

ION-SOLVENT AND ION-ION INTERACTIONS:  
ALKALI METAL TETRAALKYLALUMINATES IN NONAQUEOUS SOLUTIONS

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**Abstract** - The use of the alkali metal tetraalkylaluminates offer a unique approach to the study of ion-solvent and ion-ion interactions in non-aqueous media. Because of their solubility in nonpolar solvents such as hexane and benzene, they permit the observation of specific ion-solvent interactions without interference from the solvent. Their general application to the study of solvation numbers, ion-pair types, and ionic aggregation are discussed.

INTRODUCTION

In the last twenty years there has been a rebirth of interest in nonaqueous ionic solutions and, whereas the Debye-Huckel theory was the impetus for much of the research in this area prior to 1950, it is probable that the present interest can be traced to

- a) Winstein's proposal of two types of ion-pairs, contact and solvent separated,
- b) the development of new instrumental techniques,
- c) an attempt to differentiate between solvent dielectric constant and donicity, the latter commonly being expressed in terms of Gutmann donor numbers (1),
- d) an interest in understanding why reaction rates are critically dependent on the solvent.

Central to this present research effort is an attempt to understand solution processes in terms of a model. But of particular significance is the present interest in relating this model to chemical reactivity. In this respect, the studies of M. Szwarc on the mechanisms of anionic polymerization reactions are particularly important (2).

Experimentally, the development of spectroscopic techniques for the study of electrolyte solutions in nonaqueous media has been crucial to our present understanding. Although spectroscopic methods had previously been applied to ionic solutions (3), we might consider the present era to have begun with the uv studies of  $NR_4I$  salts by Griffiths and Symmons (4). It was based on this work that they proposed three types of ion-pairs in solution. Since that time, essentially all of the common spectroscopic methods have been utilized.

Spectroscopically it is possible to observe a) the complexing species, b) the cation, and c) the anion, although rarely is it possible to observe all three in the same system. From these we can determine something about both the ion-solvent and the ion-ion interactions and, in turn, may learn something about the identities of the species in solution. Simply to illustrate the point consider the following:

Complexing species

The complexation of the sodium ion by tetrahydrofuran was studied by observing the proton chemical shift as a function of tetrahydrofuran:sodium ion ratio with cyclohexane as the solvent (5).

Anion

Contact and solvent separated ion-pairs were detected by means of uv studies of the fluorenyl salts of the alkali metals in ethereal solvents. The fluorenyl anion shows an absorption spectrum that is strongly dependent on the nature of the cation solvation (6).

### Cation

Extensive studies of the environment of the sodium and the lithium ion have been conducted by means of  $^{23}\text{Na}$  and  $^7\text{Li}$  NMR (7). Typical is the correlation of  $^{23}\text{Na}$  chemical shifts and Gutmann donor numbers.

### ALKALI METAL TETRAALKYLALUMINATES

One of the major problems in the study of ion-solvent interactions is that of finding an acceptable electrolyte. Since most solvents are basic, solvation will occur predominantly with the cation, although anion solvation is also an important concern (8). Thus, if we can focus on cation solvation, it is important that the electrolyte have a small cation and, preferably it should be possible to vary the cation to give different cation sizes. It is also essential that it should be soluble in a variety of solvents. Inherent to the use of pure solvents is the inability to vary the solvent (complexing agent) concentration. Generally, inherent to the use of mixed solvents is competition between the mixed solvent components for sites on the cation. A particularly desirable salt would be one with a small cation that is soluble in non-complexing solvents such as hexane and benzene. Controlled amounts of a complexing agent could then be added to the solution, and the interaction of the complexing agent with the salt (usually the cation) could be directly observed.

The alkali metal tetraalkylaluminates fall into this category. Particularly interesting is sodium tetra-n-butylaluminate which is extensively soluble in saturated hydrocarbon solvents such as hexane. Smaller anion sizes and larger cation sizes both result in decreased solubility in saturated hydrocarbon solvents, but most are soluble in aromatic solvents (9).

The infrared studies of complexation of the sodium ion by tetrahydrofuran are typical of the earlier solvation studies with sodium tetrabutylaluminate (10). Using cyclohexane as a solvent, the infrared spectra were obtained as a function of the tetrahydrofuran:sodium ion ratio. The asymmetric C-O-C stretching vibration of tetrahydrofuran occurs at  $1071\text{ cm}^{-1}$ . However, in the presence of the sodium ion, a new band at  $1053\text{ cm}^{-1}$  is observed which can be attributed to complexed tetrahydrofuran. As can be seen in Fig. 1, at a ratio of tetrahydrofuran:sodium ion less than 1:1, the absence of the  $1071\text{ cm}^{-1}$  band indicates that essentially all of the tetrahydrofuran is in the complexed form. But the changes in relative intensities of both bands as the tetrahydrofuran:sodium ion ratio increases indicate an equilibrium between the 1:1 complex and additional tetrahydrofuran molecules.

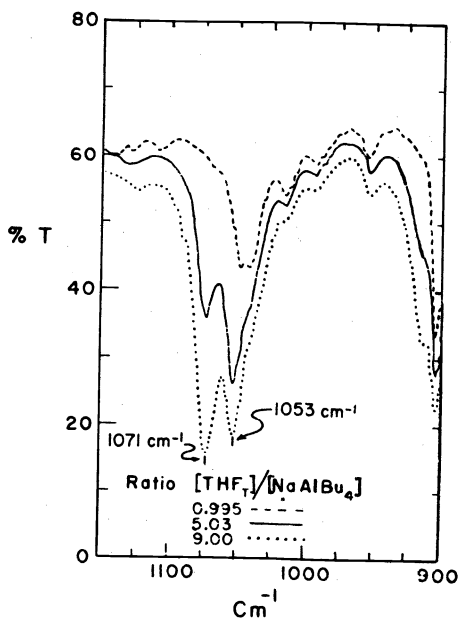


Fig. 1. Infrared spectra of  $\text{NaAlBu}_4$ -THF-cyclohexane solutions of constant salt concentration and varying THF concentration.

## ION PAIR TYPE

The first experimental confirmation of Winstein's proposal of two types of ion-pairs was made by Griffiths and Symmons based on uv studies of  $\text{NR}_4\text{I}$  salts (5). Interestingly they reported three types of ion-pairs, contact, solvent shared, and solvent separated. Subsequently Hogen-Esch and Smid reported two types of pairs based on their classic studies of the uv spectra of alkali metal fluorenyl salts in various nonaqueous solvents (7). Typical are the fluorenyllithium spectra shown in Fig. 2. Two absorption peaks can be seen at 355 nm and 373 nm. In dioxane, which is a weak complexing agent, only the band at 355 nm is observed, but in 1,2 dimethoxyethane, a strong complexing agent, only the band at 373 nm occurs.

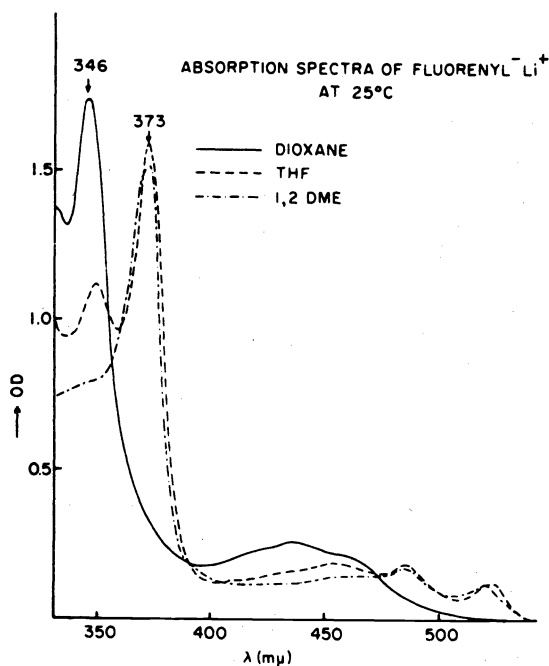


Fig. 2. Fluorenyllithium spectra in Dioxane, THF, and DME at 25°C.

Based on these observations as well as temperature dependence and cation size studies, the 355 nm band is attributed to contact pairs and the 373 nm band to solvent separated pairs. It can be seen that in THF, a solvent of intermediate donicity, an equilibrium exists between contact and solvent separated pairs.

It is to be noted that the type of experiment previously described with sodium tetrabutylaluminumate permits the observation of specific cation solvation, but it does not discriminate between the various types of ion-pairs. This problem was resolved with the interpretation of the NMR spectra of lithium tetramethylaluminumate in diethylether and 1,2 dimethoxyethane. In diethylether the methyl resonance of the tetramethylaluminumate anion is found to be a singlet whereas in dimethoxyethane it is a well defined sextuplet resulting from the spin-spin splitting by the  $^{27}\text{Al}$  nucleus (11). Theoretically it has been shown that the aluminum-proton splitting requires tetrahedral symmetry for the anion, and it is further proposed that this reflects the existence of solvent separated pairs in dimethoxyethane and contact pairs in diethylether (12). This technique has now been extended to sodiumtetraethylaluminumate (13) and, by using  $^{27}\text{Al}$ - $^{13}\text{C}$  spin-spin coupling, to sodium tetrabutylaluminumate (14). In Fig. 3, the contrast between the spectrum of a solvent separated and a contact pair is clearly evident. In dimethoxyethane, an evenly spaced nine line pattern is seen for the methylene resonance of the tetraethylaluminumate anion whereas in benzene a broadened quartet is observed.

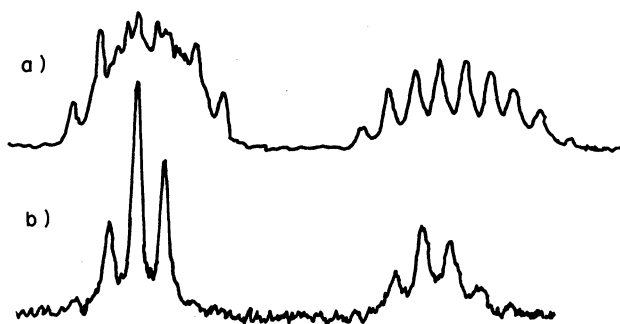


Fig. 3. NMR spectra of  $\text{NaAlEt}_4$  in (a) DME; (b) benzene

Far-infrared spectroscopy has also proven useful in differentiating between contact and solvent separated ion-pairs. Beginning with the work of Evans and Lo (15) Edgell, et. al. (16) and Popov and his coworkers (17) have made extensive studies of quantized cation motion in solvents covering a wide range of donicities. In principle, this technique can also be used to differentiate between ion-pair types with the alkali metal tetraalkylaluminum salts (17).

Interestingly, based on ESR measurements of alkali metal naphthalenide and anthracenide salts in ethereal solvents, Hirota has proposed three types of ion-pairs (18). However, these are not the same as those proposed by Griffiths and Symmons. Hirota observed two types of contact and one type of solvent separated pair. Burley and Young have also reported two types of contact pairs based on the optical spectra of alkali metal salts of 1,3-diphenylbut-1-ene in a number of ether solvents (19). They interpret these as resulting from contact pairs in two distinctly different solvation states. But based on ESR and optical spectra of alkali metal salts of triphenylene in 2-methyltetrahydrofuran, de Boer and his coworkers report three types of ion-pairs, one contact and two solvent separated (20). Since these observations, there have been a number of publications supporting the argument for three types of ion-pairs (21).

It is very likely that both proposals are correct but that the combination of instrumentation, system, and experimental conditions lends itself to favor one or the other observation. It is difficult to envision two types of solvent separated pairs but depending on the geometry of the anion, it would seem quite reasonable that different degrees of solvation of the cation would lead to different types of contact pairs. Sodium tetraethylaluminum would be particularly well suited for such a study. In Fig. 3, the extremes of contact and solvent separated pairs can be seen. With benzene as a solvent, the sodium ion should be able to maintain a position relative to the anion that is completely unencumbered by solvent molecules. This would also be the case with a 1:1 complex between the sodium ion and a complexing species. In both instances the anion would be expected to be highly distorted from tetrahedral symmetry, and the spectra should both be broadened quartets. The 4:1 complex between dimethylsulfoxide and the sodium ion gives the well defined nine line pattern (22) indicating a solvent separated pair. Thus one would expect that if a strong donor such as dimethylsulfoxide were used, the distortion of the anion should be successively less for a 2:1 and a 3:1 complex because of steric restrictions. Correspondingly, intermediate spectra should result indicative of distinctly different solvated contact pairs.

#### SOLVATION NUMBER

With the development of spectroscopic methods, it is now possible to directly observe the solvation number of an alkali metal cation. For the sodium ion this was first accomplished by noting the proton shifts in the NMR spectrum of tetrahydrofuran as a function of tetrahydrofuran:sodium ion ratio in the system tetrahydrofuran-sodium tetrabutylaluminum-cyclohexane (5). From Fig. 4, it can be seen that the  $\alpha$ -methylene signal of tetrahydrofuran is constant at 3.64 ppm.

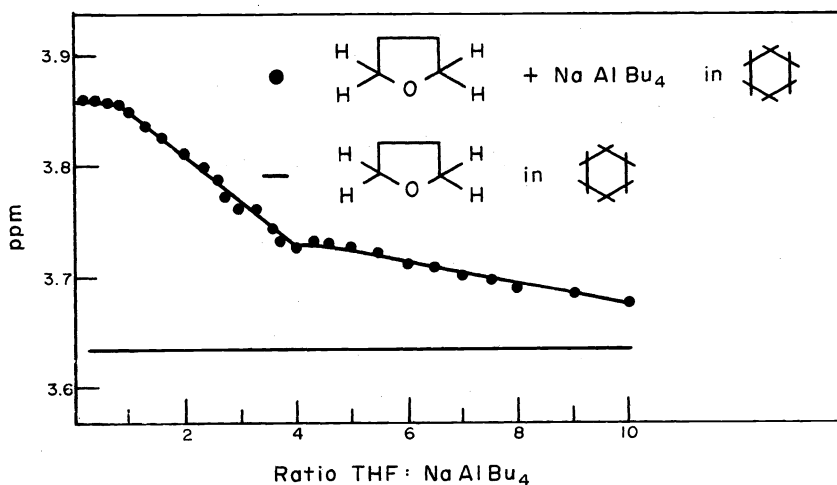


Fig. 4. Chemical shifts in the THF proton signals as a function of the mole ratio THF:NaAlBu<sub>4</sub>.

In the presence of sodium tetrabutylaluminate, the signal shifts downfield. Here it can be seen that up to a ratio of 1:1, the shift relative to the unperturbed tetrahydrofuran is very nearly constant. This implies that essentially all of the THF molecules are complexed to the sodium ion. As the ratio of tetrahydrofuran:sodium ion increases further, a distinct break is noted at a ratio of 4:1, implying the existence of a four coordinated species. Using the same method, Wuepper and Popov (23) obtained a solvation number of six with dimethylsulfoxide and four with 1-methyl-2-pyrrolidone.

The solvation number of the sodium ion has also been determined by means of infrared spectroscopy using the system tetrahydrofuran-sodium tetrabutylaluminate-cyclohexane (10). As pointed out earlier, the C-O-C asymmetric stretching vibration of tetrahydrofuran is shifted from an unperturbed value of 1071 cm<sup>-1</sup> to a value of 1053 cm<sup>-1</sup> on complexation with the sodium ion. As the ratio of tetrahydrofuran:sodium ion increases the relative intensities of the two bands permit us to determine the concentrations of the free and complexed tetrahydrofuran. In Fig. 5, an average value plot ( $\bar{n}$ ) of the ratio of bound tetrahydrofuran:salt vs total tetrahydrofuran:salt is shown. The curve tends to approach a limiting value of 4, again supporting the argument for a solvation number of 4 for the sodium ion with tetrahydrofuran.

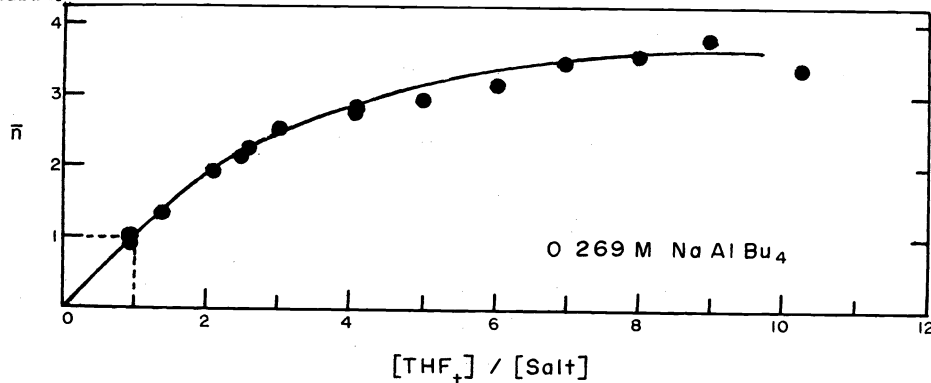


Fig. 5. Average value plot of the ratio of bound THF:salt vs ratio of total THF:salt.

Both of these methods are somewhat limited. However, another possible approach is based on the fact that sodium tetraalkylaluminates often form two phase systems in mixed solvents. For instance, the addition of 0.25 grams of sodium tetraethylaluminate and small quantities of dimethylsulfoxide to 5 ml of benzene results in two phases until the ratio of dimethylsulfoxide:sodium ion is greater than 10:1. The lower phase is composed almost in total of the salt and the complexing agent, and essentially no salt is observed in the upper phase. It seems reasonable to expect the amount of complexing agent in the upper phase to be dependent on the solvation number of the sodium ion. Thus it would seem that a determination of the amount of free complexing agent in the upper phase as a function of donor:salt ratio may offer a new means of determining solvation numbers.

### ION AGGREGATION

Since the original proposal by Fuoss and Kraus of the existence of ion-triplets, the concept has been quite generally accepted. Yet there have been some questions raised (24). In fact, Kraus has proposed an alternative explanation for the conductance curves that led to the original proposal (25). More recently, Kubas and Shriver (26) carried out molecular weight measurements on sodium tetraphenylborate in tetrahydrofuran as a solvent and found no aggregation greater than pairs. On the other hand, ESR studies have strongly supported the argument for triple ions (27) and Shirk and Shriver (28) interpreted the Raman and infrared spectra of tetrahydroaluminate salts in various ethers in terms of ion aggregates. It is likely that ion aggregates do, in fact, exist under the proper conditions, but their existence may be critically dependent on such factors as solvent donicity, cation size, and temperature.

It has been shown that in a noncomplexing solvent, a salt with a small cation does form aggregates (29). By means of vapor phase osmometry, the aggregation of sodium tetrabutylaluminate was determined as a function of salt concentration using cyclohexane as the solvent. Inasmuch as the sodium ion is unsolvated, aggregation would be expected. This can be seen to be the case from Fig. 6, where an average aggregation number approaching six is obtained at higher concentrations. On the other hand, quite different results might be expected in a more conventional solvent.

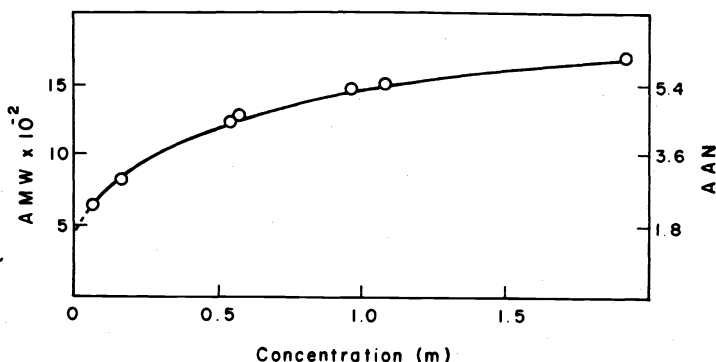


Fig. 6. Average molecular weight and aggregation number of  $\text{NaAlBu}_4$  in cyclohexane.

The extent of aggregation should be strongly dependent on cation size, and in a solvent of high donicity, the solvated cation is effectively a large ion. But the study of aggregation as a function of donor does not involve simply using different solvents. This would result in a change in bulk dielectric constant from solvent to solvent and, consequently, the ionic behavior would not be comparable.

There are two experimental features that make the tetraalkylaluminate salts particularly promising for the study of ion-aggregation by means of vapor phase osmometry (30). First, it is possible to obtain a system with a fixed bulk dielectric constant by using a tetraalkylaluminate salt in an inert solvent such as benzene. Controlled amounts of various complexing agents can then be added to determine the effect of donicity, ion-pair type, and cation size on ion aggregation. Secondly, in the use of different solvents, the behavior of the solvated electrolyte can be compared to that of a reference electrolyte such as tetrabutylammonium tetrabutylaluminate which is essentially unsolvated. Coupled with conductance (31), infrared, and NMR methods, this system should provide considerable information on ion aggregation.

## CONCLUSION

There have been many significant advances in our understanding of electrolyte solutions during the last two decades. These have been largely dependent on the development of new instrumental methods, particularly spectroscopic methods. But of equal importance has been the development of systems that permit the use of these instrumental methods. Thus, our continued advancement in the understanding of ions in solution will depend as much on the development of systems to study as on the methods we use to conduct those studies. Because of the unique properties of the tetraalkylaluminum salts, they are particularly well suited to the study of many of the problems of nonaqueous solutions and should represent one of the important systems in this research area.

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