THE THERMAL BEHAVIOUR OF SOLVATES IN THE LiCl(MgCl₂, AlCl₃) WATER-1,4-DIOXANE SYSTEMS

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The thermal behaviour of the solvates and mixed solvates in the LiCl(MgCl₂, AlCl₃)-water-1,4-dioxane systems was investigated by means of DTA measurements of the melting behaviour and by quasi-isothermal and quasi-isobaric investigations of the thermal decomposition processes.

The compounds melt incongruently. The positions of the melting points and the processes of thermal decomposition confirm the assumption that 1,4-dioxane is bonded in the first coordination sphere in the mixed solvate of lithium, but in the cases of magnesium and aluminium chloride it is bonded via hydrogen-bonds and not directly to the cations. Only for the lithium and magnesium compounds does the decomposition of the anhydrous solvates result in anhydrous chlorides.

At 298.15 K, LiCl, MgCl₂ and AlCl₃ form the salt hydrates $LiCl \cdot H_2O$, $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ in aqueous solution. Moreover, in the presence of 1,4-dioxane ($C_4H_8O_2$) the solvates and mixed solvates $LiCl \cdot H_2O \cdot C_4H_8O_2$, $LiCl \cdot C_4H_8O_2$ [1], $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$, $MgCl_2 \cdot 2C_4H_8O_2$ [2], $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ and $AlCl_3 \cdot 2C_4H_8O_2$ [3] can be obtained.

From the point of view of coordination chemistry, the incorporation of 1,4-dioxane in the solvates is interesting because this can be coordinated as a bridging ligand between the aquo complexes of the cations, as well as directly to the cation.

As a continuation of our thermoanalytical investigations of solid-phase solvates in the salt-water-organic component systems, this paper is intended to demonstrate the influence of 1,4-dioxane on the solvate structure and the coordination of the solvents to the different cations through an investigation of their thermal behaviour.

Detailed results of thermoanalytical investigations are available only for the pure salt hydrates [4–7]. As concerns the solvates and mixed solvates, the data published

so far in the literature are incomplete. Rheinboldt [8] mentioned that the separation of 1,4-dioxane from the compound $LiCl \cdot C_4H_8O_2$ is complete at 120°. Barnes [9] reported only decline curves of the $MgCl_2$ solvates under dynamic conditions, and Scheka et al. [10] gave the melting point of $AlCl_3 \cdot 2C_4H_8O_2$ as 114° and the beginning of dioxane separation at 106°.

Experimental

Preparation and characterization of solvates

With the exception of the compound $MgCl_2 \cdot 2C_4H_8O_2$, which was prepared according to the instructions of Rheinboldt [8], the solvates and mixed solvates were prepared by the addition of the anhydrous salts LiCl, $MgCl_2$ or $AlCl_3$, or the corresponding salt hydrates, to the cooled solvents and stirring at 298.15 K till the establishment of equilibrium. The resulting solid phases were separated and dried over calcium chloride before thermoanalytical investigations. The mixed solvate $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ is stable only in the mother liquor; otherwise, it decomposes even at room temperature and gives off about 1 mol of H_2O and 1 mol of $C_4H_8O_2$. The compounds were characterized by means of chemical analysis and X-ray investigations (X-ray apparatus TUR M 62, VEB Röntgen- und Transformatorenwerke, Dresden, provided with a horizontal goniometer H Z G 4–B, VEB Freiberger Präzisionsmechanik; CuK_α radiation).

In order to exclude changes of the surface due to ageing processes during the measurements, the crystals were absorbed with adherent mother liquor.

Table 1 presents the results of sample characterization. The good agreement of the lattice parameters derived from the powder diffractograms with the published results of single-crystal investigations [11–13] is clear. The lattice parameters of $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ have not been published previously.

Thermoanalytical investigations

The melting behaviour was characterized by means of DTA using the thermoanalyser made by Setaram (France), in gas-tight crucibles (consisting of TiPd 0.2) and crucible holder suspension incorporated platinel thermocouples. Parameters: DTA ± 100 μV, ± 250 μV, heating rate 2 deg/min, sample mass 8–12 mg. In addition, microscopic investigations of the crystals in closed test-tubes were carried out on a Boetius micro heating stage fitted with the observation instrument PHMU 05 produced by VEB Analytik, Dresden.

Moreover, the solid phase in the melting equilibrium was separated and analysed by means of a high-temperature centrifuge [15].

Table 1 Results of chemical analysis and X-ray investigations as compared to literature

Solvate		Chemical composition		1,4-dioxane	X-ray own results	Investigation literature
		salt	water			
$LiCl \cdot H_2O \cdot C_4H_8O_2$	pract.	28.50	12.80	58.70	$a = (597.75 \pm 1.25)$ pm $b = (1284.78 \pm 2.55)$ pm $c = 1050.48 \pm 2.93$ pm $\beta = (113.860 \pm 0.004)°$ monoclinic	$a = 597.4$ pm $b = 1285.3$ pm $c = 1049.2$ pm $\beta = 113.67°$ $P2_n/c = C_2^5 n$ [11]
	theor.	28.55	12.13	59.32		
$LiCl \cdot C_4H_8O_2$	pract.	32.63	0.3	67.07	$a = (802.20 \pm 1.42)$ pm $b = (1136.66 \pm 2.50)$ pm $c = (711.65 \pm 2.01)$ pm orthorhombic	$a = (803 \pm 2)$ pm $b = (1132 \pm 3)$ pm $c = (714 \pm 4)$ pm $P2_1 2_1 2_1 = D_2^4$ [12]
	theor.	32.49	—	67.51		
$MgCl_2 \cdot 6H_2O \cdot C_4H_8O$	pract.	32.70	37.85	29.45	$a = (1219.51 \pm 0.69)$ pm $b = (798.04 \pm 0.22)$ pm $c = (685.96 \pm 0.23)$ pm $\beta = (91.25 \pm 0.03)°C$ monoclinic	$a = 1215$ pm $b = 796$ pm $c = 686$ pm $\beta = 91.23°$ $P2_{1/m}$ [13]
	theor.	32.67	37.10	30.23		
$MgCl_2 \cdot 2C_4H_8O_2$	pract.	34.7	0.3	65.0	$a = (995.6 \pm 1.8)$ pm $c = (2507.0 \pm 1.9)$ pm tetragonal	— cf. data in [13]
	theor.	35.08	—	64.92		
$AlCl_3 \cdot 2C_4H_8O_2$	pract.	43.10	0.73	56.17	$a = 1283 \pm 3$ pm $b = 1434 \pm 1$ pm $c = 1575 \pm 1$ pm orthorhombic	
	theor.	43.08	—	56.92		
					$D_2^2 - P2_1 22 \; n = 8$	
$AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ pract. Determination by Schreinemakers-residue method					$a = (925.3 \pm 0.2)$ pm $b = (2159.5 \pm 1.7)$ pm $c = (1681.1 \pm 0.8)$ pm $\beta = 92.25°$ monoclinic	[14]
	theor.	23.82	28.96	47.22		

The investigations on the thermal decomposition were carried out under quasi-isothermal and quasi-isobaric conditions ($p \simeq 0.12 \pm 0.01$ MPa [16]) and simultaneous gas titration. In this process, the thermogravimetric signal (TG curve), the temperature difference curve for the reference material α-Al_2O_3 (ΔT curve) and the HCl titration (TGT curve) were recorded. Analyser: Q-derivatograph made by MOM, Budapest; parameters: Pt labyrinth crucible, TG = 100 mg, decomposition rate 0.3 or 0.6 mg/min, DTA = 250 µV, inert gas atmosphere = N_2, thermocouples: Pt$-$Pt/Rh 10%, titrant 0.1 N NaOH, titration at pH = 5.

Results

$LiCl$–H_2O–$C_4H_8O_2$ system

Figure 1 shows DTA plots for the dioxane adducts as compared to $LiCl \cdot H_2O$ [4]. The DTA effects reveal the incongruent melting of the compounds to form anhydrous lithium chloride. The phases $LiCl(s)$, $LiCl \cdot 1.2H_2O \cdot 0.8C_4H_8O_2(l)$ and $C_4H_8O_2(l)$ coexist in the melting equilibrium of the mixed solvate $LiCl \cdot H_2O \cdot C_4H_8O_2$ at 130°. In Fig. 2, the results of the thermal decomposition are presented. As compared to $LiCl \cdot H_2O$, were the water evaporates from the melt at 168°, the $LiCl \cdot H_2O \cdot C_4H_8O_2$ and $LiCl \cdot C_4H_8O_2$ system already decomposed just before melting. In the case of $LiCl \cdot H_2O \cdot C_4H_8O_2$, dioxane is released in the first stage at 120°, and water is released in the second stage starting at 165° from the lithium chloride monohydrate melt. The mass loss of 59% and the course of the
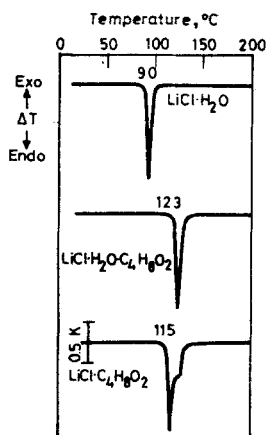

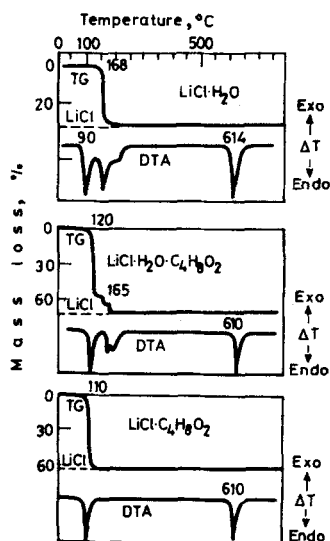Fig. 1 DTA curves of the solvates of LiCl in the closed system

Fig. 2 Thermal decomposition of the solvates of the LiCl–H$_2$O–C$_4$H$_8$O$_2$ system (TG, ΔT)

curve after interruption and resumption of the heating process at this degree of decomposition are identical with the thermal behaviour of LiCl · H$_2$O (Fig. 2) and prove the separate solvent liberation from the mixed solvate.

More than 90% dioxane separates isothermally from LiCl · C$_4$H$_8$O$_2$ at 110°.

When the solvent liberation stops, LiCl is always present in the compounds investigated. Its transition into the melt is indicated by the peaks at about 610–614° (Fig. 2). In the literature, 614° has been reported [17].

MgCl$_2$–H$_2$O–C$_4$H$_8$O$_2$ system

In Fig. 3, the DTA curves of MgCl$_2$ · 6H$_2$O · C$_4$H$_8$O$_2$ and MgCl$_2$ · 2C$_4$H$_8$O$_2$ are presented in comparison with MgCl$_2$ · 6H$_2$O. Just like the hydrate [5], the dioxane solvates melt incongruently, with the melting point of MgCl$_2$ · 6H$_2$O at 117°, intermediate between that of MgCl$_2$ · 2C$_4$H$_8$O$_2$ at 71° and that of MgCl$_2$ · 6H$_2$O · C$_4$H$_8$O$_2$ at 127°. In the case of the mixed solvate at 130°, a solid phase composed of MgCl$_2$ · 2H$_2$O · C$_4$H$_8$O$_2$ and two liquid phases approximately composed of dioxane and a melt rich in water consisting of MgCl$_2$ · 6H$_2$O · 0.5C$_4$H$_8$O$_2$ are present.

Figures 4 and 5 report the results of thermal decomposition of the MgCl$_2$ solvates. In the first stage (Fig. 4), the compound MgCl$_2$ · 6H$_2$O · C$_4$H$_8$O$_2$ isothermally releases 0.7 mol of C$_4$H$_8$O$_2$ below the melting point.
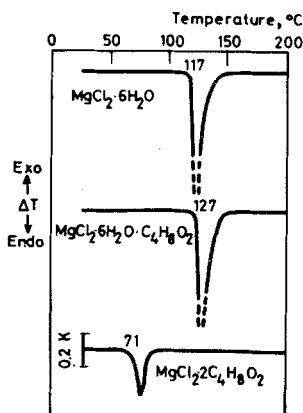
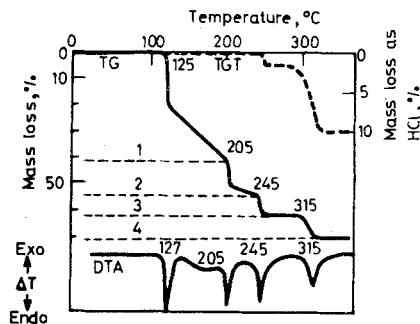Fig. 3 DTA curves of the solvates of $MgCl_2$ in the closed system

Fig. 4 Thermal decomposition of $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ (TG, ΔT, TGT). 1 $MgCl_2 \cdot 4H_2O$, 2 $MgCl_2 \cdot 2H_2O$, 3 $Mg(OH)_{0.18}Cl_{1.82} \cdot 1.03H_2O$, 4 $Mg(OH)_{0.78}Cl_{1.22}$

Subsequently, in the temperature range up to 205°, the joint evaporation of the dioxane residue (0.3 mol) and of 2 mol of water per mol of initial compound follows.

After the completion of these processes, a saturated $MgCl_2 \cdot 4H_2O$ melt is attained, whose thermal decomposition to magnesium hydroxide chloride is approximately identical with the decomposition of $MgCl_2 \cdot 4H_2O$ from $MgCl_2 \cdot 6H_2O$ [5] as described above. In contrast to this, the thermal decomposition of $MgCl_2 \cdot 2C_4H_8O_2$ results in anhydrous magnesium chloride (Fig. 5).

After melting, the evaporation of dioxane starts of 90°, with stages of solvate contents of approximately 0.5 and 0.25 mol of $C_4H_8O_2$/mol of $MgCl_2$ being observed. The slight HCl liberation of about 0.2 wt.% at about 230° should be attributed to the reaction of adhesive water with the solvate, forming $MgCl_2$ hydrate, and to the thermal decomposition of the latter.
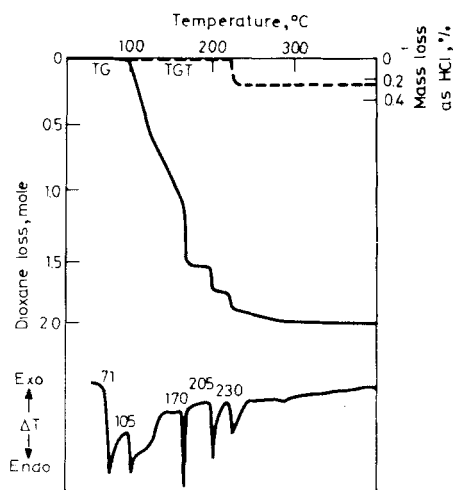
Fig. 5 Thermal decomposition of $MgCl_2 \cdot 2C_4H_8O_2$ (TG, ΔT, TGT)

$AlCl_3-H_2O-C_4H_8O_2$ system

Due to the instability of the mixed solvate $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ (Section 2), only the melting behaviour of $AlCl_3 \cdot 2C_4H_8O_2$ could be investigated. Figure 6 shows the DTA peak at 43°. By means of the heating stage microscope, extremely incongruent behaviour was observed. The evaporation of dioxane starts at 105° (Fig. 7). At the end of the first stage, $AlCl_3 \cdot C_4H_8O_2$ has been formed. This solvate was also demonstrated by Scheka [10]. No anhydrous aluminium chloride is formed

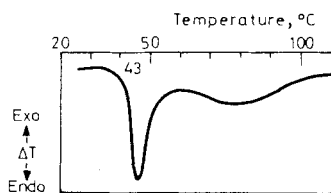**Fig. 6** DTA curves in the closed system of $AlCl_3 \cdot 2C_4H_8O_2$

with further increase of the temperature, but dissociation and polymerization reactions occur which have not been studied in detail. On the one hand, the water content of 0.7 wt.% in the solvate catalyzes the dioxane dissociation, while on the other hand, the hydrolytic dissociation of the intermediates, including HCl liberation, sets in (TGT curves in Fig. 7).
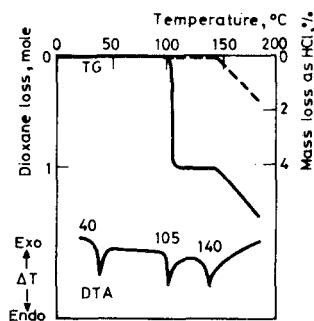
Fig. 7   Thermal decomposition of $AlCl_3 \cdot 9H_2O \cdot 2C_4H_8O_2$ (TG, ΔT, TGT)

The thermal decomposition of $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ does not result in $AlCl_3 \cdot 6H_2O$ either, but, after the simultaneous liberation of dioxane and water, Al_2O_3 is formed via $AlCl_3 \cdot 6H_2O$ (Fig. 8). Intermediate stages of dioxane liberation cannot be quantified. Moreover, Fig. 8 illustrates the instability of the mixed solvate. The liberation of dioxane already proceeds at 25°.
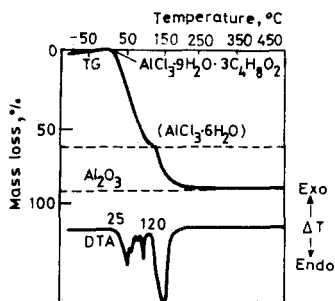

Fig. 8   Thermal decomposition of $AlCl_3 \cdot 9H_2O \cdot 3C_4H_8O_2$ (TG, ΔT)

Discussion

The thermoanalytical investigation results obtained confirm the concepts of the solvate structure and the coordination of the compounds investigated as reported in the literature. In the case of lithium chloride solvates, the compounds $LiCl \cdot C_4H_8O_2$ (melting point = 115°) and $LiCl \cdot H_2O \cdot C_4H_8O_2$ (melting point = 123°) containing dioxane always have higher melting points than the corresponding hydrates: $LiCl \cdot H_2O$ (melting point = 90°) and $LiCl \cdot 2H_2O$ (melting point = 19.4°) [18]. This increase in the melting point correlates with the

increasing stability of the coordinate bond. Due to the increase in the covalent bond character, dioxane forms stronger coordinate bonds with the lithium cation than water does. By means of X-ray investigations of the mixed solvate $LiCl \cdot H_2O \cdot C_4H_8O_2$, Durant [11] proved that the tetrahedrally coordinated Li^+ ion is surrounded by Cl^-, H_2O and two dioxane molecules forming bridges, and that the dioxane is not involved in hydrogen-bonding.

The separate solvent evaporation from the mixed solvate indicates the direct coordination of the water as well as of the dioxane to the lithium cation. In agreement with the lower donor number of dioxane as compared to water ($DN_{dioxane} = 62$ kJ/mol, $DN_{H2O} = 75.4$ kJ/mol) [19], the organic solvent is separated at a lower temperature than water.

Similarly as for the LiCl mixed solvate, the melting point of $MgCl \cdot 6H_2O \cdot C_4H_8O_2$ (melting point = 127°) is higher than that of $MgCl_2 \cdot 6H_2O$ (melting point = 117°), although the melting point is generally reduced for salt hydrates with increasing hydrate water content.

This effect is an expression of the increased bond strength of the mixed solvate, which can be attributed to the hydrogen-bonds between the dioxane and water molecules [13]. The intermolecular interactions also become obvious from the fact that the organic component is already separated in the first two stages of $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ decomposition (Fig. 4). In contrast to $MgCl_2 \cdot 6H_2O$ decomposition, the beginning of decomposition at 125° sets in from the solid phase near the melting point; according to Barnes [13], the dioxane expands the crystal lattice and thus the thermal stability is reduced in comparison to that of the hydrate.

In the initial phase, the decomposition of the mixed solvate $AlCl \cdot 9H_2O \cdot 3C_4H_8O_2$ proceeds similarly to that of the mixed solvate of $MgCl_2$, with preferred separation of dioxane and the formation of $AlCl_3 \cdot 6H_2O$, as in this case too the organic component is not bonded to the Al^{3+} cation in the first coordination sphere, but via hydrogen-bonds [20].

The decomposition of the anhydrous solvates $LiCl \cdot C_4H_8O_2$ and $MgCl_2 \cdot 2C_4H_8O_2$ results in the formation of anhydrous Li and Mg halides, but this is not the case for $AlCl_3 \cdot 2C_4H_8O_2$. Due to the increasing acidity of the salts in the series $LiCl < MgCl_2 < AlCl_3$, the reaction of the salt with the organic solvent, involving dissociation of the cyclic ether, begins in the case of $AlCl_3 \cdot 2C_4H_8O_2$.

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Zusammenfassung — Das thermische Verhalten der Solvate und Mischsolvate der Systeme LiCl, (MgCl$_2$, AlCl$_3$)-Wasser-1,4 Dioxan wurde mit Hilfe von DTA-Messungen zum Schmelzverhalten, und quasi-isothermen und quasi-isobaren Untersuchungen zum Ablauf der thermischen Zersetzung Untersucht. Die Verbindungen schmelzen inkongruent. Die Lage der Schmelzpunkte und der Verlauf der thermischen Zersetzung bekräftigen die Vorstellungen, daß 1,4 Dioxan im Mischsolvat des Lithiums in der ersten Koordinationsphäre direkt am Kation, hingegen bei Magnesium und Aluminium über Wasserstoffbrücken gebunden ist. Die Zersetzung der wasserfreien Solvate führt nur im Fall der Lithium- und Magnesiumverbindungen zu den wasserfreien Chloriden.

Резюме — Термическое поведение сольватов и смешанных сольватированных систем хлористый литий (хлорид магния, хлорид алюминия)-вода-1,4-диоксан было исследовани ДТА измерениями их плавления, а квази-изотермическими и квази-изобарными методами — процесс их термического разложения. Соединения плавятся инконгруэнтно. Положение их точек плавления и процесс термического разложения подтверждают предположение, что 1,4-диоксан связан с литием в первой координационной сфере его смешанного сольвата. В случае же хлоридов магния и алюминия, он связан с катионами не прямо, а посредством водородных связей. Только для соединений лития и магния термическое разложение безводных сольватов приводит к образованию безводных хлоридов.