served. X-ray diffraction data confirmed a lithium titanates structure.

- (II) A gel precursor fired at 750°C was treated in the Rotavapor with concentrated HNO3 and evaporated under vacuum. The process was repeated several times (generally 4) until chlorides were not observed in the evaporated solution. Chemi-
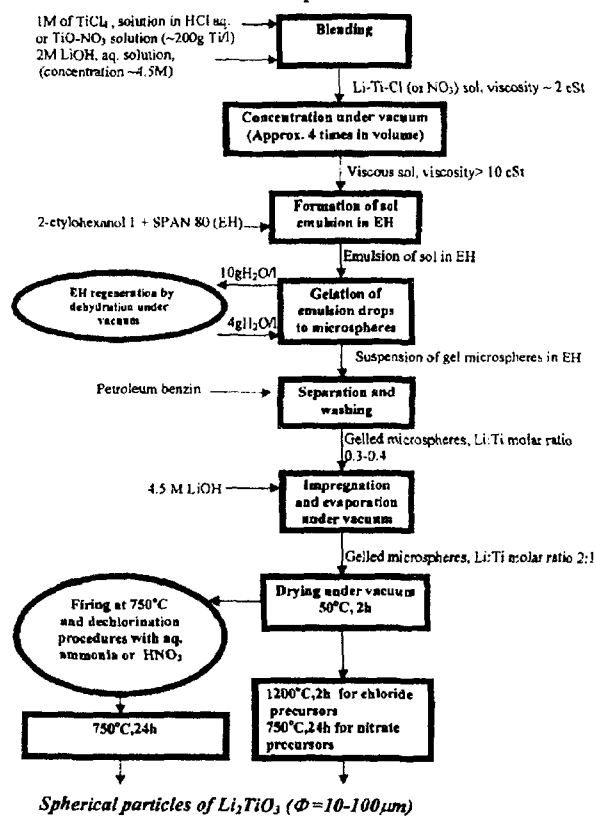

Spherical particles of Li$_2$TiO$_3$ (Φ=10-100μm)

Fig.5. Flow-chart for preparation of spherical powders of Li2TiO3 by the sol-gel process.

cal analysis (Cl<0.04) as well as thermal analysis (Fig.3) indicated that this procedure is more effective than (I).

- (III) Starting aqueous solution of TiCl4 was treated with concentrated HNO3 in a similar way as described above in (II). A concentrated solution of TiO nitrate ($\sim$ 200 g Ti/l), white in color, was prepared. To this solution LiOH can be introduced easily to MR Li:Ti=3, pH=0.4. At higher pH, precipitation takes place. A stoichiometric 2Li-Ti nitrate sol, after concentration in the Rotavapor, the concentrated sol (230 g/l, viscosity 15 cSt) was gelled to microspheres and then supplied routinely to impregnation. Thermal analysis of the fired at 750°C precursor (Fig.3), as well as the content of chloride are similar as for the former material. Micrographs of microspheres in various stages of fabrication are shown in Fig.4.

The elaborated processes of fabrication of Li2TiO3 of medium size microspheres (with diameters below 100 μm) are shown in Fig.5. These results indicate that the effective possibility of chemical, low temperature removal of chlorides from Ti-Li-Cl systems is feasible. All the described procedures do not change the spherical shape of particles. It is necessary to underline that the formation of medium sized microspheres is practically not possible by powder agglomeration processes routinely used for the fabrication of pebbles.

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PROTON NUCLEAR MAGNETIC RESONANSE STUDIES OF HYDRATION OF OXAALKANES IN BENZENE SOLUTION

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Thermodynamic studies on hydration of oxaalkanes in aqueous solution [1] put two questions: 1) whether hydrophilic properties of the oxygen atom in mono-ether molecules depend on the inductive effect of alkyl groups; and 2) how does the second oxygen atom in dioxaalkane molecules affect the hydrophilic properties of the first oxygen atom. Because the effects of hydrophilic hydration of amphiphilic solutes in aqueous solution are obscured by those of hydrophobic hydration, the answer could be obtained when studying hydration of oxaalkanes in non-aqueous solution. ^{1}H-NMR is a proper method for such a study.

We studied the formation of hydrogen bonds between water molecules and ethereal oxygen atoms [2] in a [^{2}H]$_6$-benzene solution containing ca 0.01

mol dm^{-3} water and a varying excess concentration of some oxaalkanes (given in Table) either commercial or synthesized according to Williamson reaction [3]. A Varian Gemini 2000-200 MHz spectrometer was used to collect ^{1}H-NMR data at 25°C (thermostated), using TMS as an internal standard. At the low water concentration used in this study it can be safely assumed that the proton chemical shift of about 0.4 ppm downfield of TMS is due to water monomers [4]. Upon progressively adding a large excess of oxaalkanes (up to 2 mol dm^{-3}) to such a solution, the water resonance shifts downfield, to be eventually obscured by a large signal from the methyl protons of the oxaalkanes. Given the low water concentrations throughout the study

and low values of the stability constants of the oxa-alkane hydrates, we asumed that only 1:1 hydrates are formed under the experimental conditions and the formation of 2:1 species is less probable [5]. The data in Fig. are indicative of hydration of oxaal-
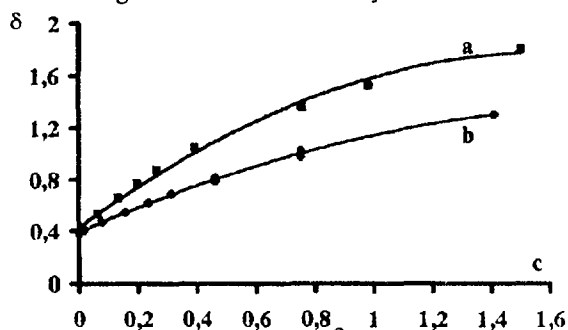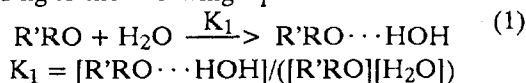

Fig. Plots of the water (0.01 mol dm^{-3}) proton chemical shifts in [^{2}H]$_6$-benzene solution containing increasing concentrations (c) of two oxaalkanes: a - 1,2-dimetoxyethane, b - dimetoxy-methane; at 25°C.

kanes by hydrogen bonding, and were analyzed according to the following equilibrium:

$$R'RO + H_2O \xrightarrow{K_1} R'RO\cdots HOH \qquad (1)$$

$$K_1 = [R'RO\cdots HOH]/([R'RO][H_2O])$$

where: R'RO - an oxaalkane molecule, R'RO$\cdots$HOH - its 1:1 hydrate, [x] - molar concentration of x, K_1 - the stability constant of the 1:1 hydrate. The data in Fig. were analysed using equation (2) which assumes that the observed shift (δ) is a weighted average of the coordinated-water (δ_h) and free-water (δ_w) positions [6]:

$$\delta = \delta_w + (\delta_h - \delta_w)\frac{K_1 c_0}{1 + K_1 c_0} \qquad (2)$$

where - under the conditions of the experiment - the equilibrium concentration of oxaalkane (c$_0$) can be approximated by its initial molar concentration (c).

Table presents the values of stability constants calculated using equation (2). Three groups of oxaalkanes of similar K_1 values can be distinguished: the values for monoethers and acetals are close to one another, while those for diethers are about twice as large as those for acetals.

The similar K_1 values obtained for two different monoethers, one of them with the terminal methyl group, show that the inductive effect of alkyl groups has small (if any) influence on the hydrophilic properties of the ethereal oxygen atom. On the other hand, nearly twice as large K_1 values obtained for diethers (practically the same for each) seem to indicate that the difference is due to the presence of

two hydrophilic oxygens in each diether molecule instead of one in the monoethers. Thus, the hydrophilicity of each ethereal oxygen is nearly the same, irrespectively of its parent molecule - either mono-or diether.

Table. Stability constants (molar concentration scale) of 1:1 hydrates of some oxaalkanes in [^{2}H]$_6$-benzene solution at 25°C.

	Oxaalkane	K_1
Monoethers	CH$_3$OC$_4$H$_9$	0.38 ± 0.02
	C$_3$H$_7$OC$_3$H$_7$	0.43 ± 0.03
Acetals	CH$_3$O(CH$_2$)OCH$_3$	0.54 ± 0.02
	C$_2$H$_5$O(CH$_2$)OC$_2$H$_5$	0.52 ± 0.08
Diethers	CH$_3$O(CH$_2$)$_2$OCH$_3$	0.96 ± 0.06
	CH$_3$O(CH$_2$)$_4$OCH$_3$	0.83 ± 0.18
	C$_2$H$_5$O(CH$_2$)$_2$OC$_2$H$_5$	1.07 ± 0.17
	C$_2$H$_5$O(CH$_2$)$_4$OC$_2$H$_5$	1.10 ± 0.05

The number of oxygen atoms in the molecules of diethers and acetals is the same (two), therefore much lower K_1 values obtained for the acetals indicate for much lower hydrophilicity of acetal oxygens than that of ethereal ones. This observation can be explained by assuming a strong mutual inductive effect of the two oxygen atoms [7] separated by only one CH$_2$ group in acetal molecules. This is also in line with our earlier experimental results showing much lower values of standard enthalpy and Gibbs free energy of water-heptane partition of acetals, compared to those of diethers [1, 8]. This well corresponds with our earlier conclusion that two oxygen atoms in diether molecules interact with water nearly independently of each other, and form hydrogen bonds of strength comparable to that in monoethers and much greater than that in acetals [8].

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X-RAY MOLECULAR AND CRYSTAL STRUCTURE
OF BIS(PENTANE-2,4-DIONATO)LEAD(II)

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Recent interest in the lead(II) chemistry [1] results not only from the role of the metal as an environmental contaminant and from the need to design drugs which could counteract the effects of lead poi-

soning [2]. Volatile lead(II) compounds, including β-diketonate complexes, are used for metaloorganic vapour deposition of lead-containing thin ferroelectric films for microelectronics [2]. Amphiphilic