All data taken at the Pacific Northwest National Laboratory
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Data Analysis: Tracy J. Baker

Composite spectrum for: Diethyl phthalate

- First Column: Position in wavenumber (cm^{-1})
- Second column: Real refractive index $n(\tilde{\upsilon})$ (dispersion index)
- Third column: Imaginary refractive index, $k(\tilde{\upsilon})$ (absorption index per unit length in centimeters)

Where the complex refractive index $\hat{n} = n(\tilde{\upsilon}) + ik(\tilde{\upsilon})$

Following Bertie (in the references below) we define the absorbance as $A = -\log_{10}(I/I_0)$ and the linear absorption coefficient K = A/d, where d is the path length. The connection between the imaginary refractive index and the absorbance coefficient arises from the following: $2.303K = 4\,\pi\,\tilde{\upsilon}\,k$

See the following references for a detailed description of terms and units:

1) Bertie, J. E., Zhang, S. L., Eysel, H. H., Baluja, S., & Ahmed, M. K. (1993). Infrared Intensities of Liquids XI: Infrared Refractive Indices from 8000 to 2 cm^{-1}, Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at 25°C. *Appl. Spec.,47*(8), 1100-1114 doi:10.1366/0003702934067973
2) Bertie, J. E., Zhang, S. L., & Keefe, C. D. (1995). Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy, 8*(2), 215-229. doi:10.1016/0924-2031(94)00038-i

Sample:

- Chemical name, formula and CAS number: Diethyl phthalate, $C_{12}H_{14}O_4$, [84-66-2]
- IUPAC name: Diethyl benzene-1,2-dicarboxylate
- Synonyms: Ethyl phthalate, phthalic acid diethyl ester
- Physical properties: FW = 222.24 g/mole; mp = -3 °C; bp = 298-299 °C; $\rho = 1.12$ g/cm^3
- Supplier and stated purity: Sigma-Aldrich, 99.5% (Lot # BCCJ6241)
- Temperature of sample: 24 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: MIR: 1.96, 2.95, 11.4, 14.6, 26.7, 49.8, 107, 208 and 478 micrometers (μm); NIR: 107, 209, 478, 925, 2073 and 4119 μm. Final data are a composite of these spectra.
- Sample cell window material: MIR = potassium bromide (KBr) except potassium chloride (KCl) for the 107 and 208 μm cells; NIR = KCl except KBr for the 478 and 925 μm cells.
- Preparation: None

NIR Instrument Parameters:

- Bruker IFS66V, purged with UHP nitrogen
- Spectral range: 12,000 to 3,000 cm^{-1} (0.83 to 3.33 microns)
- NIR source: Quartz tungsten bulb
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 5 mm
- Folding limits: 15798.0 to 0 cm^{-1}

MIR Instrument Parameters:

- Tensor II with sample stage rotated 6 degrees, purged with UHP nitrogen
- Spectral range: 7,800 to 400 cm^{-1} (1.282 to 25 microns)
- IR source: Silicon carbide glow bar
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DTGS at room temperature
- Aperture: 3 mm
- Folding limits: 11669.9 to 0 cm^{-1}

NIR/MIR Instrument Parameters:

- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz; 7.5 kHz (MIR)
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4822 cm^{-1}

a) b)

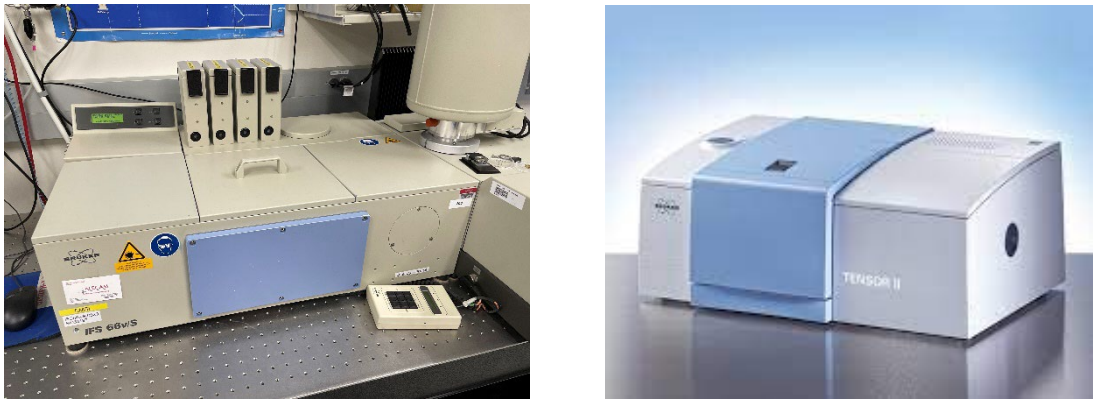

Figure 1: The Bruker IFS66V FTIR (a) and Tensor II (b).

Measured Refractive Index:

The refractive index for Diethyl phthalate was measured at 25 °C using an Atago model DR-M2/1550 Abbe refractometer. Notch filters were employed in front of a white light source to make measurements at multiple wavelengths. An infrared viewer from Atago was used to detect signal at 1550 nm. The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm: n = 1.511	486 nm: n = 1.5101	546 nm: n = 1.5037
589 nm: n = 1.4996	644 nm: n = 1.4963	656 nm: n = 1.4956
1550 nm: n = 1.4774		

The refractive index, n, vs. wavelength in microns, λ, was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data points in our experimental spectra. For Diethyl phthalate, the results were

n(7,800 cm^{-1}) = 1.4794 at 25 °C for MIR data and
n(12,000 cm^{-1}) = 1.4875 at 25 °C for NIR and merged data.

Post Processing and Related Parameters:
For the MIR, a composite spectrum was created from 9 absorbance spectra (base-10) taken at 9 path lengths: 1.96, 2.95, 11.4, 14.6, 26.7, 49.8, 107, 208 and 478 micrometers (μm). These data were collected with the sample stage rotated by -6° to minimize artifacts resulting from back-reflection into spectrometer (see Johnson et al., *Appl. Spectrosc.*, 76(5) 620-624, 2021). For the NIR, a composite spectrum was created from 6 absorbance spectra (base-10) taken at 6 path lengths: 107, 209, 478, 925, 2073 and 4119 μm. The same cells and liquid fills for the ~100, 200 and 500 μm path lengths were used for both spectral ranges. At each path length several spectra were measured and the results averaged for better signal to noise. The measured cell lengths were adjusted using Beer's law plots in which the NIR and MIR data were analyzed independently.

1) The imaginary part of the refractive index, or *k* vector, was determined for each absorbance file as per Bertie's program "RNJ46A" (see reference above). This takes into account the reflective losses due to the KBr and/or KCl windows.
2) A composite *k* vector is created via a classical, weighted, linear, least squares fit using the output files of program "RNJ46A": Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 2.5 are given zero weight. For the MIR, eleven composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 478 μm cell. This *k* vector determined the final values for the range from 7800 to 3100 cm^{-1}.
   b) The second *k* vector used the results from the 107 and 208 μm cells. This *k* vector determined the final values for the range from 3100 to 3020 cm^{-1}.
   c) The third *k* vector used the results from the 14.6 and 26.7 μm cells. This *k* vector determined the final values for the range from 3020 to 2975 cm^{-1}.
   d) The fourth *k* vector used the results from the 14.6 throguh 49.8 μm cells. This *k* vector determined the final values for the range from 2975 to 2850 cm^{-1}.
   e) The fifth *k* vector used the results from the 208 and 478 μm cells. This *k* vector determined the final values for the range from 2850 to 2400 cm^{-1} and 2225 to 1775 cm^{-1}.
   f) The sixth *k* vector used the results from the 107 μm cell. This *k* vector determined the final values for the range from 2400 to 2225 cm^{-1}.
   g) The seventh *k* vector used the results from the 49.8 through 208 μm cells. This *k* vector determined the final values for the range from 1775 to 1755 cm^{-1}.
   h) The eighth *k* vector used the results from the 1.96 and 2.95 μm cells. This *k* vector determined the final values for the range from 1755 to 1710 cm^{-1} and 1300 to 1240 cm^{-1}.
   i) The ninth *k* vector used the results from the 11.4 through 49.8 μm cells. This *k* vector determined the final values for the range from 1710 to 1370 cm^{-1}.
   j) The tenth *k* vector used the results from the 11.4 through 26.7 μm cells. This *k* vector determined the final values for the range from 1370 to 1300 cm^{-1}, 1240 to 1145 cm^{-1}, and 1065 to 400 cm^{-1}.
   k) The eleventh *k* vector used the results from the 11.4 and 14.6 μm cells. This *k* vector determined the final values for the range from 1145 to 1065 cm^{-1}.
3) A frequency correction was applied to the resulting composite MIR *k* vector.
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 0.99991 + 0.047] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
4) For the NIR, five composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 4119 μm cell. This *k* vector determined the final values for the range from 12,000 to 9000 cm^{-1}.
   b) The second *k* vector used the results from the 2073 and 4119 μm cells. This *k* vector determined the final values for the range from 9000 to 4470 cm^{-1}.
   c) The third *k* vector used the results from all the 107 through 478 μm cells. This *k* vector determined the final values for the range from 4470 to 3450 cm^{-1}.
   d) The fourth *k* vector used the results from all the 107 and 209 μm cells. This *k* vector determined the final values for the range from 3450 to 2800 cm^{-1}.
   e) The fifth *k* vector used the results from all the 478 and 925 μm cells. This *k* vector determined the final values for the range from 2800 to 400 cm^{-1}.

5) The resulting composite NIR *k* vector and the refractive index at 10,000 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 1 + 0.082] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
6) The MIR data were mapped onto the NIR x-axis using an interpolation routine, i.e. the Make Compatible command in OPUS 5.5. Then the composite MIR and NIR *k* vectors were merged to generate a final composite *k* vector across the entire spectral range. The NIR data were used exclusively above 3025 cm^{-1}, and only the MIR data were used below 3011 cm^{-1}. A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3025 and 3011 cm^{-1} was used in the overlapping spectral region. The resulting composite *k* vector and the refractive index at 12,000 cm^{-1} were used to create the final *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

Photograph of Sample Diethyl phthalate:

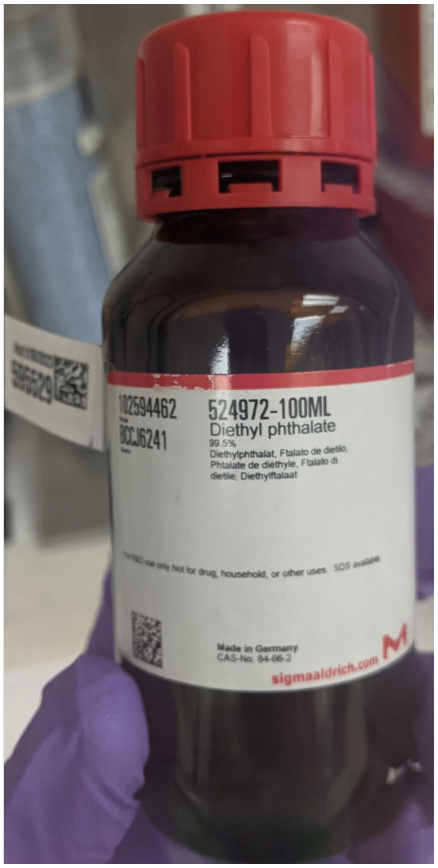

Figure 2: Diethyl phthalate in Sigma-Aldrich container for NIR and MIR measurements.