

Study of composition of adipic esters by IR spectroscopy

Abstract

In this article, the composition of the following adipic esters: isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl, isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl, isodecyl adipate and 2-phenoxy ethyl were investigated using infrared spectroscopy. The absorption spectra of isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl, isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl, isodecyl adipate and 2-phenoxy ethyl were observed at wave numbers 2958cm^{-1} and 829cm^{-1} , 2959cm^{-1} and 752cm^{-1} , 2958cm^{-1} and 752cm^{-1} respectively.

Keywords: composition, ester, adipic, spectrum, FTIR

Introduction

Infrared (IR) spectroscopy is the most suitable method for identifying the presence of polar functional groups in the structure of organic compound molecules.

Infrared (IR) radiation is that part of the electromagnetic spectrum, between the visible and microwave regions, which is characterized by wavelengths of the order of 10^{-5} m. For recording IR spectra used in determining the structure of organic compounds, only the mid-IR range is used, which contains wavelengths in the region of $2.5\text{--}25\text{ }\mu\text{m}$ (most often, the characterization is done using wave numbers in the range of $400\text{--}4000\text{ cm}^{-1}$).

IR radiation characterized by wave numbers lower than 100 cm^{-1} can be absorbed by organic compound molecules and converted into molecular rotational energy. This absorption is quantified, which determines the recording of a molecular rotational spectrum consisting of discrete lines. IR radiation in the range of $10,000\text{--}100\text{ cm}^{-1}$ can also be absorbed by molecules of organic compounds, leading to changes in molecular vibrational states. Although this absorption is in turn quantified, vibrational spectra recorded by IR spectroscopy are made up of absorption bands, because each change in vibrational energy is accompanied by changes in rotational energy.

An IR spectrum contains absorption bands due to vibrations that occur simultaneously with the participation of all atoms in the structure of the molecules of the organic compound analyzed (normal vibrations). The position of an absorption band formed by the vibrational excitation of a certain functional group is well specified in the spectrum, varying within narrow limits with the environment of the functional group within the molecule. An

absorption band characteristic of the same functional group is found at almost the same value of the wave number in the IR spectrum of any molecule (characteristic group vibrations). This fact allows the identification of the structural elements of a molecule, by assigning characteristic absorption bands in the IR spectrum.

The position of an absorption band in the IR spectrum depends on several factors such as: the relative masses of the atoms and the force constants of the bonds involved in the vibrational excitation, as well as the geometry of the molecule. The vibrational energy of a covalent bond can only have quantized values proportional to the oscillation frequency of a system formed by two masses (atomic masses) linked by a spring (covalent bond); this frequency can be deduced from an application of the law of elastic deformations (Hooke's law) to the harmonic oscillator [1-10].

$$E = h \nu(\nu + 1/2) = \frac{h}{2\pi} \sqrt{k/\mu} (\nu + 1/2)$$

where: h is Planck's constant is $4.135 \times 10^{-15} \text{ eV.s}$

ν is the vibrational quantum number with positive integer values (0, 1, 2, 3n)

ν is the oscillation frequency given by the relation:

$$\nu = \frac{1}{2\pi} \sqrt{k/\mu}$$

k is the bond force constant

μ is the reduced mass given by the relationship:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where: m_1, m_2 atomic masses

The mathematical relationship shows the direct proportionality between the vibration frequency and the bond force constant as well as the inverse proportionality of the oscillation frequency with the masses of the bonded atoms; thus, multiple bonds being characterized by higher values of the force constants, have higher oscillation frequencies while bonds formed by heavier atoms have lower oscillation frequencies [10-18].

The IR spectrum is represented as the intensity of the absorption bands as a function of the wave number (frequency ν , or wavelength λ) of the absorbed electromagnetic radiation. The intensities of the bands can be expressed either as transmittance (T) or as absorbance (A). Transmittance is the ratio of the power of the radiation transmitted through a sample to the power of the radiation incident on the sample.

$$T = I/I_0$$

$$A = \log(1/T).$$

Where: I_0 is the intensity of the incident radiation

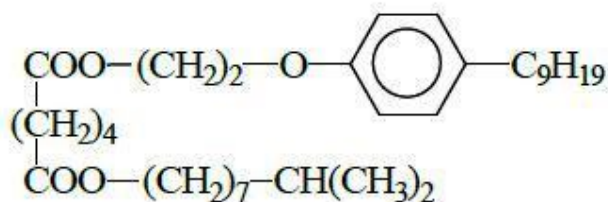
I is the intensity of the emergent radiation

For the absorption of IR radiation to occur, the electric vector of light must interact with the dipole moment of the molecule (the alternating electric field produced by the change in the charge distribution that accompanies the respective vibration couples the vibration of the molecule with the oscillating electric field of the electromagnetic radiation). A selection rule shows that only those vibrations that involve a change in the dipole moment of the molecule produce absorption bands in the IR range. Consequently, no absorption bands due to vibrations symmetrical to the center of symmetry of the molecule will be recorded - these vibrations are IR inactive. The intensity of the absorption band is usually reported in semi-quantitative terms noted: s - strong absorption, m - medium absorption, w - weak absorption.

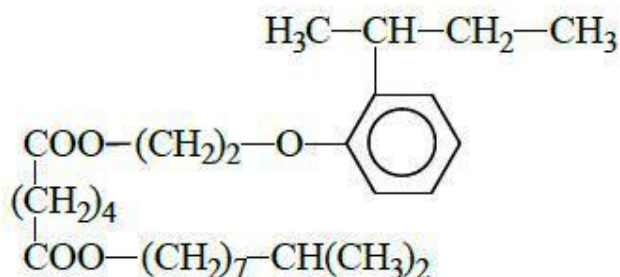
Material and methods

Synthesis of adipic esters

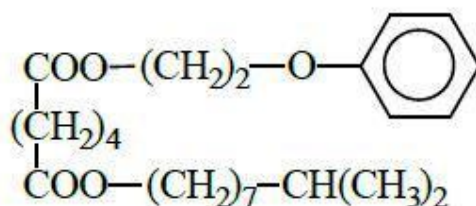
Isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl is obtained in the first stage by synthesizing 1.1 moles of adipic acid, 1.1 moles of 2-(p-nonyl-phenoxy) ethanol and 0.037 moles of p-toluene sulfonic acid. In stage I: temperature 115 - 145°C, time 5 - 7 hours, toluene 175 ml. In the second stage, 1.1 moles of isodecanol are added at a temperature between 120°C - 165°C, time 5 - 7 hours [7].



Isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl are obtained in the first stage by the reaction between 1.27 moles of adipic acid, 1.27 moles of 2-(o-sec-butyl-phenoxy) ethanol and 0.037 p-toluene sulfonic acid. In stage I: temperature 115 - 145°C, time 5 - 7 hours, toluene 175 ml. In the second stage, 1.27 moles of isodecanol are added at a temperature between 120°C - 165°C, time 5 - 7 hours [7].



Isodecyl adipate and 2-phenoxy ethyl is obtained in the first stage by the reaction between 1.45 moles of adipic acid, 1.45 2 phenoxy ethanol and 0.037 p-toluene sulfonic acid. In stage I: temperature 115 - 145⁰C, time 5 - 7 hours, toluene 175 ml. In the second stage, 1.45 moles of isodecanol are added at a temperature between 120⁰C - 165⁰C, time 5 - 7 hours [7].



Structure determination

IR spectra were obtained on a Jasco 430 FT-IR spectrophotometer (Figure 1). Samples were prepared in KBr pellets or in a film between two KBr panes. FT-IR reactions were monitored in thermostated cuvettes with 0.137 mm thick silica panes on a Jasco 430 FT-IR spectrophotometer with a resolution of 1 cm⁻¹.



Fig. 1. Spectrofotometer FT-IR Jasco 430

Results and discussion

In figures 2-4 the absorption spectra for the following compounds are presented: isodecyl adipate and 2-(p-nonyl-phenoxy)ethyl, isodecyl adipate and 2-(o-sec-butyl-phenoxy)ethyl and isodecyl adipate and 2-phenoxy ethyl. In this spectrum, the fundamental absorption bands, located in the spectral range from 3000 cm^{-1} to 829 cm^{-1} , are clearly evident.

Figure 2 shows the IR spectrum of isodecyl adipate and 2-(p-nonyl-phenoxy)ethyl.

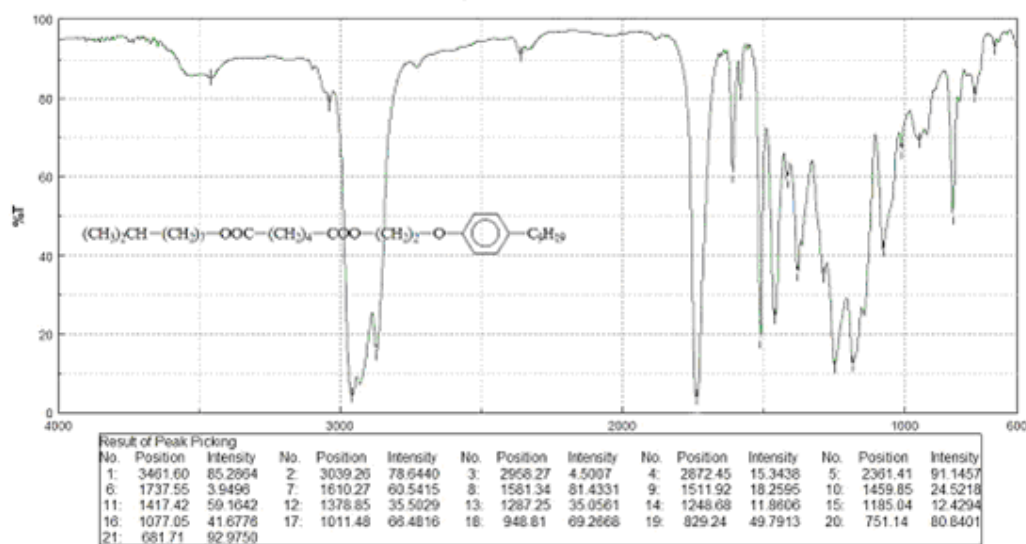


Fig.2. IR spectrum of isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl

As can be seen in the spectrum, 21 peaks appear for isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl. The most important ones are listed in Table 1.

In Table 1 we presented the assignment of peaks in the FTIR spectrum for isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl.

At the wavelength of 2958 cm^{-1} the CH_3 functional group corresponding to asymmetric aliphatic appears. At the wavelength of 2872 cm^{-1} the CH_3 functional group corresponding to asymmetric aromatic appears. At the wavelength of 1737 cm^{-1} the $\text{C}=\text{O}$ functional group corresponding to saturated esters appears. At the wavelength of 1511 cm^{-1} the $\text{C}-\text{H}$ functional group corresponding to stretch aromatic appears. At the wavelength of 1248 cm^{-1} the $\text{C}-\text{O}$ functional group corresponding to stretch aromatic appears. At the wavelength of 1185 cm^{-1} and 829 cm^{-1} the $\text{C}-\text{O}$ intensive functional group appears.

Table 1. Peak assignment in the FTIR spectrum of isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl

Wave number, cm ⁻¹	Functional grouping	Vibration mode
2958	CH ₃	Asymmetric aliphatic
2872	CH ₃	Asymmetric aromatic
1737	C=O	Saturated esters
1511	C-H	Stretch aromatic
1248	C-O	Stretch aromatic
1185	C-O	Intensive
829	C-O	Intensive

Figure 3 shows the IR spectrum of isodecyl adipate and 2-(o-sec-butyl-phenoxy)ethyl.

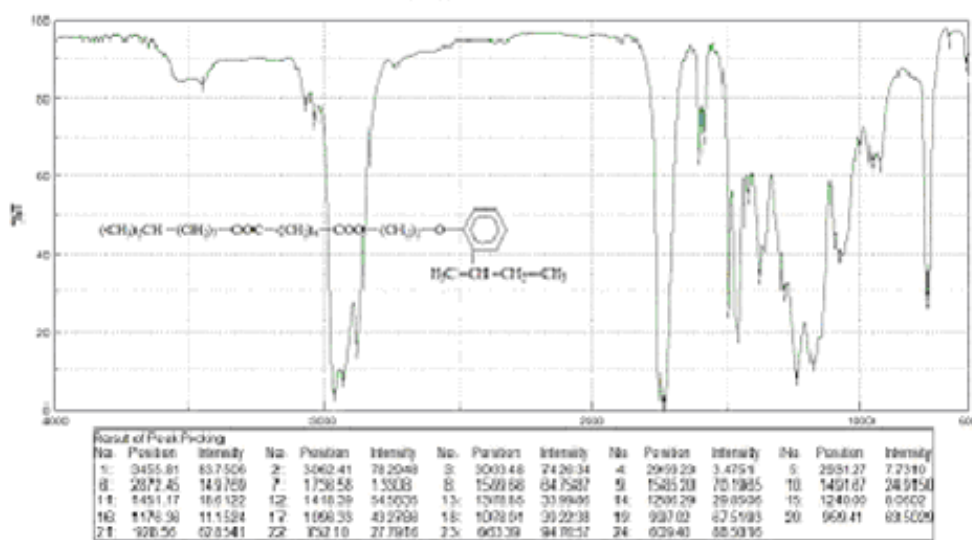


Fig.3. IR spectrum of isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl

In the spectrum of isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl several absorption bands appear and the most important ones are presented in table 2.

At the wavelength of 2959 cm⁻¹ the CH₃ functional group corresponding to asymmetric aliphatic appears. For the wavelength of 2931 cm⁻¹ the CH₃ functional group corresponding to asymmetric aromatic appears. At the wavelength of 1736 cm⁻¹ the C=O functional group corresponding to saturated esters appears. For the wavelength of 1451 cm⁻¹ the C-H functional group corresponding to stretch aromatic appears. For the wavelength of 1240 cm⁻¹ the C-O

functional group corresponding to intense symmetrical appears. For the wavelength of 1186 cm^{-1} and 752 cm^{-1} the C-O functional group intensive appears.

Table 2 shows the assignment of peaks in the FTIR spectrum for isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl.

Table 2. Peak assignment in the FTIR spectrum of isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl

Wave number, cm^{-1}	Functional grouping	Vibration mode
2959	CH_3	Asymmetric aliphatic
2931	CH_3	Asymmetric aromatic
1736	$\text{C}=\text{O}$	Saturated esters
1451	C-H	Stretch aromatic
1240	C-O	Intense symmetrical
1176	C-O	Intense
752	C-O	Intense

Figure 4 shows the IR spectrum of isodecyl adipate and 2-phenoxy ethyl.

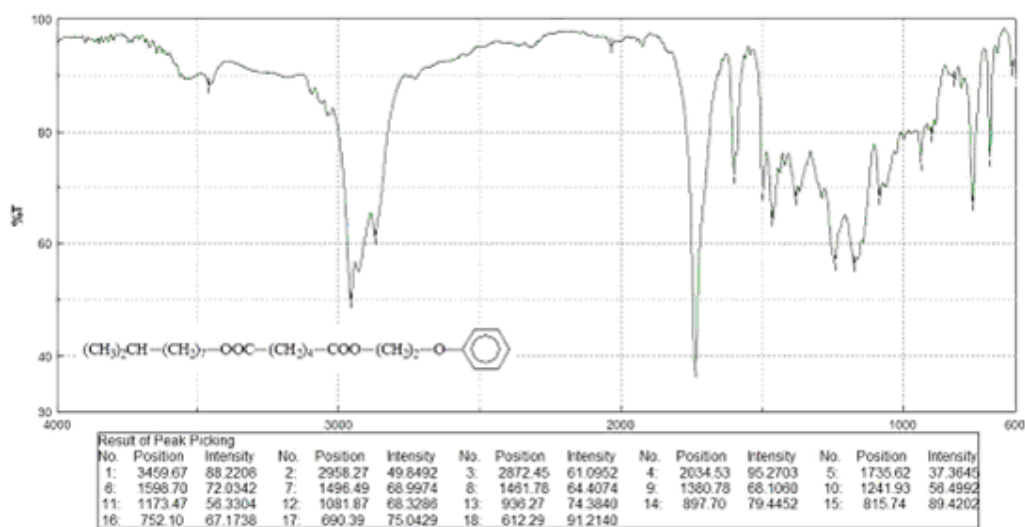


Fig.4. IR spectrum of isodecyl adipate and 2-phenoxy ethyl

The spectrum of isodecyl adipate and 2-phenoxy ethyl shows fewer absorption bands and the most important ones are presented in Table 3.

At the wavelength of 2958 cm^{-1} the CH_3 functional group corresponding to asymmetric aliphatic appears. For the wavelength of 2872 cm^{-1} the CH_3 functional group corresponding to asymmetric aromatic appears. At the wavelength of 1735 cm^{-1} the $\text{C}=\text{O}$ functional group corresponding to saturated esters appears. For the wavelength of 1241 cm^{-1} the $\text{C}-\text{O}$ functional group corresponding to intense symmetrical appears. For the wavelength of 1173 cm^{-1} and 752 cm^{-1} the $\text{C}-\text{O}$ functional group appears intensively.

Table 3. Peak assignment in the FTIR spectrum of isodecyl adipate and 2-phenoxy ethyl

Wave number, cm^{-1}	Functional grouping	Vibration mode
2958	CH_3	Asymmetric aliphatic
2872	CH_3	Asymmetric aromatic
1735	$\text{C}=\text{O}$	Saturated esters
1241	$\text{C}-\text{O}$	Intense symmetrical
1173	$\text{C}-\text{O}$	Intense
752	$\text{C}-\text{O}$	Intense

Conclusions

The absorption spectrum of the adipic esters isodecyl adipate and 2-(p-nonyl-phenoxy) ethyl, isodecyl adipate and 2-(o-sec-butyl-phenoxy) ethyl and isodecyl adipate and 2-phenoxy ethyl contain the following functional groups: CH_3 , $\text{C}=\text{O}$, $\text{C}-\text{O}$ and were determined with a Jasco 430 FT-IR spectrophotometer. Industrially, it is the most important dicarboxylic acid: approximately 2.5 billion kilograms of the white crystalline powder are produced annually, largely for use as a precursor in the production process of nylon (polyamide fiber).

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