

Solutions of Lithium Tetrahydrido Aluminates in Ethers: a ^7Li and ^{27}Al NMR Study

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Solutions of LiAlH_4 in tetrahydrofuran (THF), glycoldimethylether (monoglyme), diglycoldimethylether (diglyme) and triglycoldimethylether (triglyme) as well as solutions of $\text{LiAlH}_4/\text{THF}$ in toluene have been investigated by ^7Li and ^{27}Al NMR. It was found that $\delta^{27}\text{Al}$ is nearly independent of the solvent as is $^1J(\text{AlH})$. However, the line width of the ^{27}Al NMR signal shows strong solvent influences and, in addition, concentration and temperature dependence. Intermolecular hydride exchange becomes rapid in solutions of monoglyme and triglyme at room temperature. This can also be shown by the H/D exchange between LiAlH_4 and LiAlD_4 . $\delta^7\text{Li}$ data indicate that Li is hexacoordinated in the series of glycoldimethylethers, and LiAlH_4 in diglyme seems to be the system in which the AlH_4 moiety is least affected by ion pair or triple ion formation.

A better understanding of reductions by simple and complex metal hydrides may result from a more detailed knowledge of their solutions in aprotic solvents. In spite of the widespread use of these materials astonishingly little is known about the various species which are present in their solutions, e.g. the extent of dissociation and association, ion pair formation, etc.

Early studies on LiAlH_4 in diethylether have recognized the association of this complex hydride [1], and this was fully confirmed in more recent investigations under more rigorous conditions [2]. The suggestion [3] that the solvent, e.g. THF, coordinates not only with the Li ion but also with the Al atom of LiAlH_4 was clearly disputed by ^{27}Al NMR data. Hermanek *et al.* [4] and Wolfgang [5] have shown that $\delta^{27}\text{Al}$ of MAIH_4 is nearly independent of the solvent used. However the cation has a significant effect on the line width [4, 5]. And it has been demonstrated that the line width of the ^{27}Al NMR signal of a LiAlH_4 solution in diethylether is both temperature and concentration [6] dependent. In addition it is also strongly influenced by the solvent [4, 5, 7]. It decreases as one changes from diethylether to tetrahydrofuran (THF) and to diglycoldimethylether (diglyme). This is in consonance with the expected order of solvation of the Li cation.

^{27}Al possesses a nuclear spin of $I = 5/2$, and its sensitivity is 0.207 relative to ^1H . The local field gradient

interacts with the quadrupole moment of Al, $Q = 0.149 \cdot 10^{-24} \text{ cm}^2$, and this allows an efficient magnetic relaxation mechanism. Under the limits of fast motion [8] the quadrupole relaxation is the predominant relaxation mechanism which determines the line width. High symmetry, e.g. the nearly perfect octahedral symmetry of $[\text{Al}(\text{OH}_2)_6]^{3+}$ results in very narrow lines, ~ 3 cps for this ion [9]. Small lines are also observed for the tetrahedrally coordinated tetrahaloaluminates [10]. Deviations from the ideal symmetry results in considerable line broadening, and, therefore, it is to be expected that the line width of ^{27}Al and of ^7Li ($I = 1$, sensitivity 0.294, quadrupole moment $-4.2 \cdot 10^{-26} \text{ cm}^2$) [8] will be intimately associated with the solution state of LiAlH_4 .

Since association and dissociation are equilibrium phenomena, and since LiAlH_4 in solutions is associated, it was expected that an NMR study of LiAlH_4 in various ethers would give information about the species present in solution.

Tetrahydrofuran Solutions of LiAlH_4

The chemical shift $\delta^{27}\text{Al}$ of LiAlH_4 in THF is concentration independent in the range 0.02–5 M. Its value is 98.8 ± 0.2 ppm (lit. 97.7 [4], 100 [5]), and the 1:4:6:4:1 – quintet structure is readily recognized, $^1J(\text{AlH}) = 175.5 \pm 1.3$ cps (lit. 172 [4], 175 [5]). However, the ^{27}Al line width proved to be concentration dependent, cf. Fig. 1. There is a drastic decrease in the line width for a saturated solution (5 M) on dilution to 2.5 M; and this may, in part, be due to the viscosity of the 5 M solution.

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In spite of the rather wide lines, the splitting of the signal due to Al-H coupling is still clearly observable, and $\delta^{27}\text{Al}$ certainly suggests no solvation of AlH_4^- . Similar to LiAlH_4 solutions in diethylether [6] an increase of the line width is observed at higher dilution as shown by the shallow minimum of the curve in Fig. 1.

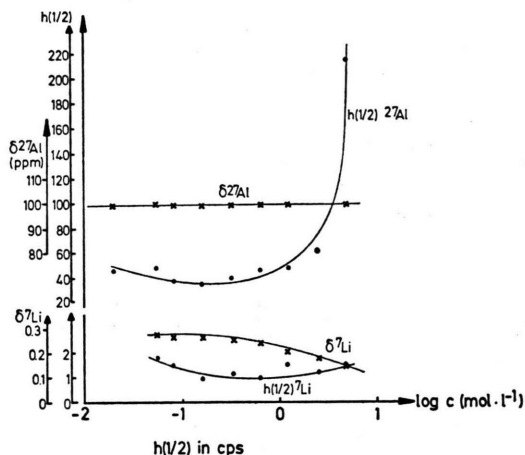


Fig. 1. Concentration dependence of the line width of ^{27}Al and ^7Li NMR signal for LiAlH_4 solutions in THF at room temperature [10].

The ^7Li NMR signal of the LiAlH_4 solutions in THF consists of a single line, and its line width remains the same on ^1H broad band decoupling. This excludes any $\text{Li}\cdots\text{H}\cdots\text{Al}$ interactions even at high concentration consistent with the assumption that Li^+ is completely solvated by THF. However, $\delta^7\text{Li}$ changes monotonically by 0.115 ppm to lower field as the 5 M solution is diluted to 0.08 M. On further dilution an increase of the line width is observed. Its minimum is found at higher concentrations as that for the ^{27}Al NMR signal.

Temperature affects both chemical shift and line width of the ^{27}Al NMR signal. Only one solution, 0.16 M in LiAlH_4 , has been investigated. The shift difference is small, since the ^{27}Al signal moves only from 99.6 ppm at -30°C to 98.5 ppm at $+60^\circ\text{C}$. The coupling constant remains unaffected. Fig. 2 shows that the change in line width with temperature varies about linearly only between -30°C and 30°C , and a similar though opposite behaviour is observed for the ^7Li line width which increases at higher temperature and remains constant at low temperatures while the signal moves slightly to higher frequencies as the temperature increases.

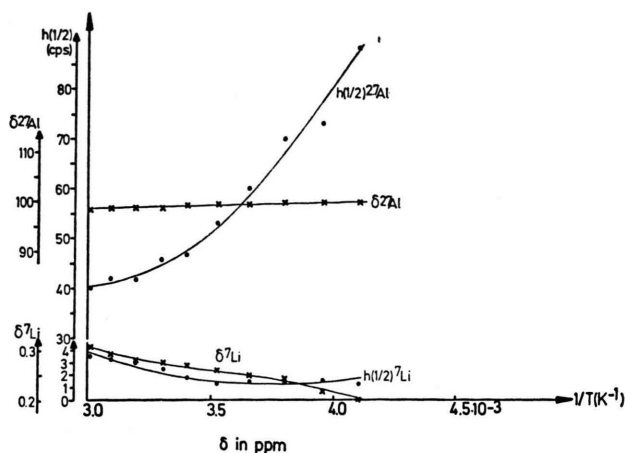
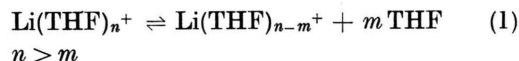


Fig. 2. Temperature dependence of the line width of the ^7Li and ^{27}Al NMR signals of a 0.16 M LiAlH_4 solution in THF.

Both, the increase in line width with increasing temperature as well as the frequency shift of the ^7Li signal is in consonance with an equilibrium (1) which is shifted to the right hand side at higher temperature.



Monoglyme Solutions of LiAlH_4

Glycoldimethylether (monoglyme) represents a bidentate ether and it solvates lithium ions more strongly than ether.

As observed for THF solutions, no significant change of $\delta^{27}\text{Al}$ for LiAlH_4 in the concentration range 2.0–0.016 M was found: $\delta^{27}\text{Al}$ 100.9 ± 0.3 ppm (lit. 100 [4], 101 [5]). Characteristic, however, is the absence of hyperfine splitting at concentrations > 1.1 M (20°C). At 1 M (see Fig. 3) the expected quintet structure of the signal has emerged, $^1J(\text{AlH}) = 174.2 \pm 0.2$ cps (lit. 172 [4], 170 [5]) and sharpens as the solution becomes more dilute. The line width of the proton coupled and decoupled ^{27}Al NMR signals are the same for 0.5 M and more dilute solutions. At higher concentrations there is considerable broadening in the proton coupled spectrum, but also a definite increase of the line width for the proton decoupled signal. Fig. 4 shows the results.

In contrast to $\delta^{27}\text{Al}$ we observe a significant low field shift of the ^7Li NMR signal on dilution: -0.84 ppm for a 2 M, -0.60 ppm for a 0.125 M and -0.47 for

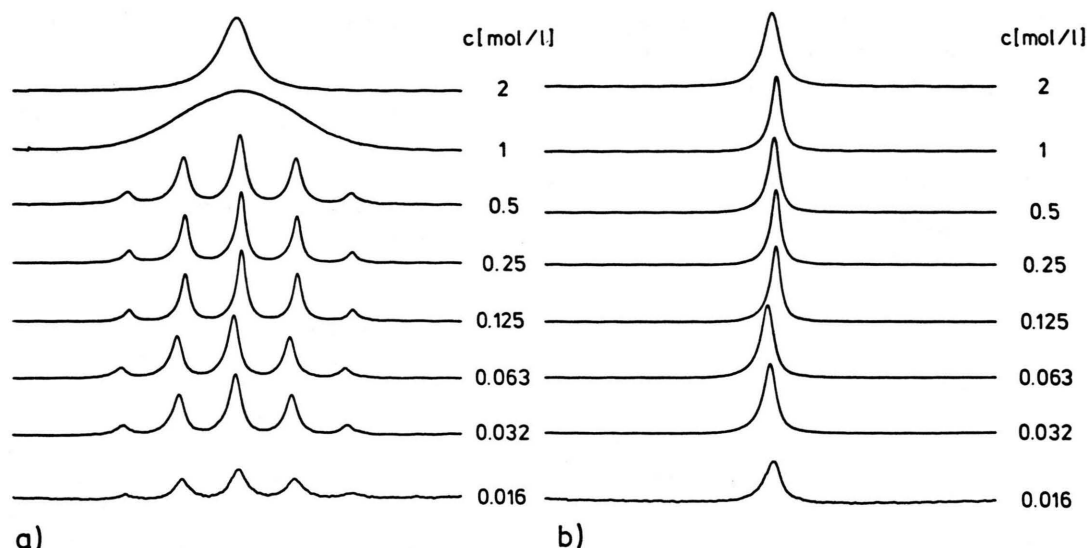


Fig. 3. ^{27}Al NMR spectra (a) proton coupled (b) ^1H broadband decoupled of LiAlH_4 in monoglyme solution at 303 K.

a 0.031 M solution. Interestingly, the ^7Li line width broadens as the solution becomes less concentrated.

The temperature dependence of chemical shifts and line width has been studied for a 0.125 M solution over the temperature range -30 to $+70^\circ\text{C}$. The ^{27}Al NMR signal moves to lower frequencies (from 101.2 to 100.5 ppm) under these conditions without any change in $^1J(\text{AlH})$. Surprisingly, an increase in the line width of the ^{27}Al NMR signal is observed as one progresses from -30°C (25 cps) to 35°C (39 cps), followed by a decrease on further raising the temperature (31 cps at 70°C) (see

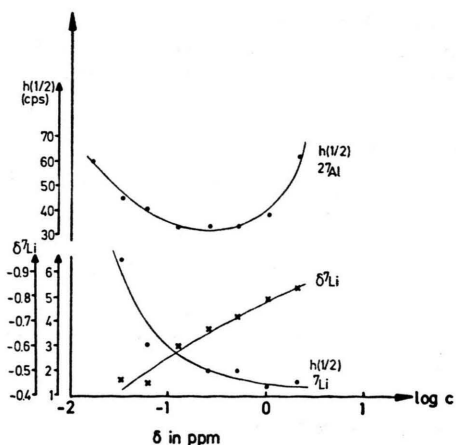


Fig. 4. Concentration dependence of the ^{27}Al and ^7Li line width for LiAlH_4 in monoglyme at 303 K.

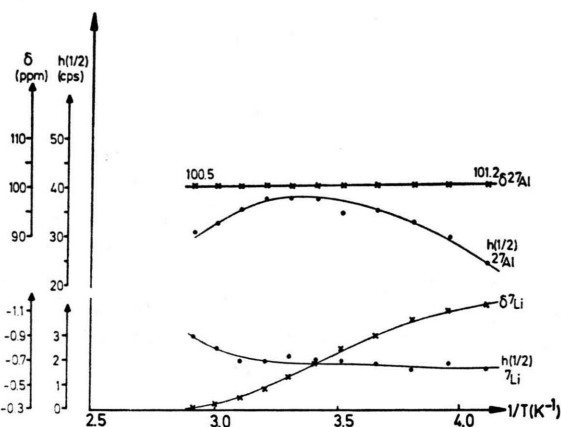
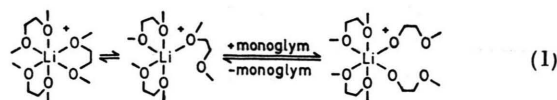


Fig. 5. Temperature dependence of the ^{27}Al and ^7Li line width for a 0.15 M LiAlH_4 solution in monoglyme.

Fig. 5). This is an *unexpected* behaviour as compared with other systems.

Changes in line width of the ^7Li NMR signal are not very pronounced, and since differences in the line width in coupled and proton broadband decoupled spectra are only marginal, any covalent Li-H-Al interaction can be excluded. However, the line width is definitely smaller at -30°C than at 30°C . In addition, the change in $\delta^7\text{Li}$ is quite drastic, -1.16 ppm at -30°C , 0.86 ppm at 0°C , -0.54 ppm at 30°C and -0.32 ppm at 70°C , representing 0.9 ppm over a 100°C temperature range.

This behaviour can be qualitatively understood by a shift towards a highly solvated Li^+ and a decrease in exchange rate of the solute with decreasing temperature.



This type of exchange is slow at low temperature where Li^+ is optimally solvated. Under these conditions ^7Li is highly shielded and the line width small due to high symmetry at this atom. As the temperature is raised the average coordination number for Li decreases, leading to a deshielding of the Li nucleus, reduction of symmetry and favouring the solvent/solvate exchange process.

Diglyme Solutions of LiAlH_4

The solubility of LiAlH_4 in diglycoldimethylether (diglyme) at a given temperature is less than in monoglyme [11]. Saturation at room temperature was reached at 0.83 M. Therefore only a limited concentration range – 0.83–0.013 M – could be investigated. No change of $\delta^{27}\text{Al}$ was observed ($\delta^{27}\text{Al}$ 100.6 ± 0.2 ppm; lit. [5] 101) as well as of $^1J(\text{AlH})$ (174.0 ± 0.7 cps, lit. 175 [5], 175.2 ± 1.2 cps [12]). The quintet structure of the ^{27}Al NMR signal due to the Al-H coupling is extremely well resolved as a consequence of the small line width (13 cps) even for a saturated solution. This signal broadens on dilution as shown in Figure 6.

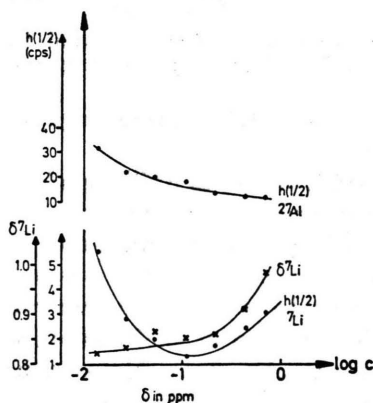


Fig. 6. Concentration dependence of the ^{27}Al and ^7Li line width of a LiAlH_4 solution in diglyme at 303 K. The change in chemical shift for the ^7Li signal is also represented.

In contrast, the line width of the ^7Li NMR signal is fairly small at high concentrations and decreases on dilution until a minimum is reached for a 0.1 M solution. Further dilution causes considerable line broadening. Again, no significant change in line width is observed on ^1H broadband decoupling. No direct correlation exists with the change in the $\delta^{27}\text{Li}$ value on dilution which is accompanied by a steady low field shift from -0.98 ppm to -0.82 ppm in the concentration range studied.

The temperature dependence of chemical shifts and line widths has been studied for a 0.41 and a 0.15 M solution. Both show the same trend, e.g. a 1.2 ppm high field shift of the ^{27}Al NMR signal in the temperature range -30 to $+60^\circ\text{C}$ (101.4 to 100.2 ppm), constancy of $^1J(\text{AlH})$ (174.2 cps) and an increase in the line width as shown in Fig. 7. The change in chemical shift as well as its value for ^7Li are identical for both solutions.

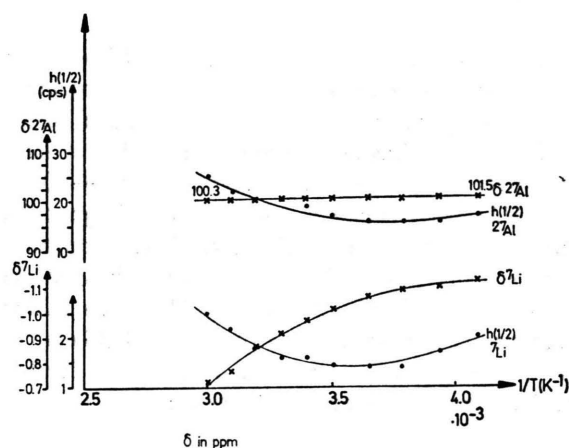


Fig. 7. Temperature dependence of chemical shift and the line width for the ^7Li and ^{27}Al NMR signal as observed on 0.41 and 0.15 M solutions of LiAlH_4 in diglyme.

In analogy to the monoglyme solution the ^7Li signal shifts to higher frequencies (low field) as the temperature is raised, the difference between the two solutions is the smaller line width for the more dilute solution which increases less at higher temperatures.

These data are in consonance with an equilibrium of type (1).

Triglyme Solutions of LiAlH_4

The concentration range studied for triglycoldimethylether was limited to 0.39–0.013 M due to the

restricted solubility of LiAlH_4 [11]. $\delta^{27}\text{Al}$ was found to be 101 ppm, independent of concentration at 303 K, $^1J(\text{AlH}) = 173 \pm 0.4$ cps. Fig. 8 demonstrates the behaviour of these rather dilute solutions which reminds to that of LiAlH_4 in monoglyme at much higher concentrations. The line width of the ^{27}Al NMR signal passes through a minimum at 0.2 M solutions. In contrast, the ^7Li line width increases steadily with dilution (from 2 to 6 cps) while the change in chemical shift is rather small, ($\delta^{27}\text{Li}$ —0.79 ppm at 0.39 M, —0.74 at 0.195 M, —0.66 ppm at 0.05 M, —0.63 ppm at 0.0125 M).

The effect of temperature on the line width was investigated for 0.39 and 0.04 M solutions. $\delta^{27}\text{Al}$ changes only slightly in both cases. The signal moves 1.5 ppm over a temperature range of 120 °C to high

field. Figure 8 represents the change in δ and line width with temperature for the 0.39 M solution.

A decrease in the line width is noted with increasing temperature for the proton decoupled signal until it passes through a minimum at $\sim 10^\circ\text{C}$. Further increases in temperature results in a steady line broadening, and at 18°C the quintet coalesces. At 90°C there is only a difference of 9 cps between the line width of the two types of spectra.

In contrast, the line width of the ^{27}Al NMR signal shows a steady increase for the 0.04 M solution with decreasing temperature. This leads to a vanishing of the structured quintet at $\sim -70^\circ\text{C}$. The reasons for the breakdown of the fine structure for the two examples is different. It is the temperature dependent quadrupole broadening of the signal in the dilute solution which prevents the observation of the quintet structure at low temperature while intermolecular hydride exchange is responsible for the coalescence of the signal in the 0.39 M solution at room temperature.

The ^7Li NMR signal of LiAlH_4 in triglyme changes with temperature in a similar manner as for the other glycol ethers: A deshielding results with increasing temperature, however, the ^7Li line width is not strongly affected.

Diglyme and Triglyme Solutions of LiAlD_4 and $\text{LiAlH}_4/\text{LiAlD}_4$

Heřmanek *et al.* [4] showed that LiAlD_4 solutions have the same chemical shifts in diglyme as LiAlH_4 . They could not detect any fine structure due to Al-D coupling. Our ^{27}Al NMR spectra in diglyme and triglyme both show an isotope shift of the ^{27}Al NMR signal as well as a fine structure resulting from spin-spin coupling. The isotope shift found for LiAlD_4 in these solutions is 0.4 ppm (to lower frequency) — see Figure 10a. The Al-D coupling leads to a nonet, and the intensities found for the lines are in good agreement with the calculated ratio 1:4:10:16:19:16:10:4:1. Due to higher resolution of the signal in diglyme the value of $26.4 \pm (0.4)$ cps for $^1J(\text{Al-H})$ is most likely the better value than the 25 ± 1.1 cps found in triglyme. Using 175.5 cps for $^1J(\text{Al-H})$ and the magnetogyric ratios for ^1H and ^2H one may expect 27.9 cps for $^1J(\text{Al-D})$.

The intermolecular hydride exchange was demonstrated by the interaction of LiAlH_4 with LiAlD_4 . Under the concentration conditions for rapid

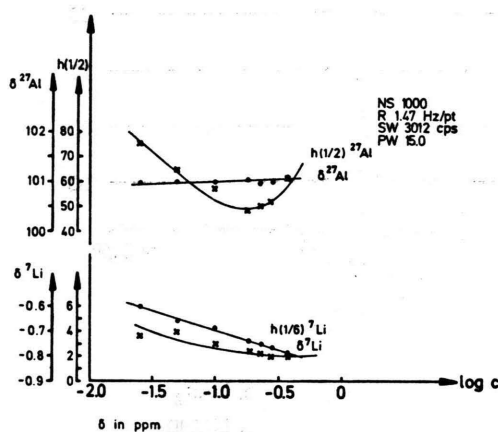


Fig. 8. Concentration dependence of the ^{27}Al NMR spectra at ambient temperature of LiAlH_4 in triglyme.

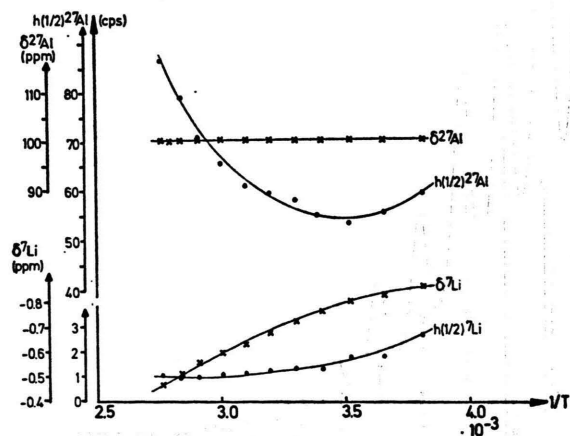
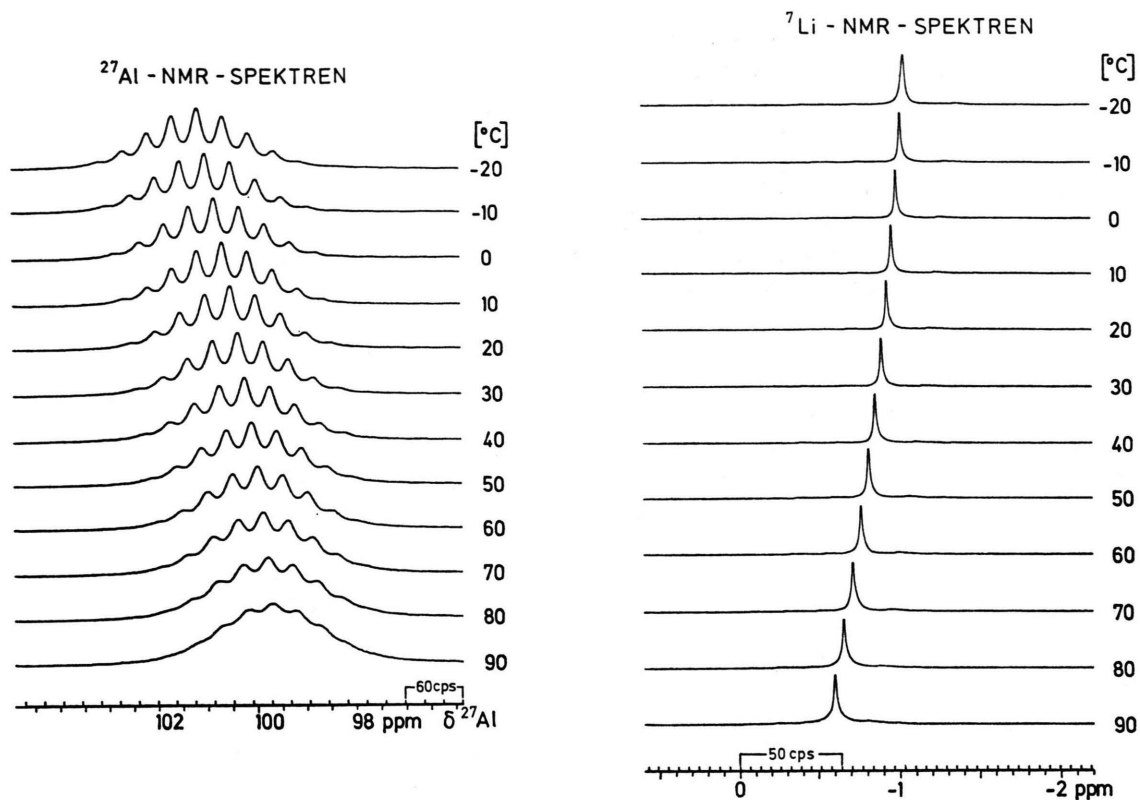
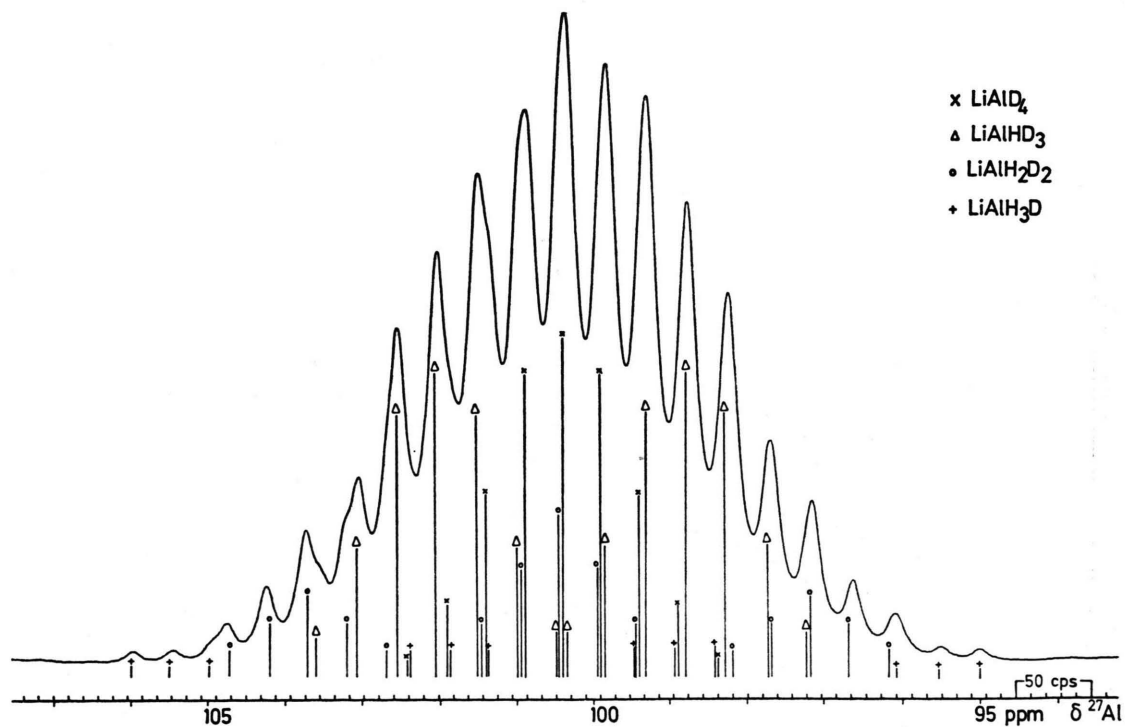


Fig. 9. Temperature dependence of chemical shift and line width for the ^{27}Al and ^7Li NMR signals of LiAlH_4 in triglyme.



a)



b)

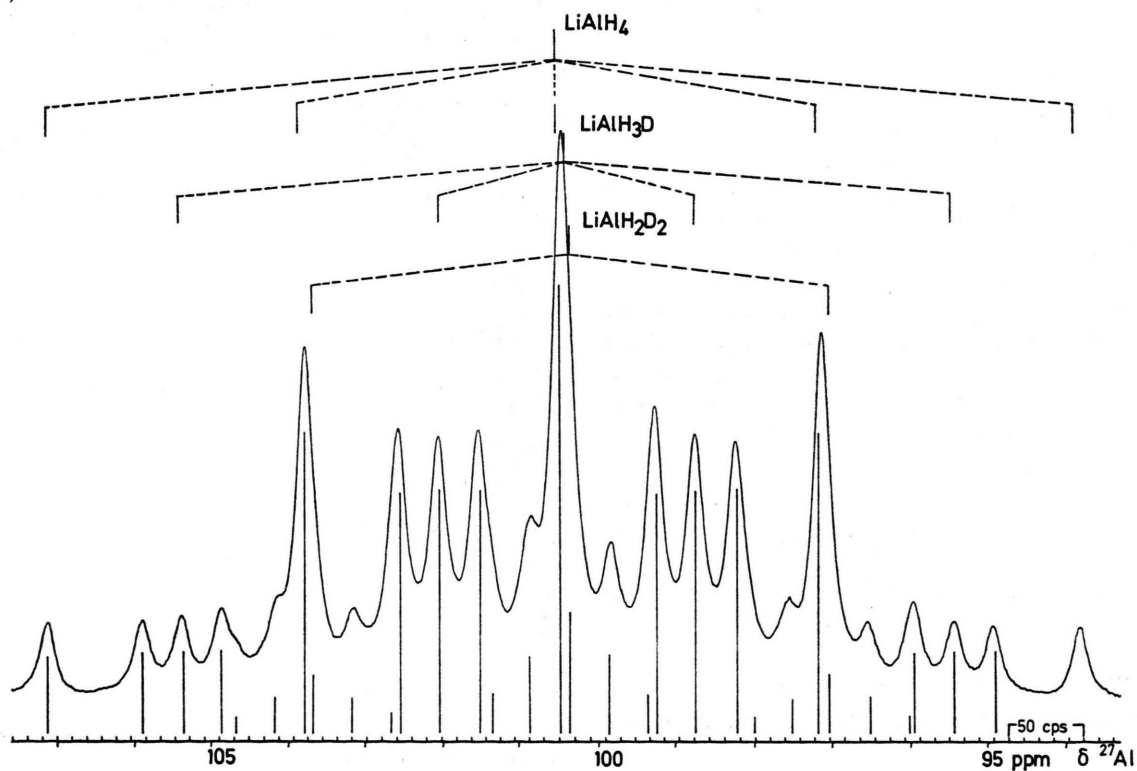
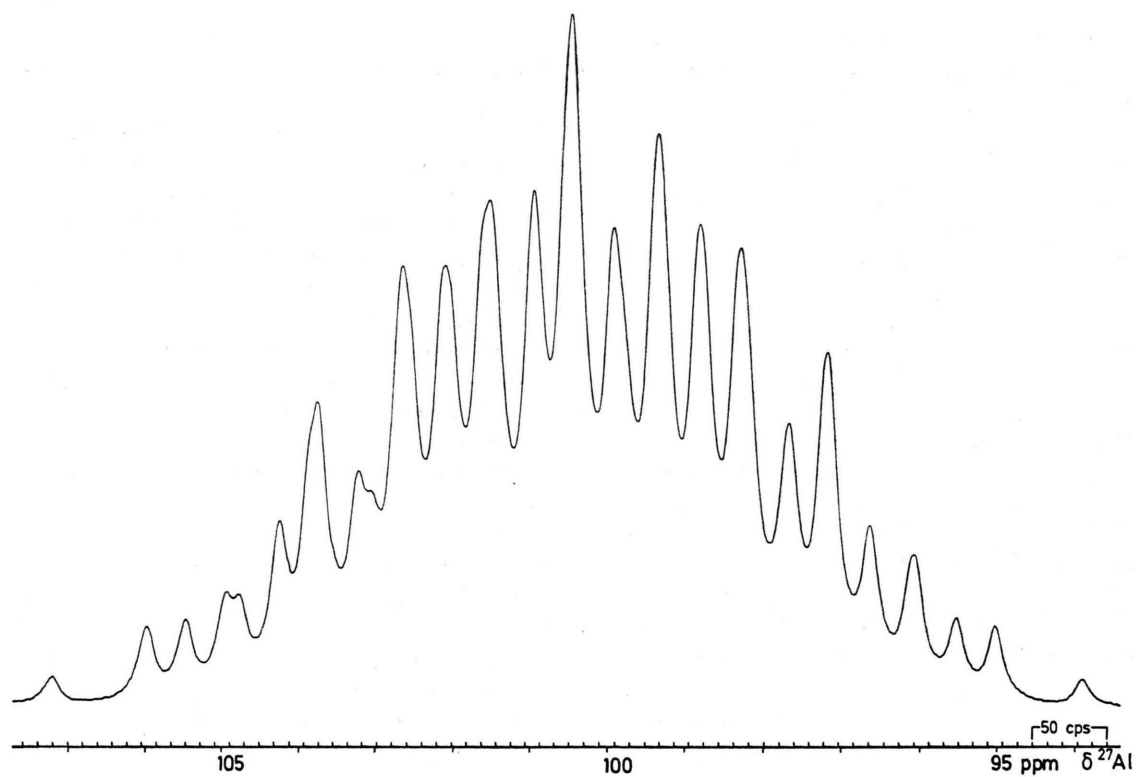


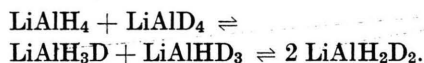
Fig. 10. ^{27}Al NMR spectra of LiAlD_4 and $\text{LiAlH}_4/\text{LiAlD}_4$ solutions (0.6 M) in diglyme at 303 K, the mixture being heated to 60 °C for 17 hours. a) LiAlD_4 ; b) $\text{LiAlH}_4:\text{LiAlD}_4 = 1:3$; c) $\text{LiAlH}_4:\text{LiAlD}_4 = 1:1$; d) $\text{LiAlH}_4:\text{LiAlD}_4 = 3:1$.

hydride exchange of LiAlH_4 in triglyme we observed rapid H/D scrambling in $\text{LiAlH}_4/\text{LiAlD}_4$ mixtures, and only a rather broad signal resulted. At more dilute solutions a LiAlH_4 quintet was recorded superimposed on a quartet whose middle lines were split into a triplet by Al–D coupling as expected for the presence of LiAlH_3D .

More information provide the ^{27}Al NMR spectra of such solutions in diglyme as a result of the smaller line width. Since H/D exchange is slow on the NMR time scale we heated the mixture to 60°C , and equilibrium was achieved in ~ 100 min. The spectra did not change on keeping the solutions for 17 h at this temperature. Figures 10b–d show the results.

Inspection of Fig. 10d reveals a quintet stemming from LiAlH_4 , the presence of LiAlH_3D as a quartet split into triplets of equal intensity due to a single Al–D bond. Moreover LiAlH_2D_2 is also recognised as a triplet superimposed on the LiAlH_4 ^{27}Al NMR signal, each line split into a quintet (ratio 1:2:3:2:1). The presence of LiAlHD_3 , a ^{27}Al doublet each split into a septet (1:3:6:7:6:3:1) can be deduced only from the intensity distribution. The presence of LiAlD_4 , however, cannot be recognised.

As the ratio of LiAlD_4 increases the proportions of LiAlH_2D_2 and LiAlHD_3 increase respectively in accord with the equilibria



This is indicated by the disappearance of the outer signals of LiAlH_4 for the $\text{LiAlH}_4:\text{LiAlD}_4 = 1:3$ reactions. Fig. 10b indicates the explanation of the experimental spectrum. It should be mentioned that the outermost signals of LiAlH_4 are observed only at higher amplification since its concentration is very low. Moreover it also appears that $^1J(\text{Al}-\text{H})$ decreases slightly with increasing D content in $\text{AlH}_{4-n}\text{D}_n^-$ and the same holds for $^1J(\text{Al}-\text{D})$ with increasing H content; however since the signals for the various species overlap, no reliable values can be given inspite of a resolution of 0.3 Hz per data point.

Attempts to deduce equilibrium constants from the data failed to give satisfying results; however an analysis of the signal heights approaches values expected for statistical scrambling.

Solutions of LiAlH_4 in Other Solvents

A number of ^{27}Al NMR spectra in different solvents have been recorded.

No change in the chemical shift ^{27}Al was observed for LiAlH_4 solutions in toluene/THF ($\text{LiAlH}_4:\text{THF}$ 1:2) comprising a concentration range from 3.9 to 0.03 M. We believe that the rather high viscosity is at least in part responsible for the enormous line width of 950 cps observed for the ^{27}Al NMR signal at the most concentrated solution; however, an intermolecular hydride exchange may be a contributing factor. No fine structure of this signal was observed at any concentration. However, a steady decrease of the line width results on dilution by recording the ^{27}Al NMR spectrum proton broadband decoupled. Nevertheless the line width never reached a point where one could expect a fine structure in the undecoupled spectrum although the line broadening which we observed at concentrations lower than 0.12 M may be an indication that a quintet structure might arise at even lower concentrations.

Considering the $\text{LiAlH}_4:\text{THF}$ -ratio it is of no surprise to find the ^7Li NMR signal at higher frequencies as compared to a THF solution. At high concentrations this signal is found nearer to tetra-coordinated Li and it moves 'downfield' on dilution. The final values observed are 0.96 ppm for the concentration range 0.5–0.03 M. The line width is not very much affected, and, importantly, there is no line sharpening on proton broadband decoupling. Fig. 11 summarizes the observed data.

The following results were obtained in the CW mode, and proton decoupling has not been possible under these circumstances. Spectra with unresolved fine structure will therefore not provide sensible line

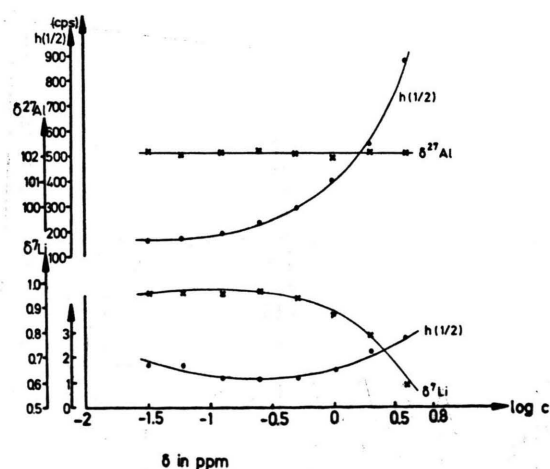


Fig. 11. Concentration dependence of chemical shifts and line width for LiAlH_4 in toluene/THF.

Table I. Chemical shifts $\delta^{27}\text{Al}$, and line width for some tetrahydridoaluminate in various solvents ($c = 0.2$ to 0.5 M).

	Solvent	$\delta^{27}\text{Al}$ [ppm]	$^1J(\text{AlH})$ [cps]	$h(1/2)$ [cps]
LiAlH_4	Tetrahydro- pyran	103	—	"390"
	2-Methyl- tetrahydro- furan	102	—	"460"
NaAlH_4	Tetrahydro- furan	97	175	220
	Monoglyme	101	170	195
	Diglyme	103	171	205
$(\text{C}_4\text{H}_9)_4\text{NAlH}_4$	Diglyme	100	172	104
	Benzene	106	—	210

width. Some results for NaAlH_4 and tetrabutylammoniumtetrahydridoaluminate are included in Table I.

Discussion

Inspection of the data presented in this study clearly indicate that solutions of LiAlH_4 in ethers vary with the nature of the ether. The conclusions drawn by Heřmanek *et al.* [4] are fully confirmed except for the interpretation of the unresolved signals in diethylether.

^7Li chemical shifts not only depend on the solvent used but also on the nature of the counter ion [8]. In this study the influence of the solvent, concentration and temperature on $\delta^7\text{Li}$ and the line width can be explained in terms of an equilibrium of type (1) and its rate of approach.

Since we are dealing here with only one species, LiAlH_4 , $\delta^7\text{Li}$ should reflect the charge density at this ion and therefore the mean coordination by the ethers. A better shielding would indicate a higher mean coordination number. According to our data (see also Table II) the following 'solvation' power

Table II. Chemical shift and line width for ^{27}Al and ^7Li at comparable concentrations at 243 K.

	Ether	THF	Mono- glyme	Di- glyme	Tri- glyme	c
$\delta^{27}\text{Al}$ [ppm]	103.3	99.6	101.2	101.5	101.5	
$h(1/2)\text{Al}$	400	88	25	17	80	
$\delta^7\text{Li}$ [ppm]	0.3	0.2	1.13	-1.13	-0.87	
$h(1/2)\text{Li}$	4	1.5	1.6	2	3.5	
$c\text{ M/l}$	0.06	0.16	0.125	0.15	0.39	

follows: diethylether < THF < triglyme < diglyme = monoglyme.

Since it has been shown that 4 molecules of THF coordinate with LiAlH_4 [13] the $\delta^7\text{Li}$ value for ether solutions of LiAlH_4 suggests the same coordination.

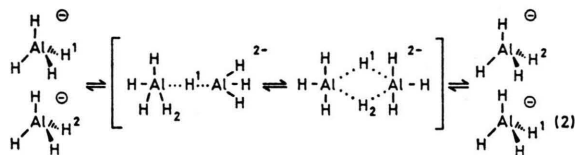
Since these ethers do not associate with AlH_4^- tetracoordinated Li cations are indicated. The considerable high field shift of the ^7Li NMR signal in monoglyme and diglyme is in consonance with hexacoordinated lithium, and this requires of course 3 molecules of monoglyme or two molecules of diglyme, these ethers acting as di- and tridentate ligands, respectively. From this point of view one can readily understand the ^7Li chemical shift for the triglyme solution. Two molecules of this ether are required for hexacoordinating Li^+ but none of these can exert its maximal denticity. This, most likely, will result in a reduced stability of the complex formed.

As can be learned from the data in Table II there is a correlation between $\delta^7\text{Li}$ and the line width of the ^{27}Al NMR signal. A better shielded Li corresponds to a smaller ^{27}Al line width. Therefore, solvation of the Li ion plays an important though certainly not the only role. One may expect that the dielectric constant of the solvent will also be of importance. However, the dielectric constants of the ethers investigated do not differ greatly and they are fairly small. Ion pairs and triple ions are therefore the dominant species present in solution in the concentration range investigated. The influence of hexacoordinated Li^+ on AlH_4^- is most likely less pronounced on solvent separated ion pairs or triple ions than with Li^+ at coordination less than 6. Thus triglyme and THF as solvents are dissimilar for the shielding of Li but comparable in its influence of the ^{27}Al line width. This width is about four times as large as for monoglyme. Since ^1H broad band decoupling has no influence on the ^7Li line width it seems that the interaction of the Li-cations and AlH_4^- anions in the ion pair and triple ions present in these solutions [13] is less efficient in these solvents than in the diglyme allowing a more rapid quadrupole relaxation.

Intermolecular hydride exchange occurs also, as observed readily at higher concentrations of LiAlH_4 in monoglyme, while much lower concentrations are necessary in triglyme ($\sim 0.3\text{ M}$ at 303 K) and diethylether ($\sim 0.15\text{ M}$) [6]. This process is accelerated with increasing temperature but is still slow on the

²⁷ Al: THF-solutions	NS 200 bzw. 800	PW 15	SW 2703	O 1 12722	R 1.111
⁷ Li: THF-solutions	NS 80	PW 10	SW 250	O 1 9108	R 0.122
²⁷ Al: Monoglyme-solutions	NS 800	PW 15	SW 950	O 1 11950	R 0.46
⁷ Li: Monoglyme-solutions	NS 100	PW 10	SW 500	O 1 9206	R 0.244
²⁷ Al: Diglyme-solutions	NS 100	PW 15	SW 2730	O 1 12722	R 1.32
⁷ Li: Diglyme-solutions	NS 400	PW 10	SW 250	O 1 9061	R 0.12
²⁷ Al: Triglyme-solutions	NS 1000	PW 15.0	SW 3012	O 1 12939	R 1.47
⁷ Li: Triglyme-solutions	NS 20	PW 24	SW 500	O 1 9200	R 0.12

NMR time scale for a 0.41 M LiAlH₄ solution in diglyme. Hydride exchange according to (2) between two negatively charged species would certainly not be a favoured process. However, one should bear in mind that this is not an exchange between free anions but rather an exchange in the realm of triple ions, where the cation/anion interaction reduces the effective charge at the anion, and therefore makes the exchange according to (2) more feasible.



Taking this process into account and the formation of triple ions the temperature dependence of the line width observed for ²⁷Al can be understood, since line narrowing will result with increasing temperature due to the temperature dependence of T₁ and line broadening due to triple ion formation and hydride exchange, the latter becoming more prominent with increasing concentration and temperature.

It follows from this study that diglyme is the solvent of choice if properties resulting from a rather undisturbed AlH₄⁻ are to be investigated.

Experimental Part

Commercial grade LiAlH₄ was recrystallized from ether or diglyme before use and desolvated in a high vacuum system. Solutions were prepared using purified ethers, freshly distilled from LiAlH₄. Stock solutions were prepared and analysed for Li, Al and H⁺.

The chemical shifts refer to Al(OH₂)₆³⁺, 1 M aqueous solution of Al(NO₃)₃, and to Li(OH₂)₆⁺ in an 1 M LiCl solution. A minimum quantity of C₆D₆ was added to the solutions as lock and for optimizing field homogeneity. As expected, no NOE was observed both for ²⁷Al and ⁷Li. The conditions for recording the spectra are given in the following sequence: Number of scans (NS), pulse angle (PW in μs), sweep width (cps), offset (cps), resolution R (cps per data point). The frequencies used were 52.14 MHz for ²⁷Al and 77.779 MHz for ⁷Li using a BRUKER WP 200 multinuclei FT-NMR spectrometer and 10 mm tubes. CW experiments were carried out using a VARIAN HA 100 instrument and a ¹⁴N probe head. To match the resonance frequency of ²⁷Al the field strength had to be reduced.

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