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COMBINED DTA - MASS SPECTROMETRY OF ORGANO-CLAY COMPLEXES

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DTA and EGA curves of montmorillonite and laponite treated with three metachromic dyes and of sepiolite and palygorskite treated with butylamine and pyridine were described, focussing on the contribution of the EGA to the interpretation of the different DTA peaks.

DTA has been used in several laboratories for the study of adsorption of organic material by clay minerals, (i) to establish whether adsorption complexes were formed or whether the clay and organic material were present merely as mechanical mixtures [1]; (ii) to study the effects of the organic material on the adsorbed water content and properties [2]; (iii) to study the thermal properties of the adsorbed organic matter [3]; (iv) to differentiate between clay minerals [3, 4] and (v) to establish the type of association between organic species and exchangeable metallic cations, water molecules or silicate layers [5]. In most studies DTA was combined with TG and hence, one could differentiate between peaks associated with weight loss and those associated with phase transitions.

Thermal analysis or organo-clay complexes is carried out either in air or under a flow of an inert gas, such as nitrogen or argon. In air, the adsorbed organic material is oxidized, giving rise to intensive exothermic peaks. Under an inert atmosphere, weak endothermic peaks are obtained which are attributed to desorption and pyrolysis of the organic material. Since these endothermic peaks are very weak, most DTA studies are carried out in air or oxygen atmosphere.

In our previous studies the identification of the reactions which were associated with weight loss and the attribution of these reactions to the various peaks, were merely speculative and the DTA curves were used only as fingerprints to differentiate between ammonium ions, free amines or amines coordinated with transition metallic cations, all adsorbed on

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montmorillonite. The differentiation between the various clay organic associations became possible because each type gave rise to the appearance of characteristic exothermic peaks.

In a previous review on the DTA of organo-clay complexes [6] the author wrote that sophisticated thermal methods and analysis of the combustion products are necessary in order to obtain a better understanding of the different peaks. A combined DTA - EGA (evolved gas analysis) seems to be the answer to this desire. In this technique the combustion products are analyzed simultaneously with the DTA and thus an unequivocal interpretation of exothermic peaks is obtained. In the present article two parallel studies are summarized, the adsorption of cationic dyes by smectites [7] and the adsorption of amines by sepiolite and palygorskite [8]. The DTA - EGA study was carried out in the clay mineralogy laboratory of the Institute for Foundation Engineering and Soil Mechanics, E.T.H., Zürich, in collaboration with Prof. M. Müller-Vonmoos, Dr. G. Kahr and Mr. A. Rub from that Laboratory, Prof. M. Steinberg from the Hebrew University and Mr. U. Shuali from the Israel Institute for Biological Research. Evolved gases were analyzed by mass spectrometry.

Thermal analysis of the adsorption of cationic dyes by smectite minerals

Montmorillonite (Wyoming bentonite) and laponite (synthetic hectorite) were saturated with three cationic dyes rhodamine 6G (R6G), acridine orange (AO) and crystal violet (CV). The adsorption of AO and CV by montmorillonite gives rise to metachromasy, namely the absorption maximum of the $\pi \rightarrow \pi^*$ transition band shifts to a shorter wavelength. Metachromasy of these dyes in aqueous solutions results from the association of two dye cations and the blue shift is the consequence of π interactions between the aggregated cations. In AO- or CV- montmorillonite [9] metachromasy results from π interactions between the oxygen plane of this mineral and the aromatic dye. π Interactions do not take place between the O plane of laponite and these cationic dyes [10]. Metachromasy in AO- or CV-laponite systems was observed only when the degree of saturation was equal to the exchange capacity of the clay. In this case metachromasy resulted from dimerization of dye cations on the solid surface. Due to steric hindrance the adsorption of R6G by montmorillonite or laponite is not accompanied by any kind of metachromasy [11].

Peak maxima in the DTA curves and in the evolution curves of H_2O and CO_2 are shown in Table 1. The maxima in the NO_2 curves appear at the same temperatures as those of the CO_2 evolution curves. The evolution of CO_2 and NO_2 results from the oxidation of carbon or nitrogen, respectively, originating from the organic cations. The temperature range in which the oxidation reactions take place are best determined from the CO_2 evolution curves. Evolution curves of laponite show that the oxidation reactions occur in the temperature range 250-660°, with one maximum at 500-575°, which is occasionally accompanied by weak shoulders. On the other hand, evolution curves of montmorillonite show that the oxidation reactions occur with several peaks, along the temperature range 250-900°.

Table 1 Endothermic (N) and exothermic (X) peak maxima in the DTA curves of montmorillonite and laponite saturated with R6G, AO or CV and peak maxima in the H_2O, and CO_2 evolution curves (in °C)

R6G-MONTMORILLONITE (40 mmole R6G per 100 g clay)						
DTA curve	100N	390X	415Xi	520Xsh	645Nvw	670Xvw
H_2O evolution	105*	390	420sh		645**	
CO_2 evolution			420	525m	640w	665w
AO-MONTMORILLONITE (50 mmole AO per 100 g clay)						
DTA curve	100N	375Xi		485Xi		665Xi, 670Xsh
H_2O evolution	110*	375			640**	
CO_2 evolution				485		655, 670sh
CV-MONTMORILLONITE (50 mmole CV per 100 g clay)						
DTA curve	100N	275Xsh 370X		485X	625Nvw	665Xm
H_2O evolution	110*	275sh 370			630**	
CO_2 evolution				490-590		675
R6G-LAPONITE (40 mmole R6G per 100 g clay)						
DTA curve	100N	370Xsh	410Xi	490Xi		735Xvw, 780Xvw
H_2O evolution	100*	375		490vw		740**, 785sh
CO_2 evolution			410sh	500	620sh	
AO-LAPONITE (50 mmole AO per 100 g clay)						
DTA curve	110N	320X		560Xi	660Xsh	775Xm
H_2O evolution	115*	330		540vw		760**
CO_2 evolution				575	660sh	
CV6G-LAPONITE (50 mmole CV per 100 g clay)						
DTA curve	110N	290Xsh 390X		500Xi	645sh	725Nvw, 775Xm
H_2O evolution	110*	290-390	450			725**
CO_2 evolution				500	630sh	

i - most intense exothermic peak; m - medium; vw - very weak; sh - shoulder. * - due to the dehydration of interlayer water. ** - mainly due to the dehydroxylation of smectite

The location and intensities of the different peaks in the CO_2 evolution curves of the montmorillonites depend on one hand on the kind of adsorbed dye and on the other hand, on the degree of saturation. In the case of R6G-montmorillonite, where no π interactions occur between the dye cation and the clayey oxygen plane, almost no changes were observed in the characteristic features of the CO_2 evolution curves versus changes in the degree of saturation. Only the intensities of the evolution peaks increased. Two intense CO_2 evolution peaks appear below 580° indicating that the greater part of the organic matter is oxidized below this temperature. Two more peaks appear above 580°, indicating that a considerable portion of the organic matter is oxidized together with the dehydroxylation of the clay. The degree of saturation has almost no effect on the thermal weight loss of R6G-laponite at temperatures 640-900°, being equal to $\approx 3\%$, whereas in the temperature range 250-640° weight loss increases from 5.25 to 18.27% with increasing degree of saturation from 3 to 60 mmole R6G per 100 g laponite. On the other hand, the degree of saturation has an effect on the thermal weight loss of R6G-montmorillonite at both temperature ranges 250-580 and 580-900°. Weight loss increases from 3.0 and 4.4% to 10.4 and 8.5% with increasing degree of saturation from 3 to 80 mmole R6G per 100 g montmorillonite, in the formed and latter temperature ranges, respectively.

The CO_2 evolution curves of AO- and CV-laponite are similar to those of R6G-laponite. Different curves were recorded with AO- or CV-montmorillonite, because these dyes form stable π interactions with the clayey oxygen plane. In AO- montmorillonite the high temperature peak at 655° is the principal peak so long as the degree of saturation is below 70 mmole AO per 100 g clay. Only when the degree of saturation is 100 mmole AO per 100 g clay does the low temperature peak at 480° become the most intense CO_2 evolution peak. This is an indication that the π interactions stabilize the adsorbed species. When excess adsorption occurs, the excess dye does not form π bonds with the clay, and is oxidized at a lower temperature. The degree of saturation has an effect on the thermal weight loss of AO-montmorillonite at both the temperature ranges 250-580 and 580-1000° up to 50 mmole AO per 100 g clay. Weight loss increases from 0.8 and 3.0% to 4.7 and 10.3% with increasing degree of saturation from 4 to 50 mmole R6G per 100 g montmorillonite, in the former and latter temperature ranges, respectively. With further increase in saturation to 100 mmole AO per 100 g clay, weight loss increases very much (from 4.7 to 10.3%) only in the 250-580° range but very slightly (from 10.3 to 11.3%) in the 580-1000° range.

CO_2 evolution curves of CV-montmorillonite show similar characteristics. The peak at 675°, which is the principal peak with degrees of saturation below 60 mmole CV per 100 g clay, is characteristic for a cation adsorbed through π interactions with the clayey oxygen plane, whereas a peak at a low temperature (585°), which is characteristic for excess dye, becomes significant with 100 mmole CV per 100 g clay.

The characteristic features of the H_2O evolution curves of both smectite minerals were independent of the degree of dye saturation. H_2O evolved below 250° originates from adsorbed water molecules initially located at the interlayer space of the smectite mineral. At higher temperatures, but below 580 or 640° in montmorillonite or laponite, respectively, the H_2O evolution results from the oxidation of the organic cation. Montmorillonite shows one intense peak at 370-390° whereas laponite shows several peaks. Above 580° in montmorillonite or 640° in laponite, the evolved H_2O originates from the dehydroxylation of the clay and to some extent also from the oxidation of the organic matter.

The DTA curves of either montmorillonite or laponite treated with the cationic dyes can be divided into three regions. In the first region, up to 250°, the endothermic dehydration of the clay is the major thermal reaction. A single endothermic peak shifts from 130 to 100° with increasing degrees of saturation. The second region, between 250-580° and 250-640° in the curves of montmorillonite and laponite, respectively, is characterized by the exothermic oxidation of the organic molecules. Comparison between the DTA and EGA curves shows that the first exothermic peak results from the oxidation of H atoms, whereas the other peaks result from the oxidation of C and N atoms. In the DTA curves of R6G treated smectites three exothermic peaks are traced (Table 1). The relative intensity of the high temperature peak increases with increasing degrees of saturation. The DTA curves of AO- or CV-laponite show two exothermic peaks and a shoulder. The presence of these peaks does not depend on the degree of saturation of the clay but the maxima are dependent. The DTA curves of AO-montmorillonite show two peaks. The second peak characterizes AO which does not form π interactions with the clay. It intensifies relatively to the other peaks only when the degree of saturation is 100 mmole dye per 100 g clay. It is weak and broad with lesser saturations. In the DTA curve of CV- montmorillonite a peak at 575°, attributed to CV which does not form π interactions with the clay, appears only when the degree of saturation is 100 mmole CV per 100 g clay.

The third region occurs above 580 or 640° for montmorillonite or laponite, respectively. The major thermal reactions of this region are the dehydroxylation and recrystallization of the smectites and, in montmorillonite, also the last stages of the oxidation of the organic matter. The DTA curve of the untreated montmorillonite shows an endothermic peak at 695°. The peak shifts to lower temperatures in the presence of dye. The oxidation reaction of the organic matter overlaps the endothermic dehydroxylation reaction. An endothermic peak is traced in DTA curves of montmorillonite saturated with less than 10 mmole dye per 100 g clay. With higher saturations exothermic peaks are detected. These peaks are small with R6G but are relatively large with AO and CV. In the case of untreated laponite the dehydroxylation is followed by recrystallization. A broad endothermic peak is recorded at 730° followed by a sharp exothermic peak at 755°. In the presence of organic matter the peaks are shifted and their shapes are modified. It can be concluded that the DTA curves or organo-clay complexes cannot give reliable information on either dehydroxylation or oxidation of organic matter. For this kind of information, combined DTA-EGA is essential.

Thermal analysis of the adsorption of amines by sepiolite and palygorskite

Sepiolite from Vallecas, Spain and palygorskite from Quincy, Florida, USA, were treated with butylamine (BA) and pyridine (PY), representing aliphatic and aromatic amines, respectively. DTA, TG and EGA curves of amine treated clays were recorded in air and under nitrogen. The peak maxima in the DTA curves and in the evolution curves of H_2O and CO_2 recorded in air are given in Table 2. Since water is evolved, in part as a result of the oxidation of organic matter and in part as a result of the dehydration and dehydroxylation of the clay, information on the oxidation of organic hydrogens was obtained by subtracting the H_2O evolution curve of the amine-treated sepiolite recorded under nitrogen from that recorded in air. The water evolution curve obtained under nitrogen is named "inorganic water evolution curve", whereas the evolution curve obtained in air is named "total water evolution curve". The calculated curve is named "organic water evolution curve". Peak maxima are shown in Table 2.

The CO_2 evolution curves of BA treated clays differ from those of PY treated clays. The aliphatic amine shows a plateau between 360-725 with a small peak at 600 in sepiolite and 390-585° in palygorskite, whereas the aromatic amine shows a single peak (Table 2). Also the organic water evolution curves of BA treated clays differ from those of PY treated clays. The aliphatic amine shows one continuous stage of hydrogen oxidation, whereas the aromatic amine shows two stages, the first at 260-275° (relatively sharp peak) and the second is a broad peak extending between 425-765 and 530-650° in sepiolite and palygorskite, respectively.

Table 2 Endothermic (N) and exothermic (X) peak maxima in the DTA curves of sepiolite and palygorskite treated with BA or PY and EGA peak maxima (in $^{\circ}$C)

BA-SEPIOLITE (112.5 mmole per 100g clay)							
DTA curve	120N	330Xsh	360Xi		600Xsh	725Xs	820X
Total H_2O evolution	140*	330	355	540sh		750vw	830**
Organic H_2O evolution		330sh	355vs				
CO_2 evolution				360 - (600) - 725 pl			830m
PY-SEPIOLITE (98.2 mmole per 100g clay)							
DTA curve	115N	238N	390Xsh	530Xi	600Xsh	725Xsh	820sh
Total H_2O evolution	120*	260		540		760sh	830**
Organic H_2O evolution		260		425 - 765 pl			
CO_2 evolution		280sh	395sh	540i		720sh	835
BA-PALYGORSKITE (62.5 mmole per 100g clay)							
DTA curve	135N	280Xsh	390Xi		590Xsh		
Total H_2O evolution	150*	295		530			
Organic H_2O evolution		290					
CO_2 evolution			390 - 585 pl				
PY-PALYGORSKITE (41.6 mmole per 100g clay)							
DTA curve	130N	280Xsh	455Xi		635Xm		
Total H_2O evolution	145*	275**		500**			
Organic H_2O evolution		275w		530 - 650 pl			
CO_2 evolution			465		660m		

i - most intense exothermic peak; m - medium; vw - very weak; pl - plateau; sh - shoulder. * - due to the dehydration of interparticle and zeolitic water. ** - due to the dehydration of bound water and dehyrdoxylation of mineral

The profiles of the exothermic region in the DTA curves are governed by the oxidation of both principal elements of the organic compounds, the carbon and the hydrogen. The hydrogen reaches a high rate of oxidation before the carbon. The temperatures of the most intense exothermic peaks are determined by the carbon oxidation, but temperatures of exothermic shoulders are determined by hydrogen oxidation. The contribution of the hydrogen oxidation to the DTA curve is considerable in the thermal analysis of the aliphatic BA and is small in that of the aromatic PY.

The locations of the exothermic peaks change with the minerals. With BA the temperature of the principal isothermic peak is lower in sepiolite compared to palygorskite, whereas with PY the opposite is observed. The fact that the peak temperatures are dependent on the minerals may serve as proof for the existence of interactions between the amines and the clays.

Conclusions

The DTA curves of organo clay complexes show exothermic peaks due to the oxidation of H, C and N atoms. The oxidation mechanism of H differs from that of C or N and the exothermic peaks associated with H oxidation differ from those associated with C and N oxidation. In the DTA curve an overlapping of the two groups of peaks is obtained. An interpretation of the different exothermic peaks can be made only if their origin is well established. This can be obtained from EGA.

In DTA runs endothermic peaks originating from dehydration or dehydroxylation of the clay, may overlap exothermic peaks of the oxidation of the organic matter. Consequently, characteristic peaks may be lost and a false interpretation can be obtained. On the other hand, CO_2 and NO_2 evolution curves are unequivocal. H_2O evolution curves can be misleading because dehydration and dehydroxylation of the clay may overlap the organic water evolution. By performing parallel runs in air and under nitrogen the two can be differentiated.

With all clay complexes studied here, exothermic peak temperatures and peak maxima in the gas evolution curves are dependent on the mineral. In those cases that different types of associations were defined, peak maxima were dependent on the type of association. No explanation is available at this stage.

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Zusammenfassung — DTA- und EGA-Kurven von nach dem Metachromverfahren behandeltem Montmorillonit und Laponit sowie von mit Buthylamin und Pyridin behandeltem Sepiolith und Palygorskit werden beschrieben. Schwerpunkt war der Beitrag der EGA zur Interpretierung der verschiedenen DTA-Peaks.