CATIONIC BINDING BY MACROBICYCLIC POLYETHERS

BY

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MASTER OF SCIENCE

FEBRUARY 1981

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ABSTRACT

Diazapolyoxamacrobicyclic compounds form exceptionally stable complexes in organic nonpolar solvents by enclosing certain cations in the tridimensional cavity. In the present work, by using hydrogen bonding properties of chloroform-d, 4,7;13;18-Tetraoxa-1,10-diazabicyclo(8.5.5) eicosane(2.1.1), 4,7;13,16;21-Pentaoxa-1,10-diazabicyclo(8.8.5)tricosane(2.2.1) and 4,7;13,16;21,24-Hexaoxa-1,10-diazabicyclo(8.8.8)hexacosane(2.2. have been investigated and shown to exist in solution in the "out,out" conformation. Hydrogen bonding of chloroform-d to the sulphate ion, SO_4^{2-}, occurs with a resultant band appearing in the infra-red at 2055cm^{-1}.

Encapsulation of Cu (II) and Co (II) by (2.1.1), (2.2.1) and (2.2.2) has been followed by infra-red spectroscopy. From the partition coefficient values (2.2.1) has been shown to be a poor selective extractant of copper and cobalt. (2.1.1) shows preference for cobalt while (2.2.2) appears to extract copper effectively.

ACKNOWLEDGEMENT

I could not have done this work if it were not for Dr Jacob Mwanza, the Vice Chancellor of the University of Zambia, who in 1978 gave me a second chance after I was proclaimed 'useless'. A student who graduates even with Merit becomes rusty after a period of five years of intellectual inactivity. This, Dr Mwanza comprehended fully and I am very grateful.

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I must acknowledge a debt of gratitude to my wife Felly for explicit encouragement and support and for painstakingly typing this work.

Finally, I must express my appreciation for the assistance and considerable encouragement I received, in the early stages of my education, from my late grand grandmother (honestly), Ba mayo banakulu Fwemba; she used to kill a chicken for me each time I obtained a first in class.

Arakan, Lusaka L. K. M

February 1981

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CHAPTER 1

HYDROGEN BONDING OF CHLOROFORM-D AS A CONFORMATIONAL PROBE OF MACROBICYCLIC POLYETHERS

1.1 INTRODUCTION

Simmons and Park (1) reported the synthesis of macrobicyclic diamines which consist of two brigehead nitrogen atoms and proposed that these compounds could exist in solution as one of three isomers. These are: the isomer in which both the nitrogen atoms are inside the molecular cavity as defined by the three hydrocarbon chains; the isomer in which both nitrogen atoms are outside the cavity and the third isomer in which one nitrogen atom is outside and the other inside the cavity. These conformations were called respectively the "in, in", "out, out" and "out, in". Lehn et. al. (2) have synthesized a series of mono- and bicyclic macrocycles containing both nitrogen and oxygen atoms. The macrobicyclic polyethers 4,7;13;18-Tetraoxa-1,10-diazabicyclo (8.5.5) eicosane (2.1.1), 4,7;13,16;21-Pentaoxa-1,10-diazabicyclo (8.8.5)tricosane (2.2.1) and 4,7;13,16;21,24 - Hexaoxa-1,10-diazabicyclo(8.8.8) hexacosane (2.2.2) (See Figure 1) can exist in solution as one of the three stereoisomers mentioned above (Figure 2).

In the present work hydrogen bonding properties of chloroform-d were used to investigate the conformation in solution of (2.1.1), (2.2.1) and (2.2.2). The free C-D stretching frequency of chloroform-d lies at 2254cm^{-1} (Figure 4.1)and the macrobicyclic polyethers, under study, have no bands in this region of the spectrum (Fig 4.2 and 4.3). A new absorption band characteristic of the hydrogen bonded complex appears at a lower frequency than the absorption due

to unassociated C-D band. Since chloroform-d is too large to diffuse into the molecular cavity of the macrocycle, the shift in the C-D stretching frequency is indicative of hydrogen bonding and the 'out' position of the bridgehead nitrogen. Thus, the presence of the associated C-D stretching frequency indicates accessibility of nitrogen atom(s).

Absorbance studies of chloroform-d using cyclehexane as a solvent were carried out in the infra-red region at 2254cm^{-1}. α_D the molar absorptivity of chloroform-d is then obtainable from Beer's law plot.

$$A_\sigma = \alpha_D \ell C \qquad (1)$$

where A_σ = Absorbance at frequency σ cm^{-1}
α = molar absorptivity, 1 mol^{-1}cm^{-1}
ℓ = cell pathlength, cm
c = concentration, M

Similar studies on triethylamine and macrobicyclic polyethers were carried out to determine α_c, the molar absorptivity of the C-D band in the associated complex. In the following equilibrium equation

$$D + A = D \ldots A = C \quad (1.2)$$

D is the electron pair donor (base)

A is the electron pair acceptor (chloroform-d)

and D ... A is the hydrogen bonded complex.

The relationships between initial and equilibrium concentrations are:

$$C_D^o = C_D + C_c$$

$$C_b^o = C_b + C_c \quad (1.3)$$

where C_c is the equilibrium concentration of complex.

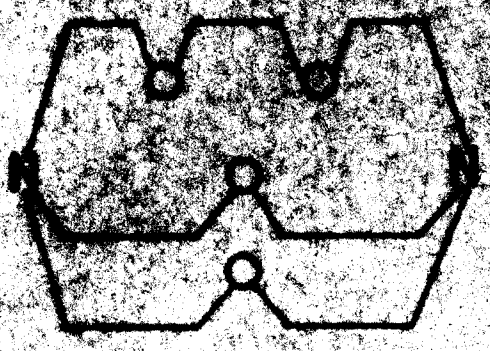
C_D , the equilibrium concentration of chloroform-d is calculated from the Beer-Lambert law (equation 1) using α_D and the observed absorbance at 2254cm^{-1}. Since C_D^o is known, C_c and C_b can be calculated. The value of C and the observed absorbance at the associated stretching frequency are used to calculate α_c from Beer's law. The values of α_c for triethylamine and those for the polyethers were compared.

The equilibrium concentrations of base C_b and of the complex C_c together with the calculated values of A, the deuterochloroform concentration, were used to calculate the equilibrium constant K defined as (3)

$$K = \frac{C_c}{(C_b)(C_D)} \qquad (1.4)$$

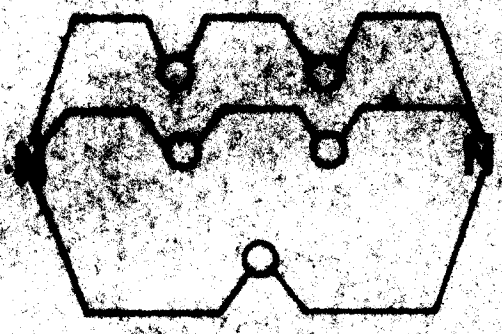
Hydrogen bonding studies were also extended to 18-crown-6 (Fig 1) in order to investigate the accessibility of oxygen atoms to chloroform-d in the polyethers.

(i)



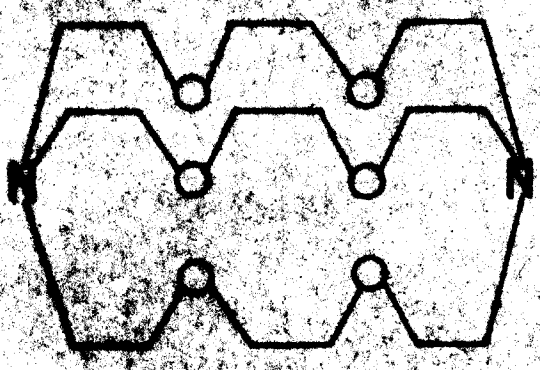
4, 7; [illegible]-TETRAONA - 1; 10-DIAZABICYCLO (8·5·5) EICOSANE [2·1·1]

(ii)



4, 7; [illegible] PENTAONA - 1, 10 DIAZABICYCLO (8·8·5) TRICOSANE [2·1·1]

(iii)



4, 7; 13, 16; 21, 24 HEXAONA - 1 - 10 DIAZABICYCLO (8·8·8) [illegible]

(iv)

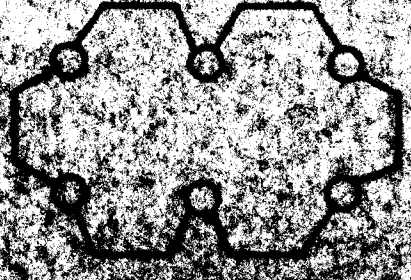
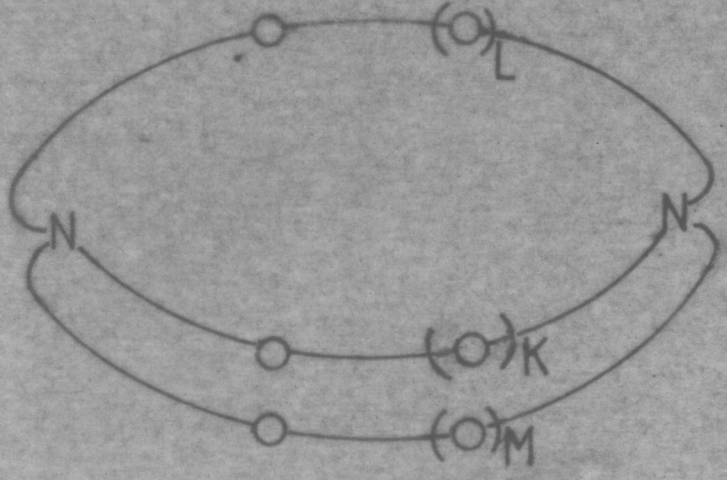


FIGURE 2

IBLE CONFORMATIONS OF MACROBICYCLIC POLYETHERS



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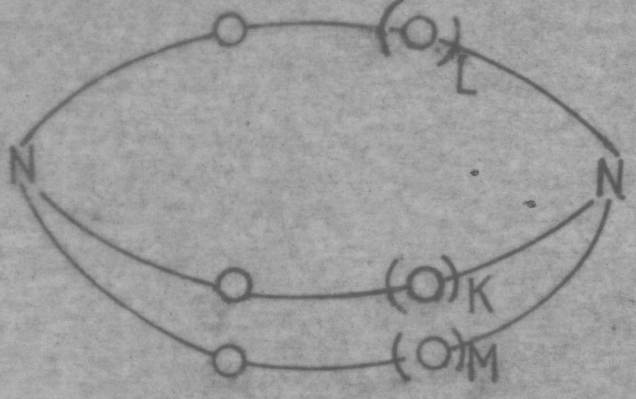
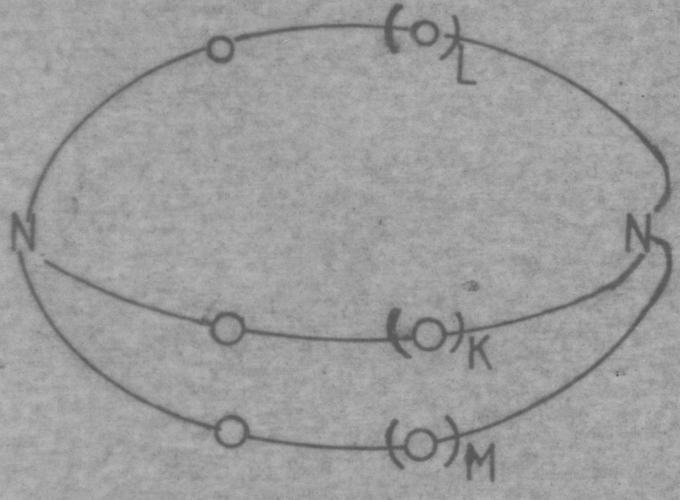


"out,out"



" out in "

L=K= M= 1 (2.2.2.)
L=K = 1 , M=0 (2 2 1)
L=1 , K=M= 0 (2.1.1)

1.2 EXPERIMENTAL

1.2.1 Materials

The macrobicyclic polyethers (2.1.1) (2.2.1) and (2.2.2) were purchased from PCR Chemicals Inc. of Gainesville, Florida, USA and were used without further purification. Chloroform-d (99.6% D) from Merck and Co. Inc. was used without further purification. Triethylamine from BDH Chemicals Ltd was refluxed over Potassium hydroxide for 1 hr and distilled. Cyclohexane was obtained from Merck and Co. Inc. and was not purified further.

Chloroform-d concentration ranged from 0.5 to 12.46 mole/litre while the concentration range of bases was from 0.04 to 0.8 mole/litre. All solutions were made up less than 1 hour before use.

1.2.2 Absorption measurements

Several NaCl and KBr liquid cells were used and their pathlengths were determined by the method of interference fringes (4). The cells were cleaned with chloroform-d and then flushed with dry nitrogen.

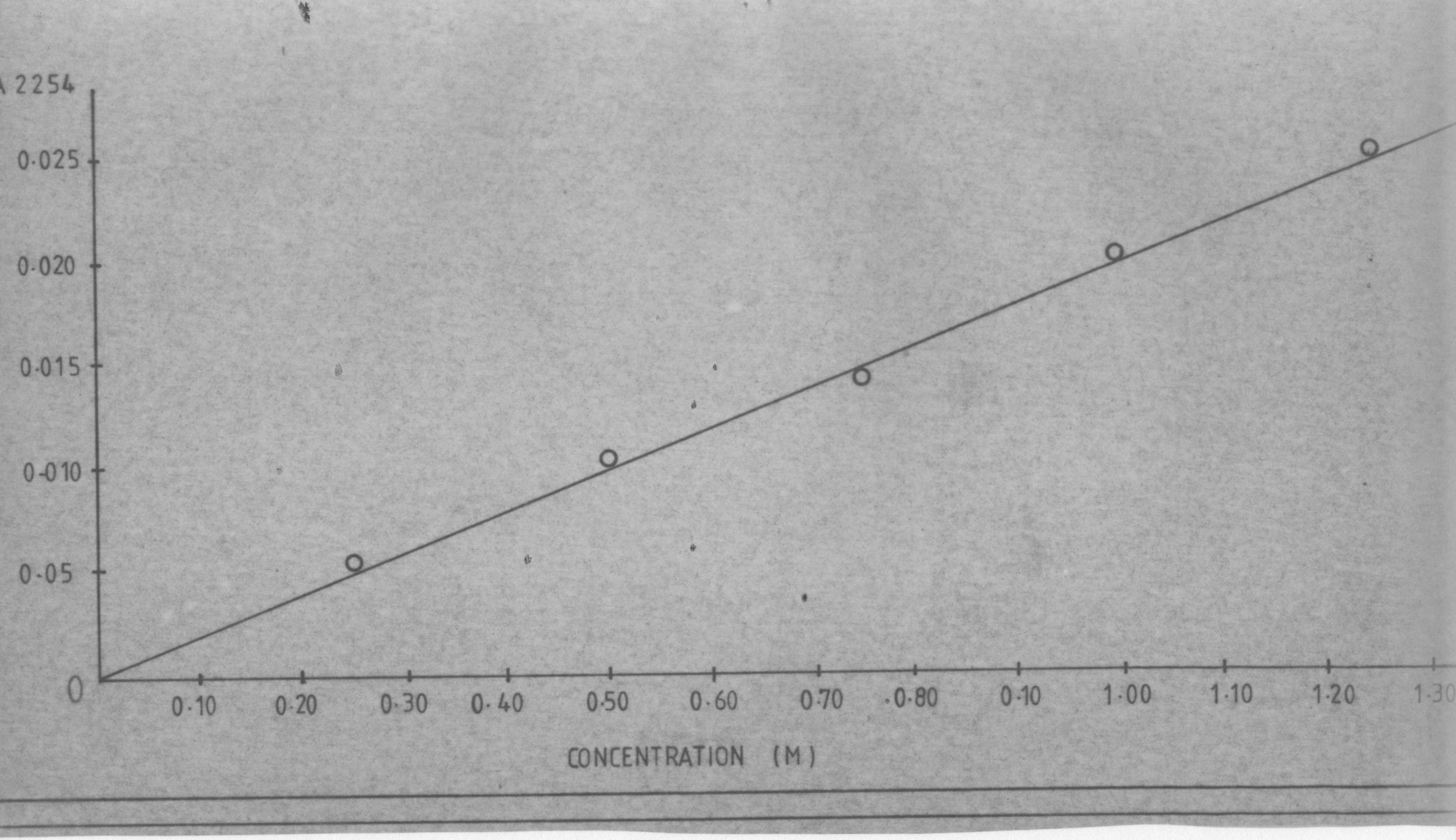
All infra-red spectra were obtained at room temperature with a Perkin-Elmer Model 197 spectrophotometer. A spectral slit width of $2cm^{-1}$ was used. Solution spectra of triethylamine in both pure chloroform-d and chloroform-d and cyclohexane were obtained. In the latter case the solvent compensation method was employed with a Perkin-Elmer variable pathlength cell (Model 5101 9525) placed in the reference beam. The pathlength of this cell could be varied from 0.095 to 0.5mm. The polyethers were dissolved in pure chloroform-d and their spectra were recorded. Spectra of pure polyethers were also obtained.

1.3 RESULTS AND DISCUSSION

1.3.1 Molar absorptivity, α_D of chloroform-d in cyclohexane at 2254cm^{-1}

The absorbance of the C-D band at 2254cm^{-1} was studied as a function of known chloroform-d concentration in cyclohexane and was found to be in excellent agreement with Beer-Lambert law (equation 1, Figure 3). The value of α_D was found to be 1.92 $\pm$ 0.06lmol^{-1}cm^{-1}; the error was estimated as a standard deviation of distribution of eight measurements. This value compares well with the value of 2.0, obtained by Lord et. al. (5) in their studies of chloroform-d bonding to pyridine and the value of 2.2 obtained by Lord and Siamwiza for chloroform-d in methylcyclopentane (6). Figure 3 shows a plot of absorbance at 2254cm^{-1} against molar concentration of chloroform-d in cyclohexane. α_D was calculated from the slope of the plot.

FIGURE 1.3: BEER'S LAW PLOT OF ABSORBANCE AT 2254cm^{-1} Vs CHLOROFORM-D CONCENTRATION IN CYCLOHEXANE


A 2254
0·025
0·020
0·015
0·010
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0·10
0·20
0·30
0·40
0·50
0·60
0·70
·0·80
0·10
1·00
1·10
1·20
1·30
CONCENTRATION (M)

TABLE 1.1

PROPERTIES OF TRIETHYLAMINE IN CHLOROFORM-D AND CYCLOHEXANE

TABLE 1.1

Initial chloroform-d concentration (M)	0.99	0.99	0.99	0.99	0.75	0.75	0.50	0.50
Initial triethylamine concentration (M)	0.43	0.29	0.29	0.22	0.22	0.22	0.22	0.22
Equilibrium chloroform-d concentration (M)	0.82	0.90	0.89	0.95	0.69	0.69	0.45	0.48
Absorbance at 2254cm^{-1}	0.016	0.018	0.018	0.019	0.013	0.014	0.009	0.095
Absorbance at 2170cm^{-1}	0.068	0.042	0.042	0.029	0.026	0.026	0.027	0.016
Equilibrium constant (M^{-1})	0.84	0.56	0.64	0.35	0.51	0.43	0.56	0.19
Average Equilibrium constant (M^{-1})	0.51 ± 0.10 (20%)							
C-D Peak absorptivity in complex, α_c (lmol^{-1}cm^{-1}	37.07	45.84	42.73	36.32	44.60	37.70	56.80	64.91
Average α_c (lmol^{-1}cm^{-1})	42.97 ± 7.08 (17%)							

1.3.2 Hydrogen Bonding of Chloroform-d to Triethylamine in Cyclohexane

The infra-red spectrum of chloroform-d dissolved in cyclohexane showed the free C-D stretching frequency at 2254cm^{-1} as in pure chloroform-d. When triethylamine was added to the solution a strong satellite, due to hydrogen bond formation between chloroform-d and triethylamine, appeared at 2170cm^{-1} (Fig 4.4). This observation is consistent with an earlier report. Lord and Siamwiza (6) reported a similar frequency shift of 84cm^{-1} to 2170cm^{-1} in their studies of hydrogen bonding of chloroform-d to triethylamine in methylcyclopentane.

The equilibrium constant, K, (equation 1.4) was obtained as 0.51 $\pm$ 0.10lmol^{-1} (See Table 1.1); the limit was obtained as a standard deviation. The value of 0.51 compares well with 0.58 $\pm$ 131mol^{-1} obtained by Lord and Siamwiza.

1.3.3 Absorbance of C-D stretching band in the Triethylamine - chloroform-d complex

The equilibrium concentration of the complex calculated above and the observed absorbance at 2170cm^{-1} were used to obtain α_c the molar absorptivity of the complex from Beer's law (equation 1). It was found to be 42.97 $\pm$ 7.08 $lmol^{-1}cm^{-1}$ (See Table 1). This value compares well with 46.1 $lmol^{-1}cm^{-1}$ obtained by Lord and Siamwiza (6).

1.3.4 Hydrogen Bonding of Chloroform-d to Triethylamine in pure Chloroform-d.

The C-D stretching frequency was shifted by 84cm^{-1} to 2170cm^{-1} as is the case when cyclohexane is used as a solvent. To calculate α_c the C-D peak molar absorptivity of the complex, the following procedure was used: First, since the concentration of uncomplexed chloroform-d was close to that of pure chloroform-d, observed absorbance at 2254cm^{-1} of the uncomplexed chloroform-d in solution was compared to that of pure chloroform-d. The concentration of free chloroform-d was then calculated. From equation 3 the concentration of triethylamine-chloroform-d complex was calculated. Second, assuming that Beer's law holds for this complex, α_c was calculated from equation 1. Data is given in Table 2.

Assuming that the initial concentration of triethylamine has been completely complexed, α_c^* is calculated from the following equation :

$$A_{2170} = \alpha_c^* \ell C_b^o \qquad (5)$$

where A_{2170} = Absorbance at 2170 cm^{-1}

α_c^* = C-D Peak molar absorptivity (1 mol^{-1}Cl^{-1})

ℓ = cell pathlength (cm)

C_b^o = initial concentration of triethylamine (base)

α_c^* was found to be 44.35 ± 4.7 (11%) lmol^{-1}cm^{-1}. This value is smaller than 54.06, the value of α_c for the same system, but compares very well with 42.97, the value of α_c obtained for the

triethylamine - chloroform-d system in cyclohexane The higher value of 54.06 for the molar absorptivity of triethylamine in pure chloroform-d system may be indicative of the large errors involved in computing the expected small equilibrium concentration C_b of uncomplexed base. Thus at equilibrium for chloroform-d $C_D o \simeq C_D$, since, $C_D o > C_b o$ (typically $C_D o = 60 C_b o$); and for triethylamine $C_b o \simeq C_c$, so that $C_b o - C_c = C_b$ is very small. Since $C_c < C_b o$, then $\frac{A_{2170}}{\ell C_c} = \alpha_c > \frac{A_{2170}}{\ell C_b o} = \alpha^*$. Thus the assumption that triethylamine is completely complexed and that the initial concentration of base could be used in equation 1 to obtain α_c^* seems to be valid. This assumption can therefore be extended to studies of polyether bonding in pure chloroform-d.

TABLE 1.2

PROPERTIES OF TRIETHYLAMINE IN PURE CHLOROFORM-D

Initial triethylamine concentration (M)	0.20	0.20	0.23	0.28	0.40	0.40
A_{2170}	0.088	0.086	0.135	0.127	0.188	0.189
Complex concentration (M), C_c	0.18	0.18	0.21	0.25	0.28	0.28
C-D Peak absorptivity in complex, α_c ($lmol^{-1}cm^{-1}$)	46.07	44.75	59.9	47.47	62.84	63.38
Average α_c	54.06 ± 8.9					
α_c* ($lmol^{-1}cm^{-1}$)	41.65	40.48	53.53	41.94	44.14	44.38
Average α_c*	44.35 ± 4.74 (11%)					

*based on assumption that initial base concentration of triethylamine is all complexed

1.3.5 Hydrogen Bonding of Chloroform-d to 18-Crown-6

Studies were extended to the hydrogen bonding properties of chloroform-d to 18-Crown-6, a macrobicyclic polyether with six oxygen atoms. A spectrum of 0.39M solution of this compound in pure chloroform-d was obtained. A shoulder, at 2214cm^{-1}, (of the free C-D stretching frequency at 2254cm^{-1}) appeared (Fig 4.5). This indicates that oxygen atoms in this polyether are accessible to chloroform-d for hydrogen bonding. The frequency shift of 40cm^{-1} appears to be the limit of hydrogen bonding between chloroform-d and oxygen atoms (6).

1.3.6 Hydrogen Bonding of Chloroform-d to Polyethers in Chloroform-d

When the macrobicyclic polyethers (2.1.1), (2.2.1) and (2.2.2) were added to pure chloroform-d, a satellite appeared at 2190cm^{-1}, a frequency shift of 64cm^{-1}. (Figures 4.6, 4.7, and 4.8). This indicates hydrogen bonding in all of the three polyethers. No shoulder of the free C-D stretching at 2254cm^{-1} was observed as in the case of hydrogen bonding of chloroform-d to 18-crown-6, dicyclohexyl-18-crown-6, dioxane and trioxane. This shows that in the polyethers, under study, chloroform-d hydrogen bonds to nitrogen atoms only and that oxygen atoms are inaccessible.

The values of C-D peak molar absorptivity, α_c for the polyethers were calculated following the procedure outlined in the case of triethylamine dissolved in pure chloroform-d. The values were found to be 89.86 ± 8.70, 91.40 ± 8.91 and 93.35 ± 14.85 lmol^{-1}cm^{-1} for (2.1.1), (2.2.1) and (2.2.2) respectively. Assuming that the polyethers were completely complexed α_c^* values were obtained from equation 5. These were found to be 90.81 ± 4.30, 90.28 ± 13.44 and 93.18 ± 12.72 lmol^{-1}cm^{-1} for (2.1.1), (2.2.1) and (2.2.2) respectively. Table 3 summarises the data.

It is interesting to compare the molar absorptivities of an open system with one nitrogen atom (triethylamine) where the nitrogen atom is clearly accessible with that of the polyethers (2.1.1), (2.2.1) and (2.2.2) where inaccessibility of one or both nitrogen atoms to chloroform-d bonding is possible.

Thus this ratio may be indicative of the nitrogen atom(s) in the latter compounds.

The ratio α_c (polyether)/α_c (triethylamine) has the values of 1.66, 1.70 and 1.73 for (2.1.1), (2.2.1) and (2.2.2) respectively. The ratio α_c^* (polyether)/α_c^* (triethylamine) gives 2.05, 2.03 and 2.10 for (2.1.1), (2.2.1) and (2.2.2) respectively. These two sets of values of the ratio show that in the polyether compounds both nitrogen atoms are accessible to hydrogen bonding by chloroform-d. This strongly suggests that in fact the polyether compounds (2.1.1), (2.2.1) and (2.2.2) in solution exist in the "out, out" conformation (Figure 2).

TABLE 1.3

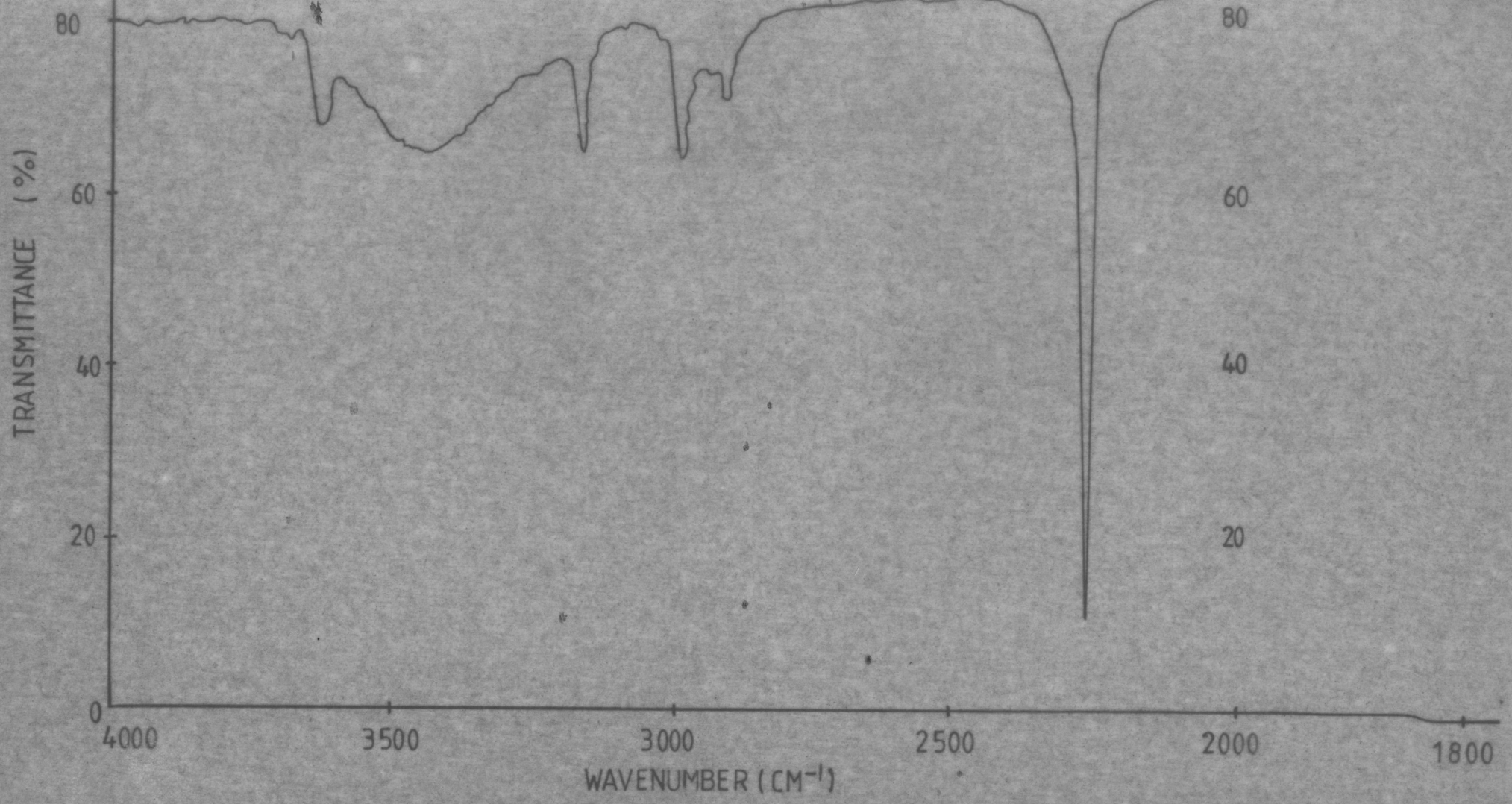
PROPERTIES OF TRIETHYLAMINE AND MACROBICYCLIC POLYETHERS IN CHLOROFORM-D

TABLE 1.3

Compound	Triethylamine	(2.1.1)	(2.2.1)	(2.2.2)	18-crown-6
Range of concentration (M)	0.20-0.53	0.076-0.36	0.10-0.26	0.17-0.42	39
Free C-D stretch (cm^{-1})	2254	2254	2254	2254	2254
Associated C-D stretch (cm^{-1})	2170	2190	2190	2190	shoulder at 2214
Frequency shift (cm^{-1})	84	64	64	64	40
C-D Peak absorptivity in complex, α_c	54.05 ± 8.90	89.86 ± 8.7	91.35 ± 14.85	93.35 ± 8.91	
C-D Peak absorptivity in complex, α_c^*	44.35 ± 4.74	90.81 ± 4.3	90.28 ± 13.4	93.18 ± 12.7	
Ratio α_c(polyether)/α_c(triethylamine)		1.66	1.70	1.73	
Ratio α_c^*(polyether)/α_c^*(triethylamine)		2.05	2.03	2.10	

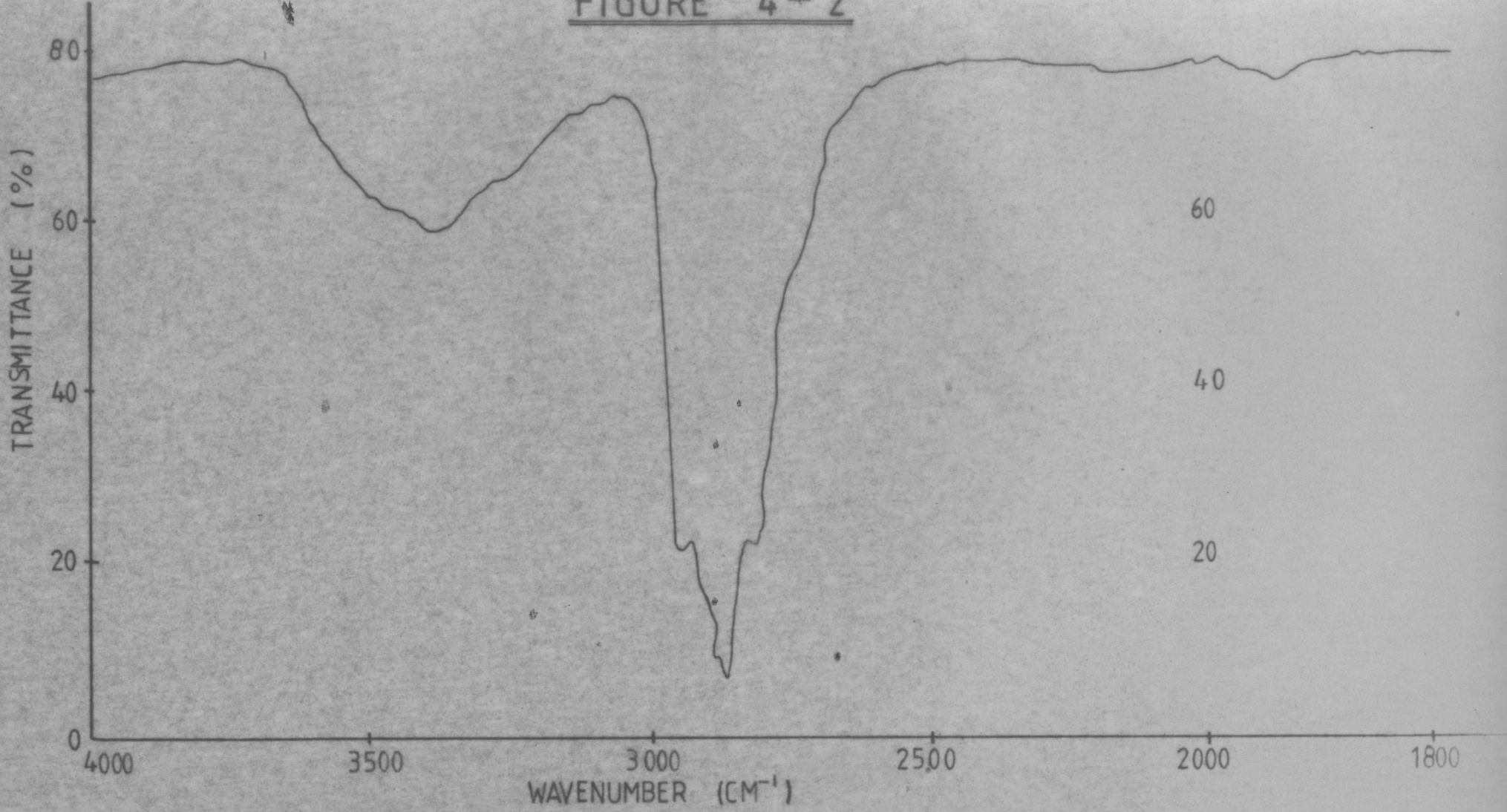
1.4 CONCLUSION

The above studies strongly indicate that the polyethers (2.1.1), (2.2.1) and (2.2.2) exist in the "out, out" conformation in solution and that oxygen atoms are inaccessible to hydrogen bonding by chloroform-d. It is therefore reasonable to assume that the molecular cavity sizes of these compounds are at their maximum in solution. This is significant because molecular cavity size is an important factor in cationic selectivity by the macrobicyclic polyethers, a subject of study in the following chapters.

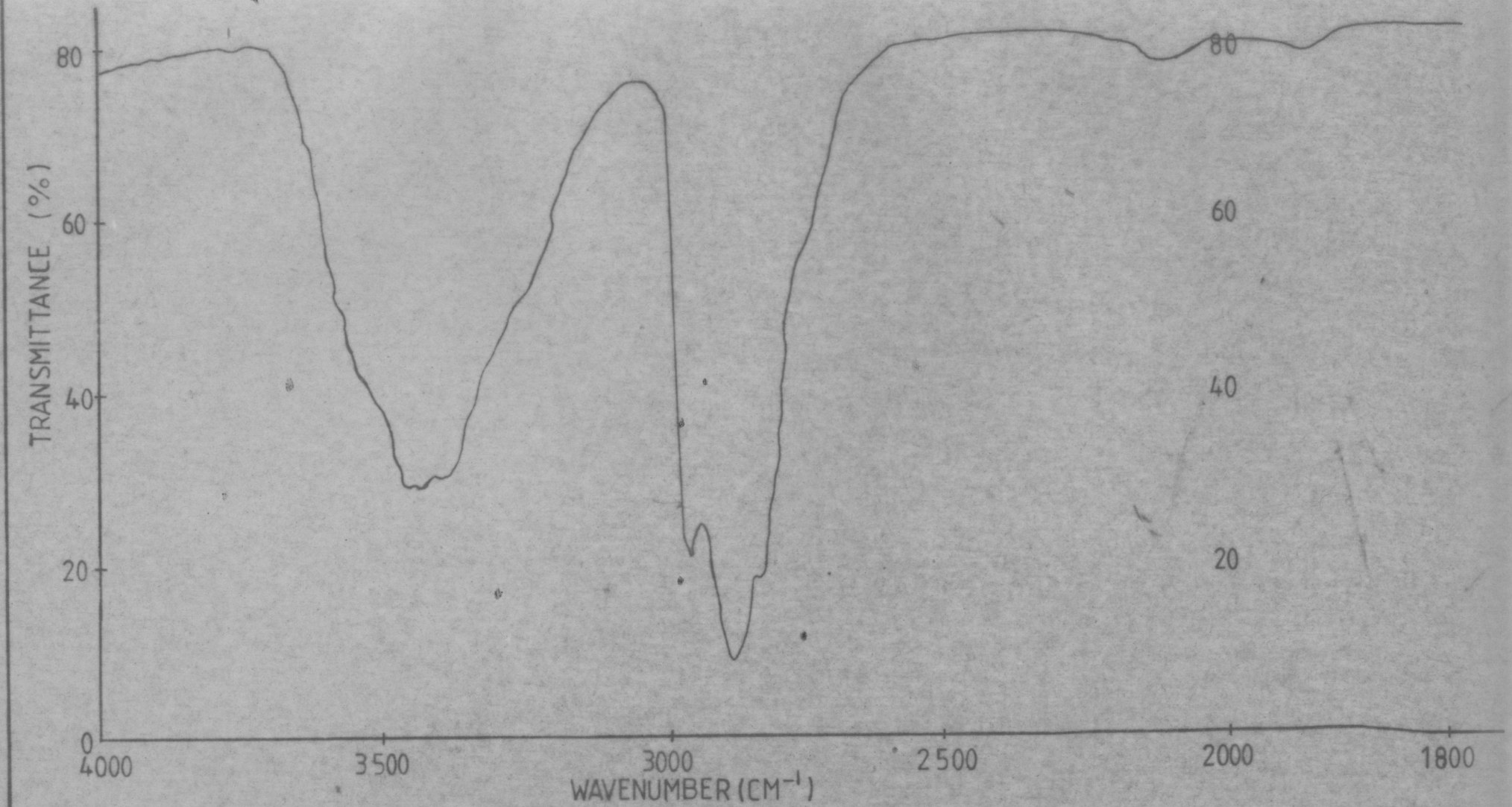


SPECTRUM OF PURE CHLOROFORM–D Vs AIR

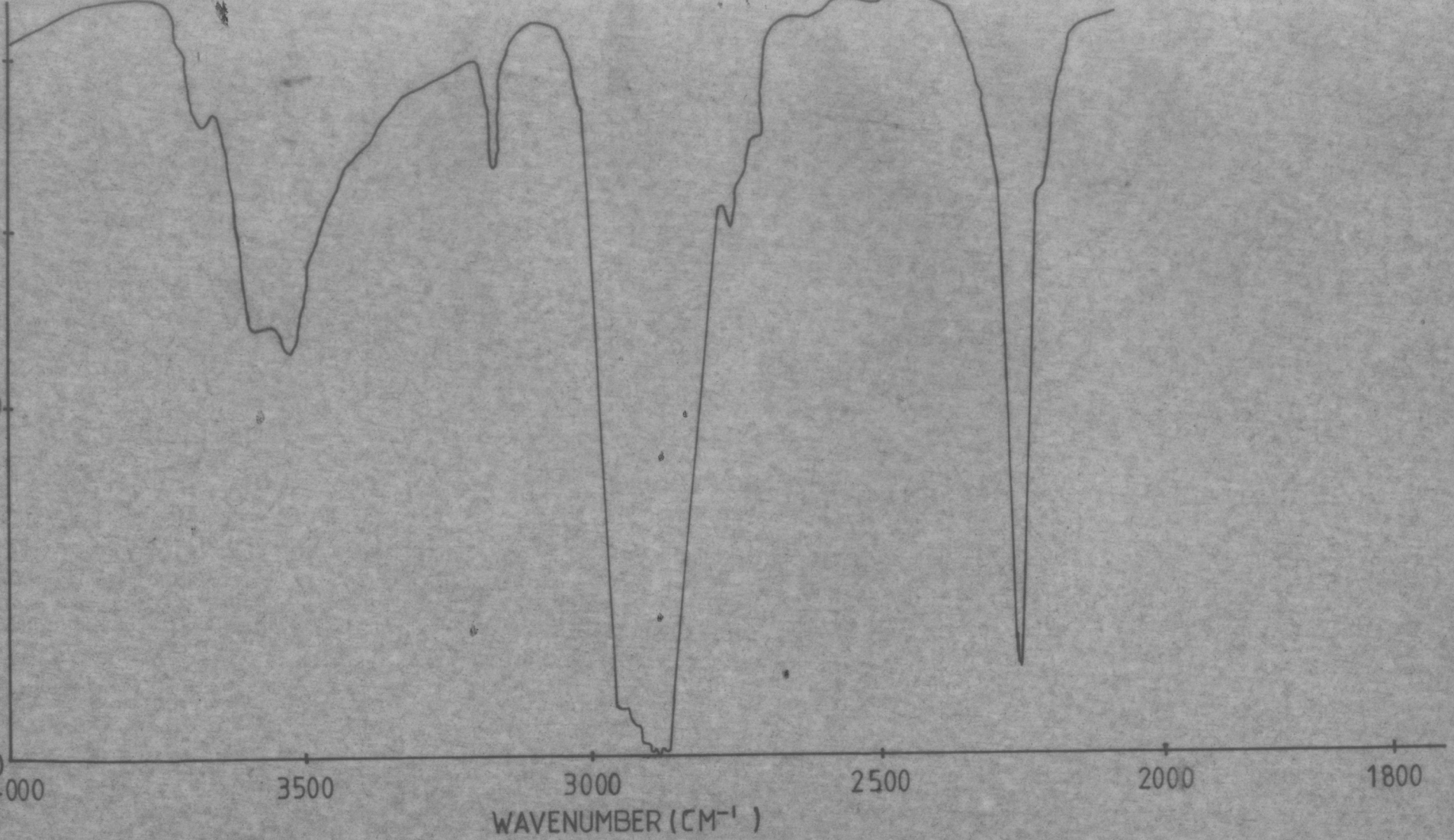
FIGURE 4.2



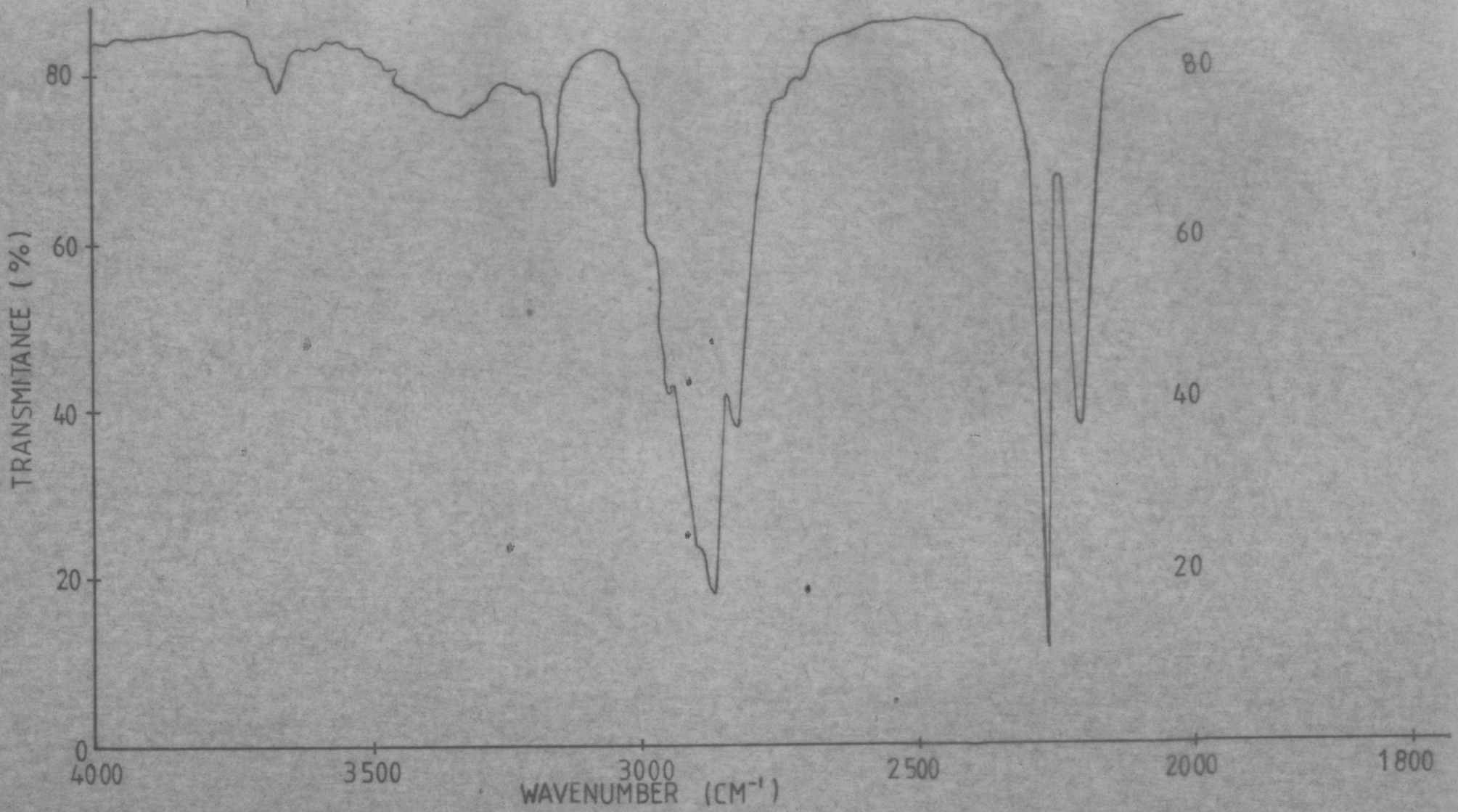
SPECTRUM OF (2·1·1) ON NACL PLATE



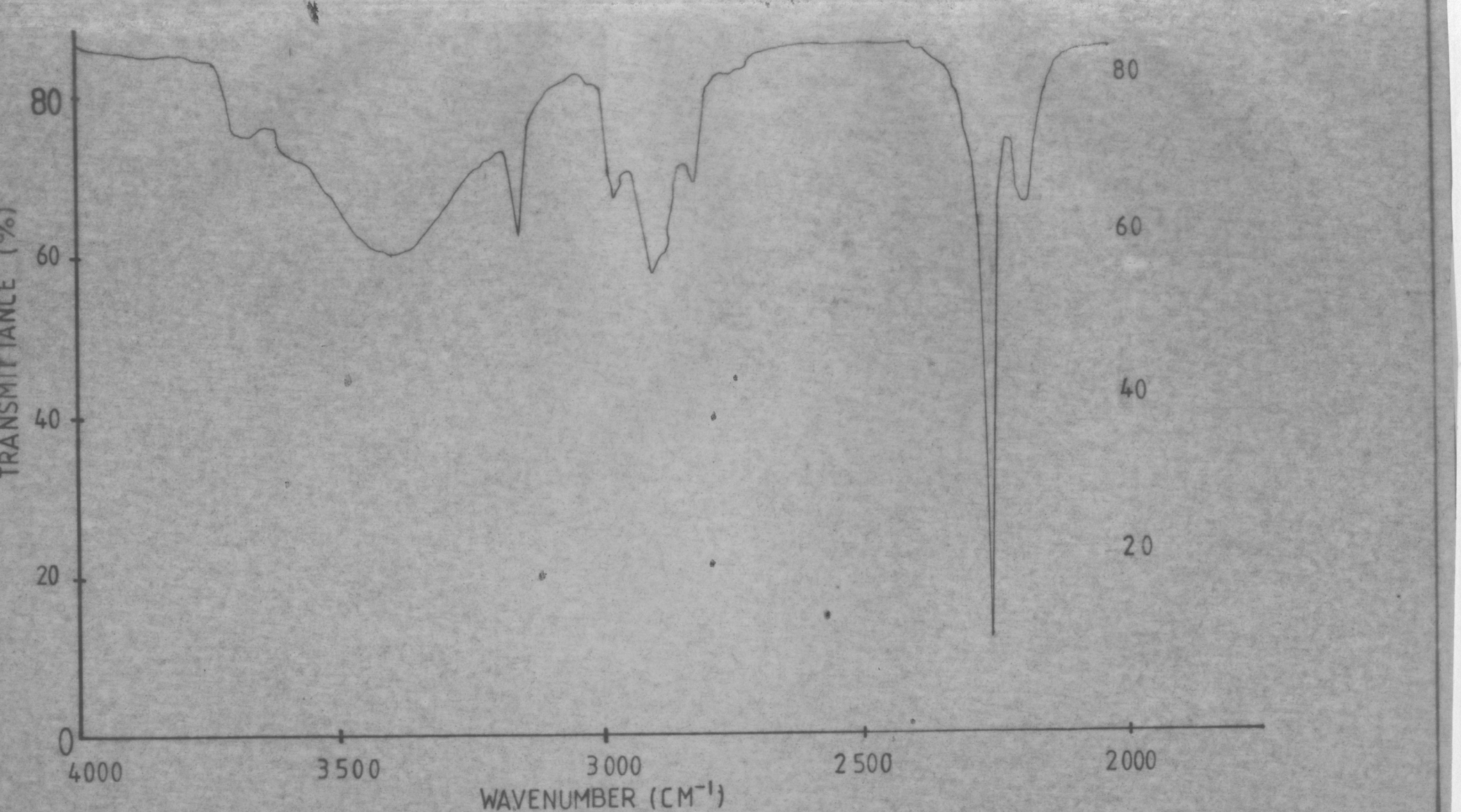
SPECTRUM OF (2·2·1) ON KBr PLATE



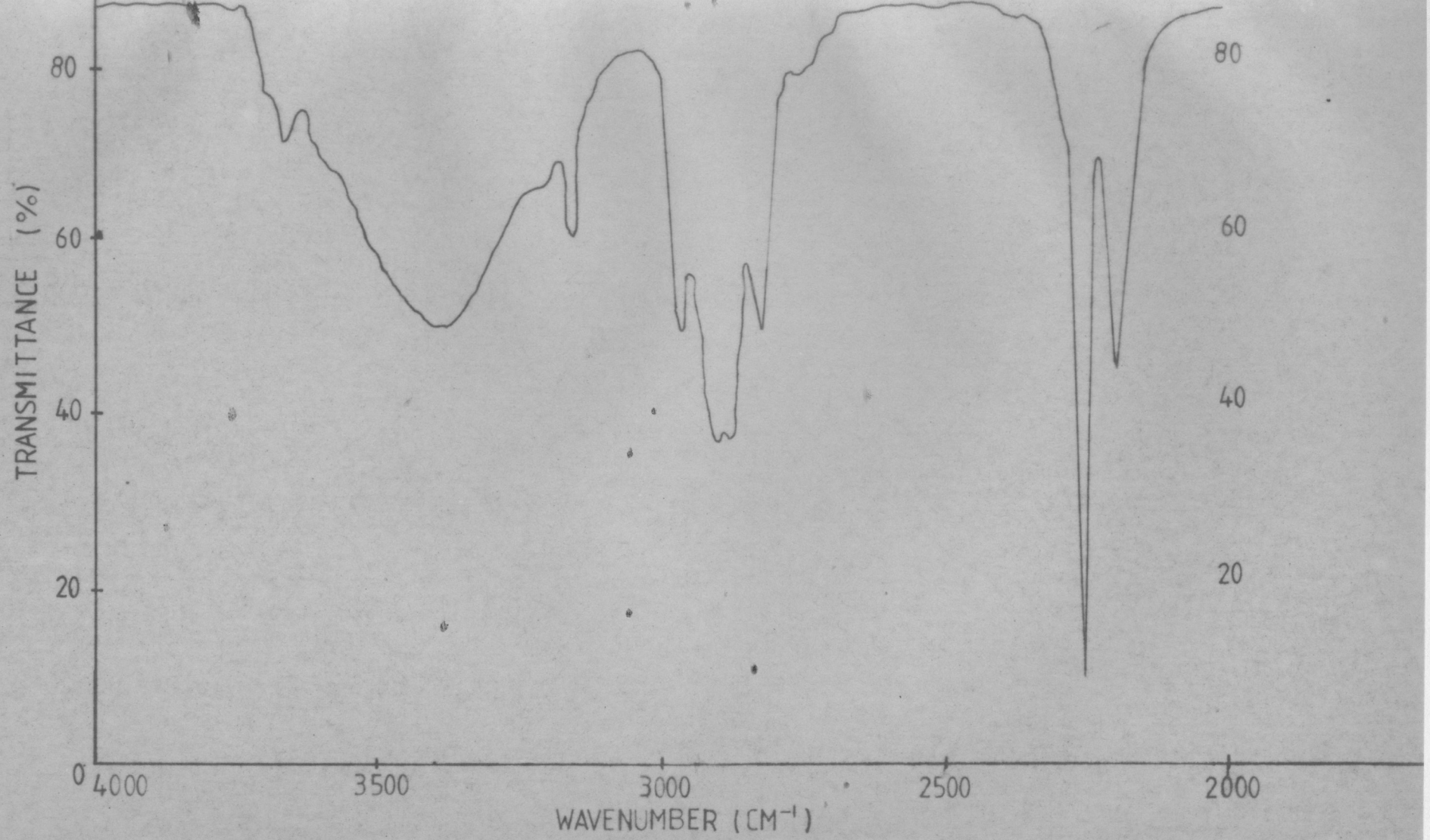
SPECTRUM OF 18-CROWN-6 (0·38M) IN PURE CHLOROFORM-D Vs AIR



SPECTRUM OF 2·1·1 (0·15M) IN PURE CHLOROFORM-D Vs AIR



SPECTRUM OF 2 2 1 (0·04M) IN PURE CHLOROFORM-D Vs AIR



SPECTRUM OF 2.2.2 (0·085M) IN PURE CHLOROFORM-D Vs AIR

CHAPTER 2

TIONIC BINDING BY MACROBICYCLIC POLYETHERS

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2.1 INTRODUCTION

Since their discovery by Pedersen in 1967 (7) macrobicyclic molecules have aroused a lot of research interest because of their highly selective binding of certain cations. These compounds have been used as models for carrier molecules in membrane studies of biological systems(8).

The macrobicyclic polyethers and other similar complexing agents have the unusual tendency to form stable complexes with alkali and alkaline earth metal ions. Complexation is shown by the solubilization of ionic compounds in nonpolar solvents such as chloroform. The resulting complexes which are termed 'cryptates' are formed by encapsulation of the cation within the cavity of the compound. Cryptation has been confirmed by X-ray analysis of the crystalline KSCN-(2.2.2) complex (9). This ability by polyethers to solubilize metal salts suggests a possible way for extracting and purifying such metals.

Complexation of metal cations by the polyethers could be followed by infra-red spectroscopy. This is based on the fact that upon complexation the polyether is in the "in,in" conformation (10) and is thus unable to hydrogen bond. The disappearance of a satellite at $2190cm^{-1}$ upon addition of the Barium thiocyanate monohydrate to the (2.2.2)-chloroform-d system was attributed to the complexation of the metal ion by the polyether (11).

In the present work, sulphate and chloride salts of copper (II), Cobalt (II) and Barium (II) were added to solutions of the polyethers and chloroform-d and

spectra were recorded. Barium was used as a reference as it has been shown to form complexes with all of the three polyethers. This work would lay down the background for further studies on selective cationic binding by the polyethers. Possible metal encapsulation would lead to the important question of whether or not Co (II) and Cu (II), ions which are currently not effectively separated could be extracted selectively by the polyethers.

2.2 EXPERIMENTAL

2.2.1 Materials

The Polyethers and chloroform-d have been described in Chapter 1. 1,1-dimethyl guanidine sulphate, $\left[(CH_3)_2NC{:}NHNH_2\right]_2 \cdot H_2SO_4$, obtained from Eastman Organic Chemicals, New York, Ferrous diaminoethane sulphate, $FeSO_4(CH_2{\cdot}NH_2)_2{\cdot}H_2SO_4{\cdot}4H_2O$, from Hopkin and Williams Ltd. and Tetraethylammonium chloride, $(C_2H_5)_4NCl$, from BDH Chemicals Ltd. were used without further purification.

Chloride salts of Ba (II) and Cu (II) were obtained from BDH Chemicals Ltd. Cobalt (II) chloride and Barium sulphate were obtained from Hopkin and Williams Ltd. The salts were used without further purification.

The concentration of the polyethers was 0.16M in chloroform-d while the concentration of the metal salts was 0.15M. And the concentration of organic salts was 0.51M.

2.2.2 Spectral measurements

Infra-red solution spectra of polyethers in chloroform-d were recorded as described in Chapter 1. Solution spectra of metal salts in solutions of polyethers and chloroform-d were also recorded. Also, spectra of ferrous diaminoethane sulphate and 1,1-dimethyl guanidine sulphate in pure chloroform-d were recorded. All spectra were recorded at room temperature.

2.3 RESULTS AND DISCUSSION

Sulphate salts of Ba (II), Cu (II) and Co (II) did not dissolve in solutions of polyethers and chloroform-d and there was no change in absorbance at 2190cm^{-1}, indicating that the cations were not complexed.

Chloride salts of Ba (II), Co (II) and Cu (II) however dissolved easily in solutions of polyethers and chloroform-d accompanied by colour change of the solutions. In the case of Co (II) the pink colour changed to blue; the copper salt changed from blue to yellowish green. Interesting spectral features were observed; there were both an increase and a decrease in absorbance at 2190cm^{-1}. Results are shown in Table 2.1. A_{2190} is observed absorbance at 2190cm^{-1} of chloroform-d hydrogen bonded to polyethers before cation encapsulation: A^{*}_{2190} is observed absorbance at 2190cm^{-1} after metal encapsulation.

Evidence for metal encapsulation by the polyethers in chloroform-d was expected to be the disappearance of the infra-red satellite at 2190cm^{-1}. It was therefore totally unexpected to observe that the satellite did not disappear. There were instead an increase and a decrease in absorbance. To try to understand these observations tetraethylammonium chloride was added to chloroform-d. A new band was observed at 2190cm^{-1} (see Table 2.2) and this was interpreted to be due to hydrogen bonding of chloroform-d to the chloride ion. Since the chloride ion can hydrogen bond to chloroform-d only after metal encapsulation has taken place (12) the above observations indicate

that the observed increase or decrease in absorbance at 2190cm^{-1} is due to chlorofrom-d bonding to the released chloride ion. It appears therefore that metal ions were encapsulated by all of the polyethers.

In both spectra of solutions of ferrous diamino-ethane sulphate and 1,1-dimethyl guanidine sulphate in pure chloroform-d a weak band interpreted as due to hydrogen bonding of chloroform-d to the sulphate ion, was observed at 2055cm^{-1} and no band was observed at 2190cm^{-1} (Table 2.2). The absence of the band at 2055cm^{-1} confirm the earlier interpretation that sulphate salts of Ba (II), Co (II) and Cu (II) were not complexed by the polyethers. Additionally, the band at 2190cm^{-1} in the spectra of metal chlorides in polyethers and chloroform-d is confirmed to arise from hydrogen bonding of chloroform-d to chloride ion.

TABLE 2.1

CHANGE ($A_{2190} - A^{*}_{2190}$) IN ABSORBANCE UPON ADDITION OF CHLORIDE SALTS (0.15M) OF Ba (II), Co (II) AND Cu (II) TO SOLUTIONS OF POLYETHERS (0.16M) IN CHLOROFORM-D

	(2.1.1)	(2.2.1)	(2.2.2)
Ba (II)	+0.11	+0.12	+0.15
Co (II)	+0.32	+0.14	-0.11
Cu (II)	-0.10	+0.22	+0.37

TABLE 2.2

PROPERTIES OF ORGANIC SALTS IN CHLOROFORM-D

Compound	Spectral observation
1,1-dimethyl guanidine sulphate	weak band at 2055cm^{-1}
Ferrous diaminoethane sulphate	weak band at 2055cm^{-1}
Tetraethylammonium chloride	Strong band at 2190cm^{-1}

2.4 CONCLUSION

On the basis of the above evidence it seems reasonable to conclude that the Chloride salts of Ba (II), Co (II) and Cu (II) have been encapsulated by polyethers (2.1.1), (2.2.1) and 2.2.2). Changes in absorbance at 2190cm^{-1} are due to hydrogen bonding of chloroform-d to chloride ion. Since covalently bonded anions are weak proton acceptors (13) the chloride ion bonds to chloroform-d after the metal ion has been encapsulated.

It is interesting to consider the decrease and increase in absorbance at 2190cm^{-1}. There are two plausible explanations. Firstly, an increase in absorbance implies that the chloride ions are completely released upon strong cationic binding by polyethers. Conversely, a decrease in absorbance shows weak complexation. Secondly, if the chloride ions are partially released an increase in absorbance would result, indicating weak complexation. To tell which of the two is the more likely explanation, it is necessary to study absorbance of triethylammonium chloride in chloroform-d at 2190cm^{-1}.

It is important to note that both Co (II) and Cu (II) have been shown to be complexed by the three polyethers. This raises the question of whether the polyethers with different molecular cavity sizes can selectively extract the two metals, with different ionic radii, from their aqueous solutions.

CHAPTER 3

SOLVENT EXTRACTION

3.1 INTRODUCTION

The separation of substances by selective extraction from one solvent into a second, immiscible with the first, is one method of de-encapsulating cations (14,15,16). In order to obtain the highest possible concentration in the solvent and the highest degree of extraction from the aqueous phase, the two phases are made to move counter-current to each other. This may be accomplished in a column where the aqueous phase sinks down and the lighter solvent rises (17). The organic phase consists of the solution of the organic extractant dissolved in an inert organic solvent.

Considerable interest is currently being shown in the use of solvent extraction in the industrial production of metals. Recently, solutions of macrobicyclic polyethers and macrobicyclic polythiaesters have been used as solvent extraction reagents for the separation of silver from mercury (18,19). The complexation of the uranyl ion with crown ethers (20) is an indicator of the possible commercial significance of crown ethers and related compounds in the mining industry.

Present metal extraction methods (21,22,23) as used on the Zambian Copperbelt are not very effective in selectively separating cobalt and copper because cobalt is lost to the copper concentrates in the form of cobalt (III) and recovery from concentrator tailings is not adequate. But copper (II) and cobalt (II) with ionic radii of 0.094nm and 0.071nm respectively appear likely to be extracted selectively by macrobicyclic polyethers, (2.1.1) (2.2.1) and (2.2.2) with different molecular cavities. An indication of this is the established relationship between the

stability of a metal macrobicyclic complex and the closeness of fit between the cation and available macrobicyclic cavity. The preferred cation is generally that which most closely fits the cavity. This requirement together with the number and nature of ligand donor atoms, provides a basis for selectivity in complex formation among metals (24).

The selective extraction of the two metals by macrobicyclic polyethers would be indicated by the partition coefficients for the species containing the metals. Assuming that both the organic and aqueous solutions obey Raoult's law the partition coefficient, D, for each solvent is given by (25)

$$D = \frac{(M)_{org}}{(M)_{aq}} \qquad (3.1)$$

where $(M)_o$ is the equilibrium concentration of the metal ion in the organic phase and $(M)_{aq}$ is the equilibrium concentration of the metal ion in the aqueous phase. Also assuming metal balance in both phases

$$(M)_{total} = (M)_{org} + (M)_{aq} \qquad (3.2)$$

where $(M)_{total}$ is the original metal concentration in the aqueous phase. Thus knowing $(M)_{aq}$, $(M)_{org}$ can be obtained from equation (3.2) and D can be calculated from equation (3.1).

3.2 EXPERIMENTAL

$20cm^3$ of aqueous chloride salts of copper (II) and cobalt (II) was mixed with $20cm^3$ of each polyether dissolved in chloroform. The concentration of cobalt (II) was $4.6 \times 10^{-3}M$ and that of copper (II) was $5.8 \times 10^{-3}M$. The solution mixtures were magnetically stirred for 25 minutes. Separation of organic and aqueous phases was done with separating funnels.

Colorimetric determination of Co (II) and Cu (II) in the aqueous phase was carried out using EEL SPECTRA colorimeter. Copper was determined as a cuprammonium ion at 650nm. This test is sensitive to about 10ppm Cu. Cobalt was complexed with ammonium thiocyanate, the complex being extracted with butyl alcohol/ether (3:1 v/v) and determined at 610nm. Also, ethylene diaminetetraacetic acid (EDTA) titrations using murexide, an ammonium salt of purpuric acid, as an indicator, were made to estimate remaining metal ion concentrations in the aqueous phase.

3.3 RESULTS AND DISCUSSION

When aqueous solutions of metal chlorides were added to solutions of polyethers in chloroform a precipitate formed at the interface, this finally settled into the organic phase.

Colorimetric and EDTA determinations were used to estimate remaining metal ion concentration in the aqueous phase. Metal ion concentration in the organic phase was obtained from equation 3.2. The partition coefficient, D, was calculated from equation 3.1. The data is given in Table 3.1.

From the data it is evident that cobalt (II) and copper (II) can be selectively extracted from their aqueous solutions by the polyethers. (2.1.1) is a very good extractant of cobalt (II) while (2.2.2) shows strong affinity for copper (II); (2.2.1) is a poor selective extractant for the two metals.

It is important to note that efficiency of the order of 80% was obtained from single extraction operations in neutral solutions (pH 7) and from small volumes of solution mixtures ($40cm^3$). Normally more than two extractions are used to obtain such efficiency levels. Further, copper is usually extracted in sulphuric acid solutions at pH 2-2.5 while cobalt is extracted at pH 5.

From the above observations two significant points emerge. First, the distribution coefficient of copper in (2.2.2) was found to be 3.7 (80% efficiency) while that of cobalt in (2.1.1) was found to be 4.8 (83% efficiency). This indicates that higher efficiency levels and possibly complete extraction could be achieved if the polyether extraction is repeated several times. The second point is that since the extractions of copper and cobalt were in

neutral solutions it may be unnecessary to separate these metals at less than pH 5. An added advantage of using solutions of the polyether (2.2.2) and (2.1.1) as extractants for copper and cobalt respectively might be the less expense and hence more economical if chloroform is replaced by kerosene as the organic phase.

TABLE 3.1

		$(M)_{org} \times 10^{-3}M$		$M_{aq} \times 10^{-3}M$		Distribution coefficient, D*	
Method	Ligand	Co^{2+}	Cu^{2+}	Co^{2+}	Cu^{2+}	Co^{2+}	Cu^{2+}
EDTA titration	(2.1.1)	3.8	1.4	0.8	4.4	4.8(83)	0.3(25)
	(2.2.1)	2.0	2.4	2.6	3.4	0.8(43)	0.7(41)
	(2.2.2)	0.9	4.6	3.8	1.2	0.2(18)	3.8(80)
Colorimetric	(2.1.1)	3.7	1.7	0.9	4.1	4.1(79)	0.4(29)
	(2.2.1)	2.1	2.2	2.5	3.6	0.8(45)	0.6(37)
	(2.2.2)	1.1	4.7	2.9	1.1	0.3(23)	4.2(81)

*Efficiency level % in brackets.

M_{total} (Copper II) = $5.8 \times 10^{-3}M$; M_{total} (cobalt II) = $4.6 \times 10^{-3}M$

Concentrations of Polyethers: (2.1.1) = $8.0 \times 10^{-3}M$

(2.2.1) = $5.2 \times 10^{-3}M$

(2.2.2) = $5.8 \times 10^{-3}M$

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