MULTINUCLEAR NMR STUDIES OF THE MACROCYCLIC EFFECT

By

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ABSTRACT

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Nuclear magnetic resonance of ^{23}Na, ^{7}Li, ^{133}Cs and ^{205}Tl were used to study the complexes of sodium, lithium, cesium and thallium(I) ions with the linear polyethers, tetraglyme (TG), pentaglyme (PG) and hexaglyme (HG) and cyclic polyethers 15-crown-5, 18-crown-6, 1,10-diaza-18-crown-6 and 21-crown-7 in various nonaqueous solvents. The stability constants of the complexes of the sodium ion with tetraglyme in the solvents studied increased in the following order, nitromethane > acetonitrile > N,N-dimethylformamide > propylene carbonate while for the pentaglyme.Na^+ complex, the stability order is as follows: nitromethane > acetone > propylene carbonate > acetonitrile. In N,N-dimethylformamide solutions, the stability constants for the thallium(I) complexes with the linear polyethers increased with increasing number of donor atoms - hexaglyme > pentaglyme > tetraglyme.

The complexation of thallium(I) ion by 18-crown-6 in acetonitrile solutions was studied by the competitive NMR technique. Plots of ^{23}Na chemical shifts as a function of 15-crown-5:Na^+ mole ratio in acetonitrile and in propylene carbonate solutions show evidence of successive formation of 1:1 and 2:1, 15-crown-5:Na^+ ion complexes. In N,N-dimethylformamide solutions, the stability

constants of the ligand:Tl^+ complexes were increased as follows: 18-crown-6.Tl^+ > 21-crown-7.Tl^+ > 15-crown-5.Tl^+. This stability order was different from that observed for the linear polyether.Tl^+ complexes where the stability increases with increasing number of donor atom.

The chemical shifts of ^{23}Na and ^{205}Tl resonances were studied as a function of ligand:metal ion mole ratio at different temperatures in acetonitrile and in N,N-dimethylformamide solutions respectively for various cyclic and their analoguous linear ligands. From the resulting data, $\Delta G°$, $\Delta H°$ and $\Delta S°$ values for the complexation reaction between the sodium and thallium ions with the ligands studied were calculated. In all the cases, a macrocyclic effect was observed for each pair of complexes, that is the stability for any cyclic complex was always higher than that of its analogous linear complex, however no definite trend was found as to the origin of this effect.

DEDICATION

In Sweet Memory of Our Daughter Ogechukwu

I can do all things through Christ who strengthens me.

Philippians 4.13

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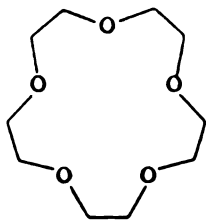
CHAPTER I

HISTORICAL PART

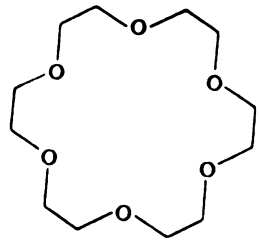
1. INTRODUCTION

Recently there has been a growing interest in the investigation of the interaction of metal ions with linear and cyclic polyethers. These interactions play a fundamental role in such processes as enzyme catalysis and inhibition, selective transport of metal ions through membranes, phase transfer catalysis and immunological response (1). There have been many studies on uncharged macrocyclic ligands, called crown ethers, which were discovered by Pedersen (2,3), and the macrobicyclic ligands, called cryptands, which were synthesised by Lehn and co-workers (4-6). A comprehensive review article has been published by Izatt et al. (7). Some studies have also been carried out with linear polyethers. Typical examples of some crown ethers, cryptands and linear polyethers are given in Figure 1.

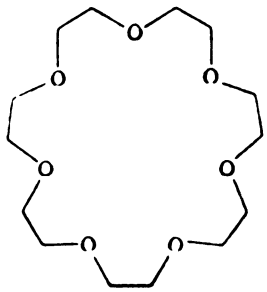
It has been observed that cyclic polyethers form more stable complexes with metal ions than with analogous linear polyethers. This increase in stability for cyclic complexes as compared to linear complexes is referred to as the "macrocyclic effect". This enhancement in stability of macrocyclic complexes over their linear counterparts could have its origin in enthalpy or entropy or both. The thermodynamic origin of the macrocyclic effect is still a controversial subject. The macrocyclic effect has been studied mainly in water and in water-methanol mixtures. Most studies have used polyaza ligands with transition metal ions. Not much work has been done with linear polyethers in aprotic solvents. It is therefore the aim of this work to investigate the macrocyclic effect of polyethers in aprotic solvents.



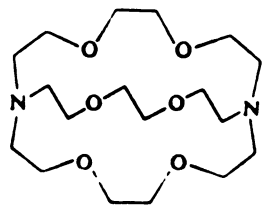
15-Crown-5
(15C5)



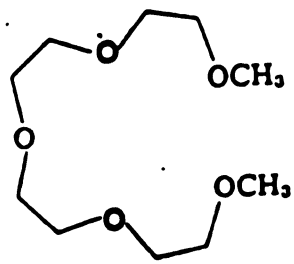
18-Crown-6
(18C6)



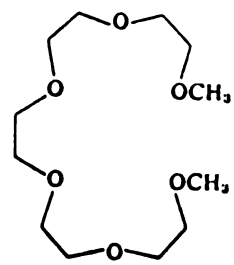
21-Crown-7
(21C7)



Cryptand-2,2,2
C222)



Tetraglyme (TG)



Pentaglyme (PG)

Figure 1: Structures of Some Macrocyclic and Linear Polyethers

2. HISTORICAL PART

a. Chelate Effect

In 1952, Schwarzenbach observed that polydentate ligands form more stable complexes with metal ions than an equivalent number of monodentate ligands with the same donor atom. This phenomenon is known as the chelate effect (8-10) and he attributed it mainly to entropy effects. For example, assuming the solvation numbers of a given metal ion is six, the formation of a complex with mono-, bi- and hexa-dentate ligands results in the release of six solvent molecules. There are however three and five new particles for the complexation processes of the bi- and hexa-dentate ligands respectively as illustrated in the following equations.

$$M(H_2O)_6 + 6NH_3 \rightleftharpoons M(NH_3)_6 + 6H_2O$$

$$M(H_2O)_6 + 3en \rightleftharpoons M(en)_3 + 6H_2O$$

$$M(H_2O)_6 + EDTA \rightleftharpoons M.EDTA + 6H_2O$$

This results in an increase in the translational entropy.

The conclusion that the chelate effect is an entropy effect was supported by subsequent work from other authors as illustrated in Tables 1 (11,12) and 2 (13-16).

Recent literature discussions on the origin and magnitude of the chelate effect have indicated that enthalpy contribution are certainly as important as entropy contributions to the chelate effect (17,18) while others have tried to throw doubt on its very existence (19,21). It should be clearly remembered,

however, that it is an experimentally observable phenomenon which finds application in the widespread use of chelating agents in areas like analytical chemistry, medicine, and bioinorganic chemistry. The factors involved in determining the enthalpies and entropies of metal chelate formation in aqueous solution are given below:

Enthalpy Effects:

Variation of bond strength with electronegatives of metal ions and ligand donor atoms.

Ligand field effects.

Steric and electrostatic repulsion between ligand donor groups in the complex.

Enthalpy effects related to the conformation of uncoordinated ligands.

Other coulombic forces involved in chelating ring formation.

Entropy Effects

Number of chelate rings.

Size of the chelate ring.

Changes of solvation on complex formation.

Arrangement of chelate rings.

Entropy variations in coordinated ligands.

Effects resulting from differences in configurational entropies of the ligand in complex compounds.

Detailed disucssion on these factors have been done by Martell (22), and by Hartley et al. (23).

A further interesting observation has been made in the case of cyclic versus linear polyethers. Consider 15-crown-5 versus tetraglyme (XXII and XXIV, Figure 2). These are both chelating ligands with the same number of chelating sites, however one is cyclic and the other is linear. Cyclic ligands form much more stable complexes with metal ions than linear ligands with the same number of donor sites. This phenomenon is known as the macrocyclic or superchelate

Table 1

Thermodynamics of Complexation of M^{2+} Ions with Mono- and Polyamine Ligands in Water

Complex	Log β_n	$\Delta H°$ kcal mol^{-1}	$\Delta G°$ kcal mol^{-1}	$\Delta S°$ cal $mol^{-1}deg^{-1}$
$Cd(NH_3)_2^{2+}$	4.95	-7.12	-6.75	-1.24
$Cd(NH_2\text{-}CH_3)_2^{2+}$	4.81	-7.02	-6.56	-1.54
$Cd(en)_2^{2+}$	5.86	-7.03	-7.97	3.12
$Cd(NH_3)_4^{2+}$	7.44	-12.70	-10.15	-8.52
$Cd(NH_2\text{-}CH_3)_4^{2+}$	6.55	-13.70	-8.94	-16.00
$Cd(en)_2^{2+}$	10.62	-13.50	-14.50	3.29
$Zn(NH_3)_2^{2+}$	5.01	6.70	-6.84	0.34
$Zn(en)^{2+}$	6.15	6.60	-8.39	6.04
$Cu(NH_3)_2^{2+}$	7.87	12.0	-10.70	-4.36
$Cu(en)^{2+}$	11.02	14.60	-15.0	1.34
$Zn(NH_3)_4^{2+}$	9.80	14.10	-13.35	-2.68
$Zn(en)_2^{2+}$	11.49	12.50	-15.67	10.74
$Cu(NH_3)_4^{2+}$	13.05	23.6	-17.8	-19.8
$Cu(en)_2^{2+}$	20.61	28.4	-28.2	-0.67

Table 2

Thermodynamic Data for Metal(II) - Polyamine Complexes In Water

M^{2+}	L	$\Delta G°$ kcal mol^{-1}	$\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal $mol\ deg^{-1}$
Ni^{2+}	dien	-5.33	-1.35	13.4
Cu^{2+}	dien	-7.24	-3.00	14.2
Ni^{2+}	trien	-8.09	0	21.7
Cu^{2+}	trien	-10.20	-1.55	29.0
Ni^{2+}	tetren	-12.10	-1.40	35.9
Cu^{2+}	tetren	-14.65	-1.75	43.3
Ni^{2+}	penten	-15.44	+1.35	56.0

dien: diethylene triamine
trien: triethylene tetraamine
tetren: tetraethylenepentaamine
penten: N,N,N',N-tetra-(2-aminoethyl)-ethylene-diamine

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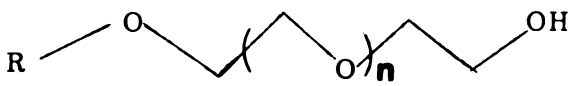
effect. The nature of this effect has not been unambiguously determined.

b. Complexes of Linear Polyethers

The thermodynamics of complex formation of non-ionic surfactants of the type,



where

$R = CH_3$,	n = 4	(A)
$R = C_{12}H_{25}$,	n = 3	(B)
	n = 22	(C)
$R = C_{16}H_{33}$,	n = 19	(D)
$R = C_{18}H_{35}$,	n = 19	(E)
$R = C_9H_{19}$	n = 11	(F)

with alkali and alkaline earth cations, have been determined by Buschman using calorimetric titrations in methanol solutions (24). Results are shown in Table 3. The author found that with an increasing number of donor atoms, the reaction enthalpies become more negative but the stability constants do not change very much due to compensating changes in entropies. The same author reported the stability constants and thermodynamic values of complex formation of several oligoethyleneglycols and their dimethylethers of the type;

$X = OH, OCH_3$,

n = 0, 1, 2, 3, 4

Table 3

Thermodynamic Parameters for the Complexation of Nonionic Surfactants with Alkali and Alkaline Earth Metal Ions in Methanol Solutions

Ligand	Cation	Log K	ΔH° kcal mol^{-1}	$T\Delta S^\circ$ kcal mol^{-1}
A	K^+	1.98	-10.3	-7.0
	Rb^+	1.77	-13.3	-9.99
	Cs^+	1.68	-8.39	-5.61
	Sr^+	3.38	-2.72	-1.70
B	K^+	3.76	-2.32	2.55
	Rb^+	4.29	-2.20	3.34
	Cs^+	3.88	-1.82	3.13
	Sr^{2+}	3.84	-0.86	3.98
	Bs^{2+}	4.40	-2.53	3.13
C	Na^+	2.07	-6.4	-3.26
	K^+	2.50	-21.0	-16.2
	Rb^+	2.56	-21.2	-16.2
	Cs^+	2.57	-17.7	13.1
	Ca^{2+}	2.48	-0.36	2.74
	Sr^{2+}	3.29	-3.37	0.98
	Ba^{2+}	2.57	-18.2	-13.5

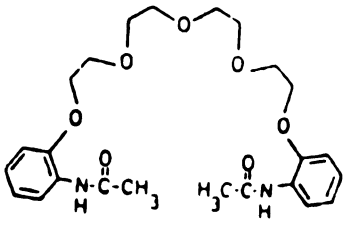
Table 3 continued

Ligand	Cation	Log K	ΔH° kcal mol^{-1}	$T\Delta S^\circ$ kcal mol^{-1}
D	Na^+	1.98	-7.15	-4.11
	K^+	2.59	-19.0	-14.2
	Rb^+	2.59	-21.6	-16.6
	Cs^+	2.42	-21.9	-17.0
	Sr^+	2.51	-5.93	-2.29
	Ba^{2+}	2.76	-14.4	-9.79
E	Na^+	2.00	-5.28	-2.35
	K^+	2.62	-17.4	-12.6
	Rb^+	2.64	-18.5	-13.7
	Cs^+	2.47	-20.5	-15.7
	Sr^{2+}	2.66	-4.61	-0.91
	Ba^{2+}	2.69	-15.6	-11.0
F	Na^+	1.52	-8.80	-6.14
	K^+	2.72	-12.6	-8.23
	Rb^+	2.77	-13.2	-8.68
	Cs^+	2.98	-10.1	-5.55
	Sr^{2+}	3.17	-3.27	0.91
	Ba^{2+}	3.68	-8.87	-3.53

with alkali and alkaline earth cations in methanol (25).

Chaput and Jeminet (26) reported that the association constants of Na^+, K^+, Tl^+ and Cs^+ ions with some polyethylene glycol ethers in methanol solutions which were obtained by potentiometric and conductometric measurements. The association constants, K_f, and the selectivity ratio, $K_f(K^+)/K_f(Na^+)$, were found to increase with the number of coordinating sites.

Attachment of rigid (e.g. aromatic) terminal groups (27-29) bearing donor atoms to oligoethylene glycol units has been found to yield neutral ligands which readily form crystalline complexes with alkali and alkaline earth metal ions in the same way as the cyclic crown ethers. Grandjean and co-workers (30) determined the thermodynamic parameters for the complexation of the ligand shown below:



with sodium cation in pyridine solution by ^{23}Na-NMR spectroscopy. A fairly strong complex (K_f of 10^3 to 101 mol^{-1} in the temperature range 5 to 50°C) is formed. From the temperature dependence of K_f, $\Delta H°_f$ = -17 kcal mol^{-1} and $\Delta S°_f$ = -48 cal mol^{-1} K^{-1} were determined. The strongly negative entropy term was explained as being reminiscent of cyclization entropy as if the Na^+ ion complexation locks the ligand molecule into a highly organized conformation;

one in which most (31,32) of the ether oxygens form van der Waals bonds with the enclosed sodium cation accounting for the magnitude of the enthalpy change. The complex formation in solution is enthalpy driven.

Tümmler and co-workers (33) studied the influences of aromatic donor end groups on the thermodynamics and kinetics of alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) complex formation with a series of open chain polyethers in methanol solutions by spectrophotometric titrations and temperature jump relaxation experiments. The ligands were found to form 1:1 complexes with the alkali metal ions with stability constants between 10^0 and 10^4 M^{-1}, depending on cation size and ligand structure as given by the number of coordinating sites and the number, donor strength and rigidity of the aromatic residue. Complex formation is characterized by large negative enthalpies (-16.7 kcal mol^{-1} < ΔH° < -4.8 kcal mol^{-1}) and by negative entropies (-43 cal mol^{-1} deg^{-1} < ΔS° < 0 cal mol^{-1} deg^{-1}) in the various systems studied. Desolvation of the metal ion and conformational change of the ligand upon complex formations contribute to different extents to changes in ΔH° and ΔS°.

Conductometric studies on the binding of alkali metal ions by poly(oxyethylenes) (with average molecular weight ranging from 200 to 2 x 10^4) indicate an increase in the K_f values in the following order Li^+ < Na^+ < K^+ < Cs^+ < Rb^+ (34). The thermodynamics for the complexation of pentaglyme with Na^+, K^+ and Ba^{2+} ions in methanol determined by microcalorimetry have been reported by Früh and Simon (35). The parameters determined are as follows:

Ligand	Cation	log K_f	ΔH° (kcal mol^{-1})	$T\Delta S^\circ$ (kcal mol^{-1})
Pentaglyme	Na^+	1.0	-9.1	-7.1
	K^+	2.1	-8.6	-5.4
	Ba^{2+}	2.3	-5.4	-2.2

The complexes are all enthalpy stabilized but entropy destabilized.

Stability constants for the reaction of Li^+, Na^+, K^+ and Rb^+ ions with polyethylene derivatives of the type $RO(CH_2CH_2O)_nR$ (R = phenyl, $6 \leq n \leq 9$) in methanol solution have been reported (36). The stability sequence for a given chain length is found to be $K^+ > Rb^+ > Na^+ > Li^+$, while for a given cation, the stability constants increases with increasing chain length. The conditional stability constants of LNa^+ complexes (where L = $HO(CH_2CH_2O)_nH$ ($5 \leq n \leq 11$) have also been determined potentiometrically in methanol solutions (37). The minimum number of oxygen atoms needed for the formation of a 1:1 complex is 6 and the maximum stability corresponds to 8 oxygens, this wraps the sodium cation completely.

Poonia et al. studied by conductometry the complexation of $M(Pic)_n$ (M = Li, Na, K^+, Cs, Mg, Cn, Sr, Ba; Pic = picrate) with glycol, diglycol and tetraglycol in water and in isopropanol (35). In water only sodium and potassium form complexes while lithium and calcium form complexes in isopropanol. The stability constants (K_f) between sodium ion and oligoethylene glycols [$HO(CH_2CH_2O)_nH$], monomethylethers [$HO(CH_2CH_2O)_nCH_3$] and dimethyl ethers [$CH_3O(CH_2CH_2O)_nCH_3$] in anhydrous methanol solutions have been reported (39). Yanagida and co-workers carried out some solvent extractions and PMR spectroscopy studies of the complexation of polyethylene glycols and the dimethyl ethers with alkali and alkaline earth cations (40-42).

Smid and co-workers studied the coordinations of fluorenyllithium, -sodium, and -potassium (F^-, M^+), and difluorenylbarium (Ba^{2+}, Fl^{2-}) with polyglycol dimethyl ethers of the general formula $CH_3O(CH_2CH_2O)_xCH_3$ ($1 \leq x \leq 6$) in dioxane and in tetrahydrofuran solutions by means of optical and nmr spectroscopy (43,44). The complexation of the glyme with the contact ion pair leads to either glymated contact ion pairs (F^-, M^+, G) or glyme separated ion pairs (F^-, G,

M^+) or to a mixture of both depending on the radius of the cation and the chain length of the glyme. The various complexation constants were found to increase with increasing number of oxygen atoms in the chain, but level off above a certain value of x depending on the size of the cation.

Höfelmann et al. conducted some esr studies on the coordination of sodium naphthalenide with tetraglyme (45). A loose ion pairs Na^+, G, $N.^-$ is formed. At sufficiently low glyme concentration ($\sim$0.006 M) both tight and loose ion pairs (Na^+, $N.^-$ and Na^+, G, $N.^-$) are formed. The gas phase basicities of several glymes have been determined by means of a pulsed electron beam high ion source pressure mass spectrometer (46). It was found that proton affinity can be correlated with the possibility of bridging two oxygens within the optimal O—H^+—O bonding distance of 2.4 A and alligning the corresponding two CH_2OCH_2 dipoles to be coaxial with the OHO axis. While the above stabilization by dicoordination is important, significant additional stabilization was obtained when the dipoles of a third and fourth CH_2OCH_2 group can be brought near the proton and placed in favorable dipole orientation. Fowles and co-workers (47) studied the reactions of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Fe^{2+} with 1,2-dimethoxyethane. Manganese, iron, cobalt and nickel halides were found to form thermally stable complexes.

c. Macrocyclic Effect

The term macrocyclic effect was first used by Cabbiness and Margerum (48) to describe the greater stability of metal complexes with cyclic polyaza ligands than those with open chain ligands of analogous structure. The macrocyclic effect is a Gibbs free energy term for the metathetical reaction given below:

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$$[ML]^{n+} + L' \rightleftharpoons [ML']^{n+} + L \qquad (1)$$

L = non-cyclic ligand

L' = cyclic ligand

For a complexation reaction

$$M^{n+} + L \rightleftharpoons ML^{n+} \qquad (2)$$

The stability constant for the complex formed is given by

$$K_f = \frac{a_{ML^{n+}}}{a_{M^{n+}} \cdot a_L}$$

where $a_{ML^{n+}}$, $a_{M^{n+}}$ and a_L represent the activities of the product and reactants respectively. The free energy for the reaction can be expressed as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_f \qquad (3)$$

where ΔH° and ΔS° stand for the enthalpy and entropy respectively while T is the temperature.

In order to understand the thermodynamics of a complexation reaction, it is necessary not only to determine the stability constant of a complex but also to divide it into enthalpic and entropic contributions. There are altogether four possible combinations of the thermodynamic parameters (ΔH° and ΔS°) which result in stable complexes ($\Delta G^\circ < 0$).

a) $\Delta H^\circ < 0$ and dominant; $T\Delta S^\circ > 0$. The complex is enthalpy and entropy stabilized with the primary contribution coming from the enthalpy of complexation.

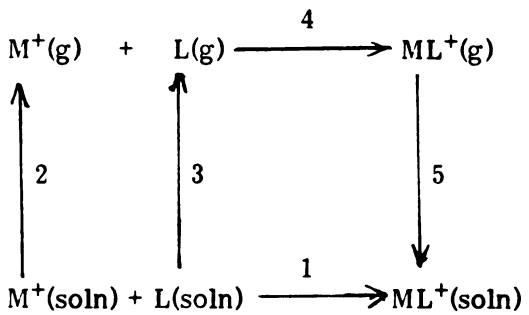
b) $\Delta H^\circ < 0$; $T\Delta S^\circ > 0$ and dominant. Again the complex is enthalpy and entropy stabilized with the primary contribution coming from the entropy of

omplexation.

c) $\Delta H^\circ < 0$ and dominant; $T\Delta S^\circ < 0$. The complex is enthalpy stabilized but entropy destabilized.

d) $\Delta H^\circ > 0$; $T\Delta S^\circ > 0$ and dominant. The complex is entropy stabilized but enthalpy destabilized.

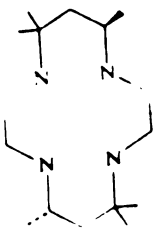
A thermochemical cycle for the complexation of a metal ion M^+ with a ligand L, is shown below:



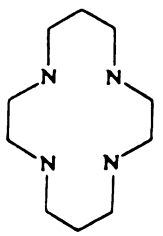
$$\Delta X_1 = \Delta X_2 + \Delta X_3 + \Delta X_4 + \Delta X_5$$

$$\Delta X = \Delta G, \Delta H \text{ or } \Delta S$$

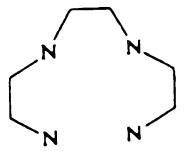
The cyclic ligands and their linear analogues studied so far by various authors are given in Figure 2. The enhanced stability of macrocyclic complexes over their linear analogues may be due to the enthalpy or the entropy changes or to both. Attempts thus far to separate the macrocyclic effect of the metathetical reaction (1) into ΔS° and ΔH° contributions have not led to unambiguous interpretations. Cabiness and Margerum (48) reported in water, an enhancement in stability for Cu^{2+} complexes of cyclic tetraamine ligand (I), Log K = 28, over that of its linear counterpart (II), Log K = 23.9. This increase in stability could not be explained simply in terms of entropy. Conformation and solvation of the ligand were proposed to be more important than entropy change.



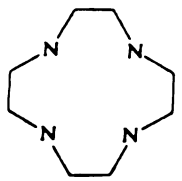
Tert a (I_a)



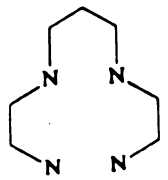
Cyclam (I_b)



2,3,2, tert (II)



cyclen (III)



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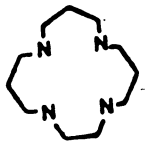
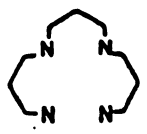
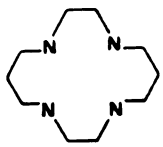


Va



VIa



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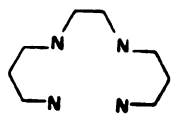
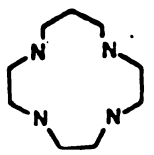


VI

Figure 2: Structures of Some Macrocyclic and Analogous Linear Ligands



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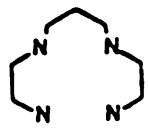
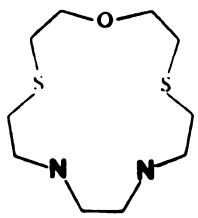
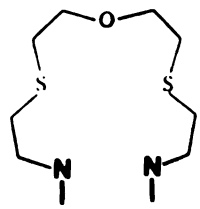


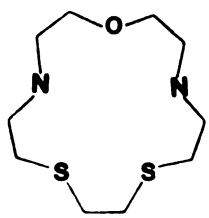
VIII



VIIa



VIIIa



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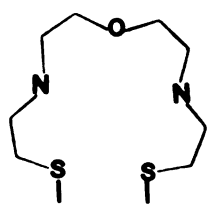

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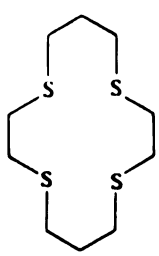

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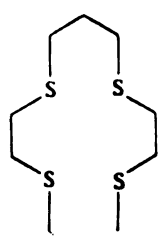
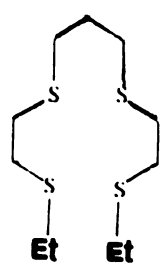
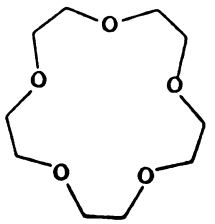


XII



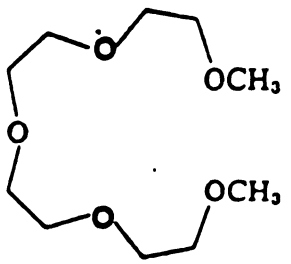
XIIb

Figure 2: continued



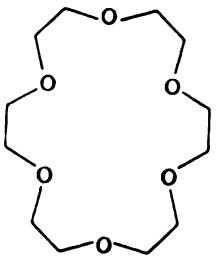
15-Crown-5

XIII



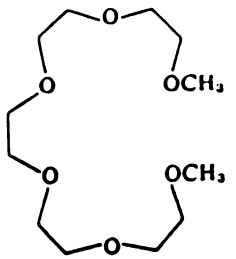
Tetraglyme

XIV



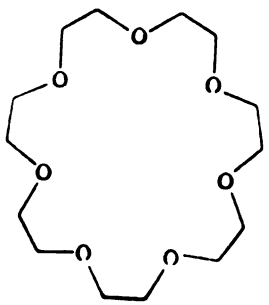
18-Crown-6

XV



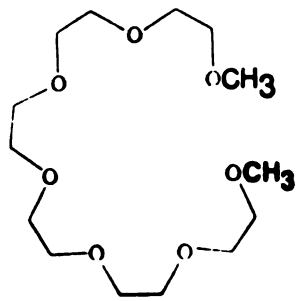
Pentaglyme

XVI



21-Crown-7

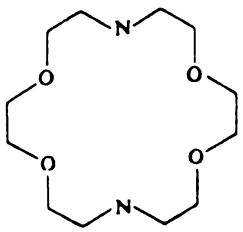
XVII



Hexaglyme

XVIII

Figure 2: continued

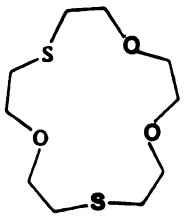


1,10 Diaza 18-Crown-6

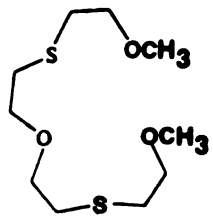
XIX

$H_2NCH_2(OCH_2)_4CH_2NH_2$

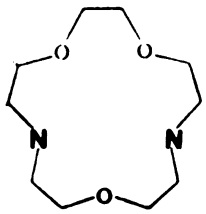
XX



XXI



XXII



XXIII

XXIV

Figure 2: continued

Later, Hinz and Margerum (49,50), as well as Smith and co-workers (51) reported that when the formation constants of Ni^{2+} complexes of cyclam(I) and those of 2,3,2 tert(II), are compared in water, the enthalpy term predominates in the macrocyclic effect. In fact, in this system, entropy changes are in opposition to the macrocyclic effect. Hinz and Margerum assumed that the desolvation step for the Ni^{2+} ion is the same in both reactions and, therefore considered the desolvation step of the ligand. For the reaction shown below, the primary solvation number (y) of the ligand is variable:

$$Ni(H_2O)_x^{2+} + L(H_2O)_y \rightleftharpoons NiL(H_2O)_z^{2+} + (x+y-z)H_2O$$

Therefore, ΔH° for the reaction increases as the enthalpy of solvation of L increases and ΔS° increases as y increases due to the additional water molecules released in the reaction. For a macrocyclic ligand, ΔH° is more negative than for a noncyclic ligand because the macrocyclic is less solvated by water due to steric hindrance. It then follows that ΔS° must be less positive because fewer water molecules are released from the ligand. There is, however, another contribution to the ΔS° of reaction, which is due to the change in the conformational entropy. One would expect a greater loss in conformational entropy of the open-chain ligand to form its complex than in the reaction of the macrocyclic ligand to form its complex.

Dei and Gori (52) reached the same conclusions with Cu^{2+} complexes of the same ligands in water. They determined the enthalpies of reaction for Cu^{2+} with cyclam(I) and 2,3,2 tert(II) in ethanol-water and in acetonitrile-chloroform mixtures. It was suggested that the macrocyclic effect is due to both stronger copper(II)-nitrogen bond interactions for the $Cu(cyclam)^{2+}$ complex and to favorable solvation enthalpy contributions. All the results discussed thus far are listed in Table 4.

Table 4

Thermodynamics of Formation of Some Nitrogen Donor Macrocyclic and Linear Complexes

Ligand	Cation	Solvent	Log K at 25°C	ΔH° kcal mol^{-1}	$T\Delta S$ kcal mol^{-1}	Ref.
Ia	Cu^{2+}	H_2O	28.0	-	-	48
II			23.9	-	-	
Ia	Ni^{2+}	H_2O	22.2	-31.0	- 0.6	49,
II			15.8	-19.4	2.1	50
Ia	Cu^{2+}	CH_3CN-	-	-61.9	-	52
II		-CH_3Cl (70%)	-	-55.0	-	
Ib	Cu^{2+}	Ethanol	-	-42.9	-	52
II		-Water (50%)	-	-31.7	-	
III	Cu^{2+}	H_2O	24.8	-18.3	15.3	54
IV			20.1	-21.6	5.8	
III	Cu^{2+}	H_2O	24.8	-22.7	9.9	59
IV			20.2	-21.6	5.3	
III	Zn^{2+}	H_2O	-	14.5	-	59
IV				-8.9	-	
Ib	Cu^{2+}	H_2O	29.1	-29.2	9.2	59
II			23.9	-27.7	4.5	
Va	H_2O	Cu^{2+}	24.4	-26.5	7.6	59
VIa			17.3	-19.5	3.5	

In 1973, Paoletti and co-workers (53) presented some preliminary studies on the thermodynamics of Cu^{2+} complexation of cyclen(III) and 2,2,-tert(IV) and proposed that the macrocyclic effect results from a combination of favorable enthalpy and entropy changes. After further studies (54,55), they found that in the above system, the entropy term was primarily responsible for the macrocyclic effect (Table 4). Thus the conclusions of Hinz and Margerum (cyclam-Cu^{2+} or Ni^{2+} in water) and those of Paoletti et al. (cyclen-Cu^{2+} in water) are completely opposite. However, it really does not seem that the apparently small difference in ligand sizes and metal ions should produce such drastically different results. Space filling models show that Ni^{2+} or Cu^{2+} fit into the cavity of the larger cyclam; this has been confirmed by crystal studies (56-58). Molecular models show that cyclen is too small to accommodate either of these ions.

In a later paper, Paoletti and co-workers (59) examined in greater detail, the disagreement between their results and those of Hinz and Margerum. They measured by microcalorimetry, the enthalpy of formation of Cu^{2+} and Zn^{2+} ions with ligand (I,III,V) and their linear analogues in aqueous solutions. They concluded that the macrocyclic effect is due to a favorable entropy term as well as to a normally favorable enthalpy term (Table 4). The favorable entropy term results from the fact that before coordination, the macrocyclic ligand, unlike its linear counterparts, is already in the conformation which is favorable for the formation of the complex. It will therefore, not lose configuration entropy to the same extent as the linear ligand upon complex formation. They also found that while the entropy went through a maximum with the best size match (cyclam.Cu^{2+}), the entropy of the macrocyclic complexes decreased steadily with increasing size and decreasing rigidity of the macrocyclic ligands. The macrocyclic effect was therefore interpreted as being due to a favorable entropy

term and to a normally favorable enthalpy term, the magnitude of which is critically dependent on the matching size of the metal ion to that of the cavity in the macrocyclic ligand.

Kodama and Kimura (60-62) studied polorographically, the equilibria and kinetics of reactions of Zn^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+} ions with 12- to 15-membered tetraamine ligands and their linear counterparts (I-VIII) in acetate buffer solutions (Table 5). They attributed the greater stabilities of the macrocyclic complexes as compared to their linear counterparts to favorable entropy changes regardless of the metal ion size. The same authors also studied in aqueous solutions, the equilibria of complex formation between Pb^{2+} and Tl^{+} ions with cyclic polyether 18-crown-6 and the linear polyether tetraglyme (62b). They reported the macrocyclic effect to be entirely due to favorable entropy countributions. It should be noted however, that tetraglyme has one fewer donor oxygen atom than 18-crown-6 and the two ligands are not strictly comparable (Table 5).

Clay and co-workers (63) determined the heats of combustion of macrocyclic and non-cyclic tetraaza ligands (I and II) and their standard enthalpies of formation were derived (-27.7 ± 0.5 and -23.9 ± 0.5 kcal mol^{-1} respectively). Enthalpies of solution of the same two compounds were determined (-2.5 and -15.8 kcal mol^{-1} respectively) in 0.5 M NaOH. The gas phase ΔH°_{f} values of the ligands were estimated and the macrocyclic enthalpy term, previously determined for both Cu^{2+} (-4.7 kcal mol^{-1}) and Ni^{2+} (-4.9kcal mol^{-1}) (64), were compared with the estimated differences in solvation energies of the two ligands (4.6 kcal mol^{-1}). These authors discussed the enthalpy term in the macrocyclic effect as originating from three terms, namely

a) differences in solvation energies of the ligands;

b) differences in solvation energies of the two complexes (which are difficult to estimate precisely), and

c) differences in metal-nitrogen bond energies in the two complexes in the

gas phase.

They suggested that the differences in solvation energies of the ligands play an important part in the macrocyclic enthalpy. Further studies by the same authors (65) on the standard enthalpies of sublimation and vaporization of the same ligands led them to conclude that in solution, the macrocyclic enthalpy is almost entirely due to the differences in solvation enthalpies of the uncoordinated ligands in agreement with the conclusion suggested by Margerum earlier (49).

Frensdorff (66) compared the complexes of sodium and potassium cations with pentaglyme and with 18-crown-6 in methanol solution. He noted a 10^3-10^4 enhancement of the stability constant in the cyclic complexes and suggested that the lower stability in the open chain ligand results from its inability to completely envelop the cation because of electrostatic repulsion between the terminal oxygens and the loss in entropy involved in wrapping the ligand around the cation. Enthalpy and entropy of complexation of some of the systems studied by Frensdorff have been determined (67). The thermodynamic values for the 18C6·Na^+, K^+, and Ba^{2+} systems in methanol (Table 5) did not yield consistent trends in $\Delta H°$ or $\Delta S°$ to explain the macrocyclic effect. While the sodium complex is entropy stabilized, the potassium complex is totally enthalpy stabilized and the barium complex is both enthalpy and entropy stabilized, but the enthalpy term is dominant. These results show that the macrocyclic effect depends very much on the systems studied and that different systems may be responding to different stabilizing factors.

Ligands with mixed types of donor atoms do not seem to show a macrocyclic effect. Frensdorff (66) studied the complexes of silver ion with 1,10-diaza-18C6 (XIX, Log K = 7.8) and a similar linear ligand (XX, Log K = 7.9) with fewer donor atoms in aqueous solution and found no indication of a macrocyclic effect. The

Table 5

Thermodynamics of Formation of Several Macrocyclic and Analogous Linear Complexes

Ligand	Cation	Solvent	Log K at 25°C	$\Delta H°$ kcal mol^{-1}	$T\Delta S°$ kcal mol^{-1}	Ref.
III	Cd^{2+}	H_2O	14.3	- 8.2	11.3	62b
IV			10.4	- 9.2	5.7	
III	Cu^{2+}	H_2O	24.8	-18.3	14.0	62a
IV			20.0	-21.6	5.0	
III	Zn^{2+}	H_2O	16.2	- 7.9	14.0	61
IV			12.1	- 8.9	7.5	
18C6	Pb^{2+}	H_2O	4.4	- 3.1	9.7	61
Tetraglyme			0.5	- 3.2	-8.3	
18C6	Na^{+}	99% wt.	4.33	- 8.11	-2.20	67
Pentaglyme		MeOH	1.0	- 9.14	-7.7	
18C6	K^{+}	99% wt.	6.05	-13.21	-4.96	67
Pentaglyme		MeOH	2.27	- 8.16	-5.06	
18C6	Ba^{2+}	99% wt.	7.0	-10.38	-0.83	67
Pentaglyme		MeOH	2.51	- 5.64	-2.22	

same ligands were studied by Anderegg (68) with Cd^{2+} and Hg^{2+} ions also in aqueous solution and again no macrocyclic effect was observed. It must again be pointed out that in these cases, the cyclic and linear ligands used are not strictly comparable since the linear ligand has fewer atoms as well as fewer donor atoms than the cyclic ligand.

Izatt and co-workers (68) reported an absence of the macrocyclic effect for ligands containing mixed donor atoms (XXI, XXII). They studied linear sulfur and oxygen containing ligands and their cyclic analogues with Hg^{2+} and Ag^{+} ions in aqueous solution (Table 6). These systems are complicated by the formation of both 1:1 and 2:1 (ligand:metal) complexes. The enthalpies for the first step in the complexation reaction of the cyclic ligand (XXI) are nearly identical with that of the linear ligand (XXII). The 2:1 cyclic complexes were found to be less stable than the 2:1 linear complexes. Crystal structures of both 1,4-dithia-18C6-$HgCl_2$ (69) and 1,4-dithia-18C6-$HgCl_2$ (68) show that the metal ions are bound externally. If similar structures exist in solution, then it is not surprising that the macrocyclic effect is absent, since only part of the ring participates in the complexation reaction.

Arnaud-Neu et al (70-73) carried out some potentiometric, spectrophotometric, and calorimetric studies on the complexation of macrocyclic ligands containing three different heteroatoms and their linear counterparts (VII-X) with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+} and Pb^{2+} ions in aqueous solutions. Their results are presented in Table 5. A macrocyclic effect was observed for Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} and Ag^{+} ions, the magnitude being strongly dependent on the nature of the cation. For Zn^{2+} and Pb^{2+} ions, an inverse macrocyclic effect was observed that is, the open chain ligands form more stable complexes than their macrocyclic analogues. Enthalpic measurements on the complexation of Cu^{2+} and Pb^{2+} with ligands (IX and X) show that in the case of Cu^{2+}, the macrocyclic effect displayed by the complex is equally

Table 6

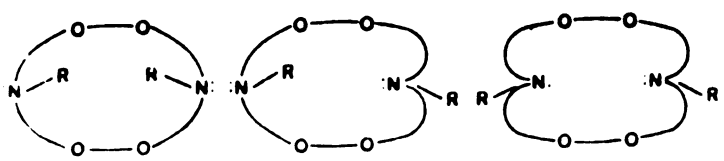
Thermodynamics of Fromation of Metal Complexes of Cyclic and Noncyclic Ligands in Water

Ligand	Cation	Solvent	Log K at 25°C	$\Delta H°$ kcal mol^{-1}	$T\Delta S°$ kcal mol^{-1}	Ref.
XXI	Ag^+	H_2O	2.70b	-16.57a (-1.0)b	2.80b	68
XXII			3.06b	-14.13a (-3.68)b	-0.68b	
XXI	Hg^+	H_2O	2.91b	-16.10a (-5.0)b	- 1.0b	68
XXII			3.22b	-14.02a (-7.09)b	-3.64b	
IX	Cu^{2+}	H_2O	13.26	-12.54	18.52	70
X			9.15	- 9.56	9.08	
IX	Pb^{2+}	H_2O	6.78	- 9.52	-0.96	70
X			7.49	- 9.54	2.25	

a) For reaction M + L ML
b) For reaction ML + L ML_2

due to favorable enthalpic and entropic contributions (Table 6). For the lead complexes, the absence of the macrocyclic effect is due to the fact that enthalpic term is negligible, while the entropy term is more favorable for the formation of the linear complex.

Buschman (74-77) studied the compelxation reactions of Pb^{2+}, Ag^{+}, Ba^{2+}, Co^{2+} and Ni^{2+} cations in methanol solution, with a variety of noncyclic ligands, crown ethers and aza-crown ethers by potentiometric and calorimetric titrations. The macrocyclic effect was observed for ligands containing only oxygen as the donor atoms, it is caused by favorable entropic contributions for the cyclic ligands. On introducing nitrogen atoms into the ligands, the macrocyclic effect disappears. No variation in complex stability was observed between the cyclic and the noncyclic ligands. The reaction enthalpies for the cyclic ligands are, in fact, equal or smaller than those of similar linear ligands. The author explained this observation by the possible existence of different conformers of the ligand (see below). These results are listed in Table 7.



exo-exo exo-endo endo-endo

Different conformational forms of uncomplexed aza-crowns.

Table 7

Thermodynamics of Formation of Metal Complexes of Cyclic and Acyclic Ligands in Methanol

Ligand	Cation	Solvent	log K at 25°C	$\Delta H°$ kcal mol^{-1}	$T\Delta S°$ kcal mol^{-1}	Ref.
15C5	Pb^{2+}	MeOH	3.92	- 5.90	- 0.56	74
Tetraglyme			2.06	- 1.72	- 1.08	
18C6	Pb^{2+}	MeOH	> 5	-10.75	-	74
Pentaglyme			2.22	-6.30	-3.27	
18C6	Ag^{+}	MeOH	4.58	-9.35	-3.10	75
Pentaglyme			1.80	-3.78	-1.43	
21C7	Ag^{+}	MeOH	2.46	-6.69	-3.59	75
Hexaglyme			1.82	-5.50	-3.11	
XXIII	Ag^{+}	MeOH	7.63	-8.27	-2.15	75
XXIV			8.55	-13.96	-2.39	
15C5	Ba^{2+}	MeOH	4.04	-5.0	0.55	76
Tetraglyme			2.15	-2.96	-0.24	
18C6	Ba^{2+}	MeOH	7.38	-11.59	-1.55	76
Pentaglyme			2.59	-4.83	-4.30	
21C7	Ba^{2+}	MeOH	5.44	-6.81	0.60	76
Hexaglyme			2.65	-6.76	-10.52	
XXIII	Co^{2+}	MeOH	6.4	1.24	10.61	77a,b
XXIV			2.25	-3.87	-0.81	
XXIII	Ni^{2+}	MeOH	4.90	5.69	12.33	77a,b
XXIV			5.32	-2.22	5.0	

Haymore (78) et al. studied K^+, Na^+ and Ba^{2+} complexes of pentaglyme, pentaethylene glycol and 18-crown-6 in methanol and water methanol mixtures by calorimetric titrations. These authors found that the macrocyclic effect results from less favorable enthalpy factors for the noncyclic ligands, but did not agree with Margerum and co-workers that the favorable enthalpy term for the cyclic ligand is mostly due to ligand solvation enthalpy. The addition of water to the methanol caused a decrease in the observed macrocyclic effect in all the cases studied, due to less favorable enthalpic changes (Table 8). They concluded that given a wide variety of solvents, ligand sizes, number and types of donor atoms, metals etc., a combination of factors at the molecular level is responsible for the presence or absence of the macrocyclic effect; in a specific case, one given factor may predominate.

Huang and co-workers (79) reported the observation of what they referred to as "mechanistic macrocyclic effect" in low pressure gas phase ion molecule reactions involving the transition metal ions Cr^+ and Fe^+ with the cyclic polyether 12-crown-4 and its linear analogue. They reported that the cyclic polyether is much more reactive to Cr^+ and Fe^+ than its linear analogue. The enhanced reactivity of the cyclic polyether as compared to the noncyclic ligand was explained as being apparently due to the fact that the cyclic ligand forces a greater number of oxygen atoms into close proximity with the metal ion during the brief ion molecule-collision, while only part of the linear polyether oxygen atoms reacts with the metal centers. Such processes they noted are not observed in solution, since the ligand interaction energy is quickly dispersed to solvent molecules.

The origin of the macrocyclic effect has also been examined from a kinetic viewpoint. The stabilities of macrocyclic complexes are due to the slow rate of decomplexation reaction. Cabbiness and Margerum (80) found that the

Table 8

Thermodynamics of Formation of Na^+, K^+ and Ba^{2+} Complexes of 18-Crown-6 and Pentaglyme in Methanol and in Methanol-Water Mixtures

Ligand	Cation	Solvent	Log K at 25°C	$\Delta H°$ kcal mol^{-1}	$T\Delta S°$ kcal mol^{-1}	Ref.
18C6	Na^+	MeOH	4.36	-8.36	-2.41	78
Pentaglyme			1.44	-4.02	-2.06	
18C6	K^+	MeOH	6.06	-13.41	-5.14	78
Pentaglyme			2.1	-8.70	-5.8	
18C6	Ba^{2+}	MeOH	7.04	-10.41	-0.81	78
Pentaglyme			2.3	-5.55	-2.4	
18C6	K^+	90% wt.	5.35	-11.77	-4.47	78
Pentaglyme		MeOH	1.95	-7.00	-4.34	
18C6	Ba^{2+}	90% wt.	6.56	-10.33	-1.38	78
Pentaglyme		MeOH	2.33	-7.10	-3.92	

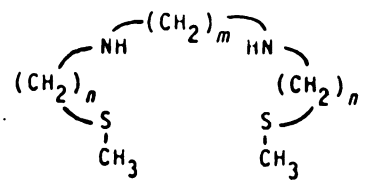
decomplexation rate for the Cu^{2+} cyclic tetraamine complex is much slower than that of its linear counterpart. The decomplexation rate is so slow that it overshadowed the slow formation rate of the cyclic complex. Busch and co-workers (81) attributed the enhanced stability exhibited by the macrocyclic complexes compared to their linear analogues to what they termed "multiple juxtapositional fixedness" (essentially configurational effects) in which emphasis has been placed on the relative rigidity of the complexed cyclic ligand resulting in an apparent increase in the difficulty of sequentially breaking the metal-donor atom bonds. A study by Jones and co-workers (82) supports this kinetic approach to understanding the macrocyclic effect. They determined the rates of forward and reverse reactions for complexes of Cu^{2+} with tetrathia analogue of the tetraamine ligands used by Margerum and co-workers. Their results show that the slow decomplexation rate of the cyclic tetrathia complex is responsible for its extra stability over the complex of the linear ligand. The authors concluded that configurational effects are responsible for the stability of the cyclic complex and that these effects should manifest themselves primarily in the entropy term. Furthermore, they suggested that solvation effect must be important only in the decomplexation step, and therefore only for the complexed species and not for the free ligand. These results are listed in Table 9.

Kanden and co-workers (83) recently reported some potentiometric, spectrophotometric and cyclic voltametric studies on some open chain N_2S_2 ligands and their macrocyclic analogues (shown below) with Cu^{2+} and Cu^{+}.

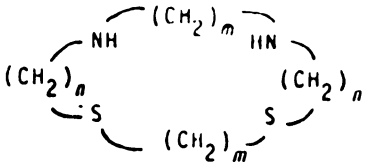
Table 9

Kinetic Data for Cu^{2+} Complexes at 25°C

Ligand	Cation	Solvent	K_f M^{-1} S^{-1}	K_d S^{-1}	Ref.
Ia	Cu^{2+}	H_2O	5.8×10^{-2}	3.6×10^{-7}	80
II			8.9×10^{4}	4.1	
XI	Cu^{2+}	80%	2.8×10^{4}	9	82
XIIb		MeOH	4.1×10^{5}	3.0×10^{4}	



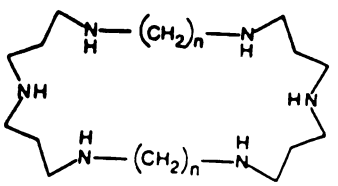
n = m = 2
n = 2, m = 3
n = 3, m = 2
n = m = 3

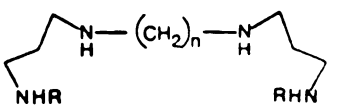


n = m = 2
n = 3, n = 2
n = m = 3

A macrocyclic effect was found in the case of Cu^{2+} complexes but not for those of Cu^{+}. The redox potentials span a larger interval for the macrocyclic than for the open chain complexes and the ligand field strength is very different for the two types of ligands. Hancock et al. (84) reported the stabilities of the complexes of the metal ions Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+} and Hg^{2+} with some nitrogen donor and mixed (O,N) donor macrocycles and open chain ligands. They observed that for all the complexes of the mixed donor ligands, the macrocyclic effect is much smaller than is the case for all nitrogen donor analogues. Their observations were discussed in terms of ligand related contributions to the macrocyclic effect such as steric hindrance to the solvation of the free ligand.

Hossein and Lehn (85) determined the stability constants of complexes between the protonated forms of some macrocyclic and acyclic polyamines (shown below) with terminal dicarboxylates, $^{-}O_2C\text{-}(CH_2)_m\text{-}CO_2^{-}$, amino-acid and dipeptide dicarboxylates by pH-metric measurements.





n = 7, 32

n = 10, 38

n = 3, 24

Compelxes of the acyclic ligands were found to be much weaker and much less selective when compared to their cyclic analogue indicating a pronounced macrocyclic effect on both stability and selectivity of binding.

Wipff and co-workers (86) reported some molecular mechanistic studies of different conformations of 18-crown-6, pentaglyme and their alkali metal complexes. Calculations gave ΔE for K^+·18-crown-6 of 61.8 kcal mol^{-1} (crystal field stabilization energy, q_o = -0.6) with the use of Ci structure for the uncomplexed crown and D_{3d} for the complex. This is comparable to the interaction energy of 59.0 kcal mol^{-1} for the reaction, K^+ + pentaglyme "(D_{3d})" ——> complex "(D_{3d})". However, pentaglyme is significantly more stable in the all-trans conformation and so the net reactions for its interaction with K^+ is reduced to 46 kcal mol^{-1} (q_o = -0.6). Thus the significantly greater affinity of K^+ for 18-crown-6 than for pentaglyme could have an important enthalpic contribution coming from the greater stability of conformations other than those that can effectively interact. The macrocyclic effect is thus expected to decrease when the dielectric constant of the medium increases.

Quantitative studies on ligand solvent interactions of several cyclic and acyclic polyether ligands in nonaqueous solvents have been conducted in this laboratory (87) by carbon-13 NMR and IR spectroscopy, to determine the effect of ligand solvation on the thermodynamics of metal ligand complexation. The equilibrium constant for metal cation ligand complexation is given by the following expression:

$$M^+ + L \underset{}{\overset{K}{\rightleftharpoons}} ML^+$$

$$K = \frac{[ML^+]}{[M^+][L]}$$

where M^+ refers to the metal cation, L to the ligand, and ML^+ to the complex. Experimentally, in solvents which also forms complexes with the crown ether, a conditional equilibrium constant, K', is measured. This conditional equilibrium constant can be defined by the following expression:

$$M^+ + L' \underset{}{\overset{K'}{\rightleftharpoons}} ML^+$$

$$K' = \frac{[ML^+]}{[M^+][L']}$$

where [L] is the concentration of the ligand uncomplexed by M^+. The concentration [L'] includes the concentration of ligand in all its solvated forms as shown:

$$[L'] = [L] + [SL] + [SLS]$$

where [L] is the concentration of crown not complexed by the solvent and [SL] and [SLS] are the concentrations of the 1:1 and 1:2 ligand:solvent complexes, respectively. The thermodynamic and conditional equilibrium constants are related to one another by the following expression:

$$K' = \alpha_L K$$

$$\alpha_L = \frac{1}{1 + K_1[S] + K_1K_2[S]^2}$$

In the above expression, [S] is the concentration of monomeric solvent and K_1 and K_2 are the formation constants for the 1:1 and 1:2 ligand-solvent complexes, respectively.

Using the above equation and the values of K_1 and K_2 obtained for some cyclic and linear polyethers with various solvents, α_L was calculated to see the effect of ligand-solvent interaction on the stabilities of ligand-metal ion complexes. The values obtained are listed in Table 10. From these values, it can be seen that the α_L value for the complex formed by nitromethane and 18-crown-6 is twenty times larger than that for the complex between nitromethane and pentaglyme (PG). On the other hand, there is no difference in the α_L values for 15-crown-5 and tetraglyme (TG) in acetonitrile, methanol and chloroform. These results indicate that differences in solvation of cyclic and linear polyethers does not account for the macrocyclic effect.

Table 10

Values of α_L Calculated for the Solvent-Ligand Interactions

Solvent	Ligand	α_L	K^a (M^{-1})
NM	18C6	3.39×10^{-3}	294.65 K'
NM	15C5	0.1495	6.69 K'
NM	21C7	6.57×10^{-2}	15.22 K'
NM	PG	0.114	8.79 K'
NM	Tg	0.155	6.44 K'
NM	C222	0.278	3.60 K'
NM	B15C5	0.269	3.72 K'
AN	18C6	1.89×10^{-2}	52.85 K'
AN	15C5	0.1759	5.69 K'
AN	TG	0.1722	5.81 K'
AN	B15C5	0.1587	6.30 K'
MeOH	18C6	3.31×10^{-3}	302.3 K'
MeOH	15C5	5.04×10^{-3}	198.6 K'
MeOH	TG	8.26 x 10-3	121.0 K'
MeOH	B15C5	4.13×10^{-3}	242.1 K'
$CHCl_3$	18C6	0.1183	8.46 K'
$CHCl_3$	15C5	0.1436	6.96 K'
$CHCl_3$	TG	0.1237	8.08 K'
$CHCl_3$	B15C5	0.2061	4.85 K'
AC	18C6	>0.363	>2.75 K'
AC	15C5	0.300	3.33 K'

[a] K and K' refer to the thermodynamic and conditional formation constants, respectively, for M^+-L complexation.

3. NUCLEAR MAGNETIC RESONANCE

a. Introduction

Since the discovery of nuclear magnetic resonance (NMR) spectroscopy in the 1940's (88,89) this technique has had a tremendous growth and a wide application to many chemical problems. Because of its steady development, both theoretical and instrumental, nuclear magnetic resonance spectroscopy has now reached such an advanced stage that it is almost an indispensable tool for chemists.

Nuclear magnetic resonance measurements are specific for each nucleus, and can be used for quantitative and qualitative determinations of species in solution. Resonance frequencies of metal ions are very sensitive probes of the immediate chemical environment of these ions and therefore can be used to detect very weak ion-ion, ion-ligand and ion-solvent interaction. Nuclear magnetic resonance of alkali cations and of the thallium ion has been used extensively for studying ionic solvation, ionic association, and preferential solvation of alkali cations and thallium ion and in complex formation with a variety of ligands in aqueous as well as in nonaqueous solutions.

b. Chemical Shift Measurements

For nuclei with adequate NMR sensitivity, observation of signals at low enough concentration to allow determination of stability constants should be possible. All of the alkali metals and thallium posses at least one isotope with a magnetic nucleus, i.e. ^{7}Li, ^{23}Na, ^{39}K, ^{87}Rb, ^{133}Cs, ^{205}Tl. The nuclear properties of these nuclei are listed in Table 11. Except for ^{205}Tl the spin is greater than 1/2, therefore, alkali nuclei have a quadrupole moment, hence broad resonance lines can be expected. In practice however, due to small values

Table 11

Nuclear Properties of Alkali Elements and Thallium

Nuclear	Resonance Frequency (MHz) at 14.09 kgauss	Natural Abundance(%)	Spin	Sensitivity Relative to ^{1}H at Constant Field
^{7}Li	23.315	42.57	3/2	0.294
^{23}Na	15.868	100	3/2	9.27×10^{-2}
^{39}K	2.800	93.08	3/2	5.08×10^{-4}
^{87}Rb	19.630	72.8	3/2	0.177
^{133}Cs	7.864	100	7/2	4.74×10^{-2}
^{205}Tl	34.319	70.48	1/2	0.192

for the quadrupole moments, $Q < 0.1/10^{28}$ m^2, with the exception of ^{87}Rb where $Q > 0.1/10^{28}$ m^2, the resonance lines are narrow and in the case of ^{7}Li, and ^{133}Cs, the natural linewidths are less than 1 Hz (90). In most cases therefore, chemical shifts can be measured precisely.

The position of a nuclear magnetic resonance signal is determined by the total shielding that the nucleus under investigation receives from various sources. This shielding is expressed by the screening constant, σ. A general formula for σ has been developed by Ramsey (91-93). According to Ramsey's equation, the screening constants, σ, is the sum of various diamagnetic and paramagnetic contributions:

$$\sigma = \sigma_d + \sigma_p$$

where σ_p and σ_d are the paramagnetic and diamagnetic components respectively.

Saika and Slichter (94) divided the screening constant into three independent contributions represented by:

$$\sigma = \sigma_d + \sigma_p + \sigma_o$$

The σ_d term is related to the local diamagnetic currents in the molecule and arises from the induced magnetic field due to the circulation of electrons around the nucleus; σ_p is usually the dominant term, and it arises from the interaction of ground state with excited electronic states in the presence of a magnetic field. The diamagnetic shielding constant is positive ($\sigma_d > 0$), while the paramagnetic term is negative ($\sigma_p < 0$). Contributions from other atoms to the shielding of the resonant nucleus are contained in the σ_o term. Unless one is considering proton chemical shifts, the σ_o term can be ignored. For

the heavier nuclei, σ_p is so much larger than σ_d that the later term can be ignored (95).

Kondo and Yamashita (96) proposed the theory of paramagnetic interaction. They suggested that the paramagnetic shift of cations and anions in alkali halide crystals is due to the short range repulsive forces between the closed shell of the ions. These forces can excite p orbital electrons of the alkali nuclei to the higher states, so that the net result would be a decrease in the shielding of the nucleus.

The success of the Kondo-Yamashita theory in interpreting chemical shifts in solids suggested that it may also provide some way for interpreting the chemical shifts in solution. In this case, however, the problem is more complex. In solids, the relative positions and distances of separation of the ions are known, but in solution, the environment of the nucleus will vary randomly with time because of the diffusion of the ions and solvent molecules through the solution and the observed chemical shift will result from an average of many instantaneous values.

Deverell and Richards (97) applied the Kondo-Yamashita theory to provide a qualitative interpretation of the cation chemical shifts in aqueous solutions. They suggested that at infinite dilution, where the only interactions present are between the ion and water molecules, the contribution to the paramagnetic shift is given by

$$\sigma_{aq}^{\circ} = -16\alpha^2 \langle 1/r^3 \rangle_{np} \cdot 1/\Delta \cdot \Lambda^{\circ}_{\text{ion-water}}$$

where α is a fine-structure constant, $\langle 1/r^3 \rangle_{np}$ is the average over the outer p orbitals of the central ion, Δ is the mean excitation energy, and $\Lambda^{\circ}_{\text{ion-water}}$

is an approximate sum of the overlap integrals of the orbitals of the central ion and surrounding water molecules.

By increasing the concentration of the solution, the interaction between the ions during collision will also contribute to the chemical shift. The chemical shift at concentration C, can be expressed as

$$\sigma = -16\alpha^2 < 1/\gamma^3>_{np} \cdot 1/\Delta \cdot [\Lambda^c_{ion\text{-}water} - \Lambda^c_{ion\text{-}ion}]$$

where $\Lambda^c_{ion\text{-}water}$ and $\Lambda^c_{ion\text{-}ion}$ represent the ion-water and ion-ion interactions respectively. Ikenberry and Das introduced a more exact equation by including the effects of overlap and charge transfer covalency. The magnitude of paramagnetic screening for an alkali nucleus is proportional to $< 1/r^3>_{np} \cdot 1/\Delta$. Since $<1/r^3>$ and $1/\Delta$ both increase with increasing atomic number (98), the magnitude and the range of σ_p increases from Li^+ to Cs^+ ions. Therefore, the range of chemical shifts varies from about 10 ppm for Li^+ to several ppm for Cs^+ ions.

c. Multinuclear NMR Studies of the Complexation of Tl^+ and Alkali Ions in Solution.

In recent years the use of multinuclear NMR for the studies of the thermodynamics and kinetics of reactions in solution has expanded very rapidly. To a very great extent, this progress is due to the development of Fourier transform NMR spectroscopy.

Lithium-7 NMR has been used for determining formation constants of lithium complexes with polymethylenetetrazole in nitromethane (99). It was found that lithium ion forms a fairly strong complexes with a convulsant tetrazole

in nitromethane (Log K_f = 3.85 - 4.97).

Lithium ion complexes with cryptands C222, C221 and C211 in water and in several nonaqueous solvents have been studied by Cahen et al. using ^7Li NMR technique (100). They showed that the first two ligands form weak 1:1 complexes with Li^+ ion solvents of low donicity such as nitromethane. One the other hand, cryptand 211 was found to form a much more stable complex and two ^7Li resonances (corresponding to the free and the complexed Li^+) were observed for solutions containing excess of the Li^+ ion. The resonance of the Li^+ ion inside the cryptand cavity was found to be independent of the solvent indicating that the ligand completely insulates the cation from the solvent.

The kinetics of the complexation reaction of Li^+ ion with cryptand 211 in water and several nonaqueous solvents have been investigated by temperature-dependent ^7Li NMR (101). The activation energy for the release of Li^+ from the complex was found to be larger in solvents with higher Gutman donor number.[a] The exchange rates and thermodynamic parameters of lithium cryptate exchange in various solvents were determined from the ^7Li NMR temperature dependent data.

Hourdakis and Popov (102) have used ^7Li, ^{23}Na and ^{133}Cs NMR to study alkali complexes with cryptand C222-dilactans in various solvents. Smetana and Popov (103) studied complexes of Li^+ ion with several crowns ethers in various solvents using ^7Li NMR.

Sodium-23 NMR measurements were used to study many antibiotic ionophores in chloroform and in methanol solutions (104). In all cases, addition of ionophores to the sodium ion broadens the ^{23}Na resonance lines. Despite the similar nature

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[a] The Gutmann donor number is a quantitative measure of the solvating power of solvents. It is defined as the negative enthalpy value (in kcal mol^{-1}) for the 1:1 adduct formation between antimony pentachloride ($SbCl_5$) and the solvent molecule (S) in 1,2,dichloro-ethane (1,2-DCE), as an inert solvent

$$S + Sb \xrightarrow{1,2\text{-DCE}} S.SbCl_5$$

$$\text{Donor Number} = - H_{S.sbCl_5} \text{ (kcal mol}^{-1}\text{)}$$

of the complexes, the ^{23}Na chemical shifts were found to be very different for different antibiotics. The complexation of Na^+ ion with pentamethylene tetrazole in nitromethane has also been studied by ^{23}Na NMR (105).

Addition of crown ethers such as 18-crown-6 derivatives, to a sodium salt solution in various solvents has been shown to result in an appreciable broadening of the sodium-23 resonance so that the resonance line could not be detected (106,107). This is because most crown ethers tend to form two-dimensional complexes with the alkali ions which could distort the spherically symmetrical electric field around the solvated sodium ion and, therefore, broaden the ^{23}Na resonance line.

Sodium-23 NMR have been extensively used to study the exchange kinetics of Na^+ ion with crown ethers (108,109) and cryptands (110-112) in different solvents. Shchori et al. (108,109) have investigated the kinetics of Na^+ ion complexes of dicyclohexyl-18-crown-6 and dibenzo-18-crown-6 and its derivatives in various solvents. The life times of free and complexed sodium ion and the pseudo first-order rate constant for the decomplexation rate have been found from line shape analysis as a function of temperature. Different substituent groups on the ligands had a significant effect on the decomplexation reaction.

Dye and co-workers (110,112) obtained two resonance signals for Na^+-C222 cryptate solutions with the excess of the sodium salt in various solvents. One signal corresponds to the sodium ion inside the cryptand cavity, and the other corresponds to the uncomplexed solvated sodium ion. The rate constants, activation energies and thermodynamic parameters for the decomplexation reaction were obtained from line shape analysis of the ^{23}Na NMR temperature-dependent data.

Strasser et al. (113) studied the influence of anions on the kinetics of complexation of Na^+ ion with the crown ether 18-crown-6 in tetrahydrofuran

solution by sodium-23 NMR. It was found that with BPh_4^- anion, the exchange of the Na^+ ion between the free and complexed sites is slow at room temperature and two distinct ^{23}Na resonances were observed in solutions which contain an excess of the Na^+ ion. The predominant exchange mechanism is the dissociative one. However, when SCN^- is the counterion, the exchange is fast at room temperature and the predominant exchange mechanism is the bimolecular process. Kinetic data were obtained by a full sodium-23 NMR line shape analysis.

Shih and Popov (114) studied complexation reaction between K^+ ion and several crown ethers and cryptands in various nonaqueous solvents by ^{39}K NMR spectroscopy. They found evidence for formation of an inclusive complex between K^+ ion and cryptand C222 but an exclusive one for K^+-C221 cryptate in solution. The K^+-18-crown-6 complexes were found to be quite stable in nonaqueous solvents. It was found that 15C5 forms both 1:1 and 2:1 sandwich complexes with K^+ in all nonaqueous solvents used.

Shporer and Luz (115) studied the longitudinal relaxation time T_1 of the potassium-39 nucleus as a function of temperature in methanol solutions in the presence of dibenzo-18-crown-6 by ^{39}K-NMR. The rate of the decomplexation reaction and the activation energy for the reaction were calculated.

Popov and coworkers (116-120) studied both the kinetics and thermodynamics of crown ethers and cryptand complexes with Cs^+ ion in nonaqueous solvents. From ^{133}Cs chemical shift measurements as a function of ligand-to-metal mole ratio, they obtained evidence of a two-step complexation reaction between Cs^+ ion and 18-crown-6. The formation of a 1:1 complex is followed by the addition of a second molecule of crown to give a 2:1 sandwich complex. The kinetics of complexation of Cs^+ ion with large crown ethers, dibenzo-21-crown-7 and dibenzo-24-crown-8 have been studied in acetone and in methanol solutions

by cesium-133 NMR (121). In all the systems studied, the predominant mechanism of exchange between the solvated and complexed Cs^+ ion sites is the bimolecular process. The kinetic parameters for the exchange were reported.

Thallium-205 has been proposed as a useful probe for the role of potassium ion in biological systems (122) becuase of its relatively large NMR sensitivity, which is 285 times higher than that of the ^{39}K nucleus. Also its ionic diameter (2.80 A) is similar to that of potassium ion (2.66 Å). The sovlent dependence of chemical shifts for ^{205}Tl is over 2600 ppm (123) in contrast to a shift of $\approx$ 8 ppm for ^{7}Li (124,107), $\approx$30 ppm for ^{23}Na (125,126) and $\approx$ 120 ppm for ^{133}Cs (128). Chemical shift measurements of ^{205}Tl have been made by Freeman et al. (127,128) for different thallium salts; thallium(I) hydroxide, fluoride, acetate, formate, nitrate and perchlorate of varying concentrations. In these salts, the ion pair formation is greatest for the hydroxide ion and least for the perchlorate ion.

Thallium-205 NMR has been used for studying preferential solvation (123,129) and the relative solvating ability of the solvent in binary solvent mixtures (130). The order of preferential solvation toward the dimethylthallium ion is hexamethylphosphoramide > DMA > DMF > pyridine.

The studies of Tl^+ ion solvation in aqueous amide, mixed amide, water/pyridine water DMSO and pyridine/DMSO mixed solvents were carried out by Hinton et al. (131,132). The results indicate that the structural effects of the solution are important in determining preferential solvation in solution. Covington's nonstatistical distribution theory was used to study preferential solvation of thallium(I) ion in nine binary solvent systems. Using this theory, the equilibrium constants and free energies of preferential solvation were obtained by Hinton et al. (133). Ion pair formation constants have also been reported by the same authors (134,135).

Popov and coworkers (152) reported formation constants of thallium(I) complexes with macrocyclic ligands of different structures but nearly the same cavity obtained by thallium-205 NMR techniques. In a given solvent, the complexing abilities of the ligand is found to vary in the order DA18C6 > DC18C6 > DB18C6 > DT18C6.

4. CONCLUSIONS

From the above discussion, it is evident that multinuclear NMR provides a very powerful tool for studies of complexation reactions in solution. Information on the thermodynamics of complexation can also be obtained by this method. The subject of this thesis is a multinuclear NMR study of the macrocyclic effect.

CHAPTER II

EXPERIMENTAL PART

1. MATERIALS

a. Salts

Sodium tetraphenylborate (Aldrich Chemical Company) was used as received except for drying under vacuum at 45°C for three days. Sodium perchlorate (Matheson Chemical Company), and sodium chloride (J.T. Baker) were dried at 110°C for three days. Thallium(I) nitrate (Alfa Chemicals) and thallium(I) perchlorate (K&K Chemical Company) were purified by recrystallization from deionized water and then dried at 120°C for three days. Lithium perchlorate (Fisher Scientific) was dried at 190°C for one week. Cesium chloride (Alfa Chemical Company) was used as received except for drying at 120°C for one week. Cesium tetraphenylborate (CsTPB) was prepared by mixing a tetrahydrofuran (THF, Burdick and Jackson Laboratories) solution of sodium tetraphenylborate with a concentrated aqueous solution of cesium chloride. A fine white precipitate of CsTPB was formed which was washed thoroughly with conductance water and dried for three days under vacuum at 70°C.

Sodium contamination was checked by atomic emission spectrophotometry and found to contain not more than 0.5% sodium on a molar basis (136). Chloride ion contamination was tested by digesting the cesium tetraphenylborate in approximately 5 ml warm (circa 40°C) concentrated nitric acid. To the resulting dark brown/black solution, an equal portion of approximately 0.1 M aqueous solution is added and the solution was inspected for a white precipitate. It should be noted that a very small grain of NaCl (circa 0.5 mg) dissolved in the warm acid solution results in a very obvious precipitate.

b. Solvent Purification

Five hundred milliliters of acetonitrile, (AN, Baker Chemical Co.) was

refluxed over about 10 g of calcium hydride (CaH_2), for one week followed by fractional distillation with the middle fraction retained. About 700 ml of acetone, (AC, Baker) was refluxed over anhydrous calcium sulfate ($CaSO_4$, 10 g) followed by fractional distillation. N,N-Dimethyl Formamide (DMF, Fisher Scientific) nitromethane (NM, Aldrich Chemical Company) and Propylene Carbonate (PC, Aldrich), 500 ml of each, were refluxed over about 10 g of calcium hydride under reduced pressure for two days then fractionally distilled under reduced pressure with the middle 60% fraction retained. All solvents except nitromethane were stored over freshly activated Linde 3Å molecular sieves in brown bottles in a dry box under nitrogen atmosphere. Nitromethane was not stored over molecular sieves (since the color changes to yellow when stored over molecular sieves for one day), but was kept in a brown bottle in a dry box under nitrogen atmosphere. The water content of all solvents except nitromethane was determined by gas chromatography. In all cases the water content was below 50 ppm (87).

House distilled water was further purified by passage through a Sybron/Barnstead Organic Removal column (#D8904) followed by passage through a Sybron/Barnstead Ultrapure mixed bed column (#d8902). The conductance of water purified in this manner is about $5 \times 10^{-8}\ \Omega^{-1}cm^{-1}$.

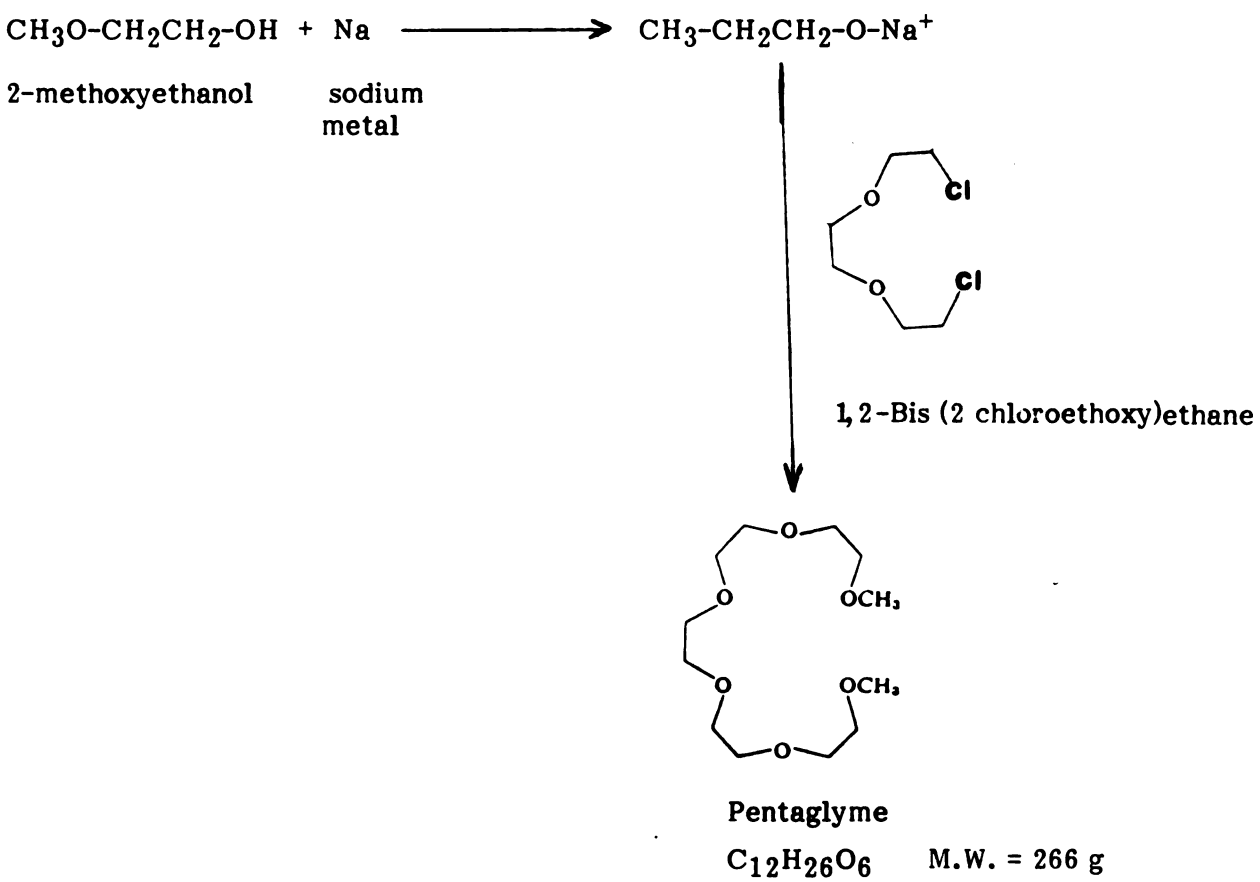
c. Ligands

The macrocyclic ligand 18-crown-6 (18C6, Aldrich), was purified as described previously (137, 138); the purified ligand was then dried under vacuum for three days at room temperature. Dry 18C6 melts at 36-37°C [Literature m.p. 36.5-38.0°C (2), 39.5-40.5°C (139), 39-40°C (3)]. The ligand 15-crown-5 (15C5) and tetraglyme (79) were obtained from Aldrich chemical Company while 21-crown-7 (21C7) and hexaglyme (HG) were obtained from Parish Chemical

Company. These ligands, except hexaglyme, were each fractionally distilled under reduced pressure and vacuum dried for three days at room temperature. Hexaglyme was used without further purification except for drying under vacuum for three days at room temperature. 1,10-Diaza-18-crown-6 (Merk Company) was recrystallized from reagent grade n-heptane and dried under vacuum at room temperature for three days. Pentaglyme was synthesized by the method described below:

Synthesis of Pentaglyme

Pentaglyme, the linear analogue of 18-crown-6 was synthesized by a method which was a modified form of that reported by Haymore and co-workers (78)



Forty-six grams of sodium were cut into small chunks (about 20 pieces) and kept under dry hexane to avoid oxidation. The freshly cut sodium chunks were dissolved in 700 ml of 2-methoxyethanol (Aldrich), [which was previously dried by refluxing over calcium sulphate under reduced pressure followed by vacuum distillation (140)], with stirring for two hours. After the reaction has ceased, the mixture was further stirred overnight, then cooled to room temperature. One hundred and eighty-seven grams of 1,2,-Bis (2-chloroethoxy)ethane was added slowly to the above mixture with vigorous stirring over a period of two hours and then refluxed overnight. The yellow reaction mixture was filtered to remove the white solid (believed to be the unreacted sodium salt of 2-methoxyethanol), and excess methoxyethanol was removed by use of a rotory evaporator. The residual liquid was vacuum distilled (1.0 torr) and two distinct fractions were obtained at 85°C and 140°C. The higher boiling fraction was carefully redistilled to give 128 g (48% yeild) of pure colorless liquid which boiled at 139-140°C (1.0 torr).

Proton NMR spectra at 250 MHz (CCl_4 25°C, TMS reference) showed two resonance 3.18 (6H, s) and 3.42 (2 OH, Br, M) which were in perfect agreement with those reported by Haymore and co-workers (78). Carbon-13 NMR at 250 MHz, (acetone-d_6 as reference) showed four resonances at 28.55 (2C), 40.73 (2C), 40.87 (6C) and 42.23 (2C). The mass spectrum showed a base peak at m/e 59 and molecular ion peak was not observed both of which are characteristics of linear polyethers (141). The M+1 peak m/e 267 was observed when the mass spectrum was taken at a higher electron volt. This also is characteristic of ethers (142). Anal. calc. for $C_{12}H_{26}O_6$ C, 54.12; H, 9.84. Found C, 54.23; H, 9.64.

2. SAMPLE PREPARATION

In order to avoid contaminations with atmospheric moisture and carbon dioxide, all the solutions were prepared in a dry box under dry nitrogen atomosphere. Two methods were employed; (i) a stock solution of the salt was prepared, various amounts of the complexing ligand were weighed into 2 ml volumetric flasks and the stock solution was then used to make up the mark. These solutions contain a constant salt concentration but varying ligand concentrations.

(ii) stock solution of metal ion was prepared and this was used to prepare the stock solution of a weighed amount of ligand (thus the ligand stock solution contains both ligand and salt). The ligand stock solution was then micropipetted into 2 ml flasks to add the desired amount of ligand, and diluted with the remaining salt stock solution to the 2 ml mark. In this way it is possible to ensure that each and every solution has the same salt concentration. The solutions were then transferred to 10 mm (Wilmad) NMR tubes, capped and wrapped with teflon tape to prevent both contamination by atmospheric moisture and solvent evaporation.

3. NMR MEASUREMENTS

All nuclear magnetic resonance measurements were made on Bruker WH-180 superconducting NMR spectrometer with a field strength of 42.3 kG. At this field, sodium-23, thallium-205, cesium-133, and lithium-7 resonante at 47.61, 103.88, 23.62 and 69.951 MHz respectively. The spectrometer was interfaced to a Nicolet 1180 computer for time averaging of spectra and for on-line Fourier transformation of data. For ^{23}Na, ^{205}Tl, ^{7}Li and ^{205}Tl measurements, acquisitions were made on the 2K, 4K, 8K and 4K memory sizes respectively. All solutions were measured in 10 mm o.d. tubes (Wilmad) with a 4 mm o.d.

insert (Wilmad) coaxially placed inside. The insert contained a chemical shift reference and the lock solvent. For sodium-23 the insert contained 0.1 M NaCl in D_2O (-0.08 ppm vs. infinite dilution sodium ion in water). For thallium-205 the insert contained 0.1 M $TlNO_3$ in D_2O (-1.5 ppm vs. infinite dilution thallium ion in water). For cesium-133, the inserts contained 0.5 M CsBr in D_2O (8.943 ppm vs. infinite dilution cesium ion in water). For lithium-7, the insert contained 0.1 M LiCl in D_2O (0.0 ppm vs. infinite dilution lithium ion in water). Downfield chemical shifts were taken to be positive.

In the studies involving temperature dependence of chemical shifts, each sample tube was left in the probe for 20-30 minutes for equilibration before acquisition of data.

4. DATA TREATMENT

All the measured chemical shifts were corrected for the differences in bulk diamagnetic susceptibility of the solution and the reference according to the equation of Live and Chan (143) as corrected for Fourier transform experiments utilizing a superconducting magnet which is as, given by Martin et al. (144),

$$\delta_{corr} = \delta_{obs} + \frac{4}{3}\pi(X_{ref} - X_{sample}) \times 10^6$$

where X_{ref} and X_{sample} are the unitless volume susceptibilities of the reference and sample solvents respectively, δ_{obs} is the observed chemical shift and δ_{corr} is the corrected chemical shift. The salt concentrations were always low (0.01-0.05 M); therefore, the magnetic susceptibility of the solution was taken to be the diamagnetic susceptibility of the solvent as Templeman and Van Geet (145) indicated. Table 12 represents the magnitudes of corrections, calculated on the basis of published susceptibilities (98), and the physical properties (146-148)

Table 12

Key Solvent Properties and Correction for Diamagnetic Susceptibility on the 180 MHz Instrument

Solvent	Dielectric Constant	Gutman Donor Number[a]	BYDS[b] x 10^6	Correction on WH-150 δ_{corr} (ppm)
Nitromethane	35.9	2.7	-0.319	1.378
Acetonitrile	38.0	14.1	-0.534	0.78
Propylene Carbonate	65.0	15.1	-0.634	-.360
Acetone	20.7	17.0	-0.460	1.09
N-N-Dimethyl-formamide	36.7	26.6	-0.500	0.616
Dimethyl-Sulfoxide	46.7	29.8	-0.605	0.482
Water	78.0	33.0	-0.720	0.000

[a]Reference (99,1000); [b]Bulk Volume Diamagnetic Susceptibility Reference (98)

for the solvents used.

The chemical shifts thus obtained as a function of mole ratio (ligand/salt) were then analyzed by the use of the non-linear weighted least squares program KINFIT (149). For all the cases studied, the exchange kinetics of the cation were such that the free and complexed sites underwent fast exchange and only one time-averaged signal was observed.

a. Determination of Formation Constant for a 1:1, Ligand:Metal Complex by the NMR Technique

The equilibrium for a 1:1 (ligand:metal ion) complexation reaction can be expressed as

$$M + L \rightleftharpoons ML \qquad (1)$$

and the concentration formation constant is given by

$$K_f = \frac{C_{ML}}{C_M \cdot C_L} \qquad (2)$$

where C refers to the molar equilibrium concentrations.

Assuming that only ligand:cation interaction is important and the rate of exchange of the metal ion between the two sites (free M and complexed M) is fast on the NMR time scale, the observed chemical shift is given by

$$\delta_{obs} = X_M \delta_M + X_{ML}\delta_{ML} \qquad (3)$$

where δ_M is the characteristic chemical shift of the free M, δ_{ML} is the chemical shift of the complexed M (ML), X_M is the mole fraction of free M, and X_{ML} is the mole fraction of M in the complexed state. Therefore

$$\delta_{obs} = X_M \delta_M + (1-X_M)\delta_{ML}$$

$$\delta_{obs} = X_M \delta_M + (1-X_M)\delta_{ML} = C_M/C_M^T (\delta_M - \delta_{ML}) + \delta_{ML} \quad (4)$$

The analytical concentration of M is

$$C_M^T = C_M + C_{ML} \quad (5)$$

and the analytical concentration of the ligand is

$$C_L^T = C_{ML} + CL \quad (6)$$

Therefore

$$C_{ML} = C_M^T - C_M \quad (7)$$

From (5) and (7)

$$C_L = C_L^T - (C_M^T - C_M)$$

$$K_f = \frac{C_M^T - C_M}{(C_M)(C_L^+ - C_M^+ + C_M)} \quad (8)$$

solving (8) for C_M

$$C_M(C_L^T - C_M^T + C_M)K_f = C_M^T - C_M$$

$$K_f C_M^2 + (K_f C_L^T - K_f C_M^T + 1)C_M - C_M^T = 0$$

$$C_M = \frac{-(K_f C_L^T - K_f C_M^T + 1) \pm \sqrt{(K_f C_L^T - K_f C_M^T + 1)^2 - 4K_f C_M^T}}{2K_f} \quad (9)$$

Since physically C_M cannot be negative, only the positive root is chosen.

Substitution of C_M from (9) into Equation (4)

$$\delta_{obs} = [(K_f C_M{}^T - K_f C_L{}^T - 1) + (K_f{}^2 C_L{}^{T2} + K_f{}^2 C_M{}^{T2} - 2K_f{}^2 C_L{}^T C_M{}^T$$

$$+ 2C_L{}^+ + 2C_M{}^+ + 1)^{1/2}][(\delta_M - \delta_{ML})/2KC_M{}^T + \delta_{ML} \qquad (10)$$

In equation (10), the total concentration of the cation and the ligand ($C_M{}^T$ and $C_L{}^T$ respectively) are known, δ_M is determined by measuring the cation chemical shift in the absence of the ligand. In order to fit the right hand side of the equation to the observed chemical shift, two constants and two parameters are used in the FORTRAN CODE:

$U(1) = \delta_{ML}$ $\qquad$ $U(2) = K_f$

$Const(1) = C_M{}^T$ $\qquad$ $CONST(2) = \delta_M$

The imput variables are the analytical concentrations of the ligand XX(1) and the observed chemical shift XX(2). The SUBROUTINE EQUATION used in the calculations is given in Appendix I.

Limitations

Using the above method, the values of formation constants to be determined have to be within the range

$$1 > K_f < 10^4$$

The implication of this limitation to our study of the macrocyclic effect is as follows: choice of linear ligand, cyclic ligand, cation and solvent has to be made in such a way that (i) the linear ligand forms a complex with the chosen cation in the chosen solvent, that is strong enough ($K_f > 1$) to be determined

while (ii) the cyclic ligand forms a complex with the chosen cation in the chosen solvent which will have a formation constant $K_f < 10^5$. This limitation imposes some obvious restrictions on the systems that could be studied in this work.

b. Determination of Formation Constants by Competitive NMR

The conventional technique used for the determination of formation constants in this study works well for $1 > K_f < 10^4$. When the formation constant to be measured is greater than 10^4, a competitive technique can be employed. A brief description of this technique is given below, more details can be found in reference 168.

For two cations, M^+ and N^+, which form only 1:1 complexes with the ligand, L, there are two simultaneous equilibria

$$M^+ + L \underset{}{\overset{K_M}{\rightleftharpoons}} ML^+ \qquad (1)$$

and

$$N^+ + L \underset{}{\overset{K_N}{\rightleftharpoons}} ML^+ \qquad (2)$$

The mass balance equations for the analytical concentrations for the cation M^+ and N^+ and the ligand C_M, C_N and C_L, respectively, may be written

$$C_M = [M^+] + [ML^+] \qquad (3)$$

$$C_N = [N^+] + [NL^+] \qquad (4)$$

$$C_L = [L] + [ML^+] + [NL^+] \qquad (5)$$

where [ ] represents the equilibrium concentrations.

By solving the equilibrium constant equations for the free cation, it could be shown that

$$C_M = \frac{[ML^+](K_M[L] + 1)}{K_M[L]} \quad (6)$$

$$C_N = \frac{[NL](K_N[L] + 1)}{K_N[L]} \quad (7)$$

Equations (6) and (7) are solved for the concentration of the complexes. These are substituted into equation (5) and the resulting equation rearranged to give the following cubic polynomial for the concentration of the free ligand:

$$K_M K_N[L]^3 + K_M K_N(C_M + C_N - C_L) + K_M + K_N \quad [L]^2$$

$$+ K_M(C_M - C_L) + K_N(C_N - C_L) + [L] - C_L = 0 \quad (8)$$

For a fast exchange of cation M^+ the chemical shift, δ_{obs} is given by the expression

$$obs = \frac{\delta_o + \delta_i[L]K_M}{1 + [L]K_M}$$

where δ_i is the chemical shift of the metal ion complexed with i ligands.

The polynomial for the free ligand equation (8) is then solved iteratively by the subroutine EQN given in Appendix II and the value of the unknown formation constant is calculated.

This method was used in the determination of the formation constants for the complexations of 18-crown-6 with thallium(I) ion and 15-crown-5 with sodium ion, both in acetonitrile solutions by sodium-23 NMR. In the case of

18-crown-6 with thallium(I) ion, a solution containing Na^+, Tl^+ ions and 18-crown-6 was used. The formation constant of Na^+ with 18-crown-6 was known and that was used, as described above to calculate the formation constant of Tl^+ with the same ligand in the same solvent. For the complexation of 15-crown-5 with sodium ion, two ligands, pentaglyme and 15-crown-5 were allowed to compete for the sodium ion in acetonitrile solution. Formation constant for the complexation of pentaglyme with sodium ion in acetonitrile is known which was in turn used to calculate that for the complexation of Na^+ ion with 15-crown-5 in the same solvent.

RESULTS AND DISCUSSION

CHAPTER III

MULTINUCLEAR NMR STUDIES OF THE COMPLEXATION OF Na^+, Tl^+, Cs^+ AND Li^+ IONS BY LINEAR AND CYCLIC POLYETHERS IN SOME NONAQUEOUS SOLVENTS

1. INTRODUCTION

Previous studies in our laboratory (150-154) and elsewhere (98,123,130,155-157) have shown that the nuclear magnetic resonance of thallium and alkali nuclei offers a very sensitive technique for the studies of changes in the immediate chemical environment of the thallium and alkali ions in solution. The chemical shifts of resonances can give information about ion-ion, ion-solvent, and ion-ligand interactions.

The complexing ability of noncyclic polyethers with metal ions has not been much investigated because they are not able to compete with crown ethers (156) and cryptands (5). In cases where the stability constants for the complexation of linear polyethers with metal ions have been reported, the studies were conducted in water, methanol and water-methanol mixtures. Very little work have been done in other nonaqueous solvents. This section reports studied on the complexation of sodium, lithium, cesium and thallous ions with tetraglyme, pentaglyme and hexaglyme, the linear analogues of 15-crown-5, 18-crown-6 and 21-crown-7 respectively in several nonaqueous solvents by sodium-23, lithium-7, cesium-133 and thallium-205 NMR techniques.

2. COMPLEXATION OF LINEAR POLYETHERS (GLYMES) WITH SODIUM, THALLIUM(I) AND CESIUM IONS IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

a. Tetraglyme (Tg) Complexes with Na^+ Ion at Room Temperature

Sodium-23 chemical shifts were determined as a function of tetraglyme/sodium mole ratio in nitromethane (NM), acetonitrile (AN), acetone (AC), propylene carbonate (PC), and N,N-dimethylformamide (DMF) solutions. The observed chemical shifts and the linewidths of resonance at half height are given in Tables 13-15 and the plots of chemical shift as a function of mole

ratio are shown in Figure 3. In all cases, only one population average resonance signal was observed indicating that the exchange of sodium ion between the free and complexed sites is fast on the NMR time scale at room temperature.

In nitromethane solutions, the mole ratio plot shows a downfield shift of the sodium-23 resonance which levels off after a mole ratio of one was reached. This clear break in the curve indicates the formation of a strong 1:1, ligand:metal ion complex. In acetonitrile solution, there was an upfield shift of the resonance as the ligand concentration was increased and the curve started to level off only after a mole ratio of two was reached. On the other hand, in N,N-dimethylformamide solution, the plot of chemical shift as a function of mole ratio shows very little curvature with no observable break at any mole ratio which indicates the existence of a weak interaction between the sodium ion and the ligand. It should be realized that while nitromethane is a solvent with low donor ability (DN = 2.7), N,N-dimethylformamide, on the other hand, is a solvent with high donor number (DN = 26.6); it has a high ability to solvate cations. Weak cation:ligand interaction is therefore expected in this solvent since complex formation is essentially a competition between the ligand and solvent for the cation. In propylene carbonate solution, no significant variation in the chemical shift of sodium-23 resonance was observed upon addition of ligand to the sodium salt solution. Consequently, in this solvent, the interaction between the ligand and sodium ion is too weak to be detected by the ^{23}Na NMR technique.

The formation constants caluclated from the chemical shift measurements are listed in Table 16.

Table 13

Mole Ratio Studies for the Complexation of Tetraglyme (TG) and Sodium Ion in Acetonitrile and in N,N-Dimethyl Formamide Solutions at Room Temperature

Acetonitrile			DMF		
Mole Ratio [TG] $[Na^+]^a$	Chemical Shifts (ppm)	Line Width (Hz)	Mole Ratio [TG] $[Na^+]^a$	Chemical Shifts (ppm)	Line Width (Hz)
0.0	-7.50	15	0.0	-4.15	39
0.3	-7.70	24	0.3	-4.20	39
0.5	-7.91	24	0.5	-4.26	42
0.7	-8.06	27	1.0	-4.31	43
0.8	-8.11	27	2.0	-4.41	44
0.9	-8.16	30	3.0	-4.46	44
1.0	-8.20	33	4.0	-4.51	47
1.3	-8.32	35	5.7	-4.68	47
2.0	-8.37	37	6.7	-4.77	54
3.0	-8.40	38	12.4	-5.18	54
4.0	-8.42	38	17.3	-5.38	56
			20.1	-5.89	56

[a] $[Na^+]$ = 0.05 M NaTPB

Table 14

Mole Ratio Studies for the Complexation of Tetraglyme (TG) with Sodium Ion in Nitromethane at Room Temperature

Mole Ratio $[TG]/[Na^+]^a$	Chemical Shift (ppm)	Line Width (Hz)
0.0	-13.5	22
0.3	-12.4	64
0.5	-11.6	110
0.7	-10.6	137
0.8	-10.3	147
0.9	-10.0	161
1.0	-9.87	171
1.3	-9.82	180
2.0	-9.77	182
3.0	-9.71	183
4.0	-9.70	183

[a] $[Na^+]$ = 0.05 M NaTPB

Table 15

Mole Ratio Studies for the Complexation of Tetraglyme with Sodium Ion in Propylene Carbonate at Room Temperature

Mole Ratio [TG]/[Na^+][a]	Chemical Shift (ppm)	Line Width (Hz)
0.0	-9.64	74
0.3	-9.18	89
0.5	-9.11	97
0.7	-9.18	110
0.8	-9.19	114
0.9	-9.15	117
1.0	-9.12	120
1.3	-9.05	123
1.5	-9.17	124
2.0	-9.14	124
3.0	-9.19	129
4.0	-9.15	130

[a] $[Na^+] = 0.05$ M

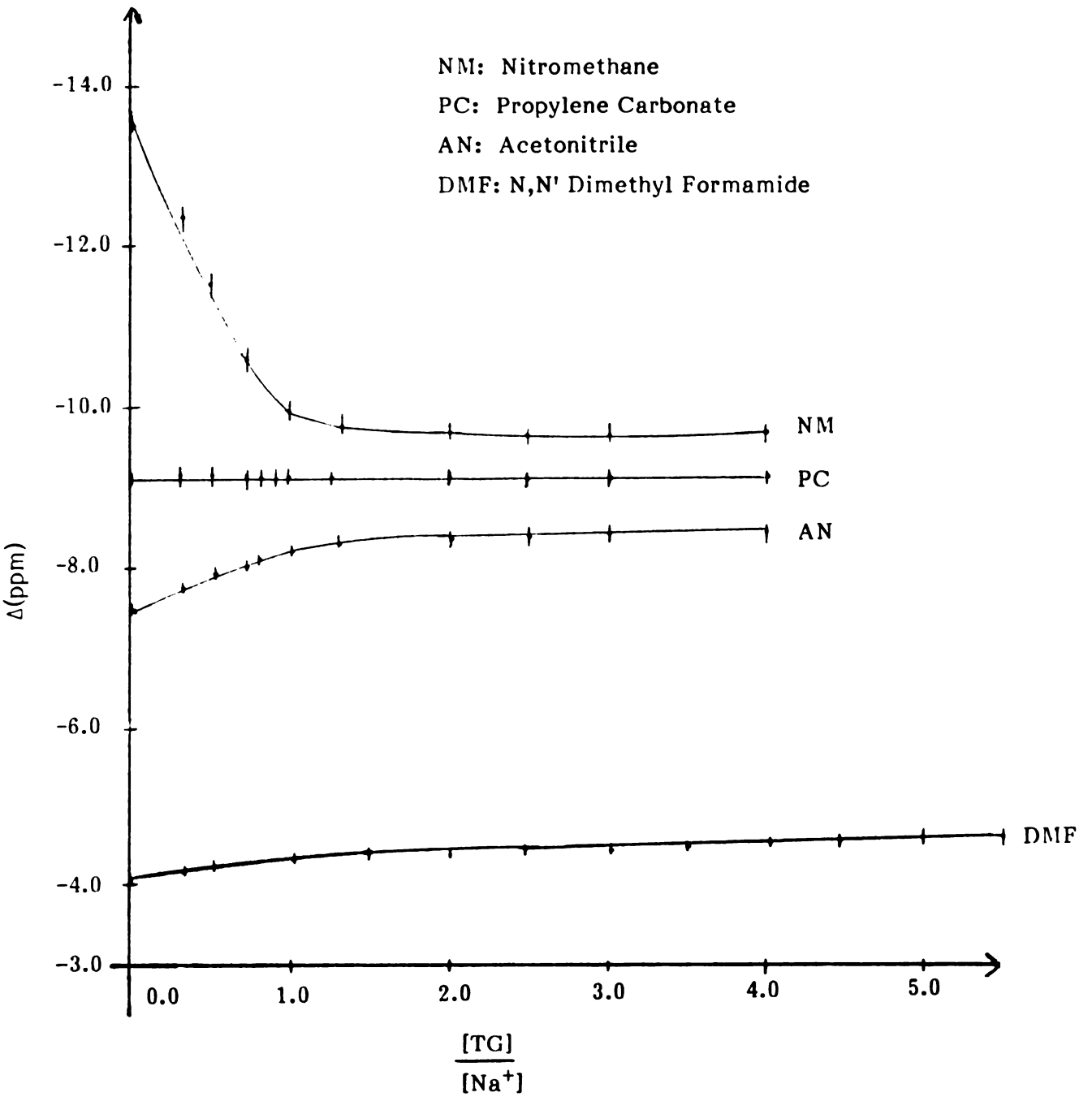


Figure 3: Sodium-23 chemical shifts vs. [TG]/[Na^+] mole ratio in various solvents.

Table 16

Stability Constants of Sodium Complexes with Tetraglyme in Various Nonaqueous Solvents at Room Temperature

Solvent	Log K_f
Nitromethane	> 4
Acetonitrile	2.43 ± 0.08
Propylene carbonate	≈ 0
N,N-dimethylformamide	K = 0.5 ± 0.12

b. Pentaglyme (PG) Complexes with Na^+ Ion at Room Temperature

The variation of sodium-23 chemical shift as a function of pentaglyme sodium ion mole ratio and the line widths of resonance at half height measured in nitromethane, acetonitrile, acetone and propylene carbonate solutions are listed in Tables 17-19. Plots of chemical shift versus mole ratio data are shown in Figure 4. In nitromethane solution, a paramagnetic shift of the sodium-23 resonance with a sharp break at a mole ratio of one was observed. This is an indication of the formation of a stable 1:1 ligand:metal ion complex (Log K_f > 4). In acetonitrile solution, a diamagnetic shift was observed until a mole ratio of one was reached after which the chemical shift showed little variation. In propylene carbonate solution, in contrast to tetraglyme, the mole ratio plot shows a downfield shift of the sodium-23 resonance which levels off after a mole ratio of one. It seems that the interaction of pentaglyme with the sodium ion is fairly strong. The formation constants calculate for these systems are listed in Table 20.

Table 17

Mole Ratio Studies for the Complexation of Pentaglyme (PG) with Sodium Ion in Nitromethane at Room Temperature

Mole Ratio $[PG]/[Na^+]$	Chemical Shift (ppm)	Line Width (Hz)
0.0	-13.5	22
0.3	-11.3	65
0.5	-10.2	115
0.8	-8.76	140
0.9	-7.94	149
1.0	-7.36	163
1.1	-7.32	175
1.5	-7.31	180
2.0	-7.30	183
3.0	-7.21	185
4.0	-7.20	185

[a] $[Na^+]$ = 0.05 M NaTPB

Table 18

Mole Ratio Studies for the Complexation of Sodium Ion with Pentaglyme (PG) In Acetonitrile and in Acetone at Room Temperature

Acetonitrile			Acetone		
Mole Ratio [PG]/[Na^+][a]	Chemical Shift (ppm)	Line Width (Hz)	Mole Ratio [PG]/[Na^+][a]	Chemical Shift (ppm)	Line Width (Hz)
0.0	-6.61	15	0.0	-7.80	22
0.3	-6.73	21	0.3	-7.00	28
0.5	-6.80	30	0.5	-8.06	29
0.7	-6.86	33	0.7	-8.16	29
0.8	-6.92	36	0.8	-8.27	29
1.0	-6.98	39	0.9	-8.32	34
1.3	-7.00	41	1.0	-8.34	34
1.5	-7.01	43	1.1	-8.37	36
2.0	-7.03	45	1.5	-8.39	36
2.5	-7.04	45	2.0	-8.40	38
3.0	-7.04	47	3.0	-8.42	38
3.5	-7.04	47	4.0	-8.42	38

[a] $[Na^+]$ = 0.05 M NaTPB

Table 19

Mole Ratio Studies for the Complexation of Pentaglyme with Sodium Ion in Propylene Carbonate at Room Temperature

Mole Ratio [PG]/[Na^+][a]	Chemical Shifts (ppm)	Linewidth (Hz)
0.0	-9.64	74
0.3	-9.32	100
0.5	-9.08	113
0.7	-8.88	120
0.8	-8.74	135
0.9	-8.57	138
1.0	-8.55	144
1.3	-8.53	144
1.5	-8.47	145
2.0	-8.44	146
3.0	-8.42	146
4.0	-8.40	149

[a] [Na^+] = 0.05 M NaTPB

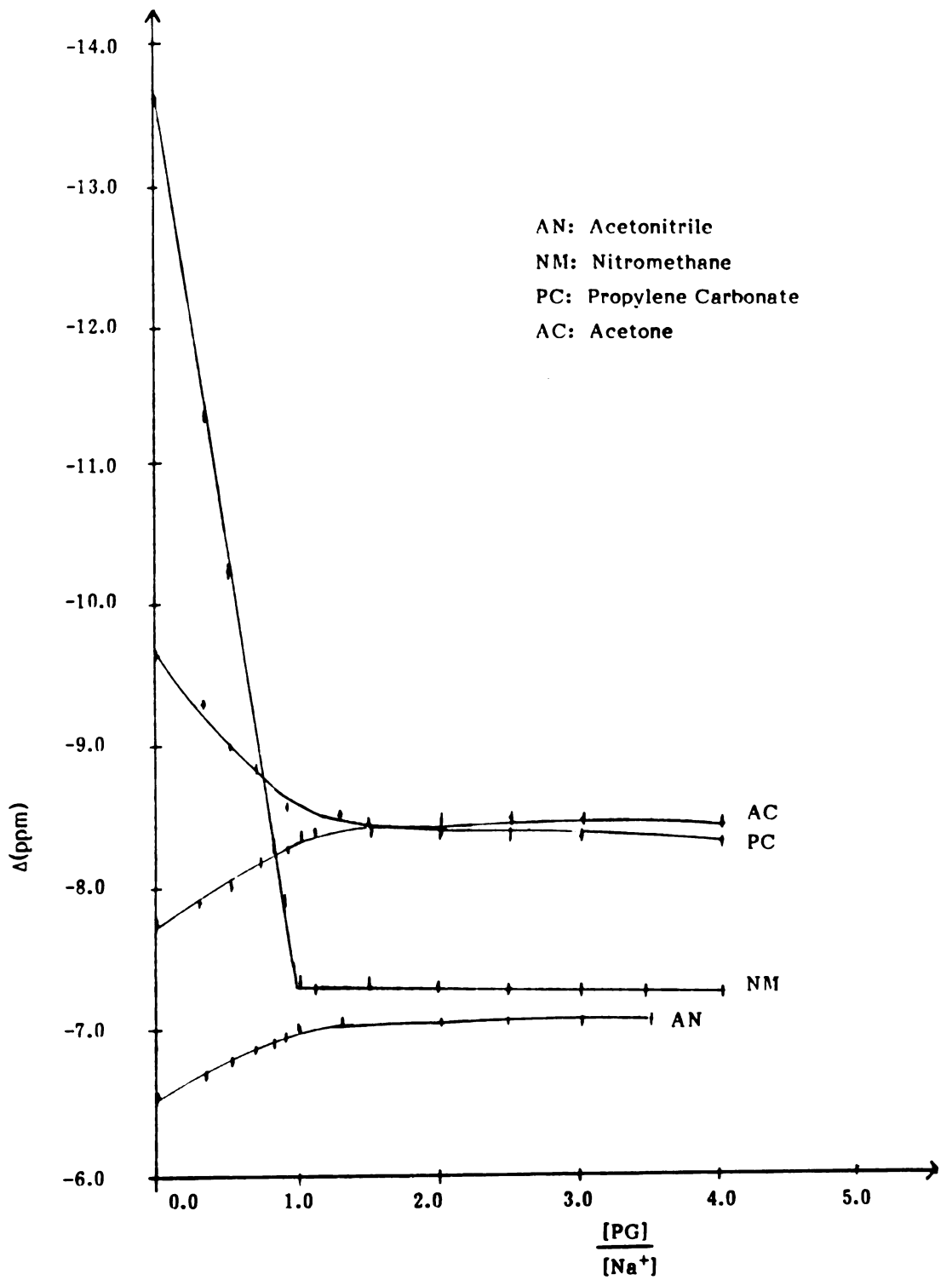


Figure 4: Sodium-23 chemical shifts vs. $[PG]/[Na^+]$ mole ratio in various solvents.

Table 20

Stability Constants of Sodium Complexes with Pentaglyme in Various Nonaqueous Solvents at Room Temperature

Solvent	Log K_f
Nitromethane	> 4
Acetonitrile	2.63 ± 0.13
Propylene carbonate	3.09 ± 0.21
Acetone	3.12 ± 0.29

For the complexes of tetraglyme and pentaglyme with sodium ion in nitromethane solutions, the formation constants (log K_f > 4) are higher than the upper limit that can be determined directly by the NMR technique. In acetonitrile solutions the formation constant for the pentaglyme - sodium ion complex (log K_f = 2.63 ± 0.13) seems to be slightly higher than that for tetraglyme-Na^+ complex (log K_f = 2.43 ± 0.08). This is due to the presence of an additional donor atom in pentaglyme as compared to tetraglyme. The strength of the interaction between sodium ion and the ligand increases with the chain length. A similar observation was made for methanol solutions by Chaput et al. (26), who found log K_f = 1.47 for pentaglyme-Na^+ complex and log K_f = 1.28 for the tetraglyme-Na^+ complex. Buschman (25) also reported, log K_f = 1.54 for the pentaglyme-Na^+ complex and log K_f = 1.44 for tetraglyme-Na^+ complex in methanol solution. In propylene carbonate solution, there is a remarkable difference in the strengths of interaction of sodium ion with tetraglyme and with pentaglyme. In fact with tetraglyme, the complex formed is too weak to be detected as there is essentially no variation in the sodium-23 chemical shift as the ligand is added to the salt solution, while pentaglyme forms a fairly strong complex (log K_f = 3.09 ± 0.21) in the same

solvent.

A stable complex is formed in acetone solution between sodium and pentaglyme (Log K_f = 3.12 ± 0.29). This is expected since acetone does not have very high donor ability based on the Gutmann donor scale (DN = 17.0). In N,N-dimethylformamide, the complex formed between sodium and tetraglyme is rather weak (K = 0.50 ± 0.12). This is due to the higher solvating ability of N,N-dimethylformamide (DN = 26.6).

c. Pentaglyme (PG), Tetraglyme (TG) And Hexaglyme (HG) Complexes with the Tl^+ Ion at Room Temperature

Thallium-205 chemical shifts were determined as a function of pentaglyme/thallium(I) ion mole ratio in acetonitrile and acetone solutions. The variation of chemical shift as a function of tetraglyme/thallium(I), pentaglyme/thallium(I) and hexaglyme/thallium(I) mole ratios in N,N-dimethylformamide solutions was also measured. The measured chemical shifts and the line widths of the resonance at half height are listed in Tables 21-24 and the plots of chemical shift versus ligand/thallium(I) mole ratios are shown in Figures 5-7.

In acetone and in acetonitrile solutions, the mole ratio plots show a downfield shift of the thallium-205 resonance as the concentrations of the ligand increased and the curve gradually levels off after a mole ratio of one. This indicates the formation of stable 1:1, ligand: metal complexes in these two solvents. When the variation of chemical shifts were measured for pentaglyme-Tl^+, tetraglyme-Tl^+ and hexaglyme-Tl^+ systems in N,N-dimethylformamide, a gradual diamagnetic shift was observed in all cases as the ligand:metal mole ratios were increased. There were no breaks in the curves even at high mole ratios as could be seen in the corresponding curves. This is due to the great ability

Table 21

Mole Ratio Studies for the Complexation of Petaglyme with Thallium(I) Ion in Acetonitrile and in Acetone at Room Temperature

Acetonitrile			Acetone		
Mole Ratio $[PG]/[Tl^+]$[a]	Chemical Shift (ppm)	Linewidth (Hz)	Mole Ratio $[PG]/[Tl^+]$	Chemical Shift (ppm)	Linewidth (Hz)
0.0	-222.2	36	0.0	-225.2	17
0.3	-198.2	112	0.3	-211.7	59
0.5	-183.1	103	0.5	-200.5	64
0.7	-167.3	84	0.7	-187.1	43
0.8	-160.9	89	0.8	-184.7	37
0.9	-154.9	68	0.9	-180.4	33
1.0	-152.7	67	1.0	-178.8	34
1.3	-144.1	68	1.1	176.2	37
1.5	-142.5	67	1.3	-175.0	37
2.0	-140.6	67	1.5	-174.9	39
2.5	-140.4	67	2.0	-171.6	45
3.0	-140.3	68	2.5	-170.6	52
3.5	-140.1	67	3.0	-170.6	52
4.0	-139.8	68	3.5	-170.5	52
			4.0	-170.4	52

[a] $[Tl^+]$ = 0.01 M $TlClO_4$

Table 22

Mole Ratio Studies for the Complexation of Pentaglyme with Thallium(I) Ion in N,N-Dimethylformamide at Room Temperature

Mole Ratio [PG]/[Tl^+][a]	Chemical Shift (ppm)	Linewidth (Hz)
0.0	129.6	39
0.3	119.6	107
0.5	113.4	115
0.7	108.1	92
0.8	105.5	109
0.9	103.1	107
1.0	100.8	92
1.1	98.12	92
1.2	95.77	92
1.5	88.42	122
2.0	78.73	122
2.5	69.53	122
3.0	59.93	122
3.5	51.70	122
5.0	37.78	122

[a] $[Tl^+]$ = 0.04 M $TlClO_4$

Table 23

Mole Ratio Studies for the Complexation of Tetraglyme with Thallium(I) Ion in N,N-Dimethylformamide at Room Temperature

Mole Ratio [TG]/[Tl^+][a]	Chemical Shift (ppm)	Linewidth (Hz)
0.0	122.5	40
0.43	116.6	46
0.89	111.6	46
1.01	107.3	46
1.27	103.4	45
1.69	100.2	45
2.17	90.78	45
2.59	89.31	43
2.96	85.49	43
4.09	73.74	45
7.42	45.54	45
9.12	34.96	46
11.61	22.91	46
14.97	7.05	46
19.99	-9.69	46

[a] $[Tl^+]$ = 0.04 M $TlClO_4$

Table 24

Mole Ratio Studies for the Complexation of Hexaglyme (HG) with with Tahllium(I) Ion in N,N-Dimethylformamide at Room Temperature

Mole Ratio $[HG]/[Tl^+]^a$	Chemical Shift (ppm)	Linewidth (Hz)
0.0	126.9	40
0.5	105.8	59
1.0	88.4	59
1.5	72.71	59
2.0	59.04	67
2.5	46.56	70
3.0	36.43	70
4.0	19.68	78
5.0	5.29	78
6.0	-10.58	86
7.0	-15.42	86
8.0	-23.50	86

[a] $[Tl^+] = 0.04$ M $TlClO_4$

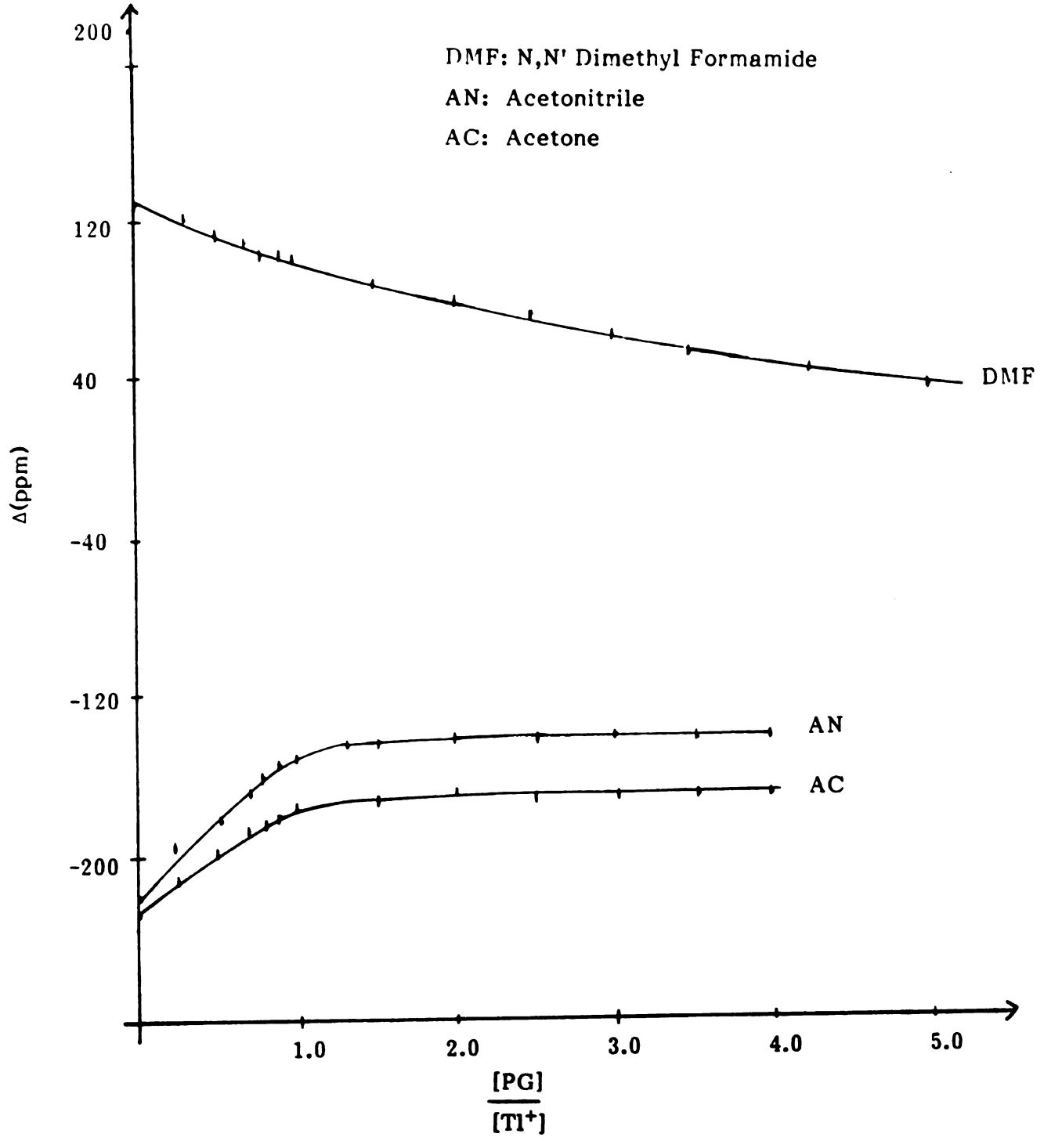


Figure 5: Thallium-205 chemical shifts vs. [PG]/[Tl^+] mole ratio in various solvents

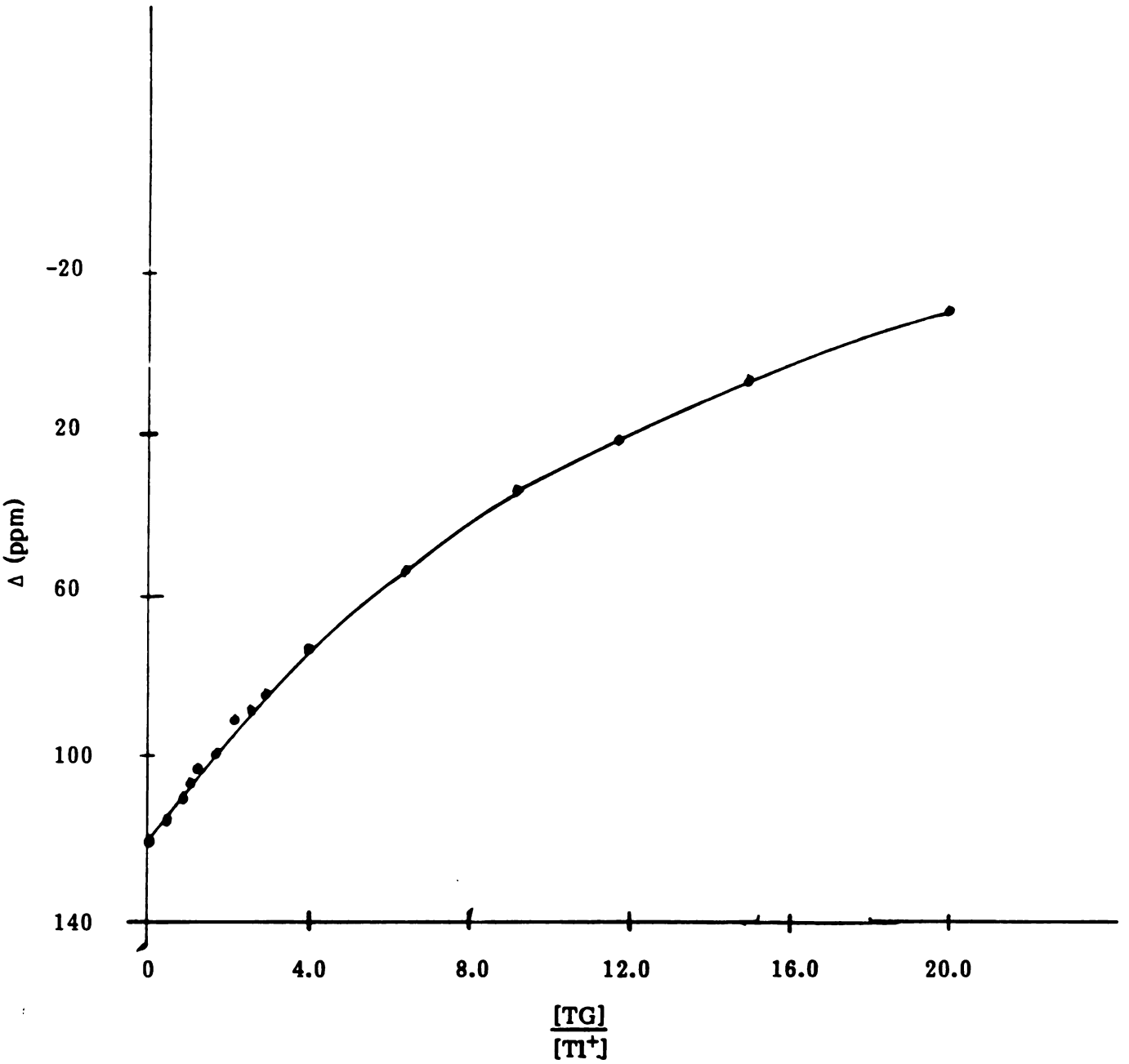


Figure 6: Thallium-205 chemical shifts as a function of $[TG]/[Tl^+]$ mole ratio in N,N-dimethylformamide solutions.

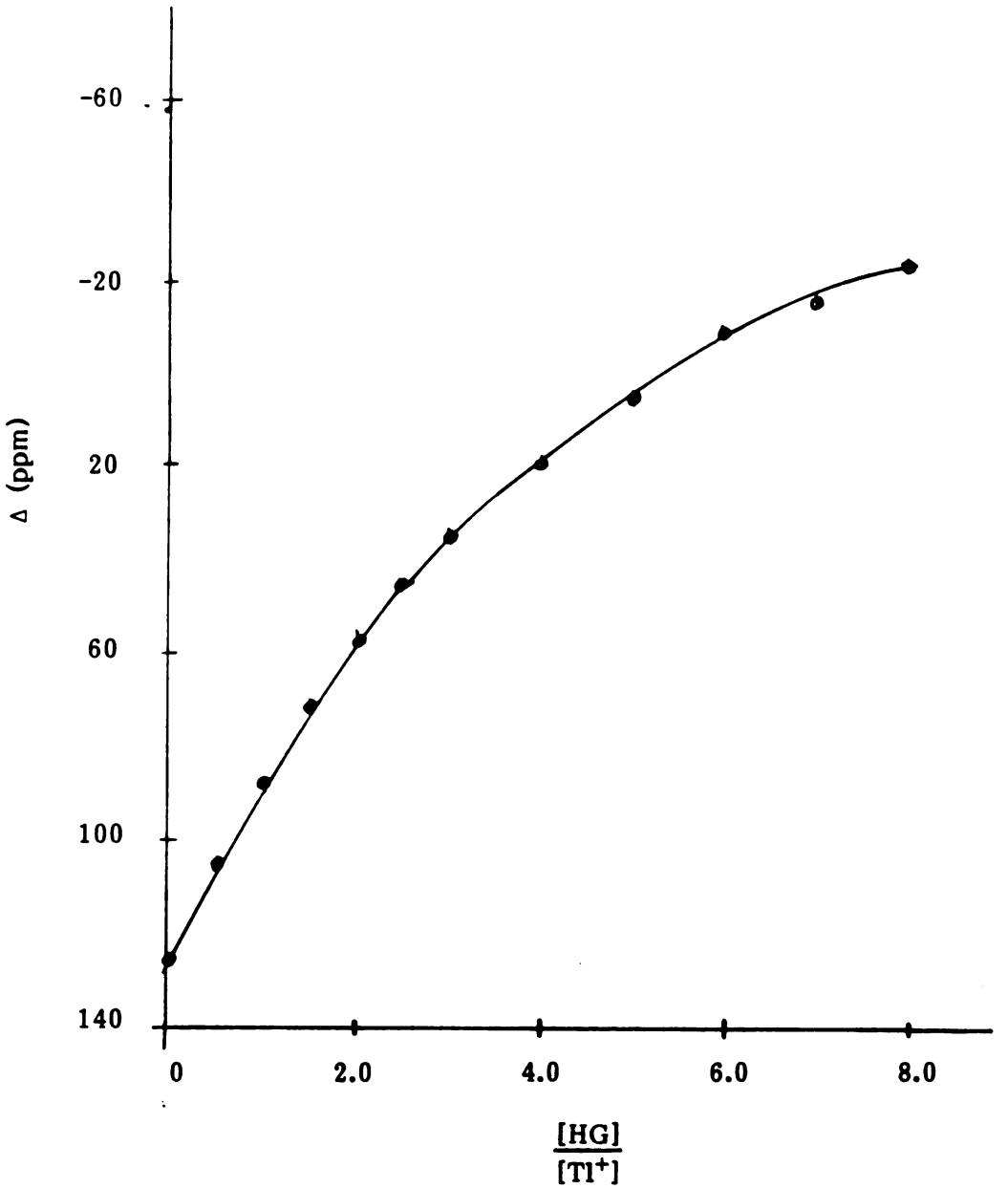


Figure 7: Thallium-205 chemical shifts as a function of [HG]/[tl^+] mole ratio in N,N-dimethylformamide solutions.

of the N,N-dimethylformamide to solvate metal ions hence weak complexes are formed in this solvent. The formation constants calculated from the measured chemical shifts are listed in Table 25.

Table 25

Stability Constants of Thallium(I) Complexes with Pentaglyme, Tetraglyme, and Hexaglyme in Nonaqueous Solvents

System	Log K_f
Pentaglyme/Tl^+/Acetonitrile	3.65 ± 0.05
Pentaglyme/Tl^+/Acetone	3.59 ± 0.13
Pentaglyme/Tl^+/DMF	0.67 ± 0.01
Tetraglyme/Tl^+/DMF	0.25 ± 0.01
Hexaglyme/Tl^+/DMF	0.76 ± 0.01

Stable complexes are formed between pentaglyme and Tl^+ ion in acetonitrile (log K_f = 3.65 ± 0.05) and in acetone (log K_f = 3.59 ± 0.13) solution. In N,N-dimethylformamide, on the other hand, the complexes formed between pentaglyme, tetraglyme, hexaglyme and Tl^+ ion, log K_f = 0.67 ± 0.01, 0.25 ± 0.01, and 0.76 ± 0.02 respectively are rather weak due to the high solvating ability of the solvent. The stability constants for the complexation of Tl^+ ion with the glymes in N,N-dimethyl formamide increase as the number of donor atoms increases. There is a larger increase in the formation constant in going from tetraglyme (five oxygen atoms) to pentaglyme(six oxygen atoms), than in going from pentaglyme to hexaglyme (seven oxygen atoms). The order of stability of thallium(I) complexes with the glymes studied in N,N-dimethylformamide is as follows, hexaglyme > pentaglyme > tetraglyme.

The same stability order was reported in methanol solution by Chaput et al. (26).

d. Complexes of Hexaglyme (Hg) with Cs^+ Ion and Tetraglyme (TG) with Li^+ Ion in Acetonitrile

The variation of cesium-133, and lithium-7 chemical shifts as a function of hexaglyme/cesium and tetraglyme/lithium mole ratios were measured in acetonitrile solution by cesium-133 and lithium-7 NMR techniques, respectively. The observed chemical shifts and linewidths at half heights are listed in Tables 26 and 27 and plots of chemical shifts versus mole ratio are shown in Figures 8 and 9. For the hexaglyme-cesium-acetonitrile system, there was an upfield shift of the cesium-133 resonance line which gradually reached a constant value after a mole ratio of one. This is an indication of formation of a stable 1:1 ligand: metal complex (log K_f = 3.33 ± 0.01). On the other hand, a gradual downfield shift was observed for the complexation of tetraglyme with lithium ion with no break in the plot at any mole ratio. The complex formed in this case is not very strong (log K_f = 1.97 ± 0.04).

3. COMPLEXATION OF CYCLIC POLYETHERS WITH SODIUM AND THALLIUM(I) IONS IN VARIOUS SOLVENTS

a. Complexes of Sodium Ion with 15-crown-5, 18-Crown-6 and 1,10-diaza-18-Crown-6 in Various Solvents at Room Temperature

The results of sodium-23 NMR studies for the interaction between the Na^+ ion and the macrocyclic ligands 15-crown-6, 18-crown-6 and diaza 18-crown-6 in some nonaqueous solvents are listed in Tables 28-31. Plots of sodium-23 chemical shifts as a function of ligand:Na^+ ion mole ratios are shown in Figures

Table 26

Mole Ratio Studies for the Complexation of Hexaglyme (HG) with Cesium Ion in Acetonitrile at 30°C

Mole Ratio $[HG]/[Cs^+]$	Chemical Shifts (ppm)	Linewidth (Hz)
0.0	15.6	5
0.3	4.57	8
0.5	0.04	9
0.7	-3.76	9
1.0	-6.53	9
1.3	-8.52	10
2.0	-10.46	11
2.5	-11.25	11
3.0	-11.79	11
4.0	-12.63	11
5.0	-13.32	11

[a] $[Cs^+]$ = 0.01 M CsTPB

Table 27

Mole Ratio Studies for the Complexation of Tetraglyme and Lithium Ion in Acetonitrile at Room Temperature

Mole Ratio [TG]/[Li^+][a]	Chemical Shift[b] (ppm)	Linewidth (Hz)
0.0	-2.01	5
0.3	-1.85	7
0.5	-1.78	7
0.7	-1.71	7
0.8	-1.70	7
0.4	-1.63	8
1.0	-1.56	8
1.1	-1.53	8
1.3	-1.52	8
1.5	-1.47	9
2.0	-1.38	9
3.0	-1.24	9
4.0	-1.18	9
5.0	-1.11	9

[a] $[Li^+]$ = 0.01 M $LiClO_4$

[b] Chemical Shifts are referred to 0.105 M LiCal in 70% D_2O

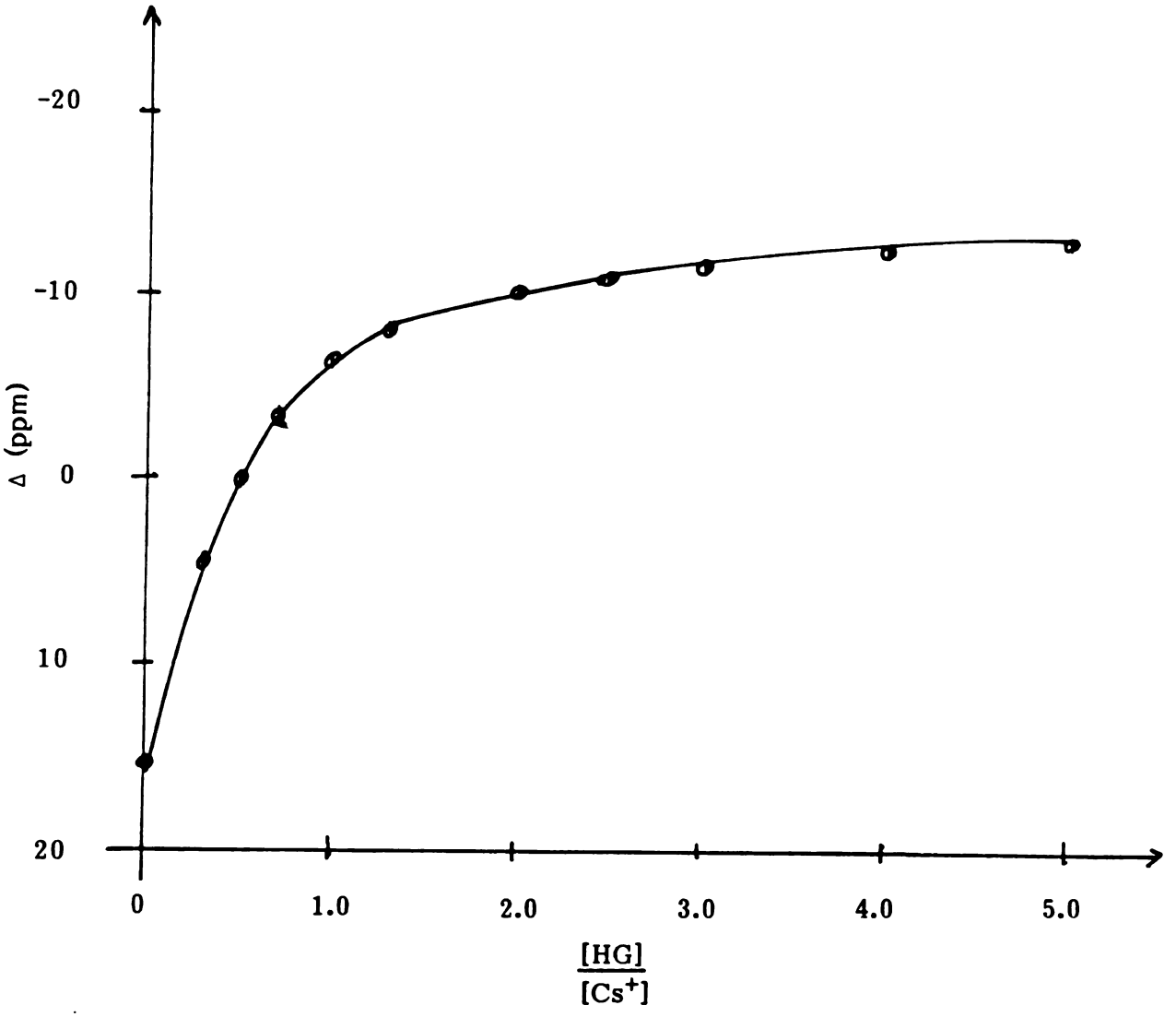


Figure 8: Cesium-133 chemical shifts vs. [HG]/[Cs^+] mole ratio in acetonitrile solutions

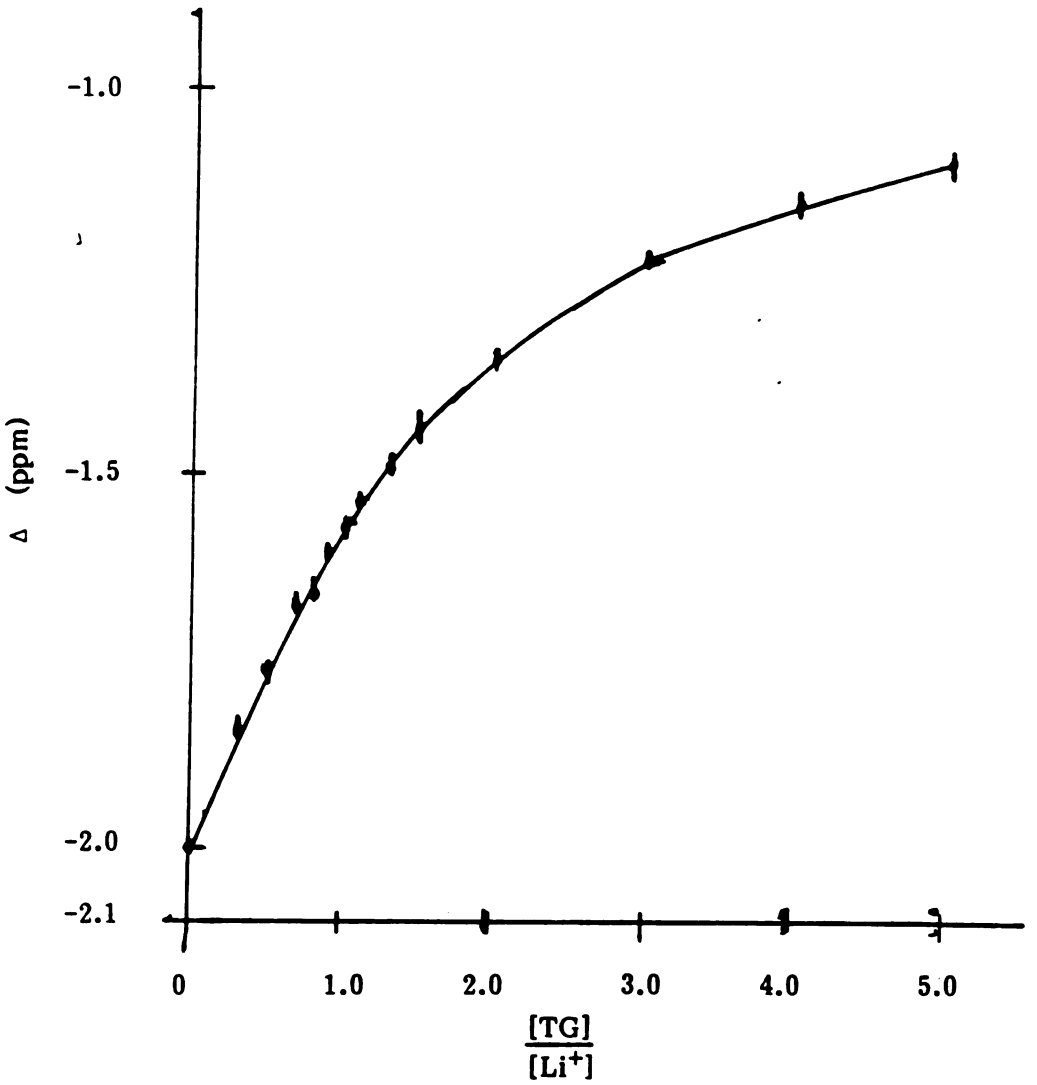


Figure 9: Lithium-7 chemical shifts vs. [TG]/[Li^+] mole ratio in acetonitrile solutions

Table 28

Mole Ratio Studies for the Complexation of 15-Crown-5 and Sodium Ion in Propylene Carbonate Solutions

Mole Ratio [15C5]/[Na^+][a]	Chemical Shift (ppm)	Linewidth (Hz)
0.0	-9.64	74
0.3	-8.61	91
0.5	-7.98	103
0.7	-7.32	105
0.8	-7.08	108
0.9	-6.87	108
1.0	-6.52	109
1.1	-6.27	111
1.3	-5.98	115
1.5	-6.03	115
2.0	-6.04	117
2.5	-6.10	118
3.0	-6.11	119
3.5	-6.20	119
4.0	-6.22	120
5.0	-6.28	121

[a] [Na^+] = 0.05 M NaTPB

Table 29

Sodium-23 Chemical Shifts as A function of 15-Crown-5 Concentration For a Solution Containing Sodium Tetraphenylborate[a], 15-Crown-5 and Tetraglyme[b] in Acetonitrile

Concentration of 15-crown-5 M	Chemical Shift (ppm)	Linewidth Hz)
0.0	-8.32	29
0.015	-7.55	58
0.030	-6.63	37
0.040	-6.06	37
0.045	-5.73	35
0.0475	-5.65	35
0.0490	-5.60	34
0.050	-5.55	34
0.051	-5.42	34
0.0525	-5.39	34
0.055	-5.29	34
0.060	-5.19	34
0.075	-5.09	34
0.090	-5.06	34
0.0975	-5.05	34
0.100	-5.05	34
0.1025	-5.04	34
0.110	-5.03	34
0.125	-5.03	34

[a] [NaTPB] = 0.05 M

[b] [Tetraglyme[= 0.01 M

Table 30

Mole Ratio Studies for the Complexation of 1,10,Diaza-18-Crown-6 with Sodium Ion in Nitromethane

Mole Ratio [DA18C6] $[Na^+]$	Chemical Shift (ppm)	Linewidth (Hz)
0.0	-11.95	24
0.3	-10.60	149
0.5	-9.58	157
0.7	-8.48	280
0.8	-7.90	285
0.9	-7.43	295
1.0	-6.75	324
1.1	-6.44	353
1.5	-6.33	357
2.0	-6.34	360
3.0	-6.33	364
4.0	-6.25	3.88

Table 31

Mole Ratio Studies for the Complexation of 18-Crown-6 with Sodium Ion in Solutions. N,N-Dimethylformamide (DMF) and in Dimethylsulfoxide (DMSO)

DMF		DMSO	
Mole Ratio [18C6]/[Na^+][a]	Chemical Shift (ppm)	Mole Ratio [18C6]/[Na^+][a]	Chemical Shift (ppm)
0.0	-4.14	0.0	-0.20
0.3	-6.61	0.1	-0.97
0.5	-8.40	0.2	-1.10
0.7	-9,82	0.4	-2.28
0.8	-10.63	0.5	-3.44
0.9	-11.32	0.7	-4.10
1.0	-11.55	0.9	-5.54
1.2	-12.23	1.0	-6.03
1.5	-12.73	1.2	-6.10
1.8	-12.88	1.5	-6.76
2.0	-12.97	2.0	-7.92
2.5	-13.10	2.5	-8.21
3.0	-13.22		
3.5	-13.44		
4.0	-13.60		

[a] $[Na^+]$ = 0.01 M NaTPB

[a] $[Na^+]$ = 0.05 M NaO

Reference = 0.1 M NaTPB in D_2O

10-13.

On the addition of 18-crown-6 to N,N-dimethylformamide and to dimethylsulfoxide solutions of the sodium ion, an upfield shift of the sodium-23 resonance was observed. Both solvents have high solvating abilities (DN = 26.6 and 29.8 for DMF and DMSO respectively), and are able to solvate the sodium cation to a great extent; hence, the complexes formed are not too strong. Log K_f values are 2.56 ± 0.05 and 1.78 ± 0.20 in DMF and DMSO solutions respectively. These values are slightly higher than those reported by Lin (161), Log K_f = 2.31 ± 0.05 and 1.41 ± 0.07 in DMF and DMSO, respectively by carbon-13 NMR techniques.

For the complexation of 15-crown-5 with the sodium ion in propylene carbonate solution, there is a paramagnetic shift of the sodium-23 resonance until a mole ratio of one is reached followed by a gradual diamagnetic shift. The behavior indicates the successive formation of both 1:1 and 2:1 (ligand:cation) complexes. Similar behavior has been observed for the complexation of 12-crown-4 with the Li^+ ion in nitromethane and in propylene carbonate solutions (103), 15-crown-5 with Na^+ ion in nitromethane and in acetonitrile solutions (161), as well as 18-crown-6 with Cs^+ ion in several nonaqueous solvents (162). In all of the above cases where two complexes are formed, the cavity size of the ligand is smaller than the size of the cation.

The formation constant for the complexation of 15-crown-5 with sodium ion, in acetonitrile solution was determined by the competititve NMR technique (168). Formation of a 2:1 (ligand: sodium) complex was not taken into account in this case since K_{f2} is considered to be quite small (161). The value of the formation constant calculated from the sodium-23 chemical shift measurement is log K_f = 4.30 ± 0.10. A value of log $K_f > 4$ was reported earlier (161).

In the case of the interaction of the sodium ion with 1,10-diaza 18-crown-6

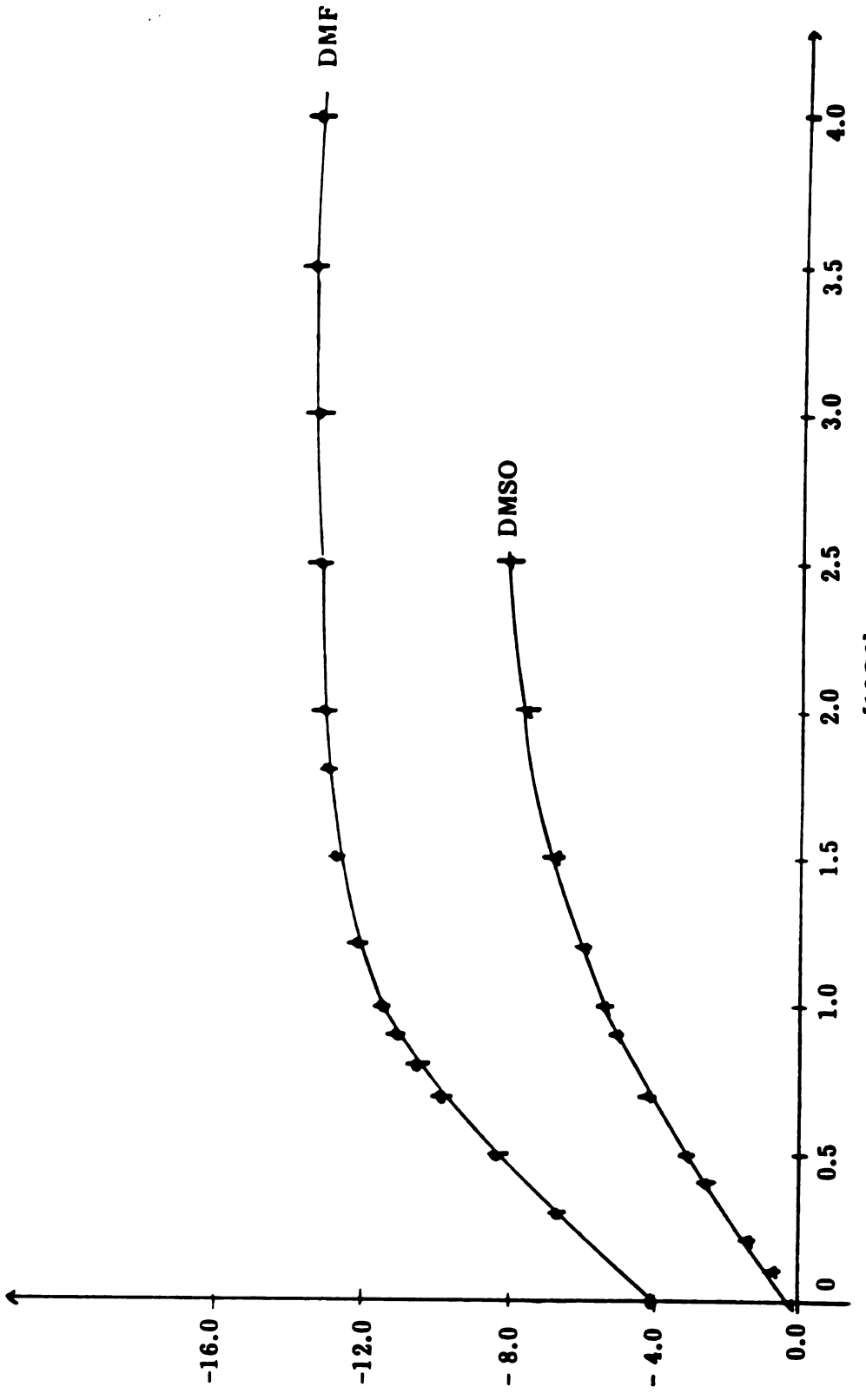


Figure 10: Sodium-23 chemical shifts as a function of $[18C6]/[Na^+]$ mole ratio in N,N-dimethylformamide and in dimethylsulfoxide solutions

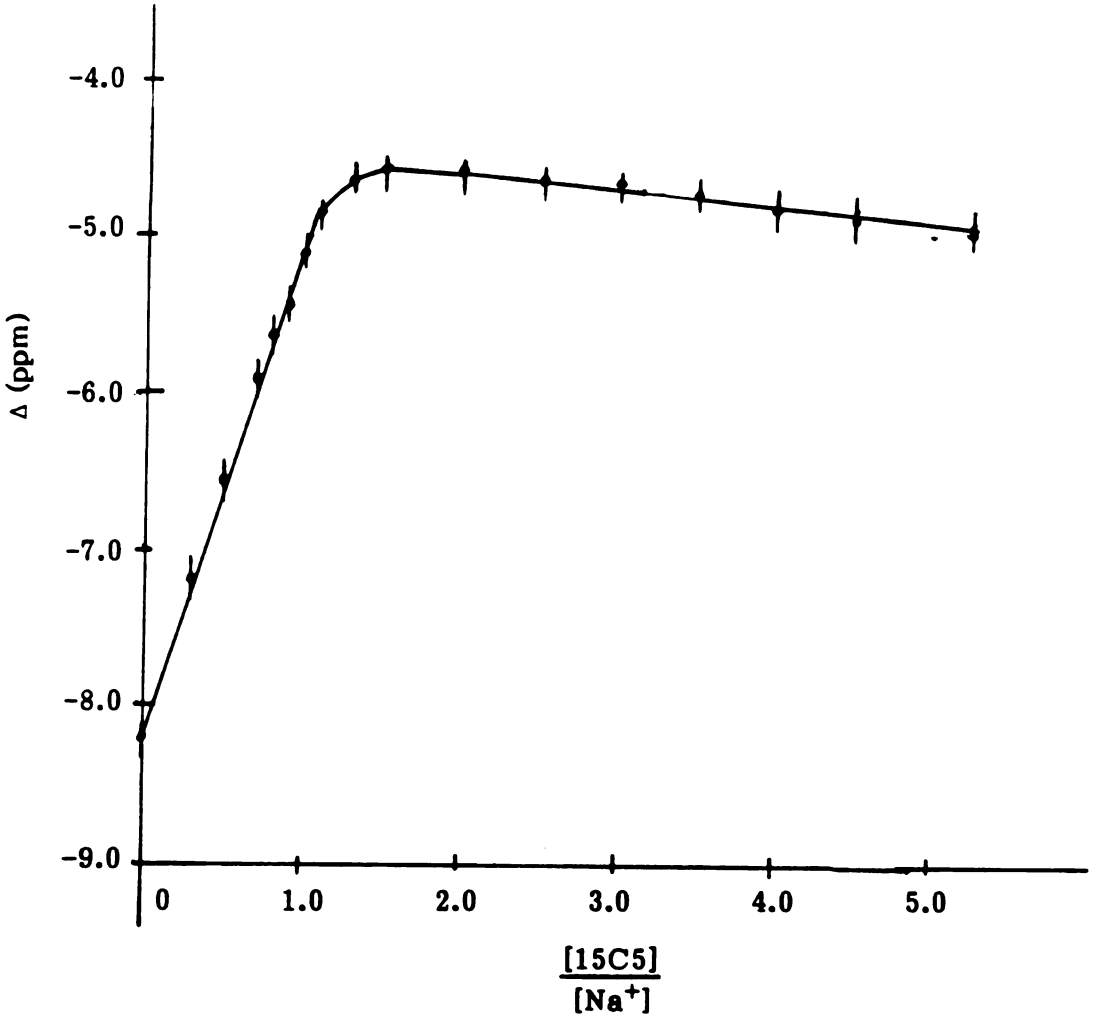


Figure 11: Sodium-23 chemical shifts as a function of [15C5]/[Na^+] mole ratio in propylene carbonate solutions

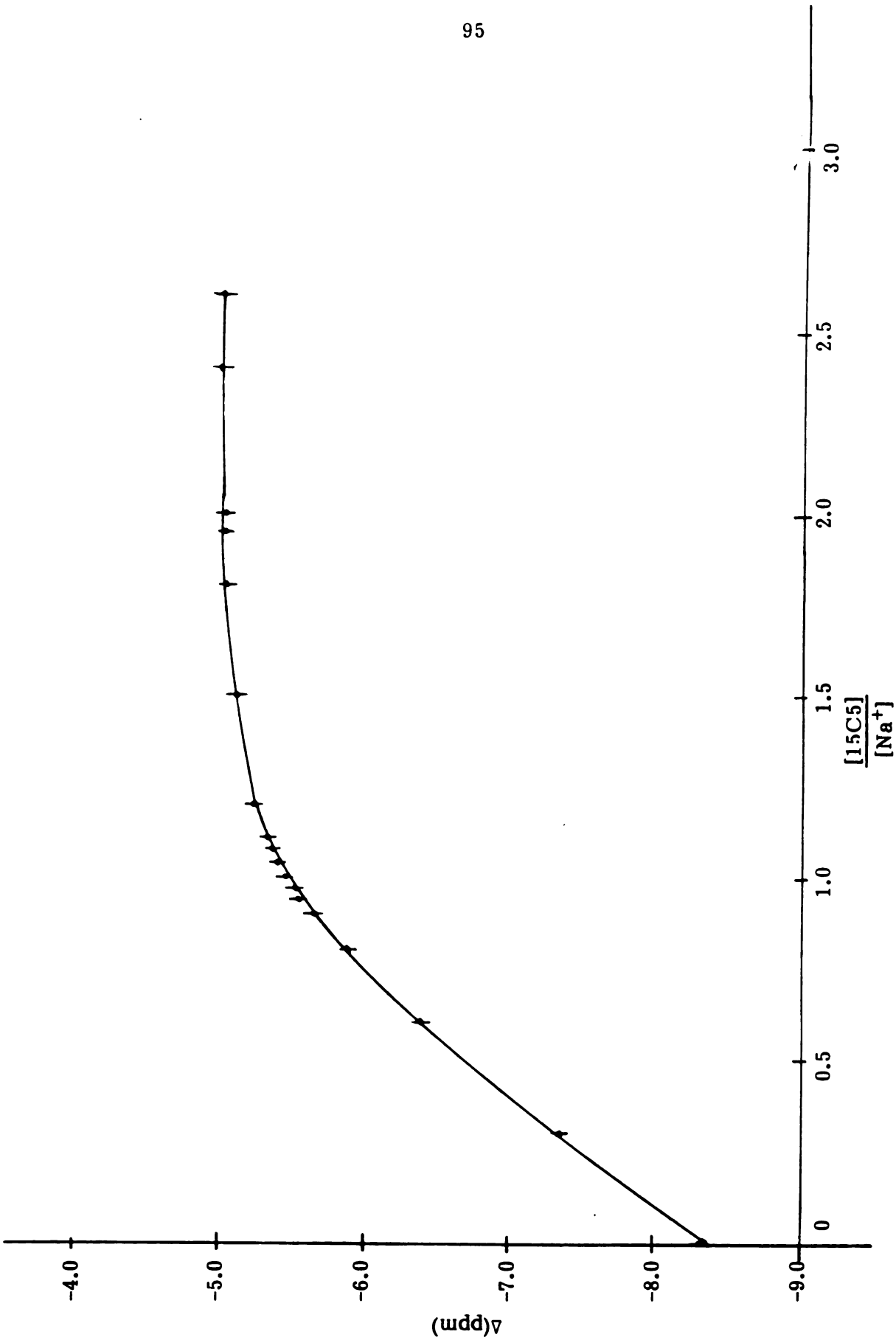


Figure 12: Sodium-23 chemical shifts as a function of $[15C5]/[Na^+]$ mole ratio for solutions containing NaTPB, tetraglyme and 15C5 in acetonitrile

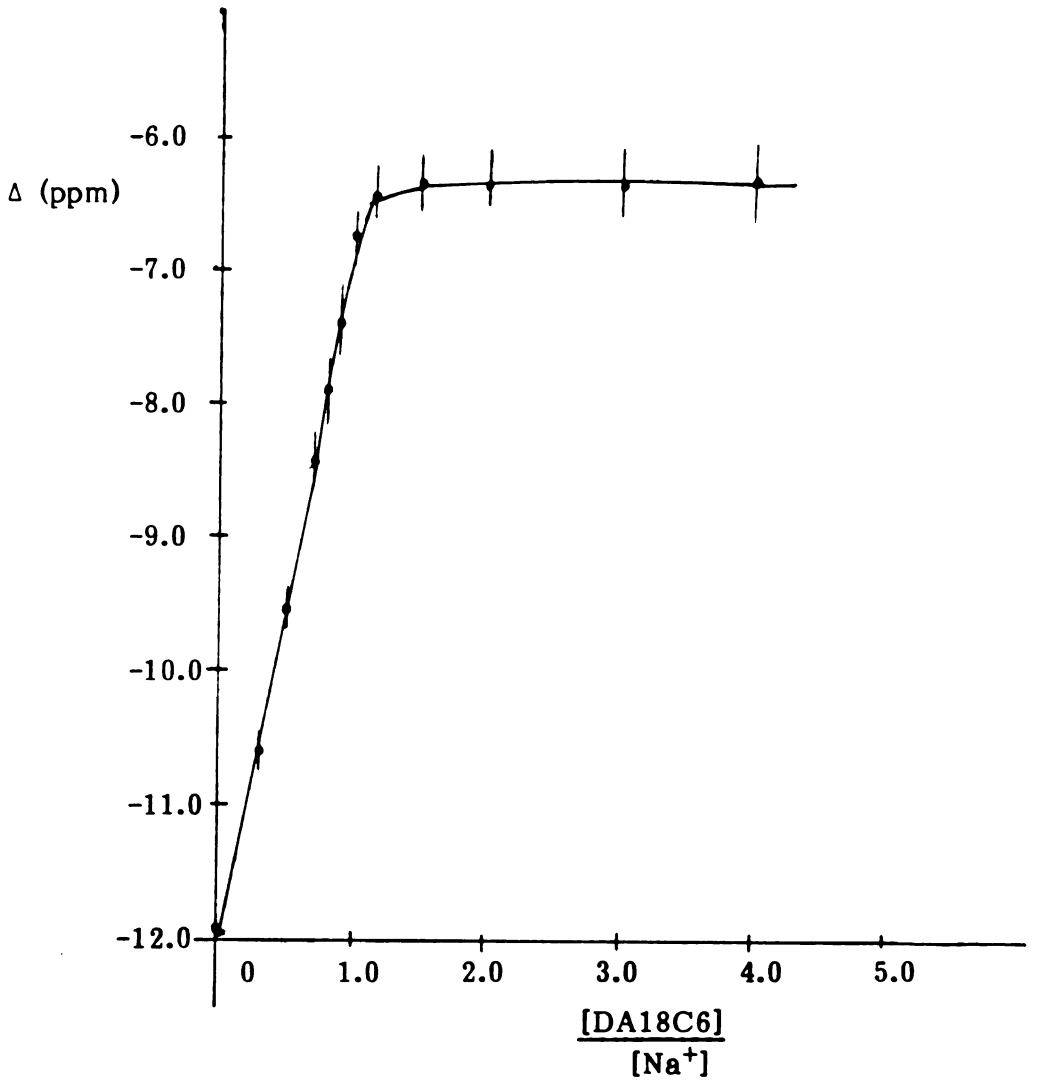


Figure 13: Sodium-23 chemical shifts vs. [DA18C6]/[Na^+] mole ratio in nitromethane solutions

in nitromethane, a downfield shift of the sodium-23 resonance was observed which reached a constant value after a mole ratio of one, indicating the formation of a stable 1:1 complex. The value of formation constant calculated from the chemical shift measurements, log K = 3.51 ± 0.12, is in relatively good agreement with the previously reported value of log K = 3.37 ± 0.13 (163). Considering the fact that nitromethane has a very poor solvating ability (DN = 2.7), one should expect a higher value for the formation constant. In the same solvent, for instance, log K_f > 4 has been reported for the interaction of 18-crown-6 with sodium ion (163) as well as for pentaglyme which the linear analogue of 18-crown-6, as found in this work.

The substitution of two oxygen atoms by two nitrogens on the 18-crown-6 macrocyclic ring seems to have a profound effect in the stability of sodium complex in this solvent. According to Pearson's hard-soft acid-base (HSAB) theory (164), the interaction of sodium ion (a hard acid) with the nitrogen atom (a soft base) should be weaker than that with oxygen atom (a hard base).

The formation constants for the systems discussed above are listed in Table 32.

Table 32

Formation Constants for the Complexes of Sodium Ion with Some Cyclic Ligands in Various Solvents at Room Temperature

System	Log K_f
Sodium/15-Crown-5/Acetonitrile	4.30 ± 0.09[a]
Sodium/18-Crown-6/DMF	2.56 ± 0.05
Sodium/18-Crown-6/DMSO	1.78 ± 0.20
Sodium/15-Crown-5/PC	> 4[b]
Sodium/DA18-Crown-6/NM	3.51 ± 0.12

[a] Obtained by the competitive NMR method.

[b] $K_{2:1}$ is too small to be calculated.

b. Complexes of the thallium(I) ion with 15-crown-5, 18-crown-6 and 21-crown-6 in N,N-dimethylformamide and in acetonitrile solutions at room temperature.

Thallium-205 NMR was used to study the interaction of macrocyclic ligands 15-crown-5, 18-crown-6 and 21-crown-7 with thallium(I) ion in N,N-dimethylformamide. The variation of thallium-205 chemical shifts as the ligand concentration increases are listed in Tables 33 35. The chemical shift plots as a function ligand/Tl^+ mole ratio are shown in Figures 14-17.

As the ligand was added to the Tl^+ solution, there was an upfield shift of the thallium-205 resonance. For 18-crown-6 and 21-crown-7, the chemical shift versus mole ratio plots level off after a mole ratio of one indicating the formation of stable 1:1 complexes. On the other hand, for 15-crown-5, there was no observable break in the curve even at high mole ratios which means that a weaker complex was formed.

The cavity sizes for the macrocyclic ligands 15-crown-5, 18-crown-6 and

Table 33

Mole Ratio Studies for the Complexation of 15-Crown-5 and 21-Crown-7 with Thallium(I) Ion in N,N-Dimethylformamide

Mole RAtio $[15C5]/[Tl^+]$[a]	Chemical Shift (ppm)	Mole Ratio $[21C7]/[Tl^+]$[a]	Chemical Shift[b] (ppm)
0.0	117.82	0.0	127.76
0.45	71.10	0.5	-21.3
0.63	49.95	0.8	-91.95
0.82	28.21	0.9	-112.52
1.02	13.22	1.0	-126.76
1.15	1.47	1.1	-137.78
1.43	-20.86	1.3	-151.30
1.73	-31.73	1.5	-158.93
2.18	-63/46	2.0	-164.22
3.00	-97.25	2.5	-166.87
4.41	-139.9	3.0	-167.10
4.77	-144.8	4.0	-167.51
6.42	-171.0	5.0	-168.32
12.19	-216.2	6.0	-168.75

[a] $[Tl^+]$ = 0.04 M $TlClO_4$

[b] Measurements made at 35°C.

Table 34

Sodium-23 Chemical Shifts as a Function of 18-Crown-6 Concentration For a Solution Containing Sodium Perchlorate[a], Thallium Perchlorate[b] and 18-Crown-6 in Acetonitrile

Concentration of 18-Crown-6 M	Chemical Shift (ppm)	Linewidth (Hz)
0.0	-7.55	14
0.003	-7.65	18
0.006	-7.80	18
0.008	-8.00	20
0.0095	-8.42	24
0.0098	-8.47	26
0.010	-8.52	28
0.0102	-8.62	29
0.0105	-8.67	31
0.0110	-9.06	33
0.0120	-9.65	34
0.0150	-11.60	34
0.0195	-14.73	35
0.0200	-14.88	35
0.0250	-14.93	36
0.0300	-14.98	36
0.0500	-14.99	36

a $[NaClO_4] = 0.01$ M

b $[TlClO_4] = 0.01$ M

Table 35

Mole Ratio Studies for the Complexation of 18-Crown-6 with Thallium(I) Ion in N,N-Dimethylformamide

Mole Ratio [18C6]/[Tl^+][a]	Chemical Shift (ppm)	Line Width (Hz)
0.0	118.98	40
0.92	96.36	700
0.39	31.73	1000
0.40	58.75	800
0.54	-13.22	550
0.79	-79.32	500
0.93	-104.58	244
1.01	-121.33	200
1.06	-126.62	152
1.19	130.14	80
1.27	131.32	61
2.06	-132.79	55
2.52	-132.80	40
3.40	-133.68	35
5.05	-133.96	30

[a] $[Tl^+] = 0.0412$ M $TlClO_4$

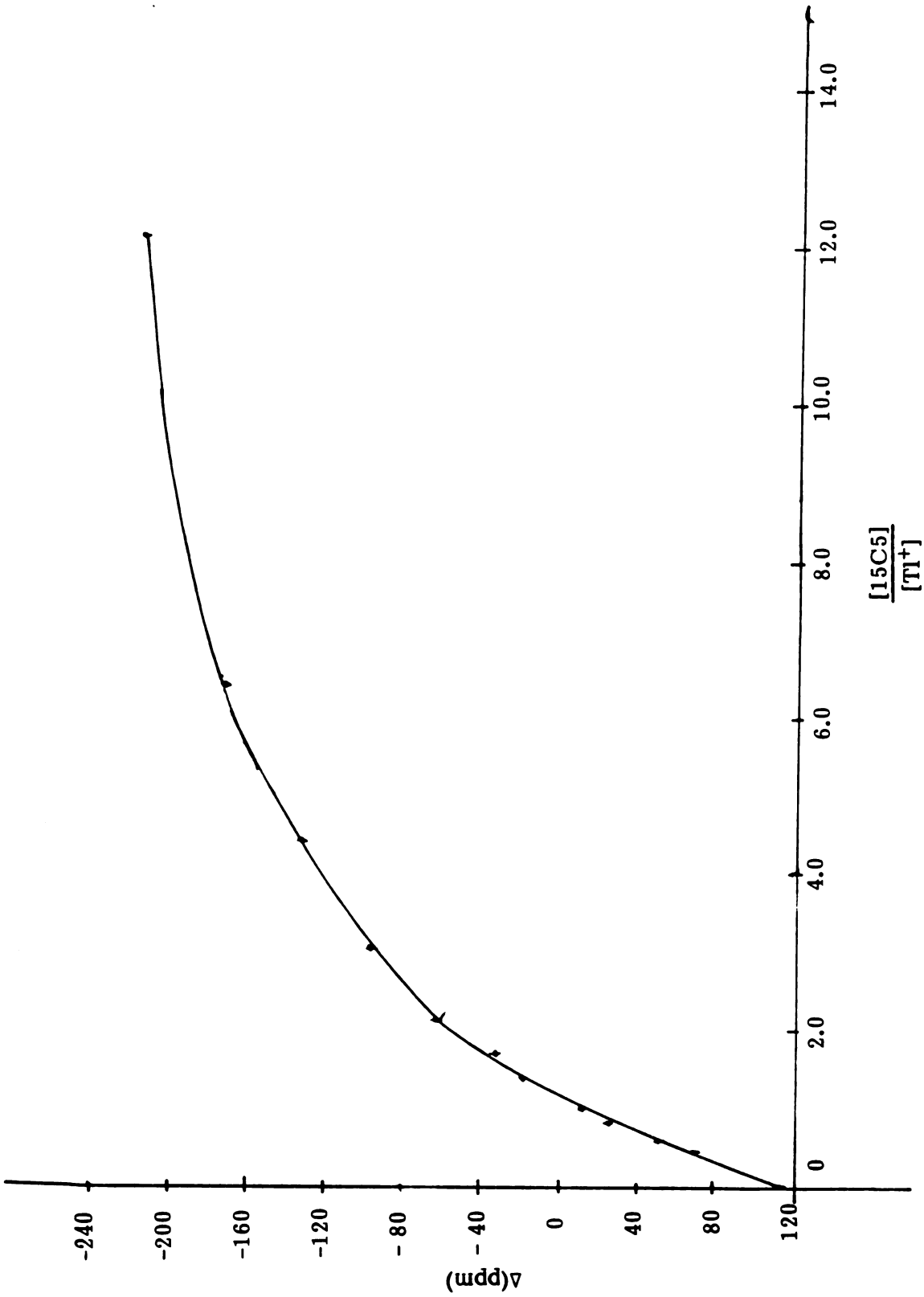


Figure 14: Thallium-205 chemical shifts as a vundtion of [15C5]/[Tl^+] mole ratio in N,N-diemthylformamide solutions

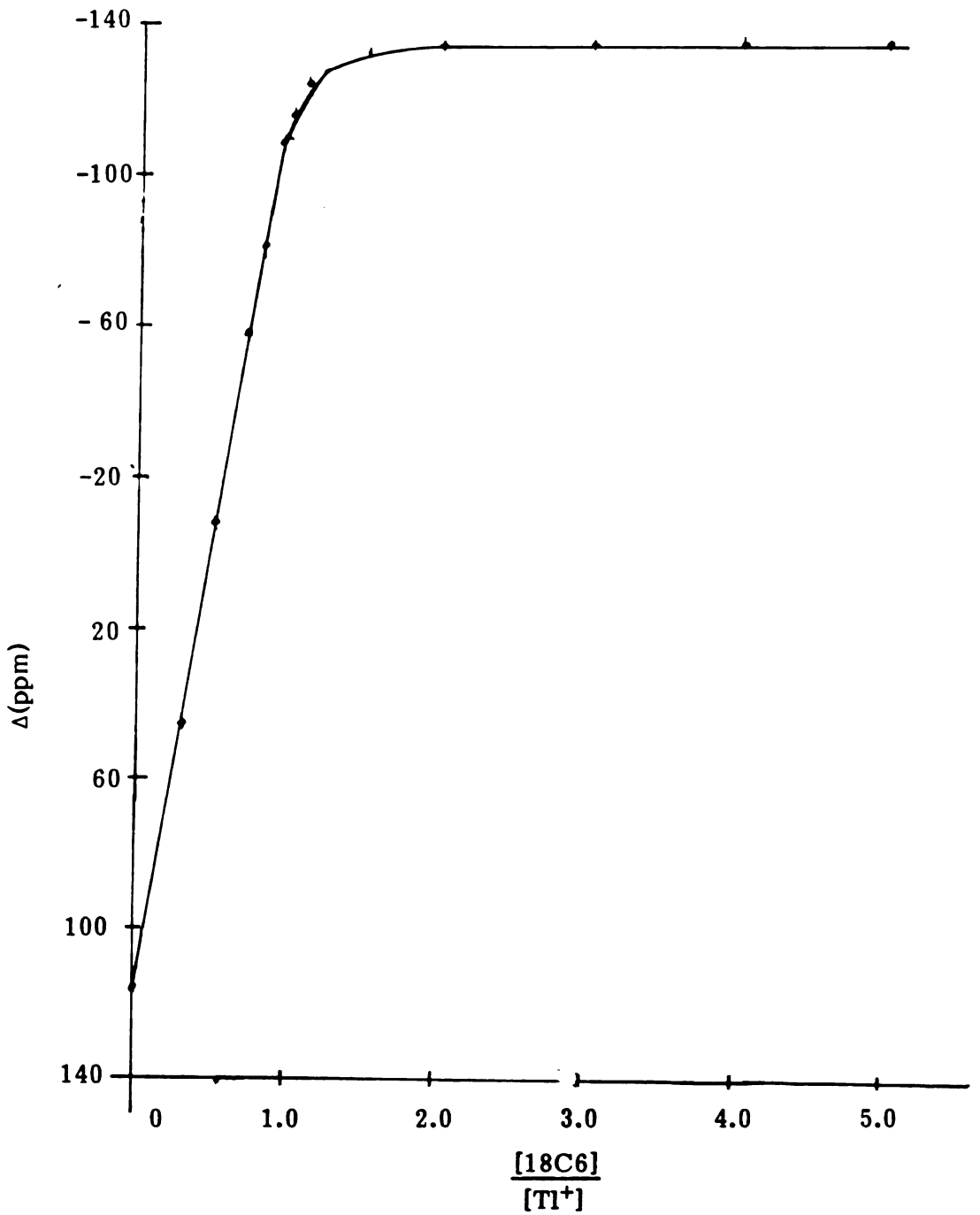


Figure 15: Thallium-205 chemical shifts as a function of [18C6]/[Tl^+] mole ratio in N,N-dimethylformamide solutions.

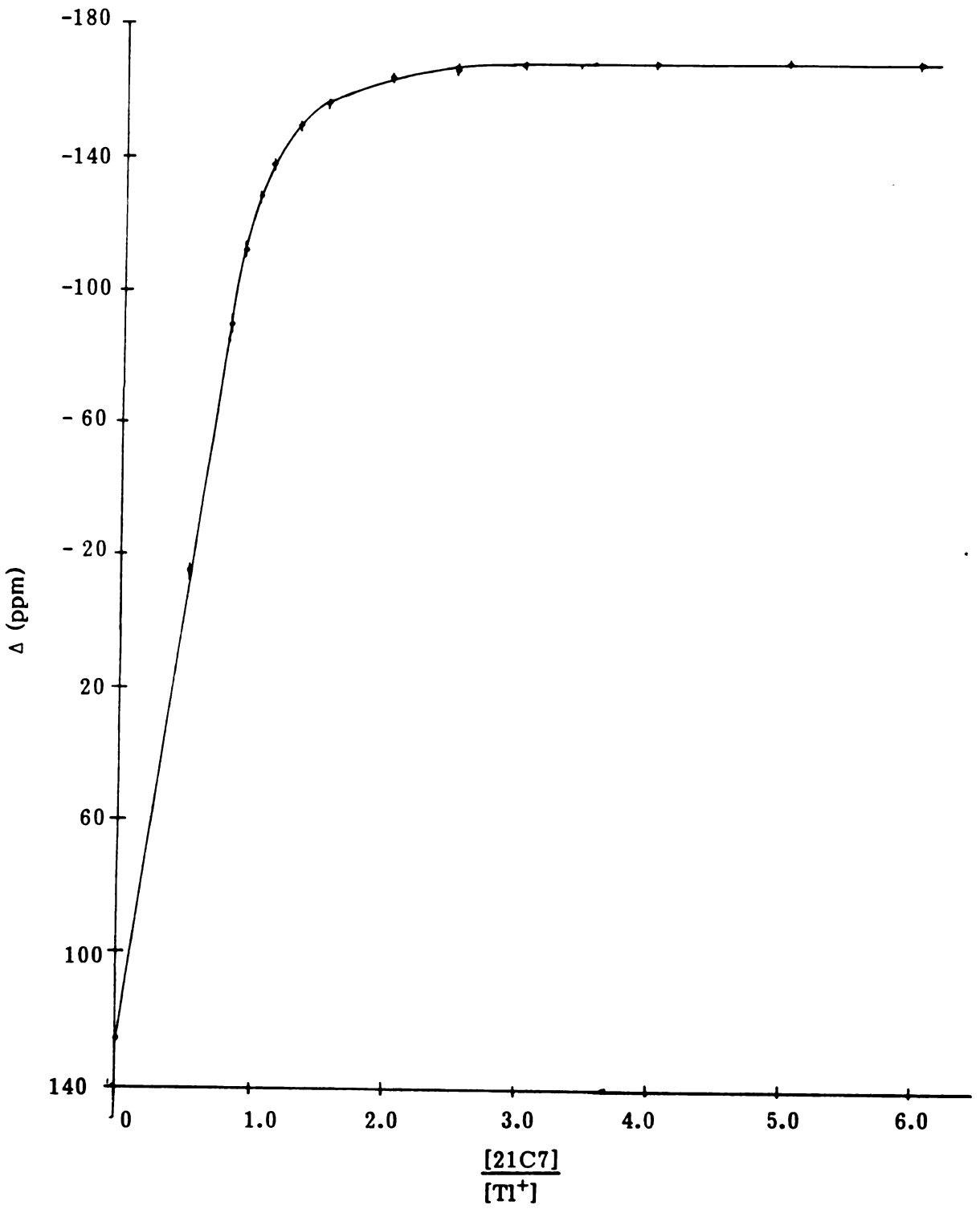


Figure 16: Thallium-205 chemical shifts vs. $[21C7]/[Tl^+]$ mole ratio in N,N-dimethylformamide solutions

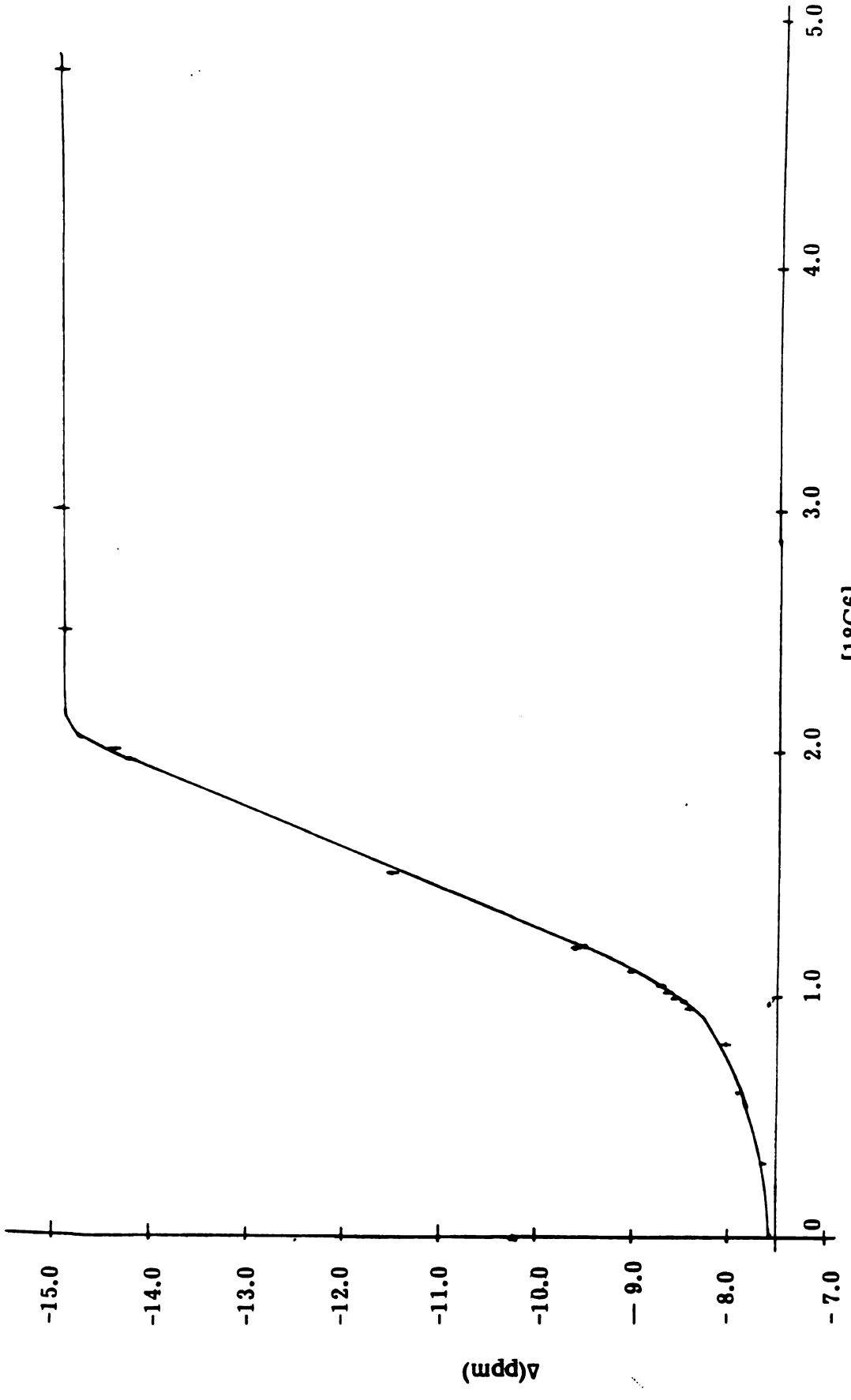


Figure 17: Sodium-23 chemical shifts as a function of $[18C6]/[Na^+]$ mole ratio for solutions containing $NaClO_4$, $TlClO_4$ and 18C6 in acetonitrile

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21-crown-7 are 1.72-2.2 Å, 2.6-3.2 Å and 3.4-4.3 Å respectively (166). According to Ladd (167), based on calculations using a combination of deduction from r_o values and experimental electron density maps, the most probable ionic radius of Tl^+ ion is 3.08 Å. Among the various factors that contribute to the stability of macrocyclic complexes with metal ions are the relative sizes of the cation and the ligand cavity. It becomes immediately obvious that the size of thallium(I) cation is too large to fit into the cavity of 15-crown-5 macrocycle. On the other hand the size of Tl^+ ion matches well with the cavity sizes of 18-crown-6 and of 21-crown-7.

The complexation of thallium(I) ion by 18-crown-6 in acetonitrile solution was studied by the competitive NMR technique (168) using sodium-23 NMR measurements.

Formation constants calculated for the systems discussed above, based on the chemical shift measurements are listed in Table 36.

Table 36

Formation Constants for the Complexes of Thallium(I) Ion with 15-Crown-5, 18-Crown-6 and 21-Crown-7 in Nonaqueous Solvents at Room Temperature

System	Log K_f
Tl^+/18-Crown-6/Acetonitrile	5.81 ± 0.05[a]
Tl^+/15-Crown-5/DMF	1.10 ± 0.01
Tl^+/18-Crown-6/DMF	3.73 ± 0.08
Tl^+/21-Crown-7/DMF	3.01 ± 0.03[b]

[a] Obtained by the competitive NMR method

[b] Formation constant determined at 35°C

It can be seen that 15-crown-5 forms a much weaker complex with Tl^+ ion in DMF solution (log K_f = 1.10 ± 0.01) than 18-crown-6 (log K_f = 3.73 ± 0.08) and 21-crown-7 (log K_f = 3.01 ± 0.03). The formation constant determined for the 18-crown-6-Tl^+-DMF system is slightly higher than the values reported by Lee (141), log K_f = 3.43 ± 0.08, and by Rounaghi (165), log K_f = 3.35 ± 0.06. These results were obtained by carbon-13 and thallium-205 NMR measurements respectively. The formation constant obtained for the 18-crown-6-Tl^+-acetonitrile system, log K_f = 5.81 ± 0.05 using sodium NMR is in excellent agreement with that reported by Boss (168) (log K_f = 5.81 ± 0.04). A value of log K_f = 3.01 ± 0.03 was caluclated for the formation constant of the 21-crown-7 complex with Tl^+ ion in DMF solution. This value is lower than that for the 18-crown-6-Tl^+-DMF system. It should be noted, however, that the stability of the former complex was measured at 35°C while that for the latter was measured at room temperature. The stability of thallium(I) complexes with macrocyclic ligands studied in N,N-dimethylformamide increases in the following order 18-crown-6 > 21-crown-7 > 15-crown-5. This order is different from what was observed in the same solvent with analogous linear polyethers where the stability increases with increasing number of donor atoms.

An interesting observation made during the course of doing thallium-205 NMR experiments on the 180 MHz instrument deserves mention at this point. At room temperature for some systems, when the mole ratio is between zero and one, the ^{205}Tl resonance cannot be observed. In these solutions, we have fast exchange between the free and bound Tl^+ ion and because of the large difference in the chemical shift of the two species, the population average signal cannot be seen. Such was not observed when thallium-205 measurements were done on a 60 MHz instrument (164, 165). The wide chemical shift range of thallium coupled with high field instrumentation becomes a disadvantage

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rather than an advantage. Attempts made to study the complexation of Tl^+ with the 15-crown-5 in low donicity sovlents like nitromethane, acetonitrile and acetone were unsuccessful for the same reason.

The purpose of the studies conducted so far was to investigate various systems, and subsequently make suitable choices for the study of the macrocyclic effect. The choice of systems has to be based on the magnitude of the formation constants of the linear and corresponding cyclic ligand with a particular metal ion in a given solvent. Recall that as discussed under the section on limitations of the technique, for direct determinations of the formation constant the range is $1 > K_f > 10^4$.

CHAPTER IV

THERMODYNAMICS OF COMPLEXATION FOR THALLIUM(I) AND SODIUM IONS WITH CYCLIC AND LINEAR LIGANDS IN N,N-DIMETHYLFORMAMIDE AND IN ACETONITRILE SOLUTIONS

1. THERMODYNAMICS OF CATION-LIGAND INTERACTION

The method for determining the enthalpy and the entropy of complexation was based on the temperature dependence of the stability constant. The stability constant (K_f) is related to the net changes in, free energy, $\Delta G°$, enthalpy, $\Delta H°$, and entropy, $\Delta S°$, of a reaction by the following relationships:

$$\Delta G° = \Delta H° - T\Delta S° \quad (1)$$

$$\Delta G° = - RT\ln K_f \quad (2)$$

$$\ln K_f = -\Delta H°/RT + \Delta S°/R \quad (3)$$

Thus a plot of $\ln K_f$ vs. $1/T$ (van't Hoff plot) gives a straight line with a slope of $-\Delta H°/R$ and an intercept of $\Delta S°/R$, providing that $\Delta H°$ is independent of temperature over the temperature range considered. From these thermodynamic functions, conclusions can be reached about the various factors governing complex formation, such as solvation effects, the character of coordinate bond and the changes of the structure often taking place during complex formation.

The measured enthalpy change ($\Delta H°$) for a complexation reaction in solution reflects the following:

a) the bond energy of the cation-donor atom bonds

b) the solvation energy of the reactants and products (ie., ion-solvent interaction, ligand-solvent interaction, and, complex-solvent interaction).

c) the contribution arising from ion-solvent interaction beyond the first solvation shell or ligation shell.

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Several factors contribute to the entropy S° of complexation which include:

1) ligand and cation desolvation
2) solvation of the complex
3) translational entropy loss on formation of a single complex from several moieties.
4) changes in internal entropy of the ligand upon complexation caused by orientation and conformational changes.

2a. Complexes of tetraglyme and 15-crown-5 with the Tl^+ ion in N,N-dimethylformamide solutions at various temperatures.

The effect of temperature on the thallium-205 resonance for the complexation of the Tl^+ ion by 15-crown-5 and tetraglyme were determined in N,N-dimethylformamide solutions. Thallium-205 chemical shifts measured at different temperatures are listed in Tables 37 and 38. Plots of ^{205}Tl chemical shifts versus ligand:thallium mole ratio at various temperatures are shown in Figure 18 and 19. In both cases in the solvent used, the thallium-205 resonance shifts upfield with increasing mole ratio and the curvature of the plots increases with decreasing temperature, which indicates the formation of more stable complexes at lower temperatures.

There were no sharp breaks in both plots even at high mole ratios which indicates formation of relatively weak complexes. This is partly due to the fact that the Tl^+ ion is too large (3.08 Å) to fit into the cavity of 15-crown-5 (1.7 - 2.2 Å) therefore, the cation cannot interact with all of the donor atoms of the ligand. Another factor that must have contributed to the formation of weak complexes for these systems is the high donicity of the solvent, DMF (DN = 26.6). A macrocyclic effect is observed, however, in that the stability

Table 37

Mole Ratio Studies for the Complexation of Tetraglyme with Thallium(I) Ion in N,N-Dimethyl Formamide at Various Temperature

Mole Ratio $[TG]/[Tl^+]$	Chemical Shift (ppm)		
	-5°C	**2°C**	**10°C**
0.0	126.5	127.0	128.0
1.0	103.1	106.5	109.1
2.0	84.91	88.44	93.28
3.0	67.14	73.75	79.77
4.0	50.54	60.23	66.99
5.0	38.64	48.48	56.56
7.0	20.95	30.85	39.37
8.0	12.35	22.63	31.44
10.3	-1.90	8.53	17.34
13.7	-16.44	-6.75	2.21
17.1	-30.40	-19.82	-12.04
	18°C	**25°C**	**32°C**
0.0	128.8	129.0	130.2
1.0	112.1	114.0	115.6
2.0	98.13	101.1	104.2
3.0	85.94	90.05	94.3
4.0	77.19	79.18	84.47
5.0	64.35	69.82	75.95
7.0	48.33	54.65	61.70
8.0	40.70	47.31	54.65
10.3	27.18	33.94	41.30
13.7	12.35	19.54	27.94
17.1	-2.34	5.0	12.93

Table 38

Mole Ratio Studies for the Complexation of 15-Crown-5 with Thallium(I) Ion in N,N-Dimethylformamide at Various Temperatures

Mole Ratio $[15C5]/[Tl^+]$	Chemical Shift (ppm)		
	2°C	**10°C**	**18°C**
0.0	127.0	128.0	128.6
0.5	66.4	75.51	83.15
1.0	25.57	33.76	43.19
1.5	-8.71	-1.84	9.56
2.0	-40.94	-31.41	-18.06
2.5	-70.09	-57.06	-42.0
3.0	-91.95	-77.93	-60.82
4.0	-127.5	-111.2	-92.09
5.0	-152.1	-135.0	-116.6
6.0	-167.2	-151.6	-134.4
7.0	-180.4	-164.8	-149.4
8.0	-190.1	-176.5	-162.2
	25°C	**35°C**	**45°C**
0.0	129.0	130.2	130.4
0.5	85.54	90.3	95.05
1.0	48.48	57.0	66.26
1.5	16.48	29.24	41.58
2.0	-8.51	6.62	22.04
2.5	-30.25	-12.48	5.74
3.0	-48.02	-27.31	-7.92
4.0	76.10	-53.75	-33.34
5.0	-100.8	-75.84	-50.23
6.0	-118.4	-91.94	-66.17
7.0	-133.7	-106.4	-79.31
8.0	-146.0	-119.3	-93.41

δ(ppm)

Figure

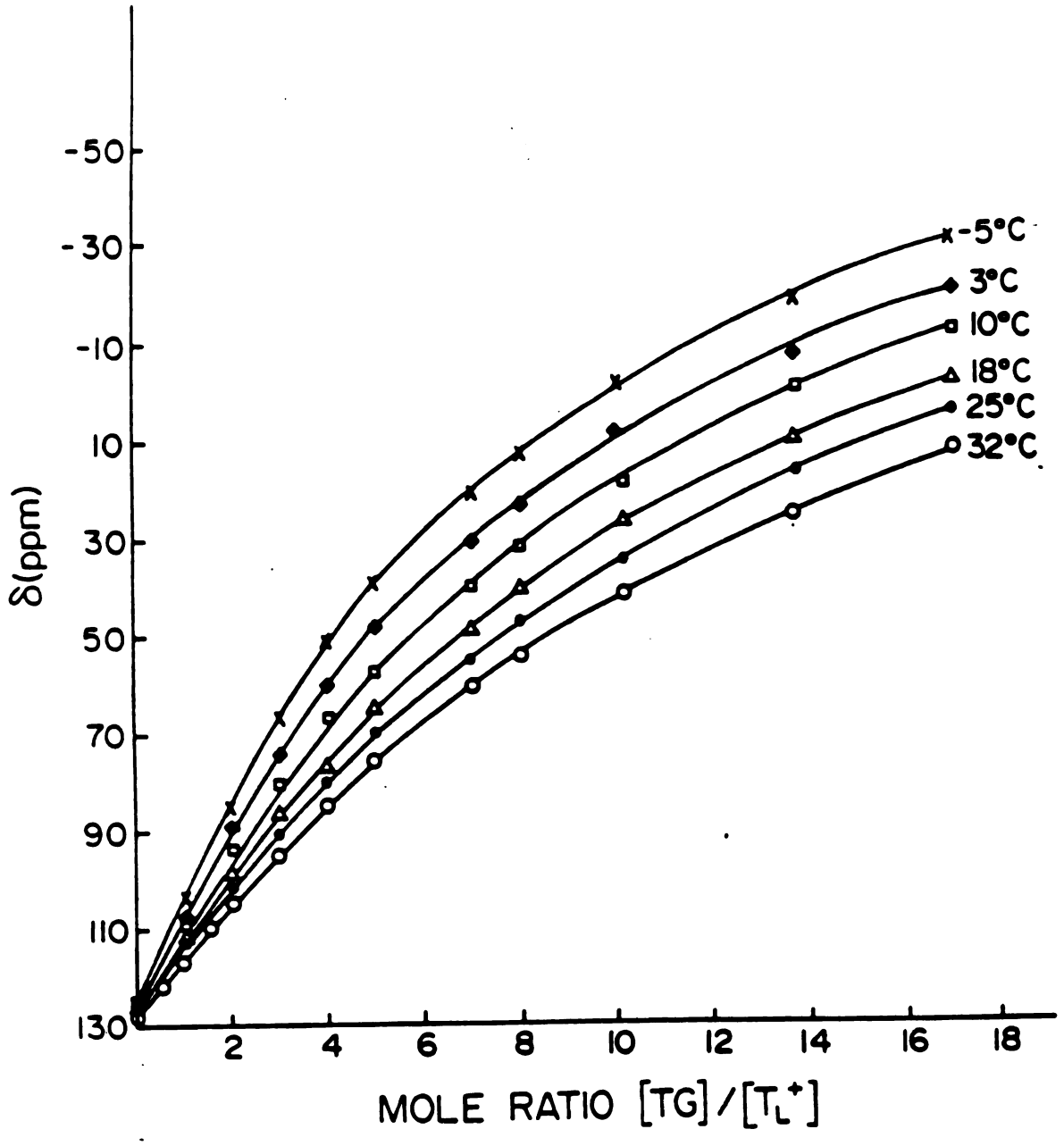

Figure 18: Thallium-205 chemical shifts vs. [TG]/[Tl^+] mole ratio in N,N-dimethylformamide solutions at different temperatures

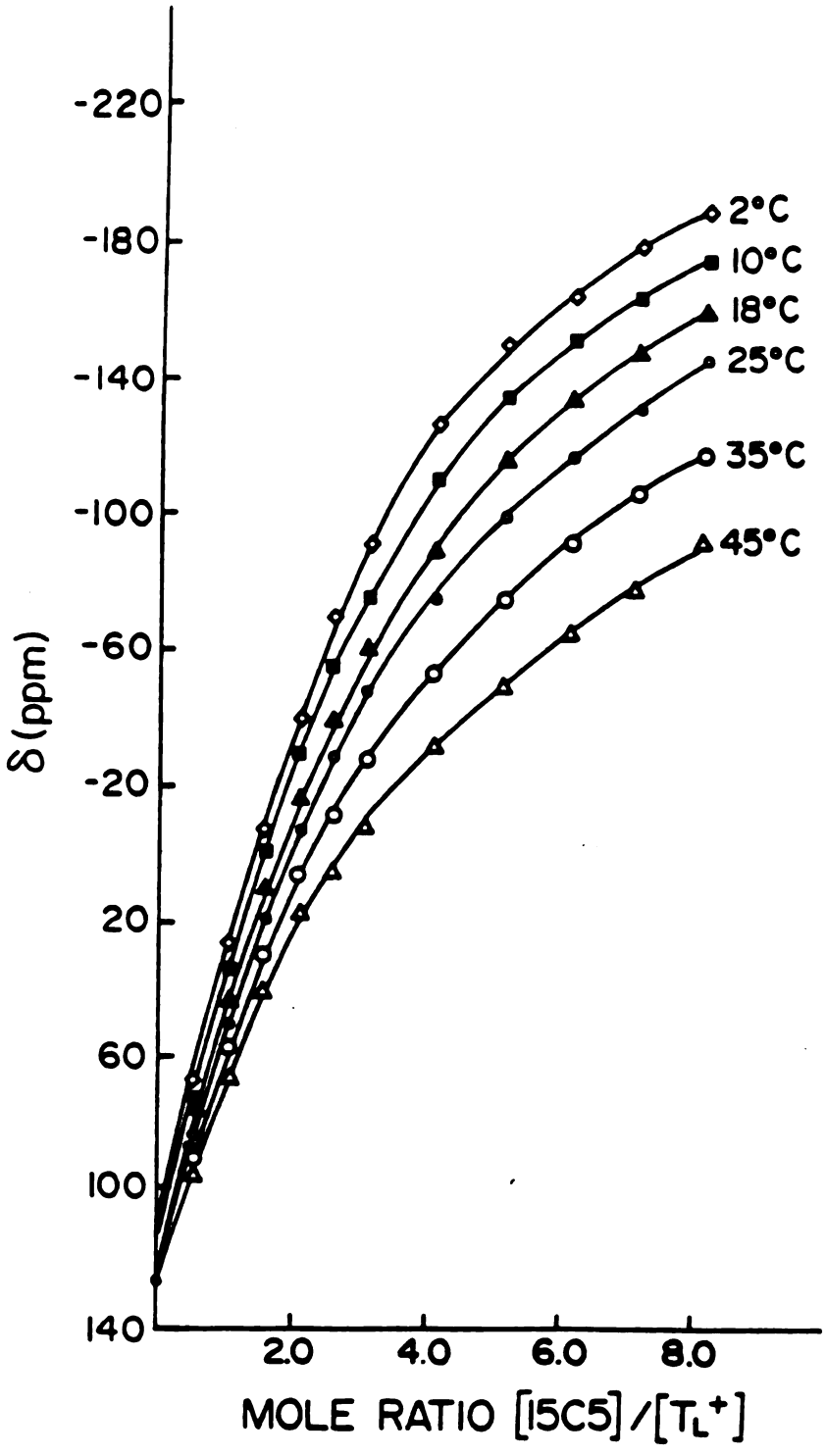

Figure 19: Thallium-205 chemical shifts as a function of [15C5]/[Tl^+] mole ratio in N,N-dimethylformamide solutions at different temperatures

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of the 15-crown-5-Tl^+ complex is slightly higher than that of the tetraglyme-Tl^+ complex in N,N-dimethylformamide solution. The formation constants calculated for these sytems are listed in Table 39.

The greater stability of the 15-crown-5-Tl^+ complex compared to that of its linear analogue is entirely due to a more favorable entropy change for the cyclic ligand reaction (Table 45). Reaction of the linear ligand with the Tl^+ ion was found to be more exothermic. In fact, the thermodynamic parameters listed in Table 45 show that enthalpy works against ($\Delta\Delta H°$) = -2.31 kcal mol^{-1}) complexation by the cyclic polyether so that the higher $\Delta G°$ value for the formation of the cyclic complex is completely due to a more favorable entropy.

b. Compelxation of the Tl^+ ion by pentaglyme and 18-crown-6[a] in N,N-dimethylformamide solutions at various temperatures.

Measurements were made on the variation in chemical shifts at different temperatures as the pentaglyme:Tl^+ ion mole ratio increases. The results are listed in Table 40. Plots of the temperature dependence of chemical shift versus mole ratio are shown in Figure 20 and 21. Again an upfield shift of the thallium-205 resonance was observed as the mole ratio increased. The curvature of the mole ratio plots decreases with increasing temperature which indicates that the reaction between the ligand and thallium ion in this solvent is exothermic.

The plots of the variation of chemical shift as a function of mole ratio at different temperatures show no break at any mole ratio indicating formation of a relatively weak complex, as was observed with tetraglyme.Tl^+ complex

[a] From reference 152

Table 39

Formation Constants at Different Temperatures for Tetraglyme·Tl^+ and 15-Crown-5·Tl^+ Complexes in N-N-Dimethylformamide

	Temperature	Log K_f
Tetraglyme·Tl^+	-5°C	0.52 ± 0.01
	2°C	0.45 ± 0.01
	10°C	0.38 ± 0.01
	18°C	0.29 ± 0.01
	25°C	0.27 ± 0.03
	32°C	0.19 ± 0.01
15-Crown-5·Tl^+	2°C	1.03 ± 0.01
	10°C	0.99 ± 0.01
	18°C	0.95 ± 0.01
	25°C	0.91 ± 0.01
	35°C	0.89 ± 0.01
	45°C	0.86 ± 0.01

Table 40

Mole Ratio Studies for the Complexation of Pentaglyme with Thallium(I) Ion in N,N-Dimethylformamide at Various Temperatures

MOle Ratio [PG]/[Tl^+]	Chemical Shift (ppm)		
	5°C	**10°C**	**20°C**
0.0	127.5	128.0	128.9
0.5	108.8	109.8	113.7
0.7	100.6	103.5	108.1
1.0	91.02	94.02	100.8
1.5	74.56	78.82	88.71
2.0	59.14	68.74	78.14
2.5	48.19	56.50	65.97
3.0	42.40	50.47	60.51
3.5	33.56	41.10	52.32
4.0	26.83	34.17	45.68
5.0	11.70	20.80	32.02
	30°C	**35°C**	**50°C**
0.0	129.4	129.7	130.2
0.5	117.0	120.0	122.5
0.7	112.3	116.9	120.2
1.0	106.1	110.4	112.6
1.5	95.52	102.2	104.8
2.0	86.20	93.31	97.77
2.5	77.0	84.35	89.99
3.0	70.25	79.36	84.20
3.5	63.25	71.81	78.95
4.0	56.30	67.02	74.84
5.0	44.25	54.68	63.84

Λ(ppm)

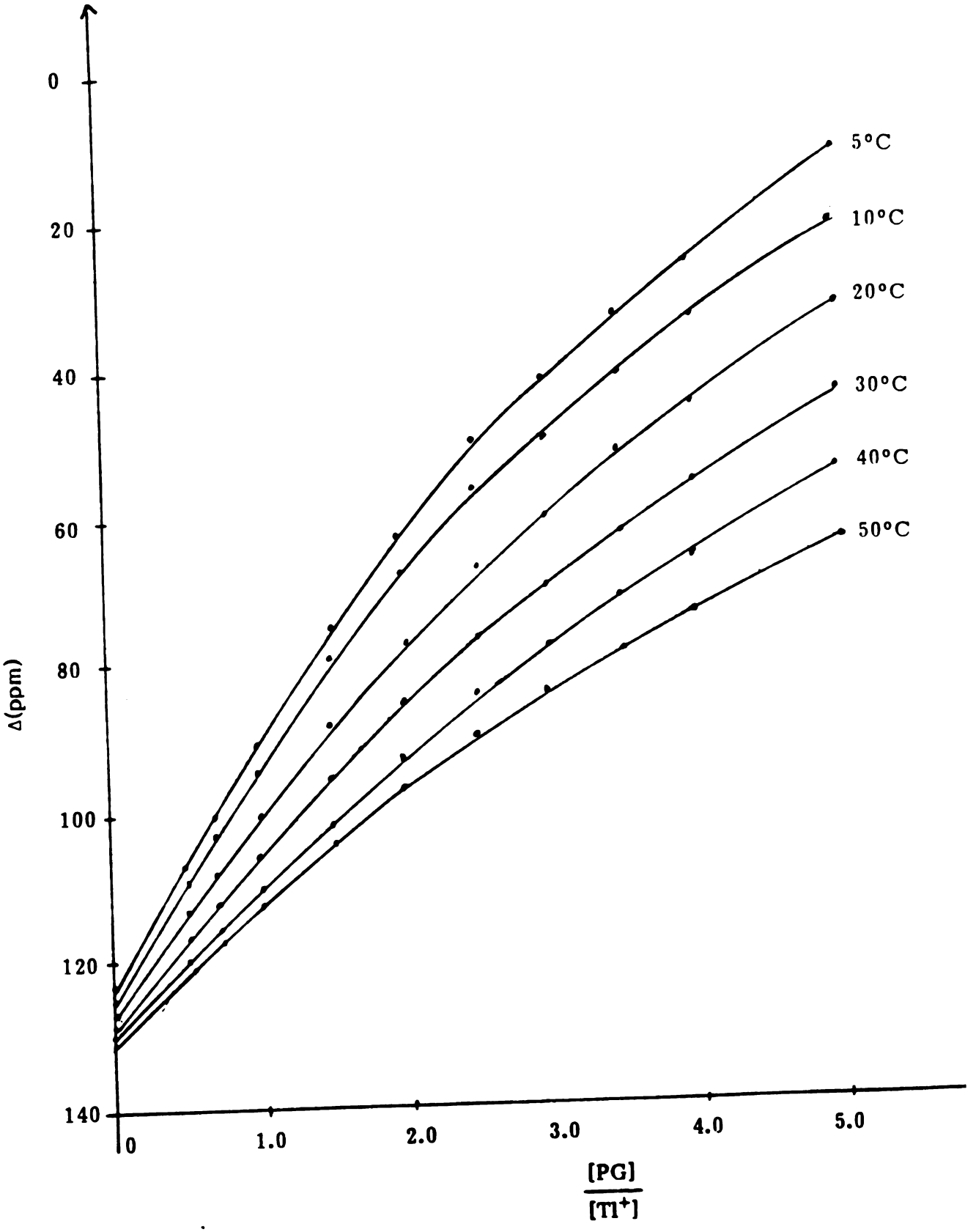

Figure 20: Chemical shifts for ^{205}Tl as a function of $[PG]/[Tl^+]$ mole ratio in DMF solutions at various temperatures.

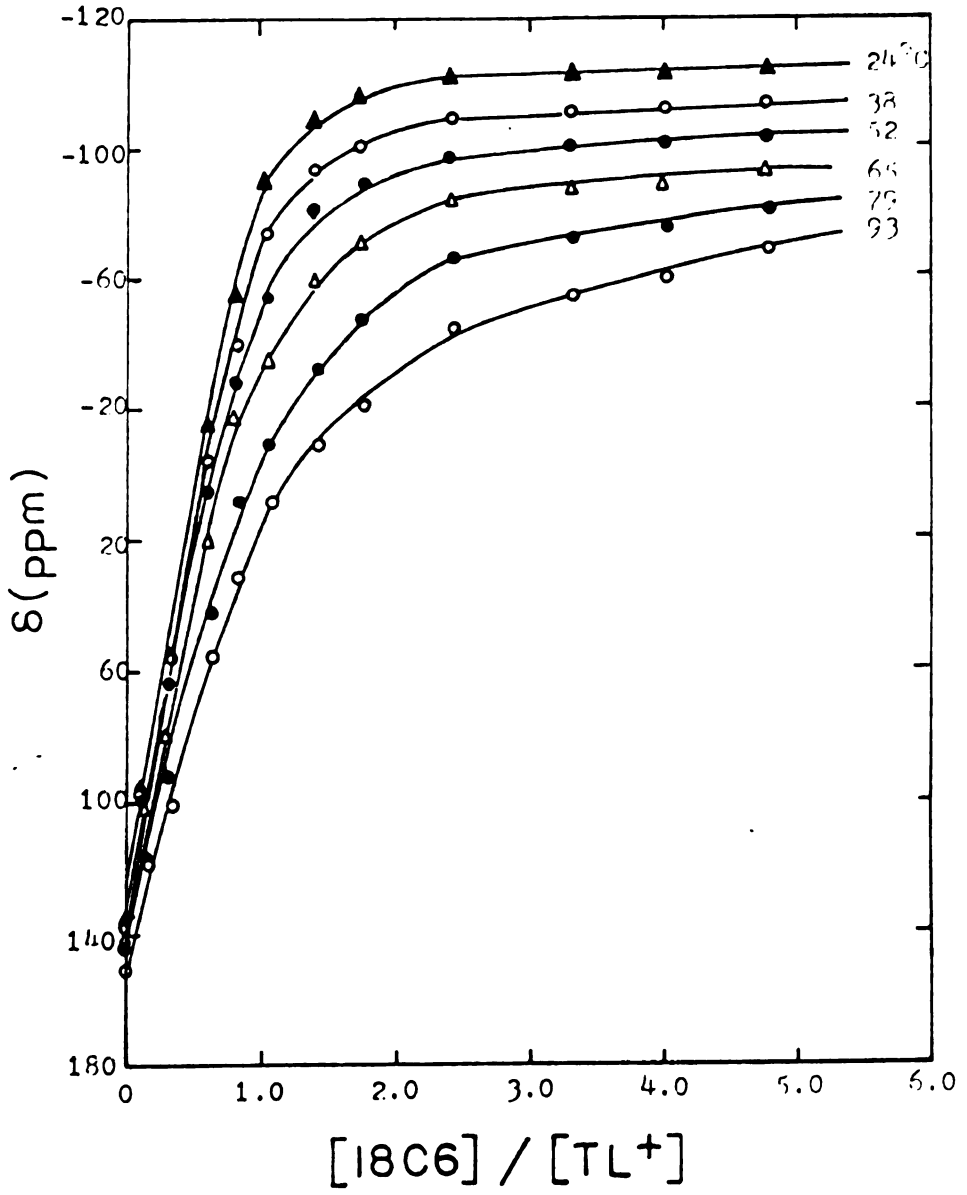

Figure 21: Thallium-205 chemical shifts as a function of [15C5]/[Tl^+] mole ratio in N,N-dimethylformamide solutions at various temperatures.

in the same solvent. On the other hand, similar plots for the 18-crown-6·Tl^+ complex levelled off after a mole ratio of 1:1 indicating formation of a stable complex. In this case (as compared with 15-crown-6) there is a better match between the size of the Tl^+ ion (3.08 A) and the cavity size of 18-crown-6 (2.6 - 3.2 Å). The formation constants calculated from these measurements are listed in Table 41.

It is seen that in DMF solution the formation constant for the cyclic complex (18-crown-6·Tl^+) is about three orders of magnitude higher than that of the linear complex (pentaglyme·Tl^+). This greater stability of the cyclic complex compared to its linear counterpart is mainly due to more favorable enthalpy and slightly more favorable entropy changes for the cyclic ligand reaction (Table 45). The more favorable entropy for the cyclic ligand results from the fact that it is more rigid in the uncomplexed form and has a preformed cavity which accomodates the cation. On the other hand, the linear ligand is highly flexible in its uncomplexed form and upon complexation is forced into a more organized state thereby loosing more conformational entropy than the cyclic ligand.

c. Complexation of the Tl^+ ion by hexaglyme and 21-crown-7 in N,N-dimethylformamide solutions at various temperature.

The effect of temperature on the thallium-205 resonance for the complexation of the Tl^+ ion by hexaglyme and 21-crown-7 were determined in N,N-dimethylformamide solutions. The results are listed in Tables 42 and 43, and plots of the measured chemical shifts versus mole ratio are shown in Figures 22 and 23. In both cases, an upfield shift of the ^{205}Tl resonance was observed at all temperatures studied, and the curvature of the plots decreases with increasing temperature. For the 21-crown-7·Tl^+ complex,

Table 41

Formation Constants at Different Temperatures for Pentaglyme·Tl^+ and 18-Crown-6.Tl^+ Complexes in N,N-Dimethylformamide

	Temperature	Log K_f
Pentaglyme.Tl^+	5°C	0.81 ± 0.05
	10°C	0.75 ± 0.03
	20°C	0.62 ± 0.04
	30°C	0.50 ± 0.03
	35°C	0.33 ± 0.04
	50°C	0.29 ± 0.03
18-Crown-6.Tl^+ [a]	24°C	3.62 ± 0.10
	38°C	3.37 ± 0.07
	52°C	3.13 ± 0.05
	65°C	2.90 ± 0.07
	79°C	2.64 ± 0.05
	93°C	2.43 ± 0.05

[a]From reference 152

Table 42

Mole Ratio Studies for the Complexation of Hexaglyme with Thallium(I) Ion in N,N-Dimethylformamide at Various Temperatures

Mole Ratio [HG]/[Tl^+]	Chemical Shift (ppm)		
	-15°C	-5°C	5°C
0.0	126.0	126.5	127.5
0.5	79.03	89.16	96.80
1.0	43.42	60.08	72.56
1.5	15.28	35.25	52.15
2.0	-1.03	17.19	35.84
2.5	-20.58	0.88	22.10
3.0	-34.52	-10.87	8.23
4.0	-47.45	-27.47	-9.89
5.0	-62.13	-43.63	-23.06
6.0	-71.04	-56.70	-37.90
7.0	-75.50	-59.93	-41.86
8.0	-77.41	-63.90	-48.77
	15°C	25°C	35°C
0.0	128.4	129.0	129.7
0.5	102.2	105.8	112.6
1.0	81.67	88.43	98.42
1.5	63.75	72.71	85.78
2.0	47.45	59.05	74.33
2.5	33.34	46.56	63.16
3.0	22.62	36.43	55.06
4.0	5.14	19.68	39.37
5.0	-8.67	5.29	25.70
6.0	-23.50	-10.58	9.55
7.0	-27.76	-15.43	4.70
8.0	-35.84	-23.50	-2.79

Table 43

Mole Ratio Studies for the Complexation of 21-Crown-7 with Thallium(I) Ion in N,N-Dimethylformamide at Various Temperatures

Mole Ratio $[21C7]/[Tl^+]$	Chemical Shift (ppm)		
	35°C	42°C	50°C
0.0	129.7	130.4	130.8
0.5	-21.30	-15.28	-10.87
0.8	-91.95	-86.52	-73.88
0.9	-112.5	-104.6	-95.77
1.0	-126.8	-117.7	-105.9
1.1	-137.8	-129.1	-117.2
1.3	-151.3	-144.5	-134.8
1.5	-158.9	-152.1	-143.7
2.0	-164.2	-158.3	-151.3
2.5	-166.9	-161.3	-157.8
3.0	-167.1	-162.2	-159.4
4.0	-167.5	-163.1	-159.5
5.0	-168.3	-163.4	-160.1
6.0	-168.8	-163.5	-160.4

Table 43 continued

Mole Ratio [21C7]/[Tl^+]	Chemical Shift (ppm)		
	58°C	**66°C**	**74°C**
0.0	131.2	131.5	131.9
0.5	-3.82	2.94	8.81
0.8	-63.46	-54.94	-48.62
0.9	-83.26	-74.46	-62.43
1.0	-95.18	-84.46	-73.59
1.1	-107.4	-95.33	-85.05
1.3	-124.4	-113.5	-102.4
1.5	-134.8	-124.7	-114.7
2.0	-143.8	-135.1	-125.1
2.5	-151.2	-143.9	-135.8
3.0	-155.1	-149.8	-143.2
4.0	-156.0	-150.8	-145.9
5.0	-156.3	-152.3	-146.6
6.0	-156.8	-152.5	-146.8

δ (ppm)

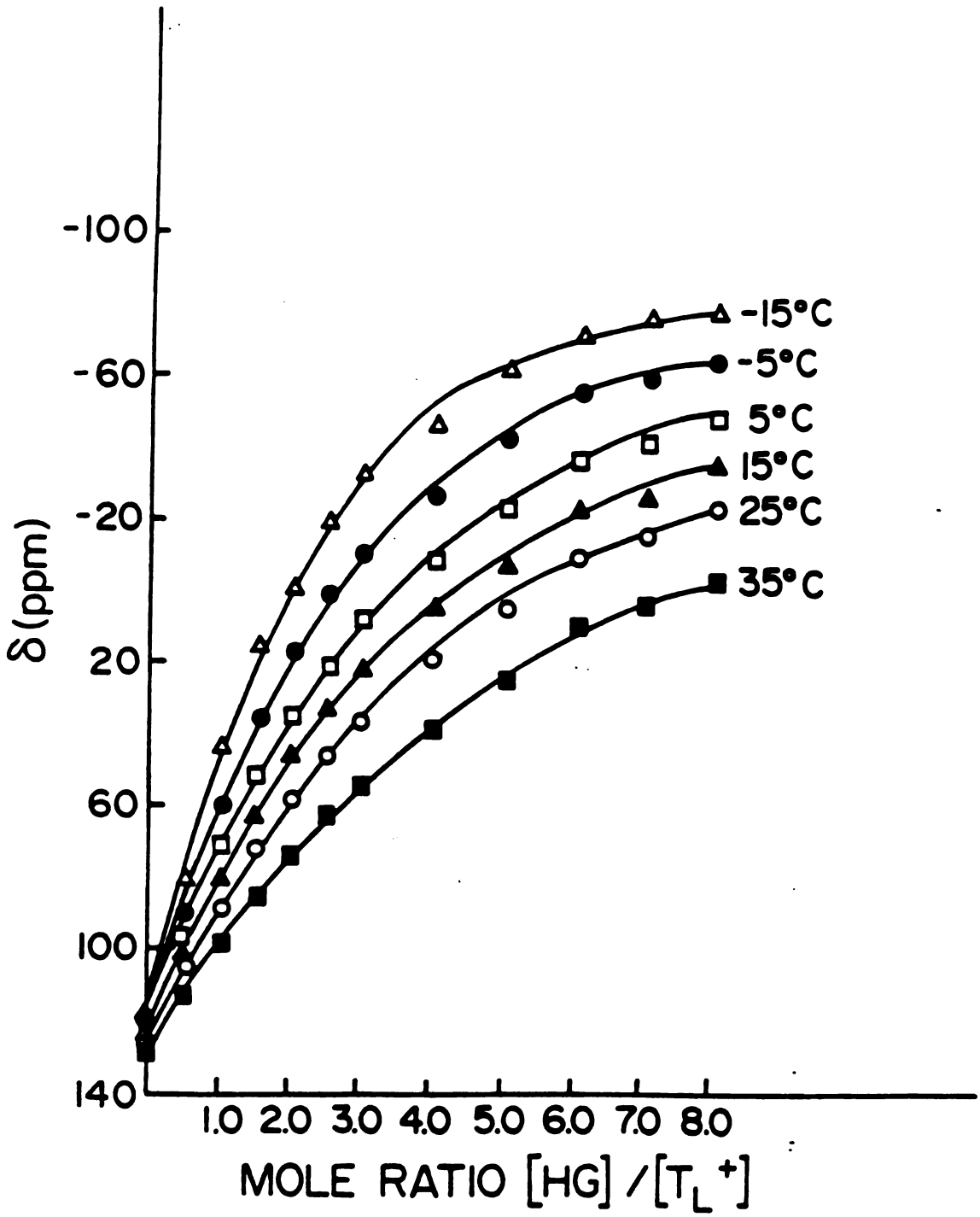

Figure 22: Thallium-205 chemical shifts vs. [HG]/[Tl^+] mole ratio in N,N-dimethylformamide solutions at various temperatures

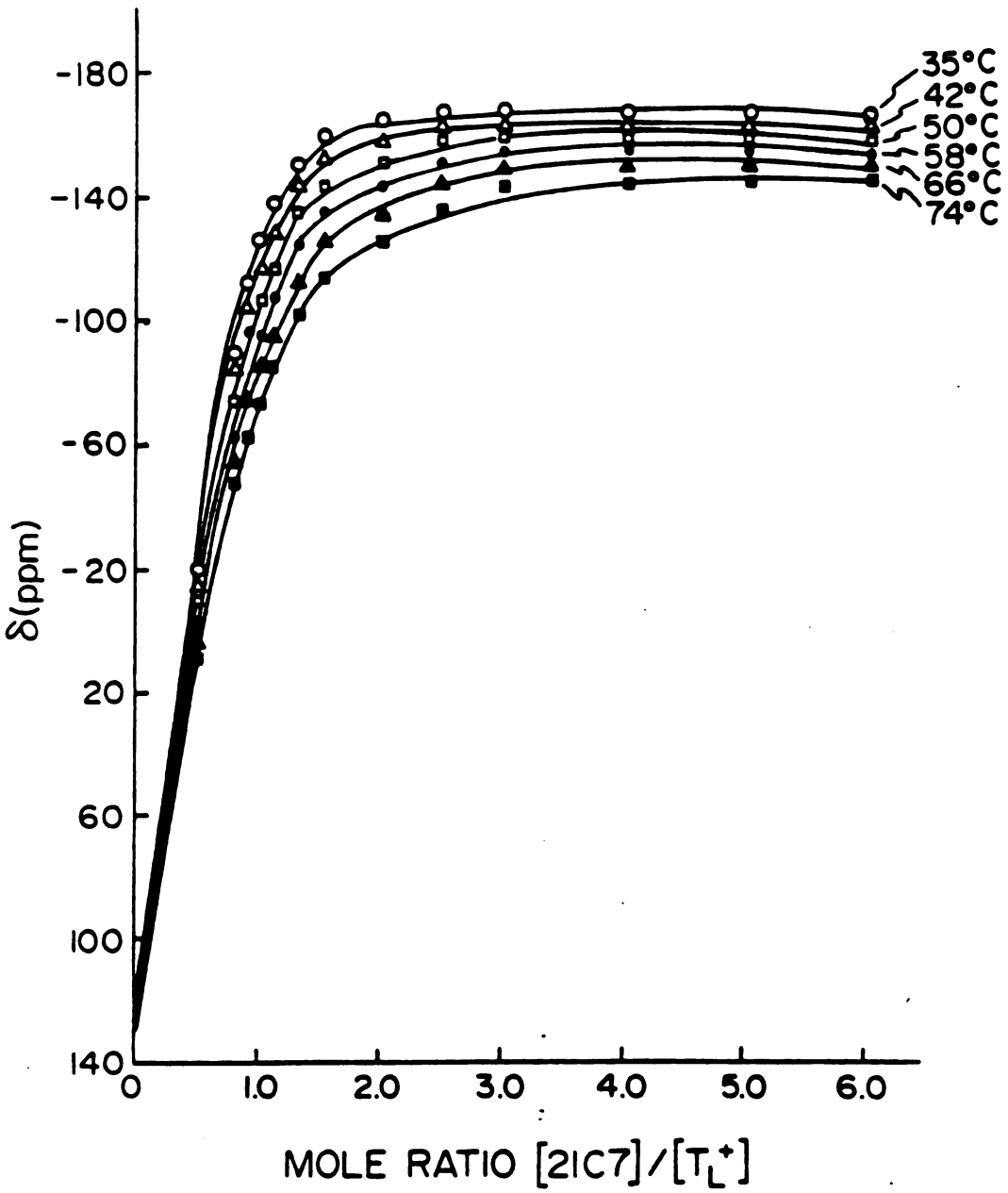

Figure 23: Thallium-205 chemical shifts vs. [21C7]/[Tl^+] mole ratio in N,N-dimethylformamide solutions at various temperatures

the curves show obvious breaks at a mole ratio of one, indicating the formation of stable 1:1, ligand:Tl^+ complex, while the plots for the hexaglyme·Tl^+ complex do not show any breaks at any mole ratio, which means that a much weaker complex is formed. Table 44 lists the formation constants calculated, based on these measurements.

Results given in Table 45 for these systems clearly show the existence of a macrocyclic effect which results entirely from a more favorable enthalpy contribution for the formation of the cyclic complex. In fact, the entropy is slightly in opposition to the cyclic ligand reaction which is contrary to expectation. Since hexaglyme is a linear ligand which is supposed to be highly flexible in the free state and 21-crown-7 is a cyclic ligand, one would expect a much more negative entropy of reaction for the linear ligand than for the cyclic.

The plots of the natural log of formation constant versus of the reciprocal of temperature (van't Hoff plots) for all the thallium(I) complexes studied are shown in Figure 24.

d. Complexation of tetraglyme and 15-crown-5 with sodium ion in acetonitrile solutions at various temperatures.

The variation of sdoium-23 chemical shift as a function of ligand:Na^+ mole ratio was measured in acetonitrile solutions at various temperatures and the results are listed in Table 46 and 47. Figures 25 and 26 show plots of the measured chemical shifts versus the mole ratios. From these plots it can be seen that for the tetraglyme.Na^+ complex, there is an upfield shift of the ^{23}Na resonance as the ligand concentration increased, the shift becomes fairly constant after a mole ratio of about one, indicating the formation of a fairly stable 1:1, ligand:metal complex. With the 15-crown-5·Na^+ complex,

Table 44

Formation Constants at Different Temperatures for Hexaglyme.Tl^+ and 21-Crown-7.Tl^+ Complexes in N,N-Dimethylformamide

	Temperature	Log K_f
Hexaglyme.Tl^+	-15°C	1.31 ± 0.01
	-5°C	1.14 ± 0.01
	5°C	0.99 ± 0.01
	15°C	0.88 ± 0.01
	25°C	0.76 ± 0.02
	35°C	0.60 ± 0.02
21-Crown-7.Tl^+	35°C	3.01 ± 0.03
	43°C	2.92 ± 0.02
	50°C	2.73 ± 0.02
	58°C	2.58 ± 0.02
	66°C	2.45 ± 0.02
	74°C	2.35 ± 0.02

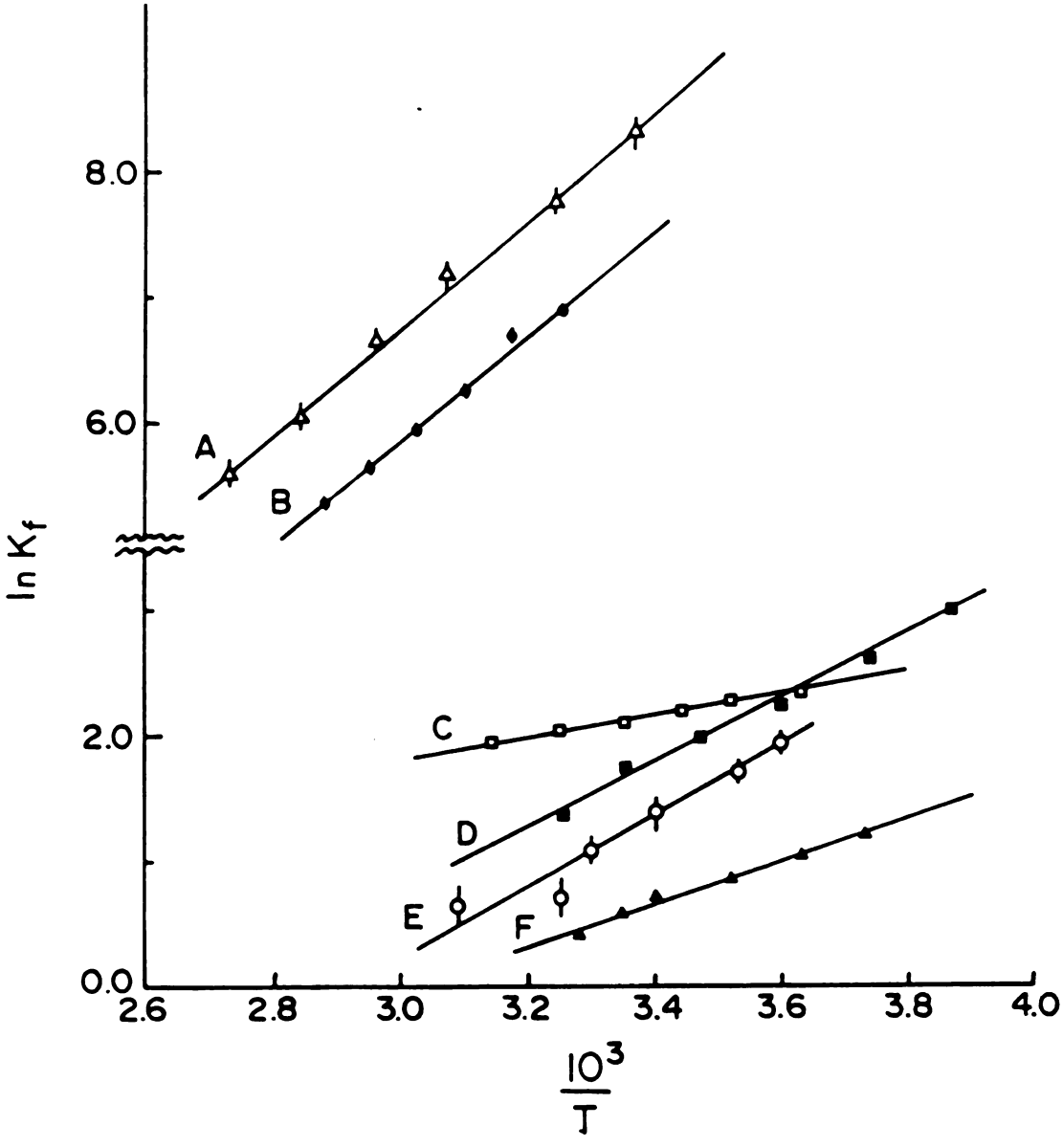

Figure 24: Van't Hoff plots for the complexation of Tl^+ ion by various cyclic and analogous linear ligands in N,N-dimethylformamide.

A: 18C6.Tl^+. B: 21C7.Tl^+, C: 15C5.Tl^+
D: HG.Tl^+, E: PG.Tl^+, F: TG.Tl^+

Table 45

Thermodynamic Parameters for Thallium(I) Complexes with Various Cyclic and Corresponding Linear Ligands in N,N-Dimethylformamide

Ligand	$\Delta G°$ (25°C) (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ cal $mol^{-1}deg^{-1}$
Tetraglyme	-0.36 + 0.04	-3.29 ± 0.13	-9.88 ± 0.44
15-Crown-5	-1.30 ± 0.18	-1.61 ± 0.06	-1.16 ± 0.20
Pentaglyme	-0.83 ± 0.05	-4.81 ± 0.15	-13.61 ± 0.36
18-Crown-6[a]	-4.89 ± 0.30	-8.66 ± 0.22	-12.44 ± 0.68
Hexaglyme	-1.04 ± 0.06	-5.0 ± 0.15	-13.40 ± 0.34
21-Crown-7	-4.41 ± 0.24	-8.64 ± 0.20	-14.21 ± 0.42

[a] From reference 152

Table 46

Mole Ratio Studies for the Complexation of Tetraglyme with Sodium Ion in Acetonitrile at Various Temperatures

Mole Ratio [TG]/[Na^+]	Chemical Shift (ppm)		
	14°C	19°C	35°C
0.0	-7.55	-7.44	-7.40
0.3	-7.75	-7.70	-8.60
0.55	-7.96	-7.76	-8.75
0.7	-8.06	-8.01	-8.41
0.8	-8.16	-8.11	-8.0
0.9	-8.27	-8.16	-8.06
1.0	-8.32	-8.21	-8.09
1.1	-8.37	-8.27	-8.11
1.3	-8.42	-8.32	-8.17
1.5	-8.45	-8.37	-8.21
2.0	-8.47	-8.40	-8.26
2.5	--8.47	-8.40	-8.29
3.0	-8.48	-8.42	-8.31
4.0	-8.48	-8.42	-8.32
5.0	-8.48	-8.42	-8.32

Table 46 continued

Mole Ratio [TG]/[Na^+]	Chemical Shift (ppm)		
	45°C	**54°C**	**64°C**
0.0	-7.34	-7.29	-7.19
0.3	-7.50	-7.44	-7.43
0.55	-7.70	-7.68	-7.49
0.7	-7.80	-7.75	-7.55
0.8	-7.85	-7.80	-7.65
0.9	-7.91	-7.85	-7.70
1.0	-7.96	-7.92	-7.75
1.1	-8.0	-7.96	-7.81
1.3	-8.08	-7.99	-7,85
1.5	-8.11	-8.08	-7.91
2.0	-8.16	-8.12	-7.96
2.5	-8.19	-8.14	-7.98
3.0	-8.21	-8.16	-8.01
4.0	-8.21	-8.17	-8.03
5.0	-8.21	-8.17	-8.06

Table 47

Mole Ratio Studies for the Complexation of 15-Crown-5 with Sodium Ion in Acetonitrile Solutions at Various Temperatures

Mole Ratio $[15C5]/[Na^+]$	Chemical Shift[a] (ppm)		
	30°C	45°C	55°C
0.0	-6.56	-6.46	-6.41
0.3	-6.00	-5.79	-5.74
0.5	-5.54	-5.28	-5.18
0.7	-5.13	-4.82	-4.77
0.8	-4.92	-4.62	-4.51
0.9	-4.67	-4.36	-4.31
1.0	-4.51	-4.20	-4.10
1.1	-4.31	-3.99	-3.90
1.3	-4.00	-3.64	-3.59
1.5	-4.00	-3.64	-3.54
2.0	-4.05	-3.69	-3.59
2.5	-4.10	-3.74	-3.66
3.0	-4.15	-3.79	-3.72
4.0	-4.26	-3.90	-3.95
5.0	-4.41	-4.00	-4.06

Table 47 continued

Mole Ratio [15C5]/[Na^+]	Chemical Shift[a] (ppm)		
	65°C	72°C	37°C
0.0	-6.36	-6.31	-6.49
0.3	-5.64	-5.59	-5.90
0.5	-5.13	-5.03	-5.31
0.7	-4.67	-4.56	-4.87
0.8	-4.41	-4.31	-4.62
0.9	-4.15	-4.05	-4.46
1.0	-3.95	-	-
1.1	-3.74	-3.69	-4.05
1.3	-3.44	-3.33	-3.78
1.5	-3.38	-3.28	-3.74
2.0	-3.38	-3.33	-3.79
2.5	-3.44	-3.33	-3.85
3.0	-3.54	-3.84	-3.90
4.0	-3.64	-3.43	-4.00
5.0	-3.69	-3.59	-4.10

[a] Chemical shifts are uncorrected

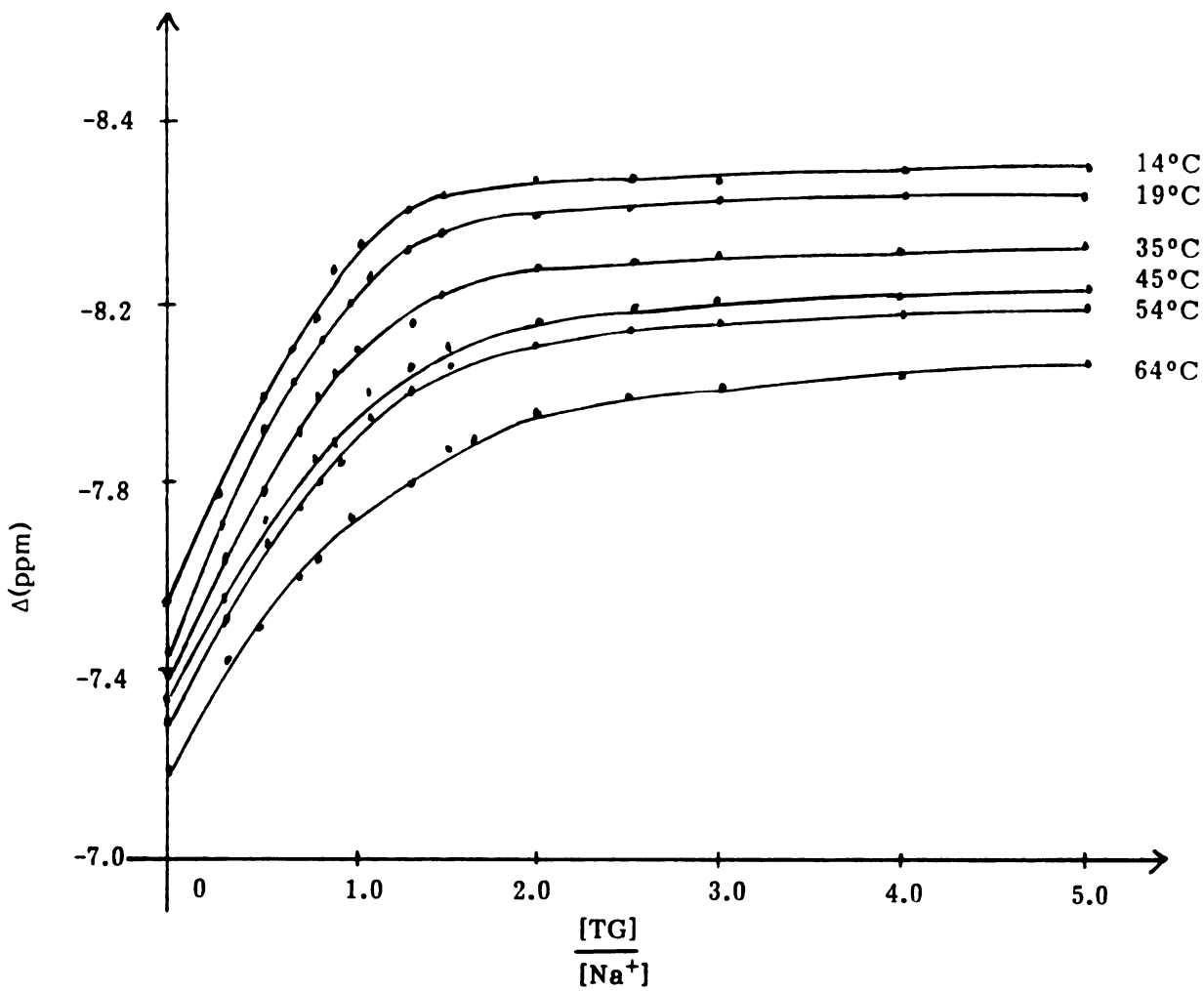

Figure 25: Chemical shifts of ^{23}Na as a function of [TG]/[Na^+] mole ratio in acetonitrile at various temperatures.

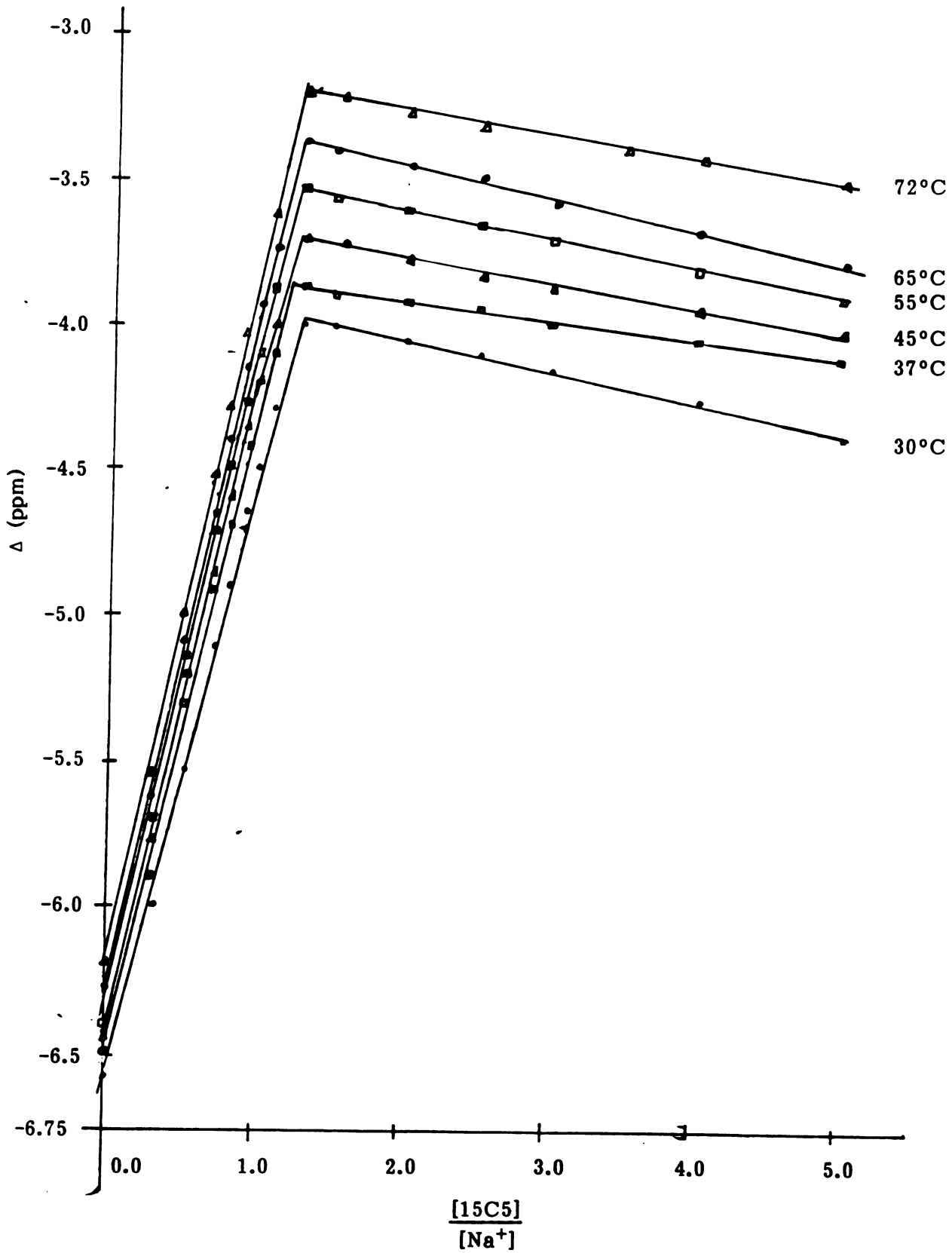

Figure 26: Sodium-23 chemical shifts as a function of [15C5]/[Na^+] mole ratio in acetonitrile solutions at different temperatures

on the other hand, a different observation was made. As the concentration of the ligand was increased, a downfield shift of the sodium-23 resonance was observed which was followed by a gradual upfield shift after a mole ratio of one. This behavior clearly indicates the formation of both, 1:1 and 2:1 15-crown-5:Na^+ complexes.

Formation constants calculated for the tetraglyme.Na^+ complex at different temperatures are listed in Table 48 and as expected, are found to decrease with increasing temperature. Repeated attempts to computer fit the data for the 15-crown-5/Na^+/acetonitrile system to a three site exchange equation in order to obtain formation constants for both 1:1 and 2:1, 15-crown-5:Na^+ complex were unsuccessful. Results from reference 160 were therefore used for comparison with the results for the linear complex. Thermodynamic parameters for these systems are listed in table 52.

There is evidently a macrocyclic effect which results strictly from a more favorable entropy contribution for the formation of the cyclic complex. The data actually show that complexation enthalpy is slightly in favor of formation of the linear as opposed to the cyclic complex. The more negative entropy for the tetraglyme and Na^+ ion complexation reaction must be due to loss in conformational entropy for the ligand upon complexation; since the donor atoms of the ligand has to be forced into a more definite orientation suitable for complex formation.

e. Complexation of pentaglyme and 18-crown-6 with sodium ion in acetonitrile solutions at various temperatures.

Sodium-23 chemical shifts as a function of ligand:Na^+ mole ratio were measured in acetonitrile solutions at various temperatures, for the complexation of 18-crown-6 and pentaglyme with sodium ion. Results of these measurements

Table 48

Formation Constants at Different Temperatures for Tetraglyme.Na^+ Complex in Acetonitrile

Temperature	Log K_f
14°C	2.54 ± 0.15
19°C	2.46 ± 0.07
35°C	2.23 ± 0.08
45°C	2.07 ± 0.07
54°C	1.96 ± 0.06
64°C	1.83 ± 0.09

are listed in Tables 49 and 50 and the plots of chemical shifts as a function of mole ratio are shown in Figures 27 and 28. An upfield shift of the sodium resonance was observed in both cases as the ligand concentration was increased. For the pentaglyme.Na^+ complex, the curves gradually levelled off after a mole ratio of one. In the case of 18-crown-6.Na^+ complex, more distinct breaks are seen in the curves after a mole ratio of one indicating formation of a much stronger complex. Again as expected, the curvature of the plots decreased with increasing temperature which is an indication of formation of weaker complexes at higher temperatures. The formation constants calculated from the above measurements are listed in Table 51. Plots of $\ln K_f$ versus 1/T (van't Hoff's plots) are shown in Figure 29 and the thermodynamic parameters calculated on the basis of these plots are listed in Table 52.

A macrocyclic effect is again observed which results from a more favorable entropy contribution for the cyclic ligand reaction. Similar to what was observed for the 15-crown-5.Na^+, tetraglyme.Na^+ pair in the same solvent, the reaction enthalpy is clearly in favor of formation of the linear complex pentaglyme.Na^+. Again it could be argued that the more negative entropy for the linear ligand reaction is due to the more organized state into which the highly flexible ligand has to be forced upon complexation with the sodium ion. This results in a greater loss in conformational entropy.

Table 49

Mole Ratio Studies for the Complexation of Pentaglyme with Sodium Ion in Acetonitrile at Various Temperatures

Mole Ratio [PG]/[Na^+]	Chemical Shift (ppm)		
	5°C	20°C	35°C
0.0	-7.54	-7.39	-7.34
0.3	-7.61	-7.53	-7.49
0.5	-7.67	-7.62	-7.58
0.7	-7.74	-7.69	-7.65
0.8	-7.79	-7.72	-7.68
0.9	-7.82	-7.75	-7.71
1.0	-7.86	-7.79	-7.74
1.3	-7.88	-7.83	-7.80
1.5	-7.89	-7.86	-7.83
2.0	-7.90	-7.90	-7.87
2.5	-7.91	-7.92	-7.89
3.0	-7.92	-7.94	-7.91
4.0	-7.93	-7.95	-7.92
5.0	-7.94	-7.96	-7.93

Table 49 continued

Mole Ratio [PG]/[Na^+]	Chemical Shift (ppm)		
	50°C	65°C	80°C
0.0	-7.29	-7.24	-7.19
0.3	-7.33	-7.37	-7.30
0.5	-7.44	-7.43	-7.36
0.7	-7.50	-7.47	-7.42
0.8	-7.54	-7.53	-7.44
0.9	-7.58	-7.57	-7.47
1.0	-7.65	-7.60	-7.50
1.1	-7.69	-7.64	-7.52
1.3	-7.73	-7.67	-7.55
1.5	-7.75	-7.74	-7.59
2.0	-7.80	-7.78	-7.65
2.5	-7.82	-7.80	-7.69
3.0	-7.85	-7.84	-7.72
4.0	-7.89	-7.86	-7.77
5.0	-7.90	-7.89	-7.79

Table 50

Mole Ratio Studies for the Complexation of 18-Crown-6 with Sodium Ion in Acetonitrile at Various Temperatures

Mole Ratio [18C6]/[Na^+]	Chemical Shift (ppm)		
	34°C	**45°C**	**53°C**
0.0	-7.39	-7.34	-7.24
0.3	-9.50	-9.39	-9,30
0.5	-11.09	-10.93	-10.78
0.7	-12.52	-12.32	-12.20
0.8	-13.14	-12.93	-12.78
0.9	-14.06	-13.85	-13.67
1.0	-14.57	-14.30	-14.10
1.1	-14.76	-14.50	-14.23
1.3	-14.78	-14.57	-14.30
1.5	-14.78	-14.57	-14.35
2.0	-14.82	-14.57	-14.38
2.5	-14.84	-14.62	-14.41
3.0	-14.86	-14.62	-14.42
3.5	-14.86	-14.62	-14.42

Table 50 continued

Mole Ratio [18C6]/[Na^+]	Chemical Shift (ppm)		
	64°C	**73°C**	**82°C**
0.0	-7.19	-7.14	-7.09
0.3	-9.19	-9.09	-9.03
0.5	-10.68	-10.56	-10.47
0.7	-12.06	-11.96	-11.85
0.8	-12.62	-12.52	-12.42
0.9	-13.55	-13.39	-13.28
1.0	-13.82	-13.68	-13.58
1.1	-14.11	-13.78	-13.68
1.3	-14.21	-14.11	-14.00
1.5	-14.24	-14.11	-14.00
2.0	-14.24	-14.15	-14.01
2.5	-14.26	-14.16	-14.01
3.0	-14.26	-14.16	-14.01
3.5	-14.26	-14.16	-14.01

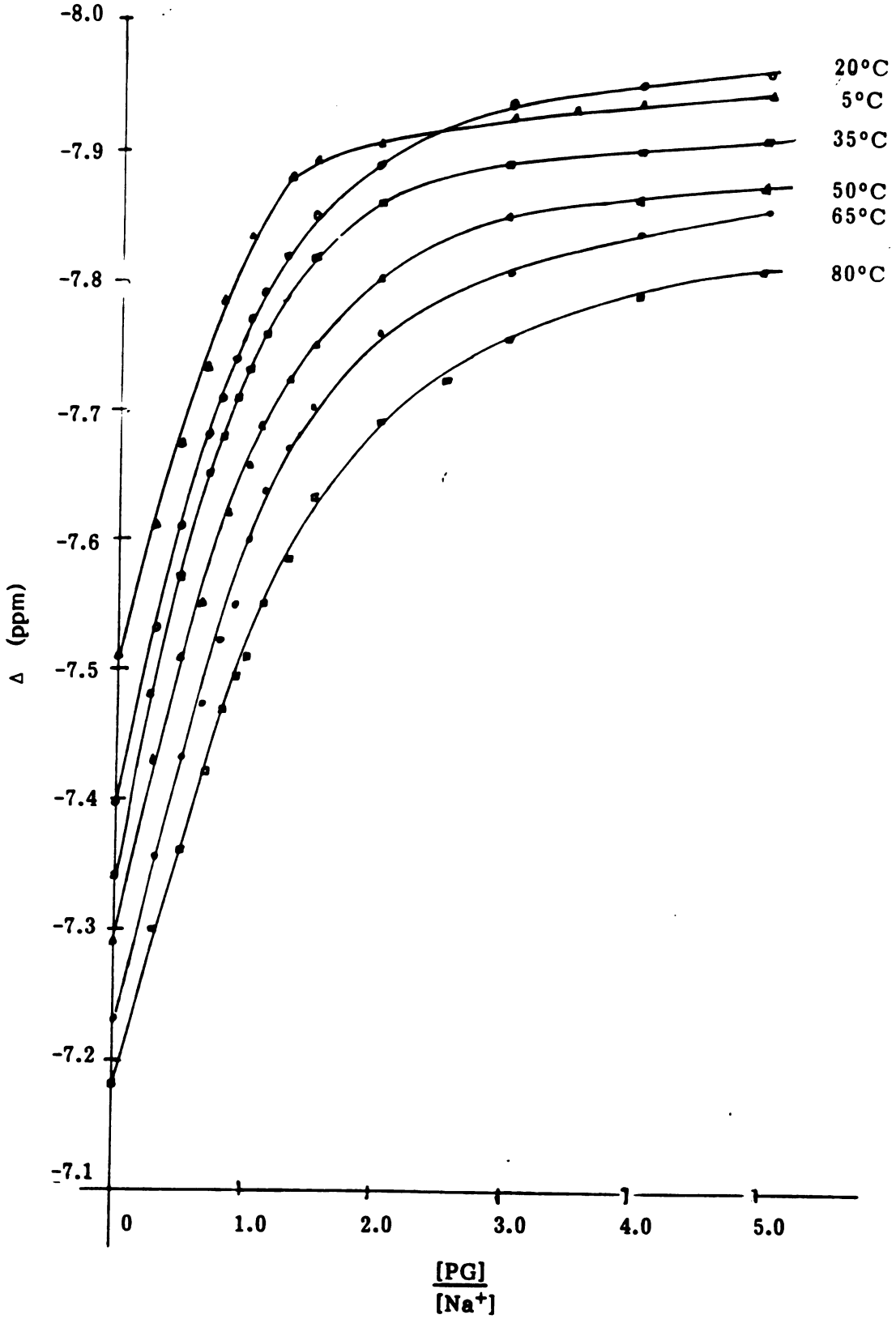

Figure 27: Sodium-23 chemical shifts vs. [PG]/[Na^+] mole ratio in acetonitrile solutions at various temperatures

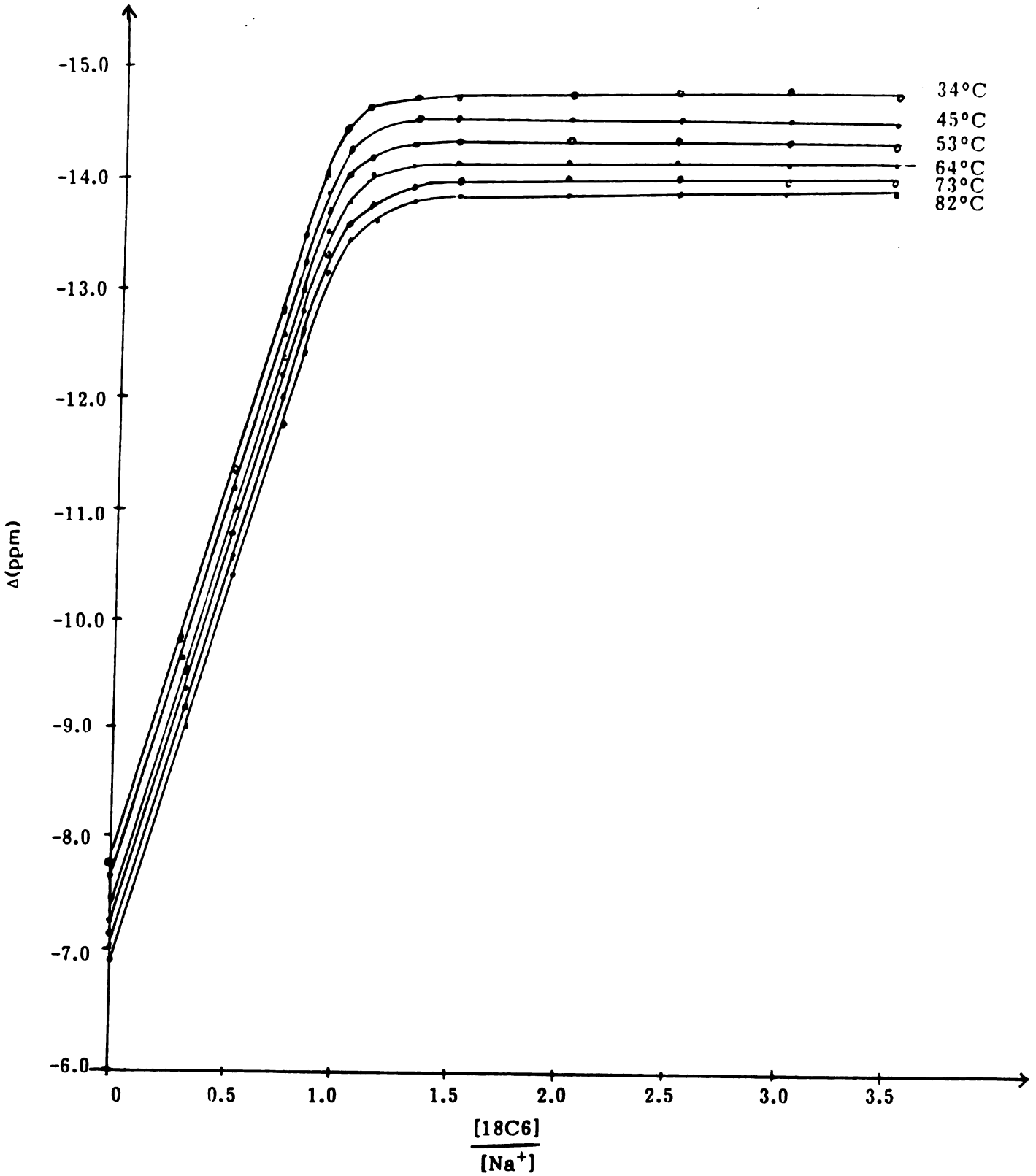

Figure 28: Sodium-23 chemical shifts as a function of mole ratio for 18C6/Na in acetonitrile at various temperatures.

Table 51

Formation Constants at Different Temperatures for Pentaglyme.Na^+ and 18-Crown-6.Na^+ Complexes in Acetonitrile

	Temperature	Log K_f
Pentaglyme.Na^+	5°C	3.04 ± 0.14
	20°C	2.63 ± 0.13
	35°C	2.27 ± 0.13
	50°C	1.97 ± 0.12
	65°C	1.71 ± 0.10
	80°C	1.44 ± 0.07
18-Crown-6.Na^+	34°C	4.28 ± 0.13
	45°C	4.07 ± 0.11
	53°C	3.98 ± 0.14
	64°C	3.77 ± 0.13
	82°C	3.53 ± 0.12

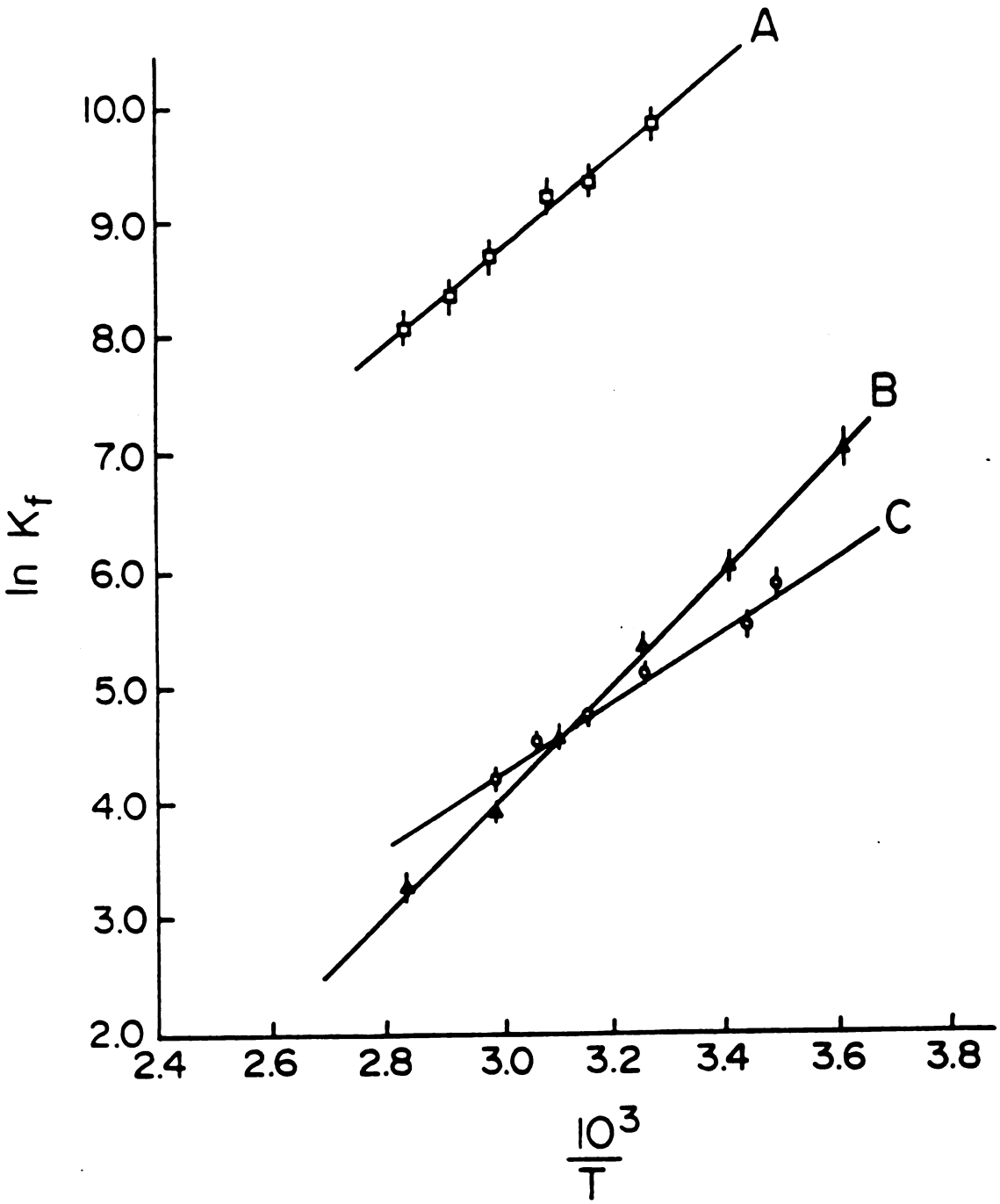

Figure 29: Van't Hoff plots for the complexation of Na^+ ion by some cyclic and analogous linear ligands in acetonitrile solutions.
A: 18C6.Na^+, B: PG.Na^+, C: TG.Na^+

Table 52

Thermodynamic Parameters for Sodium Complexes with Cyclic and Analogous Linear Ligands in Acetonitrile

Ligand	ΔG° (25°C) (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° cal $mol^{-1} deg^{-1}$
Tetraglyme	-3.13 ± 0.08 (35°C)	-6.33 ± 0.08	-10.37 ± 0.20
15-Crown-5[a]	-6.79 ± 0.02	-5.76 ± 0.48	3.94 ± 1.7
Pentaglyme	-3.59 ± 0.11	-9.47 ± 0.28	-20.3 ± 0.57
18-Crown-6	-6.02 ± 0.13 (34°C)	-7.86 ± 0.24	-6.01 ± 0.70

[a]From Reference 160

CONCLUSIONS

While our results add new information on the thermodynamics of complexation reactions, they certainly do not resolve the controversy on the nature of the macrocyclic effect. The only conclusion we can draw from our work is that the macrocyclic effect is neither purely entropic nor is it purely enthalpic. Perhaps it would be somewhat naive to expect it to be clearly one or the other. Studies of Petrucci and Eyring on the mechanism of macrocyclic complexation reactions clearly show that they follow the Eigen-Winkler mechanism

$$M^+ + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^+\cdots L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (ML^+)$$

where M^+ is the free solvated cation, L is the free solvated ligand and $M^+\cdots L$, ML^+ and (ML^+) are three different conformations of the complex. Since the macrocyclic and the linear ligands are solvated to some extent, both the change in ligand conformation and its interaction with the cation must be accompanied by changes in the solution state of the ligand, as well as that of the metal ion. Thus the overall values of the enthalpies and the entropies of complexation are sums of contributions of several processes, and therefore, each step (and especially the ligand-solvent interaction) must be much better known before the nature of the macrocyclic effect can be elucidated.

SUGGESTIONS FOR FUTURE WORK:

a. More quantitative studies on ligand-solvent interaction.

b. Comparative studies on the structures of several linear and analoguous cyclic complexes.

c. More kinetic studies on the complexation of some selected linear and cyclic ligands particularly polyethers.

APPENDICES

APPENDIX I

```
      SUBROUTINE EQN                                                    EQN4
      COMMON /JNT/ITAPE,JTAPE,IJT,LAP,XINCR,NOPT,NOVAR,NOUNK,X,U,ITMAX, EQN4
     1TX,TEST,I,AV,RESID,IAR,EPS,ITYP,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,E EQN4
     2IGVAL,XST,T,DT,L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,  EQN4
     3YYY,CONSTS                                                        EQN4
      COMMON/FREDT/IMETH                                                EQN4
      COMMON/POINT/KOPT,JOPT,XXX                                        EQN4
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),FOP(300),FO(300),FU(300) EQN4
     1,P(21,21),VECT(20,21),ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),   EQN4
     2DY(10),CONSTS(50,15),NCST(50),ISMIN(50),RXTYP(50),DX1I(50),IRX(50) EQN4
     3,MOPT(50),LOPT(50),YYY(50),CONST(16),XXX(15)                      EQN4
      GO TO (2,3,4,5,1,7,8,9,10,11,12)  ITYP                            EQN4
    1 CONTINUE                                                          EQN4
      ITAPE=61                                                          EQN4
      JTAPE=61                                                          EQN4
      RETURN                                                            EQN4
    7 CONTINUE                                                          EQN4
      NOUNK=2
      NOVAR=2
      RETURN                                                            EQN4
    8 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    2 CONTINUE                                                          EQN4
      IF(U(2).GT.0.) GO TO 1000
      U(2)=2253.7
 1000 CONTINUE
      A=U(2)*CONST(1)
      B=U(2)*XX(1)
      C=(CONST(2)-U(1))/(2.*A)
      D=(B-A+1.)**2
      CALC=((A-B-1.)+SQRT(D+4.*A))*C+U(1)
      IF(IMETH.NE.-1) GO TO 35
      RETURN                                                            EQN4
   35 CONTINUE                                                          EQN4
      RESID=CALC-XX(2)
      RETURN                                                            EQN4
    3 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    4 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    5 CONTINUE                                                          EQN4
      IF(IMETH.NE.-1) GO TO 20                                          EQN4
      RETURN                                                            EQN4
   20 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    9 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    1 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
   11 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
   12 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
      END                                                               EQN4
```

APPENDIX II

```
      SUBROUTINE EQN                                                    EQN4
      COMMON /COUNT/ITAPE,JTAPE,IWT,LAP,XINCR,NOPT,NOVAR,NOUNK,X,U,ITMAX, EQN4
     1ITX,TEST,I,AV,RESID,IAR,EPS,ITYP,XX,RXTYP,DX1I,FOP,FO,FU,P,ZL,TO,E EQN4
     2IGVAL,XST,T,DT,L,M,JJJ,Y,DY,VECT,NCST,CONST,NDAT,JDAT,MOPT,LOPT,   EQN4
     3YYY,CONSTS                                                        EQN4
      COMMON/FREDT/IMETH                                                EQN4
      COMMON/POINT/KOPT,JOPT,XXX                                        EQN4
      DIMENSION X(4,300),U(20),WTX(4,300),XX(4),FOP(300),FO(300),FU(300) EQN4
     1,P(20,21),VECT(20,21),ZL(300),TO(20),EIGVAL(20),XST(300),Y(10),   EQN4
     2DY(10),CONSTS(50,16),NCST(50),ISMIN(50),RXTYP(50),DX1I(50),IRX(50) EQN4
     3,MOPT(50),LOPT(50),YYY(50),CONST(16),XXX(15)                      EQN4
      GO TO (2,3,4,5,1,7,8,9,10,11,12)  ITYP                            EQN4
    1 CONTINUE                                                          EQN4
      ITAPE=60                                                          EQN4
      JTAPE=61                                                          EQN4
      RETURN                                                            EQN4
    7 CONTINUE                                                          EQN4
      NOUNK=2
      NOVAR=4
      RETURN                                                            EQN4
    8 CONTINUE                                                          EQN4
      RETURN                                                            EQN4
    2 CONTINUE                                                          EQN4
      U(1)=ABS(U(1))
      A=-CONST(1)*U(1)
      A1=A
      B=(XX(1)+XX(4)-XX(3))*A-CONST(1)-U(1)
      C=CONST(1)*(XX(3)-XX(4))+U(1)*(XX(3)-XX(1))-1
      IF(XX(3).EQ.0.0) GOTO 2008
      FREEL0=0.0
      FREEL1=0.00
      VALUE1=XX(3)
      FREEL2=XX(3)/1.0E+12
 2005 CONTINUE
      VALUE2=((A1*FREEL2+B)*FREEL2+C)*FREEL2+XX(3)
      IF(VALUE2.EQ.0.0) GOTO 2001
      IF(VALUE2.GT.0.0) GOTO 2000
 2004 CONTINUE
      FREEL3=(FREEL2-FREEL1)/(VALUE1-VALUE2)*VALUE1+FREEL1
      IF(ABS((FREEL3-FREEL0)/FREEL3).LT.0.0000001) GOTO 2002
      FREEL0=FREEL3
      VALUE3=((A1*FREEL3+B)*FREEL3+C)*FREEL3+XX(3)
      IF(ABS(VALUE3).LT.0.00000001) GOTO 2002
      IF(VALUE3.GT.0.0) GOTO 2003
      VALUE2=VALUE3
      FREEL2=FREEL3
      GOTO 2004
 2003 CONTINUE
      VALUE1=VALUE3
      FREEL1=FREEL3
      GOTO 2004
 2000 CONTINUE
      VALUE1=VALUE2
      FREEL1=FREEL2
      IF(FREEL2.LT.XX(3)/100.) GOTO 3000
      FREEL2=FREEL2+XX(3)/100
      GOTO 3001
```

```
      3000 CONTINUE
           FREEL2=FREEL2*10.
      3001 CONTINUE
           IF(FREEL1.GT.XX(3)) GOTO 2006
           GOTO 2005
      2001 CONTINUE
           FREEL=FREEL2
           GOTO 2007
      2002 CONTINUE
           FREEL=FREEL3
           GOTO 2007
      2006 CONTINUE
           IF(LAP.NE.3) GOTO 2008
           WRITE(JTAPE,999)
       999 FORMAT(/,5X,29H** NO NEGATIVE VALUE FOUND **)
           GOTO 2007
      2008 CONTINUE
           FREEL=0.0
      2007 CONTINUE
           H=FREEL/XX(3)

           H1=CONST(1)*FREEL*XX(4)/(1+CONST(1)*FREEL)
           H2=H1**XX(3)
           H3=1-H-H2
           CALC=CONST(2)*H+CONST(3)*H2+U(2)*H3
       3002 CONTINUE
           IF(IMETH.NE.-1) GO TO 35                                    EQN4
           RETURN                                                      EQN4
         35 CONTINUE
           RESID=CALC-XX(2)                                            EQN4
           RETURN                                                      EQN4
            3 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
            4 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
            5 CONTINUE                                                 EQN4
           IF(IMETH.NE.-1) GO TO 20                                    EQN4
           RETURN                                                      EQN4
           20 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
            9 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
           10 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
           11 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
           12 CONTINUE                                                 EQN4
           RETURN                                                      EQN4
           END
```

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