

Adsorption of alcohols onto zinc selenide (ZnSe) crystal surface

Alfred A. Christy

¹Full Department of Science, Faculty of Engineering and Science, University of Agder, 4638 Kristiansand, Norway

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Abstract. Adsorption behaviour of ZnSe, a popular material used in the manufacture of crystals for total internal reflectance techniques was studied for the adsorption of alcohols from dichloromethane solutions using infrared spectrometry. A series of n-alcohols were used in this study. The results show that the integrated area for the hydrogen bonded OH stretchings decrease and suggests that there is a continuous adsorption of alcohol molecules onto the ZnSe crystal by breaking the hydrogen bonds between alcohol molecules in solution.

Introduction

Zinc selenide is one of the infrared transparent materials that used to manufacture internal reflectance crystals for infrared analysis by internal reflectance techniques. ZnSe has a refractive index of 2.5, transparent in the mid-IR region and posses other needed qualities such as hardness, brittleness, conductivity, chemical inertness etc. for an internal reflectance crystal material [1]. The internal reflectance crystals are made in different shapes and sizes to suit different measurement purposes. Generally, in infrared internal reflectance spectrometry, the technique is based on bringing a sample in close contact with the surface of the internal reflectance crystal so that the radiation that is internally reflecting within the crystal could interact with the sample. The technique has been applied to several applications and analyses and has become one of the popular techniques to measure infrared spectra of liquids.

One of the understood requirements of the technique is that the material used for the crystal should not alter the chemical nature of the bulk of the sample whose infrared spectrum is being measured. This requirement is important because change in chemical nature of the bulk changes the infrared spectrum measured and if the induced change is dynamic then the spectrum measured will vary with time and will not represent the infrared spectrum of the sample in its natural form.

There has been very little work done on adsorption of molecules onto zinc selenide surfaces from solutions. Zinc selenide does not act as an adsorbent in most of the cases and gives representative spectra of the liquids and solutions surrounding the crystal. However, when alcohols are held in solutions of dichloromethane the adsorption process starts on the surface of the crystal.

The aim of this article is to demonstrate that the spectra measured on alcohols in solutions vary with time and therefore, caution should be taken to interpret spectra of alcohols from organic solvents.

Experimental

A set of 5 alcohols were used in this study. The alcohols include n-propanol, n-pentanol, n-hexanol, n-heptanol and n-octanol. The alcohols were prepared as 0.4 M solutions in dichloromethane. The alcohols and dichloromethane were dried over molecular sieves (4 Å) and kept in dark glass bottles.

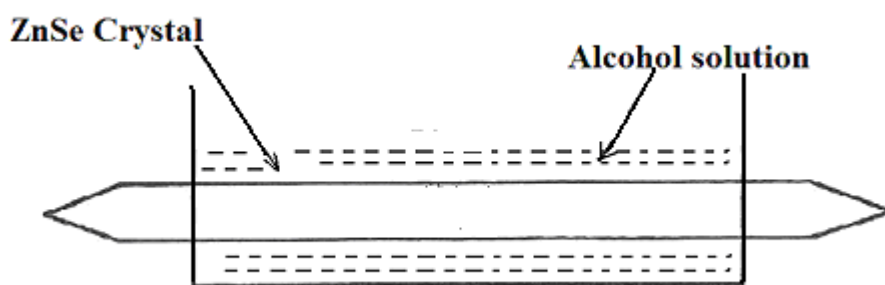
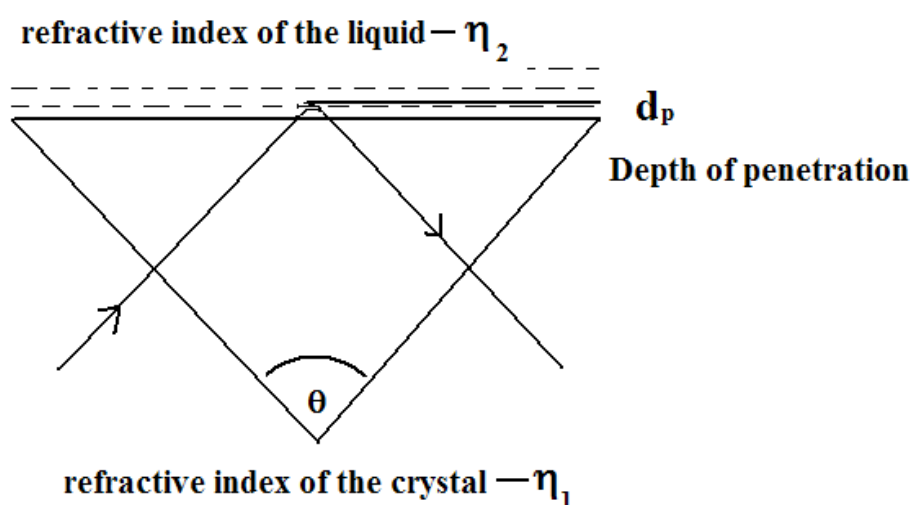


Fig. 1. Cell assembly with ZnSe ATR crystal

All the infrared measurements were performed on a Perkin Elmer Fourier Transform Infrared spectrometer equipped with a medium band mercury cadmium telluride (MCT) detector. A multi-reflection ATR cell assembly manufactured by Perkin Elmer was used in the infrared measurements. The cell assembly contained a zinc selenide crystal as the total internal reflection element. A background spectrum of the dichloromethane was made before the infrared spectral measurements of the alcohol solutions. The infrared measurements were started as soon as a solution was placed in the cell using the spectrum software of the instrument. A total of 20 scans were made at a resolution of 4 cm^{-1} in all cases.

Results and discussion

As mentioned above the internal reflectance technique based on the interaction of the infrared radiation reflected at the surface and the bulk of the liquid that is in contact with the surface. At the surface of reflection a standing wave normal to the reflecting surface is established in the denser crystal medium and an evanescent wave established in the less dense medium [2, 3]. The amplitude of the electric field in the less denser medium decays exponentially with distance from the surface. If the less denser medium absorbs evanescent radiation, attenuation occurs at wavelengths of absorption bands. The penetration depth of the evanescent radiation in the less denser medium depends on the wave length, refractive indices of the mediums involved and the crystal face angle and given by equation 1.



$$d_p = \frac{\lambda}{2\pi\eta_1\sqrt{[\sin^2\theta - (\eta_2/\eta_1)^2]}} \quad (1)$$

λ = wavelength (mm)

η_1 =refractive index of crystal

η_2 =refractive index of sample

θ =crystal face angle in degrees

Fig. 2. A figure showing the process of total internal reflection on a single reflection ATR crystal

For a particular crystal the penetration depth depends on wavelength of radiation and the refractive index of the sample. For one sample the penetration depth is the same during an experiment and the intensity of absorption at a particular wavelength can be quantitatively compared. It means that the area of the peak of absorption arising from a functional group can quantitatively represent the change in the functionality of the sample.

The variation in the area of the peaks representing the hydrogen bonded OH stretchings with time as well as the variation in the area of the peaks representing the free OH stretchings was compared. The results show that the hydrogen bonded OH stretchings absorptions decreased with time. The decrease was prominent with propanol and pentanol in solutions. The hydrogen bonded OH stretching absorptions decreased at a slower rate with higher alcohols. There was an increase in the free OH stretching absorptions. The solution in the cell can be washed and flushed for a new experiment involving the same alcohol starting afresh. All these observations clearly indicate that there is an adsorption process taking place on the cell surface with time.

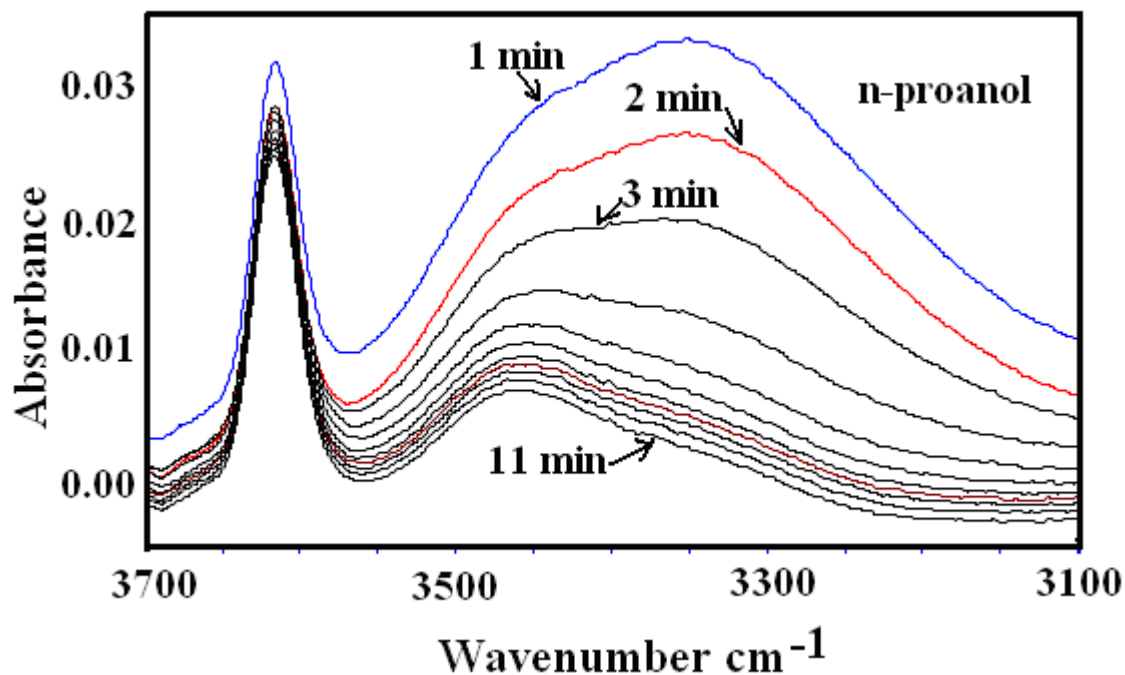


Fig. 3. Infrared spectra of propanol in dichloromethane over time

Alcohol molecules are polarized in their bond between hydrogen and oxygen. Due to the electron withdrawing power of the oxygen atom the hydrogen atom becomes positively charged and oxygen becomes negatively charged. The alcohol molecules that are in equilibrium with tetramers are being adsorbed on to the surface of the crystal.

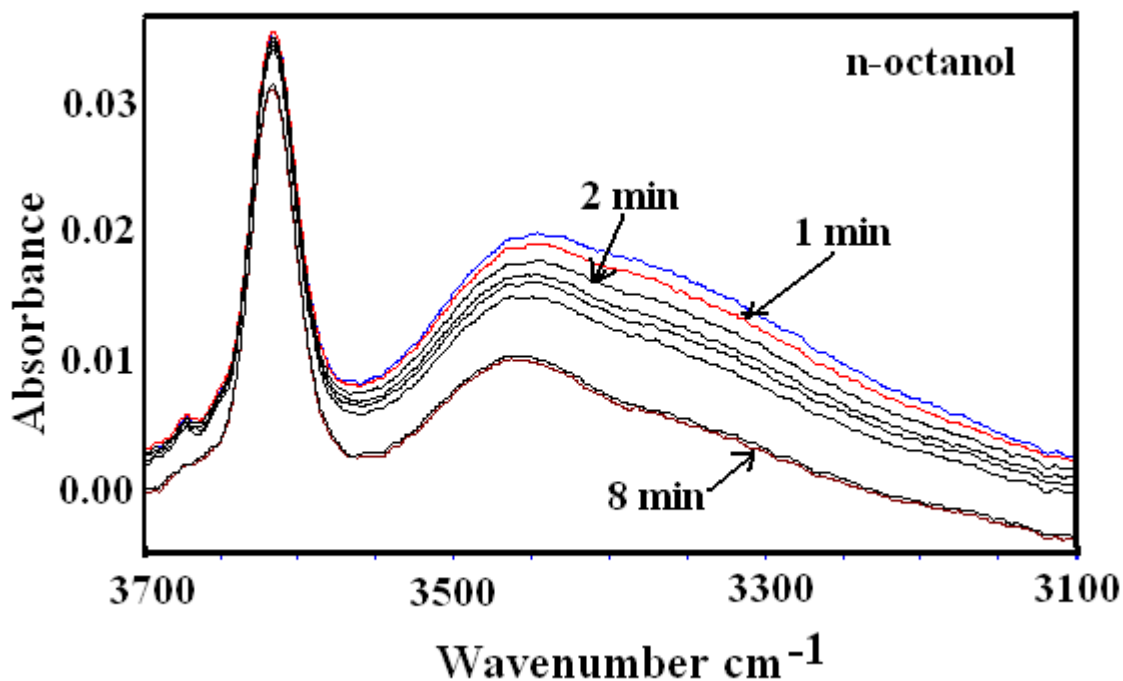


Fig. 3. Infrared spectra of heptanol in dichloromethane over time

It appears that there is a driving force that makes the molecules to approach the crystal surface. This force may be originating from the uneven surface of the crystal. An examination of the ATR crystal under a microscope reveals that the surface is uneven and full of scratches. These create potential sites for the adsorption of alcohol molecules using hydrogen bonding. This adsorption breaks hydrogen bondings between alcohol molecules and become free alcohol molecules. It is also interesting to note that the area for the free OH stretching absorptions increases for all the alcohols investigated. When alcohol molecules are adsorbed on to the crystal surface the hydrogen bonded OH stretching of the alcohol molecules are converted into free OH stretchings.

Conclusion

It has been shown in this work that the alcohol molecules are adsorbed from dichloromethane solutions onto ZnSe crystal. The hydrogen bonded network within the bulk surrounding the ZnSe crystal decrease with time. This work clearly demonstrates that any quantitative work involving alcohols using ATR as a sampling technique should be treated with caution. It is also important that those who use this technique to be aware that the alcohol molecules are being adsorbed onto the surface when a solution containing alcohol is allowed to stand in the cell.

References

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