

Chapter V

Results and discussion

Film formation optimization

1. Appropriate concentration for film preparation

It was found that the higher concentration of PVA solution, the shorter time for film drying and the thicker film obtaining, but the longer dissolving time to achieve a clear solution (as shown in figure 5.1) and the lower peeling capability of the film from casting material. As the results, an appropriate concentration for film formation should be 5 % by weight PVA in solution.

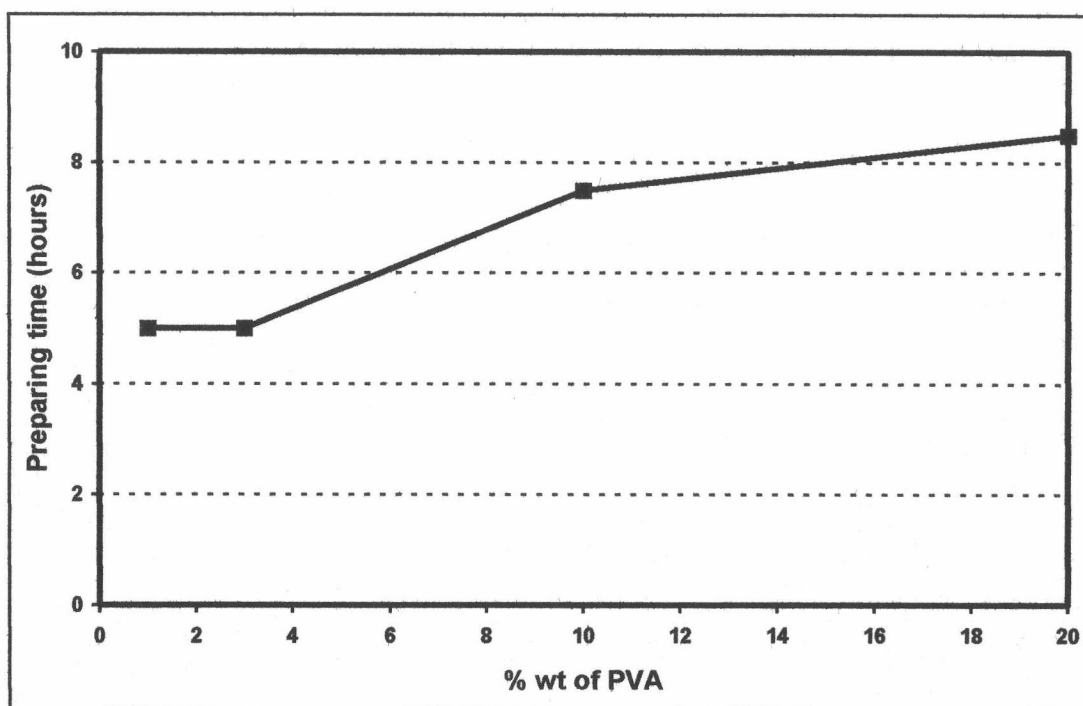


Figure 5.1 : Dependence of preparing time on PVA solution concentration.

2. Appropriate materials for film casting

As the results shown in Tables 5.1 and 5.2, it was found that appropriate casting materials for preparation of PVA and PVA films containing metal salt should be plastic sheet or plastic disc. However, PE sheet was chosen for the present study because of material available.

Table 5.1 : Dependence of peeling capability of PVA film on type of casting material.

Materials for casting	Peeling Capability	Peeling by Breaking Materials
Pyrex (glass disc)	+	+
Stainless steel disc	++	-
Ceramic disc	x	x
Teflon pan	++	-
Polystyrene sheet (PS-sheet)	+	+
Poly(vinyl chloride) sheet (PVC-sheet)	++	-
Acrylic sheet	x	x
Poly(methyl methacrylate) sheet (PMMA-sheet)	++	-
Polyethylene sheet (PE-sheet)	++	-
Foil : Front side (The higher glossy)	x	o
Foil : Back side (The lower glossy)	x	x

Footnote : + easy to remove
 ++ very easy to remove
 x cannot remove
 o can remove by breaking
 - no result

Table 5.2 : Dependence of peeling capability of PVA films containing metal salt on type of casting materials.

Films	Peeling Capability			
	Pyrex	PMMA sheet	PS sheet	PE sheet
5 wt% PVA	+	++	++	++
Li-PVA	x	+	+	+
Na-PVA	+	+	+	+
K-PVA	x	+	+	+
Ca-PVA	x	+	+	+
Ba-PVA	x	+	+	+
Fe(II)-PVA	x	+	+	+
Fe(III)-PVA	x	+	+	+
Cu-PVA	+	++	+	+
Zn-PVA	+	+	+	+
Co-PVA	x	++	+	+
Ni-PVA	x	+	+	+

Footnote : + easy to remove
 ++ very easy to remove
 x cannot remove
 o can remove by breaking
 - no result

Note : salt content 20 % by weight

3. Homogeneous distribution control of salt in film

It was found that the PVA films containing metal salt prepared by mixing the salt as powder condition showed non-homogeneous distribution of salt in the film. Whereas, the films prepared by mixing the salt as aqueous solution showed more homogeneous distribution and sequence of mixing seemed to be no effect on distribution of salt in the film.

4. Thickness regularity control

It was found that casting at temperature lower than 60 °C the resulting film showed more thickness regularity than the films casted at temperature higher than 60 °C, even below Tg of the PVA film.

It was also found that no difference can be observed between the film casted at room temperature in an autodesiccator and the film casted in an oven at the temperature higher than room temperature but not higher than 60 °C.

5. Time for complex formation

It was shown in figure 5.2 that to create polymer-metal complex, the mixture of salt solution and PVA solution should be stirred at least 6 hours in order to have time for complex formation.

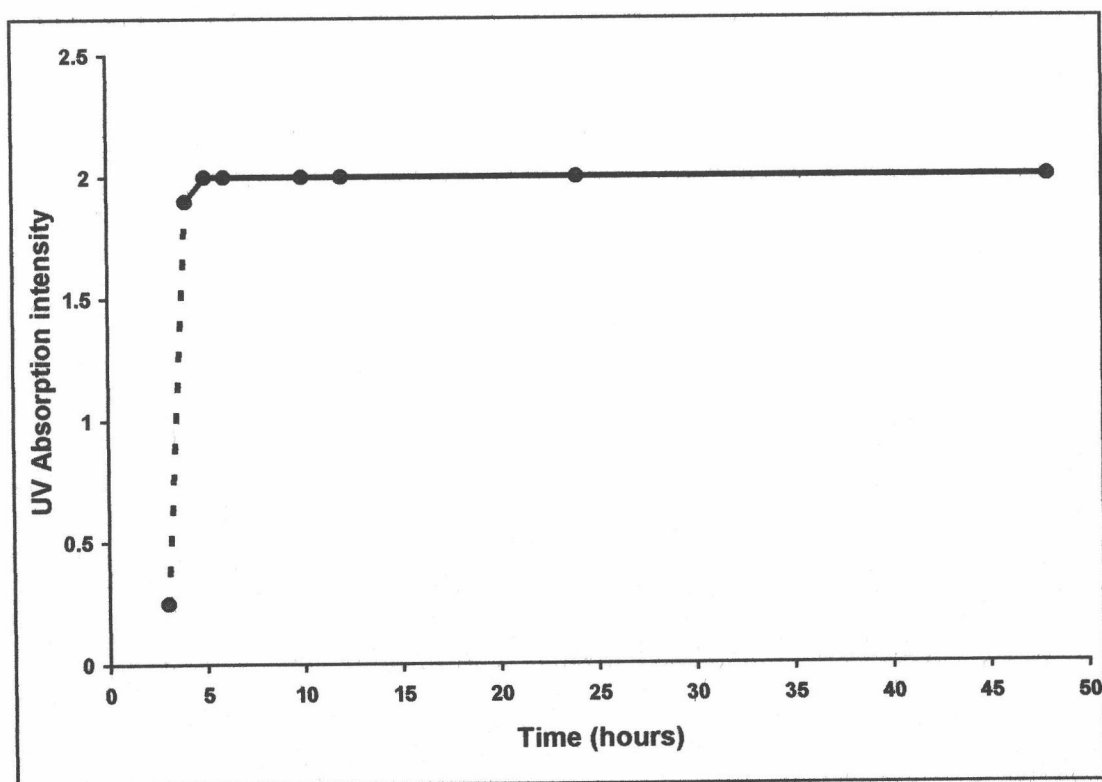


Figure 5.2 : Dependence of UV-VIS absorption at a specific wavelength of PVA film containing NiCl_2 on stirring time of the mixed solution.

Note : The other salts also showed similar behavior.

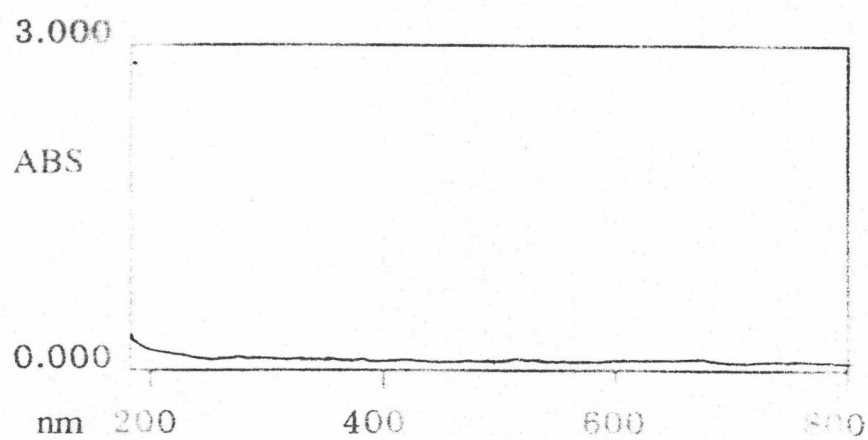
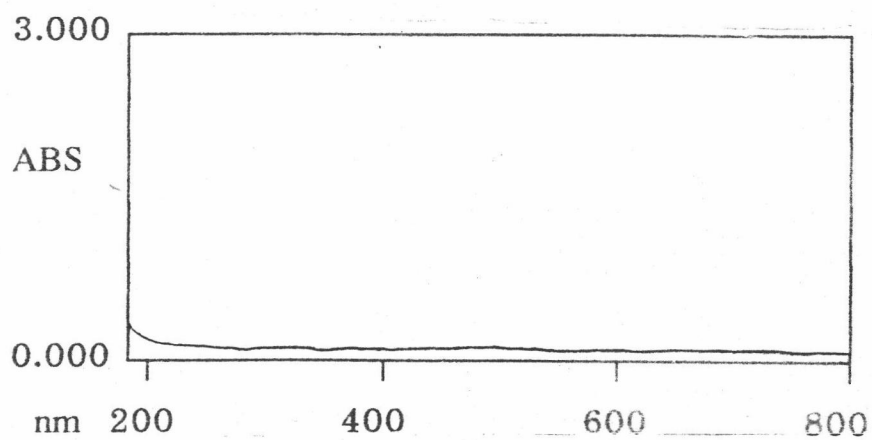
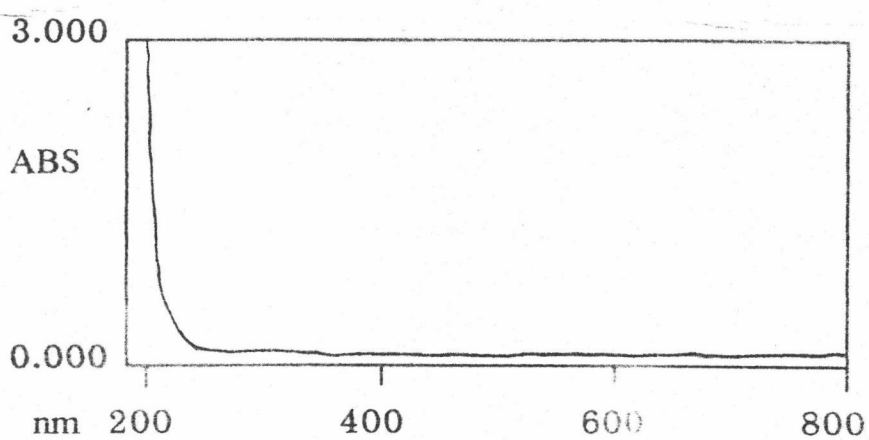


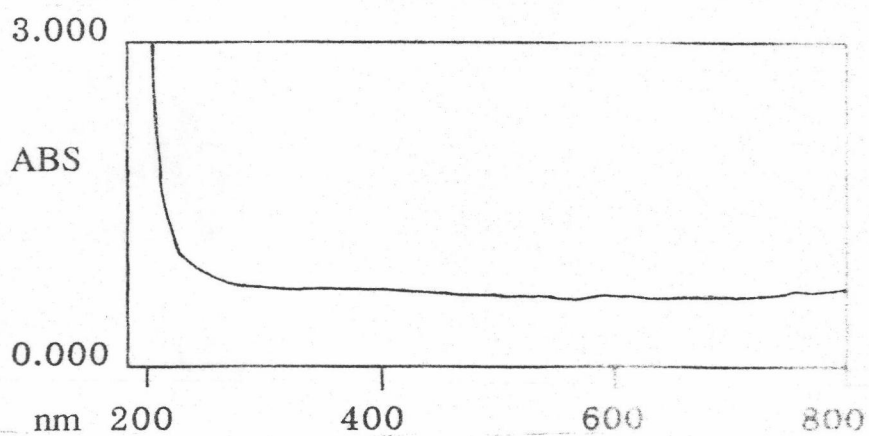
Figure 5.3 : UV-VIS absorption spectra of standard PVA film



(a)



(b)

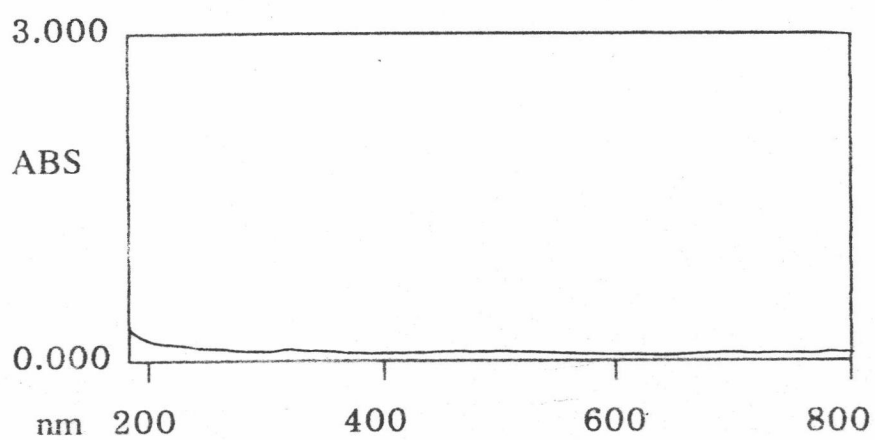


(c)

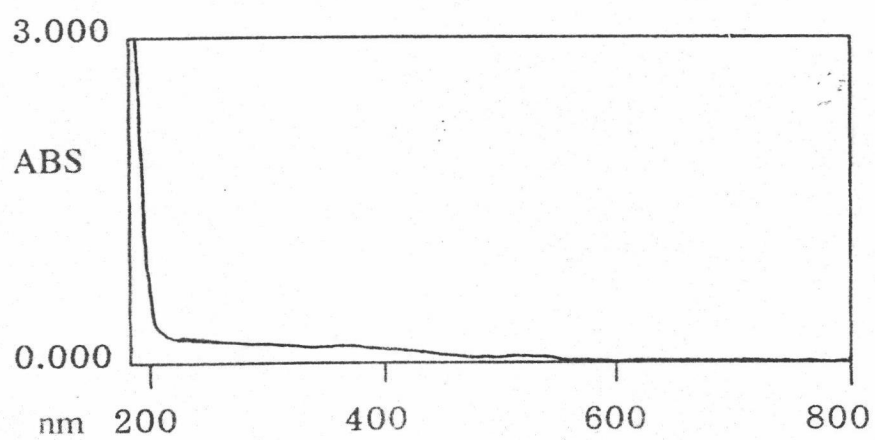
Figure 5.4 : UV-VIS absorption spectra of

(a) PVA film (b) LiCl aqueous solution

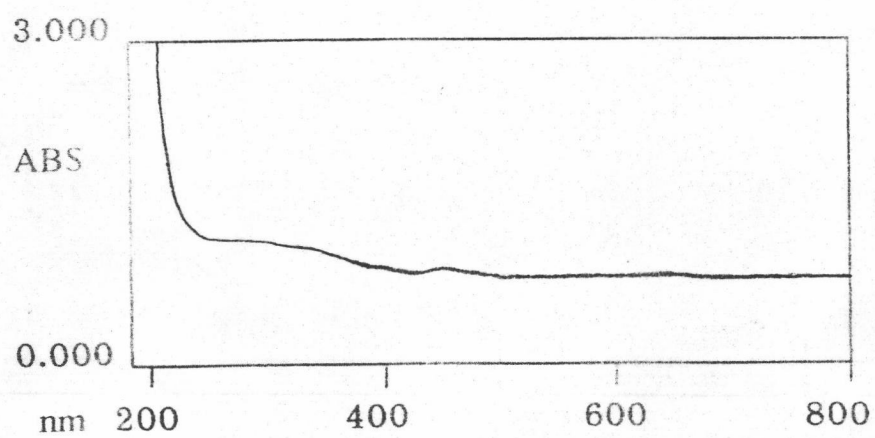
(c) PVA film containing 20% LiCl



(a)

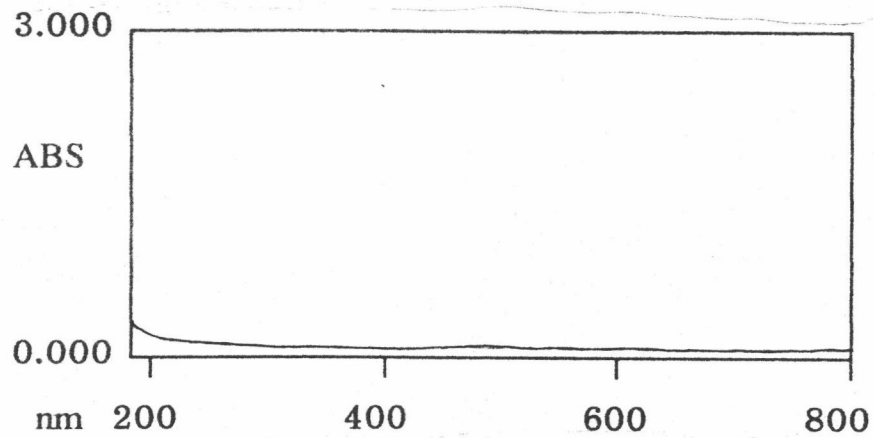


(b)

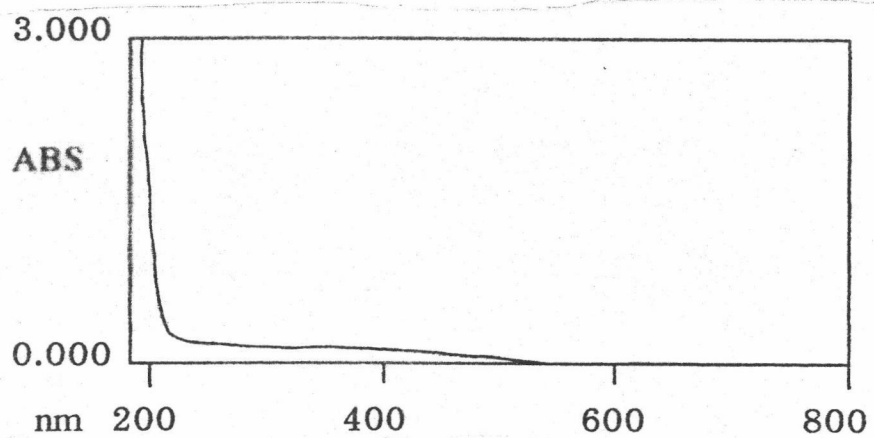


(c)

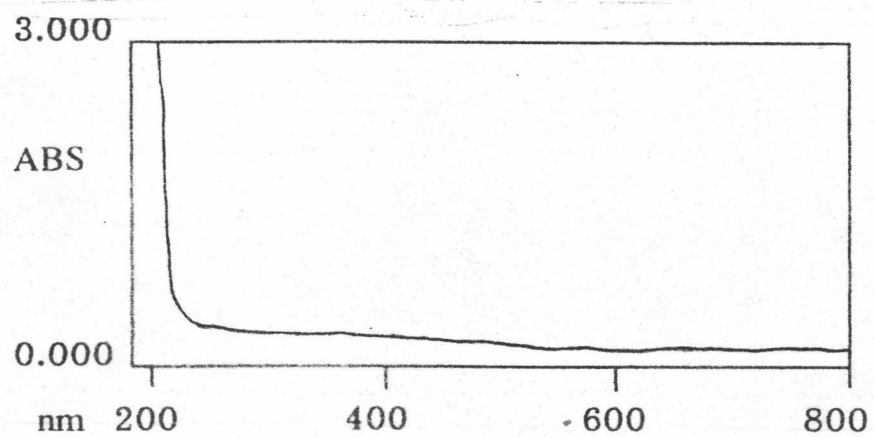
Figure 5.5 : UV-VIS absorption spectra of
(a) PVA film (b) NaCl aqueous solution
(c) PVA film containing 20% NaCl



(a)

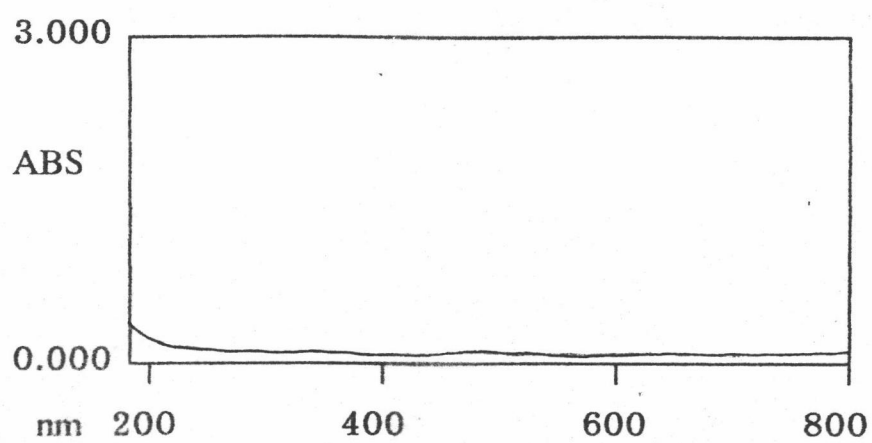


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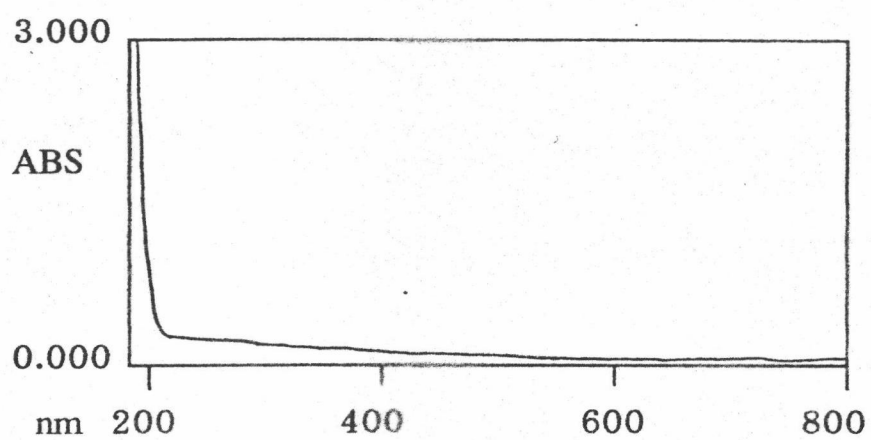


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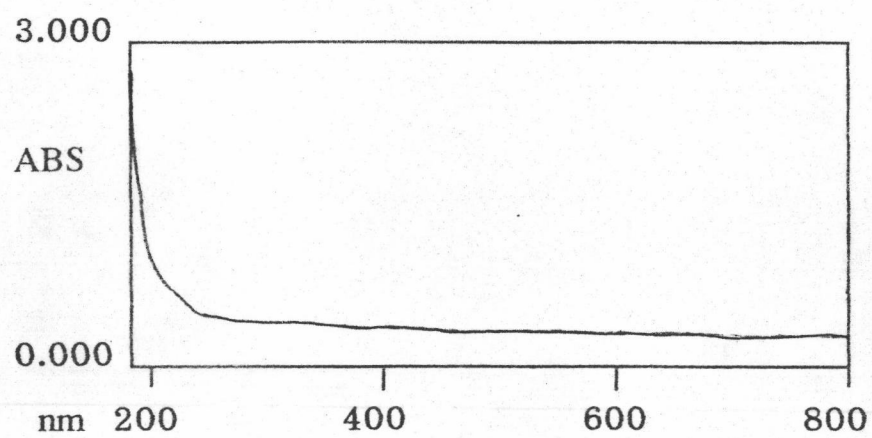
Figure 5.6 : UV-VIS absorption spectra of
(a) PVA film (b) KCl aqueous solution
(c) PVA film containing 20% KCl



(a)



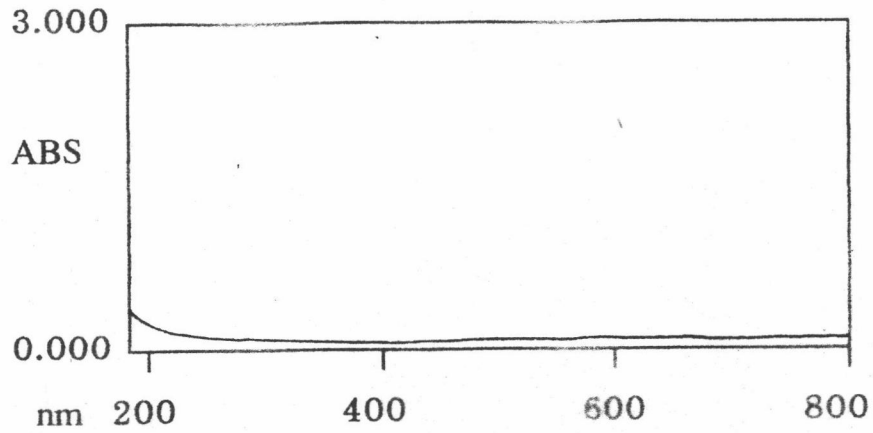
(b)



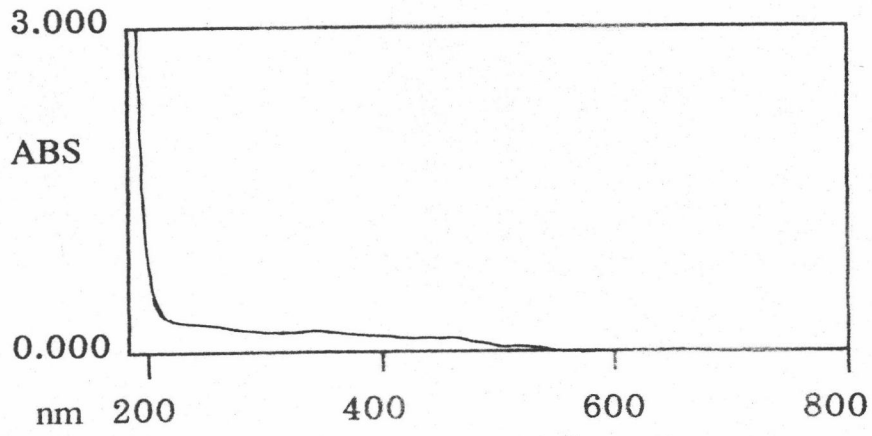
(c)

Figure 5.7 : UV-VIS absorption spectra of

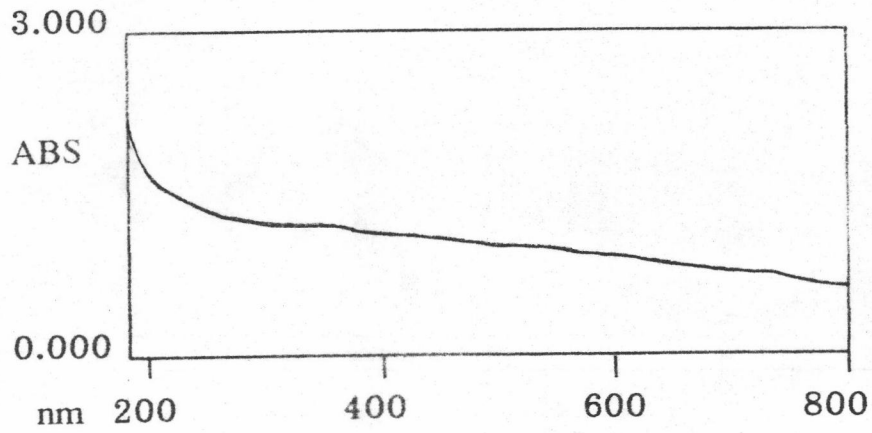
(a) PVA film (b) CaCl_2 aqueous solution(c) PVA film containing 20% CaCl_2



(a)

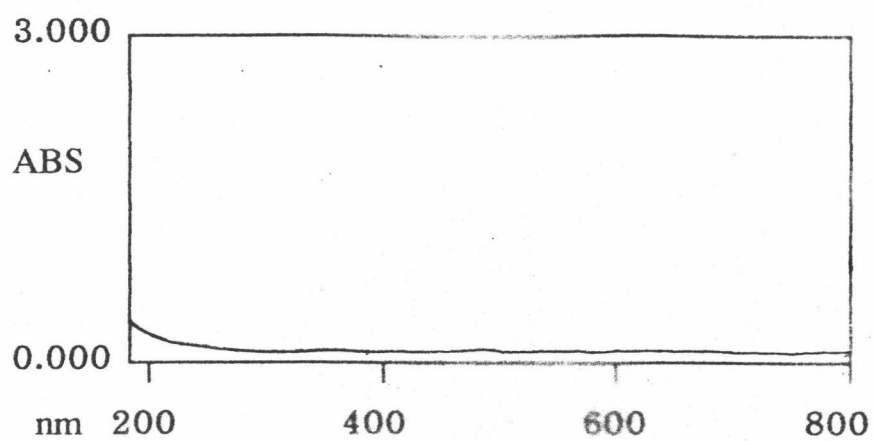


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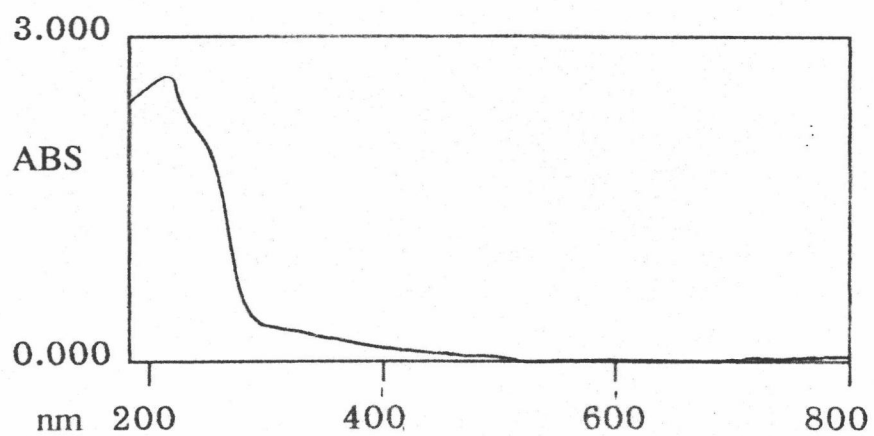


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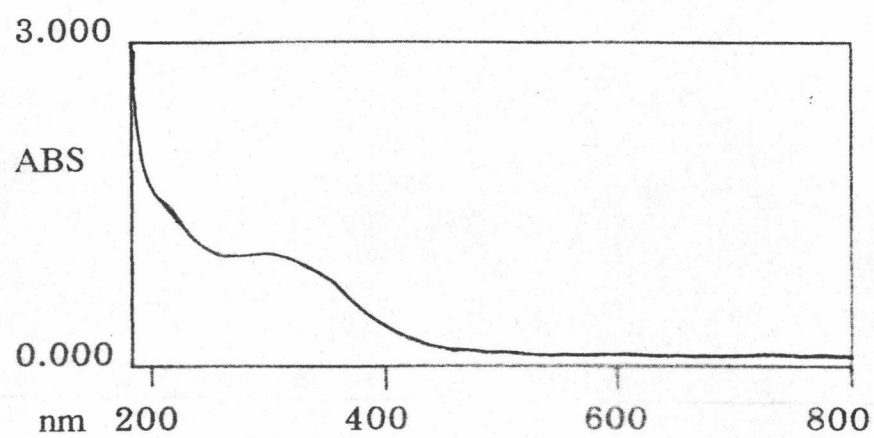
Figure 5.8 : UV-VIS absorption spectra of
(a) PVA film (b) BaCl_2 aqueous solution
(c) PVA film containing 20% BaCl_2



(a)



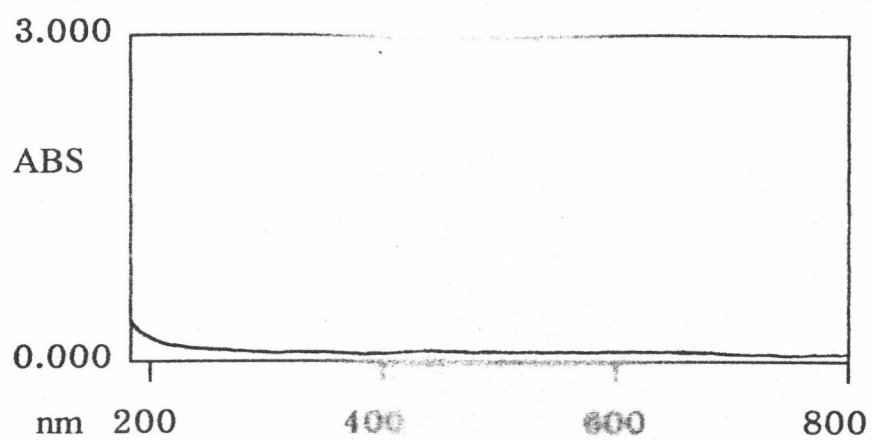
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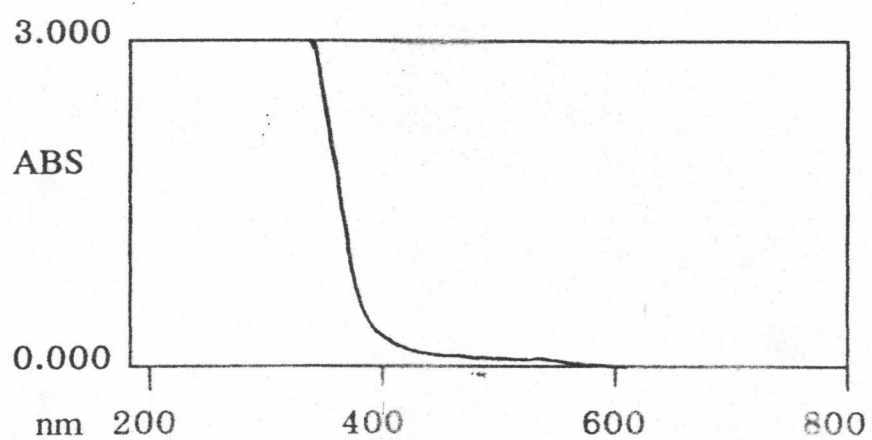
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Figure 5.9 : UV-VIS absorption spectra of

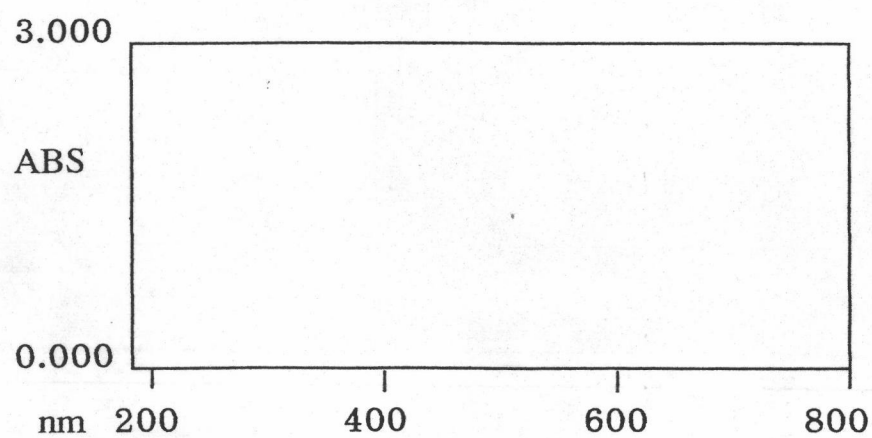
(a) PVA film (b) FeCl_2 aqueous solution(c) PVA film containing 20% FeCl_2



(a)



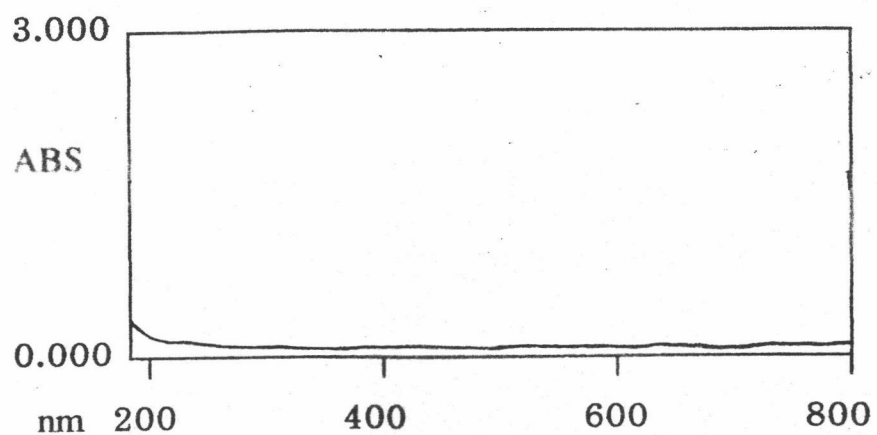
(b)



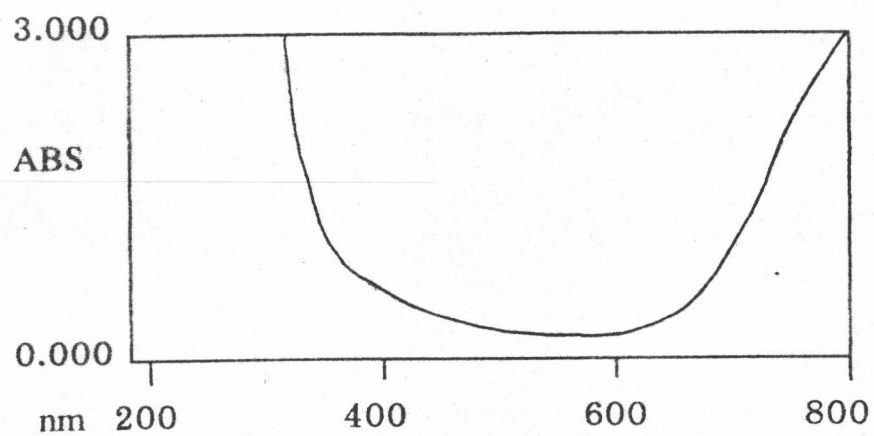
(c)

Figure 5.10 : UV-VIS absorption spectra of

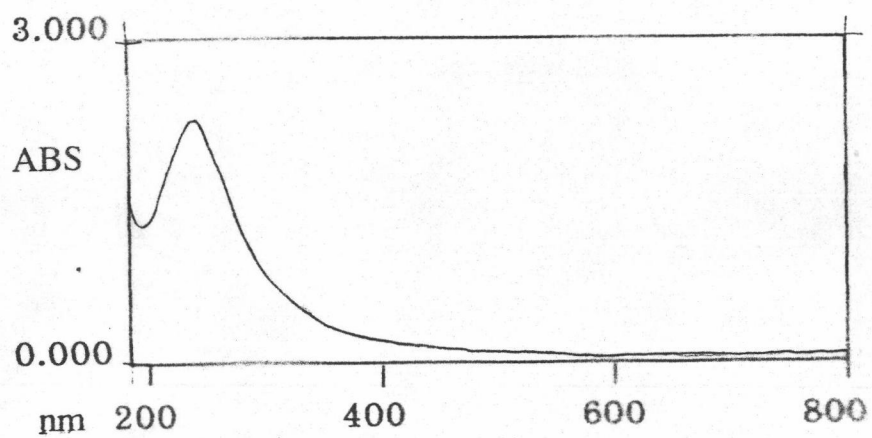
(a) PVA film (b) FeCl₃ aqueous solution(c) PVA film containing 20% FeCl₃



(a)

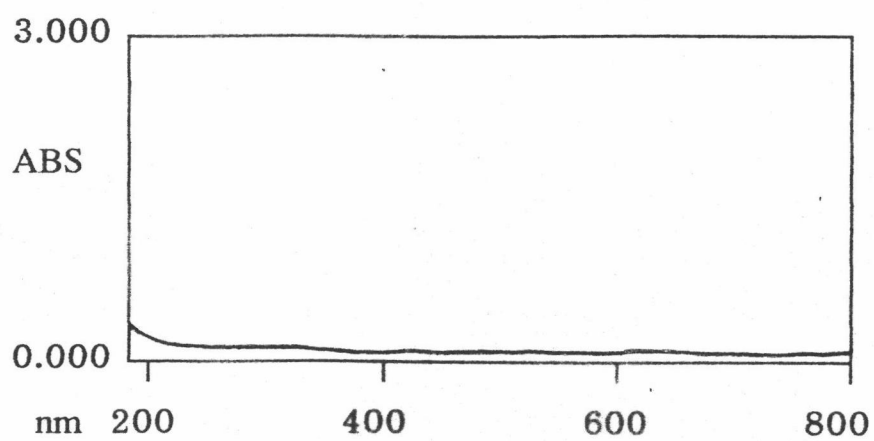


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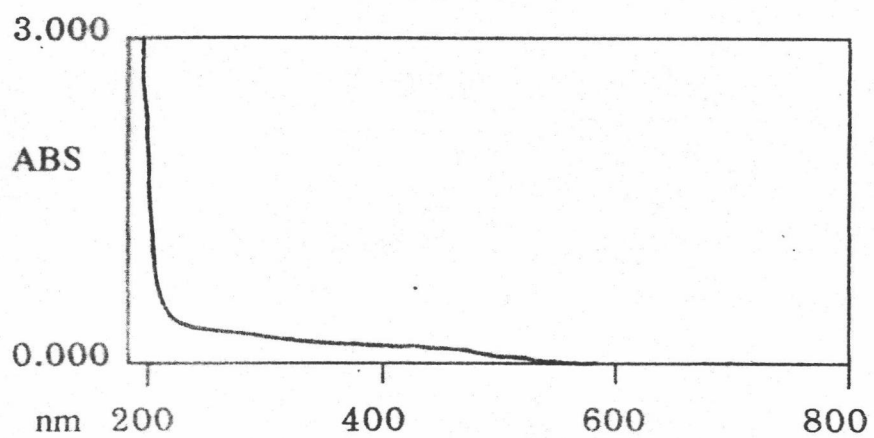


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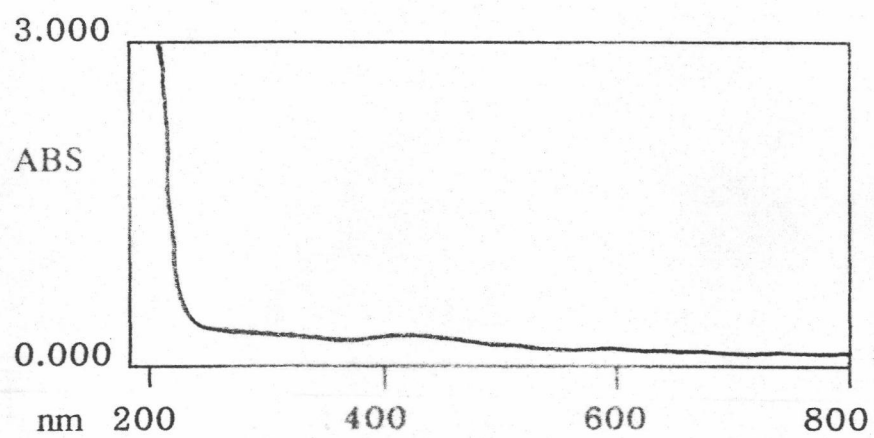
Figure 5.11 : UV-VIS absorption spectra of
(a) PVA film (b) CuCl_2 aqueous solution
(c) PVA film containing 20% CuCl_2



(a)



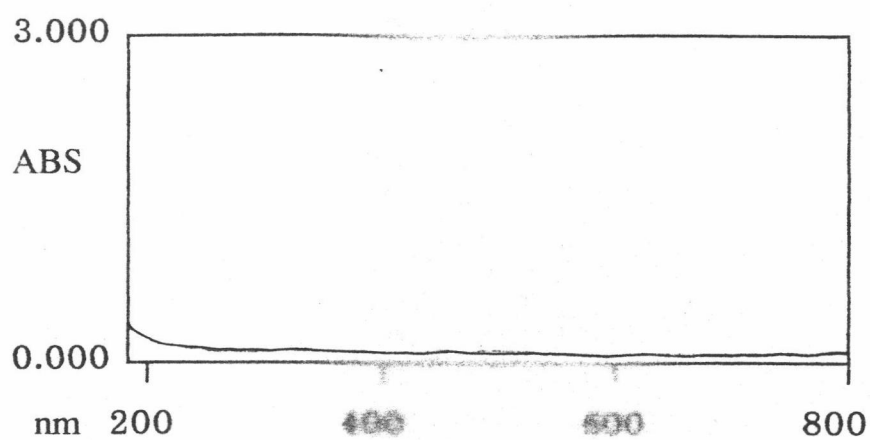
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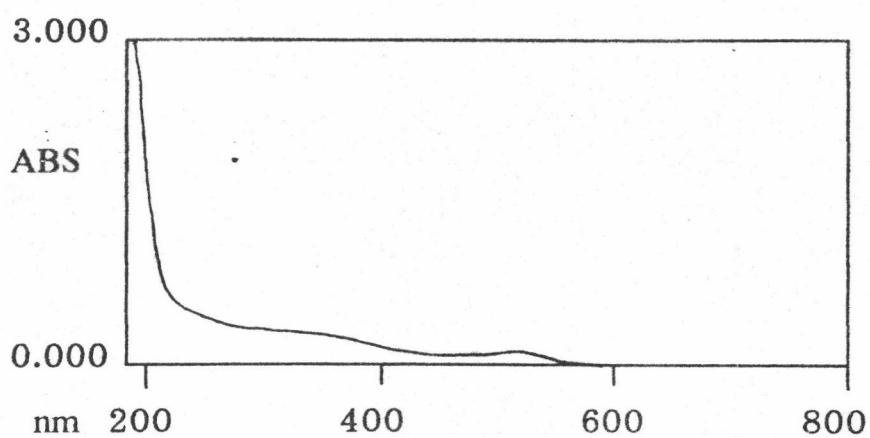
(c)

Figure 5.12 : UV-VIS absorption spectra of

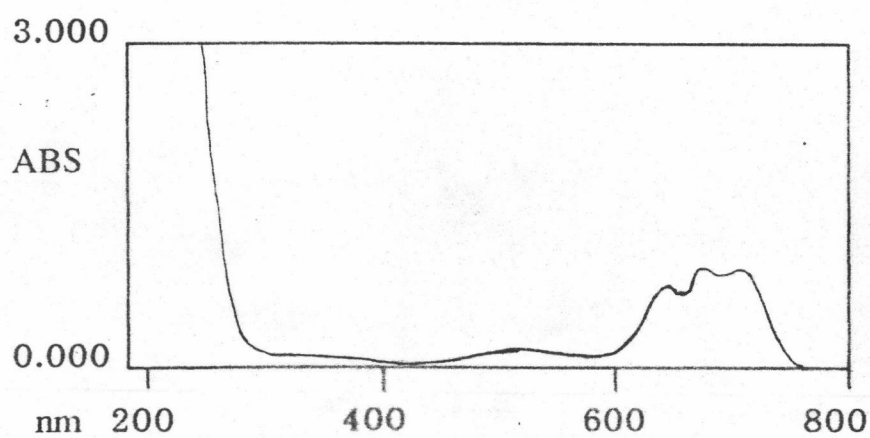
(a) PVA film (b) ZnCl₂ aqueous solution(c) PVA film containing 20% ZnCl₂



(a)

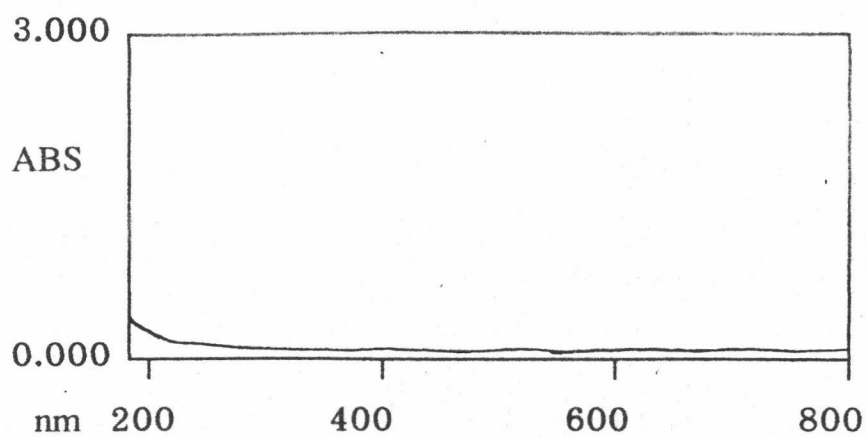


(b)

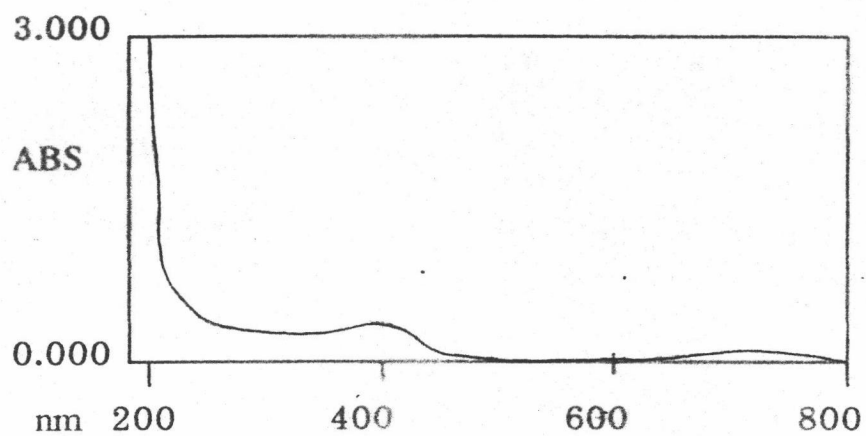


(c)

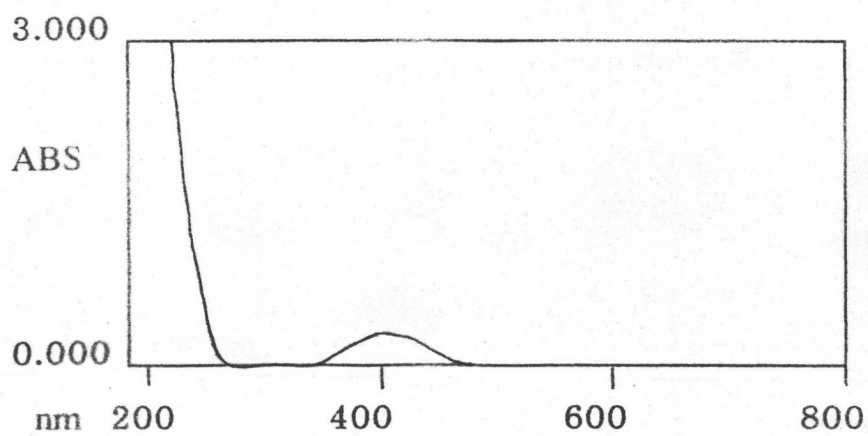
Figure 5.13 : UV-VIS absorption spectra of
(a) PVA film (b) CoCl_2 aqueous solution
(c) PVA film containing 20% CoCl_2



(a)



(b)



(c)

Figure 5.14 : UV-VIS absorption spectra of
(a) PVA film (b) NiCl_2 aqueous solution
(c) PVA film containing 20% NiCl_2

Effect of metal salt on PVA film properties

1. Determination by UV-VIS spectroscopic technique

1.1. PVA film

As shown in figure 5.3, UV-VIS absorption spectra of PVA film shows an absorption band at about 195 nm. and no more absorption band was observed in the region of 200–800 nm.. According to Bravar et. al. (1973), this absorption band should be considered as the present of residual acetate groups in PVA molecular chain.

1.2. PVA films containing LiCl

As shown in figure 5.4, UV-VIS absorption spectra of PVA film containing LiCl. The result showed that no different feature in UV-VIS absorption spectra compared to the spectra of PVA film, however, intensity of the band at 195 nm. increased with increasing metal content in PVA films. These results indicated any interaction between the metal ion and the PVA molecule.

1.3. PVA films containing NaCl

As shown in figure 5.5, the UV-VIS absorption spectra are not difference from these spectra of PVA film and intensity increasing

shows similar trend with the PVA film containing LiCl. These indicated same evidence as the film containing LiCl.

1.4. PVA films containing KCl

The UV-VIS absorption spectra of PVA film containing KCl can be seen in figure 5.6. These results may be explained as the same as evidence in the film containing LiCl .

1.5. PVA films containing CaCl₂

The UV-VIS absorption spectra of PVA film containing CaCl₂ can be seen in figure 5.7, and show the same evidence as the film containing LiCl.

1.6. PVA films containing BaCl₂

The UV-VIS absorption spectra of PVA film containing BaCl₂ can be seen in figure 5.8, and show the same evidence as the film containing LiCl.

1.7. PVA films containing FeCl₂

From figure 5.9, the UV-VIS absorption spectra of PVA film containing FeCl₂ showed absorption bands at 225 and 325 nm. which are different from the spectra of PVA film. These results

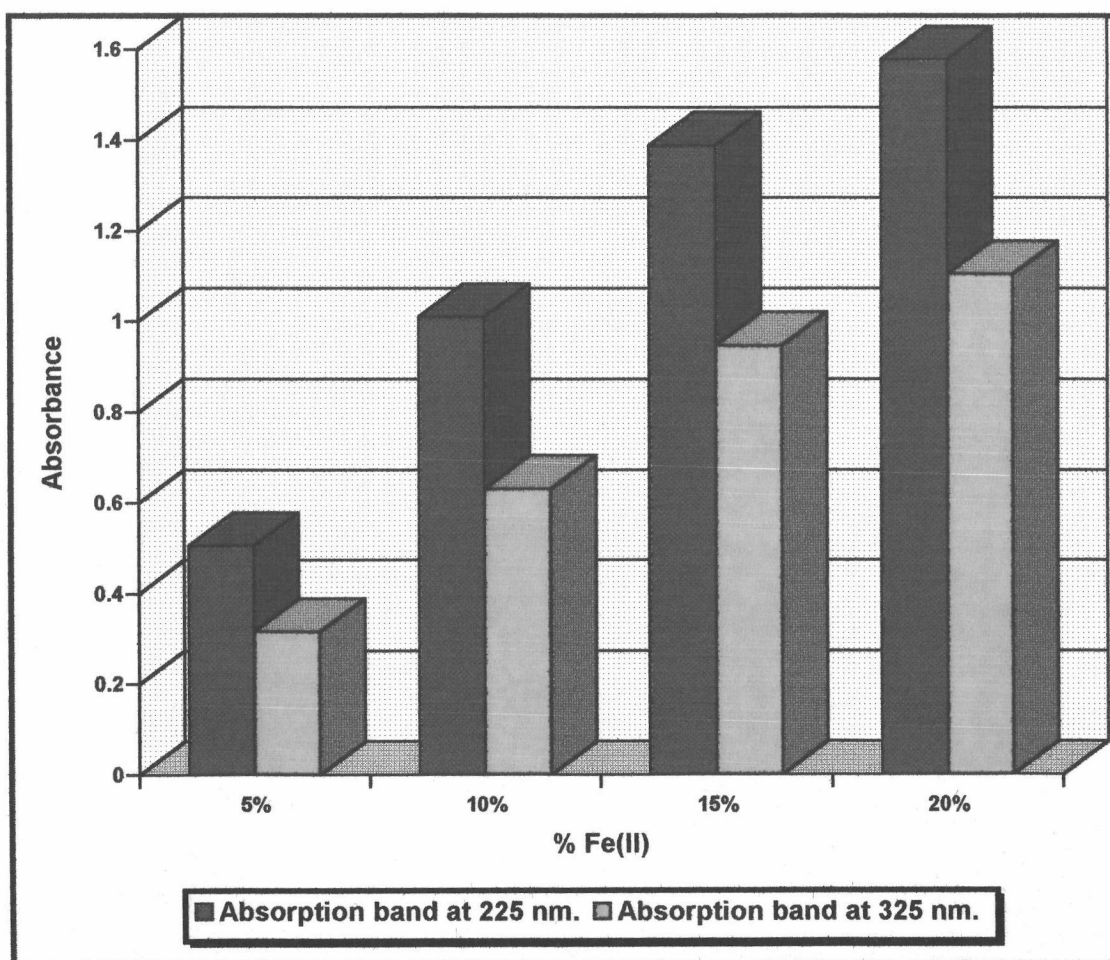


Figure 5.15 : Absorption intensity at 225 nm. and 325 nm. of PVA films containing FeCl₂ depending on salt content.

demonstrated that metal introduced into the PVA films may interact with PVA molecule leading to a new information in UV-VIS absorption spectra. In addition, intensity of these bands increased with increasing metal content as shown in figure 5.15.

1.8. PVA films containing FeCl₃

From figure 5.10, the UV-VIS absorption spectra of PVA film containing FeCl₃ showed absorption bands at 218 and 317 nm. which are different from these spectra of PVA film. These results may be explained as same as the evidence in PVA films containing FeCl₂ and intensity of these bands significantly influenced by metal contents as shown in figure 5.16.

1.9. PVA films containing CuCl₂

The UV-VIS absorption spectra were shown in figure 5.11. The different absorption band at ~260 nm. may confirm the interaction between Cu(II) ion and PVA molecule providing a new absorption band. Additionally, the intensity of these bands significantly influenced by the amounts of Cu(II) ion containing in PVA films as shown in figure 5.17.

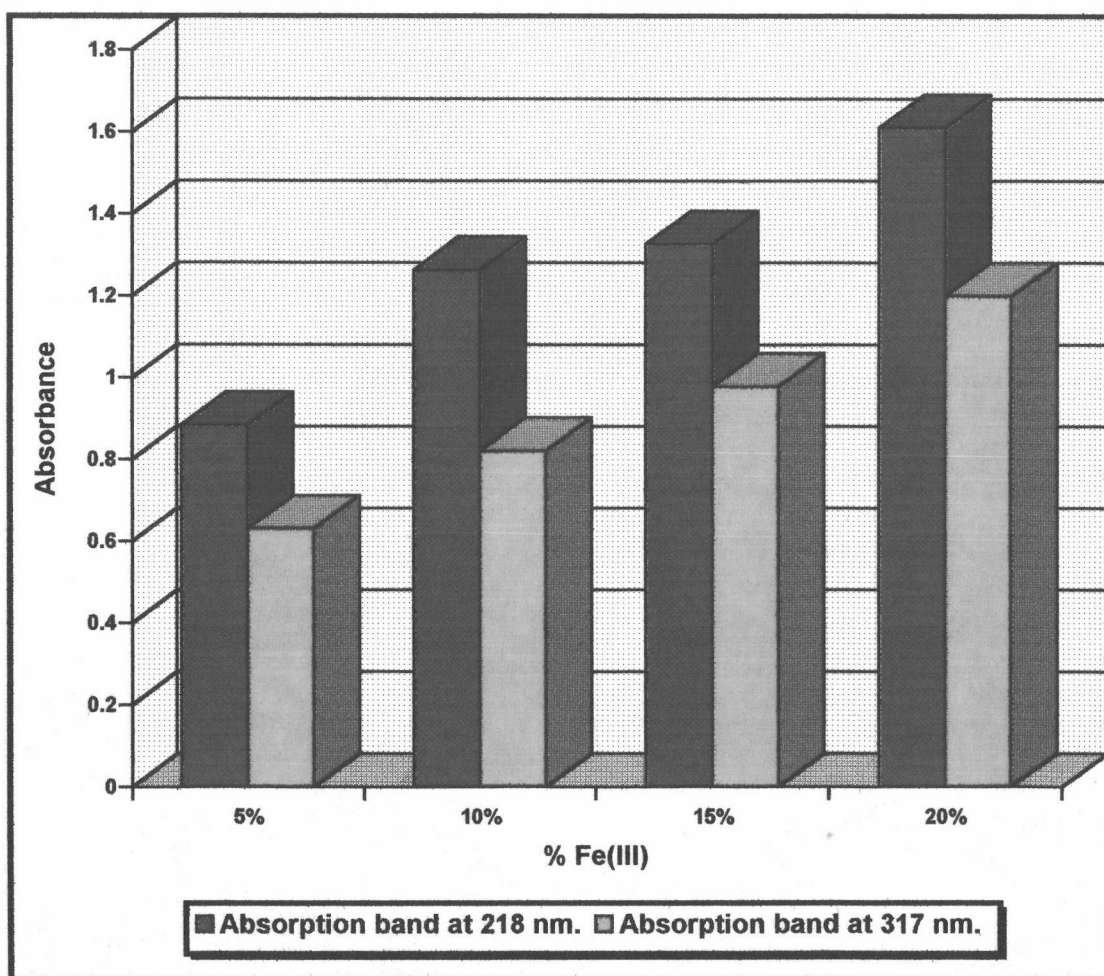


Figure 5.16 : Absorption intensity at 218 nm. and 317 nm. of PVA films containing FeCl_3 depending on salt concentration.



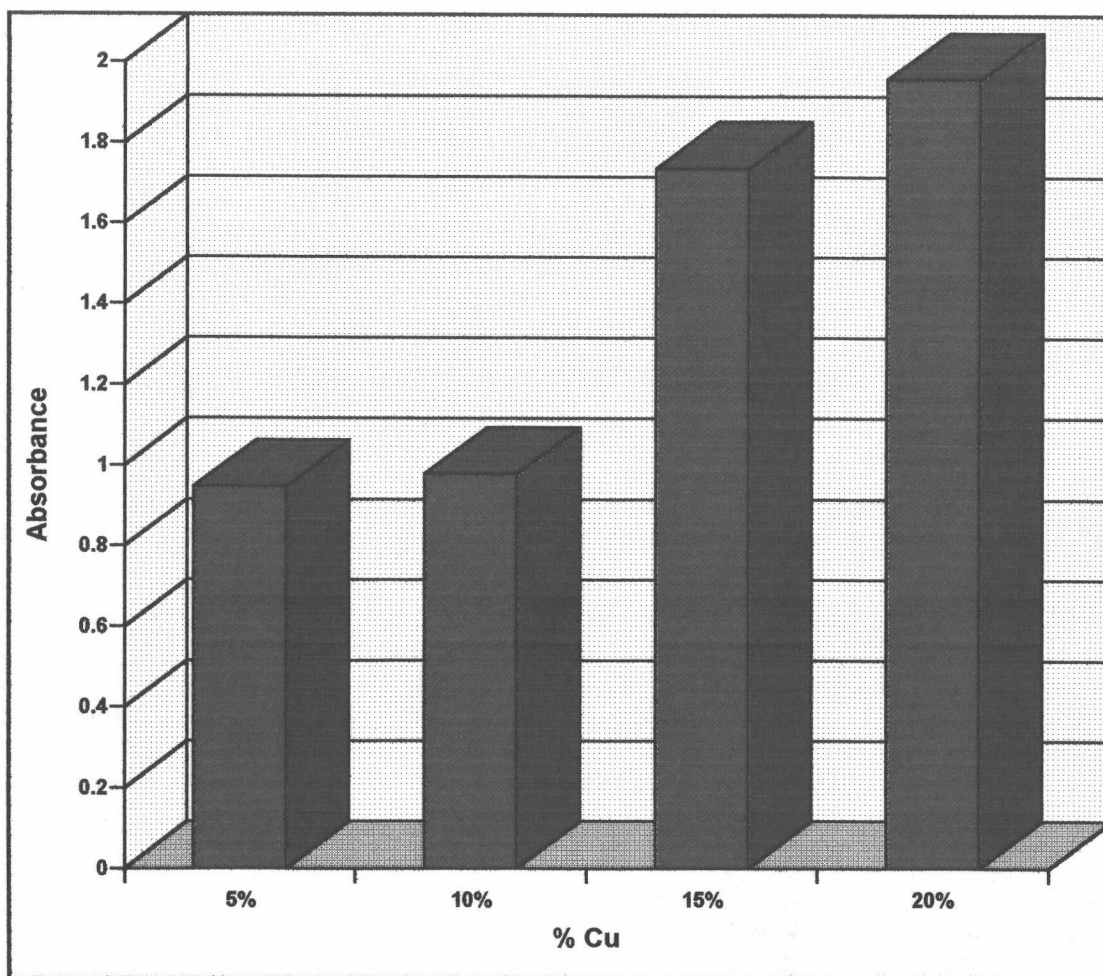


Figure 5.17 : The UV-VIS absorbance at 260 nm. of PVA films containing 5, 10, 15, and 20% CuCl₂.

1.10. PVA films containing ZnCl₂

From figure 5.12, the UV-VIS absorption spectra showed no significant different absorption features, whereas the intensity of band at ~195 nm. increased with increasing metal content. These results may be indicated that the interaction between Zn(II) ion and hydroxyl groups of PVA may be occurred and amount of Zn(II) ion influenced on intensity of absorption band at ~195 nm..

1.11. PVA films containing CoCl₂

Showing in figure 5.13, the absorption bands at ~ 260, 500 and 700 nm. significantly influenced by PVA film containing CoCl₂, moreover, the intensity of these bands obviously depended on metal content either amount of metal or thickness of obtained films as showing in figure 5.18-5.19. These results may be confirmed that metal significantly interacted with hydroxyl groups of PVA and evidence of increasing intensity of these bands directly associated with concentration of metal containing PVA films.

1.12. PVA films containing NiCl₂

In figure 5.14, the different absorption band showed at about 400 nm. and in figure 5.20, the intensity of this band increased with increasing NiCl₂ concentration. As the same way, interaction of Ni (II) ion to hydroxyl groups of PVA may be occurred and associated with metal content on the intensity of this band.

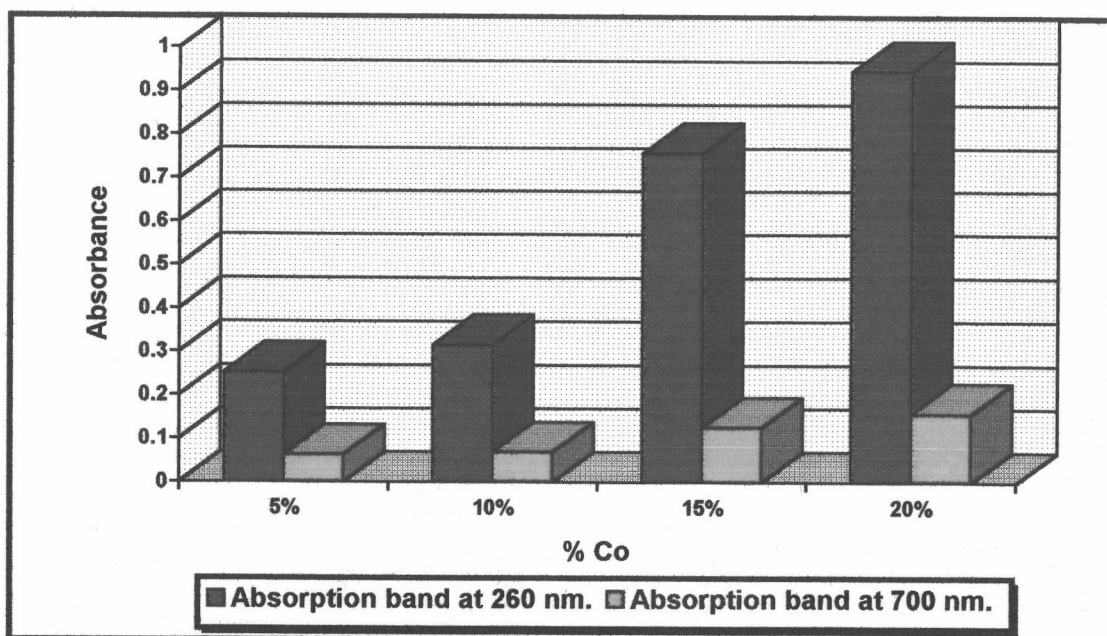


Figure 5.18 : The UV-VIS absorbance at 260 and 700 nm. of PVA films containing 5, 10, 15, and 20% CoCl_2 .

Note : Film thickness was about 0.02-0.03 mm.

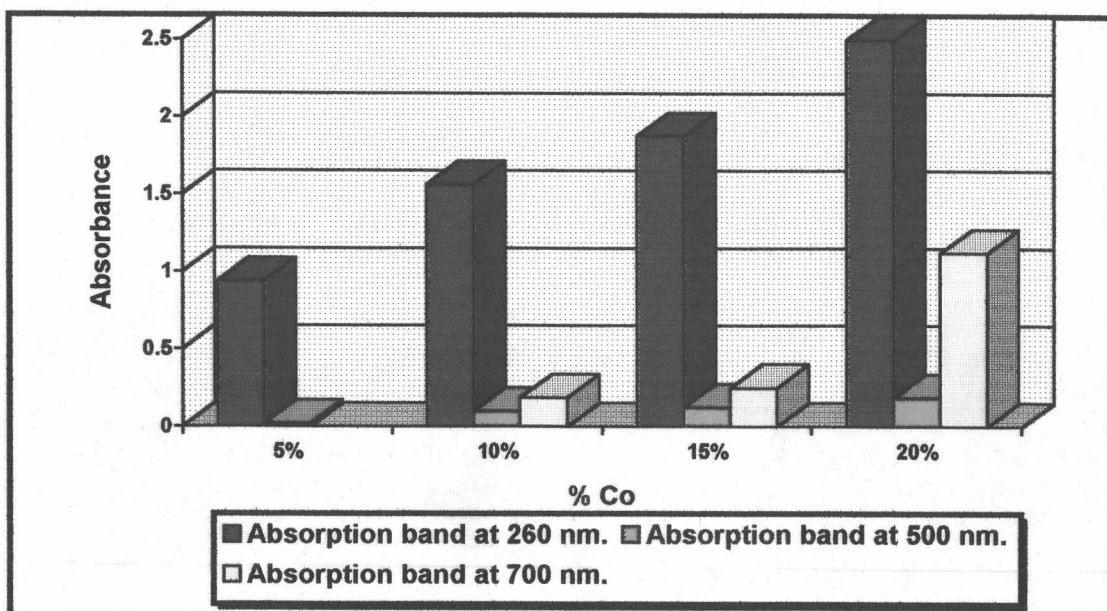


Figure 5.19 : The UV-VIS absorbance at 260, 500 and 700 nm. of PVA films containing 5, 10, 15, and 20% CoCl_2 .

Note : Film thickness was about 0.05-0.10 mm.

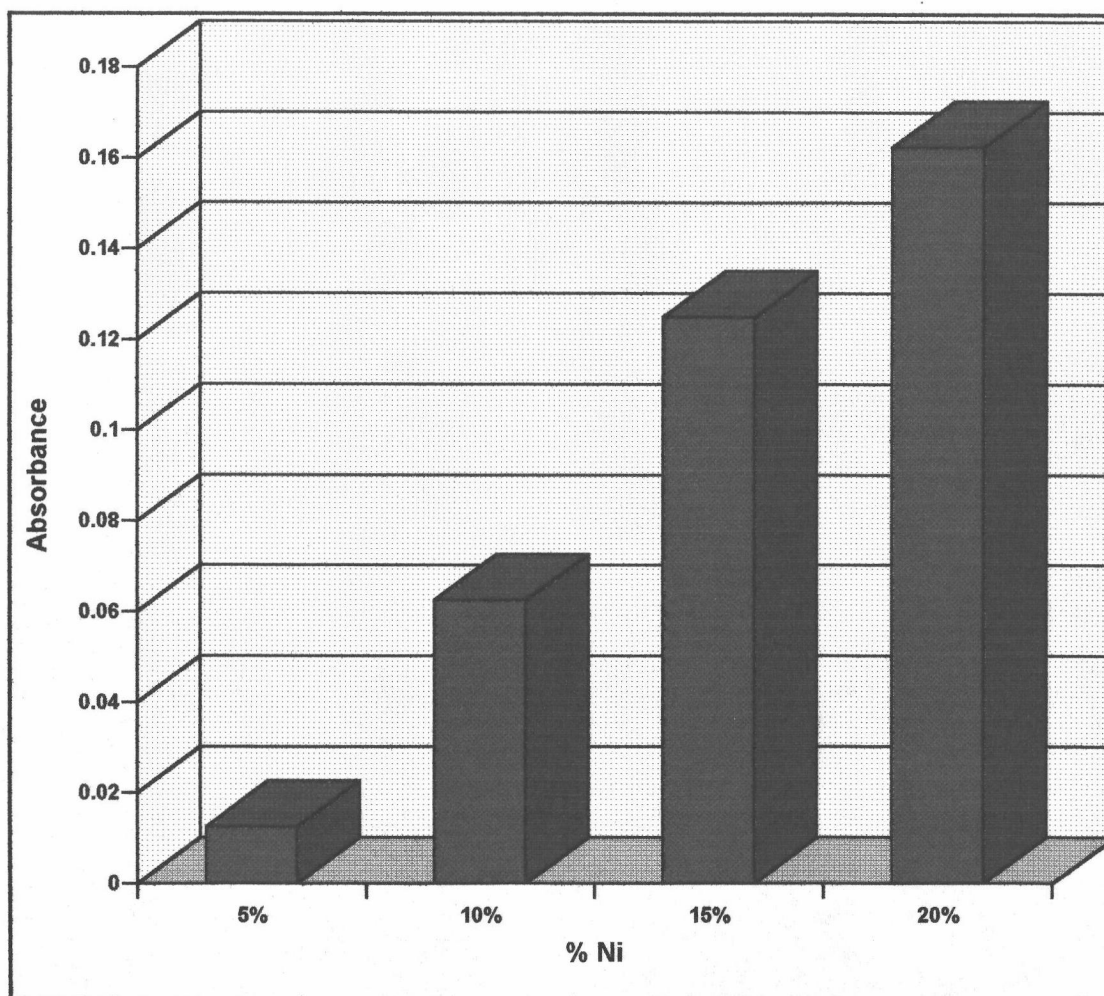


Figure 5.20 : The UV-VIS absorbance at 400 nm. of PVA films containing 5, 10, 15, and 20% NiCl₂.

From the results of UV-VIS absorption spectra, it is indicated that characteristic of metal-PVA interaction provided an individual absorption feature with particularity in transition metal group as summarized in Table 5.3. Moreover, the metal concentration significantly influenced on intensity of these bands corresponding with Lambert-Beer laws.

Table 5.3 : Specific maximum wavelength (λ_{\max}) in UV-VIS absorption spectra of each film.

Films (metal-PVA)	λ_{\max} in nm.
PVA	~195
PVA containing Li, Na, K, Ca(II), Ba(II), Zn(II)	~195
Fe(II)-PVA	225 and 325
Fe(III)-PVA	218 and 317
Cu(II)-PVA	260
Co(II)-PVA	260, 500 and 700
Ni(II)-PVA	400

2. Determination by FTIR technique

In infrared absorption spectroscopy, absorption of energy corresponding to transitions between vibrational or rotational energy states gives rise to characteristic patterns. Polymer types can often be identified in this manner, and information about sample crystallinity obtained. Advances in IR instrumentation and data processing techniques, such as Fourier transform-IR and attenuated total reflectance-IR have enhanced the power of IR even more.

The FTIR spectra of all samples investigated in the present study were shown in Appendix B (Figure B-1 to B-11). The FTIR spectrum of standard PVA film as shown in Table 5.4 shows substantial intensity of the O-H stretching band at about 3337 cm^{-1} and the C-H stretching band at 2942 cm^{-1} .

According to Swift (1994) and Philip (1983), applications of IR spectra may be used for stereoregularity estimation by using optical density ratio at 916 and 849 cm^{-1} . Data from NMR as shown in Table 5.5 indicate that syndiotactic polymer has only a peak at 916 cm^{-1} . As the result, the PVA film used in the present study, which shows IR absorption band at about 916 cm^{-1} , should be syndiotactic structure with degree of tacticity as shown in Figure 5.21. The FTIR spectra also shows the existence of residual acetate groups at 1650 and 1715 cm^{-1} of C=O stretching.

Table 5.4 : Absorption frequencies from FTIR spectra of the band region corresponding with diagnostic evidence of such a part structure in compounds.

Band at wavenumber (cm^{-1})	characteristic absorption bands
3330	O-H stretching
2942	C-H stretching
1715	C=O stretching
1650	C=C stretching
1410	O-H bending
1140	C-O stretching
917	C-H out of plane
851	C-H deformation

Table 5.5 : Results from NMR spectra corresponding with double bond absorption in FTIR spectra.

Band at wavenumber (cm^{-1})	Characteristic absorption bands	Structure features
~ 917	C-H out of plane	 syndiotactic
~ 850	C-H deformation	 isotactic

Kenney and Willcockson (1960) demonstrated that percentage of crystallinity of the samples can be determined by using the relation of two absorption bands and the baseline method as following :

$$\text{Percent crystallinity} = 92 (d/c) - 18$$

where : d is the vertical distance between the 1140 cm^{-1} peak and the intercept point of a straight line drawn across the portion of the spectrum between 1125 and 1150 cm^{-1}
 c is the vertical distance between the 1425 cm^{-1} line drawn across the band

The determined values as shown in Figure 5.22, indicate that the relative percentage of crystallinity decreases with increasing metal content in the film. However, the limitation of accuracy depends on film thickness.

The FTIR spectra of metal salt containing PVA films as shown in figure 5.22-5.23 indicate that intensity of the IR spectra is appreciable influenced by both nature and content of metal in the film.

Figure 5.21 illustrates that each kind of salts used in the present study exhibited similar effect on stereoregularity of the PVA films. It was found that degree of tacticity of the PVA films decreased with the presence of metal salt in the film and further decrease was observed with the higher content of metal salt. These results indicate the presence of interaction between PVA molecule and metal salt.

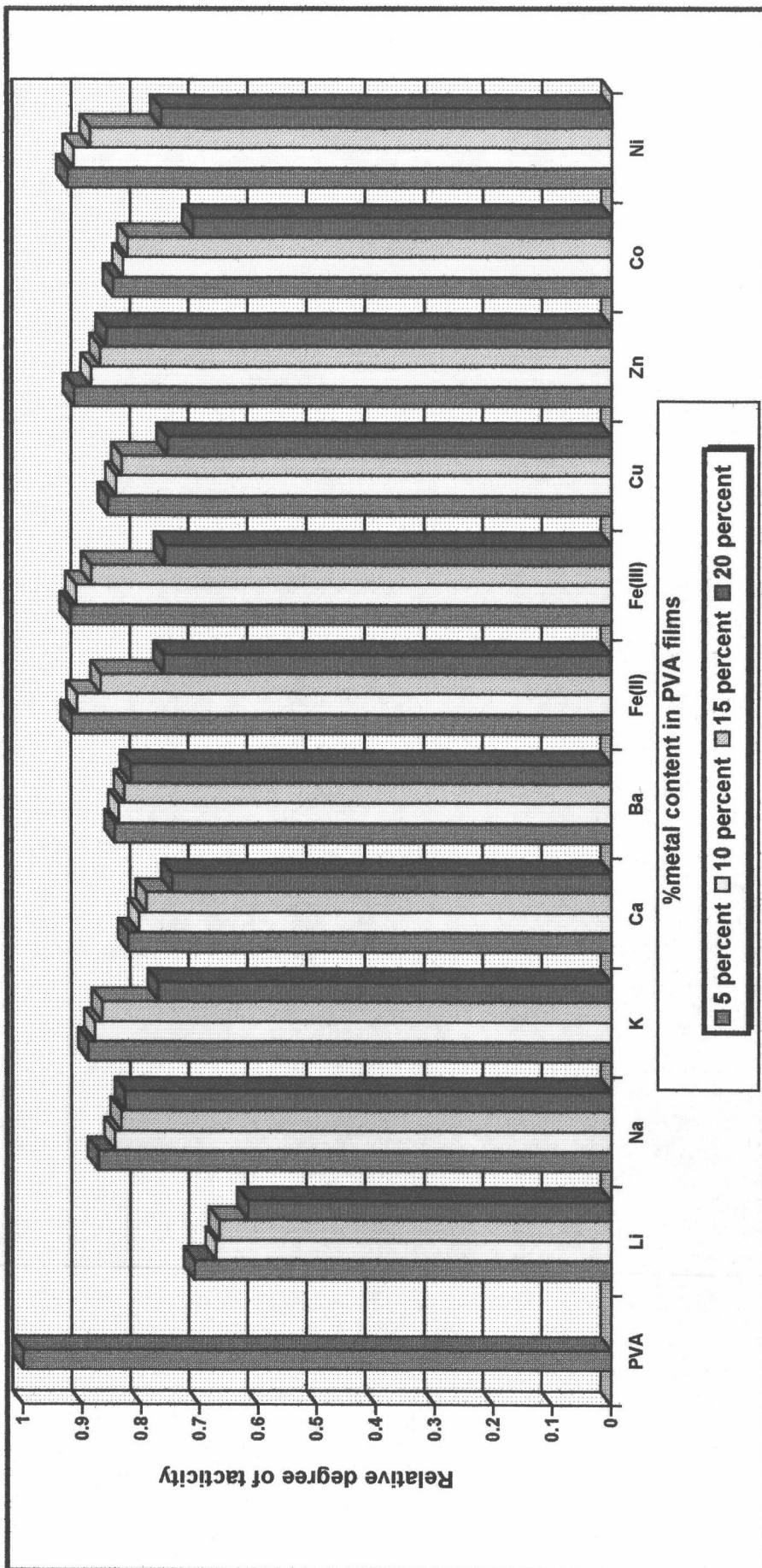


Figure 5.21 : Effect of metal salt on relative degree of tacticity of PVA film estimated from IR bands.

The presence of interaction between PVA molecule and metal salt was also confirmed by effect of metal salt on relative percentage of crystallinity and residual acetate content in the films as the results shown in figures 5.22 and 5.23 respectively. It was found that both relative percent crystallinity and residual acetate content decreased with increasing metal content in the films. The decrease of acetate content with the presence of metal salt may be considered that metal ions exhibit any interaction with C=O of acetate groups.

The interaction between metal ions and PVA molecule was expected to be bond formation between the metal ions and hydroxyl groups of PVA molecule. The degree of bond formation may be considered as relative amount of hydroxyl groups used for bond formation which can be estimated from O-H stretching band of the IR spectra. It was shown in figure 5.24 that content of the residual hydroxyl groups decreased with the presence of metal salt and further decrease was observed with the increase of metal content in the film. These results also confirm the presence of interaction between metal salt and PVA molecules in the film.

In addition, infrared absorption band around $800-600\text{ cm}^{-1}$ which indicates C-Cl stretching was also observed from IR spectra of the studied films.

Besides FTIR absorption technique, ATR-FTIR and Raman techniques were also used for the present investigation.

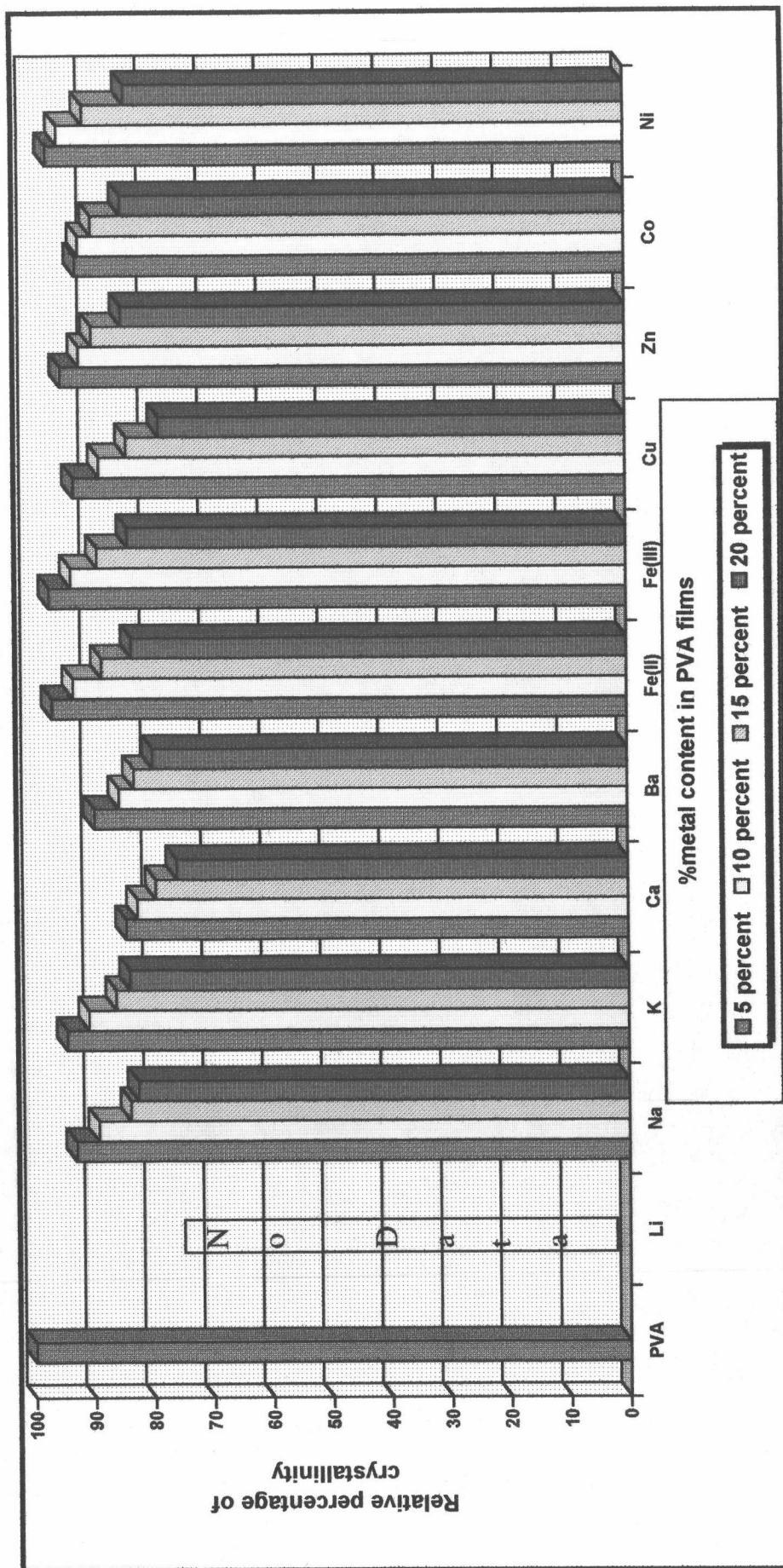


Figure 5.22 : Effect of metal salt on relative percent crystallinity of PVA film estimated from IR bands.

* No Data : Effect of LiCl salt cannot be estimated because of too high intensity of the IR band.

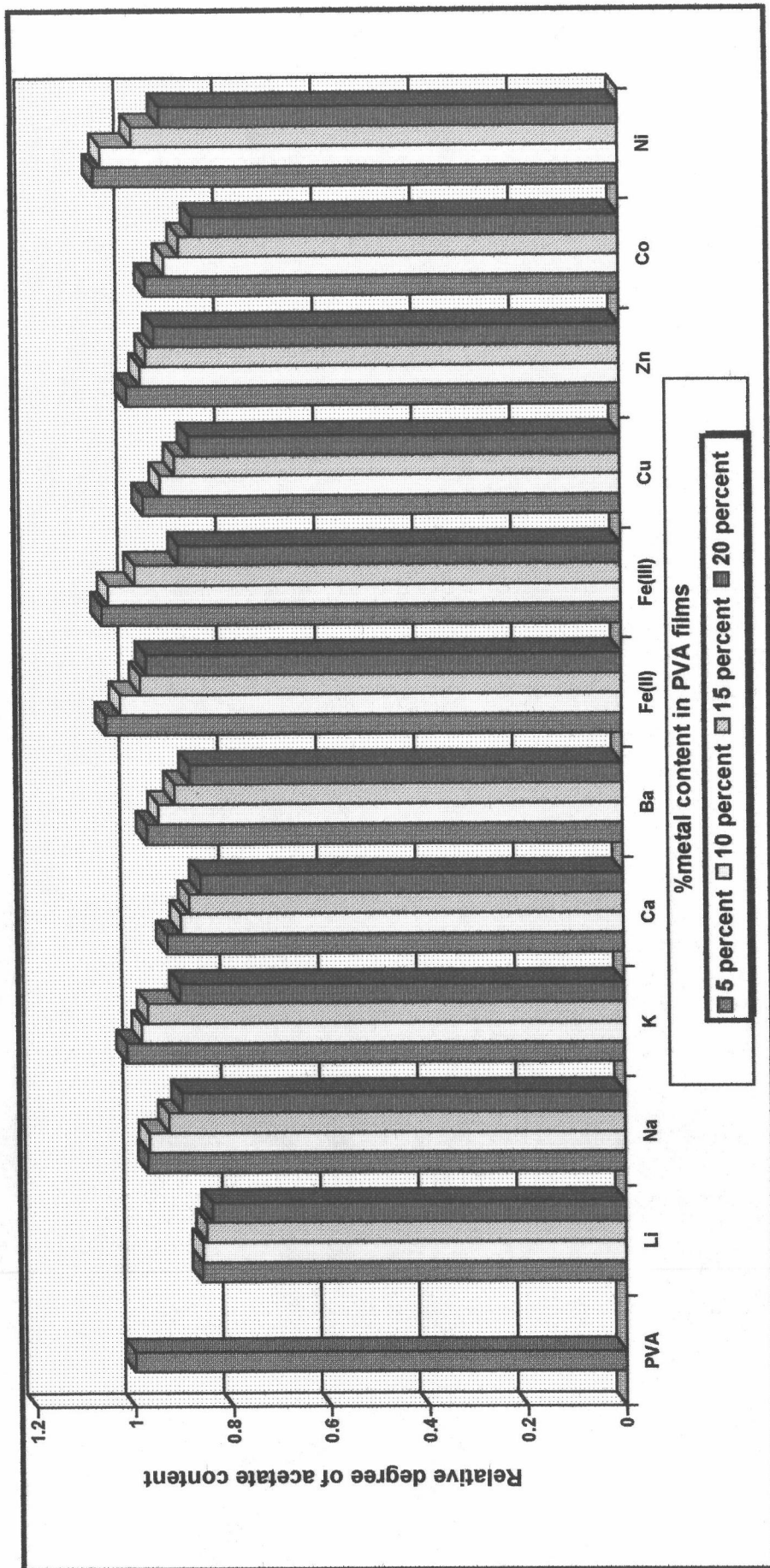


Figure 5.23 : Effect of metal on relative content of residual acetate groups of PVA films estimated from IR bands.

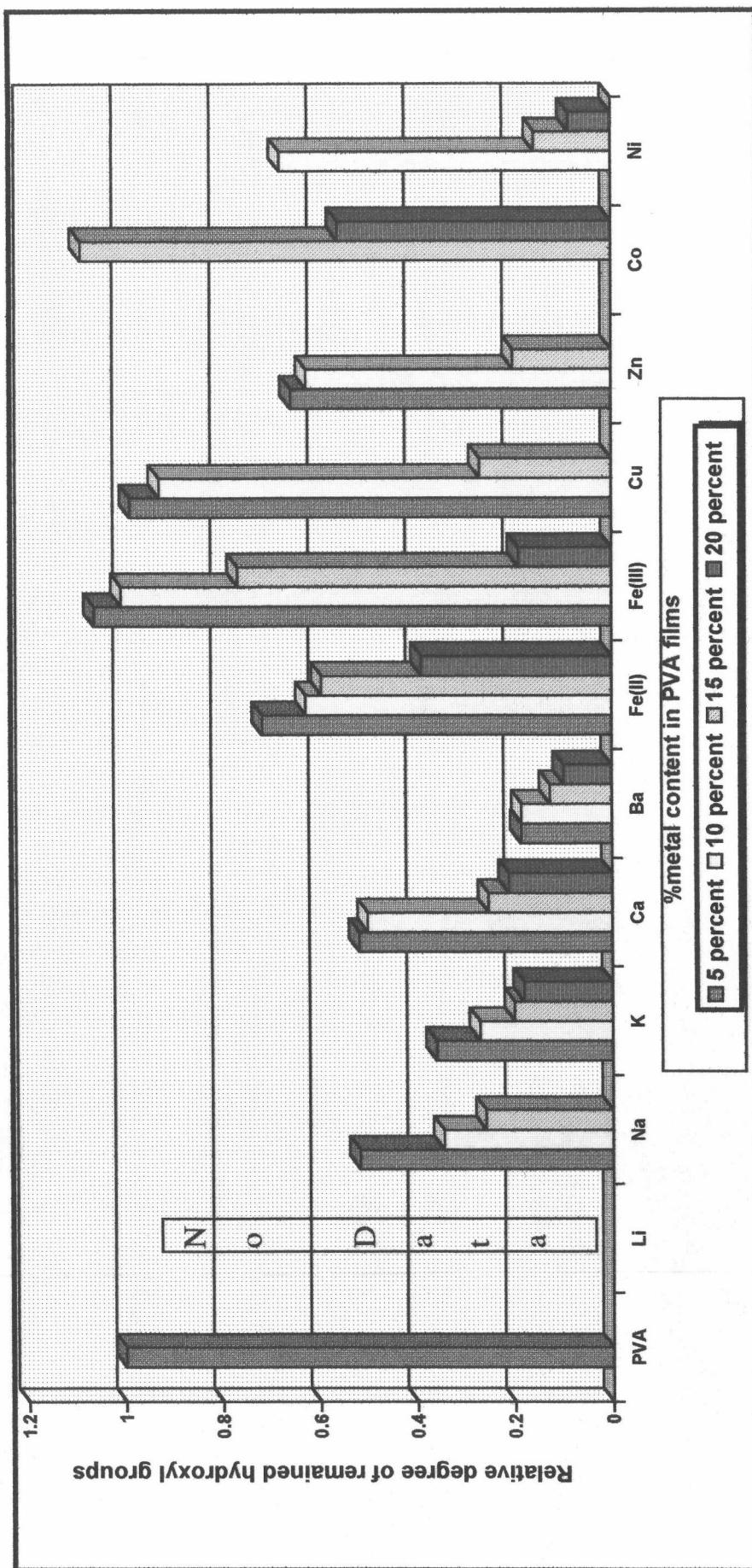


Figure 5.24 : Effect metal salt on relative degree of remained hydroxyl groups from using for bond formation

between metal ions and hydroxyl groups of the PVA films estimated from IR bands.

Note : Effect of LiCl cannot be estimated because of too high intensity of the bands.

3. Determination by ATR-FTIR technique

In case of ATR-FTIR technique, similar spectra were observed for the films containing metal salts that gave colorful film, but no significant spectra was observed for the colorless films which were the films containing LiCl, NaCl, KCl, CaCl₂, and BaCl₂. These results may be considered that the ATR-FTIR techniques was not suitable for the studied films containing alkali and alkali earth metal which were transparent or mostly transparent.

4. Determination by Raman technique

In case of Raman technique, similar spectra were observed, but resolution was not so good because the Raman technique should be used with the power upto 600 Hertz which cannot be used with organic molecule like PVA.

Effect of metal on environmental endurance properties

Because of the industrial importance of PVA, the general properties and properties under expected consideration have been dealt with various condition such as chemical resistance, solvent resistance.

1. Effect of metal on removed water

The removed water of PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ with heating temperature at 80 °C for 6 hours and further vaccuated in vacuum desiccator before observed changed weights at equilibrium state was represented in figure 5.25.

The PVA films with LiCl, NaCl, and KCl gave informations that removed water increased with increasing metal content in the films and the film with LiCl gave the highest value. Similarly, the removed water of the films containing CaCl₂ provided higher values than those derived from the films containing BaCl₂. In the films with FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂, the removed water increased with increasing metal content in the films and the values depended on nature of the metal concentration in the film.

These results may be explained in terms of crystallinity or regularity corresponding to increasing crystalline regions or regular

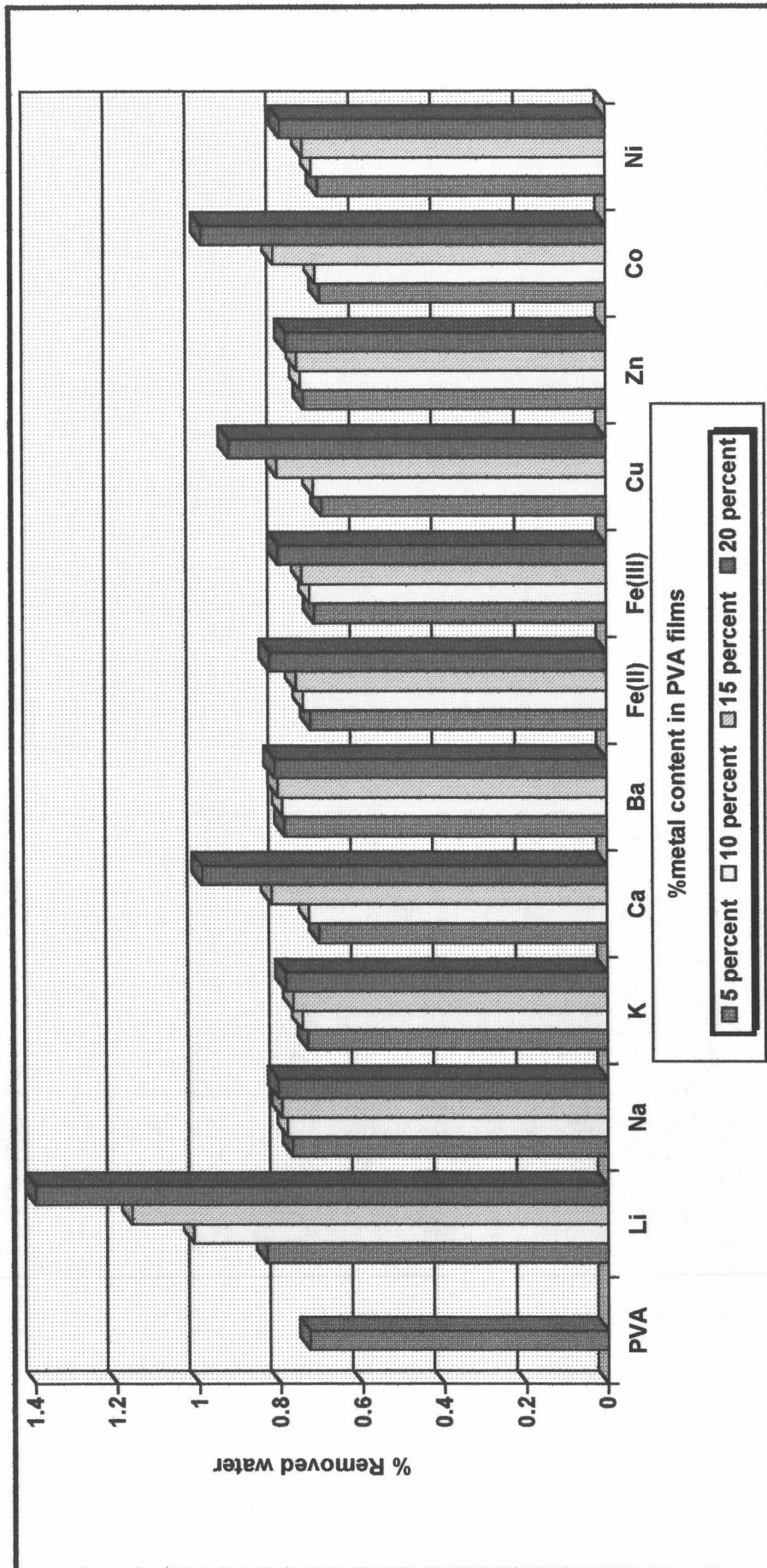


Figure 5.25 : The removed water of PVA film and PVA films containing metal after treatment the dried film under heat treatment at approximately 80 °C for 6 hours and further vacuumated in vacuum desiccator at 25 psi, room temperature for 48 hours.



structures within molecules attributed to decreasing water uptake according to previous section.

2. Effect of metal on eliminated water after heat treatment under high temperature

The PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ were heated at various temperature for 6 hours and then their changed weight after heating to various temperatures were investigated and represented in figure 5.26. It is clear from this figure that heating the sample films at 100, 150 and 200 °C caused observable changes in the total weights and elevating the heating temperature resulted in a remarkable increase in its water content. All of the salts in the films exhibited the same trend that amount of eliminated water increased with metal content in the films as shown in figure 5.26, whereas crystallinity and residual acetate contents decreased with the metal content. These results provides well-defined evidence that crystalline regions do not act as absorbing regions but amorphous regions do act simply as absorbing regions.

It was also found that water content in PVA film and PVA films containing metal salts decreased with elevation of heating temperature. These films untreated and containing metal produced marked decrease in water content after heating temperature at 100 °C , whereas these results progressive decrease after heating temperature at 150 °C

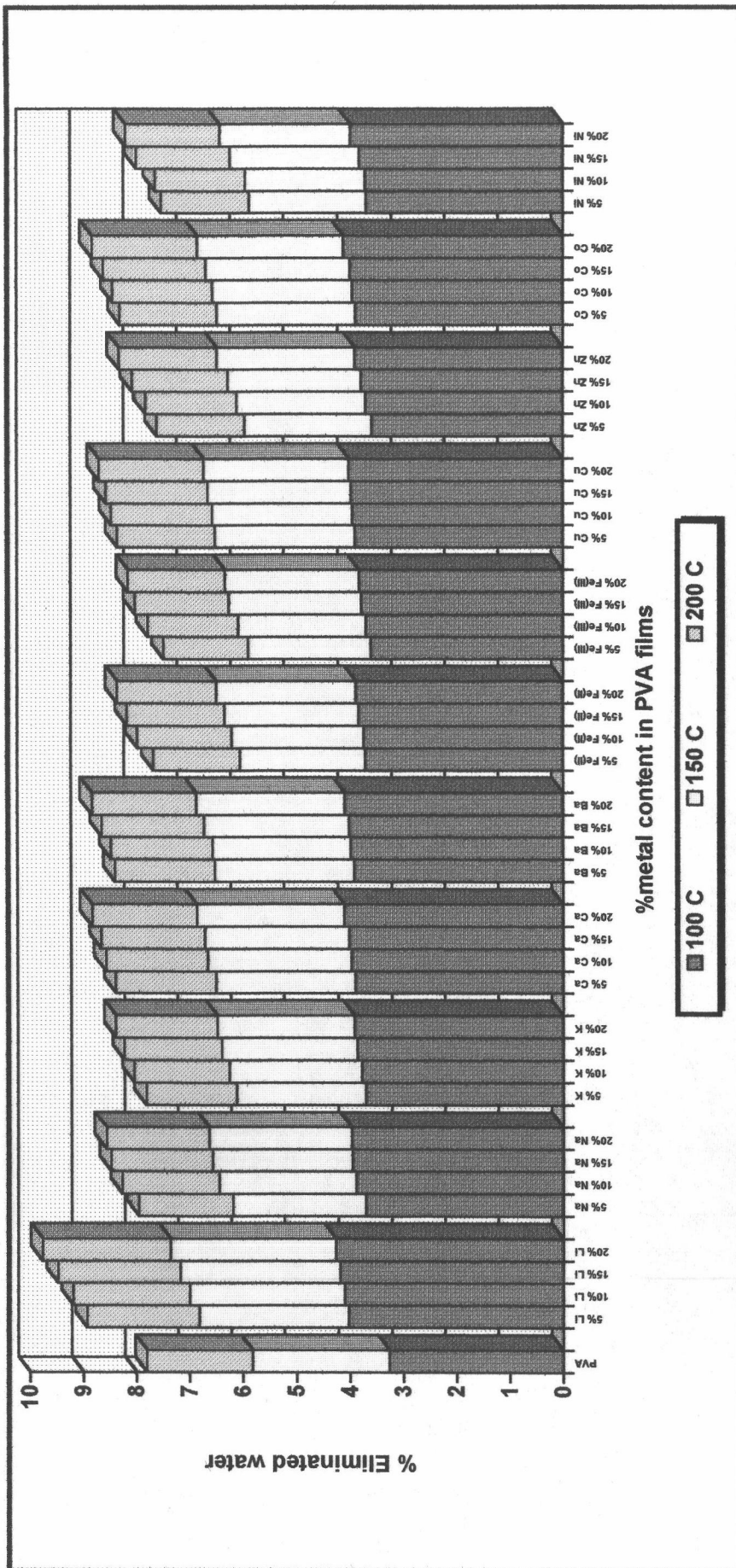


Figure 5.26 : Variation of eliminated water from PVA film and PVA films containing various salts at heating temperature of 100, 150, and 200 °C.

and 200 °C . These results are represented that elevating the heating temperature from 100 upto 200 °C resulted in a marked decrease in the water content in their films.

These results may be considered that absorbed water into films significantly influenced on properties of film because elimination of water at vigorous condition either vacuum or high temperature can not achieve. These evidences may be indicated that, at normal condition either room temperature or atmospheric pressure, absorbed water significantly affected on properties of film, however, behavior of metal favourable absorbs water.

3. Effect of metal on water swellability

PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ was soaked in deionized water for 6 hours at room temperature, then weight of each film was determined. The increased weight corresponds with amount of water swollen in the film as shown in figure 5.27.

The PVA films with LiCl became soluble in water , whereas the films with NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ gave swelling in aqueous solution. Percentage of swelling was found to be increased with metal content in the films. These results indicated the change of hydrophilicity of the film due to either

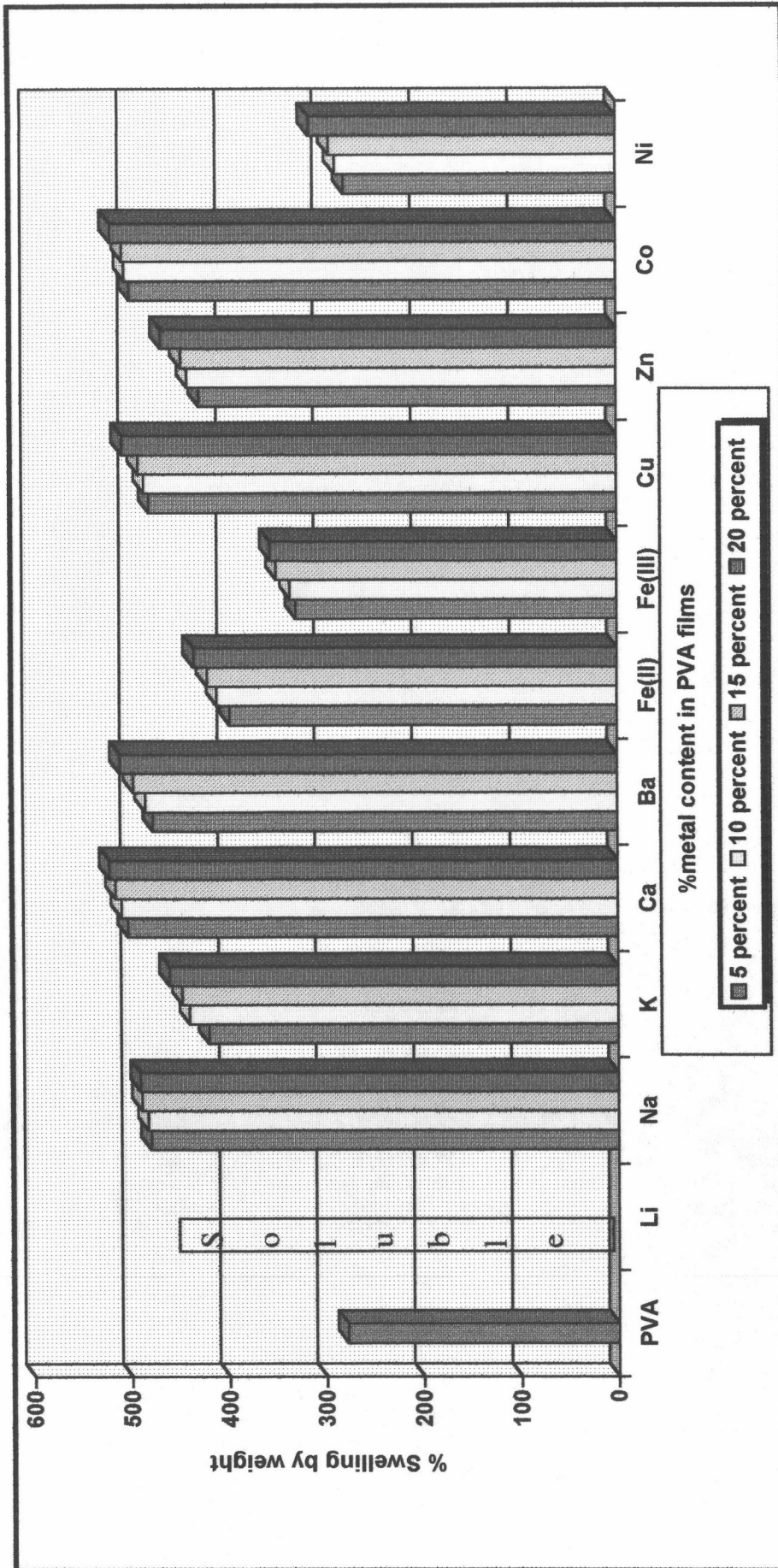


Figure 5.27 : Variation of the percentage of swelling by weight of PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂ and NiCl₂ after ageing in water.

interaction between metal ion and PVA molecule or hydrophilicity of each salt.

4. Effect of metal on solvent swellability

PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ was separately soaked in chloroform for 6 hours at room temperature and atmospheric pressure. Then percentage of swelling in chloroform was determined from the weight changed.

The results as shown in figure 5.28 showed the opposite trend with the water swellability as shown in figure 5.27 which supported the idea that variation of swellability resulting from either polymer-metal interaction or hydrophilicity difference of each salt.

Considering only effect of salt nature, the swelling percentage of the films having various metal contents was averaged and summarized in figure 5.29 for the films swollen in water and figure 5.30 for the films swollen in chloroform. It may be concluded that interaction of metal to hydroxyl group of PVA resulted to hydrophobic behavior with the following order:



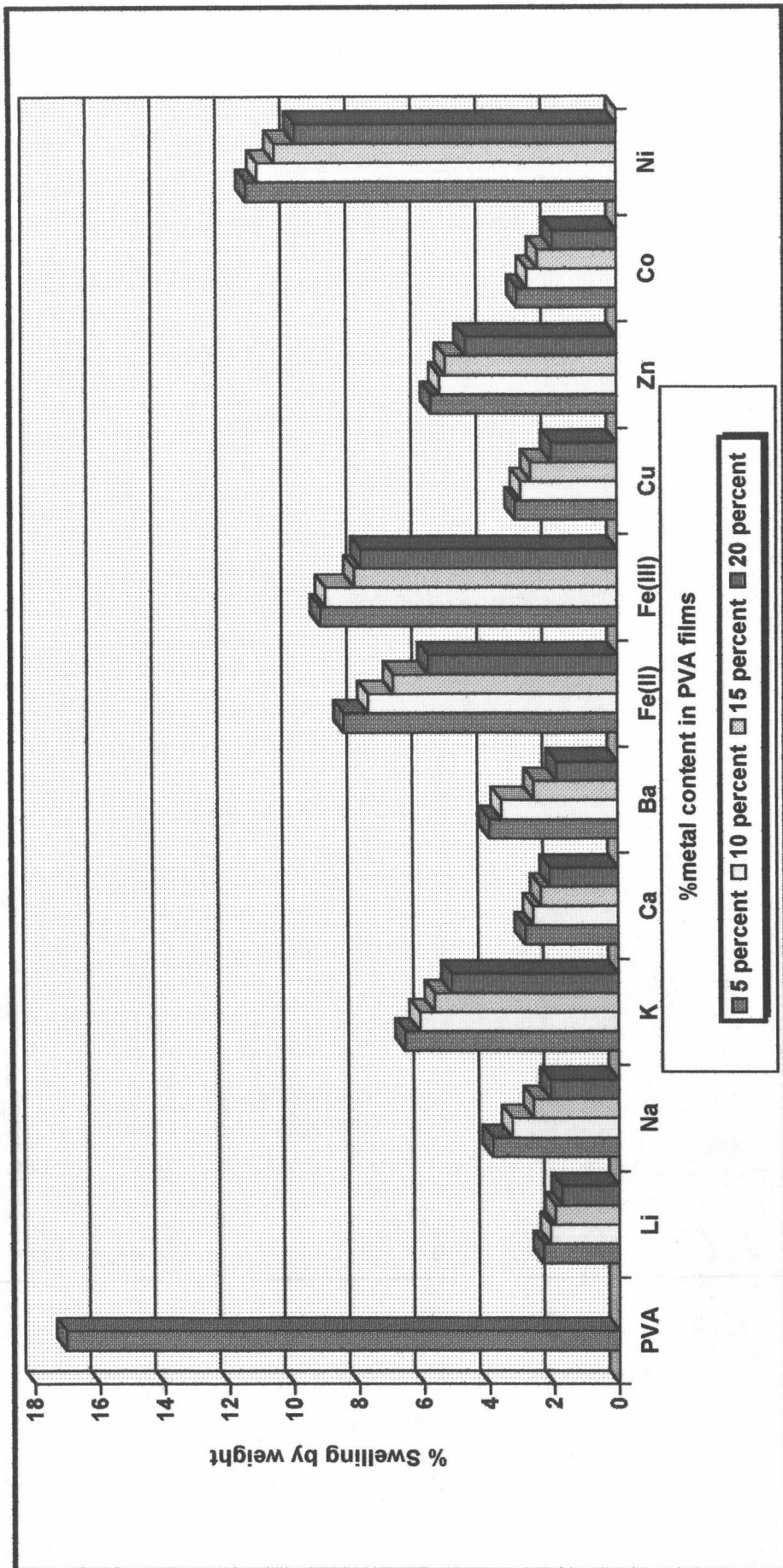


Figure 5.28 : Variation of the percentage of swelling by weight of PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂ and NiCl₂ after ageing in chloroform

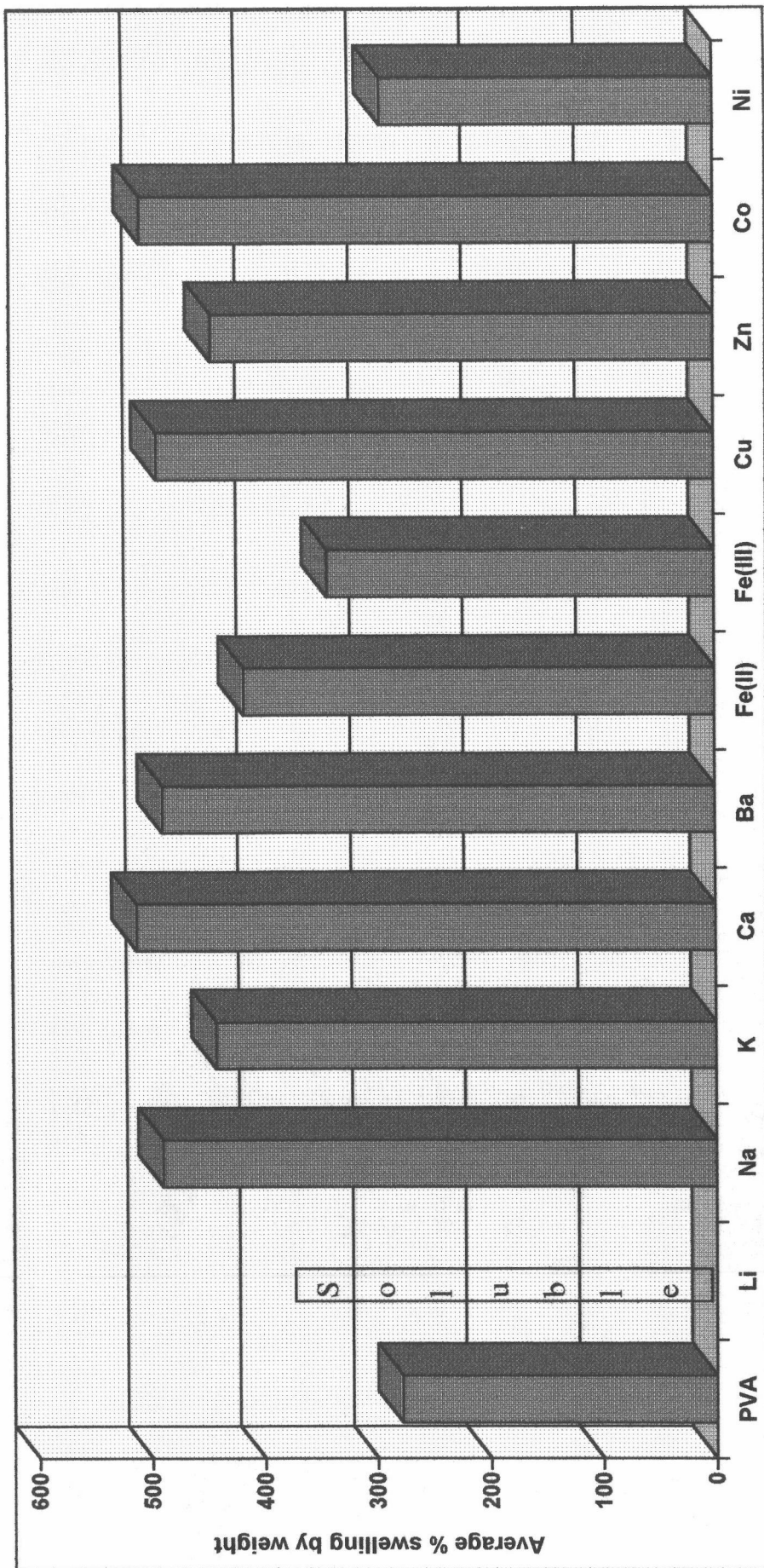


Figure 5.29 : Variation of the average percentage of swelling by weight of PVA film and PVA films containing various metal after ageing in water.

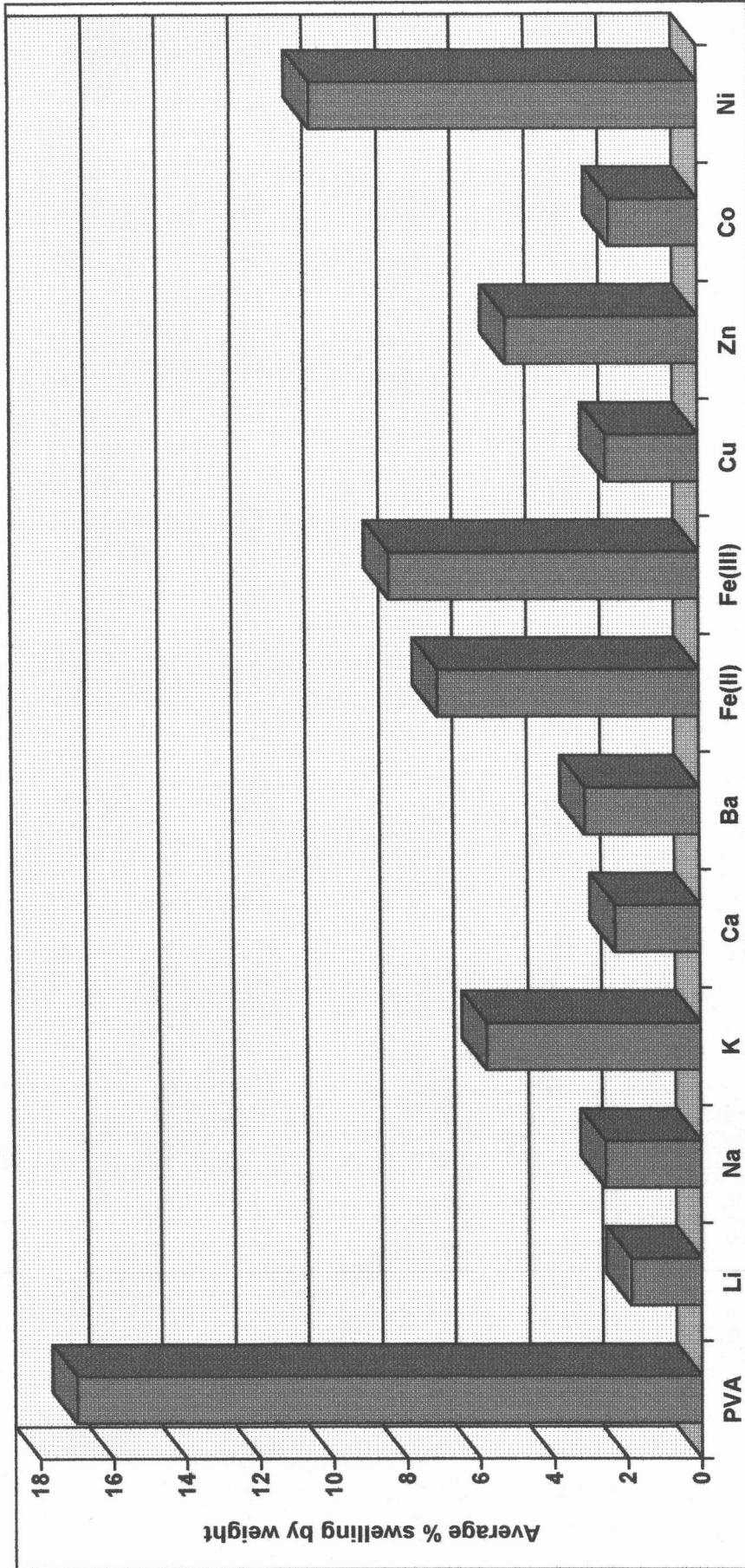


Figure 5.30 : Variation of the average percentage of swelling by weight of PVA film and PVA films containing various metal after ageing in chloroform.

As the results, it may be mentioned that transition metal groups showed higher tendency of bond formation with hydroxyl groups of PVA than the alkali and alkaline earth metal groups.

5. Effect of metal on solvent resistance

Both PVA film and PVA films containing metal salt did not dissolve in either methanol, acetic acid, chloroform or toluene after ageing at normal condition for 48 hours or ageing at 100 °C for 6 hours. These results illustrates solvent resistance of the films.

These may confirm that interaction of metal to hydroxyl groups of PVA may provide the hydrophobic behavior of molecules and leading to more resistance to organic solvent even in vigorous conditions.

Effect of metal on thermal properties

Thermal properties dependence on mechanical properties along with temperature were carried out by using DMTA MkII with bending mode at temperature ranging -40 upto 300 °C. The results were shown in figure 5.31 and 5.32.

It was shown that the modulus value falls sharply to nearly zero over the temperature range about 200 to 240 °C which is a melting range of the PVA. Measurements of bending modulus at lower temperature from -40 upto 200 °C have been used to estimate the glass transition temperature (T_g) of PVA.

As shown in figure 5.31, all of the films containing metal salt showed lower T_g than the PVA film though they were expected to have the higher T_g . These may be the effect of absorbed water.

In case of bending properties, as shown in figure 5.32, the films containing metal salts were also expected to have higher modulus than the PVA film, but the results showed opposite trend. These may be also the effect of absorbed water.

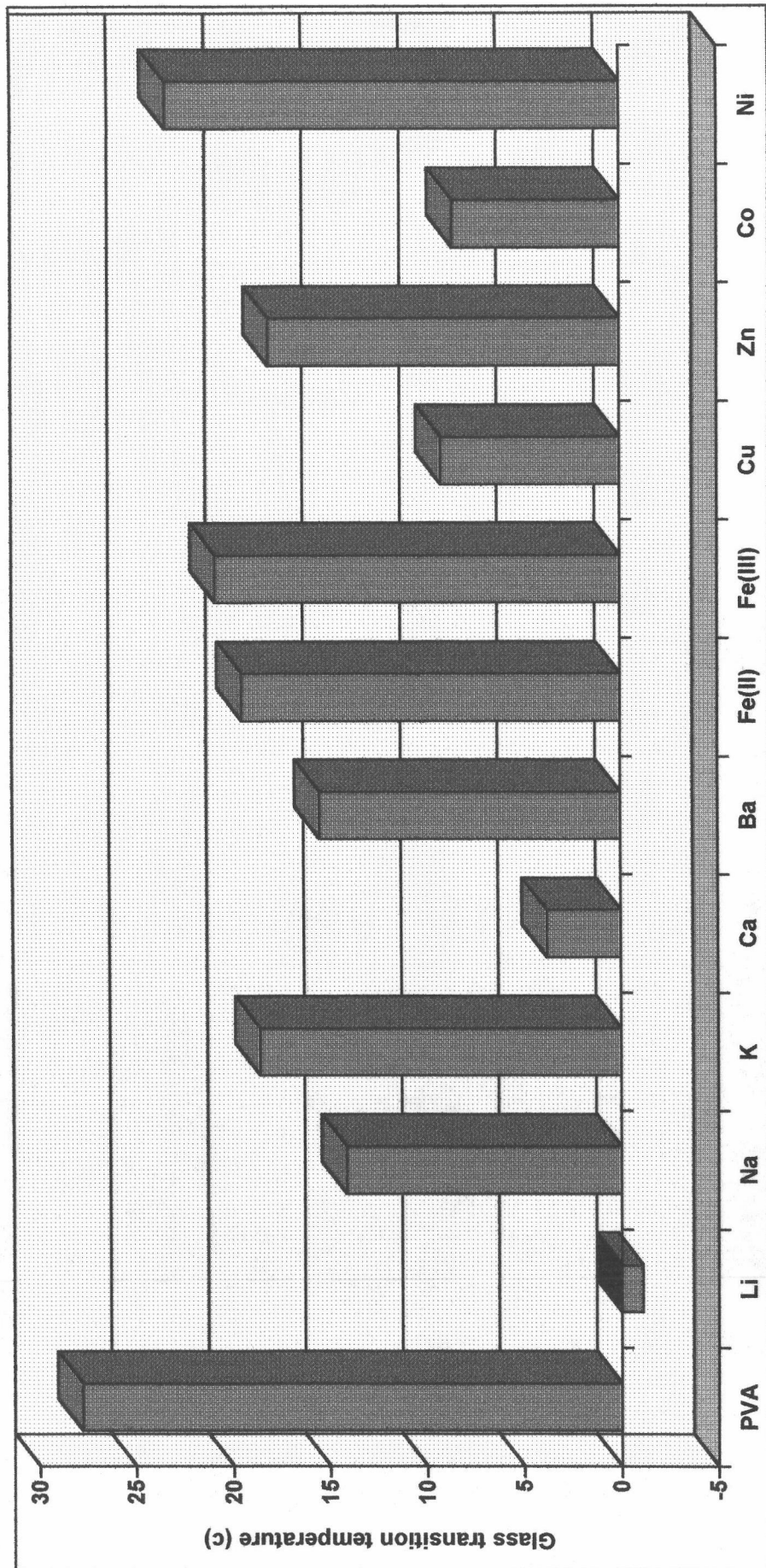


Figure 5.31 : Effect of metal salt on glass transition temperature (T_g) of PVA film and PVA films containing metal salt.

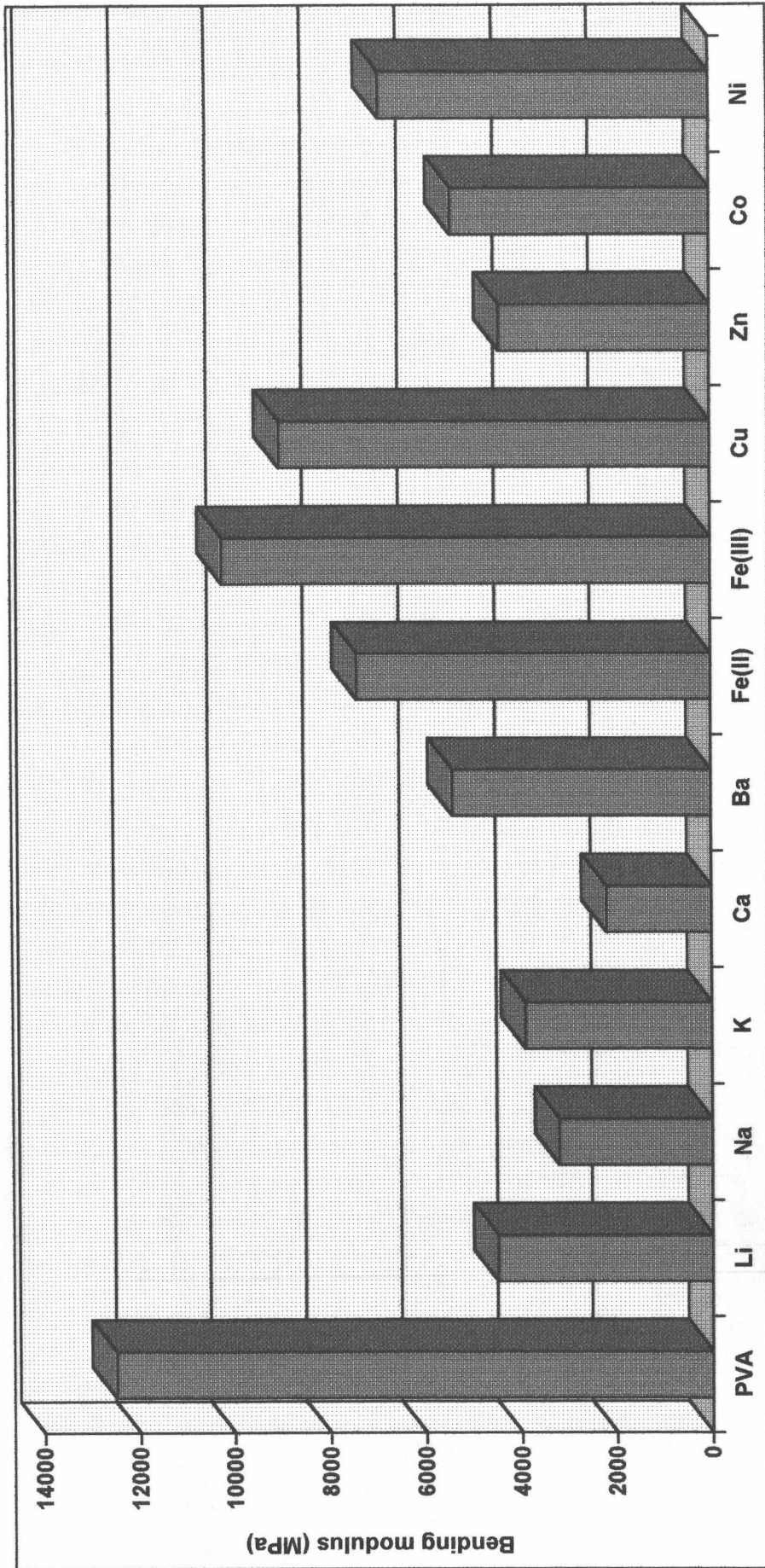


Figure 5.32 : The bending modulus (MPa) of standard PVA film and PVA films containing metal salt determined by Dynamic Mechanical Spectroscopy.

Effect of metal on mechanical properties

Effect of metal salt on tensile properties of PVA films were also investigated with Lloyd 500 Universal Testing Machine with 100 N load cell, 50 mm per minute cross head speed at room temperature. The results were showed in figure 5.33–5.35 and Appendix F.

As the results shown in figure 3.33 and 3.35, it was found that both tensile strength and tensile modulus of the films containing each salt decreased with metal content. However, the film containing 1 % metal salt content was found to have higher strength than the film in case of the film containing FeCl_2 , FeCl_3 and NiCl_2 , whereas the films containing other salts except LiCl , was found to have equal strength with the PVA film.

In case of the films containing LiCl higher than 5 % by weight, it was found to be too soft to tensile tested because of the high water content in the films.

The higher metal salt content in the film the higher water content, resulting to the increase of elastic behavior of the film, as shown in figure 5.34.

Consequently, percentage of strain at break was found to decrease with the presence of metal salt upto 1 % by weight, and then increased again with an increase of metal content. In case of the films containing LiCl , NaCl , KCl , CaCl_2 , BaCl_2 and ZnCl_2 , it was found that the strain

remarkably increased with metal content higher than 5 % by weight and became higher strain than the film without any salts when the metal content was higher than 10 % by weight.

However, in case of the films containing FeCl_2 , FeCl_3 , CuCl_2 , CoCl_2 and NiCl_2 , it was found that even the metal content was as high as 20 % by weight, the strain was still lower than the film without any salts. These results also confirmed the idea that the metal salts exhibit any interaction with the PVA molecules, consequent with the decrease of the degree of crystallinity.

As the results, it should be suggested to study the film having metal salt ≤ 1 % by weight.



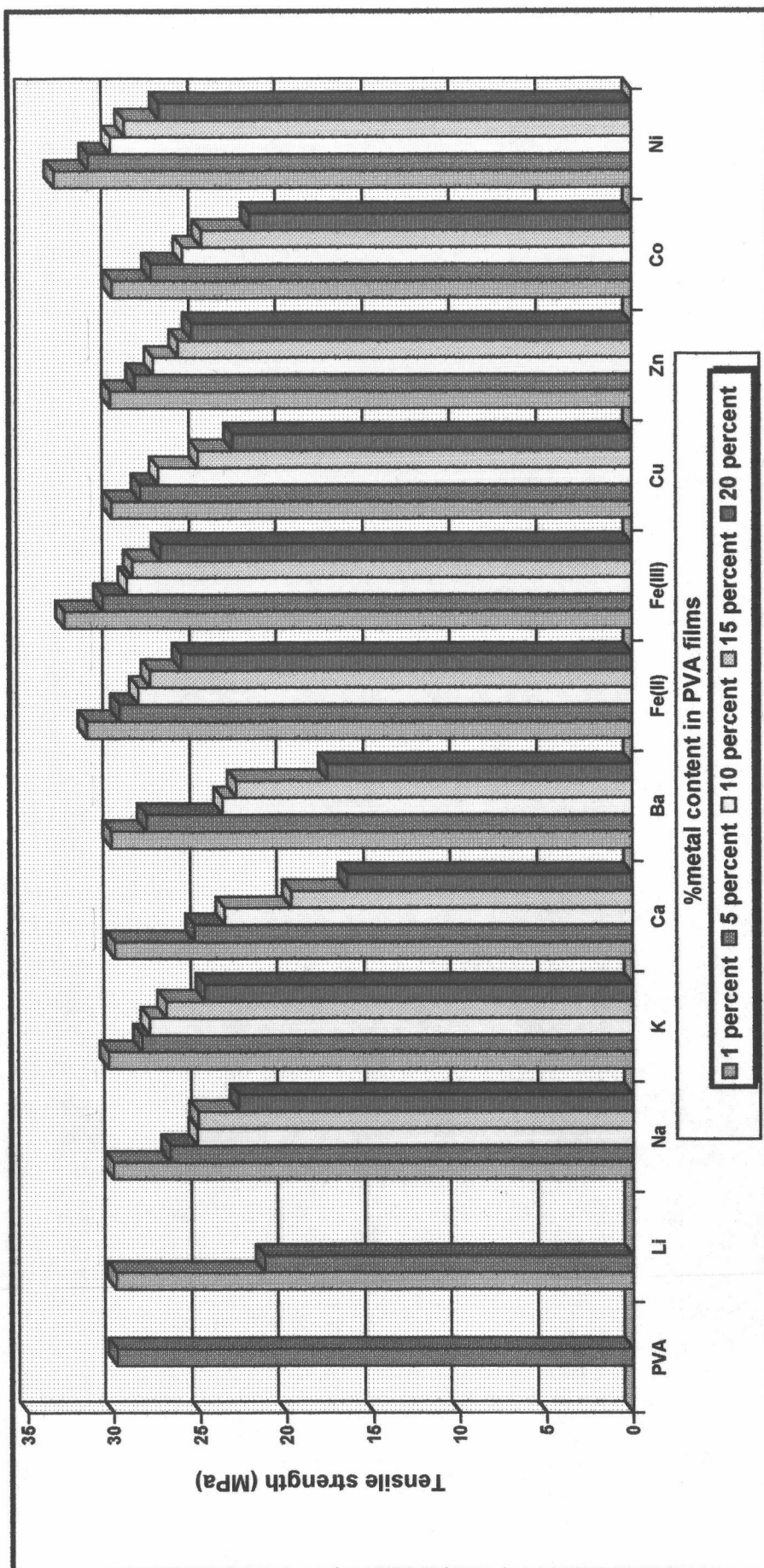


Figure 5.33 : Effect of various metal on tensile strength (MPa) of PVA films containing 1, 5, 10, 15 and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CaCl₂, ZnCl₂, CoCl₂, and NiCl₂.

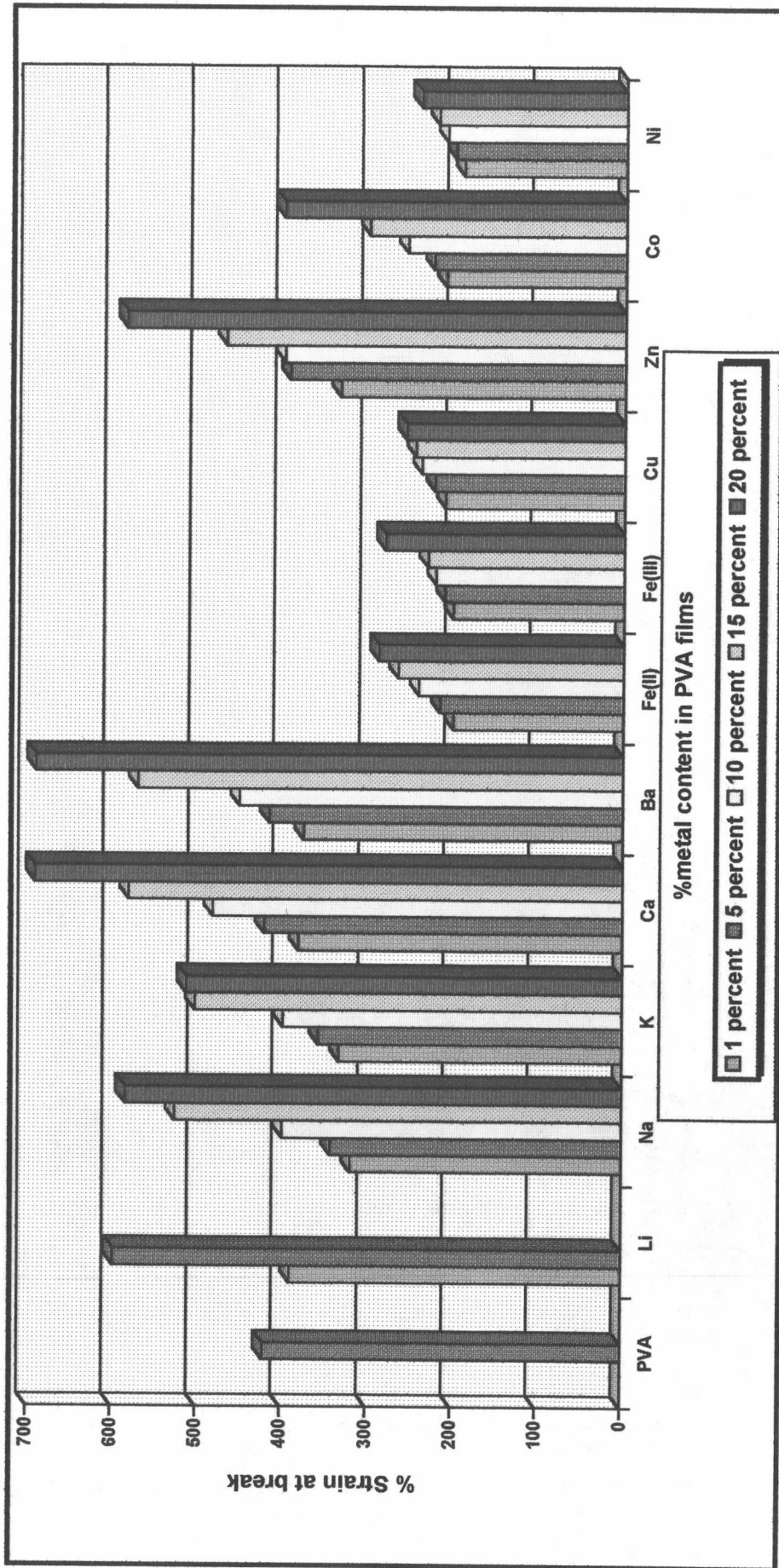


Figure 5.34 : Effect of various metal on percentage of strain at break of PVA films containing 1, 5, 10, 15 and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CaCl₂, ZnCl₂, CoCl₂, and NiCl₂.

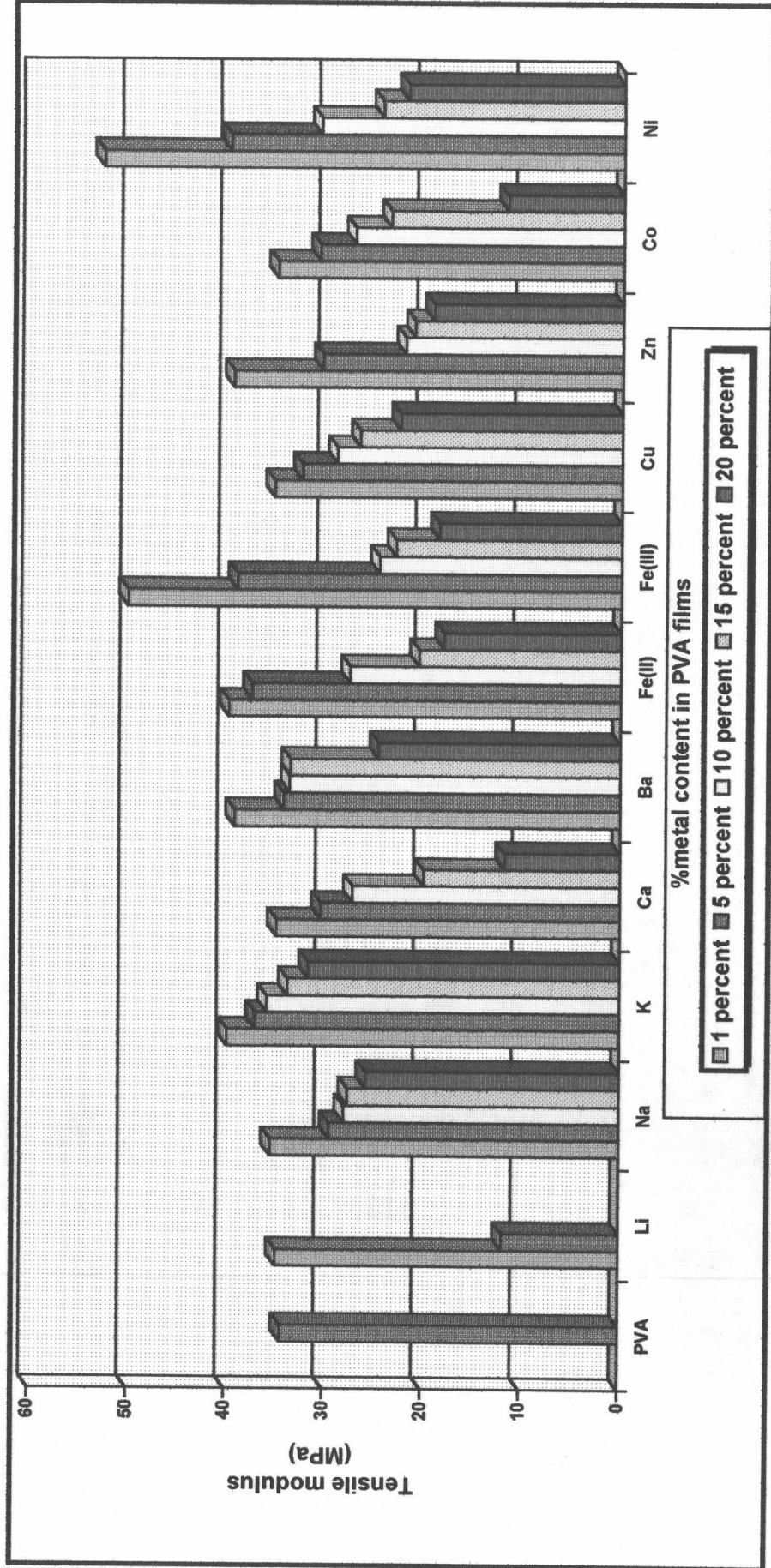


Figure 5.35 : Effect of various metal on tensile modulus (MPa) of PVA films containing 1, 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CaCl₂, ZnCl₂, CoCl₂, and NiCl₂.

Effect of metal on optical micrograph

Optical micrograph studies of the PVA films containing LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂ and NiCl₂ revealed same interesting features in the effect of metal showing in figure 5.36 and 5.37.

The PVA films containing metal under normal condition without any applying force as represented in figure 5.20 gave an understood on basis of dispersion and observable size of metal. Films containing LiCl showed higher continuous dispersion of metal, leading to greater overlapping of gain size. This alignment stated that the agglomerates of LiCl were easily took place and this features lead to failure in mechanical testing. On the other hand, the films containing NaCl and KCl exhibited random dispersion. Similarly, the films containing BaCl₂, CaCl₂, FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ provided an alignment of random dispersion of metal with small size.

Comparing dispersion of gain size, it was found that the films containing LiCl, NaCl, KCl, CaCl₂, and BaCl₂ provided smaller features with less distance between the gains, whereas the films containing transition metal salts such as FeCl₂, FeCl₃, CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ showed alignment feature of more distance between slightly large particle size. This indicated agglomeration of light metal with random dispersion. Therefore, dispersion capability depends on nature of metal interaction with hydroxyl groups and metal content in the films as shown in figure 5.36.

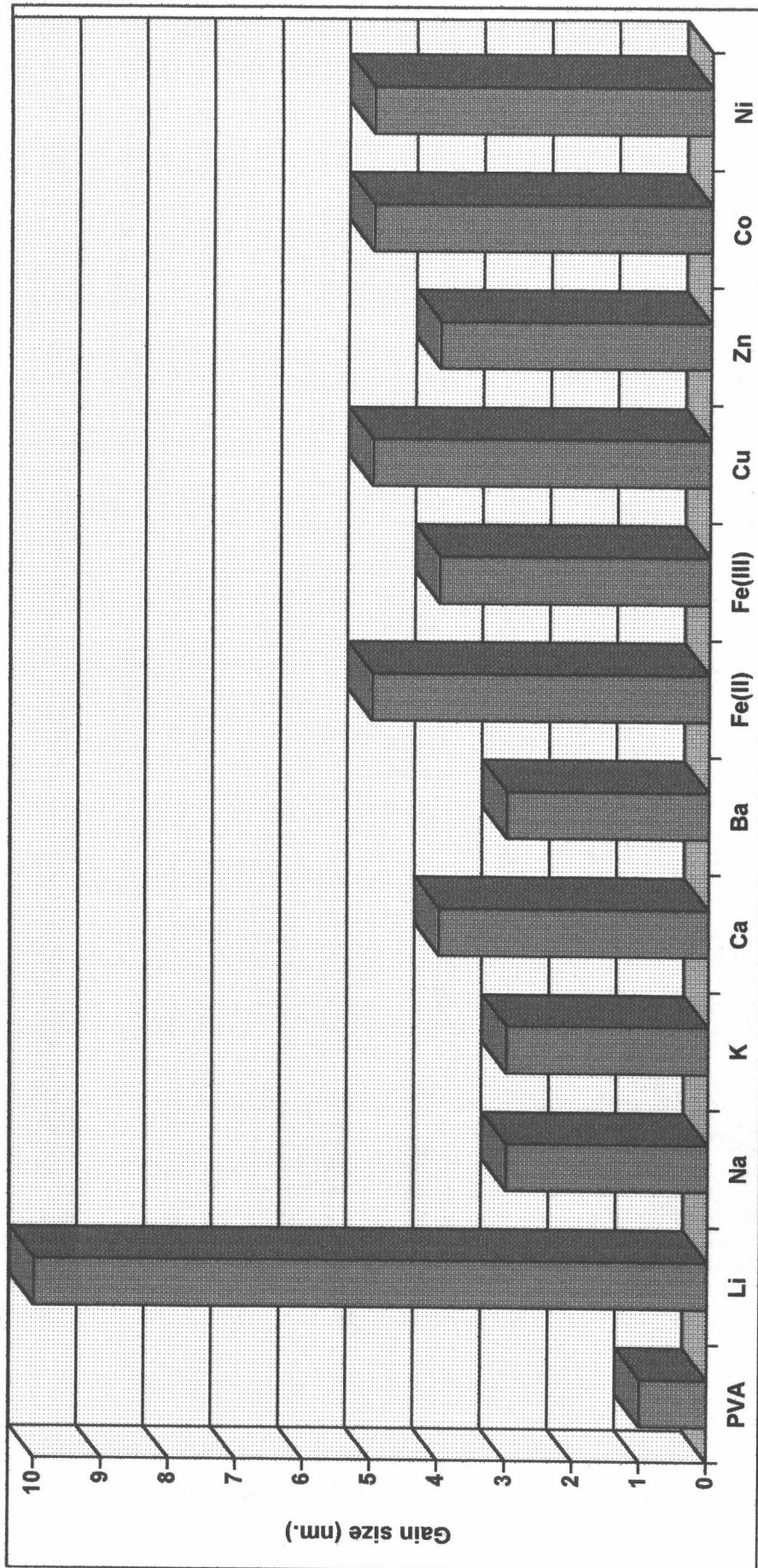


Figure 5.36 : Gain size of PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CaCl₂, ZnCl₂, CoCl₂, and NiCl₂ under normal condition.

From figure 5.37, the agglomerated ability after tensile deformation of light metals was higher than those of transition metals, whereas dispersion was found to be the lower. As a consequence, the agglomerated possibility of excess metal may lead to tensile failure which are confirmed by mechanical properties obtained from tensile testing method. It may be demonstrated that these changes in alignment features may be resulted from amount of crystalline content in the films.

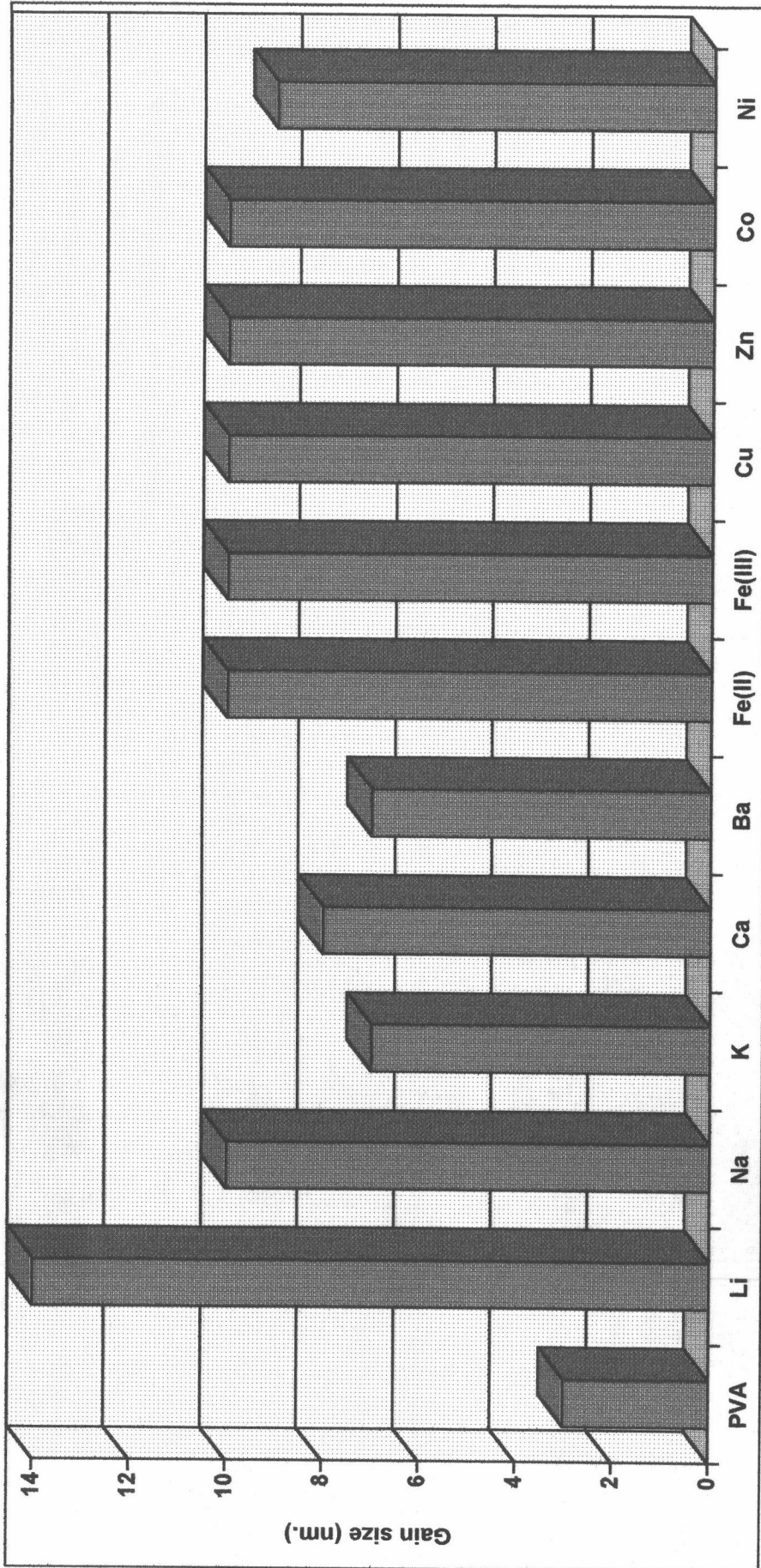


Figure 5.37 : Gain size of PVA film and PVA films containing 5, 10, 15, and 20% of LiCl, NaCl, KCl, CaCl₂, BaCl₂, FeCl₂, FeCl₃, CaCl₂, ZnCl₂, CoCl₂, and NiCl₂ after deformation under tensile testing from Lloyd at ambient condition.