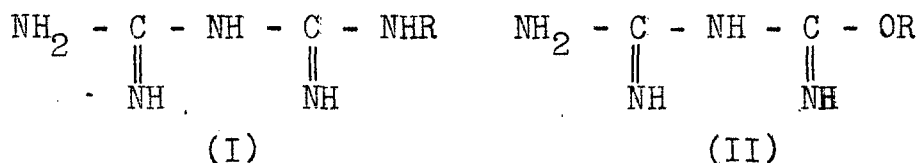


CHAPTER V :

PAPER CHROMATOGRAPHY OF SQUARE PLANAR BIS(1-AMIDINO-
O-ALKYLUREA) COMPLEXES OF COPPER(II) AND NICKEL(II).

Biguanides (BigH; I) and 1-amidino-O-alkylureas (AAUH; II) are closely related ligands^{221,244}. Both the series of ligands provide similar square planar bis(ligand) metal(II) complexes.



(Biguanide, R = H; Alkyl substituted biguanide R = alkyl group.)

(1-amidino-O-alkylurea R = alkyl group.)

Both sets of complexes have been adequately characterised via magnetic moment and electronic spectra^{221,244}. In this section the results of paper chromatographic studies of bis(1-amidino-O-alkylurea) copper(II)/nickel(II) complexes are presented and are compared with the results obtained on bis(biguanide) copper(II)/nickel(II) complexes.

Methods and materials :

The complexes were obtained by published procedures (Chapter III). Their purity was checked by elemental analysis (Table 3.2, Chapter III) and spectral measurements (Table 5.1). For the purpose of putting spots copper(II) and nickel(II) complexes of AMUH, AEUH, APⁿUH, APⁱUH (M = methyl; E = ethyl; Pⁿ = n-propyl; Pⁱ = iso-propyl for R in structure (II) were dissolved in warm water. The remaining complexes of ABⁿUH, ABⁱUH, AAⁿUH and AAⁱUH (Bⁿ = n-butyl; Bⁱ = isobutyl; Aⁿ = n-amyl; Aⁱ = iso-amyl) were dissolved in ethanol. The following developers were examined :

Developer I	:	Distilled water (~100 ml)
" II	:	100 ml 1M KCl
" III	:	100 ml 0.5M KCl + 5 ml pyridine
" IV	:	100 ml 1M KCl + 5 ml pyridine
" V	:	70 ml 0.5M KCl + 30 ml 1:1 pyridine.

Results and Discussion :

We have checked spectrophotometrically that none of the complexes undergoes any drastic change in any of the developers (Table 5.1 and Figs. 5.1, 5.2). The complexes are, therefore, chromatographed as genuine complexes.

In distilled water (Developer I), the complexes either did not travel at all or if traveled they diffused to a long distance along the filter paper like bis(biguanide) metal(II) complexes (Chapter IV). Cationic complexes are known to be strongly held on the negatively charged cellulose anion of the filter paper^{116,299,300}. Such strong attraction could be reduced by using developer II. But this developer II also was regarded unsuitable as the size of the spots are too large (16-18 cm) like what was noticed in Chapter IV. Developer III provide satisfactory spots (~ 3 cm) for bis(1-amidino-O-alkylurea) complexes of copper(II) only. Unfortunately this developer (Developer III) provided big sized spots (~ 7 cm) for bis(1-amidino-O-alkylurea) complexes of nickel(II). Suitable sized spots (2.5-3 cm) of both bis(1-amidino-O-alkylurea) copper(II) and nickel(II) complexes were obtained by using developer IV. With this developer, although increasing the chain length of the alkyl substituent led to an increase

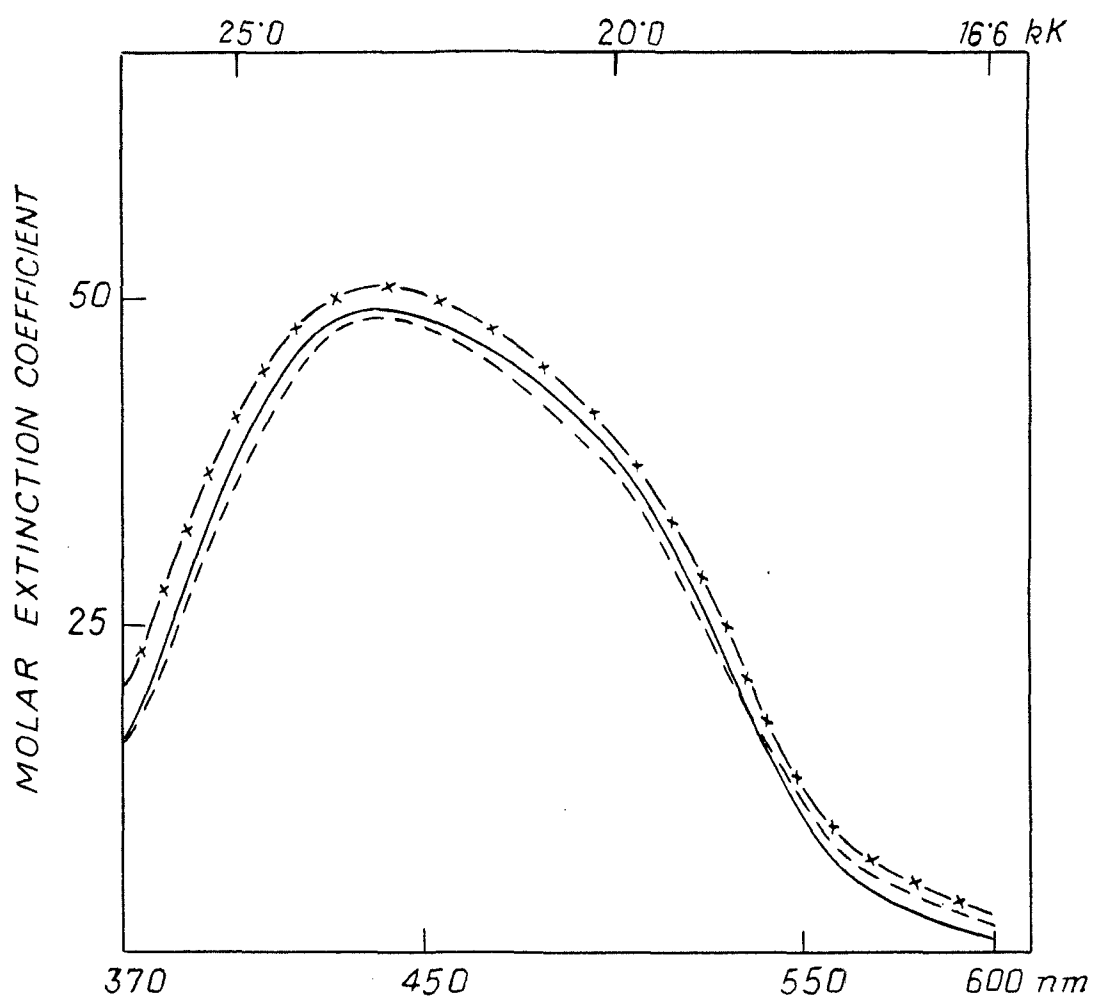


FIG. 5.1. ELECTRONIC SPECTRA OF :
 $[Ni(AMUH)_2]Cl_2$ in aqueous solution (---)
 $[Ni(AMUH)_2]Cl_2$ in the developer IV (—)
 $[Ni(AMUH)_2]Cl_2$ in the developer V (-x-)

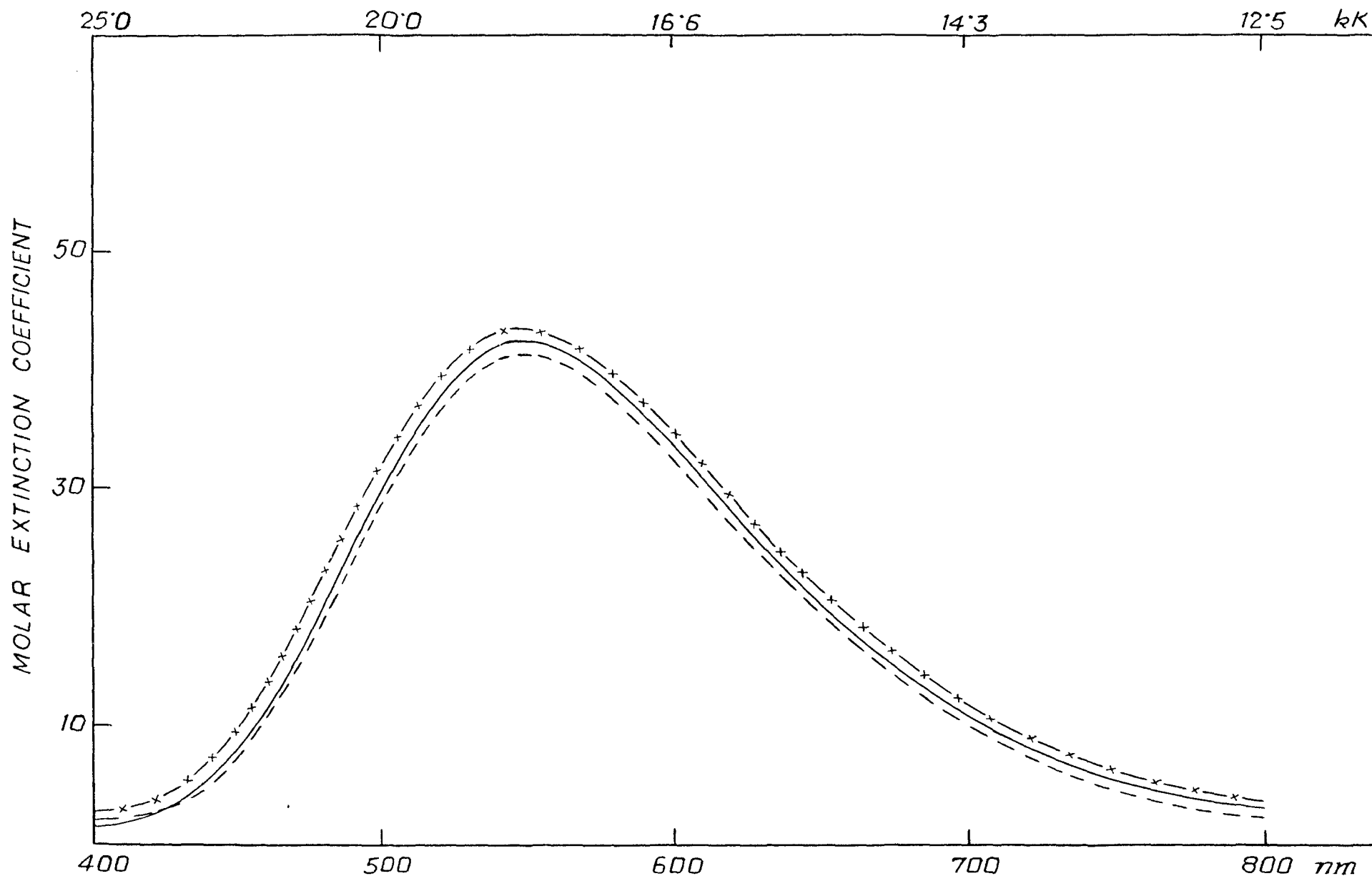


FIG. 5.2. ELECTRONIC SPECTRA OF :

$[Cu(AMUH)_2]Cl_2$ in aqueous solution (---)

$[Cu(AMUH)_2]Cl_2$ in the developer II (—)

$[Cu(AMUH)_2]Cl_2$ in the developer V (-x-)

Table 5.1. Absorption spectral data of metal 1-amidino-0-alkylurea complexes.

Complex	State	Colour	Absorption spectral band in nm	ϵ_{\max}	Ref.
$[\text{Cu}(\text{AMUH})_2]^{2-}\text{Cl}_2$	Aqueous solution	Rose red	530 - 540	43	223,244
	" "	"	530	41	This study
	Developer IV	"	530	42	
	Developer V	"	530	43	
$[\text{Cu}(\text{AEUH})_2]^{2-}\text{Cl}_2$	Aqueous solution	"	530 - 540	43	223,244
	" "	"	530	42	This study
	Developer IV	"	530	44	
	Developer V	"	530	46	
$[\text{Ni}(\text{AMUH})_2]^{2-}\text{Cl}_2$	Aqueous solution	Yellow	440 - 450	55	223,244
	" "	"	440	50	This study
	Developer IV	"	440	50	
	Developer V	"	440 - 450	52	
$[\text{Ni}(\text{AEUH})_2]^{2-}\text{Cl}_2$	Aqueous solution	"	440 - 450	47	223,244
	" "	"	440	45	This study
	Developer IV	"	440	46	
	Developer V	"	440 - 450	47	

in the R_f values for copper(II) complexes (from methyl upto isopropyl derivatives), no such increase in R_f values was marked for the corresponding nickel(II) complexes.

Effect of alkyl substitution :

In our previous studies (Chapter IV) with bis(biguanide) and bis(substituted biguanides) metal(II) complexes we have shown that on increasing the chain length of the alkyl substituent on the N^1 -atom of biguanide (I) the R_f values of the corresponding copper(II), nickel(II) and palladium(II) complexes also increase substantially. The two factors, (1) hydrogen bond formation between the cellulose anion and the N^1 -atom of biguanide and (2) the inductive effect of the alkyl group were considered responsible for increasing the R_f values. Our conjecture (Chapter IV) that on increasing the chain length of the alkyl substituent solubilities of bis(substituted biguanide) metal(II) complexes decrease in aqueous KCl-pyridine developer is shown to have a quantitative basis (Fig. 5.3 and Table 5.2). Thus solubility could not be held responsible for the increasing R_f with increasing chain length of the substituent in the cases of biguanide complexes.

In the present case of the l-amidino-O-alkylureas, the hydrogen bond formation remains invariant throughout the series because alkyl substitution does not lead to any decrease of hydrogen atoms in the ligand backbone. As against this, alkyl substitution of the N^1 -atom of biguanide does lead to a decrease

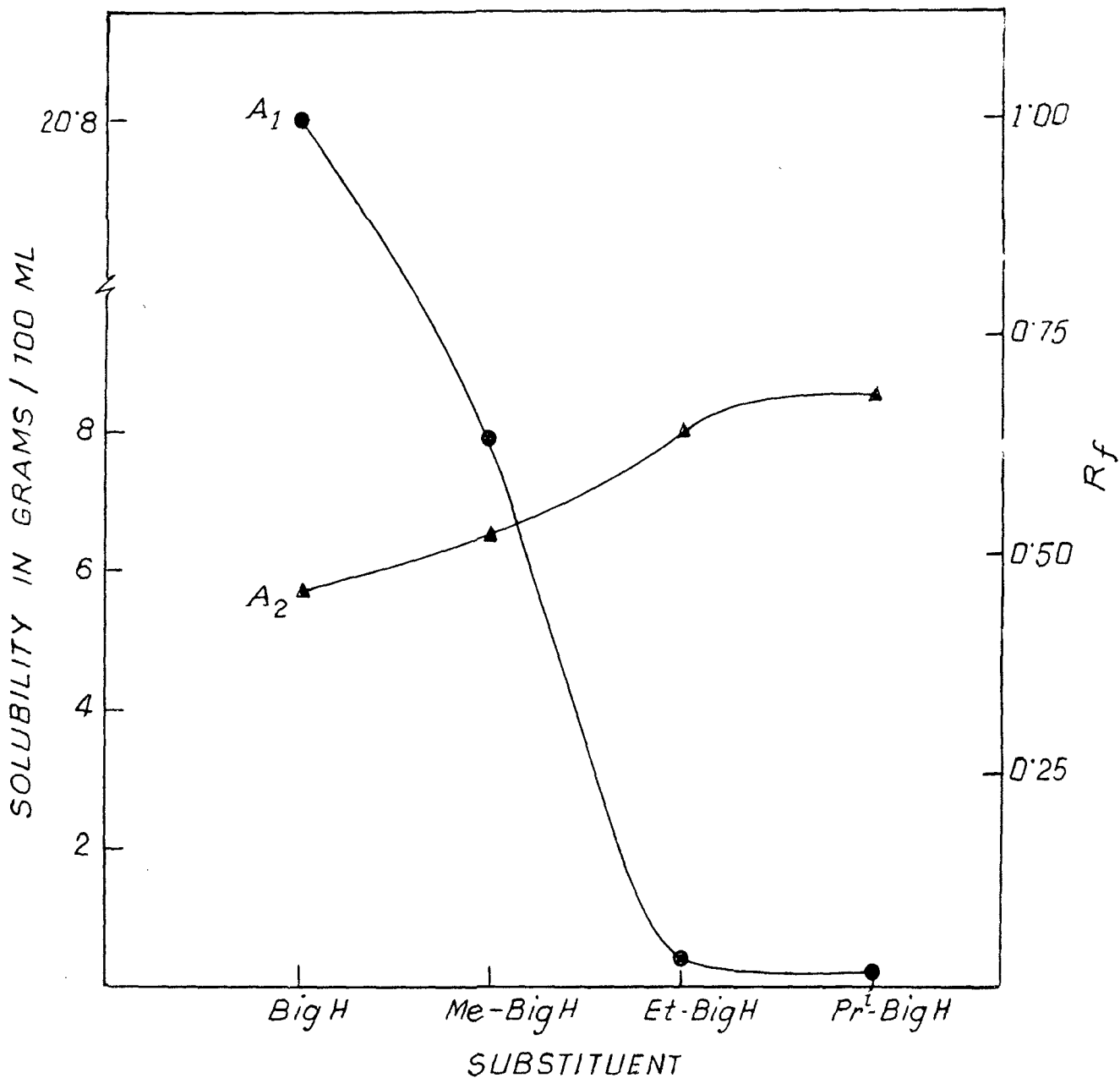


FIG.5'3. Variation in solubilities and R_f values of bis (biguanide/substituted biguanide) Copper (II) chloride in developer IV with substitution. A_1 , solubility curve; A_2 , R_f curve.

Table 5.2. Solubility and R_f values of bis(biguanide) metal(II) and bis(1-amidino-O-alkylurea) metal(II) complexes.

Complex	Developer	Solubility (in gm/100 ml of the developer)	R_f
$\text{[Cu(BigH)}_2\text{]Cl}_2$	Developer III (100ml 0.5M KCl + 5ml pyridine)	20.84	0.46
$\text{[Cu(Me-BigH)}_2\text{]Cl}_2$	"	7.96	0.52
$\text{[Cu(Et-BigH)}_2\text{]Cl}_2$	"	0.45	0.64
$\text{[Cu(Pr}^i\text{-BigH)}_2\text{]Cl}_2$	"	0.22	0.66
$\text{[Cu(Me}_2\text{-BigH)}_2\text{]Cl}_2$	"	0.32	0.72
$\text{[Cu(Et}_2\text{-BigH)}_2\text{]Cl}_2$	"	0.33	0.78
$\text{[Cu}\{\text{Et(BigH)}_2\}\text{]Cl}_2$	"	0.31	0.46
$\text{[Cu(Ph-BigH)}_2\text{]Cl}_2$	"	0.48	0.44
$\text{[Ni Et(BigH)}_2\text{]Cl}_2$	"	0.24	0.30
$\text{[Ni(AMUH)}_2\text{]Cl}_2$	Developer IV (100ml 1M KCl + 5ml pyridine)	0.26	0.85
$\text{[Ni(AEUH)}_2\text{]Cl}_2$	"	1.19	0.86
$\text{[Ni(AP}^n\text{UH)}_2\text{]Cl}_2$	"	0.62	0.86
$\text{[Ni(AP}^i\text{UH)}_2\text{]Cl}_2$	"	0.82	0.86
$\text{[Ni(AB}^n\text{UH)}_2\text{]Cl}_2$	"	0.34	0.84
$\text{[Ni(AB}^i\text{UH)}_2\text{]Cl}_2$	"	0.36	0.83
$\text{[Ni(AA}^n\text{UH)}_2\text{]Cl}_2$	"	0.30	0.73

Table 5.2.(Contd.)

Complex	Developer	Solubility (in gm/100 ml of the developer)	R _f
$\angle^- \text{Ni}(\text{AA}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	Developer IV (100ml 1M KCl + 5ml pyridine)	0.30	0.73
$\angle^- \text{Cu}(\text{AMUH})_2 \text{--} \text{Cl}_2$	"	0.055	0.67
$\angle^- \text{Cu}(\text{AEUH})_2 \text{--} \text{Cl}_2$	"	0.069	0.71
$\angle^- \text{Cu}(\text{AP}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.338	0.74
$\angle^- \text{Cu}(\text{AP}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	1.244	0.84
$\angle^- \text{Cu}(\text{AB}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.449	0.69
$\angle^- \text{Cu}(\text{AB}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.309	0.69
$\angle^- \text{Cu}(\text{AA}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.257	*
$\angle^- \text{Cu}(\text{AA}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.238	*
$\angle^- \text{Cu}(\text{AMUH})_2 \text{--} \text{Cl}_2$	Developer V (70ml 0.5M KCl + 30ml 1:1 pyridine)	0.431	0.84
$\angle^- \text{Cu}(\text{AEUH})_2 \text{--} \text{Cl}_2$	"	1.147	0.85
$\angle^- \text{Cu}(\text{AP}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	2.081	0.86
$\angle^- \text{Cu}(\text{AP}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	12.263	0.88
$\angle^- \text{Cu}(\text{AB}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	1.239	0.85
$\angle^- \text{Cu}(\text{AB}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	2.460	0.85
$\angle^- \text{Cu}(\text{AA}^{\text{n}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.839	0.82
$\angle^- \text{Cu}(\text{AA}^{\text{i}}\text{UH})_2 \text{--} \text{Cl}_2$	"	0.853	0.83

* Long tailing.

of the available hydrogen atoms. But the inductive effect of the alkyl group remains. We believe that solubility factor plays here a greater role since the solubility of the copper(II) complexes in aqueous KCl-pyridine (developer IV) is found to increase with increasing chain length of the alkyl substituent (from methyl upto isopropyl derivatives, Fig. 5.4 and Table 5.2).

The increase in R_f values of the copper(II) complexes is thus in conformity with the increasing solubility of the complexes to a certain point (isopropyl derivative), and thereafter solubilities and R_f values decrease and attain a somewhat steady level.

The solubilities of the nickel(II) complexes pass through two maxima and from isopropyl derivative onwards follow the trend of the corresponding copper(II) complexes although these solubility changes cannot influence the R_f values anymore because the R_f values have already attained a comparatively high level in the starting compound $\left[\text{Ni}(\text{AMUH})_2 \right] \text{Cl}_2$ ($R_f = 0.85$; Fig. 5.4). It is our conviction that changes in solubilities of a family of closely related complexes can influence the R_f values only when they do not start with an already high R_f value. That this suggestion is not entirely unfounded is revealed on an inspection of the R_f values and the solubilities of the complexes in developer V. In this developer, the solubility differences are enormous, (compared to those in developer IV) but the changes in R_f are minimal (Fig. 5.5). Note that the starting

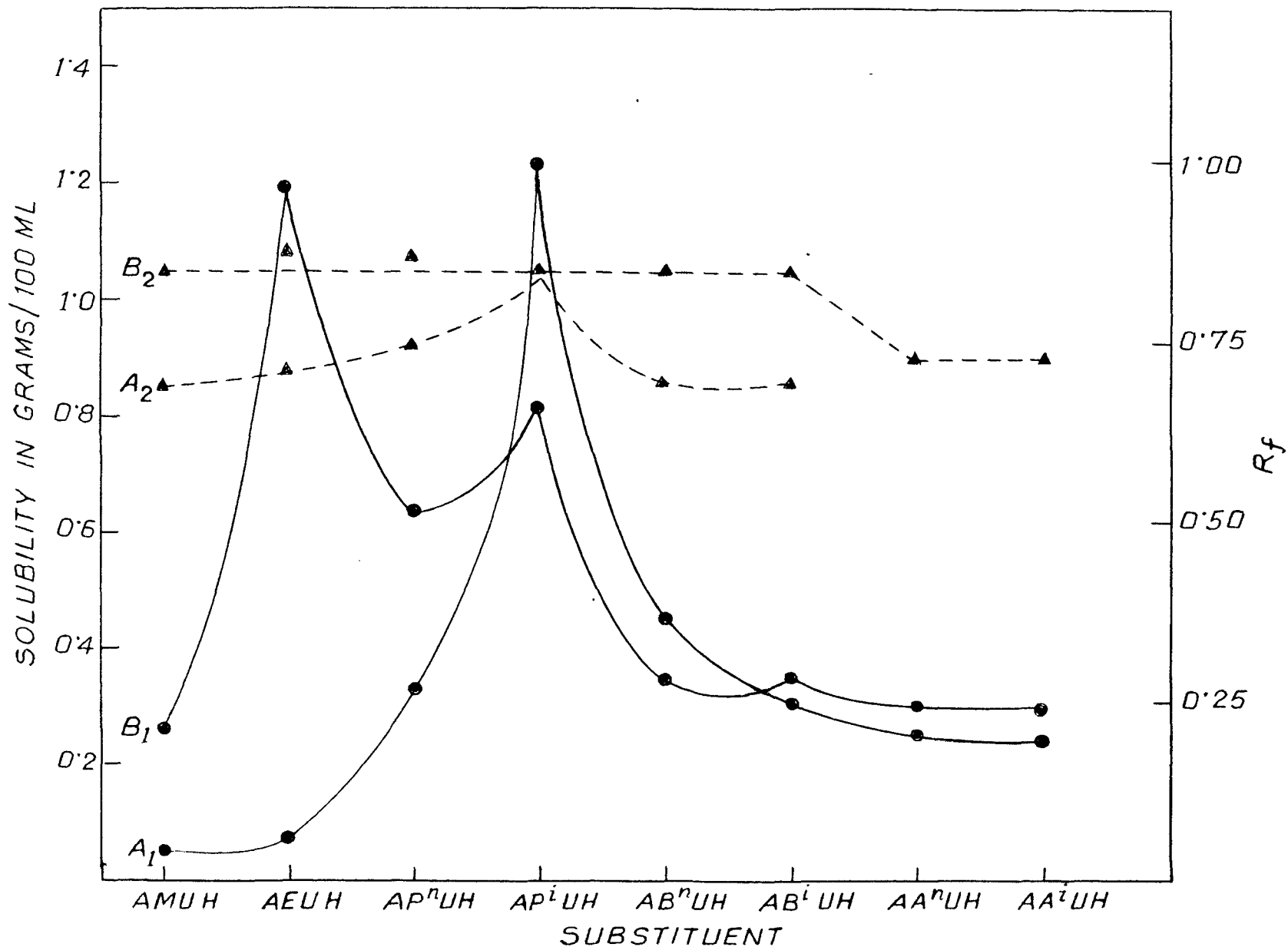


FIG 5.4 Variation in solubilities and R_f values of bis(1-amidino-O-alkylurea) Copper (II) and Nickel (II) chlorides in developer IV with substitution.
 A₁, solubility curve of Copper (II); A₂, R_f curve of Copper (II)
 B₁, " " " Nickel (II); B₂, R_f " " Nickel (II).

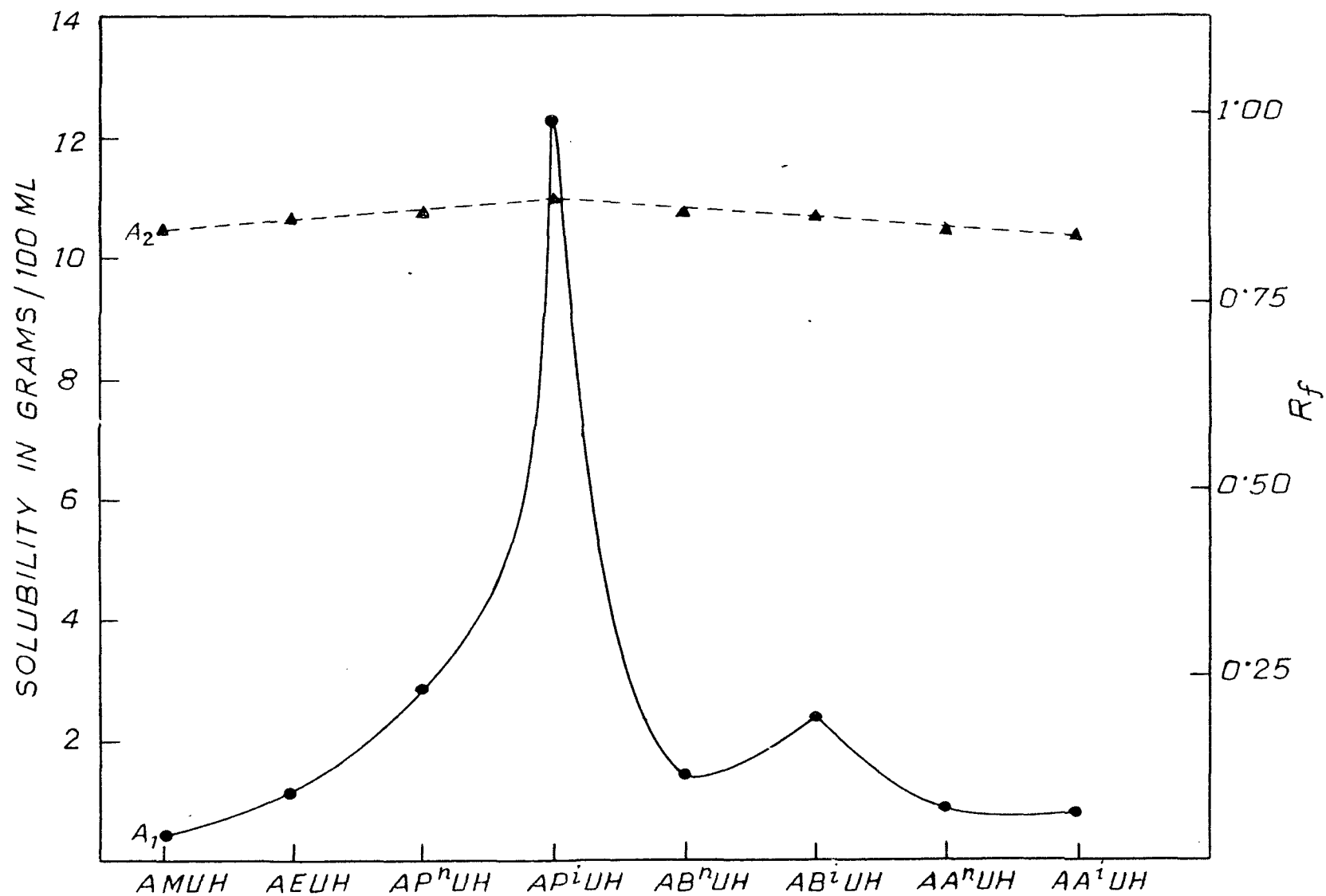


FIG. 5.5. Variation in solubilities and R_f values of bis(1-amidino-O-alkylurea) Copper (II) chlorides in developer V with substitution. A_1 , solubility curve; A_2 , R_f curve.

compound $\angle \text{Cu}(\text{AMUH})_2 \text{Cl}_2$ has an R_f 0.84 in developer V while its R_f in developer IV is only 0.64. The levelling effect of the R_f values of nickel(II) complexes in developer V is still more apparent since the R_f of starting compound $\angle \text{Ni}(\text{AMUH})_2 \text{Cl}_2$ is 0.90 instead of 0.85 in developer IV (Table 5.2 and 5.3.).

Table 5.3. R_f values of $\angle \text{Ni}(\text{AAUH})_2 \text{Cl}_2$ in the developer V.

Complex	Developer	R_f
$\angle \text{Ni}(\text{AMUH})_2 \text{Cl}_2$	Developer V (70ml 0.5M KCl + 30ml(1:1) pyridine).	0.90
$\angle \text{Ni}(\text{AEUH})_2 \text{Cl}_2$	"	0.91
$\angle \text{Ni}(\text{AP}^n\text{UH})_2 \text{Cl}_2$	"	0.91
$\angle \text{Ni}(\text{AP}^i\text{UH})_2 \text{Cl}_2$	"	0.93
$\angle \text{Ni}(\text{AB}^n\text{UH})_2 \text{Cl}_2$	"	0.91
$\angle \text{Ni}(\text{AB}^i\text{UH})_2 \text{Cl}_2$	"	0.91
$\angle \text{Ni}(\text{AA}^n\text{UH})_2 \text{Cl}_2$	"	0.90
$\angle \text{Ni}(\text{AA}^i\text{UH})_2 \text{Cl}_2$	"	0.89

Effect of size of the complexes :

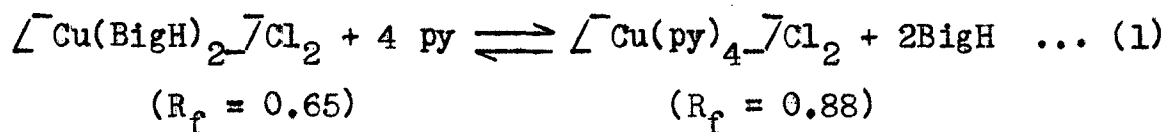
R_f values increase in the order : Cu < Ni, which is also the order of decreasing size, weight and increasing solubility.

Effect of KCl/pyridine :

Like bis(biguanide) and bis(substituted biguanide) complexes of copper(II) and nickel(II), R_f values of bis(1-amidino-O-alkylurea) complexes of copper(II) and nickel(II) also increase

on increasing the KCl concentration in aqueous KCl-pyridine developer. It is to be noted that neither KCl nor pyridine alone can give good spots. With lower concentration of KCl and high concentration of pyridine (developer V) all the complexes provided good spots (1 cm) and high R_f values compared to those with developer IV. This is also due to increased solubility of the complexes in this developer (Figs. 5.4 and 5.5).

We have seen earlier (Chapter IV) that with high concentration of pyridine and low concentration of KCl (developer V) the homochelate $\overline{\text{Cu}}(\text{BigH})_2\overline{\text{Cl}}_2$ provide two spots which were traced to be due to an equilibrium of the type :



In view of the above results with $\overline{\text{Cu}}(\text{BigH})_2\overline{\text{Cl}}_2$, it appeared likely that 1-amidino-0-alkylurea complexes of copper(II) would also provide two spots of substantially different R_f values. We have, however, obtained a single spot which was somewhat bigger in size than shown by $\overline{\text{Cu}}(\text{py})_4\overline{\text{Cl}}_2$. In view of the fact that $\overline{\text{Cu}}(\text{AMUH})_2\overline{\text{Cl}}_2$, $\overline{\text{Cu}}(\text{AEUH})_2\overline{\text{Cl}}_2$ etc. exhibit spots with about the same R_f as copper(II) in developer V, it is not unlikely that the two expected spots have got fused together (Fig. 5.6). Equilibrium of the type (1), therefore, has neither been definitely established nor dispelled in the case of bis(1-amidino-0-alkylurea) copper(II) complexes.

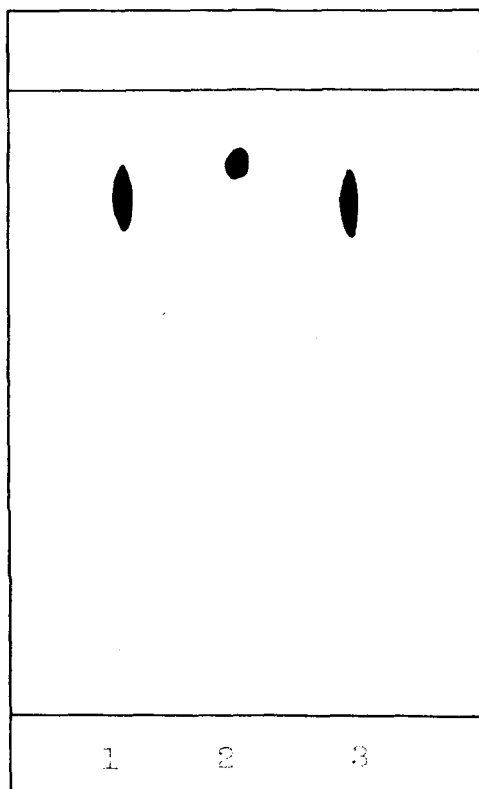


Fig.5.6. Chromatograms in
70ml 0.5M KCl + 30ml 1:1
pyridine as developer.

1. $\text{[Cu(AMUH)}_2\text{]Cl}_2$
2. CuCl_2
3. $\text{[Cu(AEUH)}_2\text{]Cl}_2$.