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Multinuclear NMR Study of Dibenzo-30-crown-10 Complexes with Sodium, Potassium, and Cesium Ions in Nonaqueous Solvents

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Abstract: Nuclear magnetic resonances of ^{23}Na, ^{133}Cs, and ^{13}C nuclei were used to study the sodium, potassium, and cesium ion complexes with dibenzo-30-crown-10 (L) in nitromethane, acetonitrile, acetone, methanol, and pyridine solutions. Potassium and cesium ions formed 1:1 complexes, but in the case of the sodium ion three complexes with the respective stoichiometries Na_2L, Na_3L_2, and NaL were identified in solutions. The NMR data support the existence of a "wrap around" structure for Cs^+–DB30C10 complex in solution. The chemical shift of the ^{133}Cs resonance was studied as a function of DB30C10/Cs^+ mole ratio at various temperatures in different solvents and from these data $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the complexation reactions were calculated. In all cases the complexes were enthalpy stabilized but entropy destabilized.

Introduction

Since Pedersen's discovery of macrocyclic polyether (crown) compounds capable of forming stable complexes with the alkali ions[1] the studies of these ligands and of their complexes became a very popular field of research. A variety of physicochemical techniques have been used for such investigations,[2] the choice of a favorite technique being dictated by the systems studied as well as by the particular expertise of the investigators. In our case we found that the nuclear magnetic resonances of the alkali nuclei offer a very sensitive technique for the studies of changes in the immediate chemical environment of the alkali ions in solutions.[3]

It was of interest to us to study the interactions of alkali ions with a large crown ether capable of forming three-dimensional complexes with these ions. In fact it has been shown by Bush and Truter[4] that dibenzo-30-crown-10 (DB30C10) has a large

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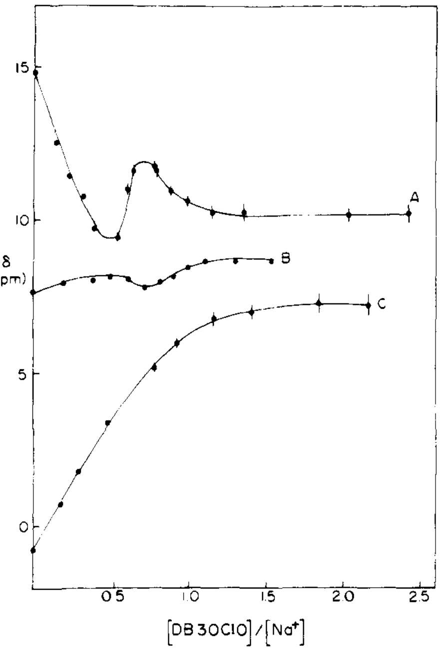

Figure 1. Sodium-23 chemical shift vs. [DB30C10]/[Na^+] mole ratio in different solvents: A, nitromethane; B, acetonitrile; C, pyridine.

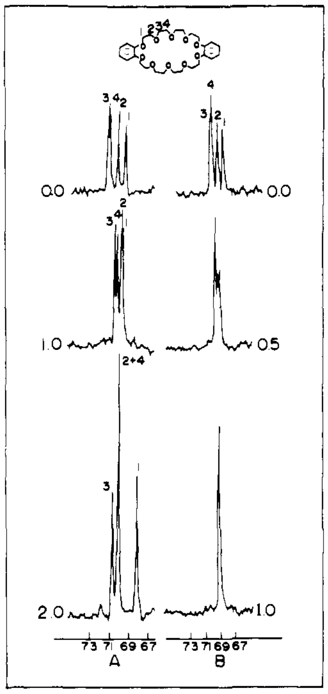

Figure 2. Carbon-13 chemical shifts at various [metal ion]/[DB30C10] mole ratios (MR) in nitromethane: A, sodium ion at MR = 0, 1.0, and 2.0; B, potassium ion at MR = 0, 0.5, and 1.0.

enough ring to twist around a metal ion of a suitable size. For example, it forms a "wrap around" three-dimensional complex with potassium iodide.

Alkali complexes of DB30C10 have been studied in aqueous, aqueous methanol, and methanol solutions by potentiometry[5] and spectrophotometry.[6] They were also studied by ^1H and ^{13}C NMR in aqueous acetone, neat acetone, and chloroform solutions.[7] In this paper we report sodium-23, cesium-133, and carbon-13 study of sodium, cesium, and potassium complexes with DB30C10 in several nonaqueous solvents

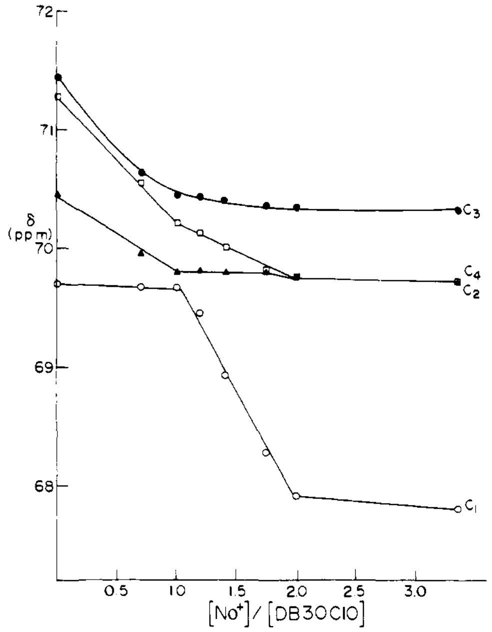

Figure 3. Carbon-13 chemical shifts for the four polyether chain carbon atoms at various [Na^+]/[DB30C10] mole ratios.

Experimental Section

Dibenzo-30-crown-10 was originally obtained through the courtesy of the Du Pont Co. Additional amounts were synthesized by a slight modification of Pedersen's method.[1] The product was recrystallized from acetone and vacuum dried. Nitromethane, acetonitrile, acetone, methanol, and pyridine were purified and dried using the previously reported methods.[8] The water content of the solvents after drying was found to be less than 100 ppm by Karl Fischer titrations.

Sodium tetraphenylborate (J. T. Baker) was dried under vacuum at 60 °C for 72 h. Potassium hexafluorophosphate (Pfaltz & Bauer) was purified by recrystallization from water and dried under vacuum at 110 °C for 72 h. Cesium thiocyanate (Pfaltz & Bauer) was recrystallized from reagent grade methanol and dried under vacuum for several days. Cesium tetraphenylborate was prepared by mixing tetrahydrofuran solution of sodium tetraphenylborate with equimolar amount of a concentrated aqueous solution of cesium chloride (Ventron Alfa Products). The resulting fine white precipitate was collected, washed several times to remove any adhering sodium salt, and dried under vacuum at 72 °C for 72 h.

^{23}Na and ^{133}Cs NMR measurements were made on a Varian Associates DA-60 spectrometer equipped with a multinuclear probe and an external proton lock and operating at a field of 14.09 kG in a pulsed Fourier transform mode. The measurements were made at 15.871 MHz for sodium-23 and at 7.871 MHz for cesium-133 nuclei using a 3 M aqueous solution of sodium chloride and a 0.5 M aqueous solution of cesium bromide, respectively, as external references. The reported chemical shifts for sodium-23 and cesium-133 nuclei are referred to infinitely dilute aqueous Na^+ and Cs^+ solutions and the chemical shifts are corrected for the bulk diamagnetic susceptibility of solvents. In order to keep the chemical shift of external reference constant, an insulated reference tube[9] was used in the measurement of cesium-133 chemical shifts as a function of temperature. *Downfield* (paramagnetic) chemical shifts from the reference are indicated as *negative*.

^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer operating at a field of 18.68 kG in a pulsed Fourier transform mode. Acetone was used as an external reference and D_2O was used to lock the system. All carbon-13 chemical shifts are reported with respect to Me_4Si.

Results and Discussion

A. DB30C10 Complexes with Na^+ and K^+. Sodium-23 chemical shifts were determined as a function of dibenzo-30-crown-10/sodium ion mole ratios in nitromethane, acetonitrile, and pyridine solutions and the results are shown in

Table I. Formation Constants and the Limiting Chemical Shifts of DB30C10–Cs^+ Complexes in Various Solvents at 30 °C

salt	solvent	log K_f	δ_L
$CsClO_4$	CH_3NO_2	4.30 ± 0.05	18.58 ± 0.04
CsSCN	CH_3CN	3.39 ± 0.09	13.56 ± 0.95
Cs^+(?)	CH_3CN	3.50[a]	
CsSCN	$(CH_3)_2CO$	3.99 ± 0.08	14.69 ± 0.01
Cs picrate	$(CH_3)_2CO$	4.04 ± 0.05	15.05 ± 0.02
$CsBPh_4$	$(CH_3)_2CO$	3.96 ± 0.07[b]	15.89 ± 0.07
$CsBPh_4$	$(CH_3)_2CO$	4.05 ± 0.06[c]	15.28 ± 0.05
$CsClO_4$	$(CH_3)_2CO$	4.23[d]	
CsSCN	CH_3OH	4.18 ± 0.07	16.50 ± 0.11
CsCl	CH_3OH	4.23[e]	
$CsBPh_4$	C_5H_5N	4.41 ± 0.10	11.35 ± 0.02

[a] Polaragraphic measurements: A. Hofmanova, J. Koryta, M. Brezina, and M. L. Mittal, *Inorg. Chim. Acta*, **28**, 73 (1978). Salt not given. Measurements made at 22 °C. [b] Concentration of $CsBPh_4$ = 5×10^{-3} M. [c] Concentration of $CsBPh_4$ = 2.5×10^{-3} M. [d] Reference 7. [e] Reference 6.

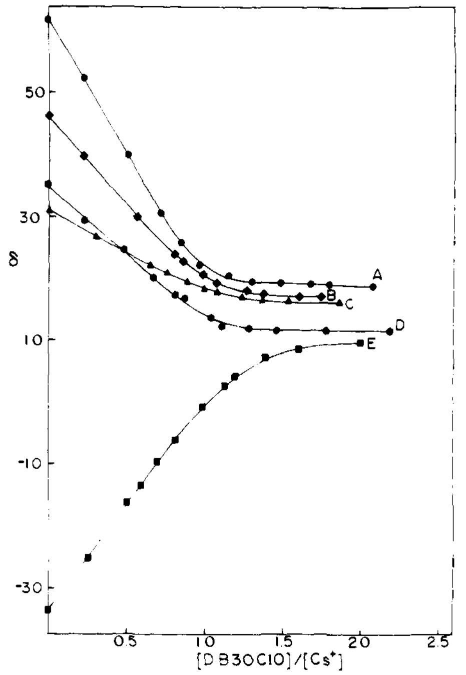

Figure 4. Cesium-133 chemical shifts at various [DB30C10]/[Cs^+] mole ratios in different solvents: A, nitromethane; B, methanol; C, acetone; D, pyridine; E, acetonitrile.

Figure 1. In all cases only one population-average resonance was observed indicating that the exchange of the metal ion between the bulk solution and the complex is faster than the NMR time scale. In the case of pyridine solutions, the addition of the ligand to the Na^+ solution produces a gradual diamagnetic shift of sodium-23 resonance which begins to level off at a mole ratio of about 1, which indicates the formation of a 1:1 complex of the sodium ion with the dibenzo-30-crown-10.

On the other hand, in the case of nitromethane and acetonitrile solutions, the chemical shift vs. mole ratio plots show three distinct inflection points at the ligand/metal ion mole ratios of about 0.5, 0.7, and 1, indicating the formation of three complexes with the respective stoichiometries L·2Na^+, 2L·3Na^+, and LNa^+. The synthesis and isolation of crystalline 1:2 and 1:1 (ligand to metal ion) complexes of sodium tetraphenylborate and dibenzo-30-crown-10 have been previously reported by Truter and co-workers.[10] It seems that the 3:2 complex is quite unstable and exists only in solutions.

It has been shown previously that carbon-13 chemical shifts of the carbons in the ether region of cyclic polyethers are sensitive to the conformational change of the ligands upon complexation with metal ions.[11] In order to get further information about DB30C10 interactions with the sodium ion we studied the chemical shifts of the polyether chain carbon atoms as a function of sodium and potassium concentrations relative to the concentration of the ligand. The results, obtained in nitromethane solutions, are shown in Figures 2 and 3.

In the case of the DB30C10–K^+ ion system, the addition of potassium hexafluorophosphate to a DB30C10 solution results in a gradual coalescence of the four resonances and only one signal is obtained at equimolar concentrations of K^+ ion and the ligand. This behavior seems to indicate an essentially equal interaction between the ten oxygens of the polyether ring and the K^+ ion. Naturally, such equal interaction is only possible if in solutions the ligand is "wrapped around" the cation as postulated by Live and Chan.[7]

Considerably different behavior is observed in the case of the sodium ion. The details are given in Figure 3. Between mole ratios of 0 and 2 all four carbons behave quite differently. While the initial addition of the sodium ion results in a chemical shift of carbons 2, 3, and 4, the chemical shift of carbon 1 remains unaffected. On the other hand, between mole ratios of 1.0 and 2.0 the chemical shifts of carbons 2 and 3 remain constant while carbon 4 and especially carbon 1 show a significant downfield shift. Beyond mole ratio of 2.0, the resonance frequencies are constant.

The results show that the addition of the sodium ion to DB30C10 results in at least two conformational changes of the ligand molecule following the formation of NaL and Na_2L complexes. No evidence for the formation of the Na_3L_2 complex was observed; however, it is to be expected that the ^{23}Na chemical shift is a much more sensitive probe of the sodium ion interaction than the ^{13}C chemical shifts. Once again, our data support the conclusions of Live and Chan[7] that the DB30C10·Na^+ complex has a different configuration from the DB30C10 complex with the potassium ion (and presumably with the Cs^+ and Ba^{2+} ions).

An attempt was made to calculate the formation constants of DB30C10 complexes with the potassium ion from the variation of the carbon-13 chemical shift as a function of K^+/ligand mole ratio as described in our previous publications.[12] This technique, however, can only be applied to relatively weak complexes with log $K_f < 5$. It was found that in nitromethane and acetonitrile solutions log K_f was greater than 5, while in acetone solutions log $K_f = 4.3 \pm 0.1$.

B. DB30C10 Complexes with Cs^+. The variation of the cesium-133 chemical shift as a function of the ligand/Cs^+ mole ratio in nitromethane, acetonitrile, acetone, methanol, and pyridine solutions at 30 °C is shown in Figure 4. It is seen that the shift is diamagnetic in acetonitrile solutions and paramagnetic in all others. The shifts begin to level off at a mole ratio of about 1 indicating the formation of a 1:1 complex. It is interesting to note that the limiting chemical shifts for the complexed Cs^+ ion tend to approach each other indicating that in the complex the cation is largely insulated from the solution and, once more, confirming the "wrap around" structure.

The formation constants for the DB30C10·Cs^+ complex in different solvents were determined from the variations of the ^{133}Cs chemical shift with the ligand/Cs^+ mole ratio. The results are shown in Table I. It is seen that in acetone solutions the stability of the complex is not affected by a change in the concentration of salt or by changing the anion. It is evident, therefore, that at the low concentrations of the cesium salts, which we used, the formation of the complex is unaffected by ion pairing. It is reasonable to assume that the same situation will exist in solvents with higher donicities and/or higher dielectric constants such as nitromethane, acetonitrile, and methanol. Comparison of our values with those reported in the

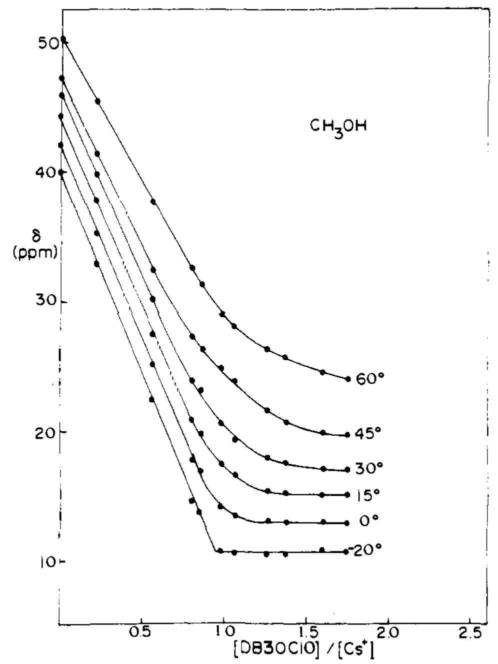

Figure 5. Cesium-133 chemical shifts vs. [DB30C10]/[Cs$^+$] mole ratio in methanol at different temperatures.

Table II. Formation Constants of DB30C10-Cs$^+$ Complex in Nonaqueous Solvents at Different Temperatures

solvent	temp, °C	log K_f
nitromethane	70	3.65 ± 0.04
	60	3.70 ± 0.02
	45	3.99 ± 0.10
	30	4.30 ± 0.05
	10	4.67 ± 0.14
	0	>5
acetonitrile	77	2.85 ± 0.07
	60	3.04 ± 0.05
	45	3.20 ± 0.08
	30	3.39 ± 0.09
	18	3.49 ± 0.10
acetone	50	3.40 ± 0.08
	30	3.96 ± 0.07
	20	4.31 ± 0.14
	10	4.92 ± 0.20
methanol	60	3.36 ± 0.08
	45	3.70 ± 0.05
	30	4.18 ± 0.07
	15	4.65 ± 0.02
	0	>5
pyridine	85	3.52 ± 0.02
	65	3.81 ± 0.05
	50	4.13 ± 0.04
	30	4.41 ± 0.10
	10	4.81 ± 0.07
	0	>5

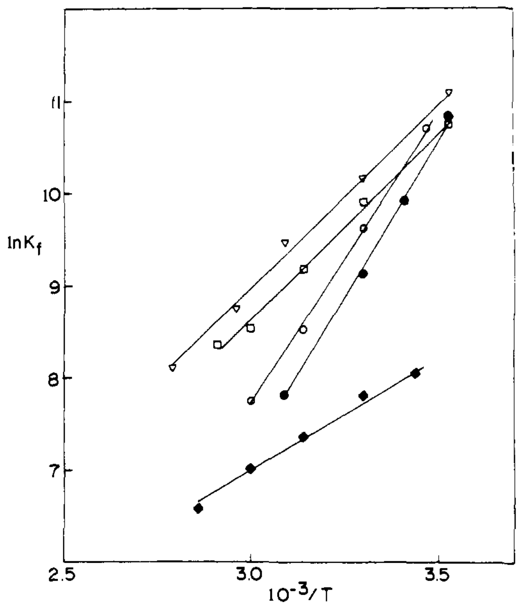

Figure 6. Van't Hoff plots: ▽, pyridine; □, nitromethane; ○, methanol; ● acetone; ■, acetonitrile.

Table III. Thermodynamic Parameters for the Complexation of Cs$^+$ Ion by Dibenzo-30-crown-10 in Various Solvents

solvent	$\Delta G°$(30 °C), kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/mol·K
nitromethane	−5.97 ± 0.07	−7.95 ± 0.39	−6.66 ± 1.25
acetonitrile	−4.71 ± 0.13	−5.13 ± 0.28	−1.53 ± 0.89
acetone	−5.50 ± 0.10	−13.48 ± 0.51	−26.19 ± 1.69
methanol	−5.81 ± 0.10	−12.72 ± 0.34	−22.82 ± 1.11
methanol[a]	−5.77	−11.2	−18.2
pyridine	−6.13 ± 0.14	−7.94 ± 0.36	−5.93 ± 1.13

[a] Reference 6.

literature (and obtained by different techniques) shows a satisfactory agreement.

Since the cesium ion is rather weakly solvated because of low charge density of the cation, it is not surprising that the stability of the complex is only marginally dependent on the nature of the solvent.

In order to determine the enthalpy and entropy of the complexation reactions, the formation constants were measured as a function of temperature in five solvents. A typical series of chemical shifts vs. mole ratio plots in methanol solutions is shown in Figure 5 and the data are given in Table II. It is readily seen that lowering the temperature increases the stability of the complex. Similar behavior was observed in the other four solvents. In most cases at lower temperatures the formation constants were greater than 10^5 and their precise value could not be determined by our technique.

Plots of ln K_f vs. $1/T$ for the five systems are shown in Figure 6. The enthalpies and the entropies of complexation were obtained in the usual manner from the slopes and the intercepts of the plots and the results are given in Table III. The results obtained in methanol solutions agree reasonably well with the results of Chock.[6]

It is interesting to note that, while the stabilities (or the $\Delta G°$ values) of the complex are not very sensitive to the solvent (at least in the case of the five solvents studied here), the enthalpy and the entropy values vary very significantly with the solvent. In all cases the complexes are enthalpy stabilized but entropy destabilized. It should be noted that similar behavior was previously observed by us and others in nonaqueous solutions. For example, in the case of the cryptate C222 exclusive complex with Cs$^+$ ion, the $\Delta H°$ and $\Delta S°$ values are −12.9 kcal mol^{-1} and −26.8 eu in acetone, −8.6 kcal mol^{-1} and −13.7 eu in propylene carbonate, and ~5.7 kcal mol^{-1} and −11.2 eu in *N,N*-dimethylformamide solutions.[12] Entropy destabilization was also observed by Izatt et al. for the complexation of Na$^+$ and K$^+$ ions by benzo-15-crown-5 and 18-crown-6 in water-methanol mixtures[13] and by Kaufmann et al. for the complexation of K$^+$ and Rb$^+$ by cryptand C221 and of Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ ions by cryptand C222 in aqueous solutions.[14] In the last case, it was assumed that the decrease in entropy was largely due to the rearrangement of water structure upon the metastatis of a small inorganic cation into a large hydrophobic organic cation. While this explanation is quite feasible for aqueous solutions, it cannot be carried over to much less structured organic solvents used in this investigation.

It seems reasonable to assume that the main reason for the negative entropy of complexation is the decrease in the conformational entropy of the ligand upon the formation of a metal complex. Large macrocyclic ligands such as DB30C10 should be rather flexible in the free state. The degree of flexibility would vary with the solvent, i.e., with the extent of ligand-solvent interaction. The formation of a rigid three-dimensional complex should decrease the conformational entropy of the ligand and thus, perhaps, give rise to a negative entropy of complexation. At the present time, however, thermodynamic data on the formation of macrocyclic complexes in nonaqueous solvents are quite sparse. Additional work is very necessary before the entropy destabilization of macrocyclic ligands in nonaqueous solvents can be explained satisfactorily.

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J-Cross Polarization in Silanes

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Abstract: The first cross-polarization NMR experiment between ${}^1H$ and ${}^{29}Si$ in the liquid state with rare-spin observation is reported. A line-shape-fitting technique is employed to directly measure the spin coupling constant, J, from the experimental results of initial magnetization vs. cross-polarization contact time. The technique has been used to enhance sensitivities of ${}^{29}Si$ measurements in Si-O- model compounds.

Introduction

The technique of cross polarizing a rare-spin species, S, by an abundant-spin species, I, is well-known.[1,2] In the early 1960s, Hartmann and Hahn[1] developed the theory of polarization transfer in liquids and solids via the coupling of two different nuclear species. They measured the ${}^1H$–${}^{31}P$ coupling constant in hypophosphorus acid, $HPO(OH)_2$, by observing the magnetization of the abundant spin, ${}^1H$, and observed the cross polarization of ${}^{35}Cl$ by ${}^{39}K$ in solid potassium chlorate, $KClO_3$.

In the early 1970s, Pines et al.[2] developed the cross-polarization technique with high-powered decoupling and rare-spin observation and recorded the first enhanced NMR spectra of rare spins in solids. Recently, Maudsley et al.[3] and Bertrand et al.[4] have utilized scalar coupling to cross polarize ${}^{13}C$ by ${}^1H$ in molecules in the liquid state, with observation of the ${}^{13}C$ magnetization.

The static dipolar coupling[1] is the interaction used for polarization transfer between I and S spins in solids. In liquids, the static dipolar coupling is motionally averaged to zero. However, the indirect or scalar coupling which results from the hyperfine interactions of electrons and nuclei remains. This indirect (or scalar, or J) coupling provides the means of polarization transfer in liquids.

Cross polarization, whenever possible, offers certain advantages in NMR studies of liquids. First, there is an enhancement in the magnetization of the rare spin, S, for suitable cross-polarization times, by a factor which can be as large as γ_I/γ_S. Second, the repetition period is determined by the longitudinal relaxation, T_1, of the abundant spin, I. The abundant spin's T_1 can be shortened through suitable "doping" with paramagnetic impurities and is usually much less than that of the rare spin.

The liquid J-cross-polarization experiment notably differs from that on most solids in that the magnetization will oscillate between the abundant and rare spins. The equations which govern the behavior of the magnetization in the liquid state for the matched Hartmann-Hahn (H-H), on-resonance experiment have been previously reported by Hartmann and Hahn[1] and Bertrand et al.[4] These equations are

$$\text{S-I} \qquad M_S = M_I' \sin^2\left(\frac{\pi J \tau}{2}\right) \tag{1}$$

$$\text{S-I}_2 \qquad M_S = M_I'' \sin^2\left(\frac{\pi J \tau}{\sqrt{2}}\right) \tag{2}$$

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