

# Use of dielectric relaxation for measurements of surface energy variations during adsorption of water on mordenite

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## Abstract

This paper tries to assess simply and quantitatively the link between classical adsorption theories and dielectric spectroscopy, in order to demonstrate that dielectric spectroscopy can be used as a tool of determination of surface energy variations due to movements of charge carriers at the surface of solids. A simple theory is developed to analyze hops of cations at the surface of mordenite, which are detected by complex impedance spectroscopy during adsorption of water. An energy of extraction of the cation can be determined from measurements and its dependence on the quantity of water molecules adsorbed is shown and qualitatively and quantitatively explained, using relationships developed in order to interpret adsorption phenomena generally. The agreement with other determinations of the adsorption energies and solid surface energy is correct.

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## 1. Introduction

Contacts between bulk phases are possible through a special zone of the space, called a surface or interface. In this region, it is possible to observe physical properties that are not observed in bulk phases. These properties are of industrial importance and it is necessary to understand and to quantify the mechanisms in order to pilot the processes. Catalysis is the most obvious application and is characterized by important energy transfers on the surface. Surface phenomena of lower energies can still be of industrial use, as for example in separation or purification and in technologies of membranes, ceramics, and glasses [1].

However, adsorption and more generally surface phenomena are still very complex problems where it is difficult to link the microscopic and macroscopic scales. In this paper, we will use the fact that dielectric relaxation spectroscopy is a tool able to give access to microscopic displacements observable at surfaces of solids [2]. Indeed, modifications of the structure of an inter-

face, induced by the intrusion of other molecules or by external field effects, modify the surface energy and the corresponding electronic density. Some of these modifications, in particular motions of ions linked to the solid framework at the surface, can be detected by DRS (in this paper, we use complex impedance spectroscopy, CIS) and can be modeled by hops over potential barriers. It is possible to quantify the dielectric effects due to these motions using macroscopic theories originally developed to describe motions in bulk glasses and thus to link dielectric relaxation to surface thermodynamics.

The studies in our laboratories are related to adsorption, and especially to adsorption of polar molecules such as water onto silicates and aluminosilicates with a large surface area [3–5]. For many years, we have focused our interest on dielectric relaxation phenomena occurring in bulk and on surfaces [6]. Solids studied contain cations, which are able to move when an electric field is applied. Following the works of Mott and Davis [7], Pollack and co-workers [8,9], and Angell et al. [10] and Martin and Angell [11], the motions of the cations are described as discrete hops of charge carriers between localized states. These localized states correspond to crystallographic sites where the cations are expected to stay at equilibrium.

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When the ion moves from its equilibrium or a metastable position, the movement implies a dielectric response. The intensity of this signal varies with the number of ions and the correlation of single motions. Obviously, at equilibrium and without an external electric field, the orientation of the resulting dipoles is random and varies with thermal agitation. When the sample is exposed to an external electric field, dipoles are oriented following the field and then polarization appears. Therefore, measurements of the electric current vs time allow the determination of the kinetics of the modification of polarization inside or at the surface of a sample. Basically, the speed of occurrence of the polarization current depends mainly on the energy associated with the orientation of the dipoles. Therefore, dielectric relaxation methods are very convenient for studying the motions of cations in systems that are insulators. Samples can be put inside a condenser setup and subjected to time variations of potential difference.

The aim of this paper is to develop a very simple theoretical representation of the mechanisms that take place during the reorientation of dipoles on the surface of a solid containing extraframework cations when adsorption of water occurs [12]. We want to use the simple idea that energies measured during dielectric relaxation are responses to microscopic constraints of the structures surrounding the cations. Afterward, we will show that it is possible to assess the enthalpies corresponding to movements of cations and the modifications of these enthalpies due to adsorption of water. The study of the adsorption of water onto an Na-mordenite presented here is considered as an example of a possible general approach, which will be applied in the near future to other ionic systems still being experimentally studied [3–6,12].

## 2. Experimental background

### 2.1. Presentation of the solid: mordenite

We have studied a mordenite, which is a zeolite with the formula  $M_{n+x/n}Al_xSi_{48-x}O_{96} \cdot zH_2O$  with M cations of charge  $n$ . Its structure is orthorhombic ( $Cmcm$ ), with unit cell parameters  $a = 18.1$ ,  $b = 20.5$ , and  $c = 7.5$  Å [13]. Its aluminosilicate network has a porous structure (Fig. 1), which consists primarily of straight channels, parallel to [001], having a slightly elliptical cross section  $6.5 \times 7.0$  Å (12-member windows) and connected secondary channels, parallel to [010], of 2.8 Å free diameter (8-members windows). Each aluminum atom introduces a negative charge, counterbalanced by extraframework cations, which strongly influence the physicochemical properties of the mordenite. These exchangeable cations are located in well-defined surface sites [14], depending on their nature and their content. In this work, we use samples with a ratio Si/Al of 5.5. This means that the number of Al per unit cell is 8. This mordenite was supplied by ZEO-CAT (France). It was originally in the hydrogen form (MOR-H), with a Si/Al ratio equal to 5.5, and the chemical structural formula  $Na_{0.09}H_{7.29}Al_{7.38}Si_{40.61}O_{96} \cdot 24H_2O$ . From this sample, the sodium form (Na-MOR) was prepared by immersion for 12 h of 5 g of anhydrous hydrogen mordenite in 100 ml of an

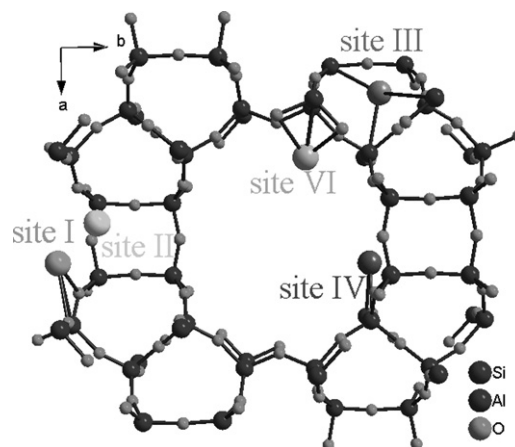


Fig. 1. Picture of the cationic sites in mordenite, denoted as from I to VI following Mortier [14].

aqueous solution of NaOH ( $0.1 \text{ mol L}^{-1}$ ) at ambient temperature. Once equilibrium was achieved, the pH of the solution was 11.4. The exchange degree was verified by atomic absorption spectrometry and chemical analysis. The number of Na can be considered as 7.4 per unit cell.

One can define four types of sites corresponding to Al or Si atoms. However, it is very difficult to know the exact repartition of atoms between these different sites. Therefore cell models are not exact representations of the diversity of actual crystals. One available information is the knowledge of distances and angles between sites and oxygen atoms, but this information is averaged for the whole crystal. Some positions are attributed by Mortier for the most probable locations of cations. Five positions are shown in Fig. 1.

The structure of mordenite can be considered rigid. However, the cations are mobile and the dimension of cycles and channels can be modified during the displacement of cations. Furthermore, the presence of adsorbed molecules can modify the local repartition of electrons and then the structure at the microscopic level. The occupancy of the six types is not a general case. Therefore, the occupancy is defined as a probability.

### 2.2. Determination of adsorbed water quantities

Before the experiments, mordenite is dried under at  $400$  °C under  $10^{-3}$  Torr. Then the sample is put in contact with water vapor in a chamber. The quantities of water molecules adsorbed on a known mass of dry mordenite have been determined by a gravimetric method using a thermal balance under argon flux with increasing temperature. Assuming that the mass loss is only due to the desorption of water molecules, we determined the water content remaining in the sample for each temperature. The adsorbed quantity is reported in Fig. 2 by a unit cell vs the temperature, which is denoted as TT (for treatment temperature).

### 2.3. CIS measurements

Permittivity measurements were performed on pellets obtained by pressing the Na-MOR powder into a disk ca. 1 mm

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