

# Alkoxohydridoaluminates: multinuclear NMR study of sodium hydrido-(2-methoxyethoxy) aluminates

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## Abstract

$^{23}\text{Na}$ ,  $^{27}\text{Al}$ , and  $^1\text{H}$  NMR spectra were obtained on benzene solutions of varying sodium alkoxohydridoaluminate compositions,  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$ , where  $x=2$  to  $0$ , and  $\text{OR}=\text{OCH}_2\text{CH}_2\text{OCH}_3$ . An extensive series was prepared by titration of initial  $\text{Na}^+\text{H}_2\text{Al}(\text{OR})_2^-$  (SDMA),  $x=2$ , by 2-methoxyethanol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$ .

The NMR data presented enabled the refinement of the structure of SDMA, sodium dihydrido-bis(2-methoxyethoxy)aluminate, proposed formerly as an individual compound. The preparation of the analogous ‘mono-hydrido aluminate’,  $\text{Na}^+\text{HAl}^-(\text{OR})_3$ ,  $x=1$ , as an individual compound, for reason of excellent selective reducing ability, failed. NMR data revealed that alcoholysis of the SDMA by 2-methoxyethanol (in molar ratio  $\text{Na}^+\text{H}_2\text{Al}^-(\text{OR})_2:\text{HOCH}_2\text{CH}_2\text{OCH}_3=1:1$ ) does not result in the desired individual  $\text{Na}^+\text{HAl}^-(\text{OR})_3$ , but in an equilibrium mixture of the  $\text{Na}^+$  salt of  $\text{H}_2\text{Al}^-(\text{OR})_2$ ,  $\text{HAl}^-(\text{OR})_3$  and  $\text{Al}^-(\text{OR})_4$  aluminate anions.

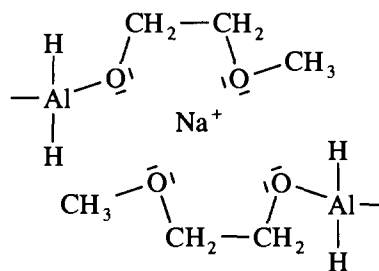
The inherently ionic sodium alkoxohydridoaluminates are stabilized in solvents of low dielectric constant and low donation strength—in benzene—via different types of aggregate: SDMA via higher, weaker ionic aggregates, and mixtures of  $\text{Na}^+$  salt of  $\text{HAl}^-(\text{OR})_3$ ,  $\text{HAl}^-(\text{OR})_3$  and  $\text{Al}^-(\text{OR})_4$  aluminate anions via ion-paired predominantly trimeric aggregates. These different types of aggregation were recognized on the basis of apparent molecular weight and conductivity measurements on the system. Multinuclear NMR data were used for discussion of these different types of aggregate in more detail.

**Keywords:** Aluminium; Hydride; Alkoxohydridoaluminates; NMR spectroscopy; Ion pairing

## 1. Introduction

Of the sodium alkoxohydridoaluminates  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$ , where  $x=2-0$ , and  $\text{OR}=\text{OCH}_2\text{CH}_2\text{OCH}_3$ ,  $\text{Na}^+\text{H}_2\text{Al}^-(\text{OR})_2$ , SDMA, represents a commercially available reducing agent produced as a 70% toluene solution under the trademarks Vitride™ or Synhydride™. The first SDMA is produced by Hexel (USA) and the second by Lučební závody Kolín (Czech Republic). A recent paper dealing with  $^{27}\text{Al}$  NMR data of SDMA [1] concluded that SDMA in benzene represents a uniform individual compound, that was probably considered previously in Refs. [2,3]. The structure of SDMA in benzene solution was proposed as open-chain oligomers associated via  $\text{Na}^+$  ions by two bidentate  $\text{OCH}_2\text{CH}_2\text{OCH}_3$  ligands belonging to two neighbouring Al atoms, Scheme 1.

The ‘mono-hydrido aluminate’,  $x=1$ ,  $\text{Na}^+\text{HAl}^-(\text{OR})_3$ , in benzene solution was widely considered as an individual compound as well [2–4]. This conclusion was particularly based on IR studies. Such individual compounds with only one hydride proton have theoretically excellent selective reducing ability compared with ‘di-hydrido aluminate’ SDMA [5]. It seems to be very attractive to prepare the mono-hydrido aluminate by a simple alcoholysis of SDMA by 2-methoxyethanol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  in molar ratio 1:1.

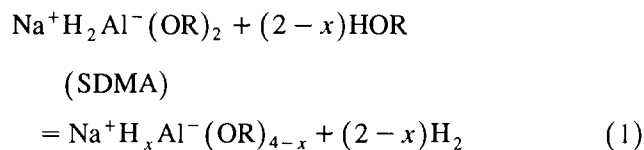


Scheme 1.

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## 2. Results

An extensive series of 0.4 M benzene solutions of alkoxohydridoaluminates  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$ , of analytical composition from  $x=2$  to 0 was prepared by alcoholysis of SDMA by 2-methoxyethanol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  at ambient temperature, Eq. (1):



The initial SDMA benzene solution was prepared by direct synthesis from Al,  $\text{H}_2$  and  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  [6]. For reason of corroboration, the samples of fundamental composition, i.e. of  $x=2$ , 1.5 and 1 were prepared by another way, namely by disproportionation reaction of the corresponding amounts of  $\text{NaAlH}_4$  and  $\text{NaAl}(\text{OR})_4$  in benzene. Regardless of the preparation method, the NMR spectra in all cases were essentially identical. The same conclusions were drawn for the sample of half (0.2 M) concentration.

Hypothetically, the disproportionation method can be used to prepare benzene solutions of alkoxohydridoaluminates  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$  of analytical composition  $x > 2$ . All efforts, however, failed. For example, preparation of  $\text{Na}^+\text{H}_3\text{Al}^-\text{OR}$  from a mixture of  $3\text{Na}^+\text{Al}^-\text{H}_4 + 1\text{Na}^+\text{Al}^-(\text{OR})_4$  resulted only in SDMA and unsolved initial  $\text{NaAlH}_4$ . Thus, from the complete theoretical range of  $4 > x > 0$ , only alkoxohydridoaluminates of just composition  $x \leq 2$  create thermodynamically stable benzene solutions. This suggests that a sufficient number of alkoxo-groups (a minimum of two) on aluminate anions is necessary.

### 2.1. Conductance and molecular weight measurements

Fig. 1 shows in the most illustrative way the changes in behaviour of 0.4 M benzene solutions of alkoxohydridoaluminates,  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$ , depending on composition of the mixture  $x$ . The molecular weight studies show that these inherently ionic compounds in benzene, i.e. in a solvent of low dielectric constant  $\epsilon \sim 2.28$  and low coordinating ability, are stabilized via high molecular aggregates. SDMA is aggregated in the most; the degree of association  $n$  is about 11. In the course of alcoholysis of SDMA, a significant breakdown of the aggregates occurs, going through a minimum at  $n \sim 2.8$  and  $x \sim 1-0.5$ . The same trend is exhibited in the viscosity of the system, 2.2 mPa s for 0.4 M SDMA is lowered to 0.9 mPa s for  $x=1$ , both at  $20 \pm 0.1$  °C.

The changes in degree of association  $n$  and viscosity are apparently controversial to the course of the conductance of the system, Fig. 1; with an increasing number

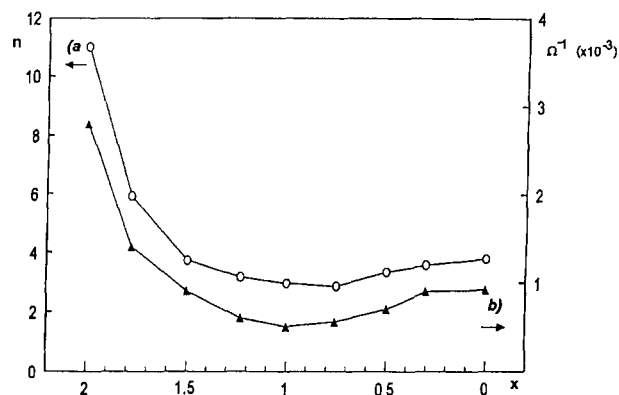


Fig. 1. Dependence of (a) degree of association  $n$ , and (b) conductivity ( $\Omega^{-1}$ ) of 0.4 M benzene solutions of alkoxohydridoaluminates of analytical formulae  $\text{Na}^+\text{H}_x\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-x}$  on  $x$ , where  $x=2$  to 0. The samples were prepared by alcoholysis of the SDMA ( $x=2$ ) by  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  in benzene at ambient temperature [6].

of species, (i.e. with decreasing  $n$ ), and also with increasing mobility, the conductivity of the system decreases. The conductance maximum corresponds to SDMA and the minimum to a degree of association  $n \sim 3$  at about  $x \sim 1$ .

The above controversial effect corresponds to a concept in which the character of the aggregates, (i.e. rather than the number and mobility of the species present), determines the conductance of benzene solutions of sodium alkoxohydridoaluminates. The higher aggregates of SDMA in this concept have features of weaker aggregates which facilitate fragmentation into lower charged entities. These ionic fragments are responsible for the observed highest conductance at  $x=2$ . The conductance minimum at  $x \sim 1$  corresponds primarily to ion-paired solutes, aggregated predominantly into trimers,  $n \sim 3$ . Such ion-pairs do not contribute to net charge transport. Beyond this minimum at  $x \sim 1-0.75$ , both the aggregation and conductance of the system increase again.

Support for the suggested concept of benzene solutions of sodium alkoxohydridoaluminates may be found in the literature from other systems of complex sodium aluminates in aliphatic or aromatic solvents, namely from sodium tetra-*n*-butylaluminate,  $\text{Na}^+\text{AlBu}_4^-$  [7]. Addition of THF to cyclohexane solution of  $\text{Na}^+\text{AlBu}_4^-$  [8] lowers the higher initial aggregates of  $\text{Na}^+\text{AlBu}_4^-$ . The magnitude of the effect increases with increasing degree of association  $n$  and with increasing THF: $\text{Na}^+$  ratio. The effect might be expected in the process of increasing complexation of  $\text{Na}^+$ . In the case of complete solvation, all coordination sites on  $\text{Na}^+$  are occupied by complexing solvent; therefore, the cation might only be able to form ion pairs, not stable higher aggregates [8]. There seems to be an interesting analogy among changes in behaviour of sodium complex aluminates in aliphatic or aromatic solvents in the course of

complexation of the  $\text{Na}^+$  cation either by THF or by complexing glycol–ether ligands on aluminate anions.

## 2.2. Multinuclear NMR data

Multinuclear NMR data of alkoxohydridoaluminate series enable discussion of the above proposed concept of alkoxohydridoaluminates over the range of composition from  $x \sim 2$  to 0 in benzene in more detail.

### 2.2.1. $^1\text{H}$ NMR spectroscopy

*General:* each  $^1\text{H}$  spectrum of  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-x}$ , of composition from  $x = 2$  to 0.5 shows

just three signals with integral ratio 2:2:3. The signals correspond to three types of proton in the alkoxy group  $-\text{OCH}_2^\alpha\text{CH}_2^\beta\text{OCH}_3^\gamma$  of the aluminate anion. The most important  $^1\text{H}$  NMR spectra for SDMA,  $x = 2$  and  $x = 1$ , are presented in Fig. 2, spectra C and D respectively. An assignment of signals of particular protons of the alkoxy group was based on the unambiguous spectrum of methoxyethanol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$ ; spectrum A, and sodium methoxyethoxide, spectrum B. Complexation of  $\text{Na}^+$  by the methoxyethoxide part results in significant deshielding of all protons.

In the region  $0 \leq x \leq 0.3$  the spectra became more complex, see spectra E for  $x = 0.3$  and F for  $x = 0$  in Fig. 2, in which each type of proton of the alkoxy group

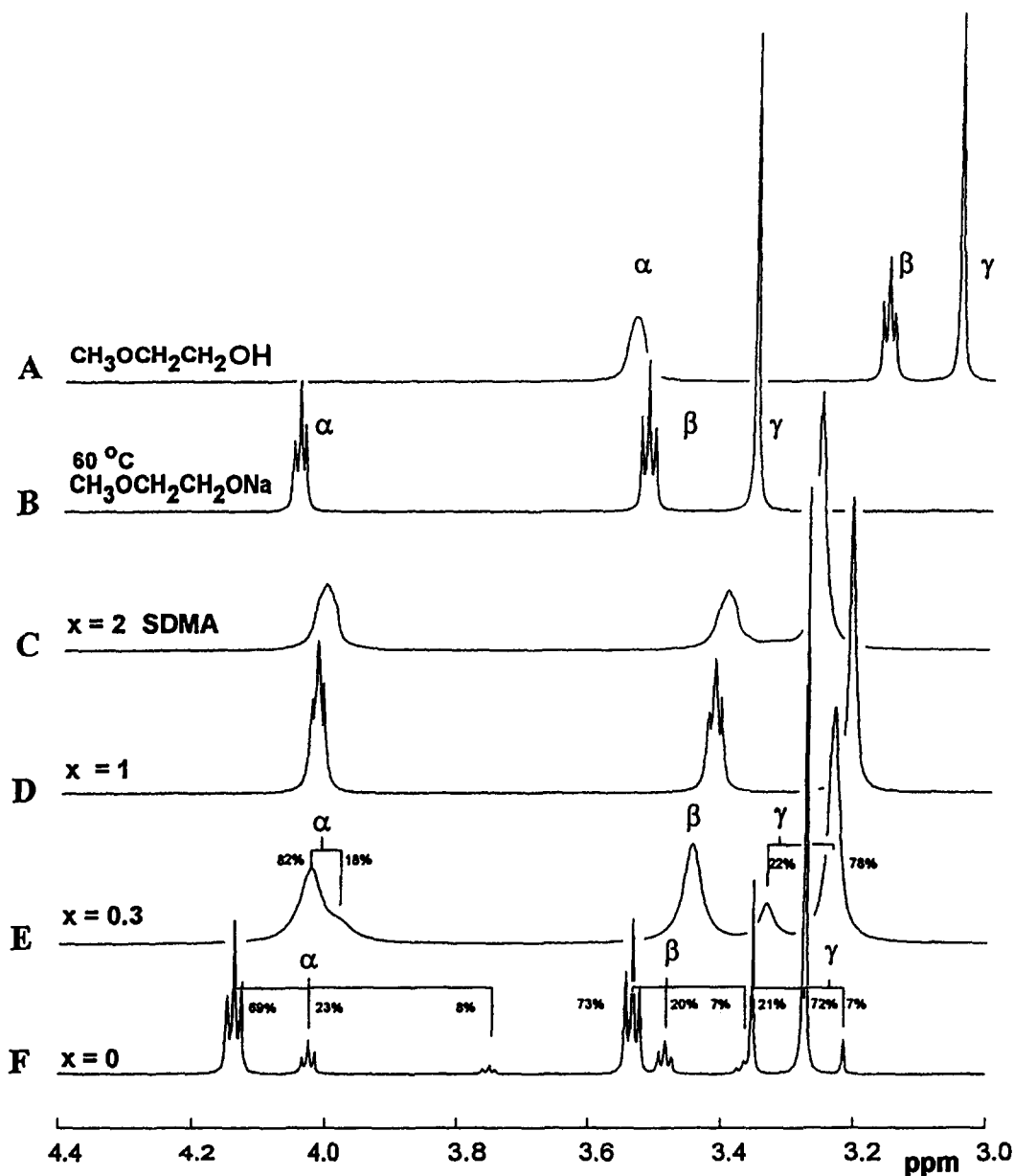


Fig. 2.  $^1\text{H}$  NMR spectra of benzene solutions of: A, methoxyethanol, (cellosolve alcohol), 8 wt.% solution; B, sodium methoxyethoxide, 8 wt.% solution (at  $60^\circ\text{C}$ ); C–F, sodium alkoxyaluminates, 0.4 M, of analytical formulae  $\text{Na}^+\text{H}_x\text{Al}^-(\text{OR})_{4-x}$ , where  $x = 2, 1, 0.3$  and 0, and  $\text{OR} = \text{OCH}_2\text{CH}_2\text{OCH}_3$  at ambient temperature.

exhibits two or three signals respectively. This indicates that at  $x = 0$  there are three different types of alkoxo-parts in the approximate ratio 1:3:12. The alkoxo groups are involved in slow chemical exchange between their different positions in the course of complexation of  $\text{Na}^+$  in predominantly tetrameric aggregates,  $n \sim 3.8$ , Scheme 2.

**Relaxation times:** in the region from  $x = 2$  to 0.5 the relaxation times show smooth increasing trends from 0.6 to 0.8 s for  $\alpha$  and  $\beta$  protons, and from 1.4 to 1.8 s for  $\gamma$  protons. This can be rationalized on the basis of the mass-size effect, i.e. the higher aggregates of SDMA tumble less freely compared with lower aggregated species at about  $x < 2$ . In the region  $x \sim 0.3$  to 0 the  $T_1$  values differentiate; the  $T_1$  values for the alkoxo-parts involved in interaction with  $\text{Na}^+$  decrease and those without the interaction increase.

A temperature study of the restricted tumbling of higher aggregates of SDMA reveals a minimum of  $T_1$  for  $\beta$ -methylene at ambient temperature and at about 5 °C for  $\alpha$ -methylene protons. This suggests that the correlation time  $\tau_c$  of the alkoxo-parts in large aggregates of SDMA is approximately proportional to the proton resonance frequency  $\omega_0$  of about 500 MHz, i.e.  $\tau_c \omega_0 \sim 1$  and  $\tau_c \sim 2 \times 10^{-9}$  s; this is a typical  $\tau_c$  for large molecules of lighter polymers [9].

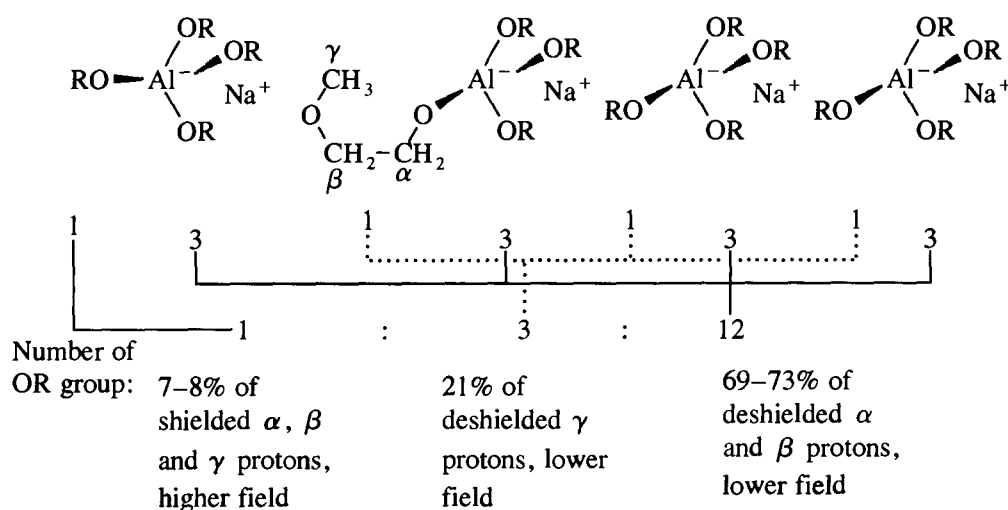
**Fine structure of signals of  $\alpha$  and  $\beta$ -methylene protons:** the fine triplet structure of the signals provides convincing evidence of our concept of gradual changes in the types of aggregate during alcoholysis of the initial SDMA. Owing to molecular tumbling of the alkoxo-parts in aggregates of SDMA on a critical level  $\tau_c \omega_0 \sim 1$ , the direct dipolar interactions between neighbouring hydrogen atoms are not completely averaged out. For this reason,  $\alpha$  and  $\beta$ -methylene proton signals lack fine structure and the spectrum shows one broad resonance

for each type of proton, spectrum C Fig. 2. During the first step of alcoholysis of SDMA, at  $x \sim 1.8$ , the degree of association  $n$  decreases from about 11 to about 6, Fig. 1. This pronounced decrease in  $n$  is sufficient to substantially reduce the correlation time  $\tau_c$  and the signals of both methylene protons are subsequently well split, see, for example, spectrum D in Fig. 2 for  $x \sim 1^\circ$  corresponding to  $J = 4$  Hz for  $\alpha$  and 4.5 Hz for  $\beta$  protons.

Starting from  $x = 0.5$ , the fine structure of  $\alpha$  and  $\beta$ -methylene proton signals collapsed into single, broad resonances again, spectrum E for  $x \sim 0.3$ , Fig. 2. Unlike the broadening at  $x \sim 2$ , this effect results from a low frequency contribution to the spin-spin relaxation time of the protons. The contribution originates from a reduction of the rate of chemical exchange of the alkoxo-parts, which differs according to presence or absence of the interaction with  $\text{Na}^+$ , see Scheme 2. Steady suppression of the chemical exchange results in three separated signals for each of the  $\alpha$  and  $\beta$ -methylene protons at  $x \sim 0$ . At about this point, a highly resolved triplet structure of signals is readily recognized again with  $J \cong 5$  Hz, spectrum F Fig. 2.

**$^1\text{H}$  NMR of hydride protons:** the  $^1\text{H}$  and  $^1\text{H}(^{23}\text{Na})$  NMR spectra of benzene solutions of sodium alkoxohydroaluminate, from  $x = 2$  to 0.15, show no signal for the hydride protons.

An apparent absence of the hydride signal may be caused by scalar relaxation of the  $^1\text{H}$  ligand nucleus coupled to metal  $^{27}\text{Al}$ . According to Abragam [9], the rate of relaxation of the  $^1\text{H}$  nucleus  $1/T_2$  ( $= 4/3\pi^2 J^2 S(S+1)(\tau_s + \tau_s/(\omega_H - \omega_{\text{Al}})^2 \tau_s^2)$ , where  $S = 5/2$  is the spin of the  $^{27}\text{Al}$  nucleus,  $\omega_H$  and  $\omega_{\text{Al}}$  are resonance frequencies, the  $J \cong 210$  Hz is the spin coupling constant between the  $^1\text{H}$  and  $^{27}\text{Al}$  nuclei derived from  $\text{Bu}_4\text{N}^+\text{H}_2\text{Al}^-(\text{OR})_2$  [10] and  $\tau_s \cong 4 \times 10^{-4}$  s is the longitudinal relaxation time of the Al nucleus at



Scheme 2.

SDMA, Fig. 3), is contributed to by about  $2000 \text{ s}^{-1}$  by the scalar relaxation. In this respect, only the  $^1\text{H}(^{27}\text{Al})$  spectrum for  $x=2$  exhibits the broad signal for the hydride protons at  $\delta = 3.78 \text{ ppm}$ ,  $W_{1/2} = 220 \text{ Hz}$  at ambient temperature and  $\delta = 3.70 \text{ ppm}$ ,  $W_{1/2} = 100 \text{ Hz}$  at  $60^\circ\text{C}$ . The signal of the hydride protons rapidly decays with increasing OR/H ratio. At  $x \sim 1.5$  the  $^1\text{H}(^{27}\text{Al})$  spectrum shows no hydride signal. The observed higher spin coupling constant between the  $^1\text{H}$  and  $^{27}\text{Al}$  nuclei for 'mono-hydrido aluminate' species  $\text{HAl}^-(\text{OR})_3$ , (about  $235 \text{ Hz}$  for  $\text{Bu}_4\text{N}^+\text{HAl}(\text{OR})_3$  [10]), faster chemical exchange (see below), and proposed larger  $\text{Na}^+ \cdots \text{H}-\text{Al}^-$  interactions correspond to the finding.

### 2.2.2. $^{23}\text{Na}$ NMR spectroscopy

Spectra show only one population-averaged signal of  $^{23}\text{Na}$  nuclei. This is indicative of the fast chemical exchange between different cationic sites, which is typical for a weak complexation of the  $\text{Na}^+$  ion by oxygen in glycol ether substituents. With increasing OR/H molar ratio, shielding of  $\text{Na}^+$  nucleus increases, Fig. 4(A). Comparison of longitudinal and transverse relaxation data, Fig. 4(B), shows that  $T_2 \cong T_1$  and that relaxation is quadrupolar dominated. The differences in  $T_2 < T_1$  at  $x \sim 2$  probably arise from additional contribution to  $T_2$  from relaxation of the  $^{23}\text{Na}$  nucleus outside the extreme narrowing limit. Such a situation is compre-

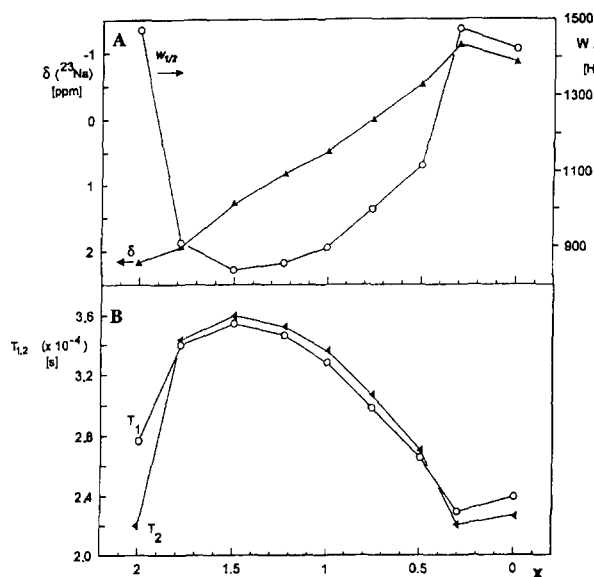


Fig. 4.  $^{23}\text{Na}$  NMR data of 0.4 M benzene solution of alkoxohydridoaluminates of analytical formulae  $\text{Na}^+ \text{H}_x \text{Al}^- (\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-x}$ , where  $x = 2$  to 0, at ambient temperature. Dependence of (A) chemical shift ( $\delta$ ), and halfwidth ( $W_{1/2}$ ), and (B) spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times on  $x$ .

hensible when the  $\text{Na}^+$  is a part of the large slowly moving higher aggregates of SDMA.

The initial increase of the  $T_1$  values for the  $^{23}\text{Na}^+$  to a maximum at  $x \sim 1.5$  correspond to mass-size reduction of the higher aggregates at high values of  $x$ . While reduction of degree of association continues up to  $x \sim 0.75$ , Fig. 1, the  $T_2$  values rapidly decrease. Such a change of the course of  $T_q$  ( $= T_1 \cong T_2$ ) has to be than attributed to an increase in the nuclear quadrupole coupling constant (NQCC) at the  $\text{Na}^+$ . The NQCC parameter is sensitive to short-range interaction [11–19] and, in the course of ion pairing, an alternation of electric field gradient at  $^{23}\text{Na}$  can be expected. The same effect has to be encountered at corresponding alkoxohydridoaluminate counter ions. Fig. 3 indeed shows a similar decrease of  $T_q$  ( $= T_1 \cong T_2$ ) values for the  $^{27}\text{Al}$  nucleus in the region from  $x \sim 1.8$  to 0.3 for signal 1, assigned to a mixture of two alkoxohydridoaluminate anions in rapid chemical exchange;  $\text{Na}^+ \text{H}_2 \text{Al}^- (\text{OR})_2 \leftrightarrow \text{Na}^+ \text{HAl}^- (\text{OR})_3$ , see below.

### 2.2.3. $^{27}\text{Al}$ NMR spectroscopy

The  $^{27}\text{Al}$  NMR spectrum, Fig. 3(A), in the case of SDMA,  $x = 2$ , exhibits a broad signal at  $\delta = 101 \text{ ppm}$ ,  $W_{1/2} = 1350 \text{ Hz}$ .  $W_{1/2}$  is only slightly sensitive to  $^1\text{H}$  and  $^{23}\text{Na}$  decoupling. The signal was assigned to the individual  $\text{Na}^+ \text{H}_2 \text{Al}^- (\text{OR})_2$  [1]. An apparent absence of splitting of the  $^{27}\text{Al}$  NMR signal owing to  $^{27}\text{Al}-^1\text{H}$  coupling may indicate: (i) both separation of the coupled atoms, i.e.  $\text{Na}^+ \text{H}_2 \text{Al}^- (\text{OR})_2 \leftrightarrow \text{NaH} + \text{HAl}(\text{OR})_2$  during chemical exchange (by 'concertant mechanism'

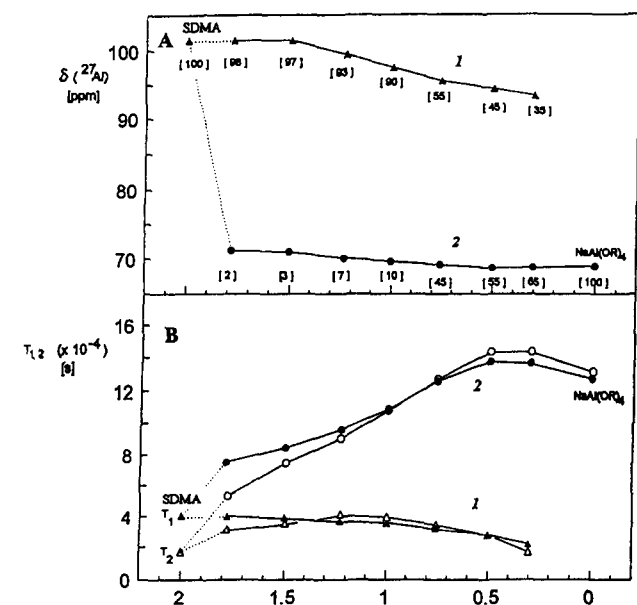
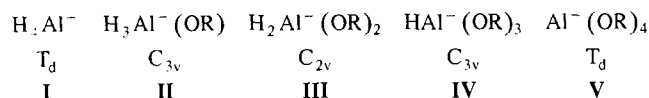


Fig. 3.  $^{27}\text{Al}$  NMR data of 0.4 M benzene solution of alkoxohydridoaluminates of analytical formulae  $\text{Na}^+ \text{H}_x \text{Al}^- (\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-x}$ , where  $x = 2$  to 0, at ambient temperature. Dependence of (A) chemical shift  $\delta$  (figures in brackets represent intensity ratio of the signals 1 and 2 in percent) and (B) spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times on  $x$ .



Chemical exchange of H/OR substituents on the central Al atom in SDMA would theoretically result in the entire range of the possible anions I–V:



For the entropic (statistic) reasons that would result in the theoretical ratio of the particular anions 1:4:6:4:1, the anion **III** would be advanced. The enthalpic part of the Gibbs free energy includes: (a) a short range electrostatic ion–dipole interaction; i.e. the **II–IV** anions with dipole moment would be favoured in the theoretical equilibrium mixture; (b) stabilization of the anions via specific interaction of the alkoxo-parts with  $\text{Na}^+$ . The latter interactions depend on the number of the alkoxo-substituents and increase in order  $\text{II} \ll \text{III} < \text{IV} \sim \text{V}$ . For this reason, the effort for preparation of  $x = 3$ , sodium ‘tri-hydrido aluminate’  $\text{Na}^+\text{H}_3\text{Al}^-(\text{OR})$  solution in benzene, failed. It may be believed that, for thermodynamic reasons, any chemical exchange of the H/OR substituent at SDMA significantly results in **III** again, i.e. the concentration of **II** and **IV** anions is negligible. Thus, in this respect, SDMA can be considered as an individual compound in Scheme 3.

**Conclusion.** While benzene solutions of SDMA involve mainly anion **III**, another situation occurs in solvents of higher dielectric constant and sufficient specific solvation abilities for  $\text{Na}^+$ . Such solvation of  $\text{Na}^+$  ion may reduce the above enthalpic factors (a) and (b) that determine the composition of the alkoxohydridoaluminate equilibrium mixture of the anions in benzene and also reduce the tendency of the ionic solutes to create the higher aggregates. One may then find the whole set of all five possible anions I–V [1] which are arranged mainly in solvent separated ion-pairs. It is important to have in mind that substrates submitted for the reduction by SDMA in benzene (and the products of the reduction as well), may emulate a solvent of sufficient donation strength. Reduction may then proceed simultaneously by the mixture of anions I–IV present. For this reason, any particular reduction by SDMA would be a subject of an individual study.

#### 4.2. $\text{Na}^+\text{HAl}^-(\text{OR})_3$ , sodium ‘mono-hydrido aluminate’, $x = 1$

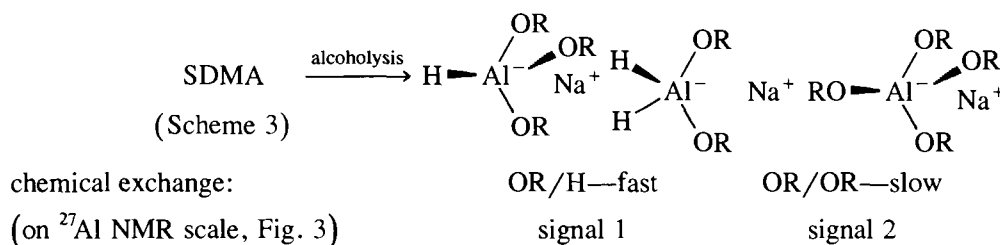
An attempt to prepare an individual  $\text{Na}^+\text{HAl}^-(\text{OR})_3$  for the purpose of a gentle selective reducing agent by alcoholysis of SDMA failed. The alcoholysis of SDMA by  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  in molar ratio 1:1 results in an equilibrium mixture of  $\text{Na}^+$  salt of **III–V** anions, arising from disproportionation of  $\text{Na}^+\text{IV}$  according to Eq. (2),  $K_{\text{disp.}} \sim 1 \times 10^{-2}$  at ambient temperature.

During the alcoholysis, the higher aggregates of SDMA break down to give rise to predominantly ion-paired trimers of different mixtures of  $\text{Na}^+\text{III}$ ,  $\text{Na}^+\text{IV}$  and  $\text{Na}^+\text{V}$  alkoxohydridoaluminates, e.g. Scheme 4.

In this case of lower aggregates,  $n \sim 3$  for  $x \sim 1$ , the ion–dipole interactions between the  $\text{Na}^+$  and **III** and **IV** anions brings the opposite ions to shorter distances and into a suitable orientation; this makes possible the fast H/OR chemical exchange between the anions, see one average signal 1 in Fig. 3. The  $T_d$  symmetric  $\text{Al}^-(\text{OR})_4$  anion **V** lacking a dipole moment is not involved in the rapid chemical exchange and exhibits an individual signal 2 in the spectrum. As the  $^1\text{H}$  NMR spectrum for  $x \sim 1$  shows only one type of alkoxo-substituent, the later ‘slow’ chemical exchange on the  $^{27}\text{Al}$  NMR scale has to represent the ‘fast’ one of the  $^1\text{H}$  NMR scale. The exchange of OR groups has to involve all three **III–V** anions, and the rate of the exchange  $1/\tau_{\text{ex}}$  is than in a narrow interval 200 (about  $\Delta$  0.4 ppm on the  $^1\text{H}$  NMR scale)  $< 1/\tau_{\text{ex}} < 3500 \text{ s}^{-1}$  (about  $\Delta$  25 ppm on the  $^{27}\text{Al}$  NMR scale).

#### 4.3. $^{27}\text{Al}$ NMR spectra of lithium alkoxohydridoaluminates

Preliminary  $^{27}\text{Al}$  NMR spectra of lithium alkoxohydridoaluminates,  $\text{Li}^+\text{H}_x\text{Al}^-(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-x}$ , provide excellent support of the above findings for the  $\text{Na}^+$  analog. The smaller cation  $\text{Li}^+$  would be expected to associate more strongly with the anions. For  $x = 2$ , the spectrum consists of one unresolved signal at about 119 ppm assigned to individual  $\text{Li}^+\text{III}$ . For  $x = 1$ , the spectrum consists of three signals assigned to the equilibrium mixture of  $\text{Li}^+\text{III}$ , (118 ppm),  $\text{Li}^+\text{IV}$ , (87 ppm) and  $\text{Li}^+\text{V}$ , (68 ppm), arising from the disproportionation reaction of  $\text{Li}^+\text{IV}$  according to Eq. (2) and corre-



Scheme 4.

sponding  $K_{\text{disp.}} \sim 1 \times 10^{-2}$ . With increasing temperature only the first two species with dipole moment, **III** and **IV**, are involved in rapid chemical exchange. The signals of these two individual anions coalesced above 60 °C into one signal resonating at 89 ppm. Starting from  $x \leq 0.5$ , the spectra show the two signals of  $\text{Li}^+\text{V}$  and  $\text{Li}^+\text{IV}$ . For this reason, reduction by a mixture of composition  $\text{Li}^+\text{H}_{0.5}\text{Al}^-(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{3.5}$  would theoretically proceed exclusively by 'mono-hydrido aluminate'  $\text{Li}^+\text{IV}$ , which promises selective reducing ability.

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