An i.r. investigation on some calcium aluminate hydrates, $\text{Ca}_2\text{Al}(\text{OH})_6 + \text{X}^-\cdot y\text{H}_2\text{O}$ ($= 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaX}_2\cdot n\text{H}_2\text{O}$, $\text{X}^- =$ univalent anion)

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An i.r. investigation on some calcium aluminate hydrates, $\text{Ca}_2\text{Al}(\text{OH})_6^+ \text{X}^- \cdot y\text{H}_2\text{O}$ ($= 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$, $\text{X}^- = \text{univalent anion}$)

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Abstract—The i.r.-spectra of some hydrated and dehydrated calcium aluminate hydrates of the type $\text{Ca}_2\text{Al}(\text{OH})_6^+ \text{X}^- \cdot y\text{H}_2\text{O}$ with $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{J}^-, \text{ClO}_3^-, \text{NO}_3^-, \text{ClO}_4^-$ ($y = 2$) and $\text{X}^- = \text{BrO}_3^-, \text{JO}_3^-$ ($2 < y < 4$), were recorded between 3800 and 200 cm^{-1} .

With increasing interaction of the interlayer water with the anions X^- , the absorption bands in the region 3600–3200 cm^{-1} due to the interlayer water are found at smaller wave numbers.

From the i.r. spectra of partially deuterated calcium aluminate hydrates it is found that, at least at room temperature, the water molecules are symmetrically bound to their surroundings. Thus, both OH groups are directed towards the anion X^- .

From the shift of the uncoupled stretching vibration, ν_{OH} or ν_{OD} , due to isotopically dilute HOD molecules, the hydrogen bond enthalpies were estimated; the hydrogen bond enthalpies vary from 1.8 kcal ($\text{X}^- = \text{ClO}_4^-$) to 5.5 kcal ($\text{X}^- = \text{JO}_3^-$).

With increasing hydrogen bond enthalpy, the enthalpies of dehydration of the calcium aluminate hydrates increase.

INTRODUCTION

The existence of two series of hexagonal calcium aluminate hydrates has been known for many years [1]. One series may be represented by the general formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$, the other by $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaX}_2 \cdot m\text{H}_2\text{O}$, in which X^- is half a divalent or one univalent anion. The amount of "water" is very different in the two series; n is about 10 and m about 32.

We will consider here the so-called monophases, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$, which can be described better by the formula:

This formula distinguishes water bound as hydroxyl groups and water present as water molecules. These compounds consist of main layers $\text{Ca}_2\text{Al}(\text{OH})_6^+$, alternated by interlayers in which anions and water are incorporated [1, 3].

Hydrates containing molecular interlayer water will be called "hydrated," those containing hydroxyl groups in the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ -layers only will be called "dehydrated."

VOLANT [4, 5] has shown that water present in calcium aluminate hydrates as hydroxyl groups is distinguishable from water present in the interlayers by i.r. spectroscopy.

BENSTED and PRAKASH VARMA [6, 7] and HENNING *et al.* [8] reported i.r. spectra of ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{18}(\text{SO}_4)_2 \cdot 22\text{--}23\text{H}_2\text{O}$) and of monosulphate $2[\text{Ca}_2\text{Al}(\text{OH})_6^+ \cdot 0.5\text{SO}_4^{2-} \cdot 3\text{H}_2\text{O}]$.

The purpose of our i.r. spectroscopic investigation was to establish a correlation between the enthalpies of dehydration of the calcium aluminate hydrates and the enthalpies of hydrogen bonds formed by water molecules and the anions X^- in the interlayers. In a previous paper [9] it was shown that the enthalpies of removing the interlayer water from compounds with different X^- anions, as determined by measuring the heats of solution of the hydrated and the dehydrated compounds in 1 N hydrochloric or 1 N perchloric acid, are connected with the enthalpies of hydration of the individual anions in aqueous solution.

There is evidence from the literature [10–18] that the interactions of water molecules in crystal hydrates with their surroundings are correlated with the positions of the absorption bands due to these water molecules.

An appropriate method to specify the bond of water molecules in crystal hydrates is the so-called isotope dilution technique [12, 19]. A hydrate prepared from a salt solution containing a small percentage of D_2O relative to H_2O , contains H_2O and HOD. The OD vibrations of these HOD molecules are both intra- and intermolecularly uncoupled. The number of the bands due to these uncoupled modes reflects the number of different OD bonds in a hydrate.

If one assumes, with BADGER and BAUER [20], that the frequency shift, i.e., the difference between

the frequency of the OH stretching vibration of HOD molecules in the gaseous state and in the crystal hydrates, is proportional to the hydrogen bond enthalpy, the strength of the hydrogen bonds between water molecules and the anions X^- can be estimated.

EXPERIMENTAL

The various methods of preparation, the identification and the chemical analysis of the calcium aluminate hydrates $\text{Ca}_2\text{Al}(\text{OH})_6^+X^-\cdot y\text{H}_2\text{O}$ have been described previously [9]. The samples were stored above a saturated aqueous solution of $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ in a vacuum desiccator. The i.r. spectra of the calcium aluminate hydrates were recorded using KBr pellets or mulls of Nujol. Nujol mulls were used preferably because with the KBr technique the hydrate crystals may be changed. In order to record the i.r. spectra of the dehydrated calcium aluminate hydrates, the compounds were kept in a vacuum drying box during at least eight hours at 1 Torr and at 140°C (at 160°C if necessary to accomplish the dehydration).

The i.r. spectra in the region between 200 and 700 cm^{-1} were recorded using Nujol mulls, between KBr plates on a Hitachi Grating Infrared Spectrophotometer, type Epi-L. The i.r. spectra in the region $700\text{--}3800\text{ cm}^{-1}$ were recorded using Nujol mulls between NaCl plates on a Hitachi Grating Infrared Spectrophotometer, type Epi-G₂. In those cases, where partially deuterated calcium aluminate hydrates were investigated, the KBr disc method was used since Nujol has absorption bands in the same region as OD groups have.

The partially deuterated samples were prepared as follows: after dehydration of the hydrates during at least eight hours in a vacuum drying box at 140°C , the compounds were rehydrated above a saturated solution of potassium acetate in mixtures of D_2O and H_2O (relative humidity 20%).

It appeared that the calcium aluminate perchlorate compound was rehydrated incompletely at this relative humidity. In that case the rehydration was performed above a saturated solution of KCNS in mixtures of D_2O and H_2O (relative humidity 47%).

RESULTS

(a) The i.r. spectra of the calcium aluminate hydrates in the region $200\text{--}1600\text{ cm}^{-1}$

The very similar pattern of the i.r. spectra of the calcium aluminate hydrates in the region $200\text{--}700\text{ cm}^{-1}$ indicates that the structure of the main layer $\text{Ca}_2\text{Al}(\text{OH})_6^+$ is in all cases almost identical, which agrees with X-ray data [1, 3, 29]. Bands between 500 and 600 cm^{-1} and bands near 780 cm^{-1} can be assigned to Al—O vibrations (c.f. the i.r. spectra of Bayerite and Gibbsite [23, 24]). According to TARTE [21, 22] condensed AlO_6 -groups, as present in the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ layers, absorb between 680 and 500 cm^{-1} .

Bands near 300 and 420 cm^{-1} can be assigned to Ca—O vibrations [23]. Besides the bands mentioned several bands due to vibrations of the anions X^- are visible in the spectra.

(b) The i.r. spectra of the calcium aluminate hydrates in the region $1600\text{--}3800\text{ cm}^{-1}$

The i.r. spectra of the calcium aluminate hydrates where $X^- = \text{Br}^-$, BrO_3^- and ClO_4^- are shown in Fig. 1(a); in Fig. 1(b) the spectra of the corresponding dehydrated compounds are shown (the absorption bands due to Nujol were omitted).

In the spectra of the hydrated calcium aluminate hydrates a broad absorption band between 3600 and 3200 cm^{-1} is visible due to OH stretching vibrations of the interlayer water (the bands disappear on dehydration).

The formation of hydrogen bonds in crystal hydrates, liquid water and salt solutions leads to broadening and shifts towards smaller wave numbers of the absorption band [10–18, 26]. So the broad absorption band due to interlayer water of the calcium aluminate hydrates is found at lower wave numbers in the direction $X^- = \text{ClO}_4^-$, J^- , ClO_3^- , NO_3^- , Br^- , Cl^- , BrO_3^- to JO_3^- . When we consider, for instance, the spectrum of $\text{Ca}_2\text{Al}(\text{OH})_6^+\text{ClO}_4^-\cdot 2\text{H}_2\text{O}$, we observe strong bands at 3615 cm^{-1} (ν_3), 3555 (ν_1) and at 1640 cm^{-1} . The bands at frequencies higher than $\nu = 3615$ can be ascribed to vibrations of OH groups of the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ layers.

Fig. 1. Parts of the i.r. spectra of the calcium aluminate hydrates: (a) hydrated compounds; (b) dehydrated compounds.

The frequencies 3615 and 3555 are comparable with those of the bands occurring in the spectra of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ [$\nu_3 = 3592 \text{ cm}^{-1}$, $\nu_1 = 3536 \text{ cm}^{-1}$] and of $\text{BaClO}_4 \cdot 3\text{H}_2\text{O}$ ($\nu_3 = 3579 \text{ cm}^{-1}$, $\nu_1 = 3529 \text{ cm}^{-1}$). In the i.r. spectrum of $\text{Mg}(\text{H}_2\text{O})_6^{2+}(\text{ClO}_4^-)_2$ bands are observed at 3564 and 3500 cm^{-1} [18]. From this analogy the $\text{Ca}_2\text{Al}(\text{OH})_6^+\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$ bands at 3615, 3555 and 1640 cm^{-1} are ascribed to vibrations of interlayer water molecules.

Clearly these stretching frequencies are found at smaller wave numbers as the cation field increases. From this point of view we can state that the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ unit behaves as a large cation. The absorption band at a wave number $= 3615 \text{ cm}^{-1}$, due to hydroxyl groups of water molecules in the interlayers, is comparable with these found at 3615 cm^{-1} in the spectra of aqueous solutions of perchlorate salts [25].

When we consider the spectra of the other calcium aluminate hydrates it is striking that with increasing hydrogen acceptor property of the anions X^- , the bands due to the stretching vibrations of the interlayer water shift towards smaller wave numbers and become more broad; the separation between ν_3 and ν_1 absorption bands disappears. Concerning the ν_2 bending vibration between 1600 and 1680 cm^{-1} , it is remarked that in the cases $X^- = \text{Cl}^-$, Br^- , J^- , ClO_4^- , ClO_3^- ($y=2$) only one band is visible. This indicates that only one type of interlayer water is present. If $y>2$ ($X^- = \text{JO}_3^-$), however, two individual bands can be discerned indicating that two types of interlayer water are present.

After dehydration the absorption bands due to the interlayer water had disappeared, see Fig. 1(b).

In addition to the bands due to the interlayer water molecules, a complex absorption band due to the hydroxyl groups of the $\text{Ca}_2\text{Al}(\text{OH})_6^+$ layer occurs between 3700 and 3500 cm^{-1} . On dehydration of the calcium aluminate hydrates this band did not disappear, but became more pronounced. A small shift toward larger wave numbers occurs. This means that the interaction of the anions X^- with their surroundings is stronger in the case they are surrounded by water molecules than when they are surrounded by hydroxyl groups of the main layers.

(c) *The i.r. spectra of partially deuterated calcium aluminate hydrates*

The i.r. spectra of the calcium aluminate hydrates rehydrated, after dehydration, above a saturated solution of potassium acetate in a mixture of about 0.017 mol.% H_2O , 93.38 mol.% D_2O , and

Fig. 2. The i.r. spectra of partially deuterated calcium aluminate hydrates: $X^- = \text{Cl}^-$, Br^- , J^- ; (a) HOD in D_2O ; (b) HOD in H_2O .

6.61 mol.% HOD, are shown in the Figs. 2(a)–4(a). The concentrations of D_2O used are given in Table 1, column 2a.

We observe in the spectra of the partially deuterated calcium aluminate hydrates only one uncoupled OH fundamental in the region between 3600 and 3200 cm^{-1} . In the region between 2700 and 2400 cm^{-1} several absorption bands are found due to OD fundamentals of D_2O molecules present in the interlayers, or to OD groups of the main layers. Thus, when D_2O molecules are present in the interlayers, some of the hydroxyl groups of the main layer become OD groups. The assignment of these bands to OD-vibrations was based upon the

Fig. 3 The i.r. spectra of partially deuterated calcium aluminate hydrates where $X^- = \text{ClO}_3^-$, BrO_3^- , JO_3^- ; (a) HOD in D_2O ; (b) HOD in H_2O .

Fig. 4. The i.r. spectra of partially deuterated calcium aluminate hydrates; (a) HOD in D_2O ; (b) HOD in H_2O .

frequency ratio ν_{OH}/ν_{OD} and the position of the OH bands of the main layer.

The i.r. spectra of the calcium aluminate hydrates in which a small percentage of the water molecules was replaced by HOD molecules, are shown in the Figs. 2(b)–4(b).

The concentrations of D_2O in the salt solutions, above which the rehydration took place, are given in Table 1, column 2b.

In the region between 2700 and 2400 cm^{-1} the uncoupled OD band of the HOD molecules and OD bands due to OD groups of the main layer are found. The frequencies of the various OH and OD stretching vibrations are tabulated in Table 1, column 3. Table 1, column 4 shows the ratio of these OH and OD fundamentals.

DISCUSSION

The anions in the interlayers of the calcium aluminate hydrates have a large influence on the frequencies due to the stretching and bending vibrations of the interlayer water molecules.

This influence is much greater than the influence of interlayer cations in clay minerals like montmorillonite [27]. The frequency shift caused by the increasing electric field of the cation going from Na^+ to Mg^{2+} is much smaller than the shift which we observe on going from ClO_4^- to JO_3^- in calcium aluminate hydrates.

The occurrence of only one ν_2 fundamental if $y=2$ indicates that in that case only one type of interlayer water is present and that the water molecules are ordered with both OH groups directed towards the anion X^- . This agrees with the crystal structure proposed by LE BEL and GRASLAND [29].

The occurrence of only one OD band and one OH band in the spectra of the calcium aluminate hydrates with small and large amounts of D_2O respectively, indicates that the hydrogen bonds between the interlayer anions and the interlayer water molecules are all equivalent, at least at room temperature.

Most convincing among the arguments for symmetrical binding of the water molecules with the anions is the feature that ν_{OH} , the frequency of the uncoupled fundamental due to an OH group in HOD surrounded by D_2O molecules is equal to the average of ν_1 and ν_3 frequencies due to water molecules in the interlayers without D_2O . We demonstrate this from the spectra of the calcium aluminate hydrates with $X^- = J^-, ClO_4^-$ and ClO_3^- :

Table 1. Frequencies of the OH en OD stretching vibrations of partially deuterated calcium aluminate hydrates

I X	II D ₂ O- and H ₂ O-contents of saturated solutions of potassium acetate employed for rehydration.				III	IV	V
	a		b				
	%H ₂ O	%D ₂ O	%H ₂ O	D ₂ O	ν_{OH}	ν_{OD}	ν_{OH}/ν_{OD}
Cl ⁻	3	97	95	5	3455	2555	1.35
Br ⁻	3	97	92	8	3460	2560	1.35
J ⁻	3	97	92	8	3465	2565	1.35
NO ₃ ⁻	3	97	90	10	3460	2545	1.36
ClO ₃ ⁻	3	97	90	8	3500	2585	1.36
BrO ₃ ⁻	3	97	90	10	3430	2535	1.35
JO ₃ ⁻	3	97	90	10	3345	2475	1.35
ClO ₄ ⁻	5*	95*	90*	10*	3585	2645	1.35

*The rehydration was performed above a saturated solution of KCNS in mixtures of D_2O and H_2O .

In these cases ν_1 and ν_3 are separated very well. The values of $\nu_1 + \nu_3/2$ are given in Table 1, column 4.

It is clear that $\nu_1 + \nu_3/2$ is equal to ν_{OH} in those cases. Another method to check whether the water molecules in a crystal hydrate are symmetrically bound has been published by BELLAMY *et al.* [30]. They established that for a series of eight different crystal hydrates, in which the water molecules are symmetrically bound, the following relation between ν_1 and ν_3 exists:

$$3657 - \nu_1 = 0.833 (3756 - \nu_3) \quad (1)$$

In this equation 3657 and 3756 are the frequencies of ν_1 and ν_3 due to water molecules in the gaseous state.

SCHIFFER and HORNIG [31] have reported the following equation:

$$\begin{aligned} \Delta\nu_{3,1} &= 0.1724\nu_{OH} - 540 \\ \Delta\nu_{3,1} &= \nu_3 - \nu_1; \nu_{OH} = \frac{\nu_1 + \nu_3}{2} \end{aligned} \quad (2)$$

Schiffer established that Equation 2 is valid in the region 3706 to 3430 cm^{-1} if the water molecules are symmetrically bound. Equation 2 is in the region 3300–3700 cm^{-1} almost equivalent to Equation 1.

In the cases $X^- = \text{ClO}_4^-$, J^- and ClO_3^- this equation is satisfied. In other cases ν_1 and ν_3 cannot be located precisely because of mutual overlap.

The enthalpy of the hydrogen bonds between the anions X^- and the interlayer water molecules

It is now generally accepted [32–34] that the enthalpy of the hydrogen bonds depends linearly on the frequency shift of the stretching vibrations in a donor/acceptor system relatively to the frequencies of the stretching fundamentals in the state with out interaction. This principle has been used for the first time by BADGER and BAUER [20]. Recently Brink and Falk estimated the enthalpy of the hydrogen bonds of the water molecules in $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ by a kind of Badger/Bauer relation:

$$\frac{\nu_{OH,g} - \nu_{OH,x}}{\nu_{OH,g} - \nu_{OH,s}} \cdot \frac{1}{2} \Delta H(\text{H}_2\text{O}) = -\Delta H_{\text{H-bond}} \quad (3)$$

$\nu_{OH,g}$ = the frequency of the uncoupled OH-stretching vibration due to the HOD molecule in the gaseous state (= 3707 cm^{-1})

$\nu_{OH,s}$ = the frequency of the uncoupled OH-stretching vibration due to the HOD

Table 2. The enthalpies of the hydrogen bonds between the anion X^- and the interlayer water molecules in the calcium aluminate hydrates

X^-	$-\Delta H_{\text{H-bond}}$, kcal
Cl^-	3.8
Br^-	3.7
J^-	3.6
ClO_3^-	3.1
BrO_3^-	4.2
JO_3^-	5.5
ClO_4^-	1.8
NO_3^-	3.7

molecules in ice with a high percentage of D_2O (= 3304 cm^{-1})

$\nu_{OH,x}$ = the frequency of the uncoupled OH-stretching vibration due to HOD molecules in a crystal hydrate with a high percentage of D_2O

$\Delta H(\text{H}_2\text{O})$ = the enthalpy of sublimation of ice at 273.15 K (= 12.2 kcal/mol).

Using Equation 3 on the data, obtained with partially deuterated calcium aluminate hydrates (see Table 1, column 3), the enthalpies of the hydrogen bonds between the anions X^- and the interlayer water molecules were estimated; they are given in Table 2.

The enthalpy of the hydrogen bonds between JO_3^- ions and water molecules in the interlayers (5.5 kcal) is found to be about three times larger than the enthalpy of the hydrogen bonds between ClO_4^- ions and these water molecules (1.8 kcal).

BRINK and FALK [10] estimated the enthalpy of the hydrogen bond between the ClO_4^- ions and

Fig. 5. The enthalpies of dehydration of the calcium aluminates vs. the hydrogen bond enthalpies.

water molecules in $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (2.0 kcal). When we compare the enthalpies of the hydrogen bonds between the anions X^- with their surrounding water molecules with the enthalpies of dehydration of the calcium aluminate hydrates (i.e., the enthalpy change of the process:

we can conclude that with increasing hydrogen bond enthalpy the enthalpy of dehydration increases (see Fig. 5). It should be remarked, however, that the enthalpy of dehydration comprises, in addition to hydrogen bond enthalpies, a number of other terms [35]. This can explain the fact that the NO_3^- compound is found off the curve.

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