An Investigation of $AlCl_3$ Solutions in Ethers by ^{27}Al NMR Spectroscopy

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^{27}Al NMR Spectra, Aluminium Compounds

^{27}Al NMR studies of $AlCl_3$ solutions in diethyl ether reveal the presence of $AlCl_4^-$ at high concentrations. This ion can also be recognized besides $AlCl_3 \cdot OR_2$ at low temperature in dilute solutions, while at 25 °C a single signal is observed, which represents the average of all species in solution. More extensive dissociation of $AlCl_3$ results in tetrahydrofuran. The main species in equilibrium with one another are $AlCl_3 \cdot 2THF$, $AlCl_4^-$ and $AlCl_2(THF)_2^+$.

Nearly quantitative dissociation to yield $AlCl_4^-$ and $[AlClL_5]^{2+}$ occurs in dilute solutions of $AlCl_3$ in monoglyme (L reprents one oxygen donor atom); at higher concentration an adduct $AlCl_3 \cdot L$ with Al in a tetrahedral environment is also present. This trend towards extensive dissociation is also observed in the solutions of $AlCl_3$ in diglyme and triglyme. Relative peak areas are in agreement with the formation of a 1:1 electrolyte $[AlCl_2L_4]^+AlCl_4^-$ in diglyme, whereas additional dissociation into $[AlClL_5]^{2+}$ and $AlCl_4^-$ occurs in triglyme.

Nonaqueous solutions of aluminium compounds have received increasing attention [1] since it was found in 1902 by Plotnikov [2] that such solutions can be used for aluminium electroplating [3]. Ethers as solvents were introduced by Brenner *et al.* [4] in their classical studies using a hydridic electrolyte prepared from $AlCl_3$ and LiH or $LiAlH_4$, respectively. This prompted an investigation of the species present in solution by conductivity measurements and IR spectroscopy. More recently, NMR methods have also been used. ^1H NMR data have shown, for example, that $AlCl_3$ in acetonitrile dissociates completely into $[Al(NCCH_3)_6]^{3+}$ and $AlCl_4^-$ [5, 6]. However, if rapid exchange (on the NMR time scale) of solute and solvent molecules occurs it is difficult to obtain reliable data on the solvation of the adducts and cations that are present in solution. Under these circumstances ^{27}Al NMR spectroscopy may be more helpful since it permits the observation of the central atom in the adducts and ions formed in these systems.

So far this latter method has been used widely in the study of aqueous solutions of aluminium salts [7]. It is, of course, applicable also for nonaqueous systems, and indeed the first two studies of this kind [8, 9] describe the spectra of aluminium chloride and bromide in ether or tetrahydrofuran (THF) as solvents. Based on these studies these solutions were regarded as solutions of molecular Al_2Cl_6 or Al_2Br_6, *i.e.*, no complex formation was assumed. In contrast, Wolfgardt [10] concluded that $AlCl_3$, dissociates in THF forming $AlCl_4^-$ although the main species present was $AlCl_3 \cdot 2THF$.

With the advent of high resolution PFT–NMR instruments and their higher resolution and sensitivity, solute species present at fairly low concentrations can also be detected, as shown by Derouault *et al.* [11] in a ^{27}Al NMR study of $AlCl_3$ in THF. Similar investigations of chloroalanes in various ethers, which we will publish shortly, prompted us to include also solutions of $AlCl_3$ in various ethers. We report here on the dependence of their ^{27}Al NMR spectra on concentration and – in part – temperature.

Aluminium Chloride and Bromide Solutions in Ethers

Ethers are excellent nonprotic solvents for aluminium halides except for AlF_3. Some of these solutions have already been studied by ^{27}Al NMR spectroscopy as have their ether adducts in aromatic hydrocarbons. These data are summarized in Table I which also contains ^{27}Al chemical shifts and line widths at half heights observed in our laboratory obtained on a CW instrument. We will discuss these data briefly before going into more detail for aluminium chloride solutions in five different ethers, which have been investigated by PFT–NMR methods.

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Table I. ^{27}Al NMR data of $AlCl_3$ and $AlBr_3$ in benzene or ether solutions as well as of AlX_3·ether adducts in benzene solution. δ-Values refer to 1 M aqueous Al^{3+} solutions; positive signs indicate signals at higher frequency.

Compound	Concentration Solvent	Molarity	$\delta^{27}Al$ [ppm]	h (1/2) [Hz]	Lit.	Compound	Concentration Solvent	Molarity	$\delta^{27}Al$ [ppm]	h (1/2) [Hz]	Lit.
Al_2Cl_6	C_6H_6	–	98	185		Al_2Br_6	C_6H_6	–	85	132	–
	$C_6H_5CH_3$	–	91	330	[9]		C_6H_6	–	75	510	[8]
$AlCl_3 \cdot OEt_2$	C_6H_6	–	98	182		$AlBr_3 \cdot OEt_2$	C_6H_6	–	93	118	
			50	160	[8]				47	210	[8]
			98		–						
$AlCl_3 \cdot OEt_2$ + 1 OEt_2	C_6H_6	–	91	210		$AlBr_3 \cdot OEt_2$ + 1 OEt_2	C_6H_6	–	98	121	
$AlCl_3$	OEt_2	–	105	145		$AlBr_3$	OEt_2	–	96	100	[9]
	OEt_2	–	105	110	[9]						
	OEt_2	1 M	100.1	126	[22]		OEt_2	1 M	91.7	–	[22]
	OEt_2	2 M	105	126	[8]		OEt_2	1.5 M	95	104	[8]
	$O(iPr)_2$	–	108	106							
	OBu_2	–	115	250			OBu_2	–	94	200	
	THF	–	64	270			THF	–	56	112	
	diglyme	–	29	broad	–		diglyme	–	11	broad	
			105	40					78	27	
$AlCl_3 \cdot THF$*	–	–	98	–	[14]						
$AlCl_3 \cdot 2THF$	C_6H_6	–	69	260							

Et = C_2H_5; *i*Pr = $CH(CH_3)_2$, Bu = *n*-C_4H_9, diglyme = $CH_3O(CH_2CH_2O)_2CH_3$, THF = OC_4H_8.
* $\delta^{27}Al$ of the molten compound.

Both $AlCl_3$ and $AlBr_3$ dissolve as dimers in aromatic hydrocarbons. These molecules contain tetrahedrally coordinated aluminium atoms, the two tetrahedra sharing a common edge. This structure is retained in crystalline $Al_2Br_6 \cdot C_6H_6$ [12]. Therefore the $\delta^{27}Al$ values observed in benzene solution for these halides correspond to coordination number 4. The aluminium resonance of Al_2Br_6 is found at a lower frequency than that of Al_2Cl_6. There is a difference of about 7 ppm for Al_2Cl_6 and 10 ppm for Al_2Br_6 in benzene solutions between our observations and literature values. Also, the reported line widths do not correspond closely with our measurements. The latter vary more strongly with concentration than the former, and this may explain the discrepancies.

Aluminium chloride and bromide form 1 : 1 adducts with diethyl ether, $AlX_3 \cdot O(C_2H_5)_2$, and the crystal structure of the chloride has been determined [13]. Therefore, it is very likely that this entity also exists in benzene solution, *e.g.* $\delta^{27}Al = 98$ ppm for the chloride and 93 ppm for the bromide can be assigned to these species. If one mole of ether is added to a solution of $AlX_3 \cdot O(C_2H_5)_2$ in benzene no change in chemical shift is observed for $AlCl_3 \cdot O(C_2H_5)_2$ but a significant broadening of the line occurs. This most likely indicates an exchange of the ether molecules. In the case of $AlBr_3 \cdot (OC_2H_5)_2$ the ^{27}Al NMR signal is shifted even further to the high frequency side as compared with Al_2Br_6 and $Br_3Al \cdot O(C_2H_5)_2$; however, this does not seem to be associated with an increase in line width. $AlCl_3 \cdot THF$ shows a similar ^{27}Al shift as $AlCl_3 \cdot O(C_2H_5)_2$ [14]. $AlCl_3 \cdot 2THF$ [15] dissolved in benzene results in a rather broad ^{27}Al NMR signal at 69 ppm. This upfield shift relative to $AlCl_3 \cdot O(C_2H_5)_2$ can be attributed to pentacoordinated aluminium atoms.

The agreement of the $\delta^{27}Al$ value observed for ether solutions of the two aluminium halides reported in the literature and our values is quite satisfactory. The presence of a single signal was noted for diethyl ether solutions, and this same holds for solutions in diisopropyl or dibutyl ether. Solutions of $AlCl_3$ and $AlBr_3$ in THF are dominated by a single signal in the δ-range of pentacoordinate aluminium [17]. However, two signals result if diglyme is used as a solvent. One signal at high frequently is quite sharp and observed in the range for tetracoordinated aluminium; it can be attributed to AlX_4^- [7]. The second signal corresponds to a highly shielded

aluminium nucleus. Its $\delta^{27}Al$ value would be in agreement with hexacoordinated aluminium. Since a tetrahaloaluminate ion is present the second signal should result from a cationic species. These observations suggested a more detailed study of these solutions.

Aluminium Chloride Solutions in Diethyl Ether

The formation of $AlCl_3 \cdot O(C_2H_5)_2$ from aluminium chloride and ether is associated with a heat of formation $\Delta H = 77.7 \pm 9.8$ kJ/mol [18, 19]. In addition it has been observed that such ether solutions conduct electricity fairly well, the specific conductivity being $\varkappa = 1.2.10^{-2}\ \Omega^{-1}\,cm^{-1}$ [20]. This led to the suggestion of an equilibrium described by eq. (1). The species $AlCl_3$ and $AlCl_2^+$ are, of course, solvated by the donor solvent. As far as we are aware no detailed

$$2\ AlCl_3 \rightleftharpoons AlCl_4^- + AlCl_2^+ \qquad (1)$$

spectroscopic data are available to fully support this equilibrium. In particular no firm evidence has yet been presented regarding the nature of the ions present, although those described by eq. (1) are the most likely ones.

Reported ^{27}Al NMR data revealed only the presence of $AlCl_3 \cdot O(C_2H_5)_2$ in ether solution. However, as shown in Figs. 1 and 2, additional signals can be observed with NMR instruments of high magnetic field strength. At rather high concentrations a second signal on the high frequency (low field) side of the $AlCl_3 \cdot O(C_2H_5)_2$ signal at 102.3 ± 0.2 ppm can be detected. This additional signal is fairly sharp, and in conjunction with a chemical shift of 105 ppm is good evidence for the ion $AlCl_4^-$. This signal disappears on dilution as shown in Fig. 1.

The signal assigned to $AlCl_3 \cdot O(C_2H_5)_2$ sharpens on dilution and passes through a shallow minimum at ~ 0.25 M. There were some solutions where a weak signal at $\delta^{27}Al = 98$ ppm was noted. This signal most likely arises from the cationic species necessary to complement the $AlCl_4^-$ ion.

This conclusion is corroborated by the ^{27}Al NMR spectra recorded at several temperatures. Fig. 2 shows three well defined signals at −60 °C for a 0.325 M $AlCl_3$ solution: a sharp signal at $\delta^{27}Al = 104.1 \pm 0.2$ ppm, and two much broader signals at 98 and 95.8 ppm. On warming these signals merge into a signal line with $\delta^{27}Al = 102.1$ ppm. Therefore the chemical shift assigned to $AlCl_3 \cdot O(C_2H_5)_2$ actually represents a signal which not only involves the most likely equilibrium depicted by eq. 1 but also solvent exchange processes since the cation must be tetracoordinate based on its chemical shift. The change in line width – a decrease with increasing temperature – would correspond with the temperature dependent line narrowing being more effective than the line broadening due to exchange processes.

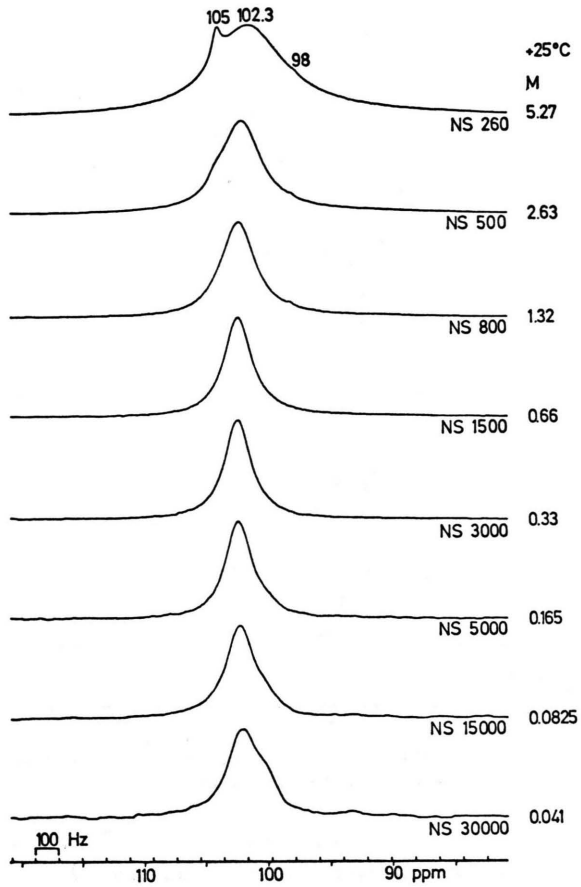


Fig. 1. ^{27}Al NMR spectra of $AlCl_3$ in ether at various concentrations at 27 °C. The number of scans as well as the line widths at half height are given. The resolution was 3.7 Hz per data point. The spectra were plotted with the most intense peak having a y-coordinate equal to 5 cm.

The law of mass action favours ion formation at high dilution. No ^{27}Al NMR signals may, however, be observed for the ionic species due to the Cl^- exchange. The line broadening on dilution supports this assumption.

Considering the merging of the two signals assigned to $AlCl_3 \cdot O(C_2H_5)_2$ and the cation, tentatively identified as $AlCl_2[O(C_2H_5)_2]_2^+$, before the $AlCl_4^-$ signal

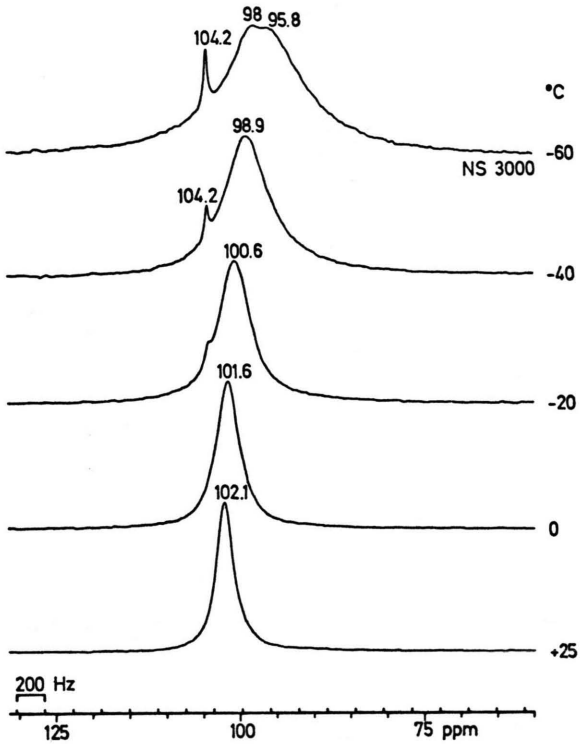


Fig. 2. ^{27}Al NMR spectra for a 0.325 M $AlCl_3$ solution in ether recorded at various temperatures.

disappears leads us to suggest that at least two processes are involved i) an exchange according to eq. (1), ii) either an association or exchange represented by eq. (2). This process

$$Cl_3Al \cdot OR_2 + Cl_2Al(OR_2)_2]^+ \rightleftharpoons$$

$$R_2O\text{–}\underset{Cl}{\overset{Cl}{Al}}\text{–}Cl\text{–}\underset{Cl}{\overset{Cl}{Al}}\text{–}OR_2\Big]^+ + R_2O \qquad (2)$$

$R = C_2H_5$

would also account for the observation of the $AlCl_4^-$ signal at high concentration since the fraction of $AlCl_3 \cdot OR_2$ present in equilibrium should increase with increasing concentration and, therefore, the rate of exchange involving the equilibrium described by eq. (2) will increase. Other equilibria cannot be excluded, but those suggested allow a qualitative description of the features observed in the ^{27}Al NMR spectra of $AlCl_3$ solutions in ether.

Aluminium Chloride Solutions in THF

This system has already been studied by Derouault *et al.* [11] by vibrational and ^{27}Al NMR spectroscopy. Our results are supplementary. The concentration range studied was 1.3–0.025 M. Three ^{27}Al NMR signals can be observed at concentrations > 0.1 M: the most intense one at $\delta^{27}Al = 64.4 \pm 0.3$ ppm attributable to pentacoordinated Al in $AlCl_3 \cdot 2THF$, a fairly sharp line at 103.5 ± 0.2 ppm resulting from the presence of $AlCl_4^-$, and a rather broad signal at ~19 ppm which represents a hexacoordinate aluminium environment. The line width of the $AlCl_4^-$ signal increases considerably on dilution and the same seems to hold for the 19 ppm signal. However, due to its broadness, it quickly disappears in the noise and no reliable line width can be measured. For the same reason we found it difficult to determine the intensity ratios for the $AlCl_4^-$ and the cationic Al species. Measurements at low temperature are in favour of a 1:1 ratio in accord with the results by Derouault *et al.* [11]. The line width of the 64 ppm signal decreases on dilution and remains fairly constant at $c < 0.1$ M.

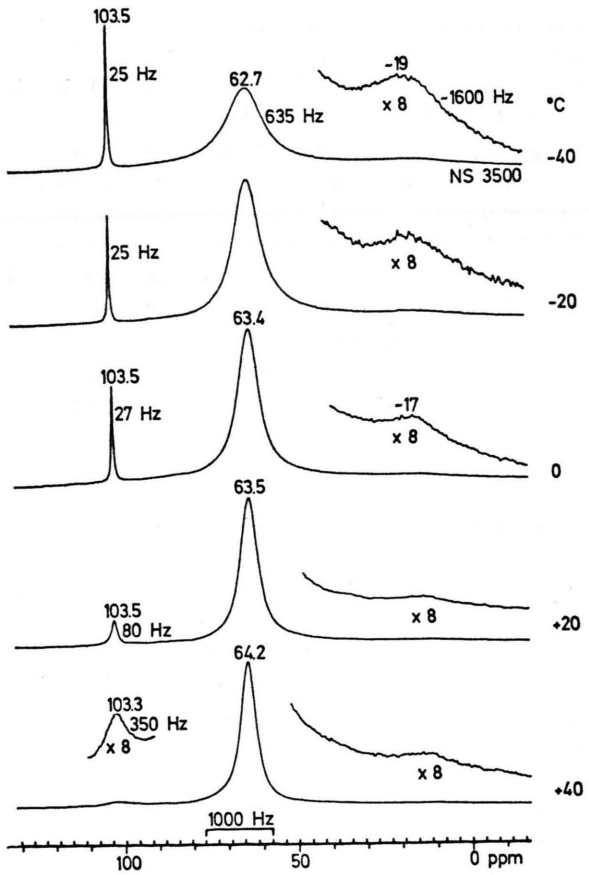


Fig. 3. ^{27}Al NMR spectra of a 0.2 M $AlCl_3$ solution in THF at various temperatures.

Table II. ^{27}Al Relaxation times T_1 measured for the $AlCl_4^-$ of an 0.2 M $AlCl_3$ solution in THF.

T [°C]	−30	−20	−10	0	20	30	40
$T_1 \cdot 10^{-2}$ [s]	7.0	6.8	5.3	1.5	0.53	0.57	0.30
h_{calcd} [Hz]	4.6	4.7	6.0	6.9	61	55.6	105
h_{found} [Hz]	24	25	27	29	84	180	350
Δh [Hz]	19	20	21	22	23	124	245

Fig. 3 represents ^{27}Al NMR spectra of a 0.2 M $AlCl_3$ solution in THF taken at various temperatures. Surprisingly, the line width of the $AlCl_4^-$ signal remains rather sharp at temperatures below 0 °C while those of the other two signals increase considerably. Although no T_1 measurements were possible for these latter signals we assume that the line broadening reflects primarily the expected temperature dependence. However, T_1 measurements were possible for the $AlCl_4^-$ species, and the results are given in Table II.

These data suggest that exchange processes contribute significantly to the line width, especially with increasing temperature. This should therefore hold also for the other two species observed and supports the interpretation of previous data [11] that the system is best described by the following equilibria

$$AlCl_3 \cdot THF + THF \rightleftharpoons AlCl_3 \cdot 2THF \quad (3)$$

$$2\ AlCl_3 \cdot 2THF \rightleftharpoons AlCl_4^- + AlCl_2(THF)_4^+ \quad (4)$$

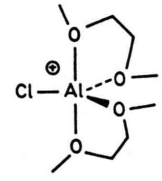
It should be noted that the exchange signal between the species $AlCl_4^-$ and $AlCl_2(THF)_4^+$ ($\delta^{27}Al = 86$ ppm) is to be expected in the 60 ppm region and would therefore coincide with the signal for $AlCl_3 \cdot 2THF$.

Aluminium Chloride Solutions in Monoglyme

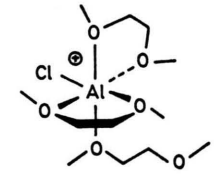
The solubility of $AlCl_3$ in monoglyme is rather low as compared with that in ether, tetrahydrofuran or diglyme. At 25 °C saturation is achieved at 0.7 M. Therefore only the rather narrow concentration range spanning 0.66 to 0.006 M could be studied by ^{27}Al NMR spectroscopy. The spectra are characterized by two prominent signals (see Fig. 4) at δ 104.2 and ~25.5 ppm. The former can be assigned to $AlCl_4^-$ based on both its $\delta^{27}Al$ value and its line width. The second signal, observed at much lower frequency (higher field) results from either a penta- or hexacoordinated aluminium species. We assign it to a cationic species. Taking into account the intensity ratios of the two signals which span a range from 2:1.7–1.0 one may deduce that the preferred dissociation is best described by eq. (5) (neglecting solvation).

$$3\ AlCl_3 \rightleftharpoons 2\ AlCl_4^- + AlCl^{2+} \quad (5)$$

The cation signal is rather broad, about three times the line width of the $AlCl_4^-$ signal in consonance with a rather low symmetry at the metal center. Since monoglyme may act as a bidentate ligand, the following structural formulae **A** and **B** can be suggested for this cation.



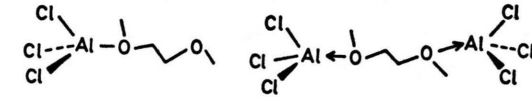
A



B

No pentacoordinated Al species showing a $\delta^{27}Al$ value <40 ppm is known at present. Therefore it is more likely that the cation is hexacoordinated.

In addition, a third ^{27}Al NMR signal can be detected at higher concentrations. The value $\delta^{27}Al = 90 \pm 1$ ppm corresponds to a tetracoordinated species. The signal itself is rather broad, about 10 times broader than that of $AlCl_4^-$. We attribute this signal to one of the following two adducts:



The line widths of all these signals do not change significantly on dilution. However, the signal at 90 ppm disappears for the most dilute solutions. This would be in agreement with increasing dissociation on dilution. Taking the spectral data for a 0.05 and 0,025 M solution an equilibrium constant

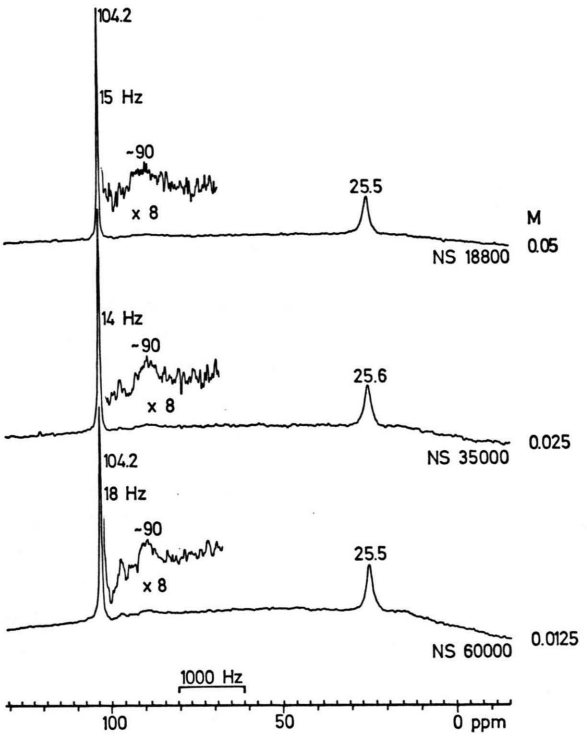


Fig. 4. ^{27}Al NMR spectra of $AlCl_3$ solutions in monoglyme.

$K = [AlCl^{2+}] \cdot [AlCl_4^-]^2/[AlCl_3]^3 = 16.3 \pm 0.5$ can be calculated from the signal intensities.

Fig. 5 depicts the ^{27}Al NMR spectrum of a 0.05 M $AlCl_3$ solution obtained in the temperature range from —10 °C to 70 °C. The $AlCl_4^-$ and AlCl (solv.)$^{2+}$ line width decreases as the temperature is increased. No change in the δ values was observed. Therefore no rapid exchange between these species is observed at higher temperature. However, two more signals appear besides the 90 ppm signal: a rather sharp one at 97.5 ppm and a broad signal at ~16 ppm. The latter has occassionally also been observed in the concentration studies. It may be due to hexacoordinated Al(solv.)$^{3+}$. It disappears on returning to lower temperatures. This does not hold for the signal at 97 ppm, which may therefore indicate ether cleavage.

Aluminium Chloride Solutions in Diglyme

A saturated solution of $AlCl_3$ in diglyme is 1.7 M at 25 °C. Its ^{27}Al NMR spectrum shows only two signals: a sharp signal at $\delta^{27}Al = 103.4$ ppm arising from the presence of $AlCl_4^-$ and a rather broad one

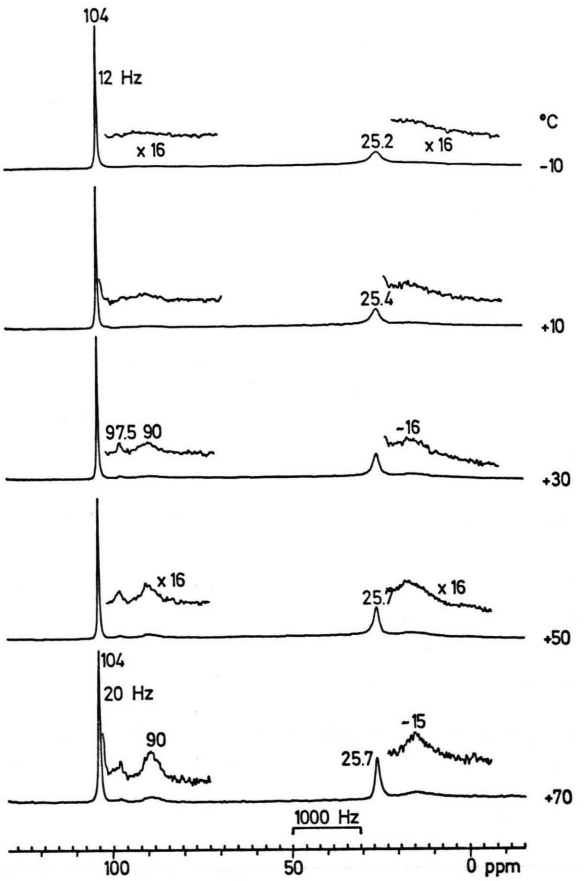
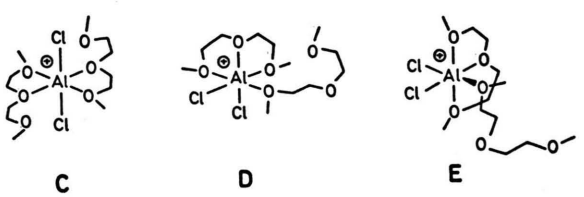


Fig. 5. ^{27}Al NMR spectra of $AlCl_3$ solutions in monoglyme at various temperatures, c = 0.05 M.

at 25 ppm. The intensity ratio was 1.3 – 1:1. Therefore dissociation occurs primarily according to eq. 1; $AlCl_3$ and Cl_2Al^+ are, of course, solvated by diglyme. The chemical shift of the cationic species suggests hexacoordination (see Fig. 6). Most likely the structure of the latter can be described by several formulae, C–E, which indicate solvent exchange. On dilution, the $AlCl_4^-$ line width runs through



C D E

a minimum at a 0.4 M concentration, while that of the signal at 25 ppm has its minimum value for a 0.21 M solution. In addition to the two signals

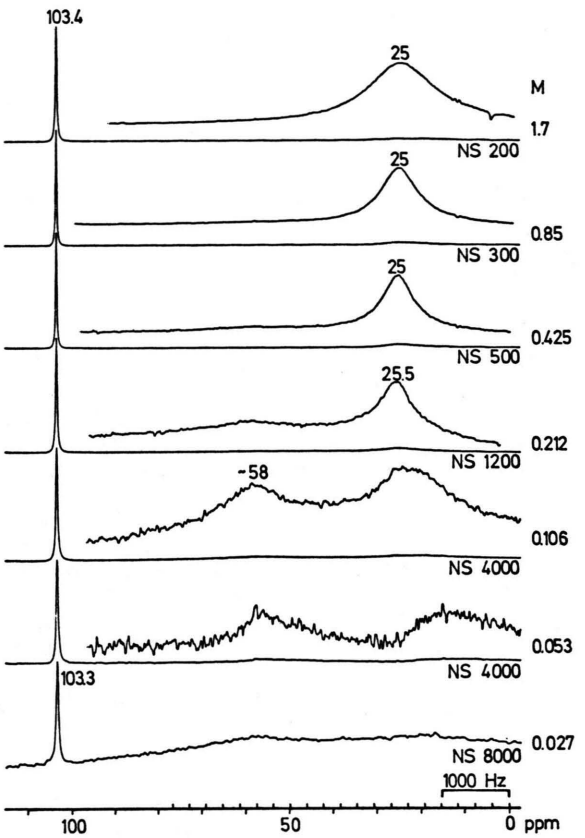
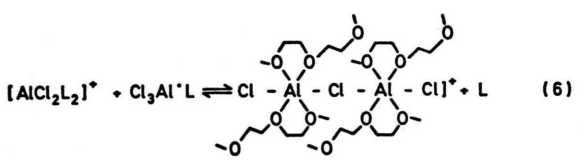


Fig. 6. ^{27}Al NMR spectra of an $AlCl_3$ solution in diglyme.

mentioned above another one at ~60 ppm appears in a 0.21 M solution. Its δ value suggests a pentacoordinated species. We assign it to a neutral moiety because the intensity for the signals at 103.4 and 25 ppm remained in the ratio 1:1. On further dilution the 25 ppm signal moves to lower frequencies ("upfield" to 15 ppm), while the signal at ~60 ppm seems to move slightly downfield. This observation may be explained by the following equilibria:



$$2\ AlCl_3 \cdot L \rightleftharpoons AlCl_2L_2^+ + AlCl_4^- \quad (7)$$

$L = H_3C\text{-}O(CH_2\text{-}CH_2O)_2CH_3$

That exchange processes of this kind as well as those involving $AlCl_4^-$ occur in these solutions is demonstrated by the temperature dependence of the ^{27}Al NMR spectra measured on a 0.2 M solution. The 25.2 ppm signal sharpens on passing from 10 °C to 40 °C (from 430 to 390 Hz) and then broadens considerably to 1000 Hz at 70 °C. It also appears that this signal splits into two (~25 and ~18 ppm) at 60 °C and merges again into a rather broad signal at 80 °C.

The ^{27}Al signal arising from $AlCl_4^-$ shows a line width at half height of 15 Hz up to 40 °C. A further increase in the temperature causes considerable line broadening, to 20 Hz at 50 °C, to 50 Hz at 70 °C and to 83 Hz at 80 °C. This indicates exchange according to the two main equilibria which describe the solution state of $AlCl_3$ in this solvent.

Aluminium Chloride Solutions in Triglyme

The concentration range 1.4 to 0.044 M of $AlCl_3$ in triglyme has been studied by ^{27}Al NMR spectroscopy. The system behaves rather similar to $AlCl_3$ in diglyme. Two signals dominate the spectrum: a signal arising from $AlCl_4^-$ at 103.1 ppm, and a rather broad signal at ~25 ppm which can be attributed to a hexacoordinated cationic aluminium species. In contrast to the solution in diglyme we observe that more $AlCl_4^-$ is formed in triglyme than would correspond to a simple chloride ion transfer according to eq. (5).

Thesefore dissociation according to eq. (5) – solvation omitted – must also be considered besides eq. (7) and both cations $AlCl_2^+$ and $AlCl^{2+}$ seem to be represented by the 25 ppm signal, the latter moving to 23 ppm for the most dilute solutions.

Discussion

^{27}Al NMR spectroscopy has revealed the presence of ionic species in $AlCl_3$ solution in all the ether solution studied. Such species have previously been postulated for ether solutions in order to explain their specific conductivity. Moreover, they have been directly observed for THF solutions by both vibrational and ^{27}Al NMR spectroscopy [10, 11, 14].

The present data allow a comparison for five solvents of the ether type. Dissociation into $AlCl_4^-$ and solvated $AlCl_2^+$ and/or $AlCl^{2+}$ increases in the series ether < THF < diglyme < triglyme. Since the dielectric constants of the solvent do not change dramatically within this series it appears that solvation of the cation plays an important role, and the

chelating effect of the glycol ethers is an inherent factor. Thus the molecular addition product $Cl_3Al \cdot O(C_2H_5)_2$ dominates in the ether solutions of $AlCl_3$, while solutions in diglyme are characterized by the ionic species $AlCl_4^-$ and $AlCl_2^+$.

The ^{27}Al NMR data also reveal the existence of exchange processes. At high concentrations, chloride ion exchange involves primarily the cationic and the neutral species. At higher temperatures and in the more dilute solutions, $AlCl_4^-$ is also involved in this process; however, at this time it cannot yet be decided whether or not this is due to a chloride exchange involving the dissociation equilibrium described by eq. (7) or the dissociation of

$$AlCl^- \rightleftharpoons AlCl_3 + Cl^- \qquad (8)$$

the tetrachloroaluminate as noted by eq. (8). This decision requires the determination of the rates of the various reactions involved. Moreover, a careful analysis of the rather broad lines will be necessary in order to ascertain the possibility of only a single species for the cation and the adduct.

Dissociation of $AlCl_3$ in other nonprotonic nonaqueous solvents has also been observed. This process in acetonitrile is best described by $3\,AlCl_3 \rightleftharpoons 2\,AlCl_4^- + AlCl^{2+}$, the cation being hexacoordinated to form $AlCl(NCCH_3)_5^{2+}$ [6]. Similarly, carbonic esters induce dissociation of $AlCl_3$ with the formation of $AlCl_4^-$ and $[AlCl(ester)_3]^{2+}$ [22]. These solvents are, however, either more basic or more polar than ethers and both stronger solvation and coordination may therefore be expected. The drastic change in the solution state of $AlCl_3$ in the investigated ethers suggests that the solution state of hydrides such as the halogenoalanes, in particular chloroalanes and also of AlH_3 can be expected to be markedly different and thereby affecting their reducing properties. We will refer on this topic in a subsequent report.

Experimental

Aluminium chloride was doubly sublimed before use, and dissolved under vacuum in the respective anhydrous ether. These latter were carefully dried by standard procedures employing $LiAlH_4$.

Stock solutions were prepared by this method and were stored under dry argon at −20 °C. Dilute solutions were prepared from the stock solution using the syringe technique and 10 mm NMR tubes.

All NMR spectra were recorded using a Bruker WP 200 multi nuclei instrument. $\delta^{27}Al$ refers to an aqueous 1 M Al^{3+} solution. 90° pulses were used in obtaining the ^{27}Al PFT NMR spectra the resolution being usually 3.7 Hz per data point. C_6D_6 was used as internal lock. The number of scans (NS) applied to obtain high quality spectra are indicated in the Figures.

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