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ION-SOLVENT INTERACTION STUDIES. I.
PREPARATION AND CHARACTERIZATION OF LITHIUM-
AND TETRAALKYLAMMONIUM TETRABUTYLALUMINATES.
II. NMR STUDY OF THE SOLVATION OF THE SODIUM
AND LITHIUM CATIONS.

The Louisiana State University and
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ION-SOLVENT INTERACTION STUDIES

I. Preparation and Characterization of Lithium- and Tetraalkylammonium Tetrabutylaluminates

II. NMR Study of the Solvation of the Sodium and Lithium Cations

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

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M.S., North Texas State University, 1965

May, 1971
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ABSTRACT

PART I

Tetraalkylammonium tetra-\(n\)-butylaluminates \([R_4NaAlBu_4; R = \text{methyl (Me), ethyl (Et), } n\text{-propyl (Pr), } n\text{-butyl (Bu)}]\) have been prepared by the addition of benzene solutions of sodium tetra-\(n\)-butylaluminate (NaAlBu\(_4\)) to saturated benzene solutions of the respective tetraalkylammonium bromides (R\(_4\)NBr). The aluminate derivatives were analyzed by nuclear magnetic resonance spectroscopy and gravimetric aluminum analyses. They were further characterized by melting point, solubility, and conductance studies.

The similarity between both physical and chemical properties of the R\(_4\)NaAlBu\(_4\) compounds and NaAlBu\(_4\) has been illustrated. This similarity provides a potentially valuable system for extending ion-solvent interaction studies which have heretofore been applied exclusively to NaAlBu\(_4\)-solvent systems.

Lithium tetra-\(n\)-butylaluminate (LiAlBu\(_4\)) has been prepared by reacting \(n\)-hexane solutions of \(n\)-butyllithium and aluminum tri-\(n\)-butyl. Analyses and physical data are presented.

The conductance data are discussed in terms of ion-ion and ion-solvent interactions. Although the data are limited and are used primarily in illustrating the ionicity of the compounds, several observations are made and interpreted in terms of the degree of association.

PART II

Proton magnetic resonance studies of ether solutions of NaAlEt\(_4\) show that spectral lines produced by protons bonded to both
α and β carbons are split into multiplets by aluminum nuclei due to the indirect (electron coupled) spin-spin interactions. The high degree of symmetry of the AlEt$_4^-$ anion in solution is considered responsible for this observation. In pure 1,2-dimethoxyethane (DME) and pure tetrahydrofuran (THF), the $^{27}$Al-$^1$H coupling is clearly resolved into discernible splittings of the ethyl group of AlEt$_4^-$. Mole ratio studies of ether:NaAlEt$_4$ indicate the existence of an equilibrium between contact and solvent-separated ion pairs in solution. The results show that the order of the coordinating ability of the ethers studied is, in decreasing order, DME > THF > diethyl ether.

An NMR temperature and concentration dependence study of NaAlEt$_4$, NaAlBu$_4$, and LiAlBu$_4$ reveals that the lithium cation forms a tighter complex with ether solvents than the sodium cation. A trend in the temperature dependence of the chemical shifts of the anion protons indicates a tendency to favor the formation of solvent-separated ion pairs at lower temperatures. The temperature and concentration dependence of the NaAlEt$_4$ line shapes further suggests the existence of an equilibrium between contact and solvent-separated ion pairs in THF solutions.
PART I

PREPARATION AND CHARACTERIZATION OF LITHIUM- AND
TETRAALKYLAMMONIUM TETRABUTYLALUMINATES
I. INTRODUCTION

"The problem of electrolyte solutions centers around the interactions of ions with one another and with solvent molecules. We have some fairly satisfactory theories of dilute solutions but these are not only limiting theories, they are also approximations in that terms of higher order are usually omitted in order to make the equations conveniently handable. The experimenter has no means of knowing whether observed deviations are due to the absence of neglected terms or to the fact that he has exceeded the concentration at which the theory is applicable. The problem confronting us today is to bring some order into the confusion presently existing in the intermediate and higher concentration ranges. These solutions bridge the gap between dilute solutions, on the one hand, and fused salts on the other.

The quest for an experimentally ideal chemical system which allows the direct instrumental observation of specific ion-ion and ion-solvent interactions is still being pursued. Intensive investigations of electrolyte systems have, in effect, illustrated the simplicity of the theories which instigated the intensive investigations, and the complexity of the microscopic world of solutions has become more and more apparent. It is now well-recognized that an ion in solution is solvated, but it is also realized that the extent and the nature of the solvation are unknown.

The effort to study solute behavior has been directed to electrolytes in nonaqueous solvents of low dielectric constant for a
number of years in an attempt to determine the influence of the dielectric constant on the solute behavior. Solvents of low dielectric constant, however, often induce a variety of ion-ion and ion-solvent interactions which are extremely difficult to evaluate. The electrostatic interactions are known to depend on the dielectric constant of the medium, but it must also be remembered that the local dielectric constant often differs from the bulk dielectric constant. This seriously complicates any treatment based on the Born approach.\textsuperscript{2,3}

The classical studies of Kraus and Fuoss\textsuperscript{4} have demonstrated the importance of the influence of the solvent dielectric constant on ionic conductances. Other early conductance studies have indicated the probable influence of both ion-ion and ion-solvent interactions, especially in solvents of low dielectric constant.\textsuperscript{1} More recently, a number of studies have employed such concepts as ion pairs, association constants, thermodynamics of dissociation, free ions, etc., in addition to solvent dielectric constants.\textsuperscript{5-10} Conductance studies have used these concepts in an attempt to include the possible influence of ion-ion and ion-solvent interactions.

Barthel\textsuperscript{11} has presented a comprehensive review of recent work which has dealt with the methods and the results of conductance studies, especially of nonaqueous solvent systems. The review depicts elaborate procedures, improved techniques, and modernized theories which have led to many suggestions about the nature of the interactions in solution, but perhaps the evaluation of Kraus\textsuperscript{12} ten years
prior is as valid as any of the recent postulations. In his evalua-
tion of the electrolyte problem Kraus surmised that "...the properties
of electrolyte solutions are, in the main, determined by the inter-
actions of the ions with one another and with the solvent molecules.
These interactions depend on the charge, size, structure, and polar-
izability of the ions and on the size, structure, dipole moment, and
polarizability of the solvent molecules." 

Although a great deal of attention has been given to con-
ductance methods in the study of electrolyte solutions, a variety of
experimental techniques have been applied to the investigation of
these systems. Spectroscopic techniques, including infrared (IR), ultraviolet (UV), nuclear magnetic resonance (NMR), electron
spin resonance (ESR), and ultrasonic absorption, have been
employed in attempts to detect and identify the interacting species.
Spectroscopy, as shown by some of the above studies, appears to offer
the distinct advantage of isolating spectral properties of individual
species in solution.

Winstein, et al. were the first to suggest the existence
of an equilibrium between two (or more) kinds of ion pairs in solu-
tion, contact and solvent-separated, and Grunwald was instrumental
in developing and extending the concept. Winstein and Robinson subsequently proposed the existence of these ion pairs in solution to

*A comprehensive survey of pertinent NMR studies is given in Part II
of this Dissertation.
rationalize kinetic data. Since the time of Winstein's proposal, the existence of the two kinds of ion pairs has been well demonstrated. The rationalization of many chemical systems has relied on these results. The rates of anionic polymerization reactions, for example, have been investigated in terms of ion-ion and ion-solvent interactions, utilizing the concept of contact and solvent-separated ionic species. These examples are but a part of the wealth of new information that has been provided by the close inspection of ion-ion and ion-solvent interactions.

In general, the study of ionic associations and the identification of specific ionic species have neglected the details of ion size effects, even though the ion size parameter has been superficially treated in many investigations. Consequently, the ion size effect has begun to receive more attention in recent years in the evaluation of ion-ion and ion-solvent interactions. An example of one of the more cogent ion size studies is that of Griffiths and Scarrow, in which it is proposed that the lithium cation in acetone is a larger species than even the (octylpropyl)N\(^+\) cation.

Although such a large variety of investigations have been used to offer possible suggestions for the behavior of electrolytes in solution, tenable theories have not been forthcoming. Usually, the inherent complexities of each solvent system obviate the extension of ideas from one solvent system to another. This is well-illustrated by the discrepancies found in the values for the solvation numbers of the alkali metal cations. Perhaps, then, the most
propitious approach would be to use as simple a solvent system as possible, one which would include as few variables as possible.

Assuming that an electrolyte system which approaches ideality can be found and can be investigated successfully, several research groups have endeavored to eliminate the greatest number of variables possible and have adopted the most apparently reasonable basic assumptions. As Day and Selbin point out in the chapter of their book on nonaqueous solvents, most conventional solvents are basic in nature. It is quite reasonable, therefore, to assume that solvation occurs primarily with the cation. A starting point is established, then, if a system is chosen such that the anion-solvent interaction is negligible in comparison to the cation-solvent interaction.

Aside from the choice of the cation as the entity which undergoes the most significant ion-solvent interaction in solution, the second most obvious consideration is the solvent itself. Coordination of the cation with the solvent must be sufficiently strong to invoke a measurable change in the chemical or the physical environment of the cation and/or the coordinating solvent molecule(s). This qualification requires the solvent molecules to exhibit themselves as distinct species, coordinated and noncoordinated. Whether the cation or the solvent molecules are to be observed, a distinct chemical entity must exist in solution. The entity, composed of the cation and the complexed solvent molecule(s), must be uniquely distinct from all other species in solution to be observed instrumentally.
This criterion has been difficult to meet, notwithstanding the many electrolyte systems which have been assembled for the express purpose of "isolating" a solvated species.

The majority of solvents which possess a sufficiently strong dipole to dissolve an electrolyte present two fundamental problems. The first involves the competition between the bulk solvent molecules and the coordinated solvent molecules for the cation. This type of competition could lead to an equilibrium process in which only an average effect can be determined macroscopically. The second complication also concerns the obstruction of the instrumental observation of the coordinated solvent molecules by the bulk solvent molecules. The spectral bands of the bulk solvent often mask any unique spectral band of the coordinated solvent molecules because of the proximity of the two absorption bands. Ordinarily, there is a relatively small energy difference between the bulk solvent molecules and the coordinated solvent molecules. For conventional spectroscopic techniques, the energy difference would indeed have to be great to overcome the much larger concentration of the bulk solvent molecules.

Mixed solvent systems have been used in an attempt to eliminate the overwhelming influence of the bulk solvent molecules, but mixed solvent systems usually present the problem of competition between the different solvents for the cation. Only if one of the ion-solvent interactions is much more pronounced will the study of a specific ion-solvent interaction be meaningful. Even then, however,
an evaluation must be made to account for the possible influence of the weaker coordinating agent. Ideally, then, the specific ion-solvent interaction under investigation should be isolated from competitive interactions and from the beclouding influence of the bulk solvent.

The unique ability of NaAlBu₄ to dissolve in solvents of low dielectric constant, including saturated hydrocarbons, has facilitated the study of specific ion-solvent interactions without interference from the bulk solvent.⁴⁶ A number of investigations utilizing this property of NaAlBu₄ have now been made on the specific complexation of the sodium cation by basic solvents.⁴⁷-⁵¹ The use of solvents such as hexane, cyclohexane, and benzene as the bulk solvent in a mixed solvent system has effectively eliminated any solvent competition for the cation, and conclusions based on the assumption that the bulk solvent does not interfere to any appreciable extent may be treated credibly.

The use of NaAlBu₄ as the source of a small cation in a relatively inert solvent is of great value, in light of the fact that the majority of ion-ion and ion-solvent interaction studies have been restricted to (a) aqueous systems, and (b) nonaqueous systems which employ solvents of relatively high dielectric constant. Generally, salts containing small cations are not soluble in noncoordinating solvents.

The disadvantages of aqueous and most nonaqueous systems are several. The use of water as the solvent is highly restrictive
in that many chemical systems do not or cannot tolerate water, either as the bulk solvent or as an impurity. Water is further disadvantaged by its high dielectric constant and its hydrogen-bonding ability, both of which are responsible for the existence of varying degrees and kinds of solvation. Nonaqueous solvents of relatively high dielectric constant inherently present complications which have been discussed previously.

Not only is NaAlBu$_4$ soluble in inert solvents, but it is also soluble in many solvents of intermediate and high dielectric constant. Furthermore, the solubility is appreciable. Often, salts of limited solubility in solvents of low or intermediate dielectric constant must be studied at such low concentrations that only theoretical considerations can be used to extrapolate results to concentrations of daily, routine usage. The high solubility of NaAlBu$_4$ allows its solutions to be studied at reasonable concentrations and with conventional spectroscopic techniques.

In summary, studies of ion-solvent interactions are usually hindered by the degree of solubility of an ionic substance in relatively inert solvents, by the concealment of the specific complexation of interest by the bulk solvent, or by the competition of the coordinating species with the bulk solvent in mixed solvent systems. The use of NaAlBu$_4$ in hydrocarbon solvents essentially eliminates all three of these complications.

Sodium tetra-$n$-butylaluminate is not, however, without its limitations. Heretofore, this research group has endeavored to use a
solvent of low dielectric constant such as cyclohexane or benzene to disperse NaAlBu₄ into a solvent medium that does not offer any appreciable or measurable interaction with the salt and yet can serve as an environment into which a coordinating agent such as tetrahydrofuran (THF) may be quantitatively introduced. The coordination between the sodium cation and the coordinating agent has been followed with nuclear magnetic resonance, infrared, conductance, and thermometric data. Unfortunately, the addition of most coordinating agents has caused the resulting solution to form two phases, which, of course, disqualifies the system for simple exploration. Only the mixed solvent system of cyclohexane and THF has yielded meaningful information to date.⁴⁶

Another more subtle disadvantage of using NaAlBu₄ in hydrocarbon solvents is the obvious lack of comparative data from analogous systems. Although this system has circumvented many of the more glaring disadvantages of other electrolyte systems, many questions still remain unanswered: How significant are the ion-ion interactions in the nonpolar solvents?; To what extent does aggregation occur - if it does?; Does the uniqueness of the NaAlBu₄-mixed solvent system prevent the extension of ideas and conclusions from this system to other systems?

In order to supplement previous work and to extend studies of this type to include the effect of ion size, several analogues of NaAlBu₄ have been prepared for future study.⁵² The characterization of the compounds was deemed necessary in order to determine the
feasibility of the use of the compounds in extending the studies of ion-solvent interactions of NaAlBu$_4$. The author feels that the simple presentation of physical data and elemental analyses is often inadequate in the identification of certain compounds, especially those which have been prepared for specific purposes and which must possess certain characteristics to be of value. Thus, an attempt has been made to characterize the compounds which have been synthesized by presenting a cursory examination of experimental results, utilizing experimental techniques which have been used in this laboratory for the study of NaAlBu$_4$.

The work reported here is not the first report of the synthesis of this general type of compound. The preparation of Me$_4$NAlEt$_4$ and Et$_4$NAl$_3$t$_4$ has been reported by Gavrilenko, et al. No analyses were given. Earlier, Lehmkuhl had already postulated the possibility of preparing R$_4$NAlR$_4$ compounds, but no preparative procedure was outlined.

Hurd reported the preparation of LiAlMe$_4$ and presented aluminum analyses which indicated the success of his procedure. LiAlEt$_4$ has also been prepared by the same general procedure. The extension of the preparative procedure to the synthesis of LiAlBu$_4$ has yielded an analogue of NaAlBu$_4$ which can also be used in the ion-solvent interaction studies and which gives yet a smaller alkali metal cation for an ion size study.
II. EXPERIMENTAL PROCEDURES

A. Preparation of NaAlBu₄

Sodium tetra-\(n\)-butylaluminate was prepared according to the procedure outlined by Höhn, et al.\(^{17}\) This procedure is a modification of the method of Frey, et al.\(^{57}\) in their preparation of NaAlEt₄ and of the method of Zakharkin and Gavrilenko\(^{58}\) in their preparation of similar alkali metal tetraalkylaluminates. One mole of aluminum tri-\(n\)-butyl (198 g) was added directly to a sodium dispersion containing a slight excess of sodium metal (ca. 23 g) in approximately 350 milliliters of \(n\)-heptane. Initially, both reactants were manipulated in the nitrogen-atmosphere dry box. The aluminum tri-\(n\)-butyl was poured into a pressure-equilizing addition funnel, and the sodium was cut and placed in a round-bottomed three-necked flask. Approximately 300 milliliters of \(n\)-heptane were placed over the sodium in the flask. Twenty to fifty milliliters of \(n\)-heptane were slowly poured over the aluminum tri-\(n\)-butyl to reduce the reactivity of the pyrophoric substance once it was taken from the dry box. The less dense \(n\)-heptane forms a thin layer over the aluminum tri-\(n\)-butyl.

After the removal of the materials from the dry box, and prior to the introduction of the aluminum tri-\(n\)-butyl into the reaction flask, a nitrogen flow was established over the reactants through one of the side arms of the reaction flask. The flask was heated until the sodium had become molten, and a high-speed stirrer was used to effect the sodium dispersion. The aluminum tri-\(n\)-butyl was added slowly over
a period of approximately one hour. The reaction mixture was allowed to continue refluxing for two more hours before it was taken into the dry box and filtered to remove the excess sodium and insoluble reaction products. Crystallization was brought about by the removal of the majority of \( n \)-heptane in vacuo, and the product was recrystallized from \( n \)-heptane. The recrystallization was induced by cooling the solution flask in an aluminum container in the dry box. The aluminum container was filled with aluminum shot and cooled by the circulation of coolant from an external low temperature bath. The white crystals of NaAlBu\(_4\) were dried with a high vacuum rotating evaporator. Last traces of solvent were removed by fusing NaAlBu\(_4\) (m.p. = 67-69°; \( \sim 80\% \) yield) in vacuo. NaAlBu\(_4\) was stored under vacuum to prevent contamination of the salt and adsorption of solvent vapors by the salt.

B. Preparation of NaAlEt\(_4\)

The preparation of NaAlEt\(_4\) consisted of adding aluminum triethyl (114 g) to a sodium dispersion (ca. 23 g) in toluene according to the method of Frey, et al.\(^{57}\) Similar to the method of preparing NaAlBu\(_4\), the reaction took place under a nitrogen atmosphere for approximately three hours. Filtration in the dry box was followed by recrystallization from toluene. The white needles of NaAlEt\(_4\) were filtered again and dried in vacuo. The addition of \( n \)-hexane to the crystals prior to filtration aided in the removal of the last traces of toluene in vacuo (m.p. = 125°; 40% yield).
C. Preparation of LiAlBu₄

The procedure for the preparation of LiAlBu₄ is similar to that of Hurd's preparation of LiAlMe₄. Equimolar amounts of aluminum tri-n-butyl (198 g) in n-hexane and n-butyllithium (64 g) as a 22% n-hexane solution were combined in the inert atmosphere of the dry box. The white crystals which formed immediately upon the mixing of the two solutions were filtered and washed with n-hexane three or four times. Recrystallization was effected from toluene. Washing again with n-hexane, followed by the application of a high vacuum rotating evaporator, gave fluffy white crystals (m.p. = 181-183°C; 69% yield).

D. Preparation of R₄NAlBu₄ Compounds

All of the R₄NAlBu₄ compounds were prepared by the same general procedure of refluxing a saturated benzene solution of the appropriate R₄NBr salt under a nitrogen atmosphere before adding a benzene solution of NaAlBu₄ dropwise to the refluxing mixture via a pressure-equalizing dropping funnel. The saturated R₄NBr solutions were refluxed for 24-48 hours to insure maximum solubility of the salts in the benzene. A slight molar excess of the R₄NBr was used, disregarding incomplete solution of the R₄NBr in the benzene. The admixture was refluxed further for approximately 24 hours to insure a quantitative reaction. The NaBr and excess R₄NBr were removed by filtration in the dry box. The resultant filtrate was subjected to a vacuum until a viscous solution was obtained; whereupon the solution was filtered again. The filtrate was washed with n-hexane.
several times (two phases formed upon the addition of \textit{n}-hexane) to extract any excess NaAlBu$_4$ and then placed under vacuum in a high vacuum rotating evaporator until a thick slurry was obtained. Filtration of the slurry gave white crystals. After having been washed with \textit{n}-hexane, the crystals were heated to 100° \textit{in vacuo} to remove the last fraction of benzene and \textit{n}-hexane. Recrystallization was never adequately effected because of the high degree of solubility of the salts in benzene and the salts’ unusual property of forming two phases in the presence of saturated hydrocarbons. Toluene, THF, and diethyl ether were also used in the attempt to induce recrystallization, but to no avail. Hence, the above procedure was repeated until a $\pm$ (or less) melting point range was obtained for each salt. Melting points for the compounds are listed in Table I, page 54. Yields were low, usually less than 20\%.

Both THF and diethyl ether were used as solvents in the preparation of the R$_4$NaAlBu$_4$ compounds, but the difficulty in the complete removal of the ethers caused the author to rely on benzene even though the R$_4$NBr salts (with the exception of Bu$_4$NBr) are not appreciably soluble in benzene. Nuclear magnetic resonance spectra indicated the preparation of the quaternary ammonium compounds in the ether solvents, but no definitive analyses were ever obtained to confirm their syntheses.
E. Melting Points and Aluminum Analyses

Melting points were ascertained by averaging the two determinations which were in closest agreement. Melting point capillaries were filled in the dry box and sealed with stopcock grease before they were brought out of the dry box. A Hoover Melting Point apparatus was used for the melting point determinations.

The aluminum analyses were carried out according to a slight modification of the procedure outlined by Kolthoff and Sandell. Each new batch of NaAlBu$_4$ was analyzed before its use in any of the preparative procedures. Because of the lack of accuracy afforded by the balance in the dry box due to fluctuations in the nitrogen pressure, the container for the salt sample was weighed outside the dry box on a Mettler H$_6$ balance before it was filled with the sample in the dry box. The filled container was weighed again on the balance outside the box. The container was fitted with an outer ground glass cap to prevent contamination by the joint lubricant. The cap was removed from the container after weighing, and water was cautiously added to the sample until decomposition was completed. Allowing the sample to stand in air for a length of time before the addition of water often made dissolution quite difficult. A dilute aqueous HCl solution (~ 20%) was slowly added to the sample solution until the appropriate pH value was obtained. The acidified solution was heated and agitated to insure the complete neutralization of Al$_2$O$_3$ and Al(OH)$_3$. The standard procedure for producing the 8-hydroxyquinolate precipitate.
was then followed. An average value of two (or more) analyses was taken for each salt. The results of the aluminum analyses are listed in Table I, page 34.

F. Conductance

Conductance cells of standard design with shiny platinum electrodes were used for all of the conductance measurements. The cells were fitted with outer ground-glass caps to prevent contamination of the solutions by the joint lubricant. The cell constants were determined by the use of potassium chloride solutions according to the method of Lind, et al. Cell constants ranged from 0.0380 to 0.1486 cm\(^{-1}\).

Conductance measurements were made with a Leeds and Northrup Model 4666 Jones Modified Conductance Bridge or with a RC-16 Conductance Bridge manufactured by Industrial Instruments, Inc. A Hewlett-Packard Model 200 D audio oscillator and a General Radio Company Type 1253 A tuned amplifier and null detector were used in conjunction with the Leeds and Northrup instrument. The oscillator was operated at 5000 cps and had an output to the bridge of 0.5 volts. The maximum resistance measurable on the RC-16 Conductance Bridge is 2.5 megohms; that on the Jones Bridge is 60 kilohms. Measured resistances were taken with the Jones Bridge whenever possible because of its higher precision. The temperature of the solutions was maintained at 30 ± 1°C during measurements.

The conductance cells were thoroughly washed with acetone, ethanol, water, 20% aqueous HCl, 50% aqueous H\(_2\)SO\(_4\), and conductivity
water (in that order) before they were dried in an oven operated at 120°C for a minimum of two hours. The cells were taken directly from the oven and placed under vacuum in the port of the nitrogen-atmosphere dry box while they cooled. The cells were kept in the port for a minimum of half an hour while the nitrogen atmosphere in the port was recirculated through a series of columns and traps to remove any residual traces of oxygen and moisture. Once the cells were filled with the appropriate solutions in the dry box, they were taken from the dry box and resistances were read within one hour of their exit.

No measurable conductances were observed for the solvents, benzene and THF; consequently, no corrections for solvent conductance were necessary. Conductance values for the solutions did not vary significantly over a 24-hour period. Each solution was run in at least two different conductance cells of significantly different cell constants; variations in resistances were insignificant, and an average value was taken.

G. Nuclear Magnetic Resonance

Nuclear magnetic resonance spectra were taken for all compounds on both the Varian Associates A-60A and HA-100 spectrometers at ambient temperatures (~37°C). NMR tubes were filled in the dry box and sealed with high pressure caps. Samples were run within approximately two hours of the time the tubes were removed from the dry box. Spectra of the tetra-n-butylaluminate salts were not significantly
altered after the samples in the sealed NMR tubes had been allowed to stand outside the dry box for a period of one week. If leakage did occur, it was not significant enough to affect the results of the NMR studies.

H. Solvents and Reagents

All solvents were purchased as reagent or higher grade chemicals. They were dried by allowing them to stand over CaH₂ until no further reaction was visible, refluxed over the CaH₂ for a minimum of eight hours, and distilled under an atmosphere of dry nitrogen gas. Collection flasks were constructed so that a positive nitrogen atmosphere blanketed the solvent at all times. The flasks were fitted with two Teflon stopcocks and a male $\text{H}\, 24/40$ ground glass joint with a glass cap. A portion of each freshly-distilled solvent was poured over small amounts of NaAlBu₄ and LiAlBu₄ in the dry box to test for traces of oxygen or water before the solvent was used. The lithium compound, in particular, is very sensitive to impurities, and solutions of the compound yield a light yellow color upon standing if reactive impurities are present in the solvent. Distillations were initially performed over LiAlH₄ or Na/K alloy, but the use of CaH₂ was found to be just as efficient in the removal of water and also provided the added advantage of working with a much less dangerous drying agent.

The R₄NBr salts were purchased as highest purity reagents (Eastman Organic and J. T. Baker). They were subjected to vacuum for several hours before they were used, even though they were stored in
the dry box in closed containers. Recrystallization of the salts was not deemed necessary for their use in the preparatory procedures.

The n-butyllithium (Alfa Inorganics) was purchased as a 28% n-hexane solution. It was filtered through glass wool in the dry box before use.

Aluminum tri-n-butyl (Texas Alkyls) was used as a 95.5% pure reagent (highest purity) without further purification. The pyrophoric chemical was stored in air-tight metal cylinders in the dry box after it was transferred from the bulk cylinder under a nitrogen atmosphere.

I. Manipulation of Compounds

Because the tetraalkylaluminates are air-sensitive, special procedures must be employed to prevent their decomposition. The nitrogen-atmosphere dry box was designed for the manipulation of air-sensitive compounds. Consequently, all of the compounds were handled in the dry box whenever possible. A copper oven was placed between the nitrogen tank and the dry box in the nitrogen gas line to remove any traces of oxygen from the nitrogen source. A nitrogen inlet valve was connected to the side of the dry box so that a positive nitrogen pressure could be maintained inside the dry box at all times. The nitrogen atmosphere in the dry box was circulated through a copper oven to remove larger solvent molecules. The dry box was periodically flushed with nitrogen to remove solvents which could not be removed
readily by the recirculation train. As a last precaution, solids were stored under vacuum in specifically designed salt flasks.

A port to the dry box was constructed so that a vacuum could be applied to glassware and chemicals before entering the dry box. Solvents or other materials which could not be evacuated were placed in the port and the port was flushed with nitrogen for half an hour. The port was then closed, and its atmosphere was circulated through the recirculation train which had been attached to the port. As a precaution, the port was recirculated even after a vacuum had been applied to the port.

Since it was necessary to synthesize all but LiAlBu₄ outside the dry box, elaborate steps were taken to blanket the reagents and solvents in a nitrogen atmosphere and to employ reliable ground glass joints in all of the glassware. Whenever possible, reagents were either covered by solvent or kept in solution.

The extreme sensitivity of the compounds to air and to a large variety of chemicals dictated caution in the preparation of the glassware. The glassware was thoroughly washed in dilute HCl and rinsed with water before being soaked in concentrated potassium hydroxide solution. The potassium hydroxide was neutralized by cleaning solution (Na₂Cr₂O₇ in H₂SO₄). The glassware was then thoroughly washed with water and rinsed with acetone before drying in an oven operated at 120°C.

The destruction of the compounds, especially the lithium and sodium salts, was carried out with care. A solution of 95%
ethanol was slowly added to a hydrocarbon or ether solution of the salt until the reactivity of the salt had been noticeably impaired. Water, followed by dilute HCl, was gradually added to the solution to complete the decomposition.
III. RESULTS AND DISCUSSION

A. Nuclear Magnetic Resonance

The NMR spectra of aqueous solutions of the $R_4NBr$ salts were recorded by a 60 MHz spectrometer, and the proton signals were analyzed. Attempts were made to record spectra of benzene solutions of the $R_4NBr$ salts, but only $Bu_4NBr$ is appreciably soluble in benzene. The proton resonance spectrum of NaAlBu$_4$ has previously been studied extensively in this laboratory,$^{46}$ and a portion of the spectrum has been published by Wuepper and Popov.$^{50}$

The spectrum of a benzene solution of NaAlBu$_4$ is presented in Figure 1. Tetramethylsilane (TMS) was used as the internal standard, and the proton absorption signals are referenced to it in parts per million (ppm). The apparent triplet furthest upfield (-0.40 ppm) is the absorption signal of the $\alpha$-methylene protons of AlBu$_4^-$. The electric quadrupole moment of aluminum has apparently caused a significant broadening of the $\alpha$-methylene triplet. The $\beta$- and $\gamma$-methylene proton signals of the butyl group are also depicted in Figure 1 (1.55 ppm). The most prominent absorption peak is part of the methyl proton resonance (1.12 ppm). This is the peak used by Schaschel and Day$^{46}$ to verify the lack of complexation between AlBu$_4^-$ and THF. The methyl peak was also used by Hammonds, et al.$^{47}$ in their investigation of the possibility of complexation of NaAlBu$_4$ by benzene and toluene. The entire spectrum of NaAlBu$_4$ is in good agreement with the recorded spectra of various other butyl groups.
FIGURE 1

60 MHz Spectrum of NaAlBu₄, 0.1 M Benzene Solution, 500 Hz Sweep Width
Massey, et al. have discussed the difference between the chemical shifts of the CH₃ and CH₂ resonances in the spectra of (CH₃CH₂)ₙX compounds in terms of the electronegativity of the atom X. For elements less electronegative than lead (2.33), the CH₃ resonance occurs at a lower field than the CH₂ resonance. The acquisition of a negative charge by the central atom X causes the CH₂ peak to assume a position upfield from the CH₃ peak because of the reduction of the electronegativity of the atom X. The acquisition of a negative charge by the central atom X causes the CH₂ peak to assume a position upfield from the CH₃ peak because of the reduction of the electronegativity of the atom X. In the case of AlBu₄⁻, the electronegativity of aluminum (1.61) is further reduced by the acquisition of its negative charge, and the α-methylene peak of AlBu₄⁻ is set apart from the other proton signals at a higher field.

Massey, et al. also observed a distinct difference between the spectra of Et₄AsBr in chloroform and in water. The spectrum of the cation in chloroform is a typical A₃B₂ spectrum, but in water the proton signals are definitely broadened. The authors consider the broadening to be due to spin coupling of the protons with the arsenic atom for which the quadrupole relaxation occurs at such a rate in the symmetrical ion that the spin-spin effects are not completely averaged out. They conclude that contact ion pair formation is probably responsible for the sharp line spectrum in the less polar chloroform. The close proximity of the anion to the Et₄As⁺ cation causes an electric field gradient at the arsenic atom in the cation which is responsible for rapid quadrupole relaxation. Hence, spin-spin effects
involving the arsenic nucleus are averaged out. An attempt to use the \(\text{AlBu}_4^-\) protons as a probe to differentiate between contact and solvent-separated ion pairs in an analogous manner was made, and the spectra of \(\text{NaAlBu}_4\) in a variety of solvents were analyzed. The spectra do not appear, however, to be affected by a change in solvent. The invariance of the spectra may be due to the small nuclear quadrupole moment of the aluminum \((Q = 0.149e \times 10^{-24} \text{ cm}^2)\),\(^{63}\) as compared to that of arsenic \((Q = 0.3e \times 10^{-24} \text{ cm}^2)\).\(^{63}\) The larger electronic polarizability of the arsenic is also a probable factor.

In the case of the \(R_4\text{NAlBu}_4\) compounds, the 60 MHz spectra which were recorded for the 0.1 M benzene solutions of the compounds were almost composite pictures of the spectra of the starting materials, \(\text{NaAlBu}_4\) and \(R_4\text{NBr}\). A 100 MHz spectrometer was used to obtain spectra of 250 hertz width to study the area of the spectra in which overlap of the proton signals from the alkyl groups on the nitrogen and the aluminum occur (Figures 2-5). Integration of the peaks did not always give clear quantitative results because of the overlapping of the signals, but the constancy of the relative peak heights of the various alkyl groups in many different samples eliminates the possibility of a simple admixture of the two starting materials in the benzene solutions. Corroborative data confirm this. Double resonance experiments were not satisfactory in a further characterization of the \(R_4\text{NAlBu}_4\) compounds.

Figure 2 shows the spectrum of \(\text{Me}_4\text{NAlBu}_4\) with the expected proton signals. The highly symmetrical \(\text{Me}_4\text{N}^+\) cation should and does
FIGURE 2

100 MHz Spectrum of Me₄NAI Bu₄, 0.1 M Benzene Solution, 250 Hz Sweep Width.

Chemical shifts are relative to TMS, measured in duplicate samples.
show a single absorption peak furthermost downfield (3.14 ppm). The similarity between the butyl proton peaks of Me₄NAlBu₄ and NaAlBu₄ can be seen by comparing Figures 1 and 2, in spite of the difference in resonance frequencies applied to the two different samples. The most obvious difference between the two spectra is the broadened α-methylene triplet of AlBu₄⁻ in Me₄NAlBu₄.

Figure 3 depicts the spectrum of Et₄NAlBu₄ with the somewhat unusual signal of the ethyl protons. The methylene proton signals of the ethyl group are found downfield as a quartet (3.56 ppm) as anticipated, but the expected methyl proton triplet of the ethyl group (0.94 ppm) undergoes further splitting. This long-range ¹H-¹⁴N coupling has been noted by several other authors as well.⁶⁴-⁶⁶ Its existence has been explained in terms of the presence of a highly symmetrical electric field gradient around the nitrogen which causes an increase in the spin-lattice relaxation time. This increase destroys the decoupling of the long-range interaction between the ¹H and the ¹⁴N to the extent that the ¹H-¹⁴N coupling constant is observable and measurable. Conveniently, the ethyl group absorption peaks do not obscure the butyl peaks, and the spectrum is easily analyzed.

Pr₄NAlBu₄ also gives a rather clear spectrum (Figure 4). The methyl protons (1.82 ppm) and the α-methylene protons (0.10 ppm) of the butyl group are easily identified, and the α-methylene protons of the propyl group (3.84 ppm) are observed downfield and broadened. The θ-methylene protons of the propyl group are somewhat obscured by the methyl protons of the butyl group, but they are distinct enough
FIGURE 3

100 MHz Spectrum of Et₄NAlBu₄, 0.1 M Benzene Solution, 250 Hz Sweep Width.

Chemical shifts are relative to TMS, measured in duplicate samples.
FIGURE 4

100 MHz Spectrum of Pr₄NAlBu₄, 0.1 M Benzene Solution, 250 Hz Sweep Width.

Chemical shifts are relative to TMS, measured in duplicate samples.
to identify (ca. 1.6 ppm). The methyl protons of the propyl group are found at 1.18 ppm.

The spectrum of Bu₄NAlBu₄ (Figure 9) is somewhat more complicated than any of the spectra of the other R₄NAlBu₄ compounds, as was anticipated. The α-methylene proton peaks of AlBu₄⁻ are obvious (0.10 ppm), as are the α-methylene proton signals of Bu₄N⁺ (1.66 ppm). Only by comparison with the other spectra, however, can the remaining peaks be readily identified. The methyl proton signals of Bu₄N⁺ are found at 1.22 ppm, furthest upfield from all but the α-methylene peaks of AlBu₄⁻. The β- and γ-methylene proton signals of AlBu₄⁻ (ca. 3.26 ppm) are still unobscured by other absorptions. There is considerable overlapping of the signals from the methyl signals of AlBu₄⁻ and the β- and γ-methylene signals of Bu₄N⁺. Figure 9 shows the final identification of the individual peaks. Spin decoupling by double irradiation was not possible because of the proximity of the irradiated signal to the other signals. Buckson and Smith⁶,⁷ have reported the NMR spectra of various n-butylammonium salts in nitrobenzene, and the assignments agree favorably with those given to Bu₄NAlBu₄. The signals in the midst of the AlBu₄⁻ α-methylene triplet are due to impurities (ca. 0.0 ppm).

Because of the limited solubility of LiAlBu₄ in benzene, its spectrum (Figure 6) was obtained in THF rather than benzene. It can be seen that the proton signals are very nearly identical to those of NaAlBu₄. The methyl proton signals appear at 0.87 ppm, and the α-methylene proton signals occur at -0.39 ppm. The β- and γ-methylene
FIGURE 5

100 MHz Spectrum of Bu₄NaBu₄, 0.1 M Benzene Solution, 250 Hz Sweep Width.

Chemical shifts are relative to TMS, measured in duplicate samples.
FIGURE 6

60 MHz Spectrum of LiAlBu₄, 0.1 M THF Solution, 500 Hz Sweep Width.
proton signals are found at 1.24 ppm, somewhat obscured by the \( \alpha \)
methylene proton signals of THF.

B. Melting Points and Aluminum Analyses

Table I lists the melting points of LiAlBu\(_4\) and the R\(_4\)NA1Bu\(_4\) compounds. The melting points of NaAlBu\(_4\), NaAlEt\(_4\), and the R\(_4\)NA1Et\(_4\) compounds have also been included for comparison. It should be noted that the melting point of NaAlBu\(_4\) is slightly higher than that reported in the earlier literature.\(^4\)\(^6\)\(^\sim\)\(^\circ\) The close agreement between the experimental and the theoretical percentages of the aluminum analyses listed in Table I and the refinement of the preparative procedure for the salt indicate that the value of the melting point reported here is the more correct one.

The melting point of NaAlBu\(_4\) is seen to be very close to the melting points of the R\(_4\)NA1Bu\(_4\) compounds. The much higher melting point of NaAlEt\(_4\)\(^5\)^6\(^7\) indicates that the forces of attraction in the crystalline state are more nearly alike among the five tetra-n-butylaluminates than for the NaAlBu\(_4\) and NaAlEt\(_4\) analogues. Moreover, the tetramethyl- and tetraethylammonium tetraethylaluminates, as reported by Gavrilenko, \textit{et al.}\(^5\)^8 show much higher melting points than any of the R\(_4\)NA1Bu\(_4\) compounds. These data imply that the presence of the tetra-n-butylaluminate anion in the crystal structure of its compounds is at least partially responsible for the lower melting points of the compounds. Perhaps the presence of AlBu\(_4^-\) is also related to the salts' greater solubilities in solvents of low dielectric constant.
<table>
<thead>
<tr>
<th>Salt</th>
<th>M.P.</th>
<th>% Al Calcd.</th>
<th>% Al Found&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlEt&lt;sub&gt;4&lt;/sub&gt;</td>
<td>ca. 125&lt;sup&gt;56,57&lt;/sup&gt;</td>
<td>16.23</td>
<td>16.11, 16.18</td>
</tr>
<tr>
<td>NaAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>67-69</td>
<td>9.69</td>
<td>9.67</td>
</tr>
<tr>
<td>LiAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>181-183</td>
<td>10.3</td>
<td>10.1</td>
</tr>
<tr>
<td>Me&lt;sub&gt;4&lt;/sub&gt;NAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>68-70</td>
<td>8.19</td>
<td>8.11</td>
</tr>
<tr>
<td>Et&lt;sub&gt;4&lt;/sub&gt;NAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>74-76</td>
<td>6.99</td>
<td>7.10</td>
</tr>
<tr>
<td>Pr&lt;sub&gt;4&lt;/sub&gt;NAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>52-54</td>
<td>6.11</td>
<td>6.02</td>
</tr>
<tr>
<td>Bu&lt;sub&gt;4&lt;/sub&gt;NAlBu&lt;sub&gt;4&lt;/sub&gt;</td>
<td>49-50</td>
<td>5.42</td>
<td>5.41</td>
</tr>
<tr>
<td>Me&lt;sub&gt;4&lt;/sub&gt;NAlEt&lt;sub&gt;4&lt;/sub&gt;</td>
<td>162-165&lt;sup&gt;53&lt;/sup&gt;</td>
<td>12.5</td>
<td>b</td>
</tr>
<tr>
<td>Et&lt;sub&gt;4&lt;/sub&gt;NAlEt&lt;sub&gt;4&lt;/sub&gt;</td>
<td>185-189&lt;sup&gt;53&lt;/sup&gt;</td>
<td>9.86</td>
<td>b</td>
</tr>
</tbody>
</table>

<sup>a</sup> Based on errors in weighing procedures alone, it is estimated that these experimental values are subject to an error of approximately 2%. Errors due to decomposition are less than 0.5%.

<sup>b</sup> Analyses not given.
Until definitive X-ray work is done on these salts, however, it would be premature to draw any conclusions.

The aluminum analyses are also included in Table I. The analyses were difficult to obtain because of the air-sensitivity of the compounds and the difficulty of completely removing the solvents from the salts. The experimental results, however, show good agreement with the theoretical values and are considered reliable.

Carbon and hydrogen analyses were not made because of their unreliability for these air-sensitive compounds. Hammonds attempted to use both % Na and % Butyl determinations as a guideline for the evaluation of the purity of NaAlBu₄ and came to the conclusion that the analysis for % Al was the only reliable test for the purity of the salt.

2. Solubility

An attempt was made to carry out a solubility study on these compounds in solvents of interest with the intent of compiling a solubility chart for the compounds. However, LiAlBu₄ is not soluble in saturated hydrocarbons and shows only limited solubility in benzene even at elevated temperatures. Furthermore, the R₄NAIAlBu₄ compounds form two phases in the presence of saturated hydrocarbons, and they appear to dissolve in benzene so readily that only an estimate of their solubilities can be made.

At higher concentrations in benzene, large globular particles can be seen on close inspection. It is possible that microscopically
fine particles exist even at the lower concentrations. The extent of this effect is dependent on the particular compound and the temperature of the solution. Further addition of benzene yields a clear solution again. The $R_4$NaN$_4$ compounds are very soluble in THF, but, surprisingly, have to be heated in order to prepare even 0.1 M solutions.

D. Conductance

Table II lists the equivalent conductances of 0.1 M and 0.01 M solutions of the tetraalkylaluminates in benzene and THF. The cursory examination of the equivalent conductances of LiAlBu$_4$ and the $R_4$NaN$_4$ compounds is intended primarily to show the extent of their ionicity. Conductance studies of NaAlBu$_4$ in cyclohexane and THF indicate that NaAlBu$_4$ exists as some sort of ionic species in these solvents; hence, an attempt has been made to show the similarity between the equivalent conductances of the synthesized compounds and NaAlBu$_4$ in order to further characterize them and to illustrate the potential usefulness of the new compounds as ionic species in solvents of low dielectric constant. NaAlEt$_4$ has also been included in Table II to supplement the conductance data.

It is obvious upon inspection of the conductance data that ionicity is clearly demonstrated for each compound in at least one solution. In addition, some rather interesting behavior is shown. A complete and elaborate conductance study would be required to finalize any considerations which might be given, and that is not the purpose of
TABLE II
SUMMARY OF EQUIVALENT CONDUCTANCES OF SOLUTIONS OF BENZENE AND TETRAHYDROFURAN

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A \times 10^2$ in Benzene $^a$ (cm$^2$ equiv$^{-1}$ ohm$^{-1}$)</th>
<th>$A \times 10^2$ in THF $^a$ (cm$^2$ equiv$^{-1}$ ohm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 M</td>
<td>0.01 M</td>
</tr>
<tr>
<td>NaAlEt$_4$</td>
<td>insol.</td>
<td>insol.</td>
</tr>
<tr>
<td>NaAlBu$_4$</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>LiAlBu$_4$</td>
<td>insol.</td>
<td>0</td>
</tr>
<tr>
<td>Me$_4$NaAlBu$_4$</td>
<td>5.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Et$_4$NaAlBu$_4$</td>
<td>0</td>
<td>1.1</td>
</tr>
<tr>
<td>Pr$_4$NaAlBu$_4$</td>
<td>0</td>
<td>1.8</td>
</tr>
<tr>
<td>Bu$_4$NaAlBu$_4$</td>
<td>32</td>
<td>1.1</td>
</tr>
</tbody>
</table>

$^a$ Since only relative orders of the magnitudes of equivalent conductances are considered, the precision of the conductance bridges was not determined; however, the equivalent conductances are well within 10% of actual values.
this study. However, the apparent anomolous conductance behavior warrants some elaboration, and speculation seems appropriate at this point.

Inspection of Table II reveals the relative magnitudes of the equivalent conductances of the alkali metal tetraalkylaluminates. Data are not available for NaAlEt₄ and LiAlBu₄ in benzene for comparison with NaAlBu₄. Of interest, though, is the fact that in benzene NaAlBu₄ shows a slight equivalent conductance at the 0.1 M concentration, but shows none at the 0.01 M concentration. It is not unreasonable to suspect that the formation of triple ions or higher aggregates is responsible for the increase in equivalent conductance with an increase in the concentration of NaAlBu₄. This same phenomenon has been observed by Hammonds for the NaAlBu₄-cyclohexane system, and Kraus has postulated the existence of triple ions at even lower concentrations in benzene (ca. 10⁻⁵ M).

The relative order of the equivalent conductances of the 0.1 M THF solutions of NaAlEt₄ and NaAlBu₄ may be rationalized in terms of apparent differences in the ionic mobilities of their free ions. If no appreciable ion-ion interactions occur in THF, the difference would then be essentially the difference between the mobilities of the AlEt₄⁻ and AlBu₄⁻ ions, assuming no significant difference in the interaction of THF with the two different anions.

The much lower equivalent conductance of the 0.1 M solution of LiAlBu₄ in THF would appear to be due to the difference in the interaction between THF with the Na⁺ cation and THF with the Li⁺
cation. Mukherjee, et al. have found that the apparent ionic size of the Li$^+$ cation in propylene carbonate is larger than either the Bu$_4$N$^+$ or the (isoamyl)$_4$N$^+$ cation. Bhattachryya, et al. have measured the equivalent conductances of several tetraphenyloborides in THF and have also concluded that the Li$^+$ cation is highly solvated by THF. These authors propose that the Na$^+$-THF interaction is substantial, though less than the Li$^+$-THF interaction.

The relative order of equivalent conductances of the alkali metal tetraalkylaluminates in the 0.01 M solutions of THF does not present such an easily-rationalized set of data. The equivalent conductance of LiAlBu$_4$ is the greatest of the three salts at this concentration. If only free ions are still considered, these data would indicate that the Li$^+$-THF interaction is less than that of the Na$^+$-THF. Obviously, there are other factors to consider.

If the equivalent conductances of the alkali metal tetraalkylaluminates for both THF solutions are compared, it becomes clear that NaAlEt$_4$ and NaAlBu$_4$ both display an increase in equivalent conductance with an increase in concentration. LiAlBu$_4$, on the other hand, shows a decrease in equivalent conductance with an increase in concentration. This very strongly indicates that ion-ion interactions are significant for all three alkali metal tetraalkylaluminates at both concentrations. This, in turn, eliminates any explanation of the conductance data solely in terms of the relative mobilities of free ions.
It is interesting to note that the extension of concepts applied to nonpolar systems to the THF solvent system can superficially rationalize the equivalent conductance data of the alkali metal tetraalkylaluminates. Bhattacharyya, et al.\textsuperscript{5} in their study of the conductance of Bu\textsubscript{4}NB\textsubscript{0} (\( \Phi = \) phenyl) and (isoamyl)$_3$BuNB\textsubscript{0} in THF, mention that deviations from theoretical considerations at the higher concentrations (> 10\textsuperscript{-4} M) are most likely due to the formation of (B\textsubscript{0}\textsuperscript{4})\textsuperscript{—}-(cation\textsuperscript{+})\textsubscript{2} species, and Randall and Shaw\textsuperscript{70} allude to the influence of "solvent-ion pair" aggregates in their study of Et\textsubscript{4}AsI to explain the results of their observations. The latter paper also points out that ion-ion and ion-solvent effects are not generally independent.

If the possibility of aggregation in THF is considered for the moment, an explanation of the conductance data may be given in terms of aggregation. The smallest possible aggregates, contact ion pairs and triple ions, will be used to illustrate. If the prevailing equilibrium is considered to be

\[
2M^+A^- \cdot n\text{THF} \rightleftharpoons M^+ \cdot (n+1)\text{THF} + A^- \cdot m\text{THF} (1)
\]

(where \( m = 0,1,...,n-1 \)), then the increase in equivalent conductance with an increase in concentration for the sodium salts can be explained. At 0.01 M concentration, both NaAlEt\textsubscript{4} and NaAlBu\textsubscript{4} may exist mainly as contact ion pairs, with triple ions present to account for the relatively small equivalent conductances. The greater equivalent conductance of NaAlEt\textsubscript{4} is due to the greater number of triple ions and the greater mobility of [Na(AlEt\textsubscript{4})\textsubscript{2}]\textsuperscript{—} relative to [Na(AlBu\textsubscript{4})\textsubscript{2}]\textsuperscript{—}. Since
the AlEt₄⁻ anion is considerably smaller than AlBu₄⁻, AlEt₄⁻ would be expected to exhibit a greater attraction toward the Na⁺ cation than would the AlBu₄⁻. Thus, as the anion size decreases, there is an increase in the degree of association. Consequently, NaAlEt₄ has a greater tendency to form triple ions, and correspondingly has a greater number of conducting species in solution.

LiAlBu₄, on the other hand, may exist primarily as free ions at the 0.01 M concentration because of the strong Li⁺-THF interaction, or, at least, solvent-separated ion pairs, which are more easily broken up than contact ion pairs. Thus LiAlBu₄ has a greater conductance at the 0.01 M concentration than either NaAlEt₄ or NaAlBu₄ because of the greater mobility of a Li⁺·nTHF species, which is obviously smaller than the triple ions of the sodium salts.

An increase in concentration of the sodium salts produces an increase in their equivalent conductances because of the increase in the number of triple ions. NaAlEt₄ has a greater equivalent conductance than NaAlBu₄, either because of the higher mobility of the NaAlEt₄ triple ion, or a higher proportion of triple ions. An increase in the concentration of LiAlBu₄ produces a decrease in its equivalent conductance because of the greater degree of association, producing an increase in the contact ion pair concentration.

It is obvious that sufficient data are not available to substantiate the consideration just given. The formation of triple ions or higher aggregates in THF is not a concept which can be readily accepted, even though the limited amount of data may be rationalized
with such a concept. It is also obvious, however, that significant ion-ion interactions appear to be responsible for the inconsistency of the data.

To complicate matters, there is also the possibility of the equilibria

\[ M^+ \cdot n\text{THF} \rightleftharpoons M^+ \cdot (n-1)\text{THF} + \text{THF} \rightleftharpoons M^+ \cdot (n-2)\text{THF} + 2\text{THF} \rightleftharpoons \text{etc.} \quad (2) \]

existing, as well as similar equilibria involving contact ion pairs or aggregates. The NMR study of Schaschel and Day indicates such a possibility. Up to a 1:1 mole ratio of THF:NaAlBu\textsubscript{4} in cyclohexane, there is no change in the chemical shift of the THF \( \alpha \)-methylene signals, indicating a "tight" complex. After 1:1, however, there is still only one \( \alpha \)-methylene signal which gradually shifts its absorption position until a 4:1 mole ratio is reached. At the 4:1 ratio, there is another distinct chemical shift which indicates a Na\textsuperscript{+} \cdot THF complex. The lack of more than one \( \alpha \)-methylene signal, although there are at least two kinds of complexed species in solution after 1:1 (e.g., at 1.5:1, there would be a 1:1 species and a 2:1 species), would indicate the possibility of an equilibrium process which is responsible for an averaging effect seen in the NMR spectra. The existence of such equilibria involving the solvent molecules, regardless of how meaningful they are, cannot assist in rationalizing the conductance data with such little information available.

Olander has discussed the concentration dependance of the solvation number of the sodium cation for the NaAlBu\textsubscript{4} \cdot THF-cyclohexane system. The average number of bound (or coordinated) THF molecules,
was determined for different concentrations of NaAlBu₄ in cyclohexane by IR spectroscopy. The higher concentrations of NaAlBu₄ show the larger $\overline{n}$ values, indicating that the competition of the AlBu₄⁻ anion for a coordination site on the Na⁺ cation is greatest at the lower concentrations of NaAlBu₄. The data are rationalized by concluding that although aggregation probably does increase with an increase in salt concentration, the stability of the aggregates must decrease with an increase in salt concentration. Olander⁷² has detected IR absorption bands which might be reasonably assigned to these aggregates of NaAlBu₄ in cyclohexane. From the $\overline{n}$ values and spectral data, he postulated the formation of "microlattices" at the higher concentrations such that the average cation-anion attraction decreases with an increase in concentration, justifying the greater tendency of cation-solvent interaction at the higher concentrations.

The extension of Olander's⁷² concepts to THF solutions is difficult. The existence of large aggregates in THF seems highly unlikely. Also, the absence of both Raman⁴⁹ and IR⁷² absorption bands of THF solutions of NaAlBu₄ which had been ascribed to aggregation in cyclohexane indicates the lack of appreciable aggregation in THF. The general consideration that the "tightness" of a contact ion pair decreases with an increase in concentration, however, may be speciously applied to the THF solutions of the alkali metal tetraalkylaluminates. Ion pair dipole-ion pair dipole interactions may become significant at the higher concentration in THF, such that
solvation of the sodium cation is enhanced to the point of disrupting a significant number of contact ion pairs.

With such scarcity of conductance data, it would be presumptuous to submit a particular model for final consideration. Although the model based on aggregation in THF does offer a simple explanation for the relative order of equivalent conductance in benzene and THF solutions, it is pure speculation and must be regarded as such. The model does illustrate, however, that a more extensive characterization of the salts must be made before any one particular model is chosen over any other.

Ionicity is also demonstrated by all of the \( \text{R}_4\text{NaBu}_4 \) compounds in at least one solution (Table II), but the equivalent conductance data of the compounds are even more difficult to rationalize than the data for the alkali metal salts. With the exception of 0.1 M \( \text{Me}_4\text{NaBu}_4 \) in benzene, the equivalent conductances of the compounds in THF are greater than or equal to those in benzene at both concentrations. In THF an increase in concentration causes a decrease in equivalent conductance for all of the compounds. In benzene an increase in concentration causes a decrease in equivalent conductance for \( \text{Pr}_4\text{NaBu}_4 \) and \( \text{Et}_4\text{NaBu}_4 \), but causes an increase in equivalent conductance for \( \text{Me}_4\text{NaBu}_4 \) and \( \text{Bu}_4\text{NaBu}_4 \). A trend which is related to ion size is not obvious, even though the order of equivalent conductances is expected to be \( \text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Bu}_4\text{N}^+ \). In terms of previous conductance studies of various tetraalkylammonium salts, the low conductance values might be attributed to a large degree of
association and/or the influence of the alkyl groups of the cation and the anion on the structure of the solvent.

A large degree of aggregation is expected to occur in benzene for most electrolytes because of the solvent's low dielectric constant and its lack of any appreciable solvating ability. At the lower concentrations of the tetraalkylammonium compounds in benzene, the equivalent conductances are almost identical. Relative magnitudes cannot be relied on because of the limitation imposed by the conductance equipment. Nevertheless, all the conductance values are quite small, indicating the prevalence of ion pairs or neutral aggregates. At a 0.1 M concentration, Et₄NAlBu₄ and Pr₄NAlBu₄ indicate the opposite effect.

Generally, a tendency to associate follows as the concentration is increased. The predominant species of all the R₄NAlBu₄ compounds at the lower benzene concentration are probably contact ion pairs. As the concentration of a R₄NAlBu₄ salt is increased, ion-ion interactions increase and the small fraction of conducting species in the benzene solutions of Et₄NAlBu₄ and Pr₄NAlBu₄ are converted to contact ion pairs.

In the case of Me₄NAlBu₄, further ion-ion interaction produces a larger fraction of conducting species. The higher surface charge density of Me₄N⁺, compared to the other R₄NAlBu₄ compounds, is well illustrated by the conductance study of R₄NX (R = CH₃, ... ,C₇H₁₅, X = Cl, I) in DMSO by Arrington and Griswold. Only the Me₄N⁺ salts showed any association to ion pairs in the highly-solvating solvent.
DMSO. Larsen's study of Me₄N⁺ and Me₃NEt⁺ salts in DMSO⁸¹ supports the contention that Me₄N⁺ displays a noticeable charge density in solution.

The increase in the equivalent conductance of Bu₄NAlBu₄ in benzene with an increase in concentration is difficult to rationalize. There is no obvious trend in the concentration dependence of the equivalent conductance with respect to ion size. Perhaps the interaction between Bu₄N⁺ and AlBu₄⁻ is not a strong one, compared to the other R₄NAlBu₄ salts, and the contact ion pair is not very stable in benzene because of the "looseness" of the aggregate. The close approach of another ion pair may direct as much influence on an ion in an ion pair as the counterion will. Although there are no other data to support such comparisons, it is quite interesting to note that the behavior of Me₄NAlBu₄ and Bu₄NAlBu₄ in benzene is very similar to that of NaAlBu₄ in benzene.

The use of THF as the solvent further complicates the picture. The equivalent conductances in the 0.01 M salt solutions indicate an appreciable degree of dissociation to free ions for all but Bu₄NAlBu₄. Only Bu₄NAlBu₄ shows any equivalent conductance in the 0.1 M THF solutions. Furthermore, the decrease in equivalent conductance of Bu₄NAlBu₄ in THF with an increase in concentration is quite small.

In the case of the three smaller R₄N⁺ salts, it would appear than an increase in concentration simply enhances the ion-ion interactions to the extent that free ions are converted to contact ion pairs. A change in concentration does not seem to have much of an influence on the conducting species in Bu₄NAlBu₄ solutions, however.
Reversal of ion-ion pair equilibria is a common phenomenon with changes in salt concentration.\textsuperscript{12} The degree of association usually reaches a maximum value at some high concentration and then decreases. Explanations for this observation are sketchy. But it is known that many factors are responsible in varying degrees. As the dielectric constant of the solvent decreases, the apparent intensity of the fields surrounding the ions increases and new types of interaction products occur.\textsuperscript{12} The properties of electrolyte solutions are primarily determined by the size and structure of the ions and the dipole moment of the ion pairs in solvents of low dielectric constant. The process of dissociation of the electrolytes to ions, as well as their association to complex polyionic aggregates, is, therefore, highly sensitive to the size and structure of the ions.

Two of the major considerations which have been used in discussing the possible types of interactions involving the \( \text{R}_4\text{N}^+ \) and alkali metal tetraalkylaluminates are: (1) ion-ion interactions which cause appreciable association, and (2) ion-solvent interactions between large cationic species and solvent molecules. With regard to the first consideration, it should be stated again at the outset that opinions concerning the significance of ion-ion interactions have been severely limited to conductance work in systems of low concentration.

Buckson and Smith\textsuperscript{67} have analyzed NMR spectra of nitrobenzene solutions (5 \( \times \) 10\(^{-3}\) to 0.25 M) of \( \text{Bu}_4\text{NX} \) salts (\( X = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \) picrate). They found a larger fraction of paired ions in this system by NMR techniques than previously assessed by conductance methods. The
authors speculate that the difference is the result of the high concentrations of Bu₄NX used in their studies. Taylor and Kuntz have also used NMR techniques to study the spectra of CH₃NR₃X salts (R = CH₃, C₆H₁₃, quinuclidinium; X = picrate, Bu₄B) and concluded that all the quaternary onium salts in solvents of low dielectric constant are highly associated in the NMR concentration range. Even in propylene carbonate, a solvent of high dielectric constant and dipole moment, viscosity and conductance studies of (isoamyl)₄NB(isoamyl)₄ and (isoamyl)₄NI reveal small but significant degrees of association for each salt at concentrations greater than 1 x 10⁻³ M. These examples, and others given in this paper, illustrate that general conclusions which eliminate the possibility of high aggregation of R₄N⁺ salts must be viewed with a certain degree of skepticism.

The second consideration, ion-solvent interactions involving large ionic species, may appear to be a weak point in the development of the proposal to explain the conductance data of the R₄N⁺ salts, especially when one considers such conclusions as that of Carvajal, et al. These authors maintain that Bu(isoamyl)₃NB⁺ dissociates into free ions in both THF and DME, and that the ions are not coordinated with solvent molecules to any extent. Bhattacharyya, et al. also state that Bu₄N⁺ and (isoamyl)₃BuN⁺ ions are not solvated by THF. Szwarc claims that Bu₄N⁺ is not coordinated with THF, although he does concede that large dipole moments of ion pairs cause them to interact strongly with polar molecules, including those of polar solvents. The resulting interaction might indeed be appreciable. Hyne
observed a relatively strong interaction between Bu₄NBr and nitrobenzene in methanol and proposed a specific orientation of the Bu₄NBr with respect to nitrobenzene to explain it. Larsen went so far as to use the rare terminology for R₄N⁺-solvent systems -- solvent-separated ion pairs in D₂O and DMSO.

Singh, et al. succinctly expressed the more recent position of many ion-solvent chemists in saying that the opinion is gaining favor of actual solvation of the R₄N⁺ ions. This opinion has emerged mainly because of the discovery that these large ions cause an enhancement of the structure of surrounding water molecules. This enhancement has been a curious phenomenon that has lead to the investigation of the possible solvation of the R₄N⁺ cations by nonaqueous solvents as well as water. Singh, et al. used conductance data of some R₄N⁺ salts (R = CH₃, ..., C₇H₁₅) in N-methylacetamide to decide that R₄N⁺ ions are also structure breakers. Gopal and Rastogi pursued the study of these ions in N,N'-dimethylformamide as well as in N-methylacetamide from a viscosity point of view and concluded that the R₄N⁺ ions also behave as structure breakers in these solvents.

Perhaps one of the more informative studies has been performed by Taylor and Kuntz. Their NMR study of quaternary onium salts in solvents of low dielectric constant led them to envision two classes of associated species in solution, contact and solvent-separated ion pairs. They give two reasons for the estimated number of contact species of large cations and anions in solvents of low dielectric constant. First, they consider unfavorable steric interactions
between bulky substituents of $R_4N^+$ ions to be responsible for the prevention of close approach of the charge sites. These effects can be nonspecific or the hindrance can be localized. Secondly, and of greater pertinence to the considerations here, they suggest that larger ions are more solvated than small ions in low dielectric constant solvents. This is due to van der Waals interactions between the polarizable groups of the ions and the solvent. These interactions facilitate the solution of salts of large ions into low dielectric constant solvents in which salts of small ions are insoluble. Such ion-solvent interactions are clearly more important for larger ions and would be expected to stabilize the solvent-separated species over the contact species. Though all dissolved solute molecules are solvated in that they are surrounded by solvent molecules, there are definite differences in the relative strengths and specificities of the various possible ion-solvent interactions. It is clear that ionic charges cause the solvent to assume a much different average orientation with respect to $R_4N^+$ ions than is postulated for nonpolar solute molecules, though it is doubtful that an ion-solvent complex of fixed stoichiometry exists as a stable kinetic entity in solution. The interactions which govern ion association in solvents of low dielectric constant may be relatively weak, but ion-dipole interactions can significantly affect the state of association. Ion size and solvent coordinating ability are important factors which can determine the nature of the associated species in solution.

Gopal and Chandra studied the solubilities of $R_4N^+$ salts in $H_2O$, N-methylformamide, $N,N'$-dimethylformamide, and formamide at
different temperatures. They concurred with other findings that the large cationic salts are hydrophobic in water and lyophilic in organic solvents, solubility increasing directly with the length of the alkyl chain in organic solvents. The heats of solution data give smaller $\Delta H_{\text{soln}}$ for the larger $R_4N^+$ cations, implying a larger heat of solvation and a stronger $R_4N^+$-solvent interaction. This deduction is at variance with the majority of considerations and the authors found the data difficult to interpret since the larger the radius of the ion, the smaller the electrostatic ion-solvent interaction is assumed to be. It could be that since the $R_4N^+$ ions and the solvents are similar in structure and origin, there are strong dispersion interactions between the alkyl chains of the $R_4N^+$ ions and the solvent molecules.

Quite obviously, the recent thinking about the role of large ions in nonaqueous solvents has undergone considerable change. It may not be possible to delineate the species of the $R_4NAlBu_4$ compounds in solution, nor to pinpoint the ion-solvent interactions. It may be possible only to offer generalizations and trends which are commensurate with the available data. Explanations are necessary for experimental results of complex systems, no matter how diaphanous, if refutations and validations are to be used to narrow the gap between speculation and fact.

E. Reactivity

A brief discussion of relative reactivities of the salts is pertinent to the study of these compounds. The utility of the compounds
in conductance and spectroscopic studies directly depends on the stability of the compounds under experimental conditions.

The \( R_4NaBu_4 \) compounds are unstable in the presence of air, water, oxygen, and alcohols, as has been observed with NaAlBu\(_4\). They appear, however, to be much less reactive than NaAlBu\(_4\) in these environs. They are about as reactive toward water as NaAlBu\(_4\) is toward ethyl alcohol. Rapid decomposition yields a white powdery substance which, from all indications, is primarily \( Al_2O_3 \) and \( Al(OH)_3 \). Slow decomposition, as occurs in the dry box upon standing for several months, yields a reddish-brown color, which indicates the decomposition of the cation.

LiAlBu\(_4\) is more reactive than NaAlBu\(_4\) and compares to the reactivity of NaAlEt\(_4\). Very dry crystals of LiAlBu\(_4\) decompose and smoke when exposed to air.

All of the compounds are quite stable in the hydrocarbons and ethers that have been used in these investigations. They will adsorb most organic vapors quite readily in the dry box. Reactivity toward air is impaired greatly when the compounds are in a hydrocarbon or ether solvent. Ether solvents are more effective in retarding decomposition than hydrocarbon solvents. The exposure of hydrocarbon or ether solutions of the compounds to air will give a yellowish solution in a matter of days. The solutions turn to a darker, more orange color on standing for a longer period of time. It has been noted that AlBu\(_3\) also decomposes to a yellow product in the presence of air before it completely decomposes to a white powder.
F. Conclusions

The usefulness of the new compounds will not be fully realized until they have been studied more thoroughly with the techniques which have been applied to NaAlBu₄. The studies which have been made by this author indicate, however, the possibility of extending the preliminary investigations to complete studies, with the possibility of gaining important insights into both ion-ion and ion-solvent interactions. Supplementation of data from NaAlBu₄-solvent systems appears to be necessary in order to verify and to expand the results which have come from the studies of NaAlBu₄.

The R₄NAlBu₄ compounds offer the advantage of relatively high solubility in at least two solvents of low dielectric constant, one of which is a relatively inert hydrocarbon, so that a solvent-dependence study can hopefully be made in conjunction with NaAlBu₄. The conductance data also indicate that an ion size study can be fruitful in the extension of ion-solvent studies initiated by this research group.

The conductance data, in particular, indicate that useful information may be gained in an attempt to explain the apparently complex results which have been reported. In the discussion of the conductance data, there were probably more questions raised than answered, but there can be no doubt that if it is experimentally feasible, the pursuit of the answers to these questions should prove meaningful.
Although LiAlBu₄ does not show solubility properties which would be ideal in gathering information that can be used to directly correlate with the NaAlBu₄ studies, it does offer the possibility of giving comparative data in solvents of intermediate and high dielectric constant which may be used to gather information about the ion size effects on ion-solvent interactions.

Until future studies prove to the contrary, this author feels that the purpose of the syntheses of these compounds has been realized.

G. Suggestions for Future Studies

The tetra-n-butylaluminates have been prepared in order to offer new compounds which may be used in the investigation of ion-ion and ion-solvent interaction studies. In the attempt to characterize the compounds, the author has observed several properties of the compounds which appear to be of value in the extension of studies which have been pursued in this laboratory.

The most obvious possibility is the use of conductance work. The quaternary ammonium compounds, in particular, show unusual behavior. A concentration and temperature dependence study in benzene and several ethers of different dielectric constants might help clarify the question of the effect of the cation size and the coordinating ability of the solvent on the degree of aggregation. Perhaps a distinction between ion-ion and ion-solvent effects can be made if the cation size is of major significance, as has been suggested.
A temperature and concentration dependence study of the solubility characteristics of the $\text{R}_4\text{NAlBu}_4$ compounds might offer some insight into the two-phasing phenomenon and the formation of globular particles in solution.

Spectroscopic studies such as IR and NMR might prove useful in the study of the complexing abilities of the lithium and the quaternary ammonium salts in various coordinating agents of varying degrees of basicity. The techniques of Schaschel and Day\textsuperscript{46} and Höhn, \textit{et al.}\textsuperscript{17} could be used to explore the possibility of determining the coordination number of the various cations in a number of the mixed solvent systems.
PART II

NMR STUDY OF THE SOLVATION OF
THE SODIUM AND LITHIUM CATIONS
IV. INTRODUCTION

The application of nuclear magnetic resonance (NMR) spectroscopy to the study of electrolyte systems has recently undergone considerable growth and expansion. Studies have encompassed a variety of chemical phenomena, such as solvation properties, solvent exchange, ionization equilibria, ligand exchange rates, ion association, etc. These measurements have taken the form of chemical shifts, the appearance of new resonance lines, variations in spin-spin hyperfine coupling, and the evaluation of line widths and shapes. Although proton magnetic resonance (pmr) has been the most widely applied use of NMR, the development of improved experimental techniques has now enabled the use of other nuclei resonances. However, in spite of the fact that a wide variety of solutes and solvents have been used in the study of ions in solution, most of the results have been obtained with aqueous systems.

The value of NMR as a probe in the study of ions in solution lies in its ability to monitor the electronic environment of a nucleus. Since the resonance frequency at which a nucleus absorbs is dependent on the electron density associated with it, any alteration in the electron density subsequently causes a change in the frequency of absorption of the nucleus. An ion in solution which interacts with another ion or a solvent molecule will therefore produce a change in the electronic environment of the interacting species. If the interaction is appreciable, a significant chemical shift will be produced,
and an evaluation of the strength and the kind of chemical bond may be possible. If the bonding interaction is subject to a rapid interchange with non-bonding or other bonding interactions, however, a weighted mean of the individual resonances will be detected as a single resonance line. In this case, other techniques must be employed in an attempt to eliminate this "exchange broadening". If the interaction equilibrium is moderately temperature dependent, variation of temperature will often allow NMR to detect and evaluate the equilibrium system.

An excellent review of studies of various ions in solution has been presented by Hinton and Amis. A perusal of the article will certainly illustrate the great variety of experimental procedures which have been applied to the studies of ions in solution by NMR. The vast majority of investigations have used water either as the pure solvent or as part of a mixed solvent system. Such systems will not be discussed herein because of this research group's interest in non-aqueous systems.

The following survey of the application of NMR to non-aqueous systems is not intended to be exhaustive, but it does represent an adequate summary of the results which have been obtained and the techniques which have been employed in the gathering of information relating to electrolyte systems.

Fraenkel has presented evidence that indicates the existence of intimate (contact) ion pairs of certain anilinium salts in several nonaqueous solvents by evaluating the effect of the
accompanying anion on the ring proton lineshapes of the anilinium ion. He concludes that the chlorides, perchlorates, and trifluoracetates of all the primary anilines exist in the form of contact ion pairs in solutions of dioxane, dimethylsulfoxide (DMSO), and 1,2-dimethoxyethane (DME).

A solvation number of 5.8 was obtained for Co(II) by Luz and Meiboom with the use of pmr spectra taken at low temperatures of solutions containing 0.24 m Co(ClO₄)₂ and HClO₄ in anhydrous methanol. Separate peaks corresponding to bulk CH₃OH and bound CH₃OH were observed, and comparison of the relative peak intensities was used to determine the solvation number of the first coordination sphere of Co(II).

Buckson and Smith obtained pmr spectra of tetra-n-butylammonium chloride, bromide, iodide, perchlorate, and picrate in nitrobenzene over a salt concentration range of 0.0005 M to 0.25 M at ambient temperatures. The position of the resonance of the α-methylene protons of the cation was found to be sensitive to both concentration and the nature of the anion. The authors interpreted their results in terms of ion association and estimated the dissociation constants of the halide salts.

La Mar has observed isotropic proton resonance shifts for the paramagnetic transition metal complexes [Bu₄N][(0₃P)CoI₃] and [Bu₄N][(0₃P)NiI₃] in deuterochloroform (CDCl₃) solutions. Isotropic shifts were observed for both the phenyl protons and the Bu₄N⁺ protons. The shifts observed for the phenyl protons were interpreted as arising
from both contact and pseudocontact interactions, and the shifts observed for the Bu₄N⁺ cation protons were attributed to a pseudocontact interaction with the metal in the complex anion through partial ion pairing.

Massey, et al. have studied the coupling constants and chemical shifts of protons of the symmetrical ions BEt₄⁻, NEt₄⁺, and AsEt₄⁺ in CHCl₃ and H₂O. The spectrum of tetraethylarsenium bromide in CHCl₃ is a typical A₃B₂ spectrum, but the peaks are broadened significantly in water. The authors conclude that the quadrupole relaxation is faster in CHCl₃ than in water because of the existence of ion pairs in CHCl₃ which induce a rapid quadrupole relaxation. The absence of any change in the spectra of NEt₄⁺ in going from water to CHCl₃ as the solvent was attributed to the small electronic polarizability and nuclear quadrupole moment of the nitrogen atom.

In a subsequent paper, Massey, et al. extended their study to the symmetrical ions BMe₄⁻, AlMe₄⁻, AlEt₄⁻, SbMe₄⁺, and PEnMe₄⁻⁺. It was found that the antimony salts show the same behavior as the arsenic salts in the previous study. The authors emphasize the importance of considering ion-solvent interactions as well as ion-ion interactions in the variation of pmr line widths under various experimental conditions.

Randall and Shaw continued the study of symmetrical ions of group III and group IV elements with NMe₄⁻⁻ and Et₄As⁺. The dependency of the chemical shift of the NEt₄⁺ protons on the counterion in CHCl₃ solutions is rationalized in terms of ion pair formation.
in solvents of low dielectric constant. It was noted that for each of
the elements in group V, the chemical shift is greater in CHCl₃ than
in water. Furthermore, the methylene protons appear to be more af­
fected by solvent and anion variations than the methyl protons. The
authors contend that ion pair formation which polarizes the ionic
center is the most reasonable explanation.

The solvation number of Co(II) in N,N’-dimethylformamide
(DMF) solutions has been determined by Matwiyoff, utilizing NMR
spectra of solutions of Co(ClO₄)₂ in DMF. Below -5° the NMR absorp­
tion frequencies of the free and the solvated solvent molecules are
separated, and from the relative intensities of these peaks, the pri­
mary solvation number of six was obtained. These results agree closely
with those obtained for Co(II) in CH₃OH.¹

Chuck and Randall examined the NMR spectra of 1,4-
diethylpyridinium halides in CDCl₃ and D₂O and found that certain
proton shifts are dependent on both the concentration and the anion
in D₂O. The shifts in ClCl₃ are clearly anion-dependent but do not
appear to be susceptible to concentration changes. The 1-methylene
and the 2,6-ring protons are most influenced by the medium effects,
and the authors choose to interpret the phenomena in terms of ion-ion
and ion-solvent interactions, assuming that the extent of ion pairing
is high at the concentrations they used in CDCl₃.

Fraenkel and Kim studied the spectra of several anilinium
salts in both polar and nonpolar solvents. They found that the NMR
spectra of primary anilinium salts in nonpolar solvents vary with the
nature of the accompanying anion, and the \( \text{NH}_3^+ \) substituent has a small deshielding effect on the ring hydrogens. Their conclusion is that intimate ion pairs are formed in the nonpolar solvents in which centers of charge are "juxtaposed". The addition of methanol to CDCl\(_3\) solutions of the salts indicates that hydrogen bonding of methanol to the NH hydrogens takes precedence over the interaction between the ion pairs to the extent that the counterions are displaced from the ammonium groups, and the resultant chemical shifts are identical to those of the salts in pure methanol.

Thomas and Reynolds\(^{97}\) found that the NMR absorption spectrum of the solvent DMSO gives two distinct signals in solutions of Al(ClO\(_4\))\(_3\) in DMSO. These signals were taken to be the free and the coordinated solvent molecule absorption peaks. A solvation number of six was determined for Al(III) directly from a ratio of the line intensities of the two distinct solvent peaks.

Maciel, et al.\(^{98}\) have studied the nature of lithium ion-solvent interactions by inspecting \(^7\text{Li}\) chemical shifts in a variety of solvents. The \(^7\text{Li}\) chemical shifts of dilute solutions of LiBr and LiClO\(_4\) were determined with respect to 23\% aqueous LiBr. No definitive ion-solvent interaction was detected, with the possible exception of the effect of solvent anisotropy on the chemical shift, as determined by the geometry of the interaction between the lithium ion and the solvent molecules. The authors state that polar, dispersion, and coordination effects on the local shielding may also be of importance.
Movius and Matwiyoff\textsuperscript{99} found a value of $6.0^{\pm}0.5$ for the solvation number of Al(III) in DMF solutions, which agrees with the solvation number of Al(III) in DMSO.\textsuperscript{97} Both proton and $^{27}$Al NMR were recorded for Al(ClO$_4$)$_3$·6DMF in DMF.

Swift and Lo\textsuperscript{100} determined the primary solvation number of Mg(II) in anhydrous liquid ammonia. The solvation number, $5.0^{\pm}0.2$, was obtained for Mg(NO$_3$)$_2$ and Mg(ClO$_4$)$_2$ solutions in NH$_3$.

Matwiyoff and Movius\textsuperscript{101} found that below 0\degree, DMF signals in the first coordination sphere of Be(II) can be seen. They determined the solvation number of Be(II) in DMF and found it to be four.

Nakamura and Meiboom\textsuperscript{102} have studied the NMR spectrum of solutions of Mg(II) in anhydrous CH$_3$OH and have determined the solvation number and exchange rate. From the broadening of the hydroxyl peaks of the free and the bound CH$_3$OH in solutions of Mg(ClO$_4$)$_2$ in CH$_3$OH, the solvation number was found to be six. The attempt to use lithium, barium, and calcium salts was unsuccessful.

Schaschel and Day,\textsuperscript{46} in their study of the solvation of the sodium ion, found experimental evidence which indicates the existence of a stable 1:1 complex and a fairly stable 4:1 complex of THF:Na$^+$ in THF. The solvent system is unique in that the bulk solvent, cyclohexane, does not interact appreciably with the salt, NaAlBu$_4$, and, as a consequence, the specific interaction between the added coordinating solvent, THF, and the sodium cation was detected without interference from the bulk solvent.
The pmr spectra have been analyzed for deuterochloroform solutions of the complexes \([\text{AsO}_2]^+\text{[PMe}_3\text{]}\), where \(M = \text{Co, Ni}\). The authors of the article were unable to unscramble the spectrum for the nickel complex, but they did observe distinct cation phenyl peaks for the cobalt complex. From calculated values based upon the postulated ion pair model with specific orientation to the anion, they were able to estimate interionic distances in solution with the use of chemical shifts and line-broadening methods. The authors admit, however, that the possibility of the existence of ion clusters in a solvent with such a low dielectric constant as CDCl\(_3\) and at high salt concentrations is worthy of consideration.

Nicholls and Szwarc\(^{104}\) found that the presence of LiClO\(_4\), AgBF\(_4\), LiBO\(_4\), and NaBO\(_4\) in THF, 2-methyltetrahydrofuran (MeTHF), tetrahydropyran, and dioxane shifts the characteristic NMR lines of the solvents. With the exception of MeTHF, the presence of the salts does not cause splitting or broadening of the solvent peaks. The authors interpret the data as indicating a rapid exchange between the solvation shell and bulk solvent. The authors evaluate their data in terms of ion pairs in solution which allow the cations of the ion pairs to coordinate with the oxygen atoms of the ether solvents.

Chan and Smid\(^{105}\) have investigated the solvating power of a series of polyglycol ethers, of the formula CH\(_3\)O(CH\(_2\)CH\(_2\)O\(_x\)CH\(_3\), with respect to alkali cations. Their research group had previously used ultraviolet and visible spectra of solutions of carbanions and radical anions as a means of observing contact and solvent-separated
ion pairs. This particular endeavor utilized NMR to study the specific complexation of the alkali ions by the polyglycol ethers. THF solutions of the salts show an upfield shift of the THF peaks compared to those of pure THF, and the addition of polyglycol ethers to the THF solutions causes the THF proton signals to assume positions very close to those of pure THF. The authors interpret this phenomenon as due to the replacement of the THF molecules around the alkali cation by the more strongly coordinating polyglycol ether molecule.

With the use of chemical shifts and $^{27}$Al-$^1$H couplings, Oliver and Wilkie have presented data to indicate that lithium tetramethylaluminate (LiAlMe$_4$) exists in solution as either a contact ion pair or a solvent-separated ion pair, depending on the solvent. They conclude that the salt exists in the form of contact ion pairs in diethyl ether and as solvent-separated ion pairs in DME.

Matwiyoff and Taube succeeded in the direct determination of the solvation number of Mg(II) in water, aqueous acetone, and methanolic acetone solutions. The authors used low resolution NMR spectra in the OH region at -25 to -80°. They conclude that acetone is a weak donor molecule, whereas methanol coordinates with the Mg(II) to form a complex Mg(CH$_3$OH)$_6^{+2}$ in methanolic solutions of Mg(ClO$_4$)$_2$.

Intending to obtain a detailed description of the ion-solvent interactions in nonaqueous solutions of sodium iodide using the $^{23}$Na nucleus as a probe, Bloor and Kidd recorded the $^{23}$Na chemical shifts of solutions of sodium iodide in various oxygen and nitrogen donor organic solvents. The range of chemical shifts is
related to changes in the paramagnetic term of the general nuclear screening equation, and a correlation between the paramagnetic term and the Lewis basicity of the solvents can be made.

Maxey and Popov, in an attempt to follow the procedure of Day and Schaschel, studied the solvation of lithium, ammonium, and sodium salts by DMSO. Contending that the hydrogen-bonding ability of 1-pentanol would not appreciably affect the coordinating ability of DMSO, the authors used 1-pentanol as the bulk solvent and added quantitative amounts of DMSO to the solutions. Both LiClO₄ and LiI data indicate the formation of a 2:1 complex of DMSO:Li⁺. NH₄SCN also gives a 2:1 complex, but the NH₄⁺-DMSO interaction appears to be weaker than the Li⁺-DMSO interaction. The use of NaI did not give clear results.

Fanning and Drago obtained the NMR spectra of [(C₀H₁₇)₃NCH₃]₃Fe(CN)₆ and [(C₆H₁₇)₃NCH₃]₃Co(CN)₆ in a variety of solvents in order to examine the influence of solvent on ion association. The proton signals due to the N-methyl and N-methylene protons of the octyl groups were identified and the shifts of these peaks were determined. The N-methyl chemical shifts of approximately 0.1 M solutions of the salts were plotted against the dielectric constants of the respective solvents and an apparent linear relationship was obtained. It was proposed that large, bulky clusters of ions are formed in the solutions so that even the hydrogen-bonding solvents obey the linear relationship because specific hydrogen-bonding is presumably sterically hindered. A concentration study showed that the N-methyl
chemical shift in solvents of high dielectric constant increases slowly as the solute concentration is increased, while for solvents of moderate dielectric constant, the chemical shift increases markedly at low concentration and remains essentially constant thereafter. In solvents of low dielectric constant, the chemical shift decreases slightly as the concentration is increased. The data are rationalized in terms of degrees of ion association.

Having noted that benzene appears to be a unique solvent in their studies of ion-solvent interactions, Hammonds, et al. used the NMR technique of Schaschel and Day to study the possibility of complexation of the sodium cation by benzene and toluene. NaAlBu₄ was used as the source of the cation, and cyclohexane was used as the bulk solvent. Chemical shifts of the benzene and the toluene proton signals were recorded as a function of the mole ratio, base:NaAlBu₄. The absence of any inflection points in the mole ratio study indicates that the small variation in chemical shifts is due to concentration effects and not to any specific complexation of the sodium cation with benzene or toluene.

An excellent presentation by Gore and Gutowsky describes the dissociation of lithium- and sodium tetramethylaluminate (LiAlMe₄ and NaAlMe₄, respectively) in solution. The authors have used proton and ²⁷Al NMR to study the salts in diethyl ether, THF, and DME solutions. The presence or absence of pmr splittings in the two salt solutions are explained in terms of an equilibrium between an intimate ion pair and a solvent-separated ion pair. In the solvent-separated ion pair, the
$^{27}\text{Al}$ nucleus will experience an electric field which has tetrahedral symmetry, and, as a result, the electric field gradient at the $^{27}\text{Al}$ nucleus is very small. Consequently, the spin-lattice relaxation rate is small enough that the $^{17}\text{Al}-^1\text{H}$ can be observed. But in the case of an intimate ion pair, the tetrahedral symmetry is destroyed by the presence of the cation. The $^{27}\text{Al}$ nucleus will, therefore, experience a large electric field gradient which will induce a large relaxation rate and average out the coupling between the proton and the $^{27}\text{Al}$ nucleus. The authors have determined the $^{27}\text{Al}$ spin-lattice relaxation rate from the proton line shapes for the methyl groups of LiAlMe$_4$ and NaAlMe$_4$ in the various solvents and have interpreted the results in terms of an equilibrium between the two different kinds of ion pairs, contact and solvent-separated. Temperature and concentration studies were employed to ascertain the existence of contact ion pairs for both LiAlMe$_4$ and NaAlMe$_4$ in diethyl ether solution, the existence of solvent-separated ion pairs for both salts in DME, and the existence of both types of ion pairs for both salts in THF. Estimates have also been made for the relative amounts of the two ion pair species and for some of the thermodynamic functions describing the proposed equilibrium.

The solvation of lithium and sodium ions in DMSO and 1-methyl-2-pyrrolidone (1M2Py) has been studied by Wuepper and Popov. They used a mole ratio study of the NaAlBu$_4$-DMSO and NaAlBu$_4$-1M2Py systems in 1,4-dioxane solutions. The authors consider 1,4-dioxane
to be an inert solvent, one which does not interact with the solute
to an appreciable degree when compared to the solvating ability of
DMSO or 1M2Py. The solvation numbers of Na⁺ in DMSO and in 1M2Py
were found to be six and four, respectively. The solvation number of
Li⁺ was determined by far-infrared spectroscopic techniques.

Ross and Oliver¹¹² have investigated the pmr spectra of
LiAlMe₄ in different solvents as a function of concentration and
temperature. From an evaluation of the results they have suggested
that in DME, LiAlMe₄ is highly dissociated into solvent-separated ion
pairs, while in nonpolar solvents, the salt exists primarily as con­
tact ion pairs. THF was shown to be intermediate in its solvating
power to the extent that a solvent separated-contact ion pair equili­
brum is established. The pmr spectrum in THF is highly dependent on
both concentration and temperature. The authors propose a complex
equilibrium of solvated contact ion pairs and solvated solvent­
separated ion pairs:

\[
\text{Solvent} \cdot \text{Li}^+\text{AlMe}_4^- \rightleftharpoons \text{Li(solvent)}^+_n\text{AlMe}_4^- \quad (5)
\]

with the equilibrium constant determined by the basicity of the solvent.

Frankel, et al.¹¹³ have employed two different techniques
for the investigation of the degree of preferential solvation in mixed
solvents. The one depends on the effect of the solvent on the NMR
chemical shift of the solute, while the other utilizes the effect of
a paramagnetic solute on the transverse relaxation time of the solvent
nuclei. The solvation of trisacetylaceton complexes of Co(III) and
Cr(III) in several solvent systems have been investigated and a thermodynamic model of preferential solvation has been devised to interpret the results, assuming that cation-solvent species interact to a significant degree and are responsible for both of the effects that the authors evaluate.

The foregoing review of selected studies of ion-ion and ion-solvent interactions should well illustrate the potential usefulness of nuclear magnetic resonance in the detection and the evaluation of these interactions. It is also seen, however, that not only must many of the experimental techniques be refined, but more amenable systems must be found to take advantage of the elaborate experimental techniques. It may also be emphasized that many of the conclusions offered by the authors of the previous articles were based on assumptions which were not thoroughly substantiated. Hence, it would appear that a great number of investigations must be undertaken with a compilation of significant data before any realistic conclusions may be drawn.

To date, this research group has expended most of its efforts in the investigation of ion-solvent interactions, utilizing NaAlBu₄ as the source of the sodium cation and cyclohexane as the inert solvent. Conductance studies have offered some information with respect to specific ion-solvent interactions and dielectric constant effects. Infrared studies have been interpreted in terms of ion-solvent interactions, and the degree and stability of aggregates of NaAlBu₄ at various concentrations have been discussed in terms of ion pair dipole-
ion pair dipole interactions.\textsuperscript{72} NMR data have been used to postulate the existence of complexes with the sodium cation.\textsuperscript{46} Unfortunately, the formation of two phase systems has all but terminated the further pursuit of the experimental techniques which have been developed so far for the system under study.

Cognizant of the inherent disadvantages of studying solvation in pure solvents of strong coordinating ability, this author has pursued a study of the solvation of alkali metal cations (Na\textsuperscript{+} and Li\textsuperscript{+}) in pure etherate solvents. Mole ratio studies of ether:cation in benzene solutions have also been made.

Ion-solvent interactions have been previously investigated in this laboratory,\textsuperscript{46,68,72} but the distinction between the kinds of ion pairs has not been made. Other studies have distinguished between the different kinds of ion pairs in solution, but have not evaluated the specific nature of the ion-solvent interactions.\textsuperscript{20,106,111,112} It is hoped that the studies herein bridge this gap.
V. EXPERIMENTAL PROCEDURES

A. Solvents and Reagents

The complete description of the preparation of the alkali metal tetraalkylaluminates and the purification of the solvents are given in Part I of this Dissertation. The handling of samples and the general procedure for operating in an inert atmosphere have also been discussed previously.

B. Preparation of Samples

Concentrations of stock solutions were determined by dissolving a weighed amount of solute in a weighed amount of solvent. The concentrations of the stock solutions were varied by the appropriate addition of weighed amounts of solvent. Transfers were made from the stock solutions to the NMR tubes with a syringe. The stock solutions were reweighed after each transfer from the stock solution to the NMR tube to determine the total loss of each constituent of the solution. From the known per cent weight composition of the original solution, the total weight of salt and solvent remaining were calculated. After the addition of a weighed amount of solvent, the new molality of the stock solution was calculated. In the case of the mole ratio studies in which an appropriate amount of ether was added to a salt-benzene admixture, the same general procedure was used to determine the total weight of ether remaining in the stock solution. A weighed amount of ether was then added to the remaining solution, and the new mole ratio of ether:salt was determined. For
salt concentrations below 0.1 molal, each solution was prepared individually to overcome potentially large errors in the dilution procedure. It is estimated that in most instances less than 5% error in the calculated molalities and less than 5% error in the calculated mole ratios resulted from the procedure of preparing sample solutions.

For those samples in which TMS was physically added as the internal standard, an appropriate amount of TMS was added directly to the stock ether solvent in the dry box before the sample solutions were prepared. The ether solvents were then stored in a cooling bath inside the dry box to prevent loss of the TMS by evaporation.

The NMR tubes were sealed with high pressure caps in the dry box and the samples were generally run within a few hours of their egress from the dry box. Samples outside the dry box which were not in use were stored under a nitrogen atmosphere in a desiccator.

The general procedure for washing glassware with ethanol, acetone, water, and dilute HCl was used to clean the NMR tubes. Cleaning solution (p. 20) was allowed to stand in the tubes for a minimum of two hours before they were rinsed with water for half an hour by inserting small diameter glass tubing into the NMR tubes and flushing with water. The NMR tubes were then rinsed with acetone and dried with dry nitrogen gas.

C. NMR Data

The pmr spectra were recorded on a Varian A-60A spectrometer, operating at 60 MHz/sec, or a Varian HA-100 spectrometer,
operating at 100 MHz/sec. All ambient temperature work was performed on the A-60A spectrometer. The concentration and temperature dependence study was performed on the HA-100 spectrometer which was equipped with a Varian V-4343 variable temperature unit.

All chemical shifts were taken with respect to TMS as the internal standard. In the case of the HA-100 spectrometer, the lock was set on the α-methylene protons of THF and their position from TMS was determined instrumentally. The TMS constituted less than 0.1% by weight in any given sample used in the concentration and temperature dependence study. The chemical shifts of samples which did not contain TMS were determined by comparison with duplicate samples containing TMS.

The limit of the low temperature measurements was imposed by the high viscosity of the concentrated solutions. Measurements were taken until it was obvious that loss of resolution was due to high viscosity effects rather than an alteration in any chemical process. The temperature of the samples was generally varied in increments of approximately 20°. At least ten minutes was allowed to elapse between temperature readings to allow time for the thermocouple to equilibrate and for the sample to attain the recorded temperature. Unless a particular sample warranted closer inspection by the display of obvious changes in line shapes and/or splittings, temperature increments were not reduced. Smaller temperature increments at the higher temperatures (> 50°) were used to safely approach the boiling points of the sample solutions.
The deviations in chemical shifts of the solvent and the solute protons caused by a variation in salt concentration were determined for each temperature. The deviations were taken to be $\Delta(\text{ppm}) = \Delta(\text{solution}) - \Delta(\text{solvent})$. The sharpest and most prominent line of a multiplet was used in the determination of the chemical shift for a particular set of protons.

A standard methanol sample was used to calibrate the temperature readings from $+40^\circ$ to $-70^\circ$. A standard ethylene glycol sample was used to calibrate the $+40^\circ$ to $+90^\circ$ temperature range.
VI. RESULTS AND DISCUSSION

A. $^{27}$Al-$^1$H Coupling

The pnm spectra of various ether solutions of NaAlEt$_4$ have been analyzed. The ability of the AlEt$_4^-$ anion to retain a rather high degree of symmetry in pure ether solutions gives rise to $^{27}$Al-$^1$H couplings which can be seen instrumentally. In mixed solvent systems in which one component is an ether, the presence or absence of the $^{27}$Al-$^1$H splittings is seen to be related to the ratio of the ether to NaAlEt$_4$. These observations have been interpreted in terms of an equilibrium process between contact and solvent-separated ion pairs.

The use of NaAlEt$_4$ as a probe for the detection of contact and solvent-separated ion pairs is based on the correlation between the extent of $^{27}$Al-$^1$H coupling and the required symmetry of the AlEt$_4^-$ anion to give such coupling. Most of the elements of group III possess nuclear spin quantum numbers greater than 1/2; consequently, most of these elements do not normally show splitting in their NMR spectra because of electric quadrupole relaxation effects.$^{1,14}$ In an environment which produces a majority of solvent-separated ion pairs in solution, however, the AlEt$_4^-$ anion assumes, on the average, tetrahedral symmetry.$^*$ Under these conditions, both the electric field gradient at the $^{27}$Al nucleus and the spin-lattice relaxation rate of the $^{27}$Al nucleus are small.$^{1,11}$ Consequently, symmetry is responsible for a spin-relaxation process that is small enough for the $^{27}$Al-$^1$H coupling

*See Appendix.
to be observed, and the splittings are clear. It is reasonably assumed
that the solvent molecules do not offer any interaction with the AlEt₄⁻
anion to the extent of destroying the symmetry of the anion.

In the case of contact ion pairs, the close proximity of the
sodium cation to the anion destroys the symmetry of the anion and ef­
facts a large field gradient at the ²⁷Al nucleus. The spin-lattice
relaxation rate is thereby increased, and the ²⁷Al-¹H coupling is ave­
raged out, yielding a broadened triplet and quartet. If the exchange
rate of the equilibrium between contact and solvent-separated ion
pairs is relatively rapid, the extent of broadening should reflect
the average number of contact ion pairs in solution.

Other authors have observed ²⁷Al-¹H splitting for NaAlMe₄
and LiAlMe₄ and have also interpreted their results in terms of an
equilibrium process between contact and solvent-separated ion
pairs.¹⁰⁸,¹¹¹,¹¹² Comparison of the spectrum of LiAlMe₄ in pure DME
with that of NaAlEt₄ in pure DME, however, reveals that the resolution
of the splittings of NaAlEt₄ is noticeably greater. The better reso­
lution and the extra long-range coupling appear to give NaAlEt₄ an
advantage over the tetramethyaluminates in the evaluation of ion-
solvent interaction studies. The NMR spectra of LiAlEt₄ have been
investigated, but no mention of observed ²⁷Al-¹H coupling is given.³³,¹¹⁵

In Figure 7, typical spectra of NaAlEt₄ in DME, THF, and
diethyl ether are presented. The spectra presented here were obtained
on the 60 MHz spectrometer. As a check, the spectra were also obtained
FIGURE 7

60 MHz Spectra of NaAlEt₄, 0.7 m Solutions,

500 Hz Sweep Width, in (a) DME, (b) THF,
and (c) Diethyl Ether
on the 100 MHz spectrometer with no observed variation in line shape or resolution.

It seems clear from the spectra in Figure 7 that each solution contains a common salt in very different environments. The spectrum of NaAlEt$_4$ in DME clearly shows well-resolved splittings. If an equilibrium between contact and solvent-separated ion pair species, such as

NaAlEt$_4$·$^3$ Solvent $\cong$ Na$^{+}$·4 Solvent∥AlEt$_4^-$

is assumed, it would appear that the predominant species in DME is the solvent-separated ion pair. On the other hand, there is a distinct loss in resolution of the AlEt$_4^-$ splittings in THF. It would seem reasonable, in light of other similar studies,$^{106,111,112}$ to attribute this difference in spectral resolution to a larger fraction of contact ion pairs in THF. The total loss of splitting in the spectrum of NaAlEt$_4$ in diethyl ether shows that the majority of species in this solvent are contact ion pairs. The $^{27}$Al-$^1$H coupling does, however, still broaden the methylene proton signals such that the quartet is not clear. This implies that there are still some solvent-separated ion pairs even in diethyl ether. As the ability of the solvent to coordinate the sodium cation increases, the fraction of solvent-separated ion pairs correspondingly increases, and this is reflected in the resolution of the $^{27}$Al-$^1$H splittings.

Similar to the method of Schaschel and Day,$^{46}$ various ratios of DME and THF were quantitatively added to weighed amounts of NaAlEt$_4$
and benzene. NaAlEt₄ is insoluble in benzene at ambient temperatures, but at a 1:1 mole ratio of ether:NaAlEt₄, complete dissolution of the salt occurs.

Figure 8 compares the spectra of the benzene solutions of NaAlEt₄ with varying ratios of DME:NaAlEt₄. Unfortunately, at a 2:1 mole ratio of DME:NaAlEt₄, two-phasing occurs and does not disappear until a 40:1 mole ratio is reached. At the 1:1 mole ratio, the resolved $^{27}$Al-$^1$H coupling is completely gone, and a broadened triplet and quartet are visibly clear. This is the expected behavior for a solution containing contact ion pairs. In the case of DME, it seems reasonable that the contact ion pair species would most likely be:

\[
\begin{align*}
\text{NaAlEt}_4
\end{align*}
\]

At higher mole ratios, up to 1.9:1, a gradual broadening of the triplet and the quartet can be seen, which results from the gradual addition of the second DME molecule to the sodium cation to give both contact and solvent-separated ion pairs in solution:

\[
\begin{align*}
\text{NaAlEt}_4 + \text{DME} & = \text{Na}^+ + \text{AlEt}_4^- \\
\end{align*}
\]  

At the 40:1 mole ratio of DME:NaAlEt₄, the $^{27}$Al-$^1$H splitting becomes clear, indicating the preponderance of solvent-separated ion pairs in solution.

The same type of mole ratio study was performed with the NaAlEt₄-THF-benzene system, and the same trend was observed.
FIGURE 8

60 MHz Spectra of NaAlEt₄, 0.7 m Benzene Solutions, 500 Hz Sweep Width, at Various Ratios of DME:NaAlEt₄: (a) 1:1, (b) 1.3:1, (c) 1.6:1, (d) 1.9:1, and (e) 4.0:1.
two-phase system does not occur in THF; thus, mole ratios beyond 2:1 can be observed. Unfortunately, the methyl proton signals of AlEt$_4^-$ are obscured by the $\beta$-proton signals of THF. However, from a mole ratio of 1:1 up to a ratio of 2:1, a broadened quartet is clearly visible. Beyond a 2:1 mole ratio the quartet becomes so broadened that even the proton splittings are no longer distinct. As in the case of the NaAlEt$_4$-DME-benzene system, a contact ion pair at a 1:1 mole ratio of the THF:NaAlEt$_4$ is indicated. Above a 1:1 mole ratio the acquisition of the second THF molecule frees the anion and the $^{27}$Al-1H splitting contributes to the averaged coupling. The major difference between the two different ether systems becomes apparent at the 1:1 mole ratio of THF:NaAlEt$_4$. Here the $^{27}$Al-1H splitting becomes visible, but the resolution is noticeably less than for the comparable DME:NaAlEt$_4$ ratio, as is the case in the pure solvents. Again, the fact is illustrated that the coordination between DME and the sodium cation is significantly greater than between THF and the sodium cation.

A mole ratio study of diethyl ether:NaAlEt$_4$ was less revealing because of the almost total lack of change in the spectra as various mole ratios of diethyl ether were added to NaAlEt$_4$. This would indicate a poorer coordinating ability of diethyl ether toward the Na$^+$ cation. The addition of increasingly larger ratios of diethyl ether do not seem to have a strong influence on the equilibrium between contact and solvent-separated ion pairs in diethyl ether. Diethyl ether and THF solutions of NaAlEt$_4$ were diluted with DME to
further illustrate the greater coordinating ability of DME. The $^{27}\text{Al} - ^1\text{H}$ splittings become more apparent in both diethyl ether and THF as a greater amount of DME is added to each solution.

From the previous results of the mole ratio study, the speculation that the sodium cation does indeed form stable 1:1 species with even weak coordinating agents appears to be substantiated by this work. Four-coordination of the Na$^+$ cation in the solvent-separated ion pair has been considered, and, by this model, one can account for the sharp difference in the spectra and the ability of the solvents to permit or prevent quadrupolar induced relaxation.

An attempt to conduct a similar study of the NaAlEt$_4$-ether-cyclohexane systems failed. At a mole ratio of 1:1, two-phasing occurs at ambient temperatures for all three aforementioned ethers.

B. Concentration and Temperature Dependence Study

The proton chemical shifts of both solute and solvent were inspected as a function of concentration and temperature. The study consisted of THF solutions of NaAlEt$_4$, NaAlBu$_4$, and LiAlBu$_4$. The 100 MHz spectrometer was locked on the $\alpha$-methylene protons of THF and the chemical shift with respect to TMS was determined instrumentally.

Tables III, IV, and V list the chemical shifts of both THF and the respective salts at various salt concentrations as a function of temperature. Nichols and Szwarc$^{104}$ detected a slight variation in the chemical shifts of both the $\alpha$- and $\beta$-methylene protons of pure
## TABLE III
PROTON CHEMICAL SHIFTS (PPM) OF THF AND NaAlEt₄ AS A
FUNCTION OF TEMPERATURE AND SALT CONCENTRATION

<table>
<thead>
<tr>
<th>Conc. (molality)</th>
<th>Temp.</th>
<th>aTHF</th>
<th>βTHF</th>
<th>CH₃</th>
<th>CH₂</th>
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<td>1.17</td>
<td>93</td>
<td>3.68</td>
<td>1.84</td>
<td>0.97</td>
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</tr>
<tr>
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<td>88</td>
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<td>1.84</td>
<td>0.97</td>
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<tr>
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<td>1.84</td>
<td>0.96</td>
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<td>3.66</td>
<td>1.82</td>
<td>0.95</td>
<td>-0.54</td>
</tr>
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<td>Conc. (molality)</td>
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<td>$\beta$THF$^b$</td>
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<td>CH$_2$</td>
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<td>----------------</td>
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a. $\alpha$THF = $\alpha$ protons of THF.
b. $\beta$THF = $\beta$ protons of THF.
TABLE IV

PROTON CHEMICAL SHIFTS (PPM) OF THF AND NaAlBu₄ AS A FUNCTION OF TEMPERATURE AND SALT CONCENTRATION

<table>
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<th>Conc. (molality)</th>
<th>Temp.</th>
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<th>βTHF&lt;sup&gt;b&lt;/sup&gt;</th>
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<th>CH₂CH₂&lt;sup&gt;c&lt;/sup&gt;</th>
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TABLE IV (Cont.)

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<th>CH$_2$CH$_2$</th>
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a. $\alpha$THF = $\alpha$ protons of THF.
b. $\beta$THF = $\beta$ protons of THF.
c. $\beta$- and $\gamma$-methylene protons of AlBu$_4^-$ are grouped together.
d. $\alpha$CH$_2$ = $\alpha$ protons of AlBu$_4^-$.

* Prepared separately, rather than by dilution from a more concentrated stock solution.
### TABLE V

PROTON CHEMICAL SHIFTS (PPM) OF THF AND LiAlBu\(_4\) AS A FUNCTION OF TEMPERATURE AND SALT CONCENTRATION

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<td>Conc. (molality)</td>
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a. $\alpha$THF = $\alpha$ protons of THF.
b. $\beta$THF = $\beta$ protons of THF.
c. $\theta$- and $\gamma$-methylene protons of AlBu$_4^-$ are grouped together.
d. $\alpha$CH$_2$ = $\alpha$ protons of AlBu$_4^-$. 
THF at different temperatures in their experimental attempt to show that there is a slight but significant variation in the chemical shifts of the solvent protons as the temperature of a salt solution is lowered. The constancy of the chemical shifts of the α- and β-methylene protons of THF for NaAlEt₄, NaAlBu₄, and LiAlBu₄ solutions does not merit a similar analysis. For a given concentration of each of the three salts, the variation of temperature does not alter the chemical shifts of the THF protons to any significant extent.

Inspection of Tables III, IV, and V does reveal, however, that there is a significant variation in the chemical shift of the THF protons as the salt concentration is varied. Since the addition of 10% of an inert solvent such as cyclopentane causes no shift in the absorption lines of THF, it appears that the variation in the chemical shift of THF with a change in salt concentration can be related to the coordination between the THF molecules and the sodium and the lithium cations. The lack of broadening of absorption lines and the lack of additional splitting with a variation in temperature and concentration indicates a rapid exchange of solvent molecules between the solvation shell and the bulk solvent under the conditions studied.

In Figure 9, the chemical shifts of the THF protons are plotted against the concentration of the three salt solutions. In all three cases, a downfield shift of the absorption lines of THF is observed. The linearity of the relationship again indicates a rapid exchange between the coordinated and the bulk solvent molecules, and also supports the assumption that only simple ion pairs, contact and
FIGURE 13

Chemical Shifts of THF Protons vs. Concentration of NaAlEt₄, NaAlBu₄, and LiAlBu₄ in THF, 60 MHz Spectra, 500 Hz Sweep Width. (a) refers to the α protons of THF and (b) refers to the β protons of THF.
solvent-separated, exist in this concentration range. The larger magnitude of the influence of the lithium cation is reasonable; for most studies have affirmed the greater tenacity of the lithium ion toward solvent molecules. The protons of THF are deshielded as a consequence of the coordination, and the presence of NaAlEt₄, NaAlBu₄, and LiAlBu₄ leads to a downfield shift of the THF protons. As the salt concentration is increased, there is a corresponding increase in chemical shift because of the larger average number of coordinated THF molecules. The effect does not seem to be temperature dependent insofar as the chemical shifts of the THF protons are concerned, indicating no significant influence of temperature on the degree of solvation over this concentration range.

As Table IV indicates, there is a lower limit in concentration which can be used to study this effect. The last four concentrations show no variation in the chemical shifts of the THF protons.

It is observed that for a given salt concentration, the influence of the temperature on the equilibrium between contact and solvent-separated ion pairs is reflected in the chemical shifts of the anion protons of each of the three salts. With the exception of the methyl protons of the AlBu₄⁻ anion, a decrease in temperature is accompanied by a decrease in chemical shift. This would indicate that as the temperature of a given salt solution is lowered, an increase in solvent-separated ion pairs results. This is based on the argument that an increase in the concentration of solvent-separated ion pairs increases the average shielding of the anion protons.
These results are in agreement with the findings of Hogen-Esch and Smid\textsuperscript{20} in their study of fluorenyllithium. Evidently, the methyl protons of AlBu\textsubscript{4} are too far removed from the influence of the alteration in shielding to be affected. This temperature dependence is not shown by the THF protons for a given concentration. This may be due, simply, to the large excess of noncoordinating THF molecules; the temperature dependence is probably averaged out.

Although the concentration and temperature dependence study in THF does not reveal as much information about the tetra-n-butylaluminate salts as was hoped, NaAlEt\textsubscript{4} does show a small, but definite, spectral dependence on both temperature and concentration. Figure 10 shows the change in line shape with a variation in temperature, and Figure 11 shows the change in line shape with a variation in salt concentration. Coalescence was never effected, however, as a result of varying both temperature and concentration. This indicates, once again, that the exchange rate for the equilibrium process is too rapid to be resolved by NMR techniques.

Gore and Gutowsky also studied the temperature and concentration dependence of NaAlMe\textsubscript{4} in THF.\textsuperscript{111} They noted that the spectra of NaAlMe\textsubscript{4} in THF exhibits only small changes with temperature and concentration, with a broad spectrum of about 10 hertz. The authors did observe a definite, though small, dependence of line shape on temperature, and concluded that the relative concentration of solvent-separated ion pairs is much smaller for NaAlMe\textsubscript{4} in THF than LiAlMe\textsubscript{4} in THF. This conclusion is consistent with the results reported herein.
FIGURE 10

Temperature Dependence of NaAlEt₄ Line Shapes, 60 MHz Spectra,

500 Hz Sweep Width at 0.69 m Concentration
FIGURE 11

Concentration Dependence of NaAlEt₄ Line Shapes,

60 MHz Spectra, 500 Hz Sweep Width at 26°C.
The results for NaAlEt₄ in THF are somewhat different from those of Gore and Gutowsky and Ross and Oliver in which they show a significant dependence of the spectrum of LiAlMe₄ in THF on both temperature and concentration. It is possible that this difference in the behavior of LiAlMe₄ and NaAlEt₄ can be related to the differences in the stability of the Li⁺·nTHF and Na⁺·nTHF complexes and the difference in the cation-anion interactions.

C. Conclusion

For THF solutions of NaAlEt₄, it is proposed that the equilibrium

\[
\text{NaAlEt}_4 \cdot \text{Solvent} = \text{Na}^+ \cdot 4 \text{Solvent} || \text{AlEt}_4^- \quad (\text{t})
\]

exists at the concentrations and temperatures studied. This equilibrium is most likely the predominant one in diethyl ether, also. For solvent molecules with two possible coordination sites, such as DME, the following equilibrium is suggested:

\[
\text{NaAlEt} \cdot 1 \text{Solvent} = \text{Na}^+ \cdot 2 \text{Solvent} || \text{AlEt}_4^- \quad (\text{i})
\]

In DME the equilibrium is shifted far to the right so that the majority of the species in solution are solvent-separated ion pairs. In THF the decrease in solvent-separated ion pair concentration and the corresponding increase in contact ion pair concentration, as compared to DME solutions, is attributed to the poorer coordinating ability of THF. Diethyl ether solutions of NaAlEt₄ appear to contain a much larger fraction of contact ion pairs than either THF or DME.
In mixed solvent systems, with benzene as the bulk solvent, a distinct difference in the NMR spectra at various ratios of ether: NaAlEt₄ clearly distinguishes between contact and solvent-separated ion pairs.

All of the above considerations are made possible by observing the influence of controlled experimental conditions on the $^{27}$Al-$^1$H coupling. The $^{27}$Al-$^1$H is almost completely destroyed by the presence of contact ion pairs and is clearly resolved into distinguishable splittings for solvent-separated ion pairs.

Although these considerations have been generally accepted by a number of research groups, it must be realized that interpretations based upon physical measurements are subject to the ability of nuclear magnetic resonance spectroscopy to differentiate between species which are quite probably undergoing rapid alterations in their conformational configurations. Molecular properties are seen as if averaged over a period of time, appropriate to the time scale of the physical measurement. In this particular instance, there are two possible rationalizations for the loss of the fine structure of the pmr lines, neither of which can be legitimately discarded at this point.

It is possible that the $^{27}$Al environment is tetrahedral at all times. In this case, there may be no quadrupole effect seen in the proton spectra. The close approach of another ion may then destroy the symmetry of the AlEt₄⁻ anion and introduce quadrupole relaxation effects which are reflected by the loss in resolution of the spectra.
On the other hand, the environment of the $^{27}\text{Al}$ nucleus may be tetrahedral only as a matter of a time average due to rotation about the Al-C bonds. The approach of another ion could then impair the rate of rotation so that the quadrupole effects are no longer averaged out. This latter explanation has been given preference only as a consequence of a reasonable attempt to concur with similar studies.*

The temperature and concentration dependence study in THF illustrates that the exchange rate is too rapid to be quantitatively analyzed in the temperature range studied. The difference in the abilities of the lithium and sodium cations to undergo coordination with ether solvents, such as THF, however, is shown. It was also shown that a decrease in temperature for a given concentration of all three salts favors an increase in the solvent-separated ion pair species.

The extension of ideas applied to NaAlEt₄ solutions cannot, at this time, be made to include NaAlBu₄ and LiAlBu₄ because of the absence of any visible variation in their spectra. Either the large AlBu₄⁻ anion does not assume a highly symmetrical configuration in solution or some other relaxation process destroys the $^{27}\text{Al}^{-1}\text{H}$ coupling. Future studies must be made to confirm any comparisons between NaAlEt₄ and the tetra-$n$-butylaluminates. The results of the NMR study of THF solutions does not irrefutably eliminate the possibility of the formation of aggregates in THF solution, as was discussed in Part I, to

* See Appendix.
rationalize the conductance data. But the NMR results do make the possibility of aggregation seem less likely.

D. Suggestions for Future Studies

The concentration and temperature dependence study of NaAlEt₄ should be extended to other ether solvents, DME in particular. If possible, $^{23}\text{Na}$ and $^{27}\text{Al}$ resonance studies should be made. The use of $^{23}\text{Na}$ would offer a more direct method of looking at the coordination of the sodium cation. $^{27}\text{Al}$ resonance would allow more quantitative information about the equilibrium between contact and solvent-separated ion pairs to be obtained.

The uniqueness of the NaAlEt₄-ether-solvent systems appears to offer a distinct system for directly determining the presence or absence of contact and solvent-separated ion pairs in solution. Mole ratio studies should be continued, similar to that of DME:NaAlEt₄ in benzene.
APPENDIX

Although it is intuitively reasonable to postulate that the AlEt$_4^-$ anion must assume a rather high degree of symmetry in solution to give such well-resolved spectra, there are several sets of data which support the idea that AlEt$_4^-$, as a free ion in solution, has tetrahedral symmetry.

Mach$^{116}$ has recorded the infrared spectra of both LiAlEt$_4$ and NaAlEt$_4$ in diethyl ether and nujol mull. By comparing the absorption bands of the tetraethylaluminates with those of other aluminum alkyls, Mach was able to make assignments which were in agreement with $C_{2v}$ or $T_d$ symmetry. A further comparison of the spectra of the tetraethylaluminates with IR spectra of SnEt$_4$ and PbEt$_4$ persuaded the author to conclude that the AlEt$_4^-$ anion has tetrahedral structure in the case of the sodium salt. The lithium salt probably exists in a tetrahedral configuration, also, but it appears that the ethyl group vibrations are affected by regularly arranged Li$^+$ cations in solution. Unfortunately, the author did not report results for a more desirable solvent; for NMR data indicate that a large fraction of contact ion pairs exist in diethyl ether.

Oliver and Wilkie$^{106}$ compared the infrared spectra of AlMe$_4^-$ in a variety of solvents to the infrared spectra of AlMe$_4^-$ in diethyl ether by Mach.$^{116}$ The results were in agreement with those of Mach for diethyl ether. Oliver and Wilkie$^{106}$ also obtained spectra in DME, which are quite different from those in diethyl ether. The authors
attribute this difference in spectra to a change from $C_{2v}$ symmetry in diethyl ether to $T_d$ symmetry in DME.

The crystal structure of LiAlEt$_4$ has been determined by X-ray diffraction methods.$^{117}$ The data indicate that the structure may be considered as consisting of alternating Li$^+$ and AlEt$_4^-$ ions. There is some evidence to indicate a weak interaction between Li$^+$ and AlEt$_4^-$ ions in the crystal. The arrangement of the carbon atoms about the aluminum nucleus approaches $C_{2v}$ symmetry. Proton and $^7$Li NMR spectra were taken in diethyl ether. The quartet lines are very broad and no information was obtained. These results, however, support the postulate that a lack of resolution in diethyl ether is a consequence of quadrupole-induced relaxation because of the formation of contact ion pairs in a weak coordinating solvent such as diethyl ether.
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VITA

Thomas Delbert Westmoreland, Jr., was born June 2, 1940, in Vivian, Louisiana, the son of Thomas D. and Marguerite B. (Moore) Westmoreland. He was graduated from Pinewood Park Elementary School in Longview, Texas, and from Judson Grove High School, Judson, Texas. In September, 1958, he matriculated at North Texas State University and was graduated from that institution May, 1965, with a Bachelor of Science in Chemistry and a Master of Science in Chemistry in August, 1965. During his academic career he was affiliated with Sigma Xi, Phi Eta Sigma, Alpha Chi Sigma, Kappa Mu Epsilon, the Baptist Student Union, and the Air Force ROTC.

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