

CHAPTER 3

EXPERIMENT

3.1. Effective Number of Reflections in an IRE

3.1.1. Materials and Equipments

1. Toluene
2. Multiple attenuated total reflection (MATR) accessories
 - 2.1. Pike Technologies accessory with 74x7x4 mm. 45° ZnSe IRE
(Theoretical number of reflections 9.25)
 - 2.2. Spectra Tech. accessory with 50x5x2 mm. 45° ZnSe and Ge IRE
(Theoretical number of reflections 10.00)
3. ZnSe disk-windows (25x3 mm.)
4. Bruker Vector 33 FT-IR spectrometer

3.1.2. FT-IR spectrometer Operating Conditions

Bruker Vector 33 FT-IR Spectrometer

Experimental Setup

Resolution	4.0 cm ⁻¹
Number of Scans	32
Result Spectrum	Absorbance

Optic Parameters

Source Setting	Globar (MIR)
Detector Setting	DTGS
Beam Splitter Setting	KBr

3.1.3. Spectral Acquisitions

1. Toluene was used as a test material for all spectral acquisitions.
2. ATR spectra of toluene were collected using two commercially available MATR accessories.
3. Transmission spectra of toluene were collected under the following conditions:

3.1. Uniform transmission cell thickness

By placing film spacers between the two ZnSe disk-windows and collecting ordinary transmission spectra, the spectra of uniform transmission cell thickness were obtained. These spectra were acquired with different cell thickness.

3.2. Non-uniform transmission cell thickness

Transmission spectra were acquired using wedge-shaped ZnSe disk-windows with different cell thickness.

3.1.4. Transmission Cell Thickness Determination

3.1.4.1. Constructions of calibration curves

1. The interference fringes in the spectra acquired via uniform thickness transmission cells were employed for calculating the transmission cell thickness.
2. The calculated thickness was used to simulate the sinusoidal interference fringes spectrum over the mid-infrared region via the optical theory with a constant refractive index of 1.47 [11]. The sinusoidal fringes in the transmission spectra were then eliminated by spectral subtraction with simulated fringe spectra.
3. Spectral intensities obtained after fringe elimination were then used in the constructions of calibration curves between the spectral intensity versus the transmission cell thickness.

3.1.4.2. Thickness determination of wedge-shaped transmission cells

The thickness of wedge-shaped transmission cells can be determined directly from the calibration curves using their spectral intensity at various frequencies.

3.1.5. The Calculation of Effective Number of Reflections

The calculated thickness from transmission experiment was used to calculate the effective number of reflections in ATR experiment. In order to suppress the error associated to an individual spectrum, the thickness obtained from calibration curve and spectral intensity from a wedge-shaped transmission cell were employed instead of those from fringe spectra.

3.2. Optical Contact in ATR Experiment

3.2.1. Materials and Equipments

1. Polycarbonate (PC)
2. Polyvinylchloride (PVC)
3. Nujol
4. *i*-propanol
5. Multiple attenuated total reflection (MATR) accessory (45⁰ IRE from Spectra Tech.) with
 - 5.1. ZnSe IRE (50x5x2 mm.)
 - 5.2. Ge IRE (50x5x2 mm.)
6. Bruker Vector 33 FT-IR spectrometer

3.2.2. FT-IR spectrometer Conditions

Bruker Vector 33 FT-IR Spectrometer

Experiment Setup

Resolution	4.0 cm ⁻¹
Number of Scans	32
Result Spectrum	Absorbance

Optic Parameters

Source Setting	Globar (MIR)
Detector Setting	DTGS
Beam Splitter Setting	KBr

3.2.3. Spectral Acquisitions

3.2.3.1. ZnSe IRE system

1. Polycarbonate was placed against ZnSe IRE by an applied pressure and ATR spectra of polycarbonate were then acquired. The applied pressure was increased and ATR spectra of polycarbonate were taken until no more significant increment of spectral intensity was observed.

2. ATR spectra of polyvinylchloride were acquired by the same procedure as described in 1.

3. Nujol was spreaded as a liquid film over ZnSe IRE and ATR spectrum of Nujol was acquired.

4. ATR spectrum of *i*-propanol was acquired by the same procedure as described in 3.

5. Nujol was spreaded over ZnSe IRE and polycarbonate was, then, placed against the IRE over the Nujol film under an applied pressure. ATR spectrum of polycarbonate/Nujol was acquired.

6. The same procedure as described in 5 was repeated using polyvinylchloride as a sample instead of polycarbonate and ATR spectrum of polyvinylchloride/Nujol was acquired.

7. *i*-propanol was spreaded over ZnSe IRE and polycarbonate was, then, placed against the IRE over the *i*-propanol film under an applied pressure which equals to the highest pressure applied to the system described in 1. ATR spectrum of polycarbonate/ *i*-propanol was acquired.

8. The same procedure as described in 7 was repeated using polyvinylchloride as a sample instead of polycarbonate and ATR spectrum of polyvinylchloride/*i*-propanol was acquired.

3.2.3.2. Ge IRE system

1. Polycarbonate was placed against Ge IRE by an applied pressure and ATR spectra of polycarbonate were acquired. The applied pressure was increased and ATR spectra of polycarbonate were taken until no more significant increment of spectral intensity was observed.

2. ATR spectra of polyvinylchloride were acquired by the same procedure as described in 1.

3. Nujol was spreaded as a liquid film over Ge IRE and ATR spectrum of Nujol was acquired.

4. ATR spectrum of *i*-propanol was acquired by the same procedure as described in 3.

5. Nujol was spreaded over Ge IRE and polycarbonate was, then, placed against the IRE over the Nujol film under an applied pressure which equals to the highest pressure applied to the system described in 1. ATR spectrum of polycarbonate/Nujol was acquired.

6. The same procedure as described in 5 was repeated using polyvinylchloride as a sample instead of polycarbonate and ATR spectrum of polyvinylchloride/Nujol was acquired.

7. *i*-propanol was spreaded over Ge IRE and polycarbonate was, then, placed against the IRE over the *i*-propanol film under an applied pressure which equals to the highest pressure applied to the system described in 1. ATR spectrum of polycarbonate/ *i*-propanol was acquired.

8. The same procedure as described in 7. was repeated using polyvinylchloride as a sample instead of polycarbonate and ATR spectrum of polyvinylchloride/*i*-propanol was acquired.

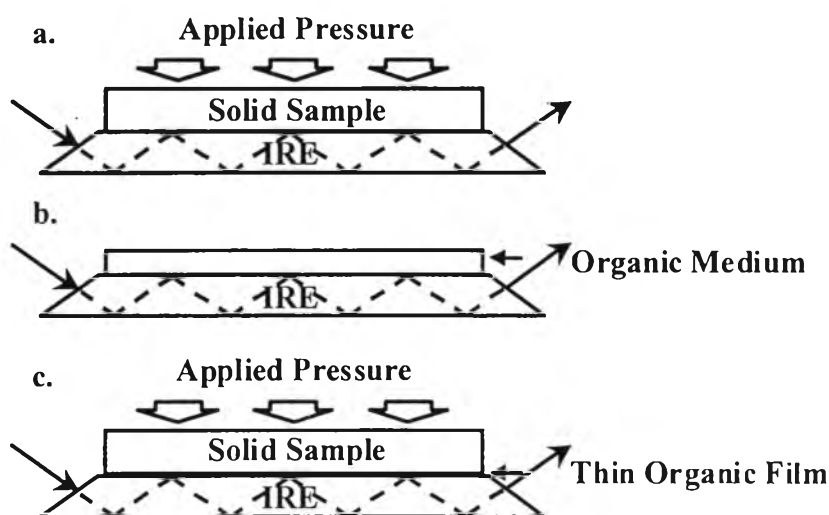


Figure 3.1 Experimental procedure for acquiring optical contact between a sample and the IRE in order to obtain bulk spectral intensity of the sample. The bulk spectral intensity obtained will later be used in the sampling depth determination experiment.

3.3. Sampling Depth in ATR FT-IR Spectroscopy

3.3.1. Materials and Equipments

1. Polycarbonate (PC)
2. Polyvinylchloride (PVC)
3. Nujol
4. *i*-propanol
5. Multiple attenuated total reflection (MATR) accessories (45⁰ IRE from Spectra Tech. with effective number of reflections 7.45)
 - 5.1. ZnSe IRE (40x5x2 mm.)
 - 5.2. Ge IRE (40x5x2 mm.)

6. Bruker Vector 33 FT-IR spectrometer

3.3.2. FT-IR spectrometer Conditions**Bruker Vector 33 FT-IR Spectrometer****Setup Experiment**

Resolution	4.0 cm ⁻¹
Number of Scans	32
Result Spectrum	Absorbance

Optic Parameters

Source Setting	Globar (MIR)
Detector Setting	DTGS
Beam Splitter Setting	KBr

3.3.3. Spectral Acquisitions**3.3.3.1. ZnSe IRE/Nujol/polycarbonate system**

1. Nujol was spreaded as a liquid film over ZnSe IRE and then polycarbonate was introduced into the system. Polycarbonate was placed over the Nujol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the Nujol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the Nujol film was squeezing out by the applied pressure until no more increment spectral intensity of polycarbonate was observed.

3.3.3.2. ZnSe IRE/*i*-propanol/polycarbonate system

1. *i*-propanol was spreaded as a liquid film over ZnSe IRE and then polycarbonate was introduced into the system. Polycarbonate was placed over the *i*-propanol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the *i*-propanol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the *i*-propanol film was squeezing out by the applied pressure until no more increment spectral intensity of polycarbonate was observed.

3.3.3.3. ZnSe IRE/Nujol/polyvinylchloride system

1. Nujol was spreaded as a liquid film over ZnSe IRE and then polyvinylchloride was introduced into the system. Polyvinylchloride was placed over the Nujol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the Nujol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the Nujol film was squeezing out by the applied pressure until no more increment spectral intensity of polyvinylchloride was observed.

3.3.3.4. ZnSe IRE/*i*-propanol/polyvinylchloride system

1. *i*-propanol was spreaded as a liquid film over ZnSe IRE and then polyvinylchloride was introduced into the system. Polyvinylchloride was placed over the *i*-propanol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the *i*-propanol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the *i*-propanol film was squeezing out by the applied pressure until no more increment spectral intensity of polyvinylchloride was observed.

3.3.3.5. Ge IRE/Nujol/polycarbonate system

1. Nujol was spreaded as a liquid film over Ge IRE and then polycarbonate was introduced into the system. Polycarbonate was placed over the Nujol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the Nujol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the Nujol film was squeezing out by the applied pressure until no more increment spectral intensity of polycarbonate was observed.

3.3.3.6. Ge IRE/*i*-propanol/polycarbonate system

1. *i*-propanol was spreaded as a liquid film over Ge IRE and then polycarbonate was introduced into the system. Polycarbonate was placed over the *i*-propanol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the *i*-propanol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the *i*-propanol film was squeezing out by the applied pressure until no more increment spectral intensity of polycarbonate was observed.

3.3.3.7. Ge IRE/Nujol/polyvinylchloride system

1. Nujol was spreaded as a liquid film over Ge IRE and then polyvinylchloride was introduced into the system. Polyvinylchloride was placed over the Nujol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the Nujol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the Nujol film was squeezing out by the applied pressure until no more increment spectral intensity of polyvinylchloride was observed.

3.3.3.8. Ge IRE/*i*-propanol/polyvinylchloride system

1. *i*-propanol was spreaded as a liquid film over Ge IRE and then polyvinylchloride was introduced into the system. Polyvinylchloride was placed over the *i*-propanol film without any pressure applied and ATR spectrum of the system was acquired.

2. Pressure was applied to the system in order to vary the thickness of the *i*-propanol film. ATR spectra were taken simultaneously as the applied pressure was increased step by step.

3. ATR spectra were continuously acquired while the *i*-propanol film was squeezing out by the applied pressure until no more increment spectral intensity of polyvinylchloride was observed.

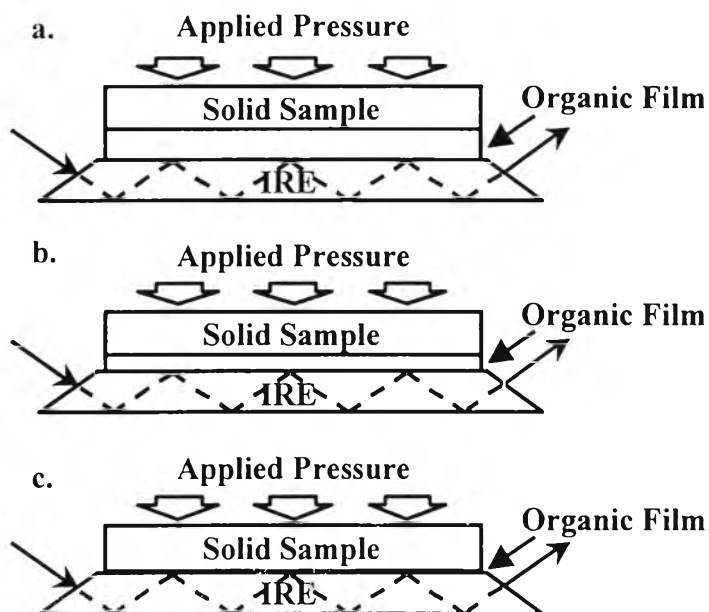


Figure 3.2 Schematic illustration of experimental setup for the sampling depth determination. ATR spectra of the system were acquired as the pressure applied was increased step by step. The ATR spectra of the system were varied in spectral intensity by the thickness of the organic film. ATR spectra of the system were collected until no significant increment of spectral intensity was observed (i.e., spectral intensity of substrate equals to its bulk intensity obtained from the optical contact experiment).