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Interim Report on Task 1.1.4

DIELECTRIC CONSTANT MEASUREMENTS ON
N-HEPTANE AND 2-HEPTANONE

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Contract 9-XG3-3453-J

January 5, 1994

DIELECTRIC CONSTANT MEASUREMENTS ON
N-HEPTANE AND 2-HEPTANONE

Norris S. Nahman

Abstract

A liquid transfer station has been built and installed in a fume hood. The dielectric properties of n-heptane and 2-heptanone have been measured using the coaxial structure of the Model 100-1, S/N 1 as the liquid measurement cell. The low (10 kHz to 1 Mhz) frequency value of the relative dielectric constant ϵ_r was measured with a HP 4275 Multifrequency LCR Meter. Also time domain reflection (TDR) and insertion time domain transmission (TDT) measurements were made using a HP 54120/54121A oscilloscope. The value of the quasi-static relative dielectric constant for n-heptane was found to be 1.923 while that for 2-heptanone was 11.735.

DIELECTRIC CONSTANT MEASUREMENTS ON
N-HEPTANE AND 2-HEPTANONE

1. Introduction.

The objective of the work reported in this interim report was twofold. The first was the construction of the liquid transfer station, and the second was the measurement of the dielectric constant parameters of n-heptane and 2-heptanone. In the final design of the waveshaping filter a dilute mixture of these two liquids will be used to form a Debye dielectric solution. n-heptane will be the solvent and 2-heptanone the solute. A Debye dielectric is one in which a small number of polar molecules (solute molecules) immersed in a sea of nonpolar molecules (solvent molecules) are free to rotate in response to an applied alternating electric field.

The dielectric parameters of these two liquids must be known for the modeling of the solution relative dielectric constant versus concentration, temperature, and frequency. In the earlier work of J. R. Andrews (NBS 1977-1981) only the relative dielectric constant of n-heptane was measured and had the value of 1.95 at 24.4 C. while that for 2-heptanone was not measured.

This report is divided into five chapters and two appendices in the following manner.

1. Introduction.
 2. The liquid transfer station.
 3. The Debye dielectric model.
 4. The dielectric parameter measurements.
 5. Conclusions and recommendations for completion of task 1.1.4.
- A1. Copies of the 1977 NBS laboratory notebook pages on liquid transfer methods.
 - A2. Data reduction for calculation of ϵ_r from capacitance measurements.

2. The liquid transfer station.

The liquid transfer station is of the same form as that built by NBS in 1977, Appendix A1, with a slight modification in that 1/8 inch stainless steel tubing has been used in place of the 1/8 inch copper interconnecting tubing used by NBS. The entire station was assembled inside of an enclosed exhaust fume hood in a vertical plane using the commercially available "Talon Lab Frame" products (rods, clamps, etc.). The fill and waste beakers were 100 cc volumetric flasks. A volumetric flask as a mixing/fill flask is necessary for establishing the molar concentration of the fill liquid.

The 1977 NBS system used filtered compressed air (2 psi) for pressurizing the fill system. In the present case dry nitrogen (2 psi) is used. The operational procedures for filling and emptying the coaxial measurement cell are the same as those used by NBS, Appendix A1.

Chemicals, flasks, and Talon Lab Frame components are available from the VWR Co., Denver CO (Tel. 303 371 0970 / 800 933 4959). The purity of the n-heptane is 99.5% (Omnisol, VWR Cat. No. EM HX0078-3), while that for 2-heptanone is 99% (VWR Cat. No. EK1138924).

The importance of the liquid transfer station and the procedures for filling and emptying the coaxial line can not be under emphasized. Keep in mind that many fillings and evacuations of a given liquid solution are required to flush out the coaxial line and achieve a pure state of the desired solution in the coaxial line.

3. The Debye Dielectric Model.

The Debye dielectric model is the simplest polar relaxation model in that it contains only one time constant. A relaxation model is one in which the real part of the complex dielectric constant $\epsilon(f, T, M)$ always decreases with increasing frequency, f . The Debye complex dielectric constant also depends upon the temperature T and the molar concentration of the molecular polar dipoles M , and is given by

$$\epsilon(f, T, M) := \epsilon(\infty, T, M) - \left[\frac{\epsilon(\infty, T, M) - \epsilon(0, T, M)}{1 + j2\pi f\tau(T, M)} \right] \quad , \quad (2.1)$$

where

$\epsilon(0, T, M)$ is the $f = 0$, DC dielectric constant.

$\epsilon(\infty, T, M)$ is the $f = \infty$, optical frequency dielectric constant.

$\tau(T, M)$ is the relaxation time of the polar molecules.

In the present case for the dilute mixtures of solute 2-heptanone in the solvent n-heptane the relaxation time τ is typically 3 to 4 ps. When a coaxial structure 30 cm long is filled with such a liquid solution, the insertion step response will be typically in the range of 25 to 300 ps depending upon the molar concentration of the solute molecules.

Though not shown explicitly in (2.1) the dielectric constant of the solution is dependent upon the dielectric constants of the solvent and the solute which are, in turn, functions of the temperature for both the solvent and the solute, and in addition a function of frequency for the solute. Consequently, the dielectric parameters of the individual liquids must be known in order to make an apriori prediction of the insertion step response of the liquid filled coaxial structure.

In the next chapter experimental results on the measurement of the dielectric constants of both n-heptane and 2-heptanone will be presented.

4. The dielectric parameter measurements.

4.1. Introduction.

The quasi-static dielectric constants were measured using capacitance and time domain reflectometry (TDR) measurements. In the capacitance technique the observable parameter is the total capacitance which is comprised of the residual capacitance of (1) the measurement system C_r , (2) the dielectric beads supporting the inner coaxial line conductor C_s , and (3) the coaxial line section or cell which holds the liquid dielectric solution C_c . See Appendix A2 for a drawing which defines the three capacitances. In the TDR technique the observable parameter is the reflection coefficient $\rho(x_1)$ at the selected point x_1 on the line which is physically and mathematically related to the characteristic impedance of the line at the selected point.

4.2. The empty coaxial line.

With the dimensions of the coaxial line and the electric permeability of free space being known the capacitance of the empty cell C_e (C_c being defined as C_e when the line is empty) and its empty characteristic impedance Z_{oe} can be calculated. The coaxial dimensions in inches are the OD of the inner conductor $a_i = 0.081$, the ID of the outer conductor $b_i = 0.276$ (which is the outer conductor of a 50 Ohm, 7 mm, precision coaxial line), and the length of the empty cell $x_i = 11.469$. Refer to appendix A2 for the calculations; the results are $C_e = 13.20$ pF and $Z_{oe} = 73.56$ Ohms. The TDR waveforms for ports F1 and F2 of the empty structure are shown in Figs. 4.2-1 and 4.2-2.

4.3. The coaxial line filled with pure n-heptane and then with pure 2-heptanone.

If the coaxial line is filled with a liquid and the same measurement setup is used, the only capacitance element which will change will be C_c which we then designate as C_f . The relative dielectric constant of the liquid is then given by the ratio C_f/C_e . Furthermore, a TDR measurement of the characteristic impedance of the filled cell Z_{of} also enables one to compute the relative dielectric constant of the liquid.

4.3. Continued.

For n-heptane a capacitance C_f of 25.30 pF would give the ratio 25.30/13.20, thus ϵ_r would equal 1.917. Also, if the TDR measurement gave a characteristic impedance of 53.1 Ohms, this in turn would give $\epsilon_r = 1.917$. A typical calculation for ϵ_r from capacitance measurements is given in Appendix 2 while that from TDR measurements is given at the end of Section 4.5.

4.4. Summary of dielectric constant measurements.

Because the coaxial cell was used to measure the dielectric constant of two different liquids, the cell had to be successively filled and emptied after the prior liquid had been evacuated in order to flush out the cell and establish a pure liquid state for measurement. Successive fillings and measurements were made until the measured value of the dielectric stabilized. Before starting the n-heptane measurements, numerous flushing operations were performed. The actual n-heptane measurements were performed with two fill cycles.

Time permitted only 4 fill cycles with 2-heptanone; note that for 2-heptanone ϵ_r is for the most part increasing with fill number. The process does not always increase ϵ_r because various nooks and crannies of the expansion bellows and piping release prior liquid in an unpredictable manner. Also, for a given fill the measured value can change with time as trapped prior liquid works its way into the coaxial cell and mixes with the liquid in the cell (by Brownian molecular motion). Note the changes between the Fill-4 and Fill-4A in the data for 2-heptanone. Listed below are the tabulated measurement data for the two liquids.

Liquid Fill No.	Meas. No.	Date	n-heptane ϵ_r Cap. Method	TDR Method
1	Cap-1	9/15/93	1.932	-
1	Cap-2/TDR-1	9/16/93	1.917	1.823 *
2	TDR-2	11/3/93	-	1.919

* TDR measurement with cold uncalibrated HP 54120/121A oscilloscope. All of the other capacitance and oscilloscope measurements were made after 24 hours of equipment warm-up. Equipment automatic calibration sequence was run just prior to making the measurements.

4.4. Continued.

Liquid Fill No.	Meas. No.	Date	2-heptanone ϵ_r Cap. Method	TDR Method
1	Cap-1	9/16/93	Trial	-
1	TDR-1	9/16/93	-	Trial
1	Cap-2	9/15/93	10.830	-
1	TDR-2	10/4/93	-	10.380
1	Cap-3	10/6/93	10.762	-
1	TDR-3	10/6/93	-	10.559
1	TDR-4	11/2/93	-	10.561
2	Cap-4	11/4/93	11.686	-
2	TDR-5	11/4/93	-	11.330
3	Cap-5	11/5/93	11.710	-
3	TDR-6	11/5/93	-	11.395
4*	TDR-7	11/5/93	-	11.454
4A**	Cap-6	11/30/93	11.735	-
4A**	TDR-8	11/30/93	-	11.416

* For this measurement the coaxial cell was nearly full of the liquid; but by tilting the coaxial line structure the liquid distribution was made uniform for the time window in use.

** Twenty five days later the filling was completed using the more of the same fill-lot held in the fill beaker attached to the filling station (thus being sealed within the filling system).

Figs. 4.4-1 and 4.4-2 are the TDR wave forms for Fill-2 n-Heptane TDR-2, and Fill-4A 2-heptanone TDR-8. Also, for Fill-4A 2-Heptanone the insertion time domain transmission waveform is shown in Fig. 4.4-3.

4.5. Discussion of the difference between the value of ϵ_r as determined by the capacity method and the TDR method for 2-heptanone.

Inspection of the ϵ_r data for 2-heptanone gives the following data.

Fill	Meas.	ϵ_r	$\delta\epsilon_r$
1	Cap-2	10.830	
1	TDR-2	10.380	-0.450
1	Cap-3	10.762	
1	TDR-3	10.559	-0.203
2	Cap-4	11.686	
2	TDR-5	11.380	-0.306
3	Cap-5	11.710	
3	TDR-6	11.395	-0.315
4A	Cap-6	11.735	
4A	TDR-8	11.416	-0.319

Notice that the TDR values are always less than those from the capacitance measurements. The impedance level at a given point on the TDR curve is always greater than the impedance level corresponding to the DC value of the dielectric constant. This is because the point of the curve where time is approaching infinity corresponds to the characteristic impedance for frequency approaching zero. The presence of frequency dependent dielectric losses increases the effect.

Consider a 50 Ohm TDR system calibrated with a 49.984 termination that has a corrected impedance level of 21.7702 Ohms which would correspond to a dielectric constant ϵ_r of 11.416. If the impedance level due to the time dependence of the TDR response is 1.3% higher than the final value (i.e., that at infinite time), the resultant ϵ_r will be low by approximately 0.3 as shown below.

4.5. Continued.

$$RL1 := 50$$

$$RL2 := 49.984$$

$$\text{Observed TDR reflection coefficient: } \rho := -39.32 \cdot 10^{-2}$$

$$Zoc := \frac{1 + \rho}{1 - \rho} \cdot RL2 \quad Zoc = 21.770235$$

$$\S Zoc := 1.3 \cdot 10^{-2}$$

$$Zoc1 := Zoc \cdot (1 + \S Zoc)$$

$$\epsilon_r := \left[\frac{60}{Zoc} \cdot \ln \left[\frac{0.276}{0.081} \right] \right]^2 \quad \epsilon_{r1} := \left[\frac{60}{Zoc1} \cdot \ln \left[\frac{0.276}{0.081} \right] \right]^2$$

$$\epsilon_r = 11.416238$$

$$\epsilon_{r1} = 11.125105$$

$$\S \epsilon_r := \epsilon_r - \epsilon_{r1}$$

$$\S \epsilon_r = 0.291133$$

The effect will decrease for large enough TDR time windows or fast enough transient processes. However, time windows are dependent upon our ability to terminate the sample cell in its characteristic impedance which is not a simple resistor or a lumped network due to distributed losses in the metal walls and in the dielectric sample.

5. Conclusions and recommendations for the completion of Task 1.1.4.

5.1. Conclusions.

The measured value of the static relative dielectric constant for n-heptane was found to be 1.923 (the average value of Cap-1, Cap-2, TDR-2). This is in agreement with the published value of 1.924 (American Institute of Physics Handbook, McGraw Hill, 1957, p. 5-139.).

An estimated value for the static relative dielectric constant for 2-heptanone given by the measurement Cap-6 is 11.735. In the handbook cited previously for n-heptane the static ϵ_r for 4-heptanone is given as 12.5. Both 2 and 4-heptanone have the same molecular weight but their structures are different. Both of them contain the following number of atoms: 7 carbon, 14 hydrogen, and one oxygen. From the Handbook of Physics and Chemistry their formulae are

2-heptanone	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$
4-heptanone	$\text{C}_3\text{H}_7\text{COC}_3\text{H}_7$

Their different structures will have different dipole moments which will make ϵ_r different, but not too different. Consequently, the value 11.735 is probably a very reasonable estimate of the exact value for (the purity of) this sample.

5.2. Recommendations for the completion of task 1.1.4.

The next phase should consist of the following work:

- (1). Measure the temperature dependence of the static dielectric constant for 2-heptanone.
- (2). Experimentally determine the solution concentrations and their quasi-static dielectric constants which will provide insertion step responses in the range 15 to 200 ps.
- (3). Provide the Debye model for the solutions in (2) above.
- (4). After P14 selects the solution that has the desired insertion transmission step response (namely, transition duration), complete the construction of the coaxial filter making the quasi-static characteristic impedance equal to 50 Ohms.

FL, Input TDR Model 100-1, SINL
17.1800 ns Normalized, 30ps Filter

Empty Cell. *CV Ref*

18.4300 ns

LANL 9/15/93

19.6800 ns

Timebase = 250 ps/div
Memory 1 = 10.00 mVolts/div
Timebase = 250 ps/div
Start = 17.4350 ns
Cursor on Memory 1
-50.4 ps from ref. plane

Stop = 25.3578 ns
Impedance = 49.7 Ohms
Distance = -6.923 mmeters

Delay = 17.1800 ns
Offset = 201.0 mVolts
Delay = 17.1800 ns
Delta T = 7.9228 ns
Rho = -223.5 m%
Ref Plane = 17.4854 ns

	Time, ps.	Rho	Z, ohms
① Ref. Plane	0.4	558.8 m%	50.5
② SMA/AP7	79.6	-878.1 m%	49.1
③ APC7/RPG APC7	254.6	-8,318 %	42.3
④ RPG Coax Line	949.6 ps	19.35 %	73.9

Fig. 4.2-1

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LANL 11/15/93 1084

F2, output TDR Model 100-L, S/n L Empty Cell

17.1800 ns Normalized, 30ps Filter

18.4300 ns

LANL c/det, 9/15/93

19.6800 ns

Timebase = 250 ps/div
 Memory 1 = 10.00 mVolts/div
 Timebase = 250 ps/div
 Start = 17.4350 ns
 Cursor on Memory 1
 -80.4 ps from ref. plane

Stop = 25.3578 ns
 Impedance = 50.0 Ohms
 Distance = -11.04 mmeters

Delay = 17.1800 ns
 Offset = 209.2 mVolts
 Delay = 17.1800 ns
 Delta T = 7.9228 ns
 Rho = 0.000 %
 Ref Plane = 17.4854 ns

	Time, ps	Rho	Z, Ohms
(1) Ref. Plane	0.4	351.2 m%	50.3
(2) SMA/APC 7	79.6	-494.9 m%	49.5
(3) APC7/RPG APC7	234.6	-3.37 %	46.7
(4) " "	299.6	22.25 %	78.6
(5) RPG Coax Line	944.6	19.49 %	74.2

Fig. 4.2-2

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LANL 9/15/93 Page 3
 c/det

TDR F1 Input, Normalized 60ps filter, Heptane filled cell.

24.3850 ns

25.6350 ns

26.8850 ns

Ch. 1 = 10.00 mVolts/div
Timebase = 250 ps/div
Memory 1 = 10.00 mVolts/div
Timebase = 250 ps/div

Offset = 175.7 mVolts
Delay = 24.3850 ns
Offset = 175.7 mVolts
Delay = 24.3850 ns
Rho = 17.97 m%
Ref Plane = 24.6854 ns

① Cursor on Memory 1 Impedance = 50.0 Ohms
-85.4 ps from ref. plane Distance = -8.272 mmeters

① 50 ohm level

{HP APC 7 Ref. 50 Ω Load, Model HP909C, S/N 2638A-00716}
DC: 49.984 ohms

Time, ps	Rho	Z ₀ , ohms
-85.4	17.97 x 10 ⁻³ %	50
② 29.6	-6.562 %	43.8
③ 949.6	3.074 %	53.1

$$\epsilon_r = \left[\frac{n_0}{2\pi Z_0} \ln\left(\frac{r_0}{r_i}\right) \right]^2$$

$$= \left[\frac{3.97}{2\pi(53.1)} \ln\left(\frac{0.276}{0.081}\right) \right]^2$$

$$\epsilon_r = 1.9192$$

n-Heptane TDR-2
LHNL v2.0 11/3/93
F11-2

Fig. 4.4-1

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Fig. 4.4-2

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24.0900 ns

26.5900 ns

60ps Normalization

29.0900 ns

Ch. 1 = 10.00 mVolts/div
 Timebase = 500 ps/div
 Memory 1 = 10.00 mVolts/div
 Timebase = 500 ps/div
 Cursor on Memory 1
 3.1910 ns from ref. plane

Impedance = 21.7 Ohms
 Distance = 309.1 mmeters

Offset = 150.5 mVolts
 Delay = 26.5900 ns
 Offset = 150.5 mVolts
 Delay = 26.5900 ns
 Rho = -39.32 %
 Ref Plane = 24.6490 ns

LAUL 11/30/73
 2-Heptanone
 TOR-8
 F.I. # 44

Fig. 4.4-3

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wdd

New Filling Tech.

all 1/8" copper tubing Swagelok fittings

Filling Tech.

1. Close valves 1 & 2, open valves 3 & 4
turn on vacuum pump & remove any fluids
that may be trapped in xfer std. move
xfer std. around to facilitate removal.
2. When xfer std. is empty close valve 4.
3. Open valve #2 slightly & allow 50ml
of clean fluid to run into the waste
beaker.
4. Close valve #2 & open valve #4
& allow wait several mins. to evacuate line.
5. Disconnect air line & open valve #1
to set std. air pressure in main beaker.
6. Close valve 3, then open valve #2
& observe on TDR the filling of the line.
7. Close valve #1 & reconnect air hose.
8. With special tool unscrew slightly
the center conductor on output connector
to provide a leak.
9. Open valve #1 slightly to get a flow
out the loosened center conductor. Continue
this flow until all air bubbles are
eliminated as seen on the TDR.

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10. Close valve # 1
11. Retighten (gently) the center conductor.
12. Close valve # 4.
13. ~~Disconnect~~ Close valve # 2
14. Disconnect fill line from
Xfer 5+d.

This is a data reduction program which calculates the relative dielectric constant ϵ_r of a coaxial dielectric sample in a coaxial cell from measured values of the following capacitances: (1) the measurement system residual capacitance, C_r , (2) the calculated capacitance of the empty cell, C_e , (3) the total measured capacitance of the empty cell and the cell end supports C_s , $C_{te} = C_e + C_s + C_r$, and (4) the total measured capacitance of the filled cell, C_f , and the end supports, $C_{tf} = C_f + C_s + C_r$, Fig. A2-1.

1. Measured Empty Capacitances.

Empty Measurement System Capacitance: $C_{re} := 37.5 \cdot 10^{-12}$

Empty Cell Total Capacitance: $C_{te} := 52.4 \cdot 10^{-12}$

2. Measured Full Capacitances.

(Note: The full measurement system capacitance C_{rf} can be different from the above empty measurement system capacitance C_{re} if the measurement system must be changed to make the full measurements.)

Full Measurement System Capacitance: $C_{rf} := 34.1 \cdot 10^{-12}$

Full Cell Total Capacitance: $C_{tf} := 61.1 \cdot 10^{-12}$

3. Computed capacitance of the empty cell, C_e .

Note: MCAD Precision set to 7 places.

$$\epsilon_o := \frac{10^{-9}}{36 \cdot \pi} \quad \epsilon_o = 8.8419413 \cdot 10^{-12}$$

$a_i := 0.081$, in. $b_i := 0.276$, in. $x_i := 11.469$, in.

$a := 25.4 \cdot 10^{-3} \cdot a_i$ $b := 25.4 \cdot 10^{-3} \cdot b_i$ $x := 25.4 \cdot 10^{-3} \cdot x_i$

$a = 0.0020574$, m. $b = 0.0070104$, m. $x = 0.2913126$, m.

$\frac{b}{a} = 3.4074074$

File: MCAD EPSMEA01.NSN 8/23/93.

$$C_e := 2 \cdot \pi \cdot x \cdot \frac{\epsilon_0}{\ln \left[\frac{b}{a} \right]} \quad C_e = 1.32012 \cdot 10^{-11} \text{ F.}$$

4. Deduced Capacitances.

$$C_s := C_{te} - C_{re} - C_e \quad C_s = 1.6988003 \cdot 10^{-12}$$

$$C_f := C_{tf} - C_s - C_{rf}$$

$$C_f = 2.53012 \cdot 10^{-11}$$

5. Deduced Relative Dielectric Constant of the Sample.

$$\epsilon_r := \frac{C_f}{C_e} \quad \epsilon_r = 1.9165834$$

APPENDIX-A2

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* Cable to HP 4275 LCR Meter

$F_1 + F_2$ are modified APC 7's.

$$C_r = C_{r1} + C_{r2}$$

$$C_s = C_{s1} + C_{s2}$$

Connector, Cable, Cell and Cell Support Capacitances.

Fig. A2-1.

APPENDIX-A2

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