STUDY OF THE INTERACTION BETWEEN CAESIUM BROMIDE AND KAOLINITE BY DIFFERENTIAL THERMAL ANALYSIS

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The reaction occurring during the wet grinding of kaolinite with CsBr was studied by simultaneous Differential Thermal Analysis -Thermogravimetry (DTA-TG), supplemented by infrared spectroscopy of isothermally treated CsBr disks. The DTA and TG curves were compared with those of untreated kaolinite and of kaolinite mixed or air ground with different alkali halides. A new endothermic DTA peak at 75–115°, accompanied by weight loss, is due to the desorption of surface and interparticle water located mainly at the "interface" between the mineral and the salt. A second endothermic peak at about 500° represents the simultaneous dehydroxylation of the clay and thermal hydrolysis of CsBr. The presence of a separate CsBr phase was identified from two endothermic peaks which characterize melting and boiling of the salt; only mixtures with more than 140 mmol CsBr per 100 g kaolinite show the presence of this phase. All of the CsBr below this concentration occurs in the CsBr–HOH–kaolinite intercalation complex. This degree of saturation is smaller than that obtained previously for CsCl.

It has been shown previously by both conventional and photoacoustic infrared (IR) spectroscopy that the grinding of kaolinite with caesium chloride or caesium bromide leads to its delamination and the formation of an intercalation complex in which the caesium salt, together with water, is located between the layers of the mineral [1–6]. In the case of CsCl, water needed for the intercalation complex can be adsorbed from the atmosphere (air grinding), whereas for CsBr–kaolinite, the moistening of the mixture

during the grinding process (wet grinding) is essential for the formation of a complex. In these complexes, the large Cs ion, which serves as a water 'structure breaker', perturbs the ice-like structure of water clusters in the vicinity of the clay, and the monomeric water molecules coordinated to Cs^+ take part in hydrogen bonds in which
1. protons are donated to the oxygen planes of the kaolin-like layers;
2. protons are accepted from the hydroxyl planes of the kaolin-like layers;
3. protons are donated to the halide ions.

No intercalation complex is obtained with CsI either by wet grinding or by air grinding. This might be due to the fact that I^- is too big and cannot penetrate into the interlayer space of kaolinite, or that the water molecules do not form the hydrogen bonds with I^- that are essential for the intercalation reaction [6]. The air grinding of kaolinite with alkali halides leads to prototropy and partial delamination of the clay [1, 7].

Infrared spectroscopy can give direct proof only of the intercalation pf water or organic molecules between the layers of kaolinite [8, 9], but not of the intercalation of the salt, which lacks characteristic absorption bands. In our previous IR study we showed that the exact locations of the bands of the intercalated HOH were dependent on the Cs salt, and from this observation concluded that the salt was intercalated together with water [6]. Differential thermal analysis (DTA) was previously used to prove that kaolinite was intercalated by the CsCl and to determine the degree of saturation. This was possible because the presence of a separate CsCl phase in the CsCl-kaolinite mixture was identified from the appearance of endothermic peaks in the DTA curves due to melting and evaporation of the CsCl.

Only a few investigations are known which deal with the thermal behaviour of intercalation complexes [4, 10, 12]. In the present study we examined the thermal behaviour of wet ground mixtures of kaolinite and CsBr at various ratios. Our purpose was to identify the different phases which occur in each mixture, to determine whether CsBr intercalates between the layers and measure the degree of saturation. We applied simultaneous DTA and thermogravimetry (TG), and supplemented this with an IR study of isothermally treated samples. Isothermal weight loss measurements were published elsewhere [6].

In order to characterize specific thermal reactions of the intercalation complex, understand the nature of these reactions, and differentiate between them and those occurring between kaolinite and alkali halides in mixtures, the DTA–TG curves of wet ground CsBr–kaolinite mixtures were

compared to those of kaolinite air ground with KBr, KI, CsCl, CsBr, and CsI.

In a previous study of the CsCl–HOH–kaolinite system, air ground samples were aged for three weeks to obtain the intercalation complex before recording the DTA [4]. However, in the present study our goal was to observe the DTA of a mixture of kaolinite with CsCl, and not that of the complex. For this reason the DTA curve of the air ground CsCl–kaolinite mixture was recorded a short time after its preparation.

Experimental

Materials

Natural jurassic kaolinite from Makhtesh Ramon, Israel was used in this study. The clay powder was obtained by carefully abrading the rock in an agate mortar. The fraction passing an 80 mesh (0.177 mm) sieve was used. The halides were suprapure grade reagents, supplied by Merck.

Methods

The two different grinding techniques mentioned above were employed. In the first, mixtures containing 500 mg of kaolinite and 500 mg of the alkali halide (KBr, KI, CsCl, CsBr, or CsI) were ground in a mechanical 'Fisher' mortar grinder for 30 minutes at ambient atmosphere (air grinding). In the second technique, 1000 mg of mixtures containing kaolinite and CsBr at various ratios were ground mechanically for 60 minutes, but 2–3 drops of water were added every 5 minutes in order to keep the mixture moist (wet grinding).

Simultaneous DTA–TG curves were recorded in flowing nitrogen using a Stanton-Redcroft apparatus (STA 781). Calcined alumina was used as a reference. The quantity of kaolinite-salt mixture for each run was between 10 and 50 mg; the net amount of kaolinite in each sample was 10 mg. Alumina crucibles were used for the specimen and the reference material. The samples were heated from room temperature (r.t.) to 1170°. The heating rate in most experiments was 20 deg·min^{-1}, although in a few representative runs the heating rate was 10 deg·min^{-1}.

Infrared spectra of the wet ground CsBr–kaolinite mixtures were recorded with a Perkin–Elmer model 597 spectrophotometer. For this purpose, CsBr disks were prepared by carefully mixing 0.5–2 mg of the ground

mixtures with 150 mg of CsBr. Spectra were recorded for the freshly prepared disks, and after heating them at 100, 200, 300, and 400° for 24 h at each temperature. The disks were repressed after the heat treatment before their spectra were measured.

Results

Infrared study of thermally treated disks of wet ground CsBr-kaolinite mixtures

In our previous study [6], we showed that the intercalation complex is identified by the perturbation of characteristic OH, Si−O, and Al−OH bands of kaolinite. The 3692 cm^{-1} band becomes weak and a new band appears at 3597 cm^{-1}. Moreover, absorption at 1040 and 918 cm^{-1} shift to 1034 and 910 cm^{-1}, respectively. The present spectra show that the relative intensities of the absorption bands which characterize the intercalation complex increase with the concentration of CsBr in the mixture up to a maximum of 65%, indicating that the degree of intercalation increases. However, even at such a high concentration of CsBr, only part of the kaolinite is involved in the formation of the intercalation complex.

Some representative spectra recorded after heating the disks at several temperatures are shown in Fig. 1. The broad absorption at 3350–3500 and 1630 cm^{-1} are due to stretching and bending vibrations, respectively, of adsorbed water on the external surfaces of the mineral and the salt crystals. These bands are very strong in the spectra of the unheated disks. They become slightly weaker after heating the disks at 100°. In the spectrum of pure kaolinite, these bands do not appear after heating the disks at 200°, although they persist in the spectra of the wet ground mixtures up to 300°, indicating that the samples had not lost their 'adsorbed' surface water at this temperature.

The kaolinite OH stretching vibrations at 3590–3700 cm^{-1} are very weak in the spectra recorded after heating the disks at 400°, indicating that the dehydroxylation of the clay started at this temperature but was not completed after 24 hours. The Si−O stretching and deformation vibrations at 1000–1120 and 430–480 cm^{-1}, respectively, and the Al−OH vibrations at 900–920 and 540–570 cm^{-1} became broad, indicating that part of the clay had been transformed into the amorphous meta-kaolinite phase. The broadening of the peaks is more pronounced in the spectra of the intercalation complexes, indicating that their decomposition is faster than that of untreated kaolinite.
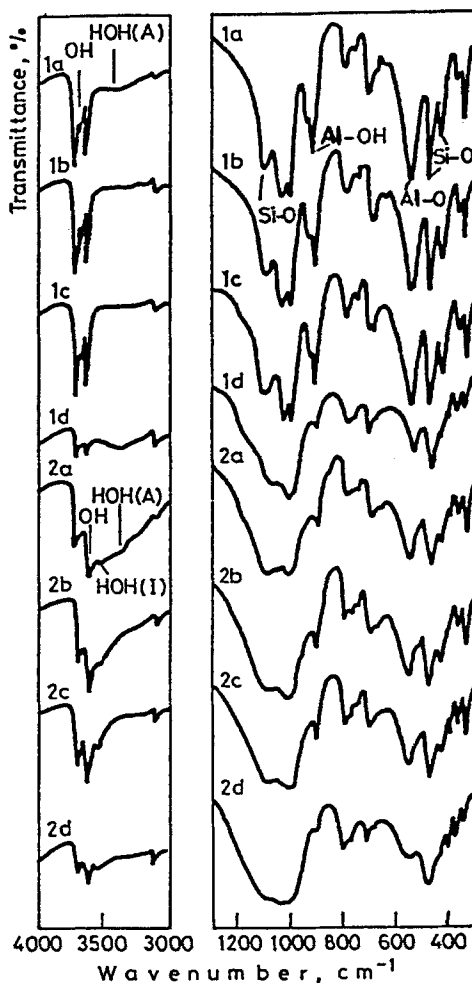
Fig. 1 Infrared spectra of CsBr disks of kaolinite (curves 1a–1d) and the CsBr–H2O–kaolinite intercalation complex obtained by wet grinding a mixture containing 60% kaolinite and 40% CsBr (curves 2a–2d). a, b, c, and d denote the temperatures (100, 200, 300, and 400°C respectively) at which the disks were heated for 24 h

Intercalated water gives a characteristic absorption band at 3541 cm^{-1} [6]. This band also appears in the spectra which were recorded after heating the disks at 300°. It becomes weak together with the OH stretching vibrations of the kaolinite only when the disks are heated at 400°. This is an indication that the intercalation complex is dehydrated together with the dehydroxylation of the clay.

DTA and TG of untreated kaolinite

The DTA curve of untreated kaolinite shows an endothermic peak at 530°, which is due to the dehydroxylation of this mineral and the formation of meta-kaolinite. An exothermic peak at 990° is due to the crystallization of the amorphous meta-kaolinite (Fig. 2). The endothermic peak is associated with a weight loss of 10.6% in the temperature range 335–685°. Another 0.4% is lost in the temperature range 685–1170° (Fig. 3).
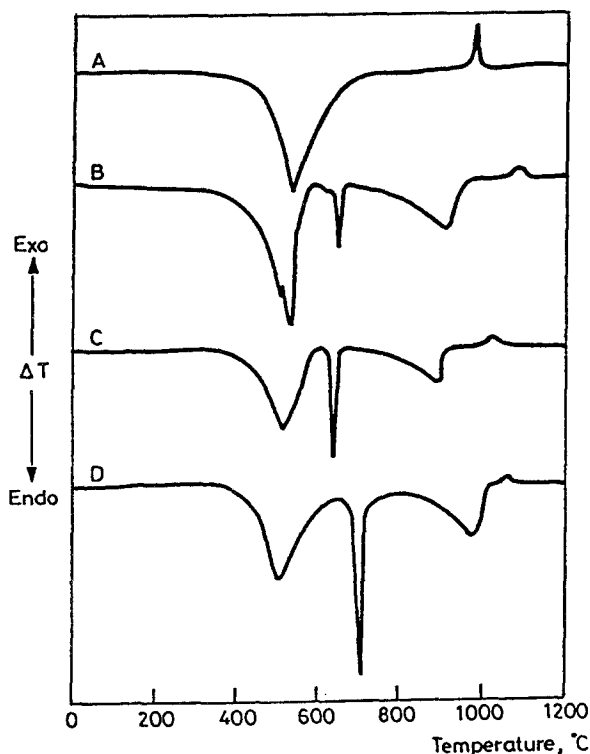

Fig. 2 DTA curves of untreated kaolinite (curve *A*), and of kaolinite air ground with CsCl (curve *B*), CsBr (curve *C*), and KBr (curve *D*). Each mixture consisted of 50% kaolinite and 50% alkali halide

DTA and TG of kaolinite mixed or air ground with alkali halides

The DTA curves of kaolinite mixed or air ground with alkali halides show the characteristic endothermic and exothermic reactions of kaolinite. The exact temperatures of these peaks are given in Table 1. Two additional endothermic peaks characterize the melting and evaporation of the alkali halide [13]. The first peak is very sharp and its location does not depend on

the heating rate. In contrast, the second one is very broad and its location depends on the heating rate. Some representative curves are shown in Fig. 2.

The TG curve of each of these samples can be divided into five regions of weight loss (the result for the air ground CsBr-kaolinite mixture in Fig. 3 serves as a typical exsample). This division correlates with the corresponding DTA curves. In the first region weight loss is due to the thermal drying of the salt and the surface of the kaolinite. The second region occurs simultaneously with the DTA peak arising from dehydroxylation of the kaolinite. The amount of weight loss is greater than that for untreated kaolinite in this temperature range. The third region occurs simultaneous with the melting of
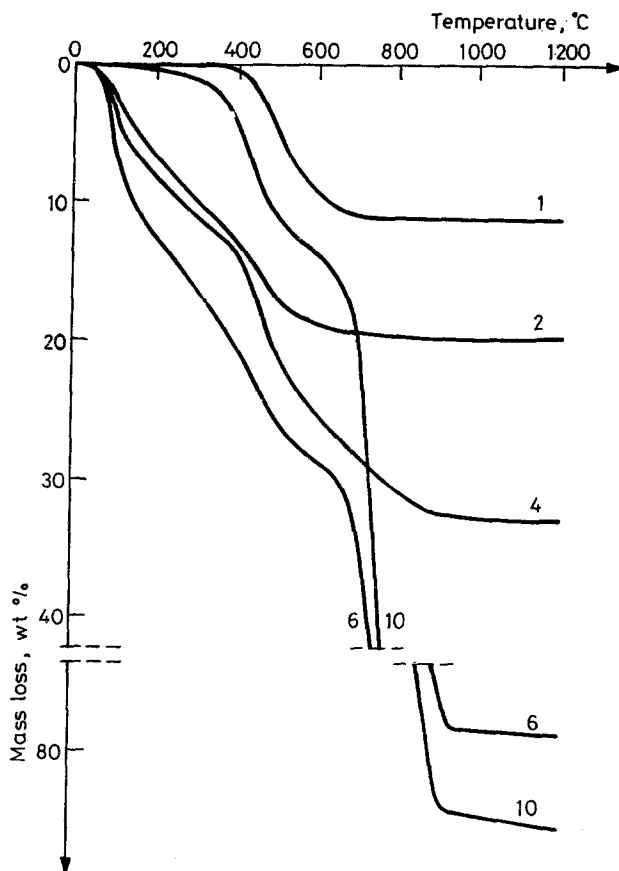

Fig. 3 TG curves of untreated kaolinite (curve 1), 50% kaolinite in air ground with CsBr (curve 10), and of 90/10, 70/30, and 50/50 weight % mixtures of kaolinite wet ground with CsBr (curves 2, 4 and 6, respectively). Numbers in this Fig. correspond to sample numbers in Table 2

Table 1 TG regions, temperature ranges, weight loss percentages (calculated on the basis of kaolinite), and DTA exothermic (ex) and endothermic (en) peaks ($^\circ$C) in the thermal analysis curves of kaolinite mixed (u) and air ground (g) with alkali halides

TG region	Temperature range, $^\circ$C	Weight loss, %	DTA peak temp., $^\circ$C
	1. 50% kaolinite + 50% KBr (g)		
1st	50– 355	1.0	—
2nd	355– 645	21.0	500 en
3rd	645– 720	3.65	710 en
4th	720–1025	71.35	990 en
5th	1025–1170	0.3	1060 ex
	2. 50% kaolinite + 50% KI (g)		
1st	r.t.– 355	1.0	—
2nd	355– 640	27.5	525 en
3rd	640– 685	4.0	680 en
4th	685– 965	33.0	935 en
5th	965–1170	0.5	1065 ex
	3. 50% kaolinite + 50% CsCl (u)		
1st	r.t.– 295	—	—
2nd	295– 570	13.0	525 en
3rd	570– 690	2.0	640 en
4th	690– 945	49.0	895 en
5th	945–1170	1.5	1025 ex
	4. 50% kaolinite + 50% CsCl (g)		
1st	r.t.– 280	2.5	—
2nd	280– 570	11.5	525 en
3rd	570– 690	2.0	645 en
4th	690– 970	62.0	925 en
5th	970–1170	1.3	1085 ex
	5. 50% kaolinite + 50% CsBr (u)		
1st	r.t.– 305	1.5	—
2nd	305– 605	12.5	540 en
3rd	605– 685	4.0	640 en
4th	685– 935	59.0	900 en
5th	9325–1170	1.5	1035 ex
	6. 50% kaolinite + 50% CsBr (g)		
1st	r.t.– 295	1.0	—
2nd	295– 590	12.5	515 en
3rd	590– 685	4.5	630 en
4th	685– 925	66.0	900 en
5th	925–1170	1.5	1025 ex

Table 1 (continued)

TG region	Temperature range, °C	Weight loss, %	DTA peak temp., °C
		7. 50% kaolinite + 50% CsI (u)	
1st	r.t.– 385	1.5	—
2nd	385– 590	16.0	525 en
3rd	590– 685	6.0	620 en
4th	685– 895	62.0	870 en
5th	895–1170	0.5	1035 ex
		8. 50% kaolinite + 50% CsI (g)	
1st	r.t.– 385	3.0	—
2nd	385– 590	16.5	525 en
3rd	590– 685	6.5	620 en
4th	685– 895	54.5	845 en
5th	895–1170	1.0	1020 ex

the salt. To a small extent, weight loss in this temperature range is due to the dehydroxylation of the clay, but it is principally due to the evaporation of the salt which starts in this region. The fourth region corresponds to the evaporation of the salt. Finally, in the fifth region a very small loss occurs during recrystallization of the meta-clay.

DTA and TG of wet ground CsBr–kaolinite mixtures

All the DTA curves of kaolinite ground with caesium bromide in the presence of water show a new endothermic peak at 75–115° which, according to the IR study, is associated with the evaporation of "adsorbed" water from the external surface of the clay. The dehydroxylation endothermic peak appears at temperatures slightly lower than that of the untreated clay. The DTA curves also show one or two exothermic peaks due to the crystallization of the amorphous meta-kaolinite. The exothermic reaction was not traced when the concentration of the clay in the system was less than 50%. The two endothermic peaks which characterize the melting and evaporation of CsBr occurred only when the clay concentration was > 40%. The exact temperatures of these peaks are given in Table 2. Some representative curves are shown in Fig. 4.

The TG curve of each of these samples can be divided into six regions of weight loss (Fig. 3 and Table 2). This division correlates with the corresponding DTA curves. The first region (r.t.–170°) occurs simultaneously with the first DTA endothermic peak and is associated with the dehydration of the external surface of the kaolinite. The second (170–400°) is charac-

terized by an almost constant rate of weight loss. The third region (400–590°) occurs simultaneously with the dehydroxylation DTA peak of kaolinite. For some of the mixtures the amount of weight loss is smaller than that of untreated kaolinite in the same temperature range. This is an indication that the dehydroxylation has already started at temperatures in the second region. In the fourth region (590–685°), melting of the excess salt occurs. In samples 1–4, weight loss is due to the dehydroxylation of the clay which continues in this region; however, in samples 5–8, it is mainly due to the evaporation of the salt which starts in this temperature range. Evaporation of the salt occurs in the fifth region. In samples 2–4 only traces of CsBr survive to evaporate at this temperature range, but in samples 5–8 this region is associated with a high weight loss that increases with increasing concentration of CsBr in the system. In the sixth region a very small weight loss is recorded corresponding to the recrystallization of the meta-clay.
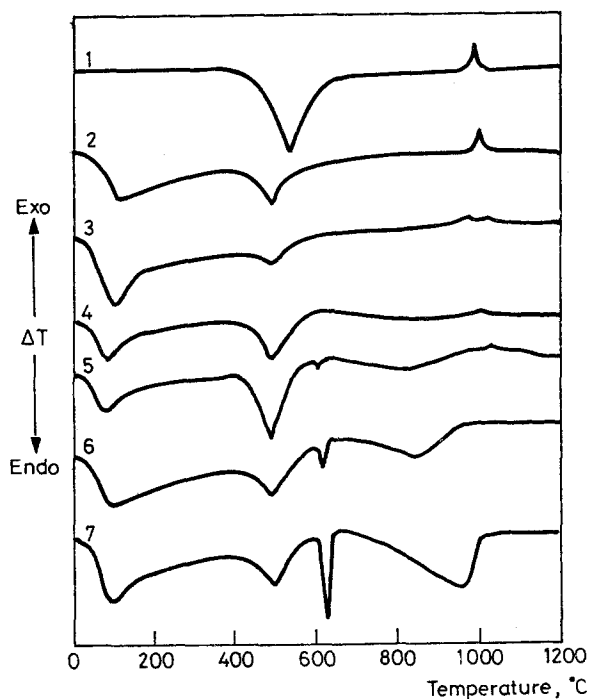
Fig. 4 DTA curves of untreated kaolinite (curve 1), and of 90/10, 80/20, 70/30, 60/40, 50/50, and 35/65 weight % mixtures of kaolinite wet ground with CsBr (curves 2, 3, ...7, respectively). Numbers in this Fig. correspond to sample numbers in Table 2

Table 2 TG regions, temperature ranges, weight loss percentages (calculated on the basis of kaolinite), and DTA exothermic (ex) and endothermic (en) peaks (°C) in the thermal analysis curves of wet ground CsBr–kaolinite mixtured (samples 2–8). The composition of the mixtures is given in the Table. For comparison, data are included from the TG and DTA curves of untreated kaolinite (sample 1) and mixed (u) and air ground (g) CsBr–kaolinite mixtures (samples 9 and 10) recorded in the same temperature ranges as for the wet ground CsBr–kaolinite mixtures

TG region	Temperature range °C	Weight loss, %	DTA peak temp., °C
	1. 100% kaolinite		
1st	r.t.– 170	—	—
2nd	170– 400	0.3	—
3rd	400– 590	8.2	530 en
4th	590– 685	2.1	—
5th	685– 950	0.3	
6th	950–1170	0.1	990 ex
	2. 90% kaolinite + 10% CsBr		
1st	r.t.– 170	5.8	115
2nd	170– 400	6.9	—
3rd	400– 590	5.2	490 en
4th	590– 685	1.2	—
5th	685– 950	0.5	—
6th	950–1170	0.1	1000 ex
	3. 80% kaolinite + 20% CsBr		
1st	r.t.– 170	8.5	100 en
2nd	170– 400	9.0	—
3rd	400– 590	6.5	485 en
4th	590– 685	1.75	—
5th	685– 850	1.75	—
6th	850–1170	0.5	980 ex
			1025 ex
	4. 70% kaolinite + 30% CsBr		
1st	r.t.– 170	7.5	75 en
2nd	170– 400	6.15	—
3rd	400– 590	10.5	490 en
4th	590– 685	3.6	—
5th	685– 870	4.3	—
6th	870–1170	0.7	1010 ex
	5. 60% kaolinite + 40% CsBr		
1st	r.t.– 170	8.85	75 en
2nd	170– 400	5.85	—
3rd	400– 590	11.3	495 en
4th	590– 685	4.7	605 en
5th	685– 935	17.3	825 en
6th	935–1170	0.5	1025 ex

Table 2 (continued)

TG region	Temperature range, °C	Weight loss, %	DTA peak temp., °C
6. 50% kaolinite + 50% CsBr			
1st	r.t.– 170	11.4	100 en
2nd	170– 400	9.4	—
3rd	400– 590	7.6	490 en
4th	590– 685	5.2	620 en
5th	685– 950	44.5	885 en
6th	950–1170	0.4	—
7. 35% kaolinite 65% CsBr			
1st	r.t.– 170	12.0	100 en
2nd	170– 400	9.15	—
3rd	400– 590	9.15	495 en
4th	590– 685	2.85	630 en
5th	685–1000	122.3	960 en
6th	1000–1170	1.5	—
8. 20% kaolinite + 80% CsBr			
1st	r.t.– 170	7.5	85 en
2nd	170– 400	5.0	—
3rd	400– 590	11.0	515en
4th	590– 685	5.5	640 en
5th	685–1060	340.0	1040 en
6th	1060–1170	3.0	—
9. 50% kaolinite + 50% CsBr (u)			
1st	r.t.– 170	0.5	—
2nd	170– 400	1.0	—
3rd	400– 590	12.0	540 en
4th	590– 685	4.5	640 en
5th	685– 935	59.0	900 en
6th	935–1170	1.5	1035 ex
10. 50% kaolinite + 50% CsBr			
1st	r.t.– 107	0.3	—
2nd	170– 400	1.7	—
3rd	400– 590	12.0	515 en
4th	590– 685	4.0	630 en
5th	685– 925	66.0	895 en
6th	925–1170	1.5	1025 ex

Discussion

### Thermal analysis of mixtures of kaolinite with alkali halides obtained by mixing or air grinding

There were no differences between the thermal curves of the air ground CsBr– or CsI–kaolinite mixtures and those of the unground mixtures. This is an indication that changes in the thermal behaviour of kaolinite during the dehydroxylation and recrystallization stages result from thermal reactions between the salt and the clay, and not from mechanochemical reactions which occur during the air grinding of the mixtures. For CsCl–kaolinite, the air ground mixtures show weight loss in the temperature range r.t.–400 °, greater than that of the unground mixture; this can be attributed to partial formation of the intercalation complex.

In order to understand the reactions between the salt and the kaolinite which occur during the thermal analysis, two observations must be considered:

1. The amounts of weight loss recorded in each region of the TG curves for the different mixtures are always higher than those lost by the untreated kaolinite in the corresponding temperature ranges.

2. The total amounts of weight loss recorded in the whole run (up to 1170°) are much smaller than those to be expected if the salts are completely evaporated.

According to Heller–Kallai [14] and Gabor et al. [15] when salts are heated together with kaolinite they undergo thermal hydrolysis during the dehydroxylation of the clay. Following these investigators, it is assumed that the difference in the weight loss occurring during the dehydroxylation stage between the mixtures and the untreated kaolinite is in part due to the evolution of hydrogen halide which results from the following thermal hydrolysis:

$$2\,SiO_2 \cdot Al_2O_3 \cdot 2HOH + 2nMX \rightarrow$$

$$\rightarrow 2\,SiO_2 \cdot Al_2O_3 \cdot nM_2O + 2nHX + (2-n)HOH$$
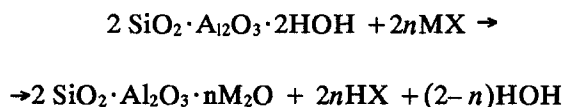
where M is K or Cs and X is Cl, Br, or I. On the clay surface a liberated water molecule associates with X^- to form volatile HX. The volatilization of HX, instead of HOH, is responsible for the great thermal weight losses of dry ground or mixed MX–kaolinite mixtures, especially in the temperature range of the dehydroxylation of the clay.

That part of the salt which reacted with the evolved water molecules forms a non-volatile oxide. Thus, the thermal hydrolysis is also responsible for the fact that the total amounts of weight lost during the recording of the TG curves are much smaller than expected.

The exothermic peak of the kaolinite, which appears at 990° in the DTA curve of the unground sample, is lowered after grinding the clay in the absence of salts. This peak was observed in the DTA curves of KCl–kaolinite mixtures at higher temperatures, after the evaporation of the excess salt [4]. In the present study it is seen that all the salts investigated cause the same effect, namely, the recrystallization peak is shifted to higher temperatures and becomes very small. In a previous X-ray study by Heller–Kallai and Frenkel [16], it was shown that the products of the thermal decomposition of kaolinite depend on the presence of various additives in the mixture. In the presence of potassium salts, thermal dehydroxylation at 500° results in an intermediate between metakaolinite and kalsilite, whereas in the absence of additives the dehydroxylation of kaolinite yields metakaolinite. The shift of the exothermic peak to high temperatures in our study is probably associated with the presence of the oxides of the alkali metals.

Thermal analysis of the CsBr-HOH-kaolinite intercalation complex obtained by wet grinding

The DTA curves of the wet ground CsBr-kaolinite mixtures show a new endothermic peak at 75–115°, which is accompanied by weight loss. This peak is not observed in the DTA curves of un–, air and wet ground kaolinite or of kaolinite mixed and air ground with alkali halides. On the other hand, a similar peak was observed in the DTA curves of wet ground CsCl–kaolinite (unpublished work). According to the IR study of the thermally treated CsBr disks, the intercalation complex is not decomposed in the first TG region; this loss must be due to the desorption of surface and interparticle water which had been adsorbed by the clay and the salt during the wet grinding process. This water is probably located primarily at the 'interface' between the mineral and the salt.

The second TG region is specific for wet ground mixtures and is not observed for air ground mixtures. In order to understand the reactions that occur within the second region, the following one must be considered. In this third region the dehydroxylation of the clay and the thermal hydrolysis of CsBr occur simultaneously. However, weight losses of mixtures 2 and 3 in the third TG region are smaller than that of the untreated kaolinite (sample 1). This is because these reactions have already started at the

temperature range of the second region in the CsBr intercalation complex. According to the IR results, weight loss in the temperature range 300–400° is partly due to the dehydroxylation of the clay. From the isothermal weight loss, determined by heating the samples overnight at different temperatures [6], we showed that the greater weight loss of the CsBr $-$ H$_2$O-kaolinite complex occurred at 350°. On the other hand, the greatest weight loss of dry ground kaolinite, in either the absence or the presence of alkali halides, occurred at 400°. With unground kaolinite [4], higher temperatures were needed for dehydroxylation and the reaction was completed only at 575°. The total weight loss in the second and third regions increases with the concentration of CsBr in the system, indicating that the degree of intercalation increases with CsBr concentration. In sample 8 the total weight loss in the second and third regions is relatively small, but this is due to the reduced efficiency of the mechanochemical intercalation when the clay concentration is small.

The presence of a separate CsBr phase can be identified in the corresponding DTA curves from the two endothermic peaks which represent the melting and boiling of this salt. Of the wet ground mixtures examined in the present study (samples 2–8 in Table 2), only mixtures 5–8 show the presence of a separate CsBr phase. Samples 2–4, with 10, 20 and 30 weight percent CsBr, do not have any excess salt and the entire amount of CsBr used for their preparation is adsorbed by the kaolinite in the formation of the CsBr $-$ HOH-kaolinite intercalation complex. The degree of saturation is thus > 140 mmol CsBr per 100 g kaolinite. This is much smaller than that obtained previously for the chloride salt, which is >297 mmol CsCl per 100 g clay [4]. These results are in agreement with our IR studies showing that kaolinite can be completely intercalated by CsCl, while in the case of CsBr a considerable fraction of the clay does not form an intercalation complex.

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References

1 S. Yariv, Powder Technol., 12 (1975) 131.
2 S. Yariv, J. Chem. Soc. Faraday Trans. I, 71 (1975) 674.
3 S. Yariv and S. Shoval, Clays & Clay Minerals, 24 (1976) 253.
4 S. Yariv, E. Mendelovici and R. Villalba, Proc. Seventh Intern. Conf. Thermal Anal., Ed. B. Miller, Kingston, Canada, 1982 Vol. 1, p. 533.
5 S. Yariv, Intern J. Trop. Agri., 4 (1986) 310.

6 K. H. Michaelian, S. Yariv and A. Nasser, Can. J. Chem., 69 (1991) 749.

7 S. Yariv, Clays & Clay Minerals, 23 (1975) 80.

8 R. L. Ledoux and J. L. White, Clays & Clay Minerals, 13 (1964) 289.

9 O. Anton and P. G. Rouxhet, Clays & Clay Minerals, 25 (1977) 259.

10 M. Adams, Clays & Clay Minerals, 26 (1978) 169.

11 M. Adams and G. Walti, Clays & Clay Minerals, 28(1980) 130.

12 C. H. Horte, Ch. Becker, G. Kranz, E. Schiller and J. Wiegman, J. Thermal Anal., 33 (1988) 401.

13 L. Erdey, G. Liptay and S. Gal, Talanta, 12 (1965) 257.

14 L. Heller-Kallai, Clay Minerals, 13 (1978) 221.

15 M. Gabor, L. Poeppl and E. Koeroes, Clays & Clay Minerals, 34 (1986) 529.

16 L. Heller-Kallai and M. Frenkel, Proc. Intern. Clay Conf. 1978, Eds. M. M. Mortland and V. C. Farmer, Elsevier, Amsterdam 1979, p. 629.

Zusammenfassung — Mittels simultaner DTA-TG wurde die sich während des Naßmahlens von Kaolinit mit CsBr stattfindende Reaktion untersucht, ergänzt durch IR-spektroskopische Untersuchungen von isotherm wärmebehandelten CsBr-Plättchen. Die DTA und TG Kurven wurden mit denen von unbehandeltem Kaolinit und von Kaolinit, vermischt oder an Luft gemahlen mit verschiedenen Alkalihalogeniden. Ein neuer endothermer DTA-Peak bei 75-115°C, begleitet von einem Gewichtsverlust, wird der Desorption von oberflächen- oder interpartikelgebundenem Wasser zugeschrieben, das hauptsächlich an den Übergangsflächen Mineral/Salz lokalisiert ist. Ein zweiter endothermer Peak bei 500°C steht für die gleichzeitige Dehydroxylierung der Tonerde und die thermische Hydrolyse von CsBr. Aus zwei für Schmelzen und Sieden des Salzes charakteristischen endothermen Peaks konnte auf eine separate CsBr-Phase geschlossen werden; nur Gemische mit mehr als 141 mmol CsBr pro 100 g Kaolinit zeigen die Gegenwart einer solchen Phase. Unterhalb dieser Konzentrationsgrenze ist alles CsBr in CsBr-HOH-Kaolinit Durchdringungskomplexen vorhanden. Dieser Sättigungsgrad ist niedriger als der für CsCl.