

On the Hydrolytic Stability of Organic Ligands in Al-, Ti- and Zr-Alkoxide Complexes

DAGOBERT HOEBBEL, THOMAS REINERT AND HELMUT SCHMIDT
Institut für Neue Materialien, Im Stadtwald, D-66123 Saarbrücken, Germany

ERTUGRUL ARPAC
Akdeniz University, 07200 Antalya, Turkey

Abstract. The complexation degrees of Al-, Ti- and Zr-butoxide (M) with unsaturated and saturated β -diketones (3-allylpentane-2,4-dione-APD, acetylacetonate-ACAC) and β -ketoesters (methacryloxyethyl-acetoacetate-MEAA, allylacetoacetate-AAA, ethylacetoacetate-EAA) as organic ligands (L) were examined by IR and ^{13}C NMR spectroscopy and were found to be $L : M \geq 1.5$. The hydrolytic stability of the ligands of the metal alkoxide complexes ($L : M = 1$) during hydrolysis/condensation reactions at the molar ratio h ($\text{H}_2\text{O} : \text{OR}$) = 0.5–2.0 decreases with increasing $\text{H}_2\text{O} : \text{complex}$ ratio. Furthermore, the ligand stability depends on the type of metal in the complexes and decreases in the order $\text{Al} > \text{Zr} > \text{Ti}$ -butoxide complexes at $h = 1$. The ACAC ligand likewise shows in the Al-, Ti- and Zr-butoxide complexes a high hydrolytic stability (95–100%) at $h = 1$ within 7 days. The Ti- and Zr-butoxide complexes with β -ketoesters as ligand show at $h = 1$ a release to a different extent e.g., up to 60% in the case of the MEAA-ligand in the Ti-butoxide complex after 2 days. In general, the hydrolytic stability of the ligands in the Ti-butoxide complexes ($L : M = 1, h = 1$) decreases in the order $\text{ACAC} > \text{APD} > \text{AAA} > \text{EAA} \geq \text{MEAA}$. The hydrolysis/condensation reaction of complexes having a weak ligand stability leads to larger particle sizes in the sols than those with stable ACAC ligands. The results contribute to a more controlled synthesis of sols and of new inorganic-organic hybrid polymers via the sol-gel process.

Keywords: metal alkoxide complexes, β -keto ligands, hydrolysis, particle size, IR, ^{13}C NMR

1. Introduction

Metal alkoxides and their organic derivatives play an important role in synthesis of glasses, ceramics and inorganic-organic materials using the sol-gel process [1–8]. In this process the silicon alkoxides and their organic derivatives with non-hydrolysable C–Si bonds play a dominant role [5, 9–12].

In contrast to the silicon compounds the direct attachment of organic groups via C–M bonds to other metals (M) such as titanium, zirconium and aluminium is not useful because of the hydrolytic instability of the more ionic C–M bonds [9, 10]. Therefore, the

common way for the organic modification of e.g., Al-, Ti- and Zr-alkoxides is the partial complexation with carboxylic acids, β -ketoesters or β -diketones. These organic ligands of the metal alkoxide complexes are more stable towards hydrolysis than the ligands with C–M bonds due to the chelate bond formation and sterical hindrance effects [9–11, 13, 14]. The organic complex ligands act as modifier of the condensation degree of metal alkoxides. If organic ligands with reactive e.g., unsaturated bonds are used, additional organic networks between metal alkoxide complexes can be build up by polymerisation or additive reaction. This organic network is linked

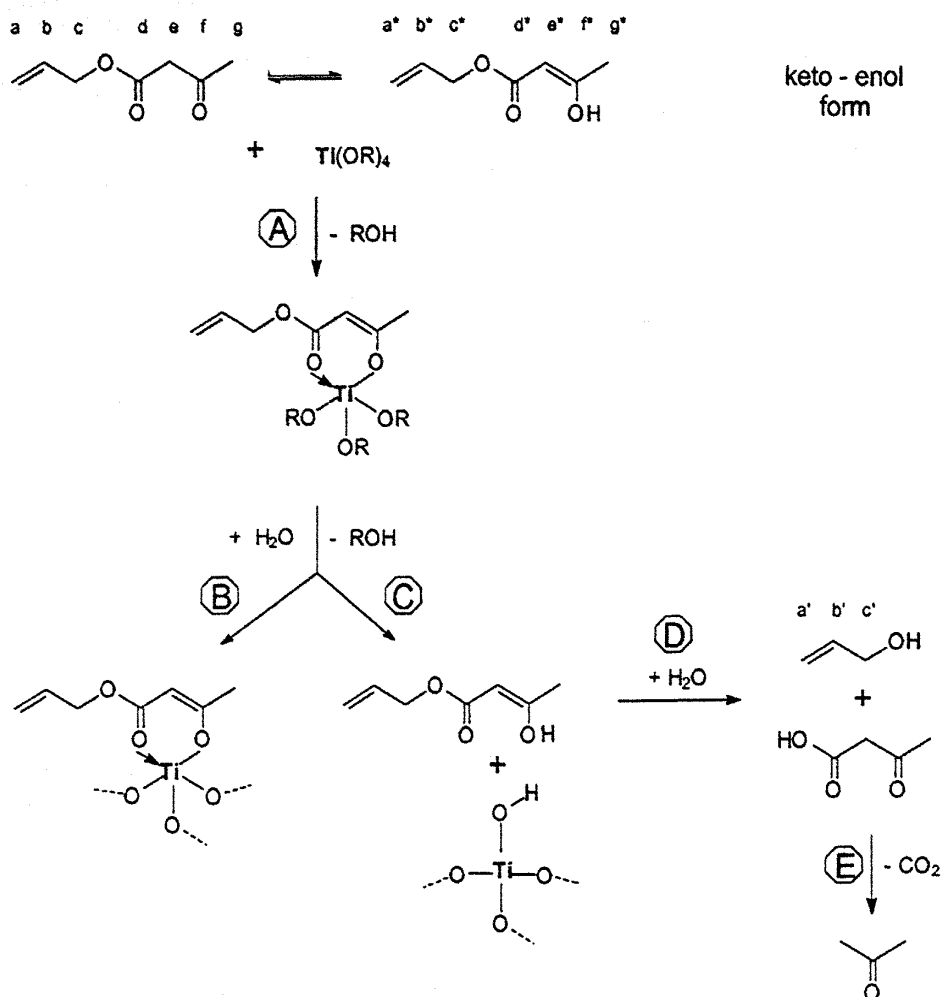


Figure 1. Scheme of the complexation of Ti-alkoxide with AAA and of the complex hydrolysis.

with the inorganic one via C-O-M-O-M bridges [10, 11, 15, 16].

Unsaturated compounds used as ligands for the metal alkoxide complexes are mostly organic acids such as acrylic-, methacrylic- or methacrylamidosalicylic acid [9, 10, 15, 17–19]. Other complexing acids containing unsaturated bonds are cinnamic acid [19, 20], sorbic acid [19], 2-acrylamido-2-methyl-propanesulfonic acid and itaconic anhydride [21, 22]. A second group of complexing compounds with unsaturated bonds involves β -ketoesters such as allylacetoacetate (AAA) [9, 11] and methacryloxyethyl-acetoacetate (MEAA) [9, 23]. A third group of complexing compounds are β -diketones. The 3-allylpentane-2,4-dione (APD) is the only described complexing β -diketone with unsaturated groups [24].

The complexation degree of metal alkoxides with unsaturated organic compounds is sparsely described in the literature. Furthermore, not much emphasis has been laid on the ligand stability of the complexes with saturated and unsaturated groups towards hydrolysis with the exception of a few works [6, 14, 21, 22, 25–29].

A scheme of the complexation reaction ($L : M = 1$) and of the hydrolysis of the complex ligand is shown in Fig. 1. It is known from the literature [29] that the Ti-alkoxide complexes ($L : M = 1$) do not exist exclusively in the given $Ti(OR)_3L$ structure but rather in an equilibrium with $Ti(OR)_4$ and $Ti(OR)_2L_2$ species. Our work does not differentiate between the different complexed species but considers only the simplified $Ti(OR)_3L$ structure at the ratio $L : M = 1$. According to Fig. 1(C) a low hydrolytic stability of the metal alkoxide complex results in an additional, mostly indefinite, number of OH or OR groups at the metal atoms which entail a higher extent of condensation reaction compared to a stable complex with a defined OR functionality. Furthermore, a weak hydrolytic stability of functional organic ligands diminishes the bonds of the organic with the inorganic network and leads finally to more inhomogeneous hybrid polymers.

The objectives of this article are the determination of the complexation degree of Al-, Ti- and Zr-butoxide complexes with unsaturated β -ketoesters (allylacetoacetate, methacryloxyethyl-acetoacetate) and the

unsaturated β -diketone 3-allylpentane-2,4-dione. For comparing examination the complexes with saturated ligands (acetylacetone, ethylacetoacetate) were included. Furthermore, we tried to get more quantitative information on the hydrolytic stability of unsaturated and saturated ligands by means of IR spectroscopy and on the relations between complex stability and particle size in hydrolysates of the metal alkoxide complexes.

2. Experimental

Chemicals. The used titanium *n*-butoxide $\text{Ti}(\text{O}i\text{Bu})_4$ and aluminium-sec-butoxide $\text{Al}(\text{O}i\text{Bu})_3$ were purchased from FLUKA and zirconium-*n*-butoxide $\text{Zr}(\text{O}i\text{Bu})_4$ in *n*-butanol (84%) from ABCR. Aluminium-*n*-butoxyethoxide was prepared as follows: 100 g (0.41 mole) aluminium sec-butoxide were mixed with 203 ml (1.55 mole) 2-butoxyethanol and were stirred for 15 h at room temperature. 2-Butanol is slowly removed at 60°C in vacuum up to 5 mbar. Aluminium *n*-butoxyethoxide is then obtained by the distillation of the residual 2-butoxyethanol at 80°C and 10^{-2} mbar.

The used ethylacetoacetate (EAA, >99%) and acetylacetone (ACAC, >99.5%) were obtained from FLUKA, allylacetoacetate (AAA, 98%), *n*-butanol (99.8%) and sec-butanol (99%) from ALDRICH, and methacryloxyethyl-acetoacetate (MEAA, 98%) from KODAK. The chemicals were used without further purification.

3-Allylpentane-2,4-dione (APD) was prepared as described in [30] by reaction of acetylacetone and allyl bromide in a sodium methylate solution. GC: purity >98%, ^{13}C NMR: enolic C—OH $\delta = 191.9$ ppm, keto C=O $\delta = 203.7$ ppm, intensity ratio of the signals nearly 1 : 1, ^{17}O NMR: enolic C—OH $\delta = 276.0$ ppm (60%), keto $\delta = 576.8$ ppm (40%), IR: two absorption bands $\nu(\text{C}=\text{O})$ for keto groups at 1701 and 1733 cm^{-1} , enol bands $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ at 1600 cm^{-1} and $\nu(\text{C}=\text{C})$ vibration of the allyl group at 1638 cm^{-1} . The water content of the chemicals and solvents was determined by Karl-Fischer-titration [31] and was found to be below 0.08%.

Procedure. The complexations were carried out in tightly closed glass vessels at 25°C. *n*-butanol was added to titanium- or zirconium-*n*-butoxide and sec-butanol to aluminium-sec-butoxide, respectively, to get a molar ratio alcohol : metal alkoxide = 5 : 1. The β -diketones or β -ketoesters were added dropwise to the stirred metal alkoxide solution in molar

ratios of ligand : metal alkoxide = 0.5 : 1 to 3 : 1. The Ti-concentration in $\text{Ti}(\text{O}i\text{Bu})_3\text{AAA}$ solution was 1.07 mol/l. The Al- and Zr-concentration in the $\text{Al}(\text{O}i\text{Bu})_2\text{AAA}$ and $\text{Zr}(\text{O}i\text{Bu})_3\text{AAA}$ solutions were 1.18 and 1.04 mol/l, respectively.

The hydrolysis of $\text{Ti}(\text{O}i\text{Bu})_3\text{L}$ and $\text{Zr}(\text{O}i\text{Bu})_3\text{L}$ complexes (L = ligand) were carried out with a water/*n*-butanol solution, and the hydrolysis of $\text{Al}(\text{O}i\text{Bu})_2\text{L}$ complexes with a water/sec-butanol solution at 25°C. The molar ratio of water : butanol was 1 : 3 in both solutions. The hydrolysis ratio *h* refers to the molar ratio of water/OR groups bonded at the complexed alkoxide (see simplified complex structure in Fig. 1(A)) and was chosen to be *h* = 0.5, 1.0, 1.5, 2.0. The metal ion concentration of all hydrolysates (*h* = 0.5–2.0) was kept in the range of 0.88–0.37 mol/l. Only transparent solutions were examined by IR, ^{13}C NMR, Photon Correlation Spectroscopy (PCS) and Karl-Fischer-titration for 1 h, 1 d, 2 d, 3 d and 7 days after the start of the hydrolysis.

Measurements. The liquid state ^{13}C NMR spectra were obtained using a Bruker AC200 spectrometer operating at a field of 4.7 Tesla. The measurements were carried out with CDCl_3 and TMS as external lock and reference at 25°C. The inverse gated pulse sequence was used in order to eliminate the ^1H - ^{13}C interactions and NOE effects. The experimental NMR conditions were: 60° pulse, 10 s recycle delay and 400–2000 scans. The conditions of the ^{17}O NMR spectra of the complexing compounds were taken from the literature [32].

The FT-IR spectra were obtained by using a Bruker IFS25 spectrometer. Data acquisition and processing were performed using the OPUS software package. Liquid-state spectra were recorded between 650 and 4000 cm^{-1} in the attenuated total reflection (ATR) mode with a ZnSe-45°-crystal. The measurements were carried out under ambient atmosphere and within one minute. For the evaluation of the IR spectra which is based on the integration of the IR bands the following points have to be taken into consideration. The dependence of the IR band intensities in the range 1500–1800 cm^{-1} on the wavelength is assumed to be neglectable. The two point integration method with baseline correction was used for the determination of the integral extinction in the absorption spectra. The bands of the stretching vibrations $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the enolic forms of the β -diketones around 1600 cm^{-1} and of the β -ketoesters at about 1615 and 1525

cm^{-1} were integrated (region A). Additionally, the integrals of the stretching vibrations $\nu(\text{C}=\text{O})$ of the keto forms of free β -diketones and β -ketoesters at about 1740 and 1710 cm^{-1} were measured (region B).

In the following, the ratio $A/A + B$ of the different bands within one and the same spectrum are compared to receive information on the complexation degree and the release of ligands, respectively. This procedure is supported by the following additional calibrations;

- (i) comparing measurements of the keto-enol ratio in the complexing compounds by ^{13}C and ^{17}O NMR show a good coincidence with the IR results (max. deviation 10%);
- (ii) the examination of the ratio of IR band intensity in dependence on the concentration of complexing compounds was found to be nearly constant (max. deviation 10%). It follows from the results that the ratio of keto-enol band intensities in the IR spectra of the complexing compounds represent almost the correct equilibrium between the two species;
- (iii) the bands of the enol form of the β -diketone complex at 1590 cm^{-1} and the β -ketoester at 1613 cm^{-1} are overlapped (a) by the $\nu(\text{C}=\text{C})$ vibration of the allyl- or methacryl-group around 1630 cm^{-1} , (b) by the $\delta(\text{H}-\text{O}-\text{H})$ vibration at 1640 cm^{-1} of the water in the hydrolysates and (c) by the enol-band of the released complexing compound.

The intensity of the $\nu(\text{C}=\text{C})$ band of the allyl- or methacryl-group is low and does not change during hydrolysis and was taken into account to 5% of the overall band intensities ($A + B$). The contribution of the broad water band to the sum of ($A + B$) band intensities decreases with increasing hydrolysis time and remains relatively constant at 8% after 1 h reaction time. The share of the enol form of the released ligand to the band around 1615 cm^{-1} depends on its ratio of keto/enol form. The corresponding part was subtracted from the band of the enol form of the complex.

The water content in the hydrolysates was examined by Karl-Fischer-titration [31] using a KYOTO MK210. The solvent used was Hydranal working medium K (Riedel de Haen) which contains 2-chloroethanol and trichloromethane. The reagent for volumetric titration was Hydranal Composite 5K. The hydrolysed solutions for the Photon Correlation Spectroscopy (PCS) were prepared by filtration of the sols through filters with $0.45 \mu\text{m}$ pore size directly into cuvettes. All

measurements were made at 20°C with an ALV-5000 Multiple Tau Digital Correlator (ALV-Laser, Langen-Germany). The measurements were carried out at the angles 35° , 45° , 60° and 90° . Additional measurements were made at 75° and 105° to get a better statistical distribution. The differences in the metal ion concentration of the hydrolysates (0.37–0.88 mol/l) were neglected. The refractive indices n^{20} and the viscosities η^{20} of the solvents, taken from the literature [33], were used for the calculation of the PCS-parameters and the averaged particle sizes (diameter) by the computer program CONTIN [34].

3. Results

3.1. Complexation of Metal Alkoxides with β -Ketoesters and β -Diketones

The $\text{Al}(\text{OBU}^n)_3$, $\text{Al}(\text{OEtOBU}^n)_3$, $\text{Ti}(\text{OBU}^n)_4$ and $\text{Zr}(\text{OBU}^n)_4$ were used for the complexation with the unsaturated β -ketoesters (AAA, MEAA) and the β -diketone APD. The strong chelating ACAC [27, 35, 36] and EAA [37] were used as saturated ligands for comparing examination of the complexation degree and the hydrolytic stability of the metal alkoxide complexes.

Figure 2 illustrates the changes in the IR absorptions before and after complexation reaction and after the hydrolysis of the complex one example of $\text{Zr}(\text{OBU}^n)_3\text{AAA}$ and $\text{Ti}(\text{OBU}^n)_3\text{APD}$ complexes.

The IR spectra of the metal alkoxides $\text{Zr}(\text{OBU}^n)_4$ and $\text{Ti}(\text{OBU}^n)_4$ are similar and show no absorption bands in the region of $1500\text{--}1800 \text{ cm}^{-1}$. Two bands at 1460 and 1375 cm^{-1} are due to $\delta(\text{C}-\text{H})$ deformation vibrations (Fig. 2(I)). The absorption bands of AAA (Fig. 2(II)) are assigned as follows: The strong bands at 1740 and 1715 cm^{-1} are due to $\nu(\text{C}-\text{O}$, ester) and $\nu(\text{C}=\text{O}$, ketone) vibrations. Two bands at 1650 and 1633 cm^{-1} are assigned to $\nu(\text{C}=\text{C}$, $\text{C}-\text{O})$ of the enolic form of AAA and $\nu(\text{C}=\text{C}$, allyl). The keto-enol ratio of AAA was determined by IR, ^{13}C and ^{17}O NMR spectroscopy and was approximately 9 : 1. The absorption bands of APD (Fig. 2(II)) at 1727 and 1700 cm^{-1} are caused by $\nu(\text{C}=\text{O}$, ketone) vibrations, a broad band at 1600 cm^{-1} is assigned to $\nu(\text{C}=\text{C}$, $\text{C}-\text{O}$, enol) and a small band at 1638 cm^{-1} to $\nu(\text{C}=\text{C}$, allyl). The keto-enol ratio of APD is about 1 : 1 as determined by IR. The evaluation of the corresponding ^{13}C and ^{17}O NMR spectra of APD support the IR spectroscopic result.

Figure 2(III) shows the IR spectra of $\text{Zr}(\text{OBU}^n)_3\text{AAA}$ in *n*-butanol. No free AAA is observed in the 1 : 1

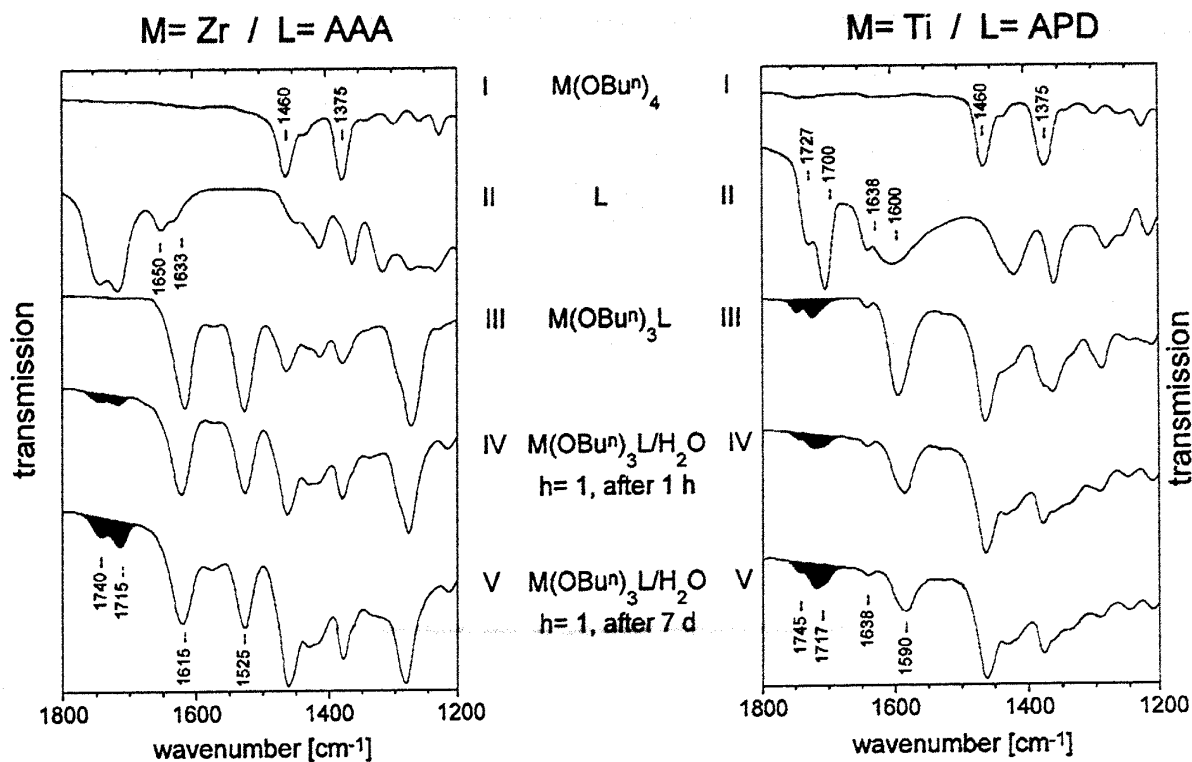


Figure 2. IR spectra of $Zr(OBu^n)_4$, $Ti(OBu^n)_4$ (I), AAA, APD (II), $Zr(OBu^n)_4/AAA$ and $Ti(OBu^n)_4/APD$ solutions ($L:M=1$) and of the hydrolysates of the complexes (IV) and (V).

mixture of $Zr(OBu^n)_4$ and allylacetacetate but the two stretching vibrations ($C=C$ and $C-O$) of the enolic form of the β -ketoester at 1615 and 1525 cm^{-1} show that all of AAA is bonded to the Zr-butoxide. The corresponding $Ti(OBu^n)_3APD$ spectrum (Fig. 2(III)) shows one broad band at 1590 cm^{-1} due to stretching vibrations ($C=C$ and $C-O$) of the enolic form of the β -diketone which indicates the presence of complexed bonded APD. But there are also absorption bands of free APD at 1745 and 1717 cm^{-1} . From the integration of the IR bands follows that about 15% of the added APD remain uncomplexed in the $Ti(OBu^n)_3APD$ solution.

Figure 3(I) shows the ^{13}C NMR spectrum of AAA in the region from $\delta = 210$ till 100 ppm. The six signals are assigned as follows: 201.4 ppm $-H_2C-\underline{C}(O)-CH_3$ (f), 177.0 ppm $C=CH-\underline{C}OOR$ (d^*), 172.9 ppm $C=C-\underline{O}H$ (f^*), 168.3 ppm $C-CH_2-\underline{C}OOR$ (d), 133.0 ppm $C-\underline{H}C=CH_2$ (b) and 118.5 ppm $C-\underline{H}C=\underline{C}H_2$ (a). The ^{13}C NMR spectrum of the $Zr(OBu^n)_3AAA$ complex (Fig. 3(II)) shows four signal groups: the two signals of the allyl group (133 ppm , 118 ppm) and the two signal groups of the enol form of AAA bonded to Zr: $\delta = 187 - 185\text{ ppm}$ $C=C-C-O-Zr$ and $173.5 - 172.5\text{ ppm}$ $C=C-O-Zr$. The splitting of the signals in Fig. 3(II) is caused by the different bonds of the ligand to the metal atom, probably due

to the $Zr(OR)_3AAA/Zr(OR)_2(AAA)_2$ equilibrium and the different association degree of the complexed metal alkoxide. The ^{13}C NMR result agrees with those of the IR-spectra (Fig. 2(III)) and shows that all of AAA is bonded to Zr.

The results of the IR spectroscopic evaluation of the maximum complexation degree of Al-, Ti-, and Zr-butoxides are summarised in Fig. 4. The graph shows that unsaturated and saturated β -keto compounds are able to form a metal alkoxide complex with a molar ratio ligand:metal $> 1:1$. One special feature was found in metal alkoxide complexes with APD. After the reaction of APD with the metal alkoxides at a molar ratio $1:1$ a degree of complexation < 1 was found: Aluminium-sec-butoxide = 0.6, Titanium- and Zirconium-*n*-butoxide = 0.85 and 0.95, respectively. A longer reaction time (24 h) and higher temperatures (60°C) did not significantly increase the complexation degree. Complexation degrees greater than 1 can be realised however with an excess of APD. For example a complexation degree of 1.6 (Fig. 4) was found for the Al atom in a solution of $APD/Al(OBu^n)_3 = 2$. In one case aluminium-butoxyethoxide $Al(OEtOBu^n)_3$ was used instead of Al-sec-butoxide to avoid undesirable precipitations of aluminium-sec-butoxide complexes. This is marked by the abbreviation "albe" in Fig. 4.

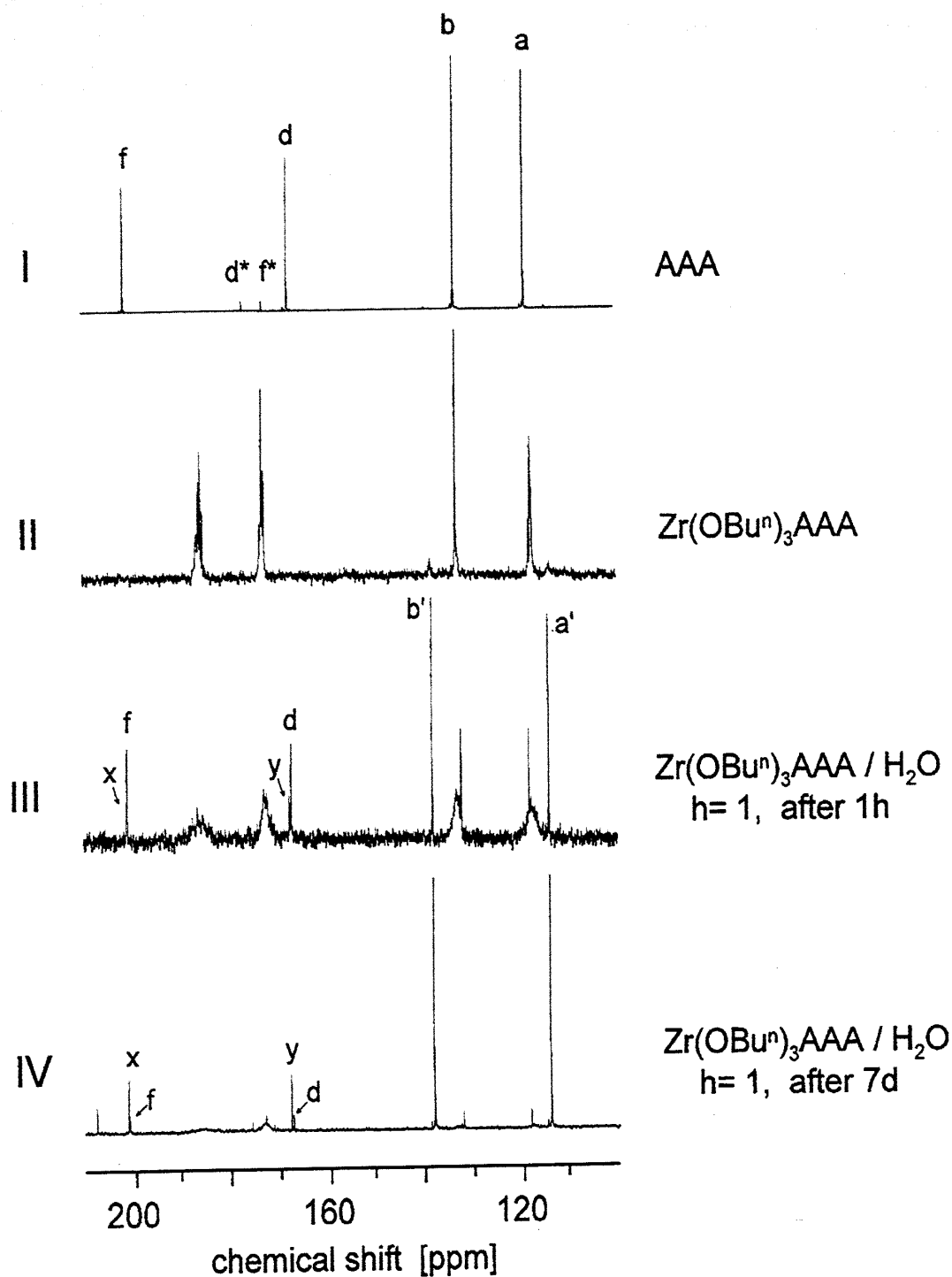


Figure 3. ^{13}C NMR spectra (detail) of AAA (I), $\text{Zr}(\text{OBu}^n)_3\text{AAA}$ complex (II) and its hydrolysis products (III) and (IV).

In the following, metal alkoxide complexes with a molar ratio $\text{L}:\text{M}=1$ were only chosen for the examination of their hydrolytic stability. In the case of APD/metal alkoxide complexes, solutions with the molar ratio $\text{APD}:\text{M}=1$ were used with a lower complexation degree than 1 as mentioned above.

3.2. Hydrolysis of the Metal Alkoxide Complexes

Figure 2(IV, V) shows as an example the IR spectra of the $\text{Zr}(\text{OBu}^n)_3\text{AAA}$ hydrolysates ($h=1$) after 1 h and

7 d ($c(\text{Zr})=0.54$ mol/l). The appearance of the bands of uncomplexed AAA at 1740 and 1715 cm^{-1} with increased hydrolysis time indicates that AAA ligands are partially released from the complex by the addition of water.

The ^{13}C NMR spectra of the $\text{Zr}(\text{OBu}^n)_3\text{AAA}$ hydrolysate (Fig. 3(III, IV), $h=1$) show sharp signals at $\delta=201.0$ ppm (f) and 167.3 ppm (d) for the $\text{C}=\text{O}$ and COOR group of the free AAA and signals at $\delta=132.2$ ppm and 118.1 ppm caused by the allyl group in the keto form of AAA. These signals confirm in accordance with the IR data the presence

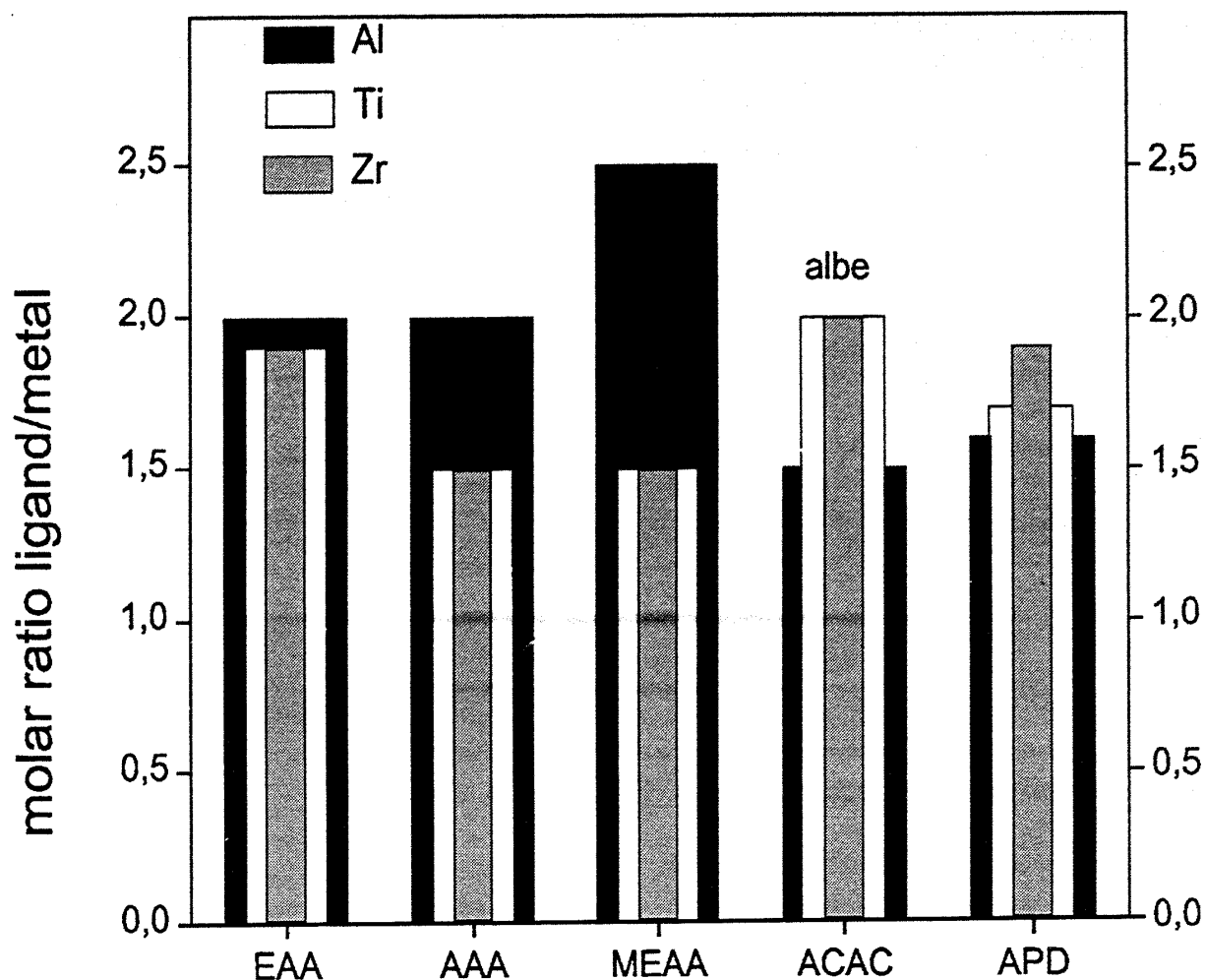


Figure 4. Maximum complexation degree of $\text{Al}(\text{O}i\text{Bu}^n)_3$, $\text{Al}(\text{OEtO}i\text{Bu}^n)_3$ [albe], $\text{Ti}(\text{O}i\text{Bu}^n)_4$ and $\text{Zr}(\text{O}i\text{Bu}^n)_4$ with the unsaturated β -keto compounds AAA, MEAA, APD and the saturated EAA and ACAC.

of released AAA. The signals of the enol form of AAA bonded to Zr at $\delta = 173$ and 186 ppm are now very broad because of the different environment of the C-atoms caused by the different condensation degree of the $\text{Zr}(\text{OR})_{3-x}(\text{OH})_{x+y}\text{AAA}_{1-y}$ precursors and the increasing molecular weight of the particles in the solution.

The ^{13}C NMR spectra of the $\text{Zr}(\text{O}i\text{Bu}^n)_3\text{AAA}$ -hydrolysates (Fig. 3(III, IV)) show in addition to the already mentioned signals f and d at 201.0 and 167.3 ppm two narrowly neighboured signals (see arrows) at $\delta = 201.1$ and 167.7 ppm (x, y) whose intensities increase with time. Simultaneously, the intensity of the signals b' and a' at $\delta = 138.1$ and 118.1 ppm which are attributed to the $\text{C}=\text{C}$ group of free allyl alcohol increases. It can be concluded from the detected signals that a re-esterification of the AAA by butanol under release of allyl alcohol took place with increasing time of hydrolysis. Furthermore, the allyl alcohol can be derived from the cleavage of AAA to a 3-oxo-butanoic acid and allyl alcohol according to the scheme shown in Fig. 1(D). This reaction is supported

by the two additional signals at $\delta = 207.5$ and 30.0 ppm in the ^{13}C NMR spectrum of the hydrolysates caused by acetone which is released by the decarboxylation of the unstable 3-oxo-butanoic acid according to the scheme shown in Fig. 1(E). Similar side reactions of the organic ligands were identified in hydrolysates of $\text{Zr}(\text{O}i\text{Bu}^n)_3\text{EAA}$, $\text{Zr}(\text{O}i\text{Bu}^n)_3\text{MEAA}$ and also of $\text{Ti}(\text{O}i\text{Bu}^n)_3\text{AAA}$ complexes.

The signals of the ^{13}C NMR spectra of the hydrolysates were integrated for a quantitative comparison with the results of the IR measurements. It follows from the comparison that the amount of free AAA in identical hydrolysates found by NMR was two times higher than those measured by IR. The differences in the quantity of the IR and NMR results can be explained by the uncertainty in the integration of broad lines and the long relaxation times of the carbonylic atoms in the ^{13}C NMR spectra. In the following, the results of the IR spectroscopy were used for the determination of the hydrolytic stability of the complex ligands. Additional ^{13}C NMR measurements were only used to support the IR results, in particular for identification

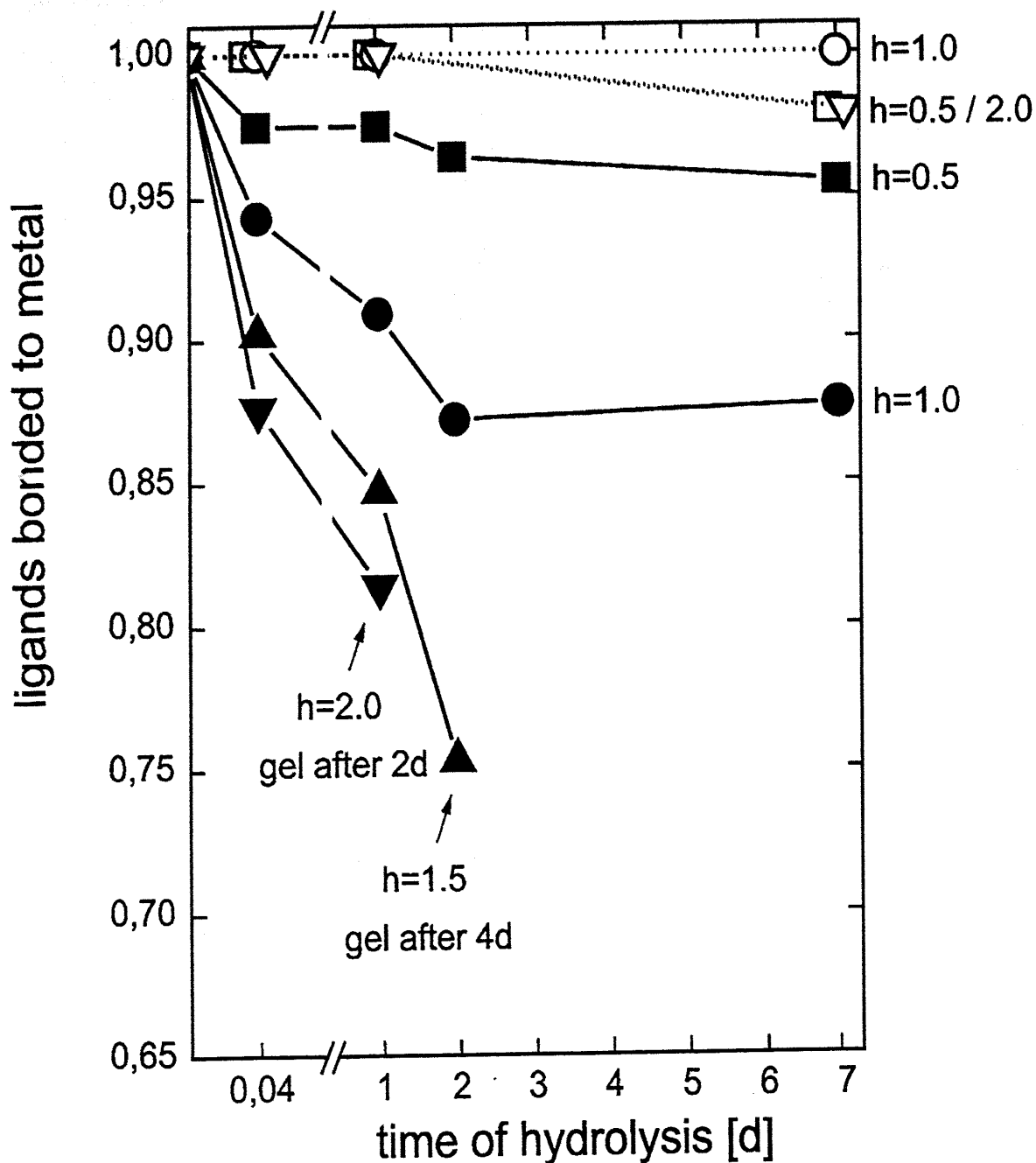


Figure 5. Effect of the amount of water ($h = 0.5\text{--}2.0$) on the hydrolytic stability of the ligands of $\text{Zr}(\text{OBU}^n)_3\text{ACAC}$ (unfilled symbols) and $\text{Zr}(\text{OBU}^n)_3\text{AAA}$ complexes (black symbols).

of low amounts of released ACAC and APD ligands because these diketones are difficult to identify by IR due to their large ratio of enol to keto form.

Figure 5 shows the effect of the ratio h ($\text{H}_2\text{O}/\text{OR}$) on the hydrolytic stability of the ligands of $\text{Zr}(\text{OBU}^n)_3\text{AAA}$ and $\text{Zr}(\text{OBU}^n)_3\text{ACAC}$ complexes. At $h = 0.5$ a low release of AAA from the complex up to 5% is only observed. The degradation of the complex ligand at $h = 1$ was found to about 10% after 1 day. At $h = 1.5$ about 10% of the AAA ligands is released already after 1 h. The strongest release of AAA is observed at the ratio $h = 2$ after 1 d hydrolysis. A gelification of this solution occurs already after

2 days. The $\text{Zr}(\text{OBU}^n)_3\text{ACAC}$ complex shows a high hydrolytic stability between 97–100% up to 7 days at all examined molar ratios h (Fig. 5). The following experiments on the hydrolytic stability of the complex ligands were only carried out at the hydrolysis ratio $h = 1$.

Figure 6 summarises the IR spectroscopic results on the hydrolytic stability of different ligands attached to Al-, Zr- and Ti-alkoxides in molar ratio 1 : 1. The Al-sec-butoxide complexes show a high hydrolytic stability of their different ligands between 95 and 100% within a reaction time of 7 days. The APD ligand shows a comparable good stability considering the

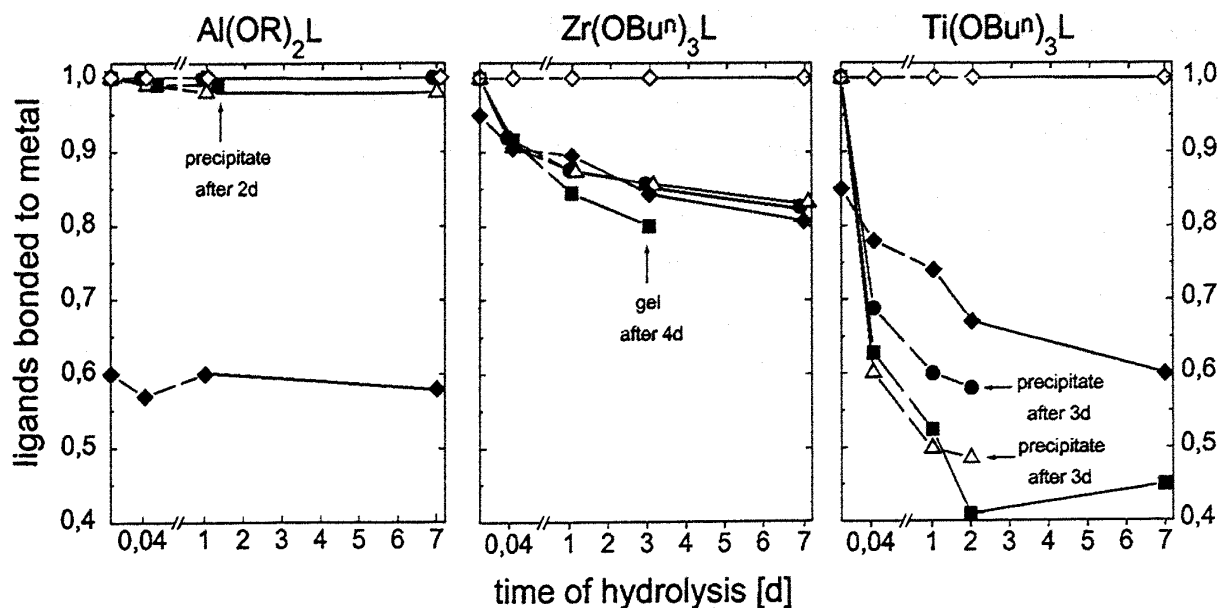


Figure 6. Hydrolytic stability of the ligands in Al(OBuⁿ)₂L, Al(OEtOBuⁿ)₂ACAC [albe], Ti(OBuⁿ)₃L and Zr(OBuⁿ)₃L complexes (L : M = 1, h = 1); (L = ◇ ACAC, ◆ APD, △ EAA, ● AAA, ■ MEAA).

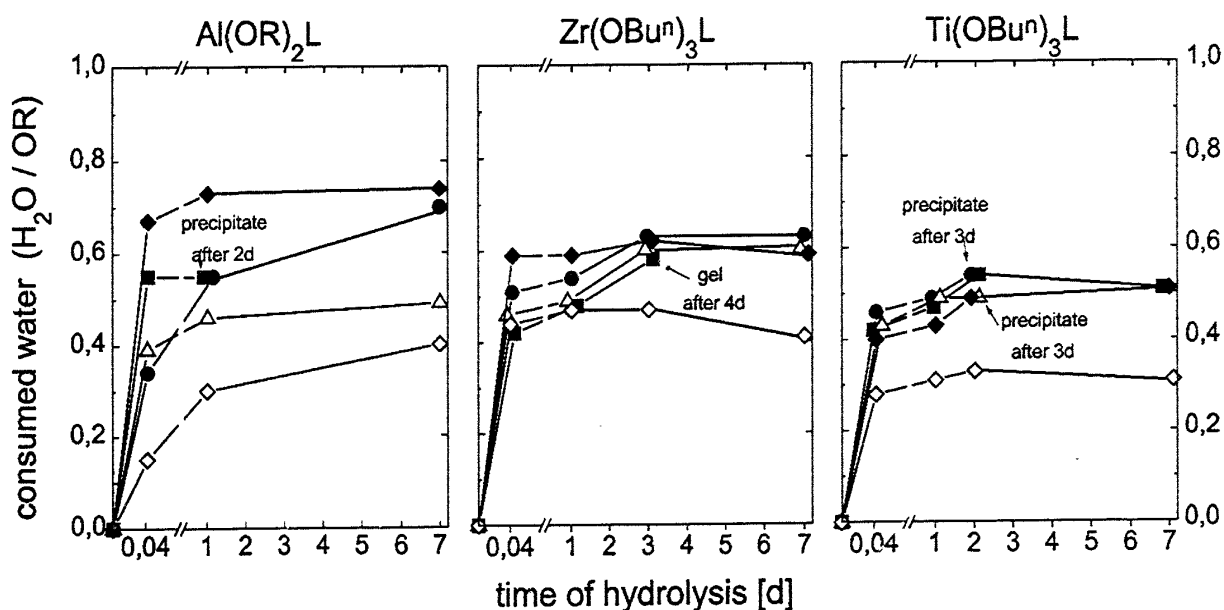


Figure 7. Consumption of water in hydrolysates (h = 1) of Al(OBuⁿ)₂L, Al(OEtOBuⁿ)₂ACAC [albe], Ti(OBuⁿ)₃L and Zr(OBuⁿ)₃L complexes with different ligands; (L = ◇ ACAC, ◆ APD, △ EAA, ● AAA, ■ MEAA).

lower degree of complexation (60%) in the graph. The ACAC ligand of Ti- and Zr-alkoxide complexes show a likewise high hydrolytic stability. The other ligands of Ti- and Zr-alkoxide complexes, especially the β -ketoesters AAA, MEAA and EAA, show a decreased hydrolytic stability. About 15% of the AAA and MEAA are released from the hydrolysed Zr-alkoxide complexes after 1d, whereas up to 50% of the EAA- and MEAA-ligands of the Ti-alkoxide complexes are released after the same time.

Figure 7 indicates the consumed amount of water in hydrolysates (h = 1) of Al-, Zr- and Ti-butoxide

complexes. It follows from the graph that the hydrolysates of the Al-, Ti- and Zr-alkoxide complexes with ACAC as ligand consume the least amount of water, i.e., 0.3–0.4 mol H₂O/OR for the hydrolysis of the alkoxo-groups. This result corresponds to the high hydrolytic stability of the ACAC ligand which does not use additional water for the ligand hydrolysis. The metal alkoxides with more unstable ligands MEAA, AAA and EAA consume higher amounts of water, i.e., between 0.4 and 0.7 mol H₂O/OR due to the additional ligand hydrolysis. More detailed correlations between the amount of consumed water and

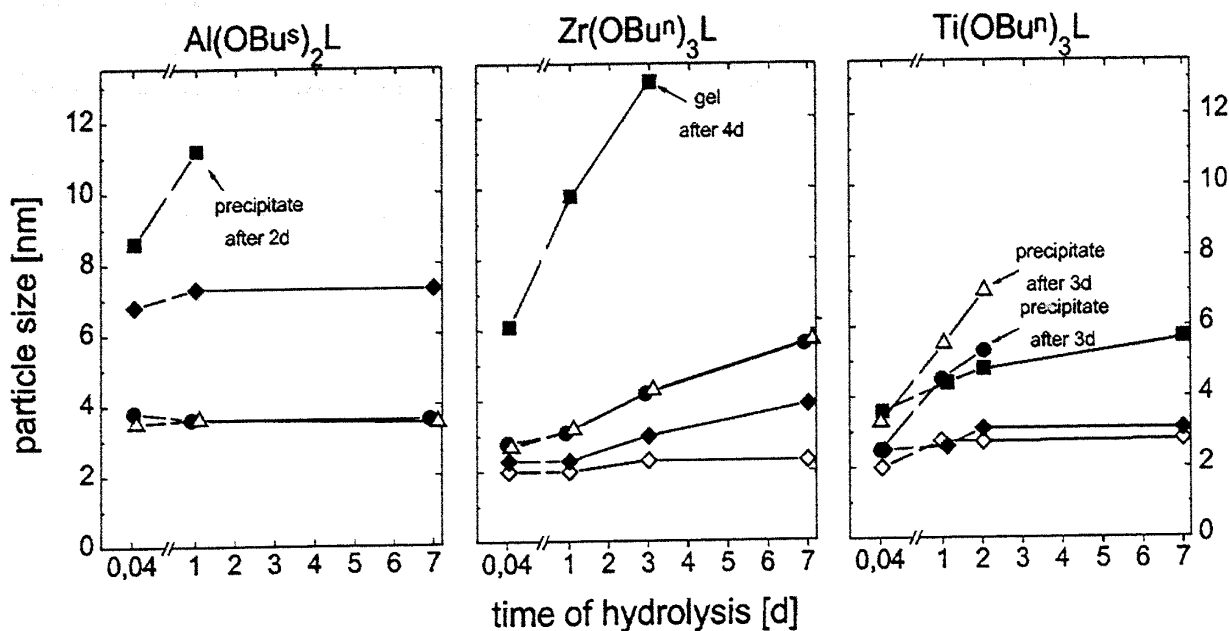


Figure 8. Averaged particle sizes in hydrolysates ($h = 1$) of $\text{Al}(\text{OBu}^s)_2\text{L}$, $\text{Ti}(\text{OBu}^n)_3\text{L}$ and $\text{Zr}(\text{OBu}^n)_3\text{L}$ complexes with different ligands ($\text{L} = \diamond$ ACAC, \blacklozenge APD, \triangle EAA, \bullet AAA, \blacksquare MEAA).

the observed different complex stabilities of the ligands cannot be established due to the overlapping of hydrolysis reactions of the OR groups with the condensation reactions and the side reactions of the ligands.

The results of the light scattering method (PCS) on the averaged particle sizes in hydrolysates of complexes in dependence on the reaction time are shown in Fig. 8. Small particles with a slow increase in the particle diameter from 2 to 3 nm can be observed in hydrolysates of ACAC complexed Zr- and Ti-alkoxides within 7 days. This result corresponds with those in the literature [35]. Particles of larger size are found in hydrolysates of complexes with hydrolytically unstable ligands. Particles with a diameter of about 7 nm are already formed e.g. in a $\text{Ti}(\text{OBu}^n)_3\text{EAA}$ hydrolysate after 2 d, but after 3 d the hydrolysate transforms into a gel. The largest particles with diameters of about 13 nm were found in hydrolysates of $\text{Zr}(\text{OBu}^s)_3\text{MEAA}$ after 3 d. One day later the sol condenses to a gel.

4. Discussion and Conclusions

The explanation of the different complexation degrees of the metal alkoxides by ACAC, AAA, EAA and MEAA as shown in Fig. 4 requires a detailed knowledge on the association degree of the metal alkoxide complexes, the type of bonds of the ligands with the metal alkoxide (chelating, bridging ligands), the equilibrium constant of different complexed species in

dependence on the L : M ratio, the coordination state of the metal atoms and the steric effects of the ligands. Because of the lack of sufficient structural data of the synthesised metal alkoxide complexes a discussion of the different complexation degrees is not meaningful.

The incomplete complexation degree of the complexes with APD as ligand may have its reason in a hindered keto-enol equilibrium of the APD caused by the allyl group attached to the C-3 atom and by its additional steric effect [19]. The different complexation degrees with APD in dependence on the metal alkoxide type suggest an influence of the metal alkoxide on the keto-enol equilibrium to a different extent. Obviously, the Al-sec-butoxide influences the shift of the equilibrium from the keto to the enol form, which is required for a complete complexation, only to an insufficient extent. The found complexation degree of 60% in a APD : Al-butoxide = 1 : 1 solution corresponds approximately with the original keto to enol ratio of the APD, whereas a nearly full complexation (95%) is obtained in the corresponding APD/Zr-alkoxide = 1 : 1 solution.

It is known from the literature that with increasing water to metal alkoxide ratio both the condensation rate and the particle size increase [35]. Additionally, the results of this work show an increasing complex degradation with increasing water to metal alkoxide complex ratio. The results make sure that the hydrolytic stability of the complex ligands is significantly

influenced by the structure of the ligands and the type of the metal alkoxide used. It can be seen from Fig. 6 that the different ligands of the Al-sec-butoxide complexes have the highest hydrolytic stability (95–100%) followed by the Zr-butoxide and Ti-butoxide complexes. The lowest stability of the ligands is shown by Ti-butoxide complexes, especially the MEAA/Ti-butoxide complex, which releases about 60% of its ligands after 2 days hydrolysis.

Furthermore, the results show that the saturated β -diketon ACAC as complex ligand has the highest hydrolytic stability in Al-alkoxide complexes as well as in Ti- and Zr-alkoxide complexes ($h = 1$). The unsaturated β -diketon APD as ligand shows a lower stability in Ti- and Zr-alkoxide complexes in comparison to the complex stability of the β -diketon ACAC but a higher one as compared to the saturated and unsaturated β -ketoesters (Fig. 6). The lower hydrolytic complex stability of the β -ketoesters compared to the diketones cannot be explained by different negative partial charges of the ligands according to the partial charge model [38]. Beside the differences in the charges, the isomerism of the bonds and the steric effect of the ligands should influence the hydrolytic stability of the complex ligands.

The different hydrolytic stability of the ligands at one and the same metal alkoxide is clearly visible in the Ti-butoxide complexes in which it decreases in the order ACAC > APD > AAA > EAA \geq MEAA. The strongest degradation of the Ti-complexes with β -ketoesters as ligands is observed within the first 2 h hydrolysis. The different hydrolytic behaviours of the metal alkoxide complexes in dependence on the metal alkoxide type and on the structure of the ligands show the necessity of a detailed knowledge on the ligand stability for a more controlled condensation reaction of such complexes to obtain well defined sols and hybrid polymers.

The added amount of water to the metal alkoxide complexes is mainly consumed for the hydrolysis of the metal alkoxide groups and for the release of hydrolytically unstable ligands and their degradation (see Fig. 1(B, C, D)). From the results in Fig. 7 it follows that the Al-, Ti- and Zr-butoxide complexes with stable ACAC ligands consume the lowest amount of water (30–40%), mainly for the hydrolysis of the M–OR groups. The relatively large water consumption in hydrolysates of the Al-alkoxide complex with APD as ligand is due to the incomplete complexation (0.6 : 1)

and the higher OR : M ratio (2.4). The complexes with unstable β -ketoester ligands consume 40–70% of the added water. Obviously, the larger fraction of consumed water is used for the partial release of the complex ligand and the establishing of additional MOH or MOR groups at the metal atom (Fig. 1(C)). Additional water is also necessary for the detected degradation of the AAA, EAA or MEAA corresponding to the reaction scheme in Fig. 1(D).

Particles with diameter up to 40 nm can be detected in hydrolysates of low or non-complexed metal alkoxides [36, 39]. Lower sized particles are present in hydrolysed solutions of metal alkoxide complexes (1 : 1) due to the lower OR to M ratio [11, 29, 35]. It follows from Fig. 8 that the particles in hydrolysates of the Ti- and Zr-complexes with stable ACAC and APD as ligands are very small with diameters of 2–4 nm. The averaged particle size is changed only to a small extent within 7 days of reaction time. The relatively large particles of 7 nm in hydrolysates of Al(OBu^t)₂APD complexes can be explained by the low complexation degree (60%) of the Al-sec-butoxide with APD in comparison with the Ti- and Zr-alkoxide complexes (see Fig. 6). The high hydrolytic stability of the AAA and EAA complexed Al-butoxide similarly results in a small particle size as in the hydrolysates of complexes with ACAC ligands. At present, the large particle diameter and the early formation of a precipitate in Al(OBu^t)₂MEAA hydrolysates is surprising in spite of the high ligand stability of this complex.

Corresponding to the theory, the more unstable β -ketoester ligands of the Zr- and Ti-alkoxide complexes lead to larger particles and to a significant increase of the particle size with increased reaction time than in sols with stable ligands. From the studies can be concluded that the significant differences in the hydrolytic stability of the organic ligands (β -diketone and β -ketoester) in Al-, Ti- and Zr-alkoxide complexes are to be taken into consideration for a more controlled synthesis of sols with a defined particle size, of organically modified polymers and of inorganic-organic hybrid polymers. A highly hydrolytically unstable ligand is connected with additional condensation reactions of the MOR/OH groups and leads to larger particle sizes in the sols. Furthermore, the hydrolytic instability of unsaturated complex ligands can entail incomplete connections between inorganic and organic networks in the hybrid polymers.

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