FTIR Study of Weak Hydrogen Bonding of Brönsted Hydroxyls in Zeolites and Aluminophosphates

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FTIR spectroscopy is used for the investigation of hydrogen bonding of the Brönsted hydroxyls in H-ZSM-5 zeolite with a number of weak bases (Ar, H_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, CO, C_2H_4). The following correlation for the increase in intensity of the hydroxyl band, due to its shift resulting from perturbation, is observed: $\Delta A/A_0 = 0.018\Delta\nu_{OH}$. Applying this correlation to the HF–LF pair in the infrared spectra of H-Y, H-EMT, and H-EMO zeolites, it is shown that the distribution of Brönsted hydroxyls between super and β cages is approximately 1:1 whereas in SAPO-37 samples this ratio is close to 3:1. This is in agreement with results for the deconvolution of the hydroxyl region of the ^1H MAS NMR spectra. The estimated values of the extinction coefficients for the HF and LF band in H-Y zeolite (Si/Al = 2.7) are 3.2 and 8.5 cm·μmol^{-1}, respectively.

Introduction

Although FTIR spectroscopy is one of the most powerful methods for the study of Brönsted acidity in zeolites,[1] there are still some complications regarding quantification. The overall hydroxyl band quite often consists of several contributing components some of which can arise from perturbation by hydrogen bonding. The reason for this phenomenon can be, for instance, an interaction with the framework oxygens if hydroxyls vibrate in smaller than 10-membered[2] rings. The hydroxyl region of the spectrum of conventional H-Y zeolite with its two components, high frequency (HF) at about 3640 cm^{-1} and low frequency (LF) at about 3540 cm^{-1}, can be considered as a classic and simple example of such a case. Other reasons for perturbation by hydrogen bonding include interaction with extraframework species as occurs in US-Y zeolites. In both cases, however, the source of the inhomogeneity of the infrared mode is the same: a weak perturbation by hydrogen bonding of part of the Brönsted hydroxyls by bases, be they zeolitic oxygens or extralattice aluminooxide species.

Although new approaches for decomposition of the complex hydroxyl bands have appeared recently,[3,4] the next step in the FTIR analysis, determination of the relative amounts of the various hydroxyls, present in the sample, has not yet been achieved. According to the theory of hydrogen bonding, the perturbation of the OH bond leads to an increase in its intensity and, consequently, all the shifted components have different extinction coefficients.[5,6] Determination of the extinction coefficients is a complicated problem. A conventional method reported in the literature involves titration of the OH bands with strong bases such as ammonia or pyridine.[7–12] However, the following conditions should be satisfied: (1) absence of Lewis acidity in the sample; (2) absence of physisorption of the base under the conditions of the titration; (3) accessibility of all the hydroxyls for the titrating base; (4) 1:1 interaction of the base with the hydroxyls; (5) separate poisoning of each spectroscopic component.

Even in the case of H-Y zeolite, the reported results are rather controversial,[7–12] whereas for the more complex systems, direct titration is unlikely to give correct results.

Another notion is to combine the infrared measurements with ^1H MAS NMR results. ^1H MAS NMR spectra contain the same signals of bridging OH groups in the large cavities at 3.8 and 3.9 ppm and in the six-membered oxygen rings of the sodalite cages at 4.3 and 5.0 ppm observed for SAPO-37 and HY zeolite,[13] respectively, and their intensities, in contrast to FTIR, do not depend upon their positions. However, the ^1H MAS NMR lines are less well resolved than the IR peaks, which limits the application of this method.

In the present paper we report a new approach for determination of the distribution of different types of Brönsted hydroxyls. It is based on a study of weak hydrogen bonding in the model system, hydroxyls in H-ZSM-5, perturbed by adsorbed weak bases. The correlation obtained from this study of the increase in the intensity of the band, resulting from the perturbation, with the frequency shift, can then be transferred to the perturbation caused by oxygens in six-membered rings of β cages in faujasite-like materials. The distribution of Brönsted hydroxyls between super and β cages obtained from the FTIR spectra, using this correlation, agrees with ^1H MAS NMR results. An estimation of the extinction coefficients for the HF and LF bands in H-Y is made.

Experimental Section

Spectroscopically pure gases (Ar, H_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, CO, C_2H_4) were supplied by Messer Griesheim. The chemical composition of the zeolite and aluminophosphate samples is given in Table 1.

The spectroscopic technique was described in detail elsewhere.[14] Briefly, FTIR studies were carried out using a Cygnus-100 Mattson FTIR spectrometer and a special IR cell having a thermostated zone which facilitated high-temperature treatment of samples *in situ*. The cell was also connected to a vacuum rig and a calibrated volume, fitted with a pressure gauge, for quantitative gas adsorption. The samples were pressed into self-supporting disks (m = 5–10 mg, ρ = 2–6 mg·cm^{-2}), placed into the cell, heated at 1 °C/min to 350 °C under vacuum, and then held at this temperature overnight (vacuum of 10^{-5} Torr). Aluminophosphate samples were additionally heated under oxygen (300 Torr, 550 °C, 2 h) to remove organic templates. Pyridine adsorption showed that no Lewis acidity was formed after such a pretreatment. Results for ammonia adsorption (Table 1) also proved that in zeolite samples all the aluminum was in the framework. As regards the SAPO-37 samples, a more comprehensive characterization was reported elsewhere (samples 1 and 8 in ref 15). For spectroscopic/adsorption measurements on the H-ZSM-5 reference sample, the IR cell was lowered into a quartz dewar situated inside the spectrometer chamber and filled with liquid nitrogen (temperature of the sample was 100–120 °C), and small increments of the gases were admitted stepwise into

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TABLE 1: Chemical Composition of the Samples

no.	sample	unit cell composition (chemical analysis)	N_{OH} per unit cell (ammonia titration)
1	H-ZSM-5	$H_{5.6}Al_{5.6}Si_{90.4}O_{192}$	7.6
2	H-Y	$H_{51.4}Na_{0.5}Al_{51.9}Si_{140.1}O_{384}$	51.8
3	H-EMT	$H_{19.2}Al_{19.2}Si_{76.8}O_{192}$	19.9
4	H-EMO	$H_{40.0}Al_{40.0}Si_{152.0}O_{384}$	38.0
5	SAPO-37a	$H_{11.5}Al_{94.1}P_{82.6}Si_{15.3}O_{384}$	13.1
6	SAPO-37b	$H_{19.2}Al_{84.5}P_{65.3}Si_{42.2}O_{384}$	17.6

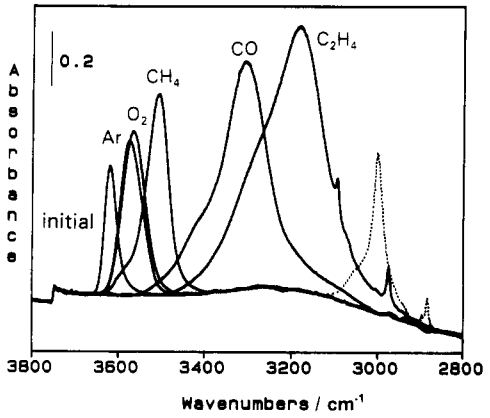

Figure 1. FTIR spectra of the Brönsted hydroxyls in H-ZSM-5 hydrogen-perturbed by different weak bases. CH vibrations in CH_4 are denoted by a dotted line.

the cell. All the spectra were collected using 100 scans and a resolution of 2 cm^{-1} in the wavenumber interval of 2500–4000 cm^{-1}. The spectroscopic parameters (position of the bands, their intensity and half-width) were determined at high fractional coverage of the hydroxyls with adsorbed molecules, θ = 0.8–1.0, and the intensities were recalculated to θ = 1.0.

For the deconvolution of the hydroxyl region in the faujasite-like materials (samples 2–6, Table 1), FTIR spectra were collected at room temperature. To reduce the experimental error arising from pretreatment in the case of each sample, the experiment was repeated for the number of self-supported disks (usually not less than four). The average spectrum, which was used for the analysis, was obtained by summing these spectra followed by reducing the scale by the number of the components (using spectroscopic software @First@).

^1H MAS NMR measurements were carried out using a Bruker MSL 400 spectrometer and a homemade probe to rotate sealed glass ampules. The MAS frequency was set to 3 kHz, the $\pi/2$ pulse to 3 μs, and the repetition time to 10 s. The ^1H MAS NMR spectra were simulated using the program LINESIM, taking into account the intensity contributions of the MAS NMR sidebands. For each spectrum 200 scans were recorded. The calcination of the NMR samples was performed under vacuum with a temperature sweep of 10 °C/h. At the final temperature of 350 °C the samples were kept for 20 h in a vacuum of 0.01 Pa and sealed off.

Results and Discussion

I. Perturbation of the Hydroxyl Band in H-ZSM-5 with Weak Bases. An infrared study of hydrogen bonding in zeolites was made using the hydroxyl group in H-ZSM-5, which has a single rather narrow absorption band in the infrared, as a model system. The perturbation of this hydroxyl by several weak bases (viz. Ar, H_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, CO, C_2H_4) was then used to establish a correlation between the increase in absorbance and bathochromic shift in OH frequency. Weak bases which gave shifts in the OH stretching frequency less than 400 cm^{-1} were used to avoid band splitting by Fermi resonance.[16]

Figure 1 illustrates this weak perturbation by some of the bases used. With an increase in the strength of the base, (i) the shift

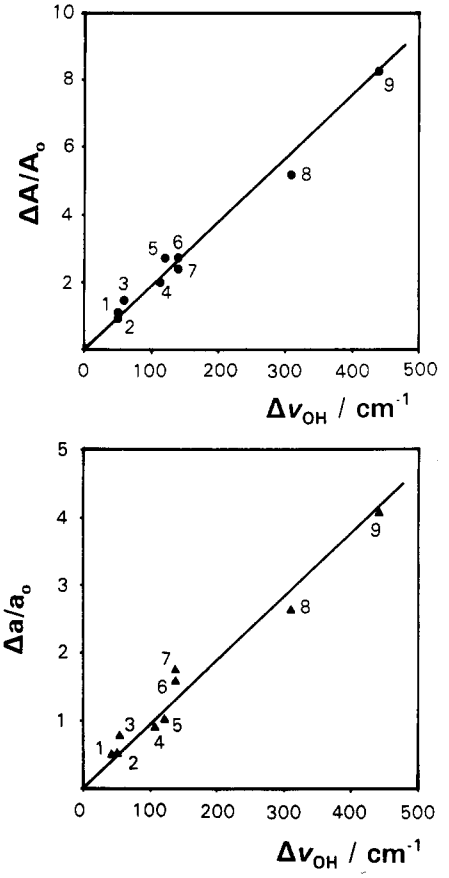

Figure 2. Plot of the increase in the intensity (a, top) and in the half-width (b, bottom) of the hydrogen-bonded Brönsted hydroxyls in H-ZSM-5 against their shift. The bases used were (1) Ar, (2) H_2, (3) O_2, (4) CH_4, (5) N_2, (6) C_2H_6, (7) C_3H_8, (8) CO, and (9) C_2H_4.

from the initial position of the band at 3601 cm^{-1} increases, (ii) its shape becomes more asymmetrical, (iii) it widens, and (iv) the intensity increases. The shift in the band position, $\Delta\nu_{OH}$, is usually considered to be a measure of the strength of the perturbation. Correlations of the intensity of the hydroxyl band and its half-width with this shift are well-known for hydrogen bonding in solution.[5,6] However, they have not been properly analyzed, to our knowledge, in the case of zeolite systems.

Figure 2 shows the growth in the intensity of the hydroxyl band during the perturbation, $\Delta A/A_0$, and the widening of the band, $\Delta a/a_0$, where $\Delta A = A - A_0$, $\Delta a = a - a_0$, A and A_0 are the intensities, and a and a_0 are the half-widths of the perturbed and unperturbed bands, respectively.

Both correlations are linear and can be described by the equations

$$\Delta A/A_0 = 0.018\Delta\nu_{OH}/cm^{-1} \quad (1)$$

$$\Delta a/a_0 = 0.010\Delta\nu_{OH}/cm^{-1} \quad (2)$$

II. Hydroxyl Distribution between Super and β Cages in the Faujasite-Like Materials. In zeolite H-Y, Brönsted hydroxyls are present in both large and small cages. The perturbation of hydroxyls in the six rings of the small β cages, by proximate oxygens, results in the typical infrared spectrum showing two distinct hydroxyl bands. A direct determination of the ratio of Brönsted hydroxyls, vibrating in the different cages, from the intensities of the bands, is not possible because of the difference in their extinction coefficients. However, using the following assumption, one can apply the correlation $\Delta A/A_0 \propto \Delta\nu_{OH}$, obtained for the model system studied above, to the faujasite-like systems.

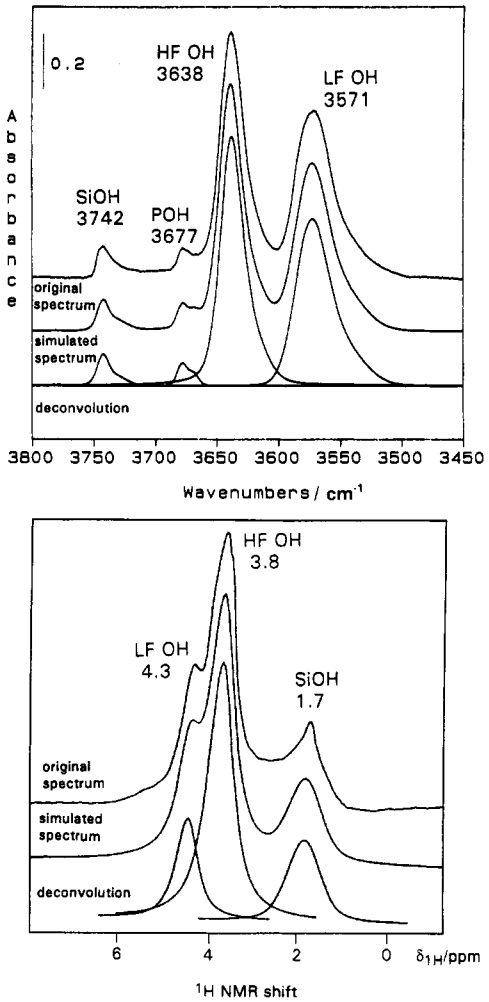

Figure 3. SAPO-37b: Deconvolution of the hydroxyl region in (a, top) FTIR spectra and (b, bottom) ^{1}H MAS NMR spectra.

Assumption. The changes in the O–H mode due to hydrogen bonding with a weak base (the shift in the position, $\Delta\nu_{OH}$, and the growth in the intensity, $\Delta A/A_0$) depend on the strength of the perturbation and not on the nature of the base.

Consequently, if two different bases perturb an O–H bond with the same strength (resulting in the same $\Delta\nu_{OH}$), the increase in the intensity of the shifted band should also be the same. Thus, considering the HF component unperturbed and the LF component as a perturbed band, shifted by $\Delta\nu_{OH}$, it becomes possible to determine the relative increase in the intensity due to the hydrogen bonding. ^{1}H MAS NMR results are used for comparison, as the intensities of the bands in this case do not depend on their positions.

To measure the intensities of the contributing bands, the hydroxyl region in FTIR and ^{1}H MAS NMR spectra was deconvoluted into HF and LF components. Figure 3 illustrates a typical pattern in the case of the SAPO-37b as an example. Each of the HF and LF single components in the FTIR spectra (Figure 3a) is taken as a composite of at least two mixed Gauss–Lorentzian functions. Lorentzian functions are used for deconvolution of the hydroxyl region in ^{1}H MAS NMR spectra (Figure 3b).

Table 2 presents the distances between the HF and LF peaks in the FTIR spectra for the samples studied, $\Delta\nu_{OH}$, and relative intensities of the products of the deconvolution, A_{HF} and A_{LF}. Also listed are the values for the coefficient k reflecting the relative increase in the extinction of the LF in comparison with the HF component, which according to eq 1 is

$$k = 1 + 0.018\Delta\nu_{OH}/\text{cm}^{-1} \tag{3}$$

TABLE 2: FTIR and ^{1}H MAS NMR Spectral Characteristics, and Brönsted Hydroxyl Distribution between Super and β Cages in Faujasite-like Materials

	FTIR						^{1}H MAS NMR	
sample	A_{HF} (%)	A_{LF} (%)	$\Delta\nu_{OH}$ (cm^{-1})	k	OH_{HF} (%)	OH_{LF} (%)	OH_{HF} (%)	OH_{LF} (%)
H-Y	29	71	92	2.66	52	48	53[a]	47[a]
H-EMT	30	70	84	2.51	52	48	58	42
H-EMO	30	70	85	2.53	52	48	58	42
SAPO-37a	55	45	66	2.19	73	27	77	23
SAPO-37b	52	48	67	2.21	70	30	72	28

[a] Literature result from ref 21.

This allows for the calculation of the distribution of Brönsted hydroxyls between the two cages

$$OH_{HF}\,(\%) = \frac{A_{HF}}{A_{LF}/k + A_{HF}} \tag{4}$$

$$OH_{LF}\,(\%) = \frac{A_{LF}}{A_{LF}/k + A_{HF}} \tag{5}$$

which is also given in Table 2.

The results for the deconvolution of the ^{1}H MAS NMR spectra (Table 2) are in good agreement with the FTIR results. Together they show that the distribution of the Brönsted hydroxyls between super and β cages in faujasite-like zeolite materials (H-Y, H-EMT, H-EMO) is the same and close to 1:1. In the case of the aluminophosphates (SAPO-37), it is approximately 3:1, on average, and is slightly lower for the samples with the high silicon content (SAPO-37b) as compared to the low-silicon material (SAPO-37a).

There are four crystallographically different oxygen sites in faujasite-like materials. Two of these, O_1 and O_4, point directly into the large cages whereas O_3 points clearly into the β cage and O_2, in the six-ring between the super and β cages, points slightly into the small cage. A statistical distribution then would give a 1:1 distribution between hydroxyls vibrating into 12 rings (O_1 and O_4) and six rings (O_3 and O_2). X-ray and neutron diffraction results have been interpreted in terms of distribution on O_1 and O_3,[17,18] and theoretical calculations[19] support these oxygens as energetically favored sites for protic hydrogens and suggest a distribution between the two sites (cages) close to 1:1, in agreement with the present FTIR results. An alternative view which assumes that protic hydrogens on O_2, O_3, and O_4 vibrate into the small cages with only O_1, giving rise to vibration in the large cages (which on a statistical basis gives a 1:3 ratio for HF vs LF),[20] appears not to be in accord with experimental, structural, or theoretical evidence.

The good agreement between the FTIR and ^{1}H MAS NMR results in the present study provides support for the validity of the proposed method for calculating the relative increase in extinction coefficients of hydroxyl bands in zeolites which are shifted because of weak perturbation by hydrogen bonding.

III. Extinction Coefficients for the HF and LF OH Bands in H-Y Zeolite. A first question concerns the quantitative study of zeolites which requires that Beer's law is applicable. Its form, adapted for the case of solid samples, can be written as

$$A = \epsilon N \rho \tag{6}$$

where A is the intensity of the band (cm^{-1}), ϵ is the integrated extinction coefficient (cm·μmol^{-1}), N is the concentration of the vibrating species (mmol·g^{-1}), and ρ is the thickness of the disk (mg·cm^{-2}).

A series of experiments with samples of H-Y zeolite having different thicknesses, in the range 2–6 mg·cm^{-2}, does not show any deviation from linearity (Figure 4). The experimental error is ±13% (95% confidence limits). However, the averaging of

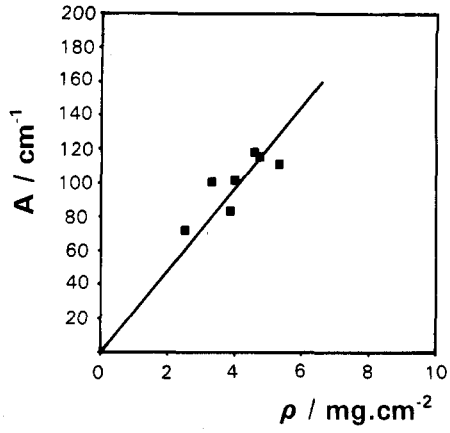

Figure 4. Checking the validity of Beer's law in the case of H-Y zeolite. (A is a total intensity of the HF + LF Brönsted hydroxyls.)

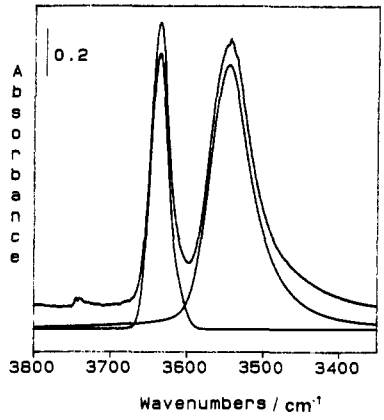

Figure 5. Deconvolution of the hydroxyl region in the FTIR spectrum of H-Y zeolite; ρ = 5 mg·cm^{-2} (dry basis).

seven experiments decreases the error to ±5%. The spectrum corresponding to the average in the series (the sum of the seven spectra divided by 7), recalculated to ρ = 5 mg·cm^{-2} (dry basis), and its deconvolution into HF and LF components are shown in Figure 5.

The approach described in part II leads to the following system of equations:

$$\epsilon_{LF} = k\epsilon_{HF}$$

$$A_{HF} = \epsilon_{HF}N_{HF}\rho$$

$$A_{LF} = \epsilon_{LF}N_{LF}\rho \qquad (7)$$

$$N_{HF} + N_{LF} = N_{OH}$$

Parameters for the spectrum in Figure 5 are

$$k = 2.66$$

$$A_{HF} = 37.2 \text{ cm}^{-1}$$

$$A_{LF} = 91.1 \text{ cm}^{-1}$$

$$\rho = 5 \text{ mg·cm}^{-2}$$

$$N_{OH} = 4.5 \text{ mmol/g (Table 1)}$$

This results in the following extinction coefficients

$$\epsilon_{HF} = 3.2 \ \mu\text{mol·cm}^{-1}$$

$$\epsilon_{LF} = 8.5 \ \mu\text{mol·cm}^{-1}$$

TABLE 3: Integrated Extinction Coefficients for H-Y Zeolite

no.	ϵ_{HF} (cm·μmol^{-1})	ϵ_{LF} (cm·μmol^{-1})	method of determination	ref
1	12.2	19.9	Py and Pi sorption	7
2	5.28	9.5	NH_3 sorption	8
3	2.8–4.4[a]		Py sorption	9
		9.4–13.4[a]	NH_3 sorption[b]	9
		9.4–9.6[a]	Pi sorption[b]	9
4	0.6–3.1[a]		Py sorption	10
5	3.0–8.0[a]	4.5–6.7[a]	Py sorption	11
6	3.1[c]	3.1[c]	Py sorption	12

[a] The extinction coefficient changes depending on the degree of the exchange and calcination temperature. [b] ϵ_{LF} was determined after the HF band was poisoned with Py. [c] Determined with the assumption that the HF and LF bands have the same extinction coefficients.

There have been several attempts in the literature to determine these extinction coefficients.[7-12] A summary of the results is given in Table 3. It can be seen that the range of the values is very wide. The values determined in the present work can probably clarify the problem.

Conclusions

The perturbation of the OH mode in H-ZSM-5 with a number of weak bases (Ar, H_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, CO, C_2H_4) was used to study weak hydrogen bonding of Brönsted hydroxyls in zeolites. The increase in the intensity of the perturbed hydroxyl band and its widening were related linearly to its shift as

$$\Delta A/A_0 = 0.018\Delta\nu_{OH}/\text{cm}^{-1}$$

$$\Delta a/a_0 = 0.010\Delta\nu_{OH}/\text{cm}^{-1}$$

An application of these correlations to the shift between HF and LF components in the faujasite-like materials allows for the determination of the distribution of Brönsted hydroxyls between the super and β cages. In the case of zeolites (H-Y, H-EMT, H-EMO), this ratio is approximately 1:1 whereas for the aluminophosphates it is close to 3:1. This agrees with the ^{1}H MAS NMR results which justify the transfer of the correlation for the model system H-ZSM-5/weak bases to the hydroxyls interacting with framework oxygens when they are situated in rings smaller than 12-membered.

With the same approach and an average of a series of experimental spectra for H-Y zeolite (Si/Al = 2.7), the extinction coefficients of the HF and LF hydroxyl bands were determined:

$$\epsilon_{HF} = 3.2 \text{ cm·}\mu\text{mol}^{-1}$$

$$\epsilon_{LF} = 8.5 \text{ cm·}\mu\text{mol}^{-1}$$

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