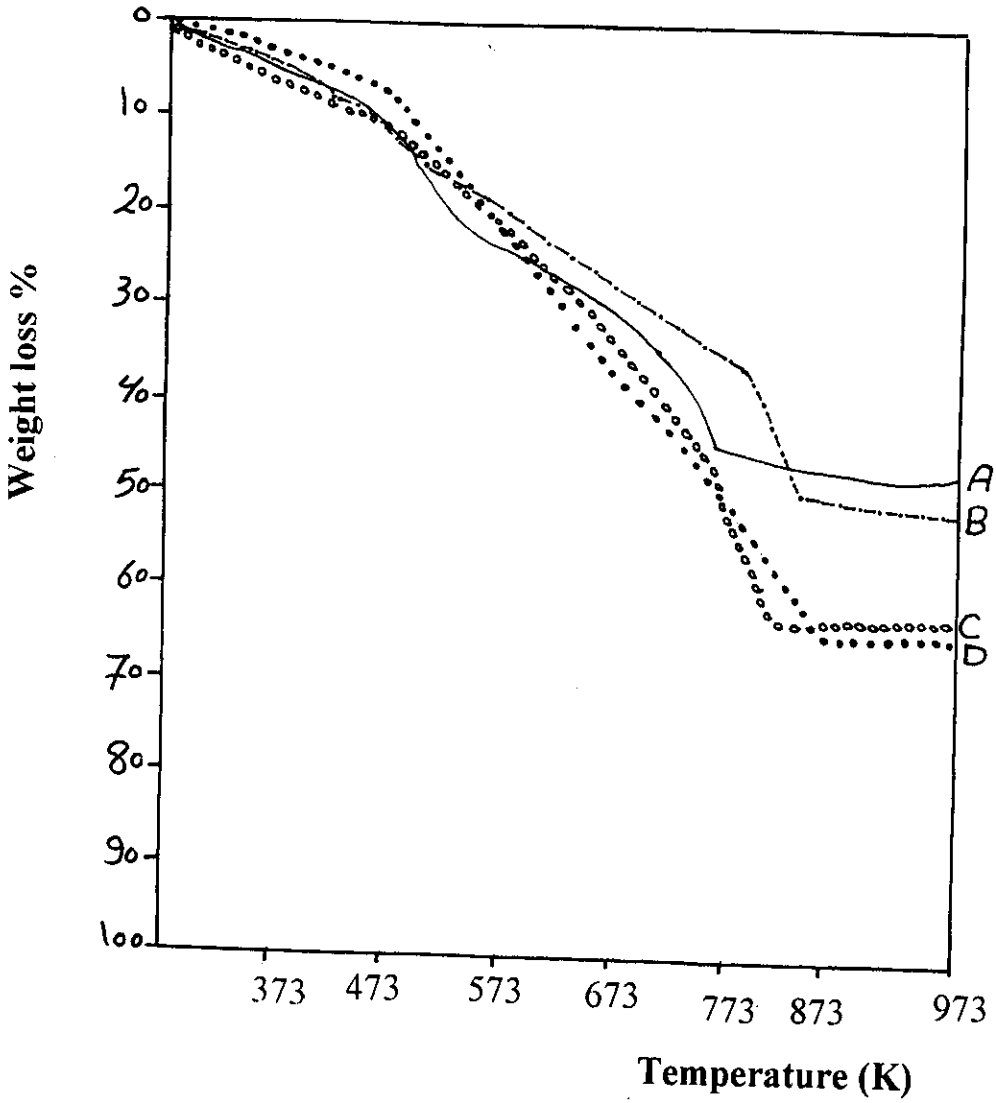
(C) PHMA- Cd(II) Complex

(D) PHMA-Co(II) Complex

(E) PHMA-Ni(II) Complex

(F) PHMA-Polyester

Figure (16): TGA of PDEA and Its Metal Complex.



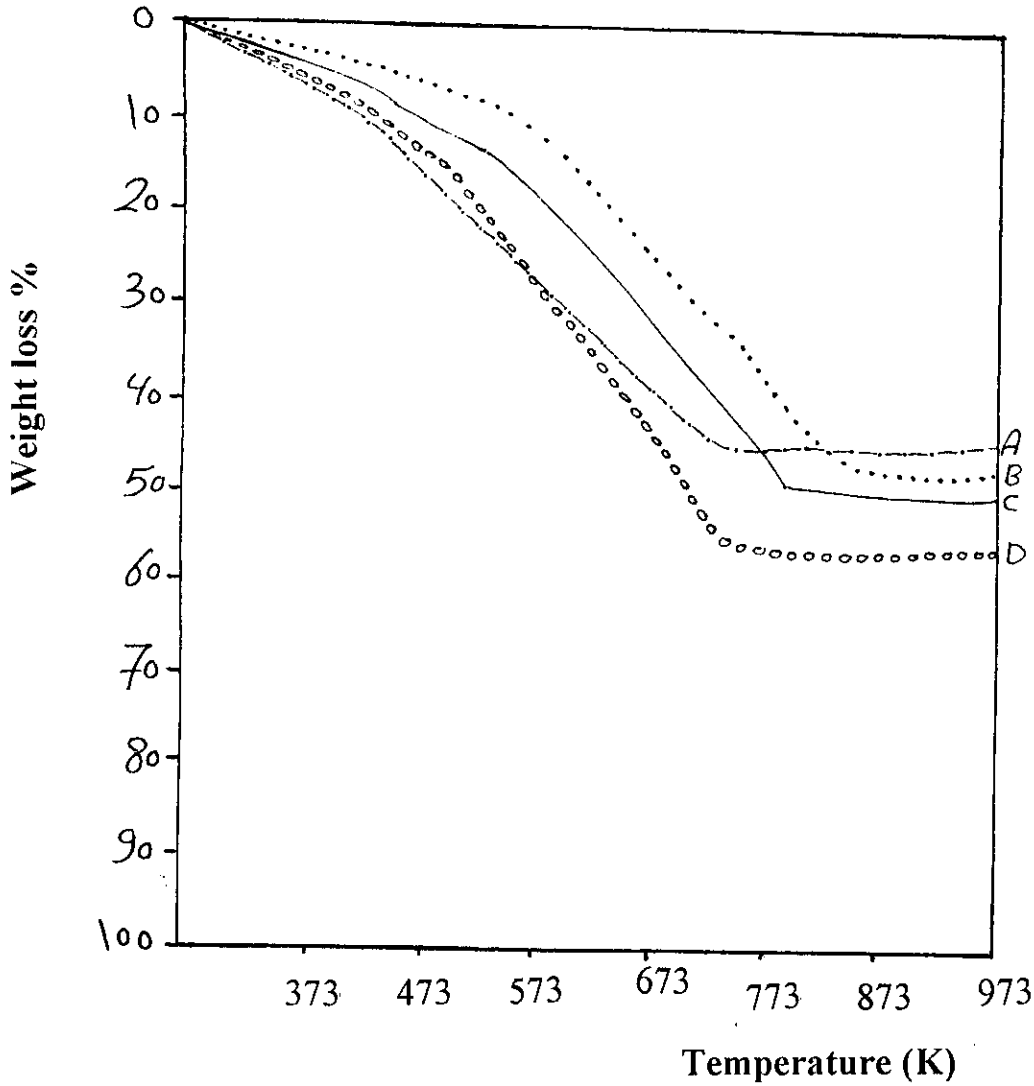
(A) PDEA-Pb(II) Complex

(B) PDEA-Ni(II) Complex

(C) PDEA-Cu(II) Complex

(D) PDEA Polyester

Figure (17): TGA of PPA and Its Metal Complex.



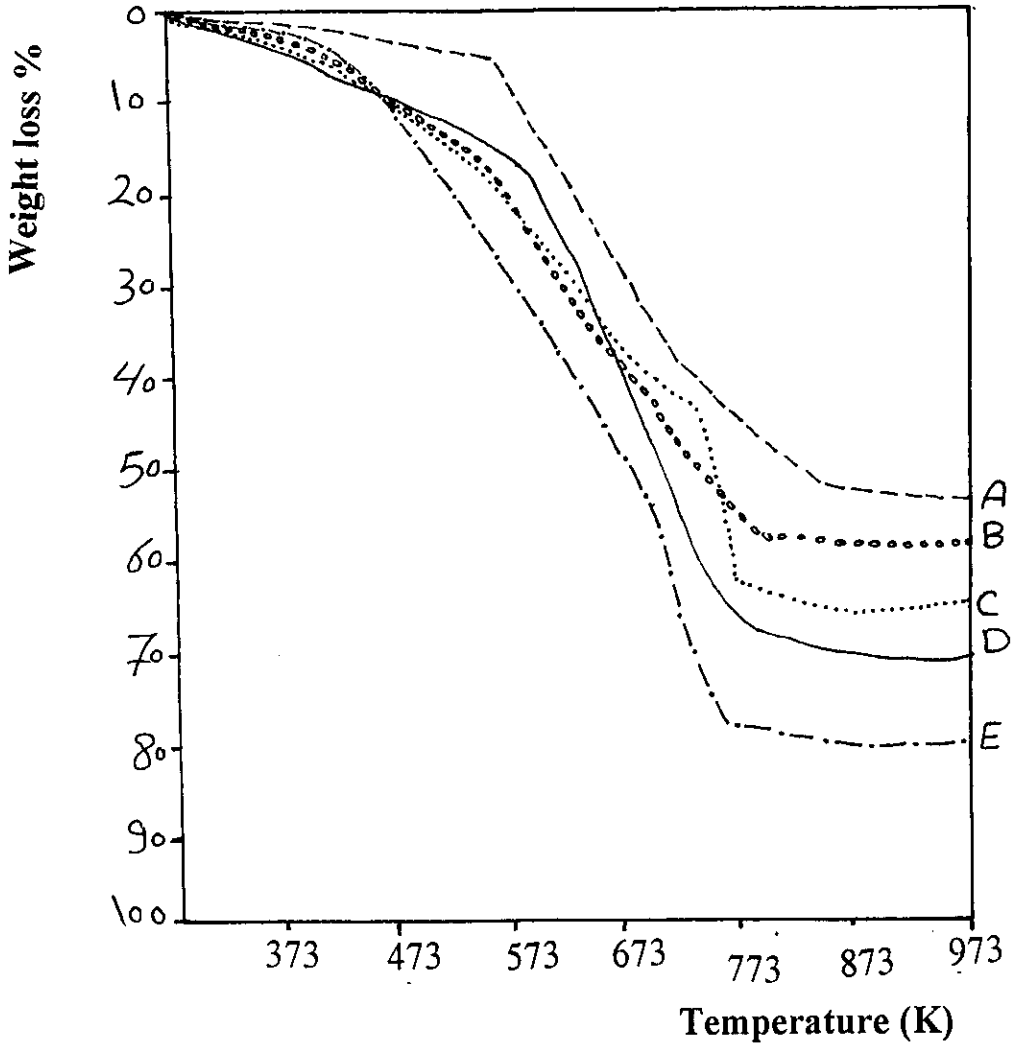
(A) PPA-Ni(II) Complex

(B) PPA polyester

(C) PPA-Co(II) Complex

(D) PPA Cu(II) Complex.

Figure (18): TGA of PDPA and Its "Metal and Double Metals Complex"



(A) PDPA polyester

(B) PDPA –Ni(II) Complex

(C) PDPA-Ni(II), Cu(II) Complex

(D) PDPA-Ni(II), Co(II) Complex

(E) PDPA-Cu(II), Co(II), Complex

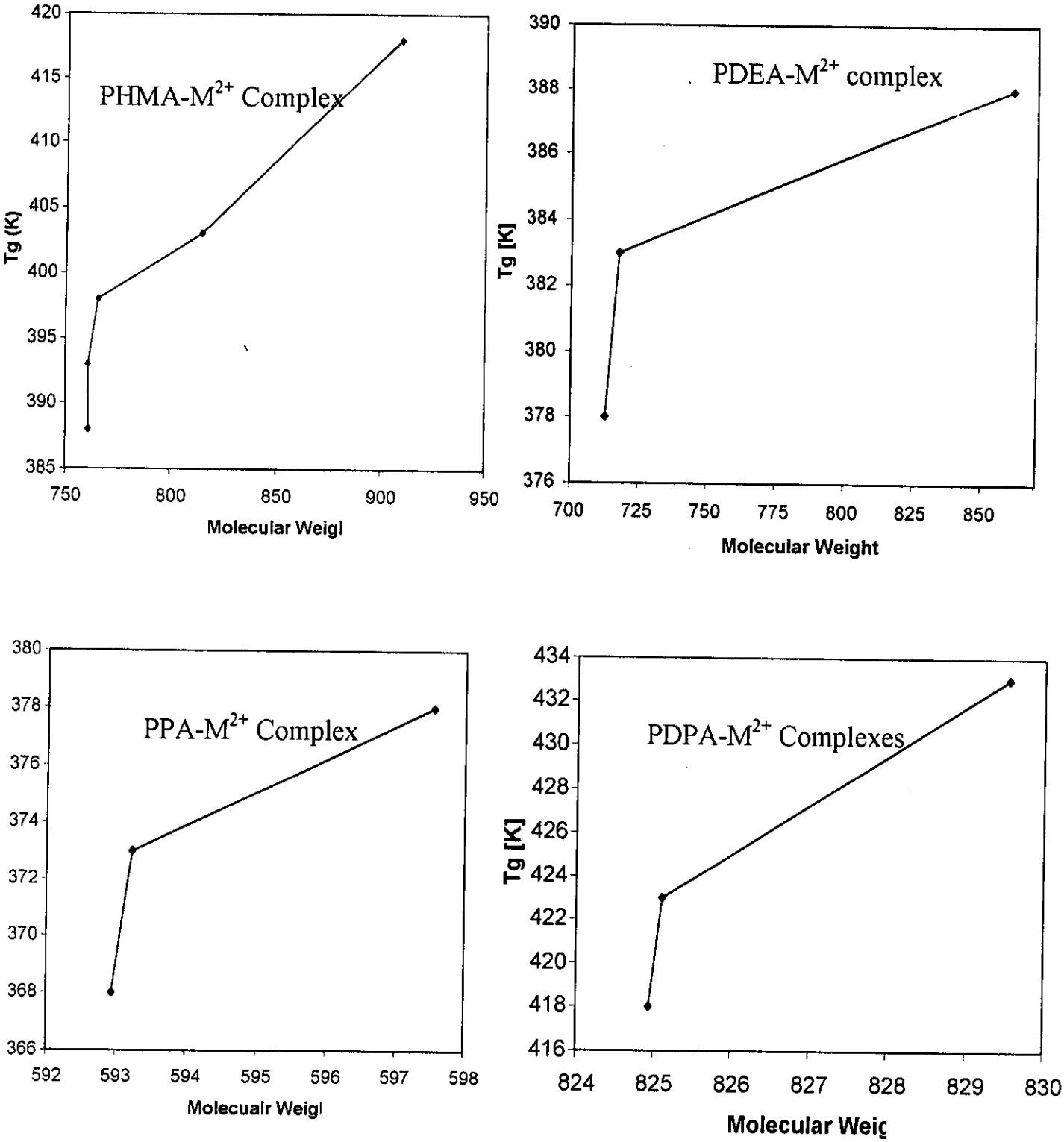
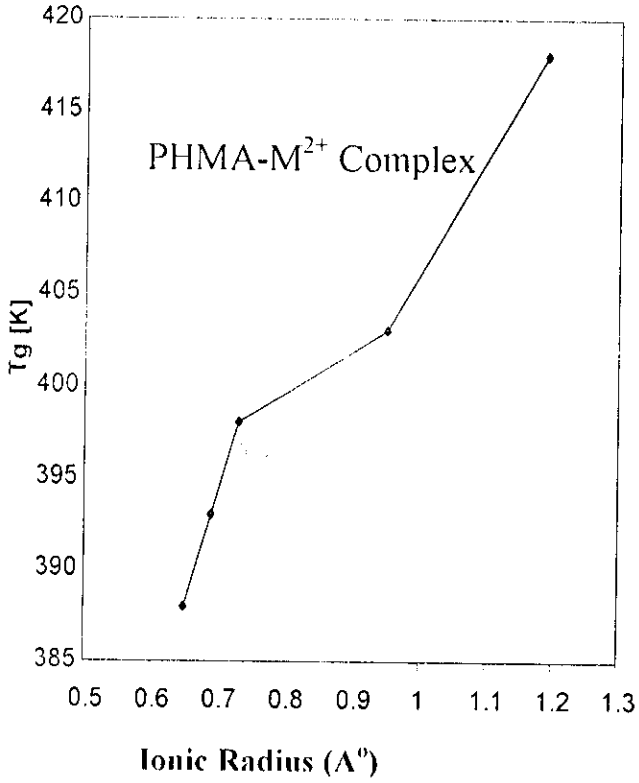
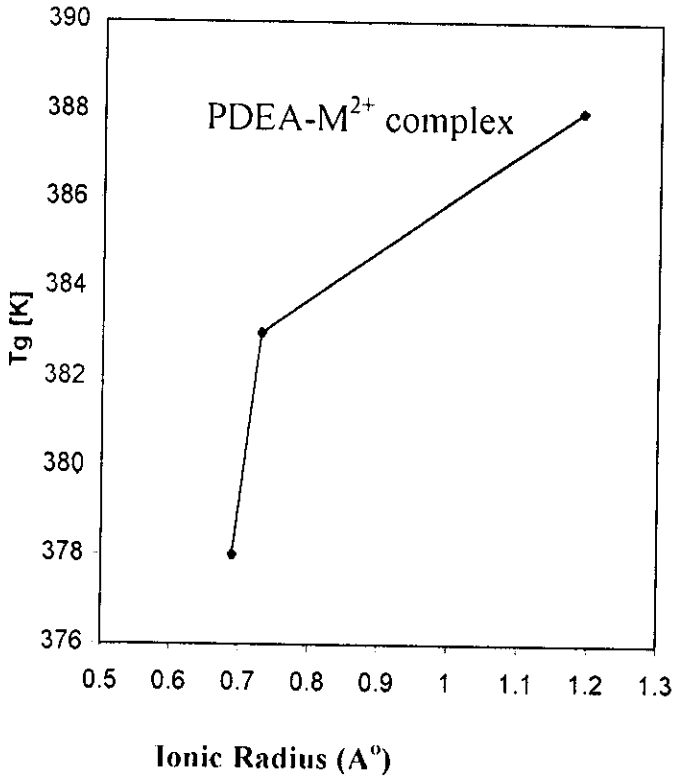
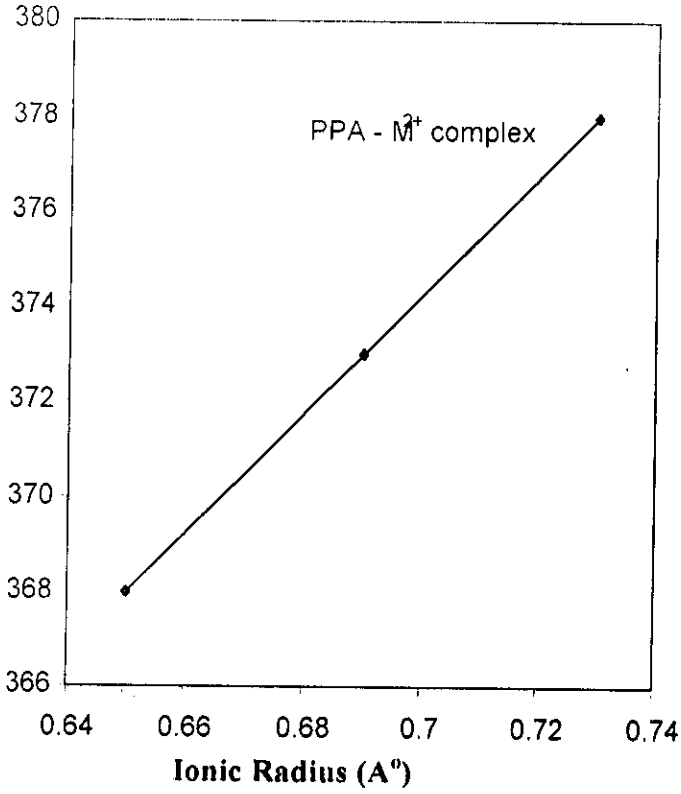


Figure (19): Relation between Thermal Gravimetry and Molecular Weight of Investigated Compounds.







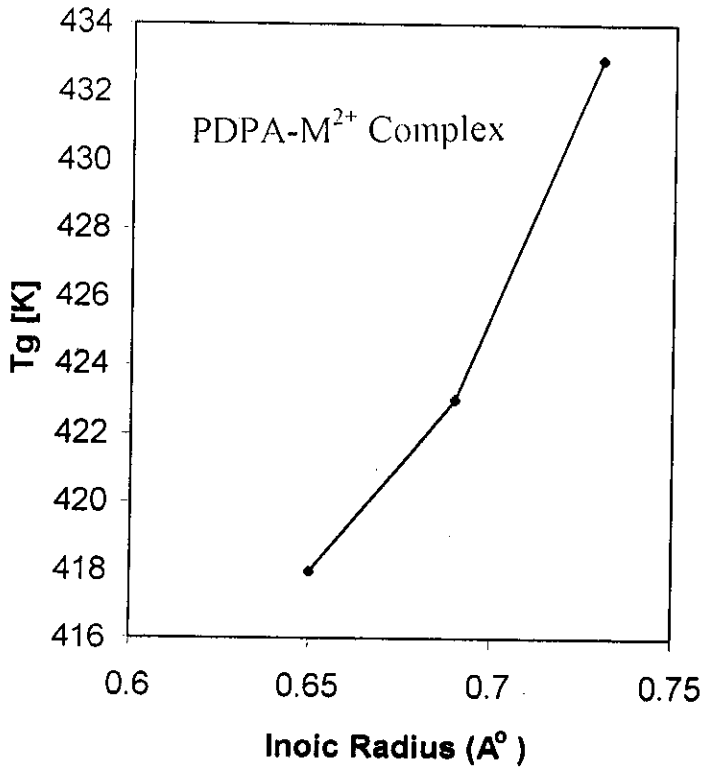


Figure (20): Relation between Thermal Gravimetry and Ionic Radius of Investigated Compounds.

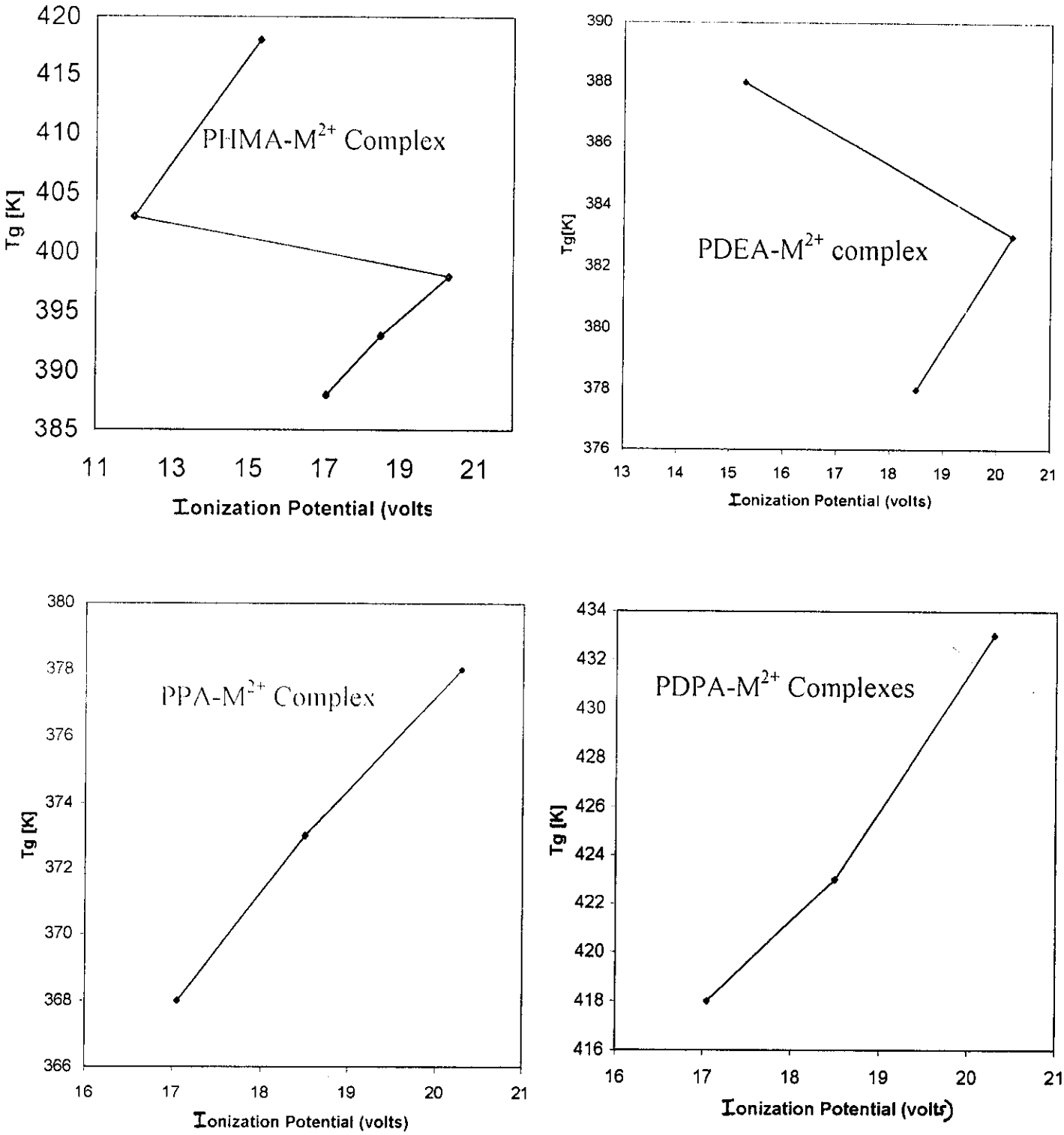
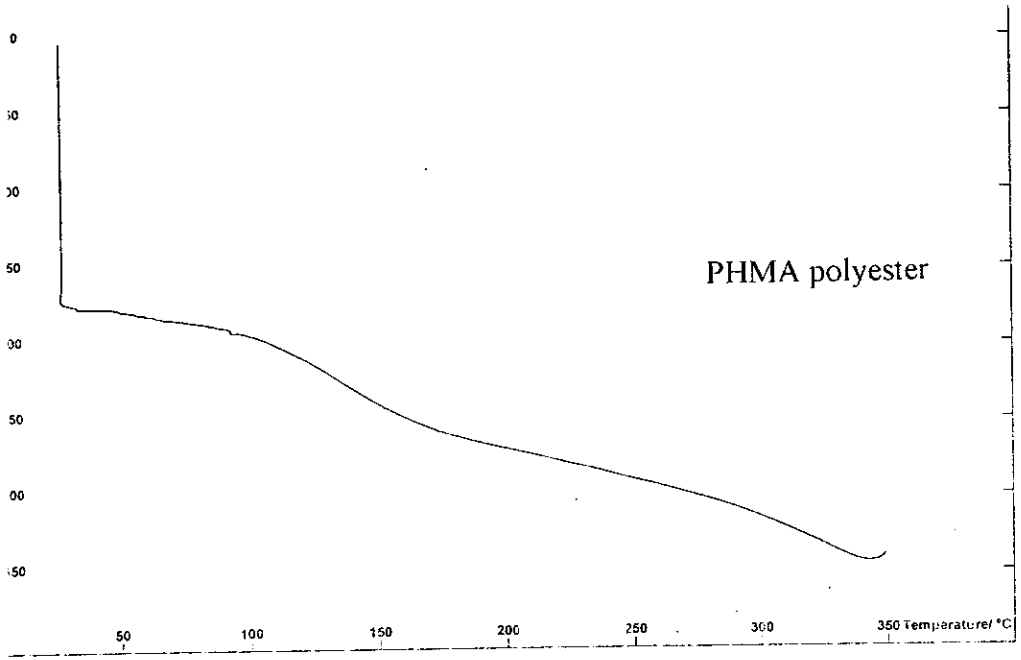
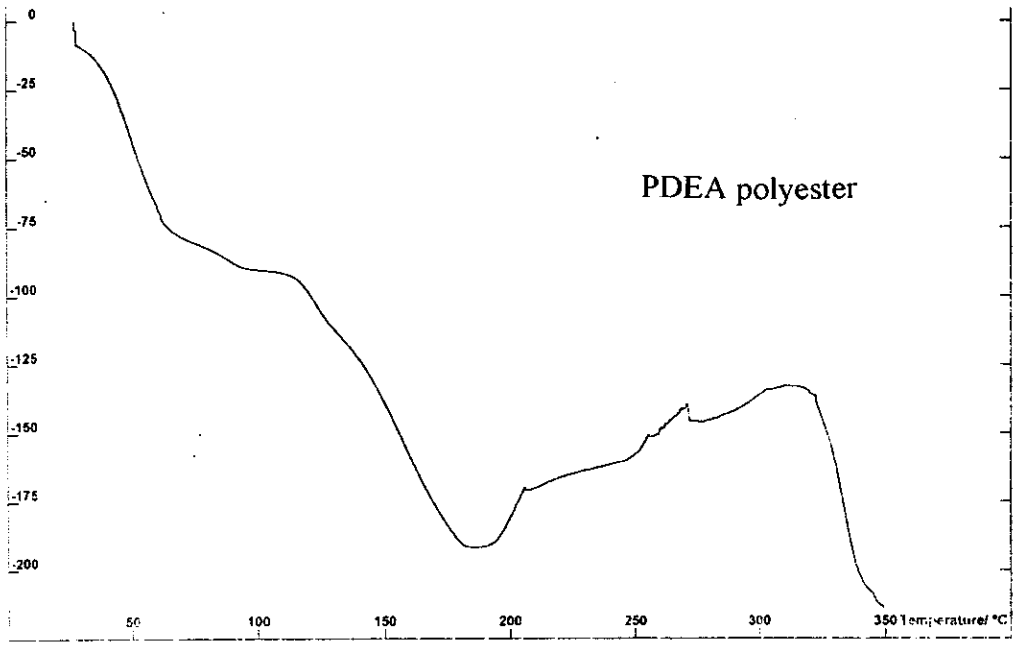
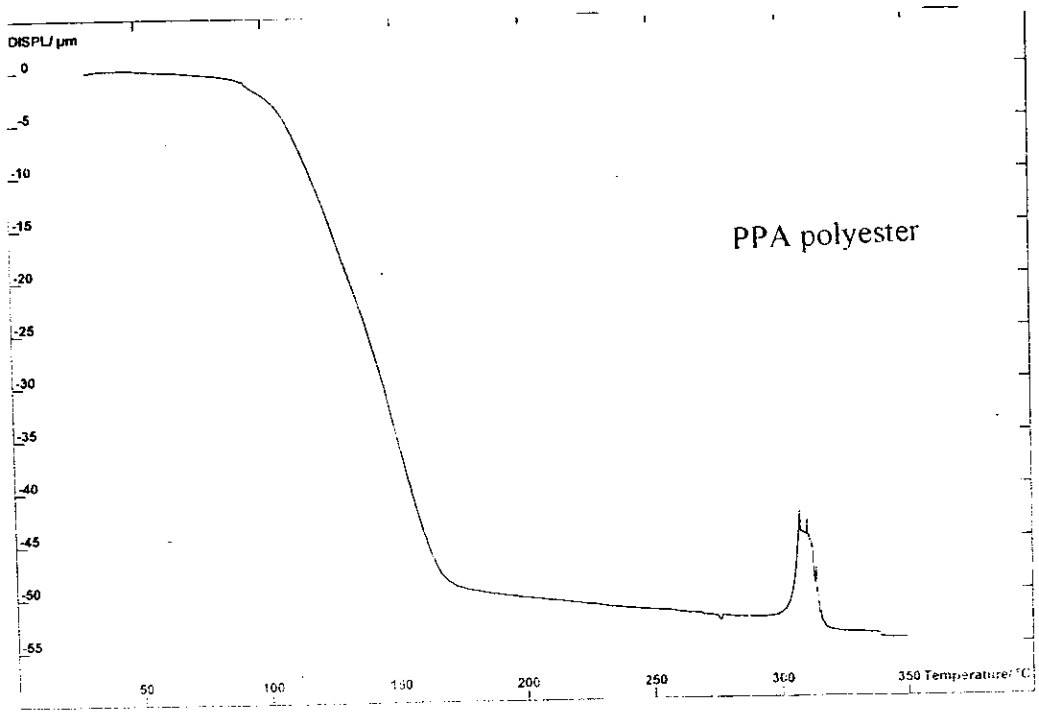


Figure (21) : Relation between Thermal Gravimetry and Ionization potential of Investigated Compounds.







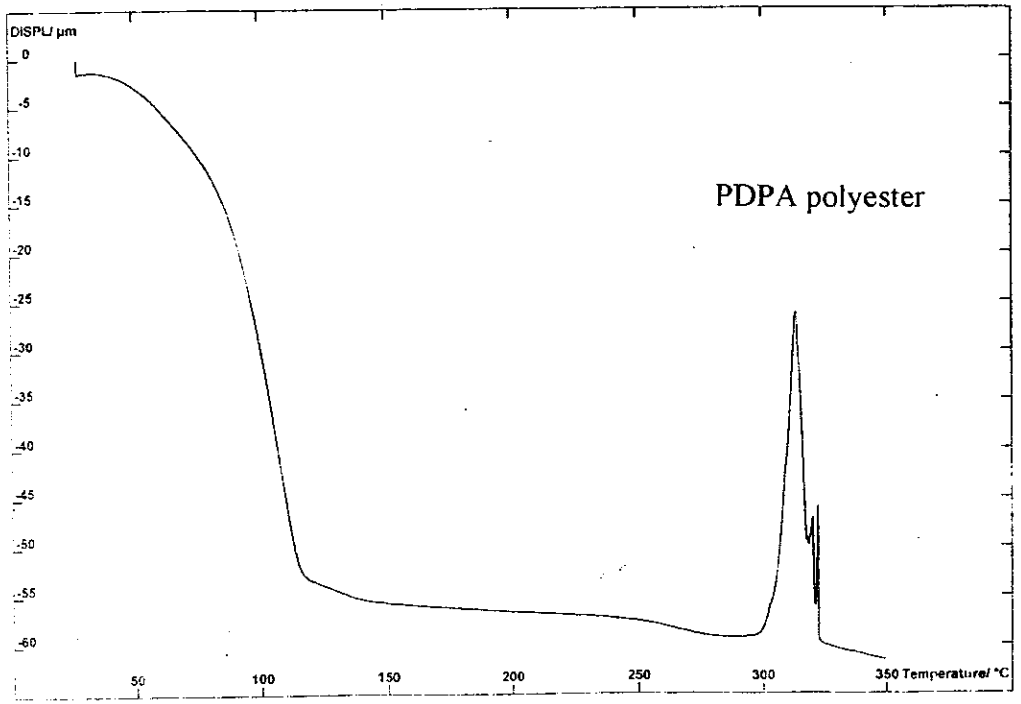


Fig.(22): TMA curves for the investigated polyesters.

Temperature (C^o)

III-D-Electrical properties of polymer sample

III-D-1-Electrical conductivity:

The electrical properties of polyester (PDPA) are affected by many factors such as the types of hard and soft segments, molecular weight of the components, the chain extender, the stoichiometric composition and the polymerization method[106-108]. In this work the effect of composition on the electrical properties of one of the investigated polymers has been studied. The polydipropylen asparate (PDPA) and its complexes are chosen as a representative for our study.

The electrical conductivity (σ) was measured at different frequencies 0 – 10^6 Hz and over a temperature range from 300 K to temperature just below the decomposition temperature of the component. This is done to prevent a catastrophis loss in electrical conductivity when the polymer melts or expands.

The effect of temperature and frequency on electrical conductivity for PDPA sample is shown in Fig. (30). The plot shows the same behaviour at all measuring frequencies. At each frequency the plot of ln σ vs. $\frac{1}{T}$ shows two regions, their temperature break lie at 318 K. However in the lower temperature region the conductivity was found to increase with increasing the temperature indicating metallic behaviour. This is because as the temperature is lowered scattering of conduction electrons by phonons decreases because the phonon frequencies decrease with temperature and the conductivity goes up[46]. In the second region (at high temperatures) the conductivity increases with increasing temperature (semi conducting behaviour). Figs (31-36) shows also that at any

temperature the ac- conductivity is higher than the dc-conductivity referring to the presence of polarization effect in the investigated polymer. At the same time the ac- conductivity increases with increasing frequency due to the decrease in the barrier effect with increasing the frequency. The high frequency acts as a pumping force helps the charge carriers to jump between the different localized states. Also the field accompanied with frequency increases leading to an increase in the polarizability of the sample appearing then as an increase in conductivity.

The frequency dependence of the ac-conductivity at different temperatures for the pure polymer was found to obey the relation[96]: $\sigma = A\omega^s$. The value of the exponent s are listed with the other conductivity data (n = number of charge carrier, μ = the mobility of charge carrier calculated from $\sigma = n\ q\ \mu$) in Table (17).

The values of exponent s lies in the range 0.13 – 0.54 referring to the transfer of charge carriers through hopping mechanism[109]. The change in the values of s` entail strongly frequence dependent susceptibility, i.e., strong dispersion due to the ionic polarization which occurs in the crystal structure of the investigated compounds.

The breaks in σ-T curves at T = 318 K is corresponding to an abrupt change in conduction mechanism or structural modification in the polymer. But because the thermal analysis did not show any change in DTA signal at 318 K, therefore this change in conductivity should be attributed to change in the number of charge carries at this temperature (intrinsic defects occurring in the polymer).

The temperature dependence of conductivity σ at different frequencies for the investigated polymer metal complexes are shown in Figs (30-36). The plots for all samples have the same character as that of pure polymer, where two regions are observed. One can also see that the presence of metal ion in the polymer back bone improve the conductivity in the order:

PDPA – Ni(II), Cu(II) > PDPA – Co(II) > PDPA – Cu(II) > PDPA – Co(II), Cu(II)> PDPA- Co(II), Ni(II) > PDPA-Ni(II) > PDPA.

The activation energy E_a for the conduction process was calculated in semiconductor region from the Arrhenius plots shown in Fig. (30-36). The conductivity data are summarized and listed in Tables (17-18). The values of activation energy of the pure and the polyester complex indicate that the electrical properties of these compounds at higher temperatures are similar to those of semiconducting materials[110].

The conductivity data present in Tables (17-18) suggest that the coordinated metal ion play an important role in the conduction process and the conduction pathway in the complexes is not going via the ligand molecules. More looking on the electrical properties of the polymeric complexes, Table (17) shows that the E_a values for the conduction in the ligands are affected by complexation. Where in case of polymer PDPA, the E_a values of the conduction in the complexes are lower than that of the pure polymer. This can be attributed to the enrichment of electrons by the metal ion and the partial ionic bond character in such complexes leads to a decrease in energy of activation according to :

Polyester > PDPA – Ni(II) > PDPA – Ni(II), Cu(II) ≃ PDPA- Ni(II), Co(II) > PDPA-Cu(II), Co(II) > PDPA – Cu(II) > PDPA – Co(II).

It means that the introducing of metal ion in the polymer occurring through a formation of new orbitals appearing in the gap energy of the ligand (polymer) which will cause a decrease in the activation energy of conduction process.

The mobility μ of the charge carriers in the complexes were calculated at T = 350 K using Equation (4):

$$\sigma = n\, q\, \mu$$

And the results listed in Table (17). The fact that μ values are much smaller than 1 $Cm^2\ V^{-1}s^{-1}$ can be used as a criterion for applying the hopping model for the description of the mechanism of the conductance. Therefore the conduction process is the excitation of Π-electron from the upper most filled Π-orbital to the lowest empty Π-Mo. The electron is then transferred to an empty level of the neighboring molecule.

Table (17) : DC-conductivity data for PDPA and its complexes.

Compound	σ^* Ohm^{-1}. Cm^{-1}	E_a (eV)	S$^{\#}$ Temp. Range K	Temp. Breaks K	n* Cm^{-3}	μ^{**} Cm^2 V^{-1} s^{-1}
Polyester PDPA	6.8×10^{-8}	0.19	318-370	318	5.5×10^{22}	7.7×10^{-12}
PDPA-Cu(II)	1.2×10^{-6}	0.12	330-370	330	5.6×10^{23}	1.33×10^{-11}
PDPA-Ni(II)	1.3×10^{-7}	0.17	318-370	318	1.07×10^{23}	7.6×10^{-12}
PDPA-Co(II)	6.2×10^{-6}	0.11	318-370	330	6.0×10^{23}	6.4×10^{-11}
PDPA Ni(II),Cu(II)	4.5×10^{-5}	0.15	330-370	330	2.1×10^{23}	1.3×10^{-9}
PAPA Ni(II),Co(II)	6.2×10^{-7}	0.15	318-370	318	2.1×10^{23}	1.8×10^{-11}
PAPA Cu(II),Co(II)	8.4×10^{-7}	0.13	318-370	318	4.0×10^{23}	1.3×10^{-11}

σ_{dc}* at 350 K.

S$^{\#}$ temperature range at which the activation energy E_a was calculated.

* Density of charge carriers at 310 K.

** Mobility of charge carriers at 310 K.

Table (18): Ac- Conductivity data for PDPA and its complexes.

Compound	Temp. Break (K)	σ* at 350 K for			S
		5 kH_z	50 kH_z	10^3 kH_z	
Polyester PDPA	318	7.9×10^{-6}	2.2×10^{-5}	8.6×10^{-5}	0.45 ± 0.09
PDPA-Cu(II)	330	4.8×10^{-5}	1.09×10^{-4}	3.1×10^{-4}	0.35 ± 0.11
PDPA- Ni(II)	318	2.8×10^{-6}	5.5×10^{-6}	1.3×10^{-5}	0.29 ± 0.07
PDPA- Co(II)	330	8.7×10^{-5}	1.5×10^{-4}	3.2×10^{-4}	0.25 ± 0.05
PDPA-Ni(II),Cu(II)	330	5.7×10^{-4}	9.9×10^{-4}	2.0×10^{-3}	0.24 ± 0.07
PDPA-Ni(II),Co(II)	318	7.1×10^{-6}	1.2×10^{-5}	2.4×10^{-5}	0.23 ± 0.10
PDPA-Cu(II), Co(II)	318	1.0×10^{-5}	1.9×10^{-5}	3.8×10^{-5}	0.24 ± 0.09

Fig. (30): Temperature dependence of electrical conductivity for PDPA polyester.

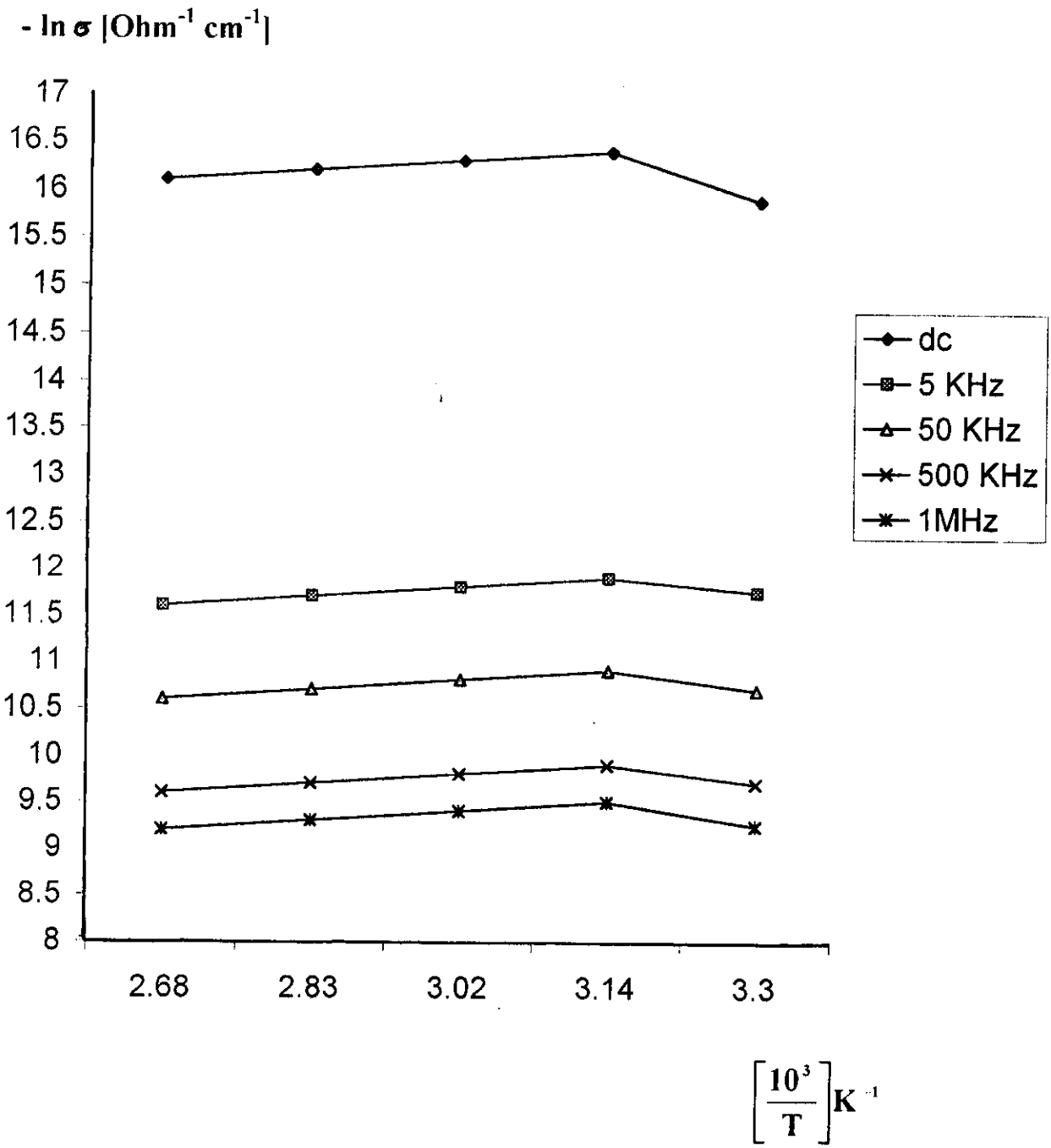


Fig. (31) : Temperature dependence of electrical conductivity for PDPA-[Cu(II), Co(II)] complex.

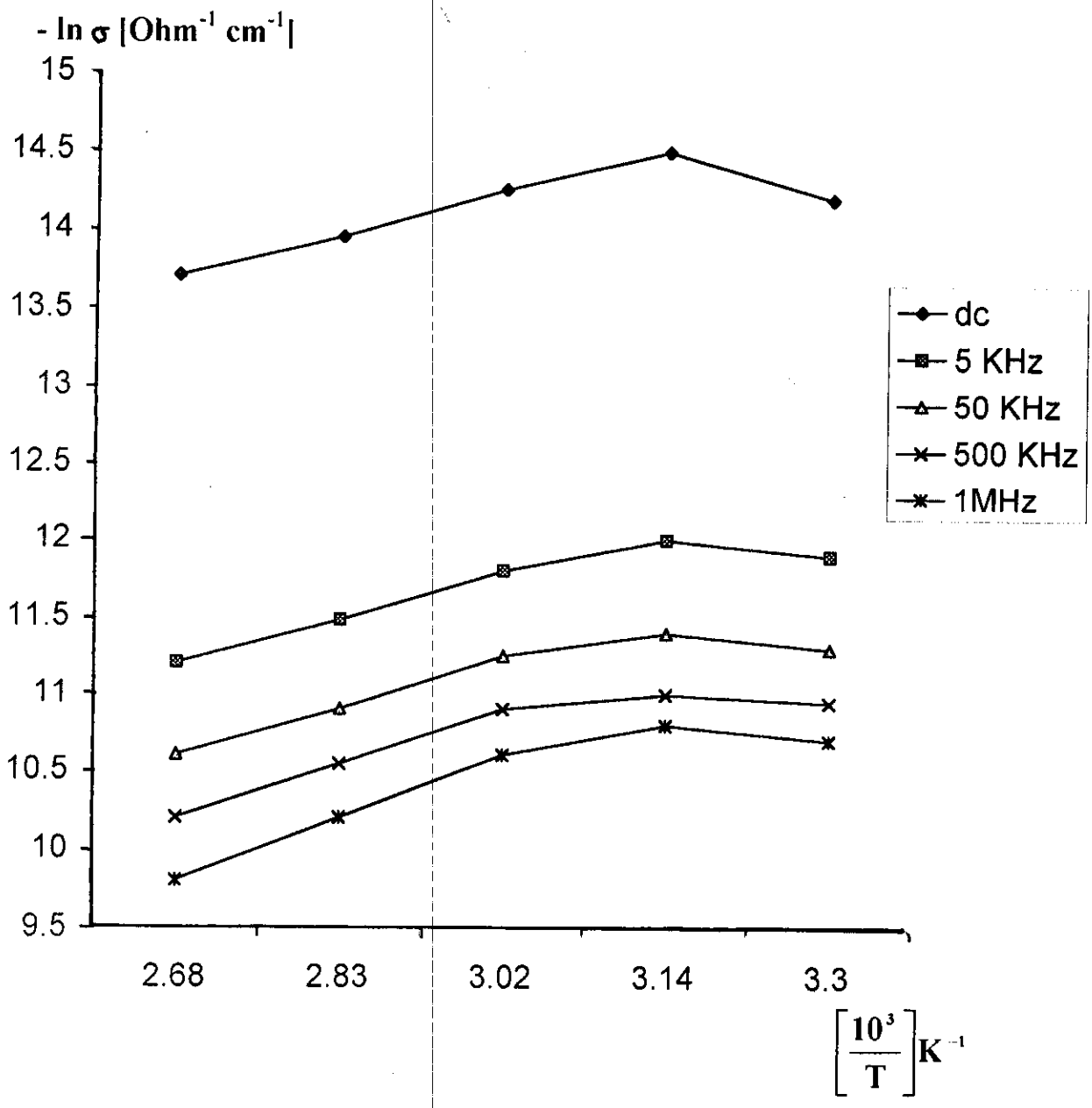


Fig. (32): Temperature dependence of electrical conductivity for PDPA-[Ni(II), Cu(II)] complex.

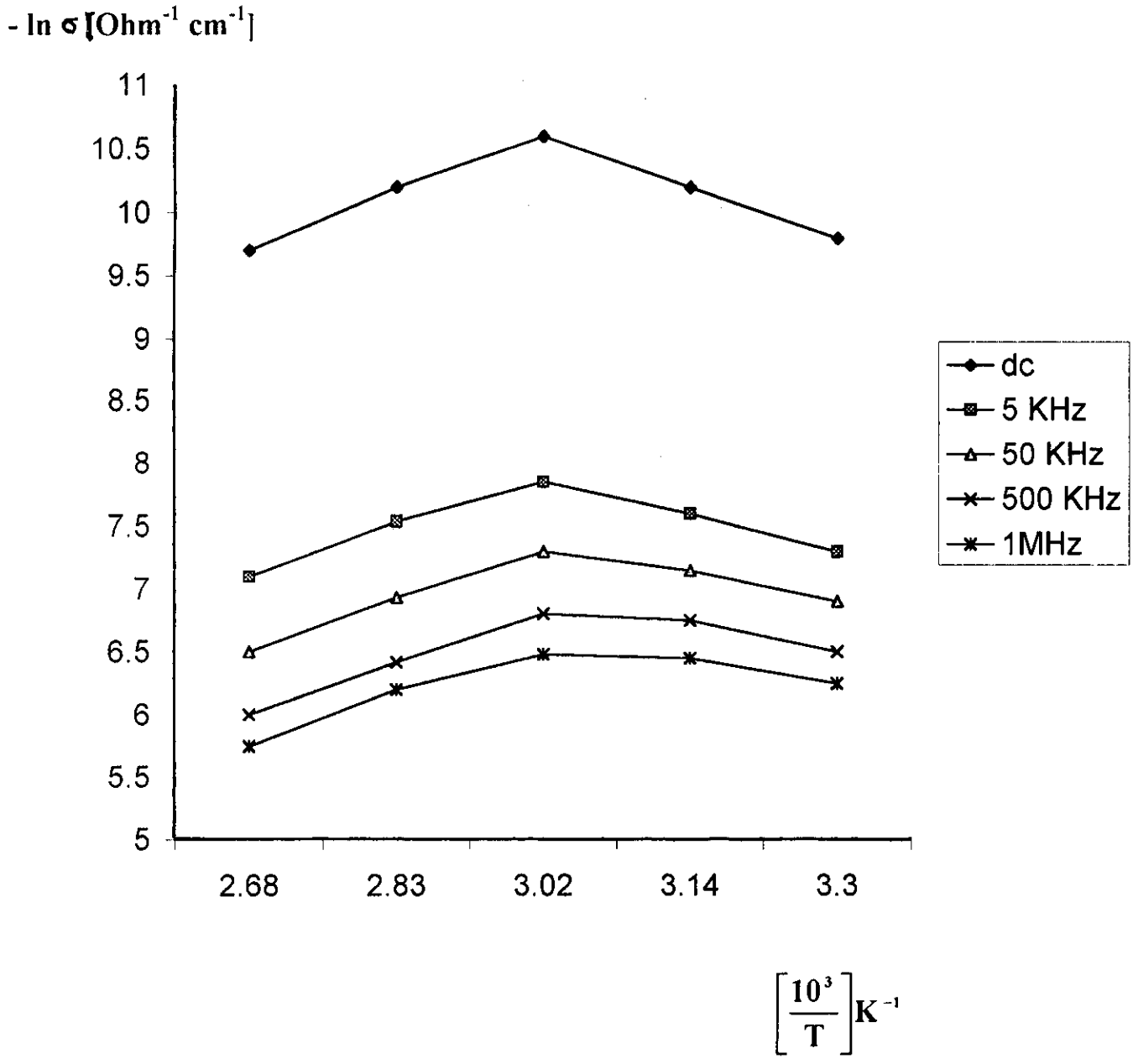


Fig. (33): Temperature dependence of electrical conductivity for PDPA-[Ni(II), Cu(II)] complex.

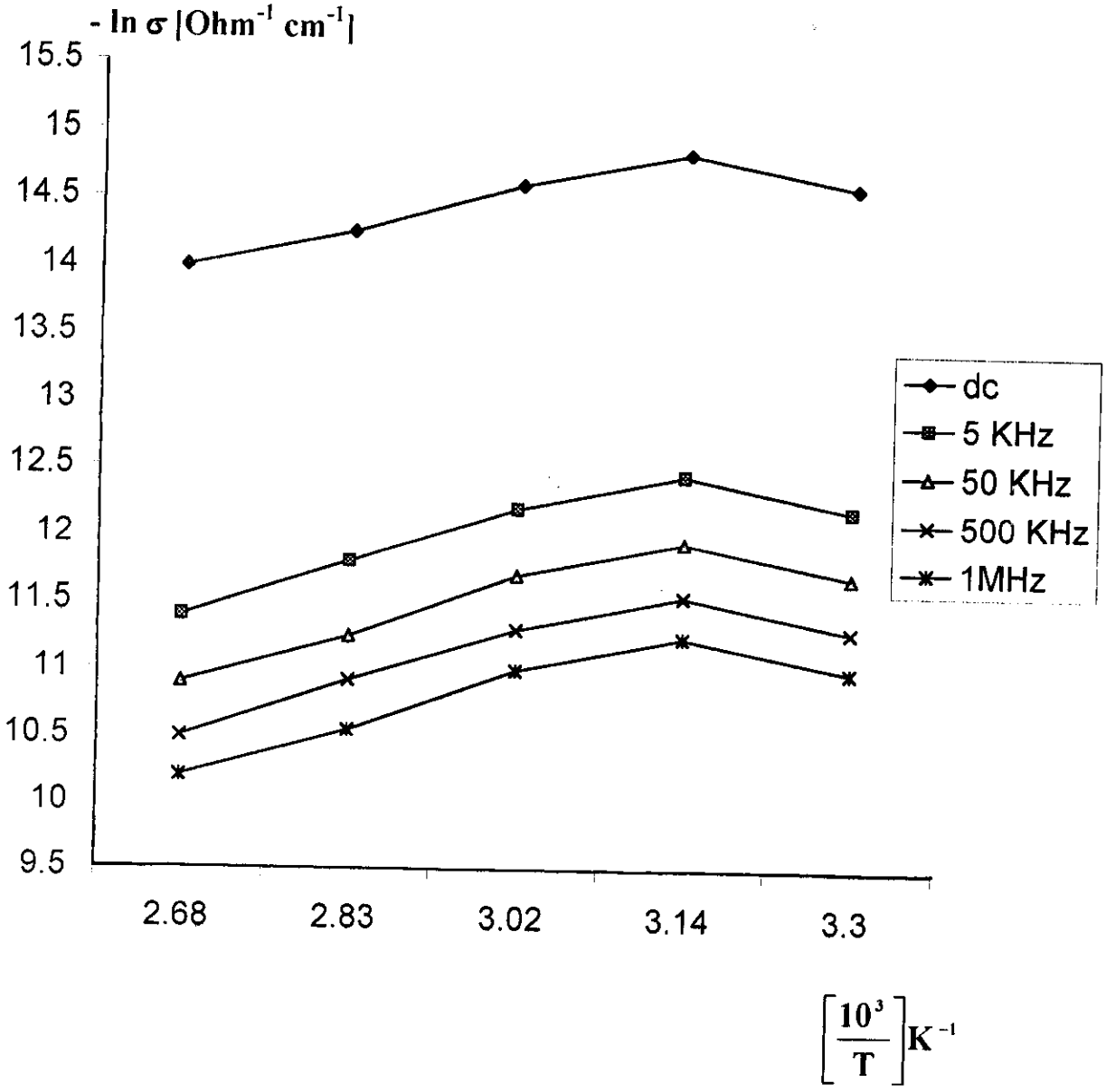


Fig. (34) : Temperature dependence of electrical conductivity for PDPA- Co(II) complex.

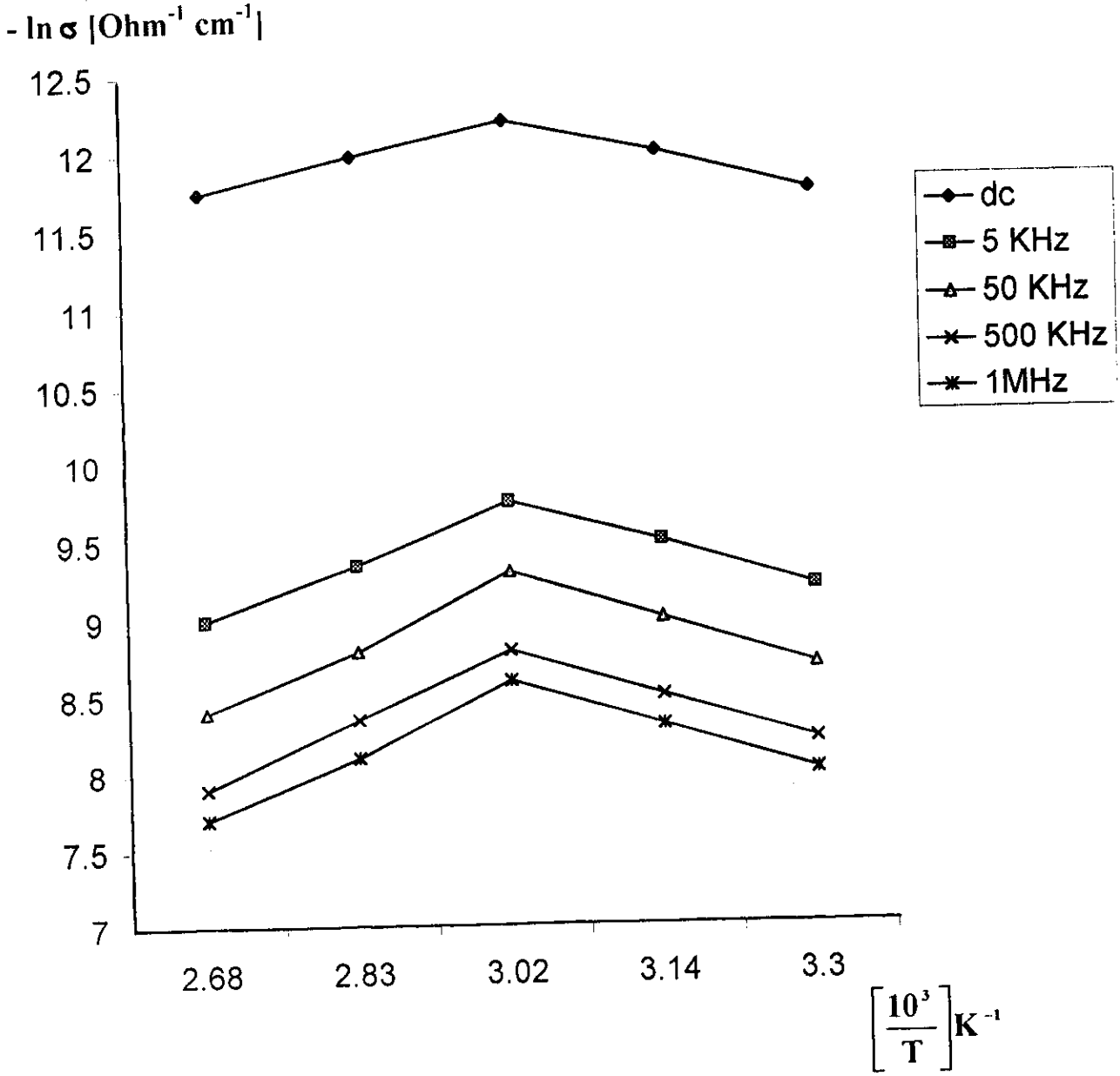


Fig. (35): Temperature dependence of electrical conductivity for PDPA-Cu(II) complex.

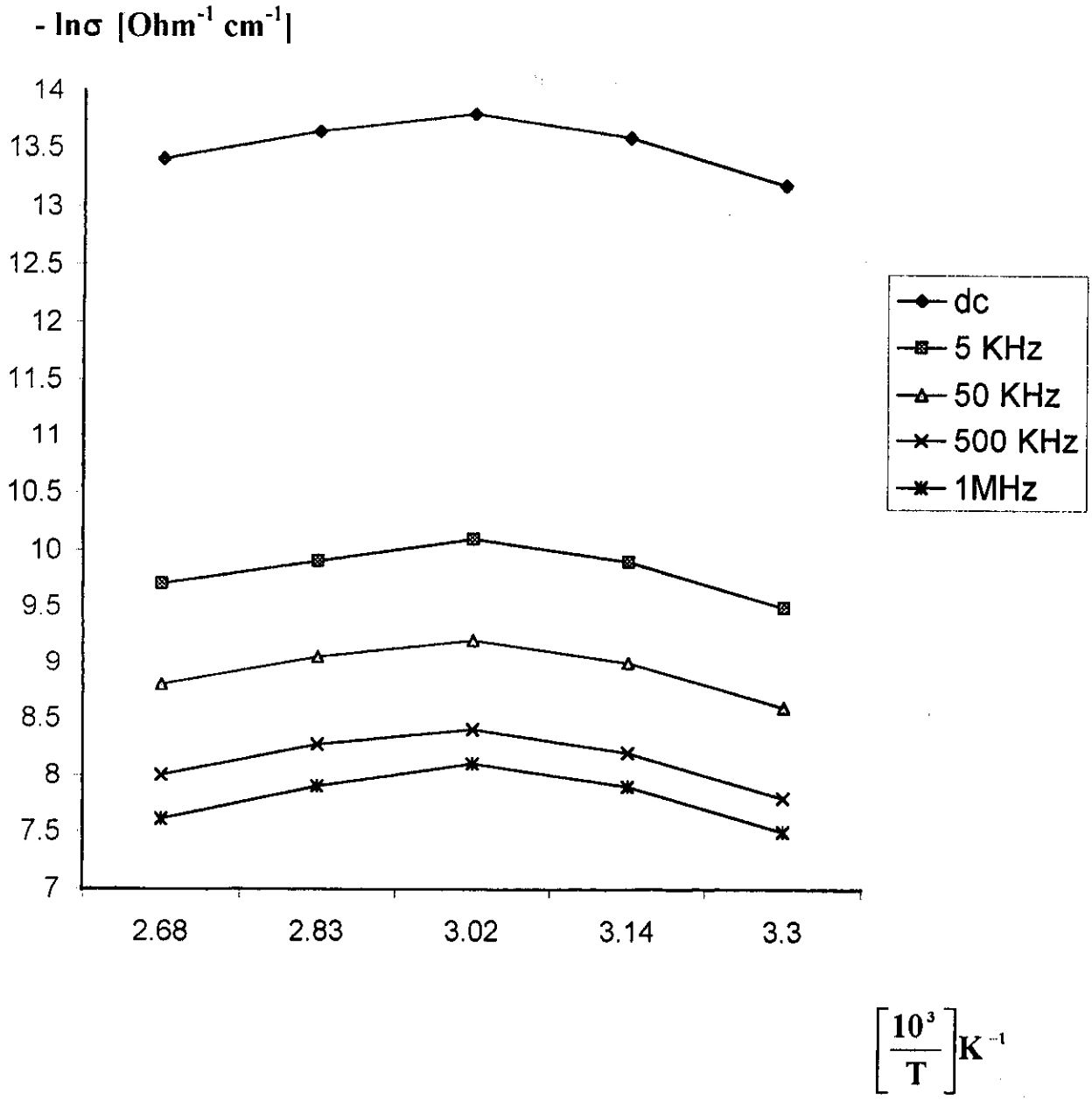
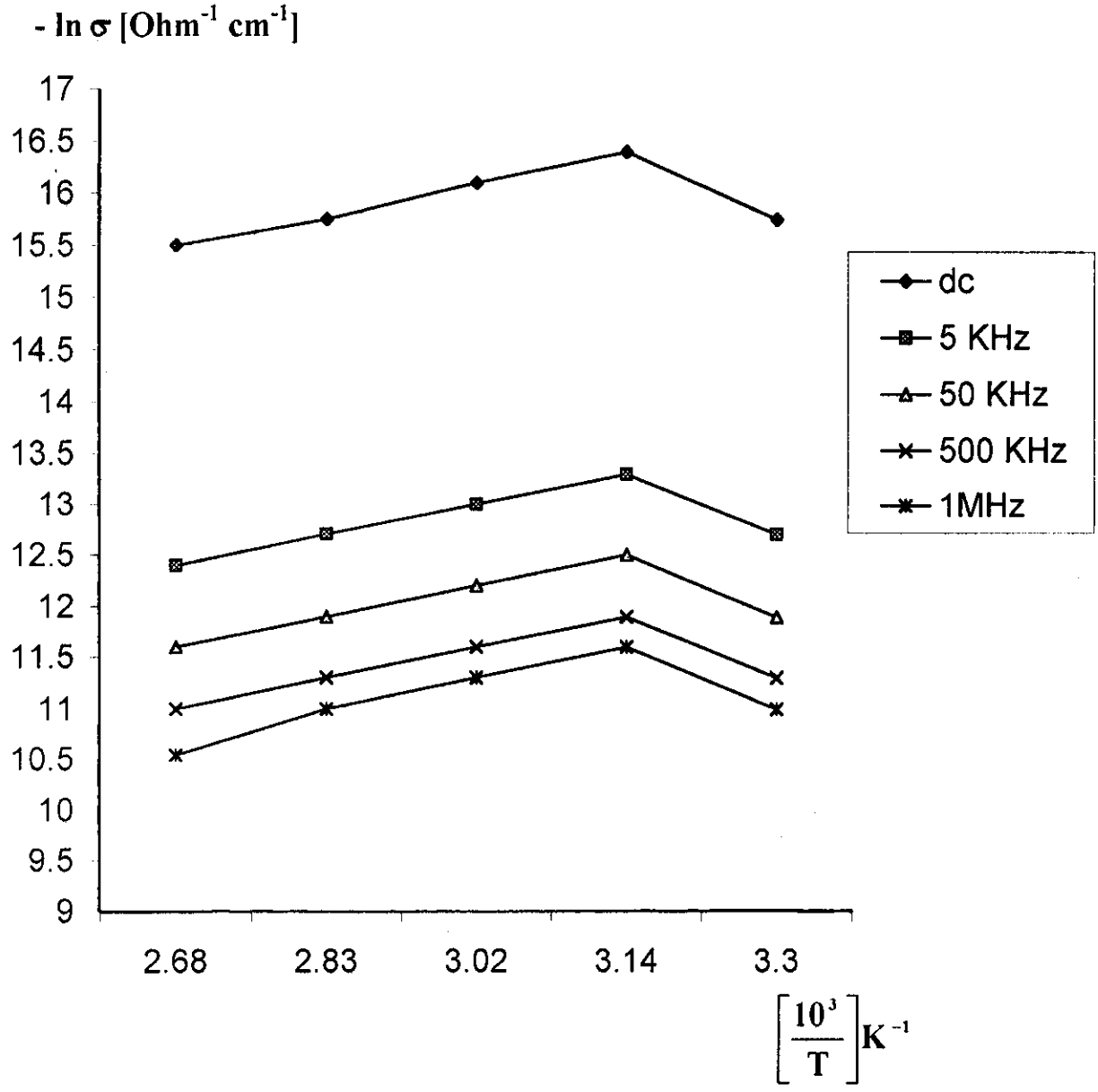


Fig. (36): Temperature dependence of electrical conductivity for PDPA-Ni(II) complex.



III-D-2-Relative permittivity and dielectric loss:

Owing to the change in $\ln \sigma$ vs $\frac{1}{T}$ behaviour of the pure polymer and its complexes under DC and AC voltage, we have emphasized the relative permittivity and dielectric loss in order to through light on the relaxation phenomena and type of polarization inside the sample.

The relative permittivity ε' plotted versus two variable factors, frequency for a wide range from 5×10^3 to 1×10^6 Hz and at temperature from 300 to $\simeq$ 380 K for the pure polyester PDPA and its complexes, are shown in Figs (23-29). Different behaviours are observed, depending on the composition of the investigated samples. Generally, all samples showed break in ε'- values at temperature coincide well with those observed in conductivity measurements. For all samples ε' values increase with increasing the frequency. This is because by increasing the frequency, the electric dipoles will no longer be able to rotate sufficiently fast to follow the field variations. This will lead to a decrease in the relative permittivity of the different metal polymeric complexes with frequency. This phenomenon is known as anomalous dielectric dispersion. For all polymeric complex, the relative change of ε'_r with increasing temperature is small because the oriental moment will not have the time to be developed and it behaves like a non-polar material. In this case, only a deformational moment will be observed.

Generally, the results at Table (19) show that ε' at 5 KHz and 300 K decreases in the order :

PDPA-Ni(II), Cu(II) > PDPA-Co(II) > PDPA-Ni(II) >

PDPA-Cu(II), Co(II) > PDPA-Ni(II), Co(II)> PDPA-Cu(II) > PDPA

They exhibit ε` values in the range of 0.02 – 2.2, so they may be classified as simple dielectric with a slightly ionic polarization.

The plot of ε` versus ionic radius of chelated compounds, Fig (37), shows a linear relation. It indicates that, the polarization of the compound increases with decreasing bond length between the polymer and the metal ions.

The temperature dependence of dielectric loss ε″ at different frequencies ranging from 5 x 10^3 to 1 x 10^6 Hz and temperature from 300 to $\simeq$ 380 K is shown in Figs (23-29). The plots showed behaviour similar to those observed for ∈`-T plots. Break in ε″ values are observed at temperatures coincide well with those obtained from ε` and σ values. For all samples, ε″ a value was found to decrease with increasing the frequency.

Table (19): Relative permittivity ε` and dielectric loss values for polyester PDPA and its complexes at room temperature and frequency of 1MHz.

Compound	ε'	ε''	Temp. break
Polyester PDPA	0.51	0.55	318
PDPA-Cu(II)	1.33	0.57	330
PDPA-Ni(II)	1.7	0.107	318
PDPA-Co(II)	1.9	0.05	330
PDPA-Ni(II),Cu(II)	2.2	0.068	330
PDPA-Ni(II), Co(II)	0.9	0.018	318
PDPA-Cu(II),Co(II)	1.6	0.33	318

Fig. (23) : Temperature dependence of relative permitivity and dielectric loss for PDPA polyester

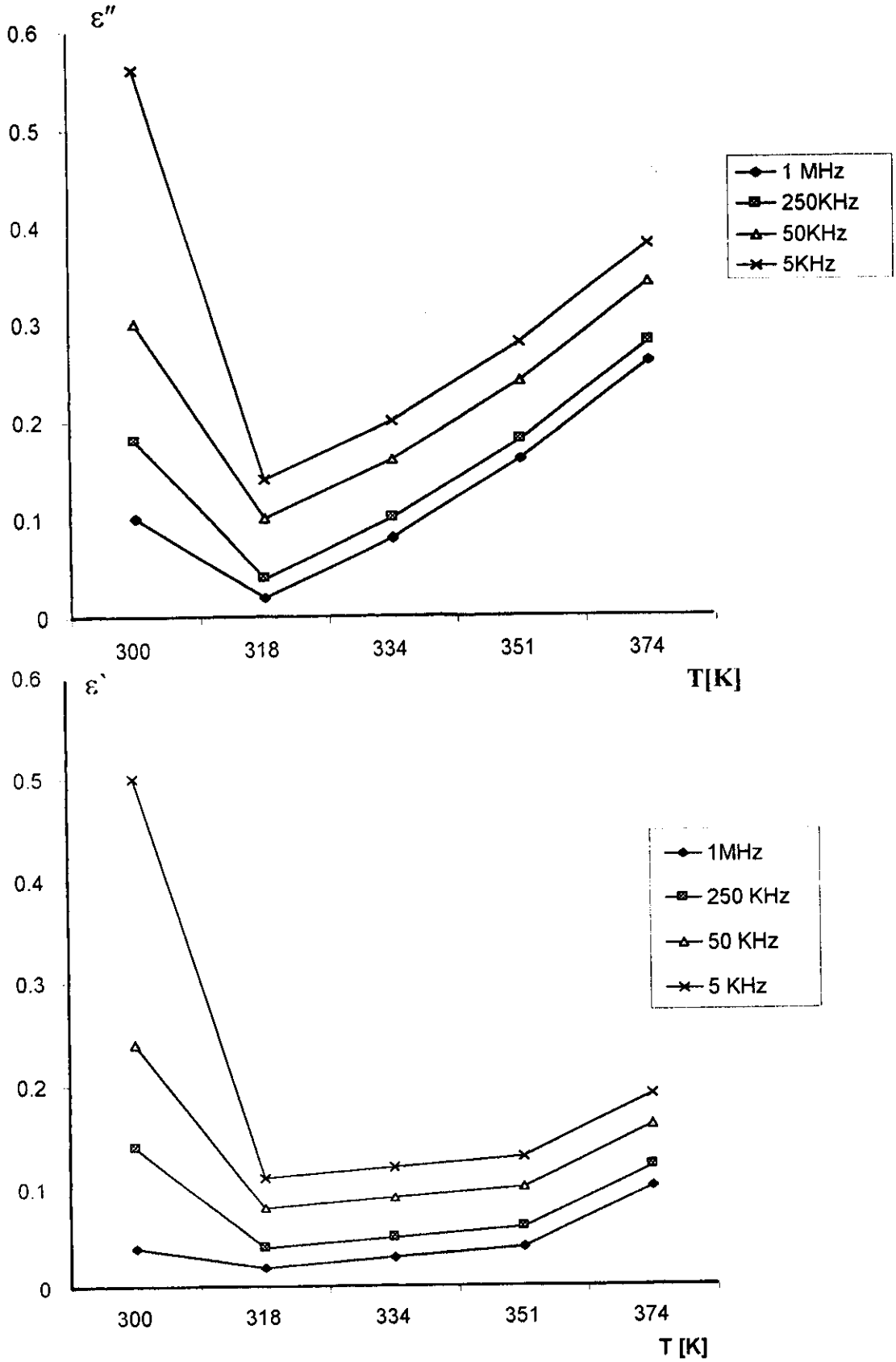
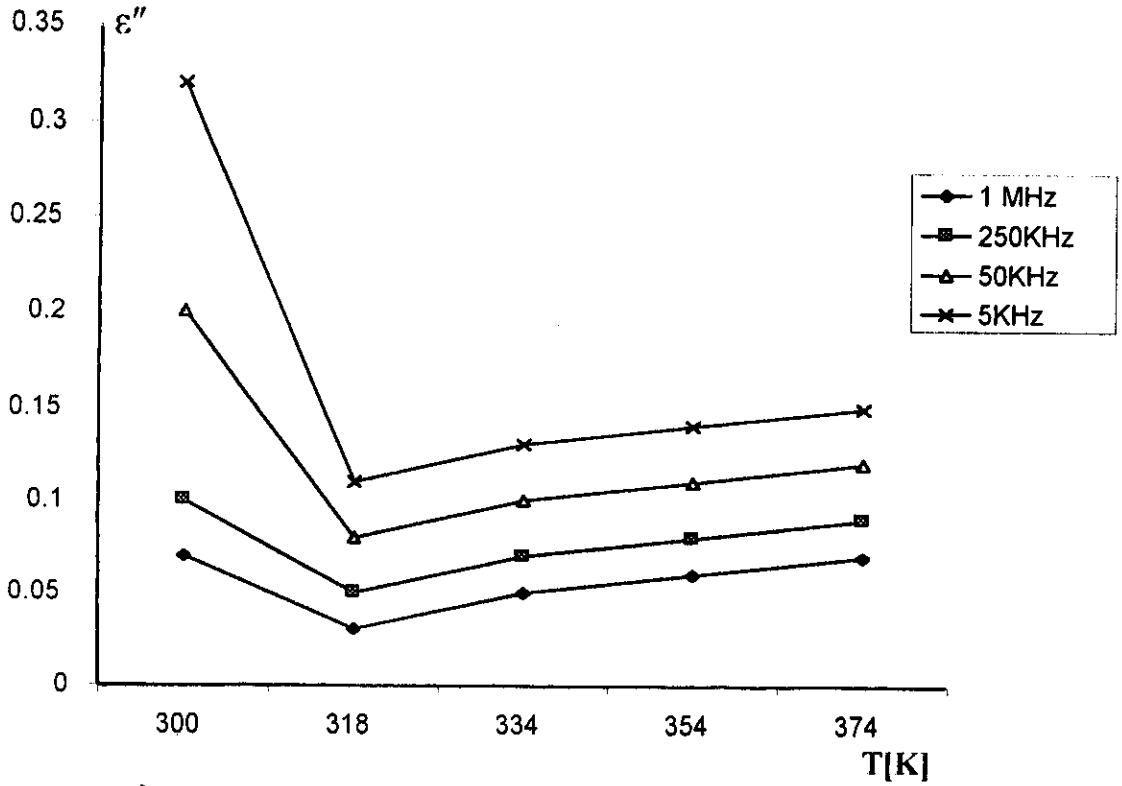


Fig. (24) : Temperature dependence of relative permitivity and dielectric loss for PDPA-[Cu(II), Co(II)] complex



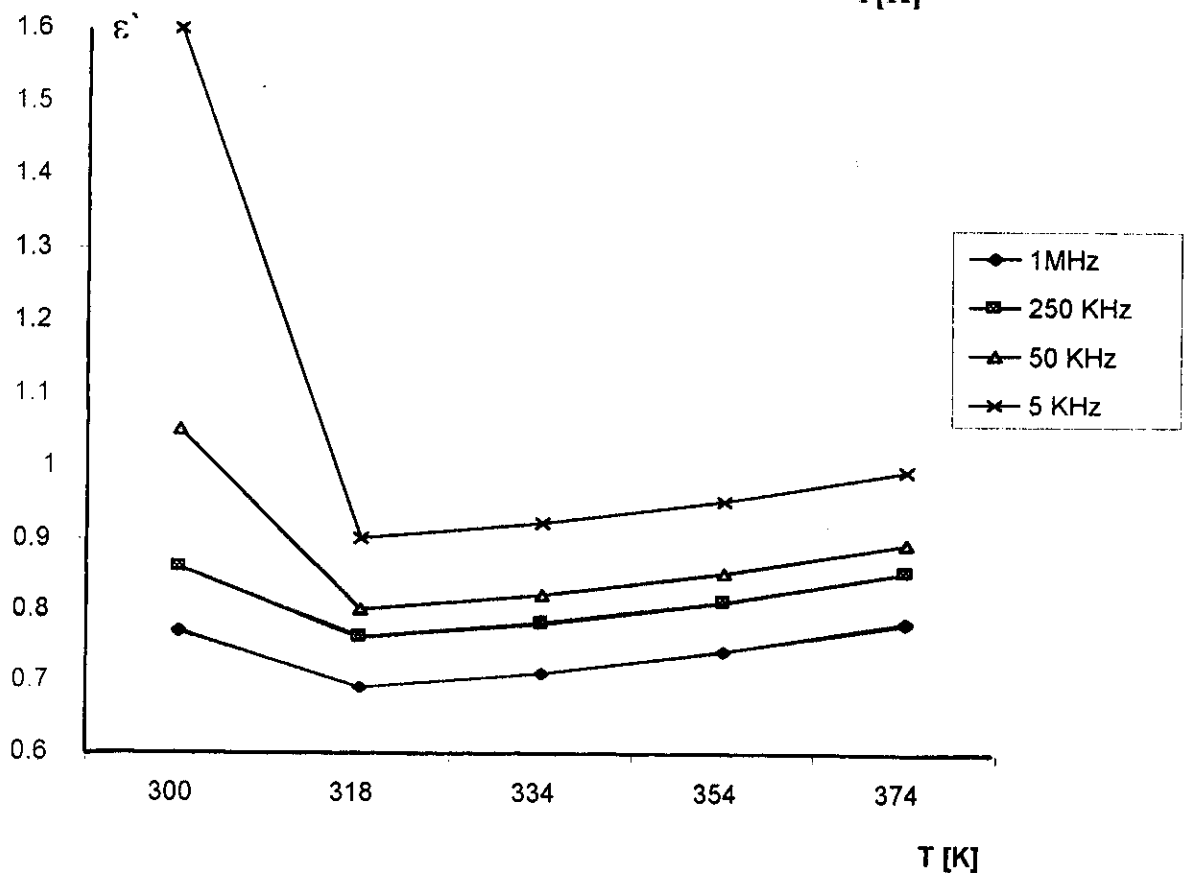


Fig. (25): Temperature dependence of relative permitivity and dielectric loss for PDPA-[Ni(II), Co(II)] complex

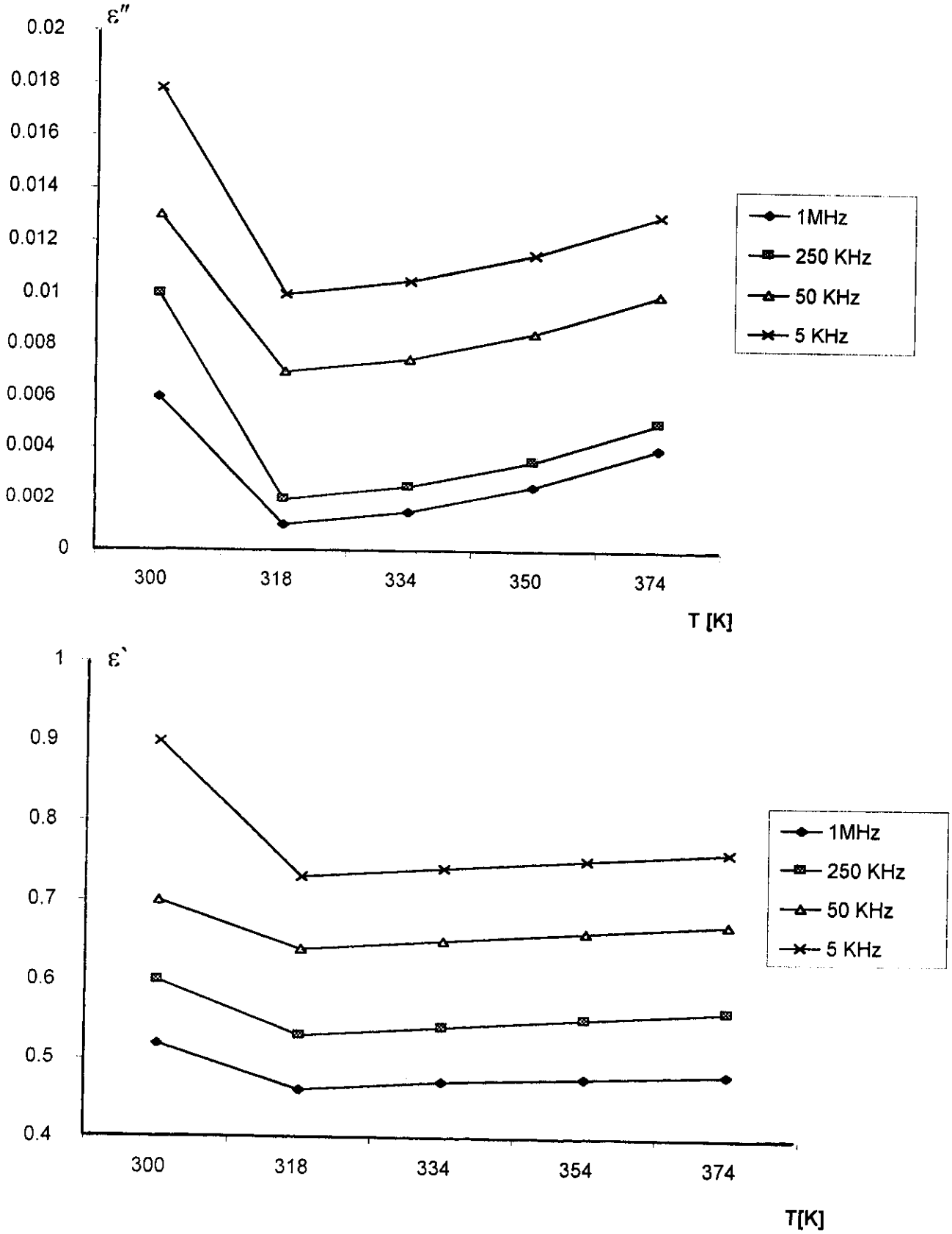
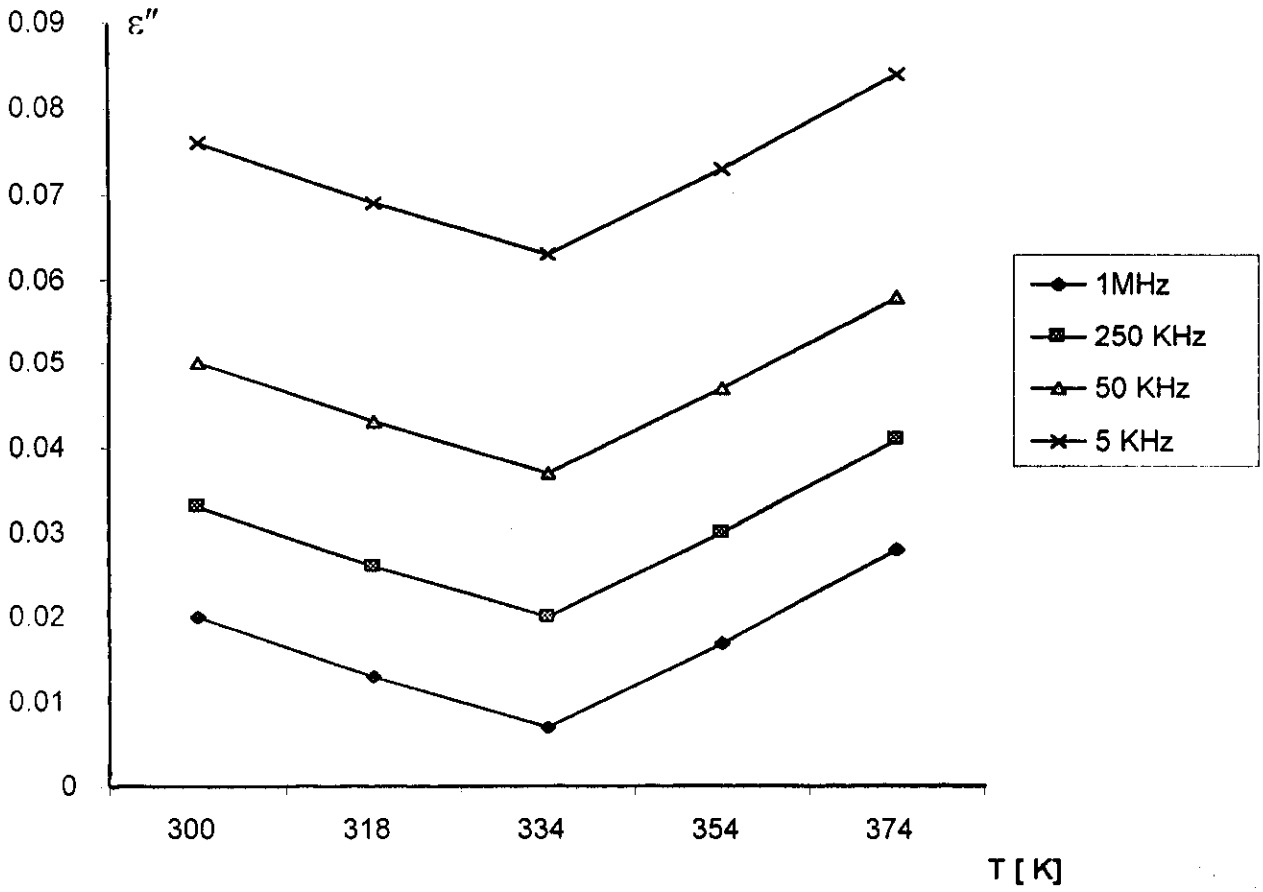


Fig. (26) : Temperature dependence of relative permitivity and dielectric loss for PDPA-[Ni(II), Cu(II)] complex



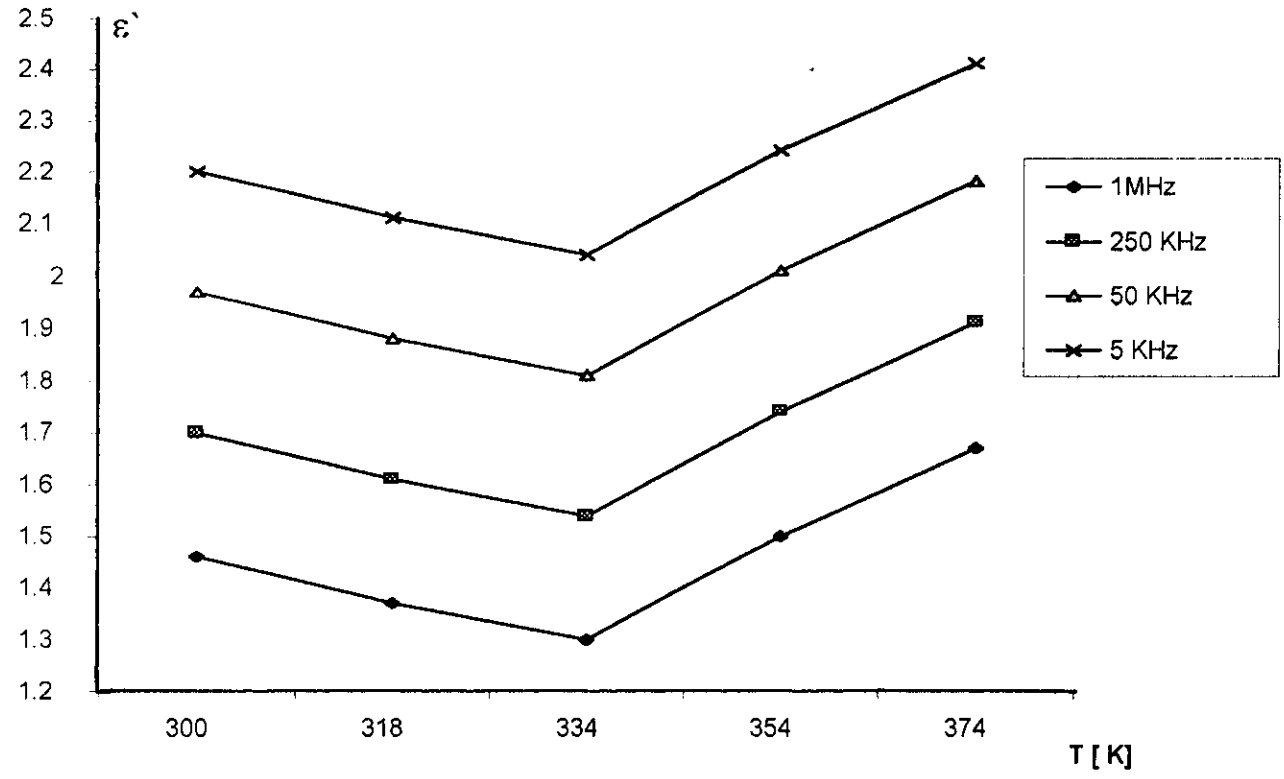
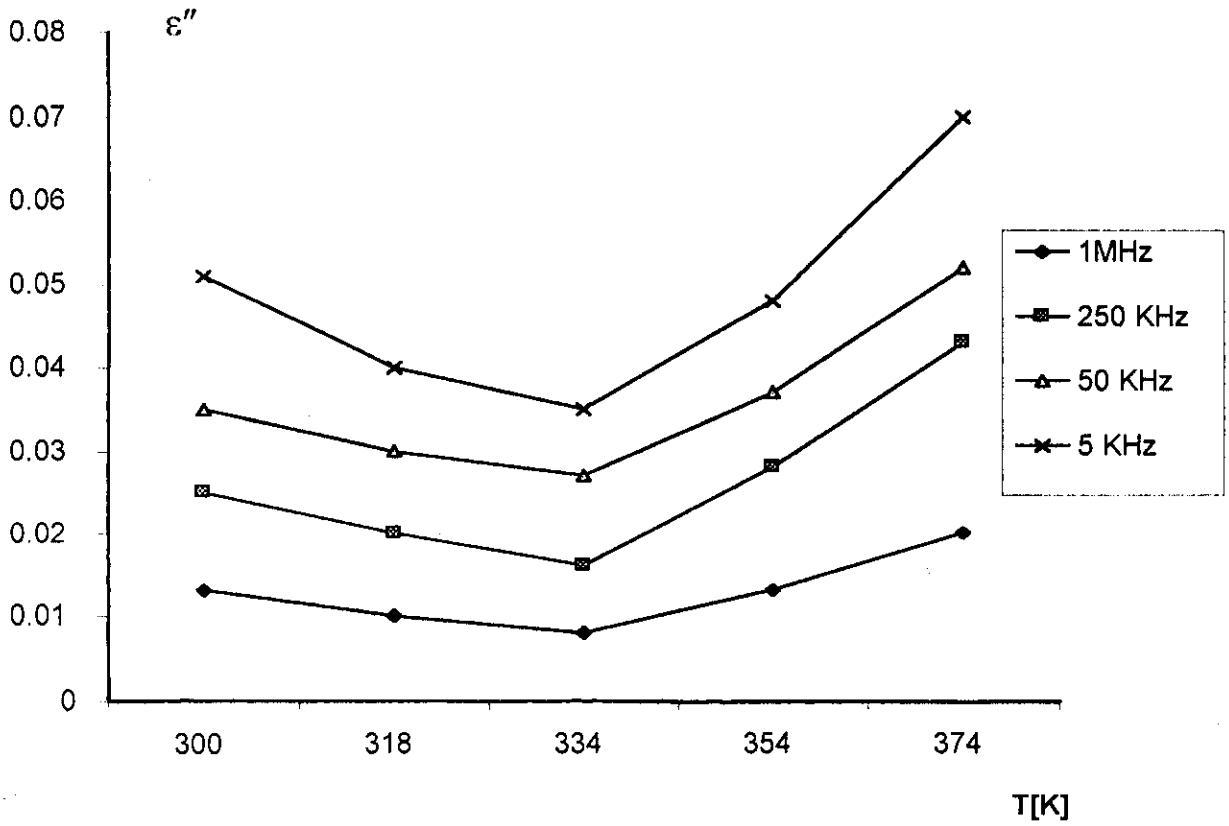


Fig. (27) : Temperature dependence of relative permitivity and dielectric loss for PDPA-Co(II) complex.



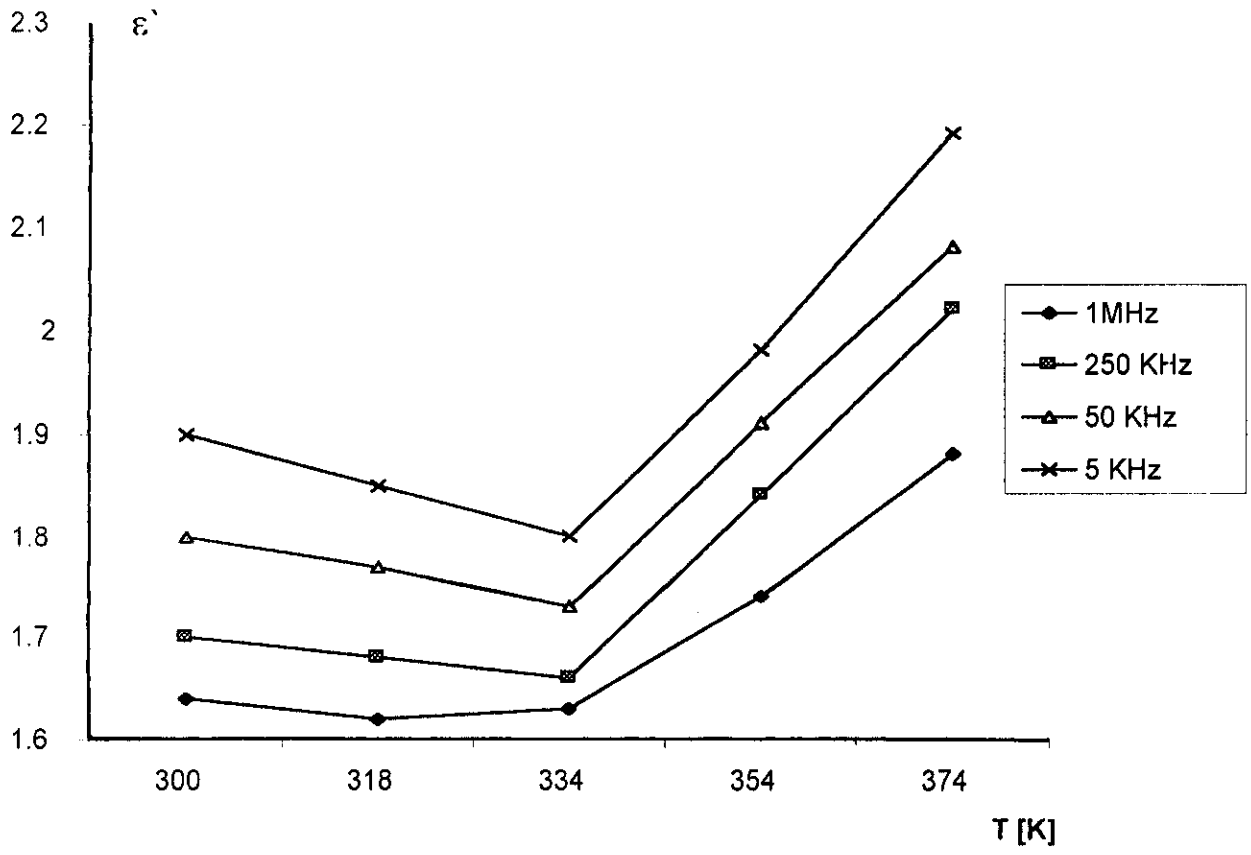
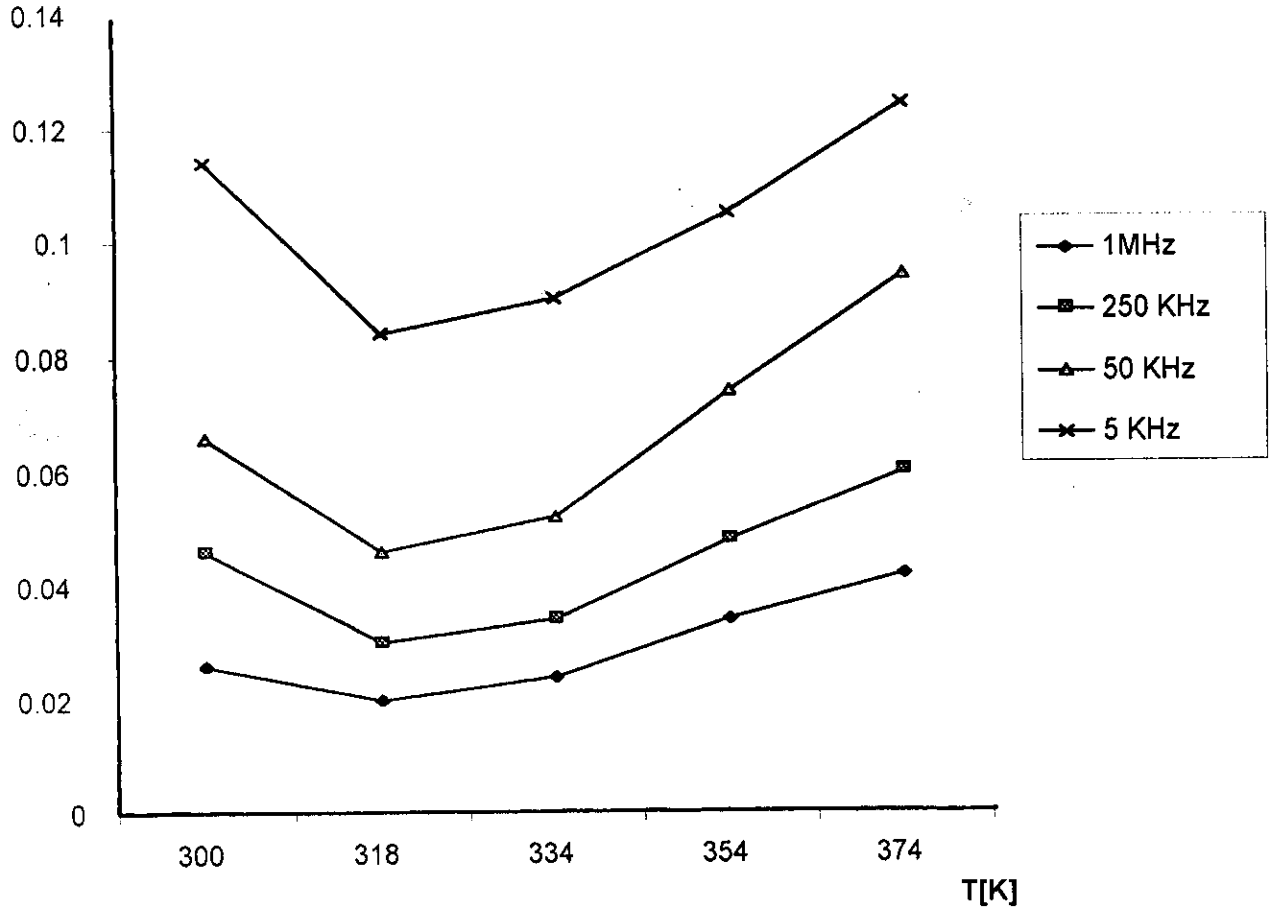


Fig. (28): Temperature dependence of relative permitivity and dielectric loss for PDPA-Ni(II) complex.



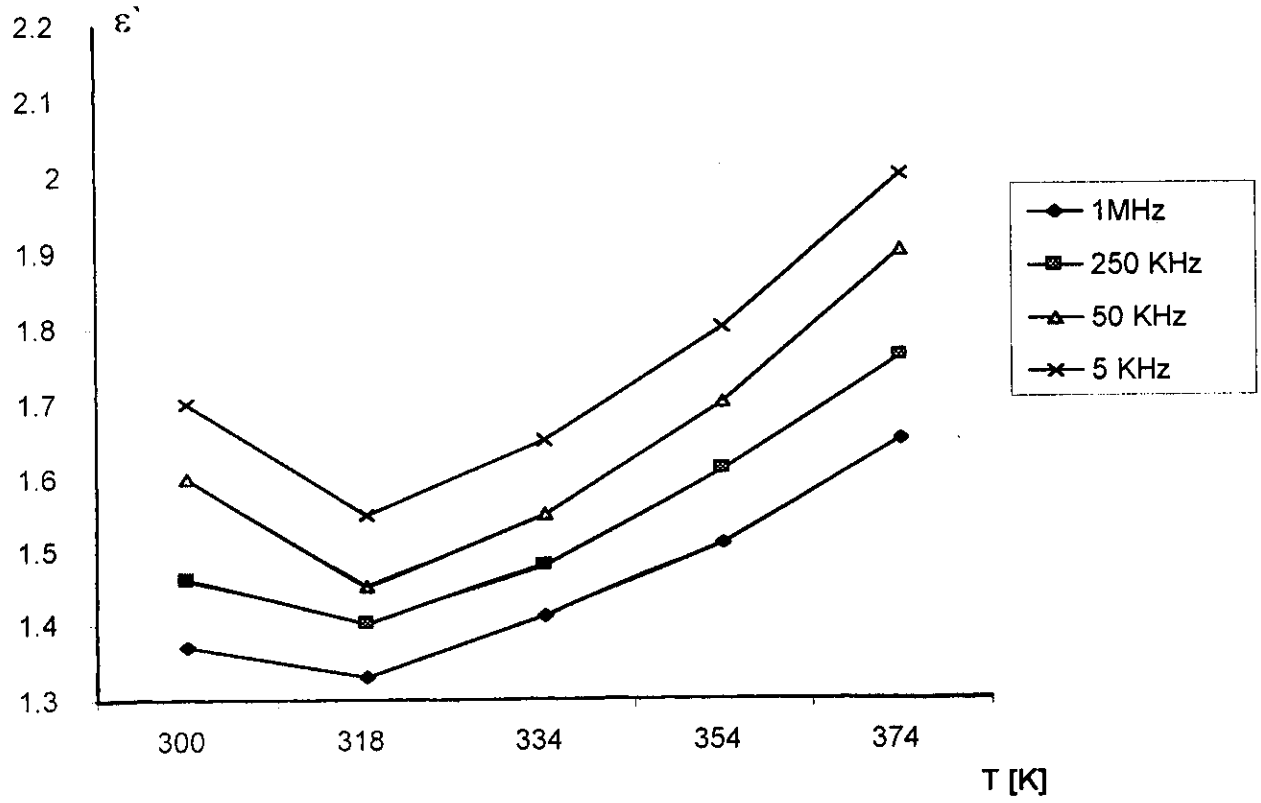
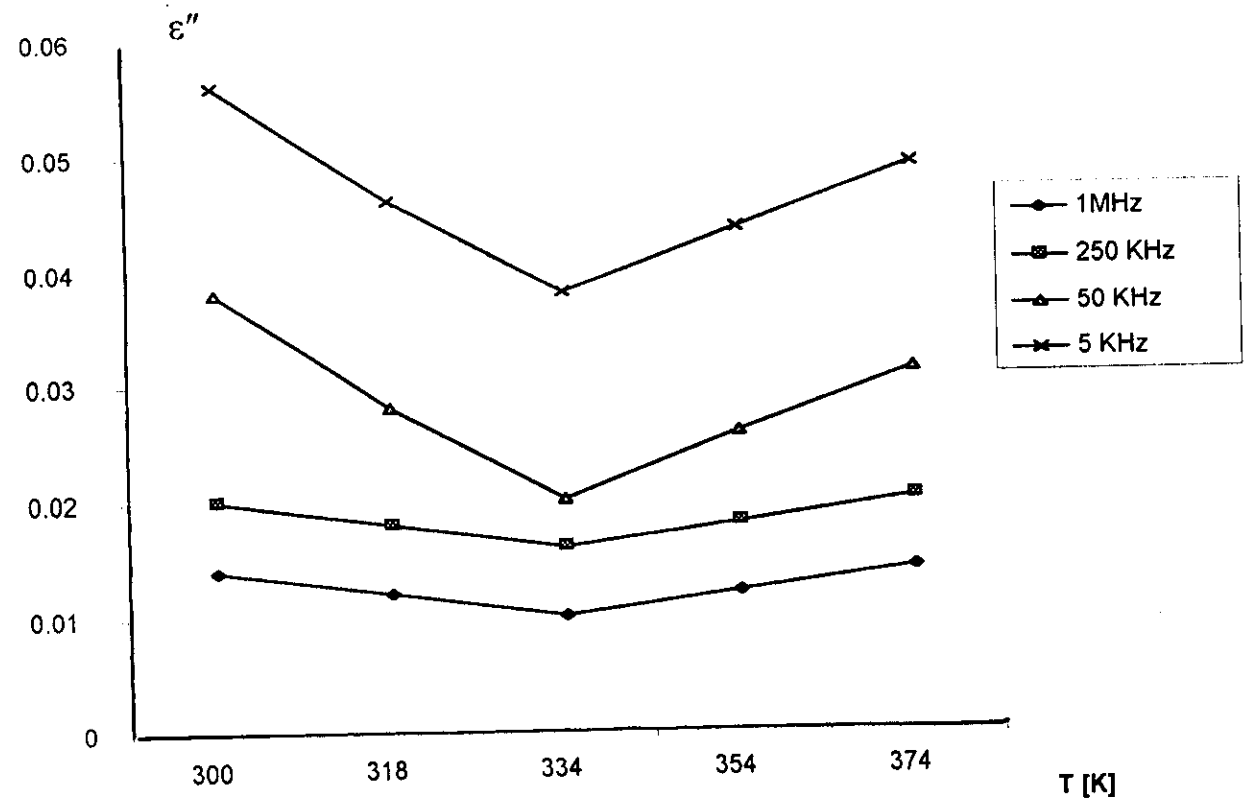


Fig. (29): Temperature dependence of relative permitivity and dielectric loss for PDPA-Cu(II) complex.



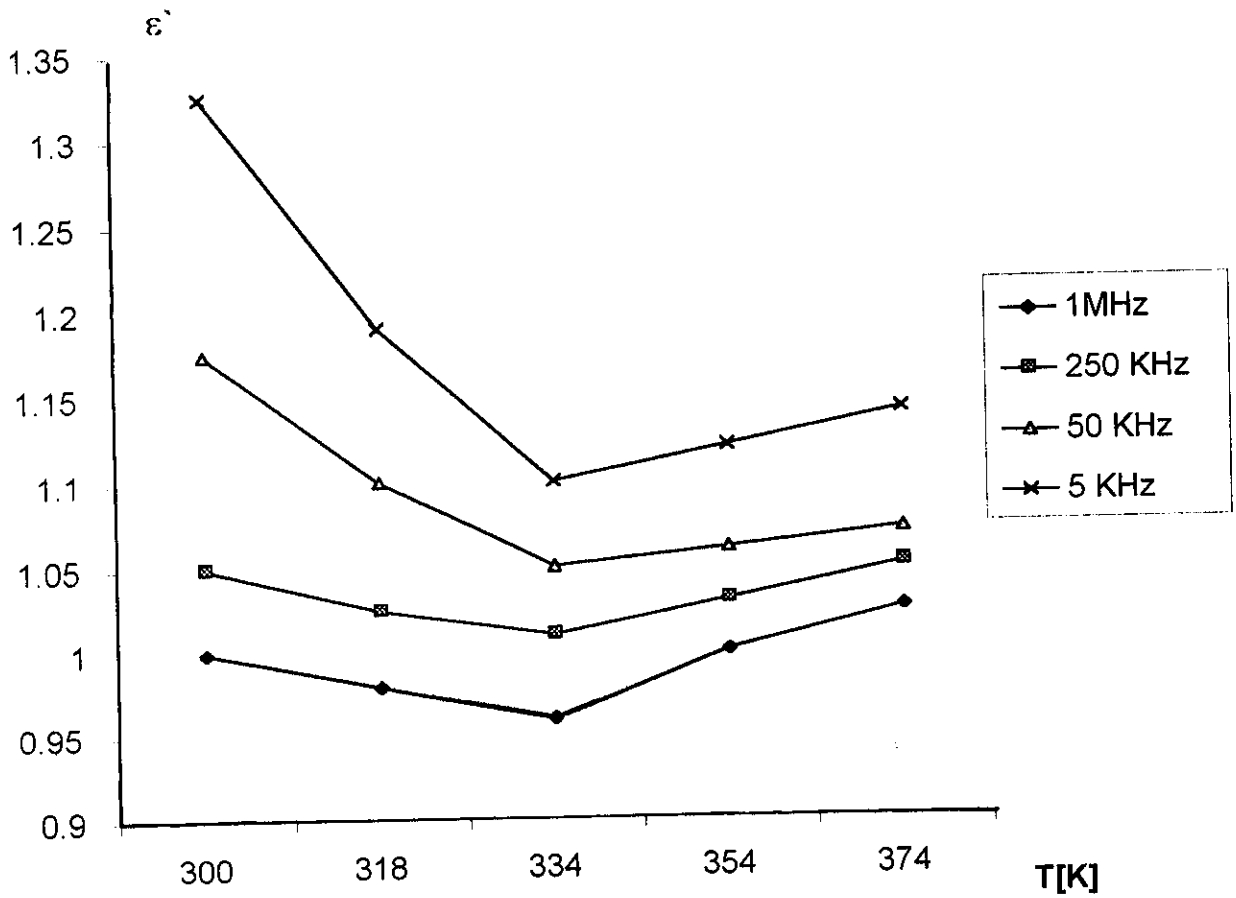
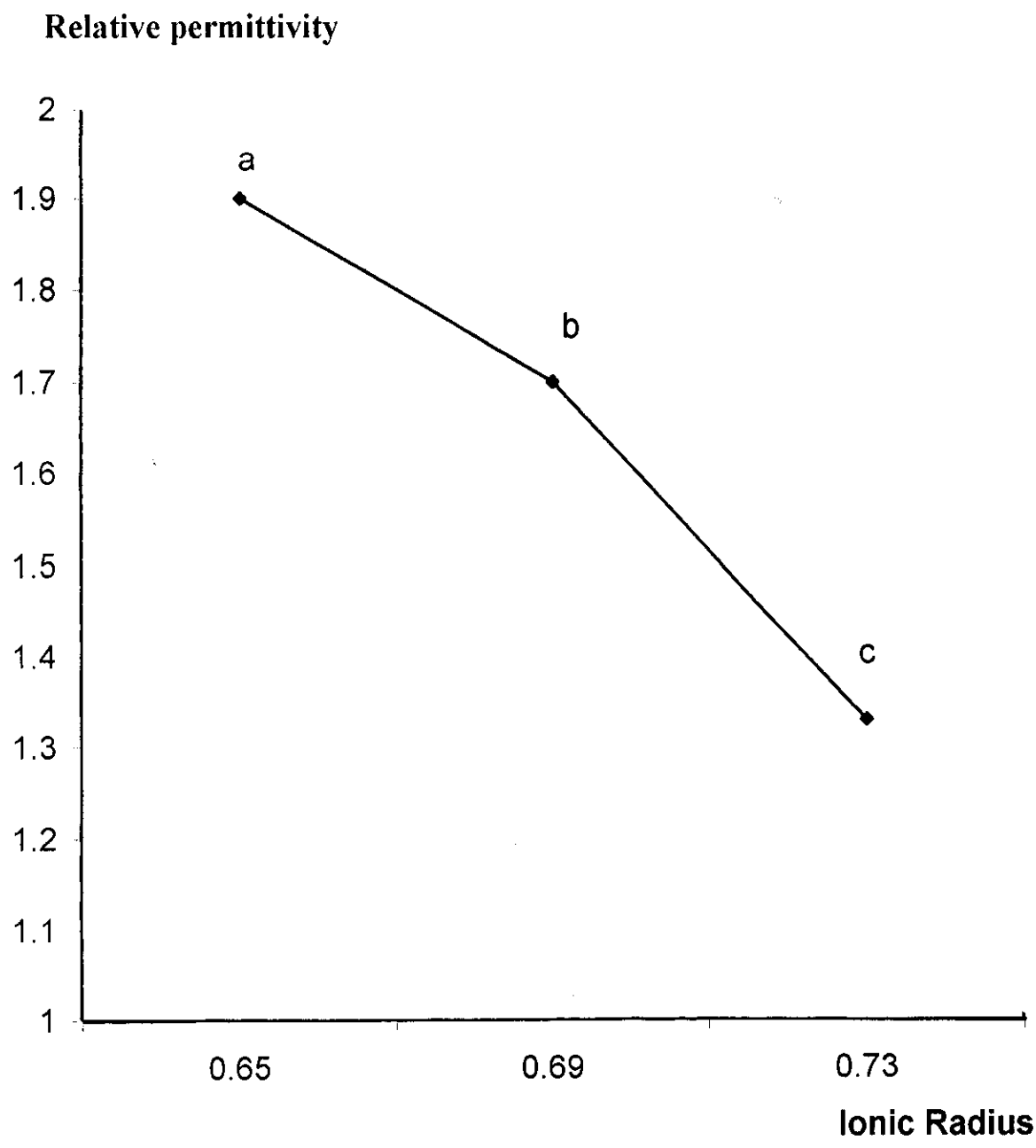


Fig. (37): Relation between Relative permittivity and Ionic radius of PDPA-Metal complexes.



a : PDPA-Co(II) complex

b: PDPA – Ni (II) complex

c: PDPA-Cu(II) complex