Electrically Induced Motion in Room Temperature Ionic Liquids

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Abstract

Room temperature ionic liquids (RTILs) are ideal solvents for transporting large biomolecules, for analysis using time-of-flight secondary ion mass spectroscopy (TOF-SIMS), because of their high stability and negligible vapor pressure. However, in order for TOF-SIMS to be successful in differentiating large biomolecules, the biomolecules need to be concentrated at the surface of the RTIL. This experiment investigated the electrically induced transport processes present in solutions of the RTIL $[C_8H_{15}N_2][PF_6]$ ($[BMIM][PF_6]$) and the pH indicator dyes bromophenol blue and crystal violet. Moving the dyes first through a solution using water as a solvent and then through one using RTIL as a solvent gave insight into how the charge of the dye affected its movement and how RTIL affected movement. It is shown that although dye always appears to move towards the positive electrode in a $[BMIM][PF_6]$ solution, crystal violet dye is actually modified at the electrodes and diffuses throughout the solution.

1 Introduction

The analysis of large biomarker proteins is an important process in the diagnosis of many diseases. Time-of-flight mass spectrometry offers a method for the sensitive detection of these larger biomolecules through the promising new process of serum proteomic profiling. Improving the process of TOF-SIMS would thus be an important milestone in the field of disease profiling [1].

TOF-SIMS analyzes molecules at the surface of a sample, so in order for it to be effective as a mass analyzer the molecules in a sample need to be brought from throughout the sample to a specific spot on the surface of the sample. Room temperature ionic liquids (RTILs) would be very effective as a matrix for transporting molecules for TOF-SIMS because they allow molecules to be transported thorugh them in order to concentrate the test molecules at a specific location on the surface of the RTIL and also because they are very stable and have negligible vapor pressure. Having negligible vapor pressure removes the risk of vaporized molecules interacting with test molecules once they have been ejected from the surface by an ion beam in the TOF-SIMS apparatus and thus allows for more accurate measurements of the molecules' masses [2][3].

In order for RTILs to be effective matrices for TOF-SIMS an understanding of the transport mechanisms at work in the RTILs is necessary. Electrical transport using an applied electric field seems to be an effective mode of transporting molecules in RTIL with the main mechanisms for describing this motion being electrophoresis and electroosmosis. Understanding how molecules move through RTIL requires that the motion of both the test molecules and RTIL ions be understood, as well any possible interactions between these molecules in solution. The goal of this research is to investigate how an RTIL-dye solution behaves under the influence of an electric field in order to gain a greater understanding of the transport properties of RTIL solutions.

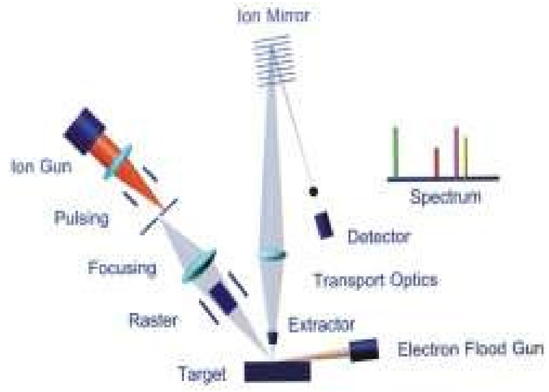
2 Theory

2.1 TOF-SIMS

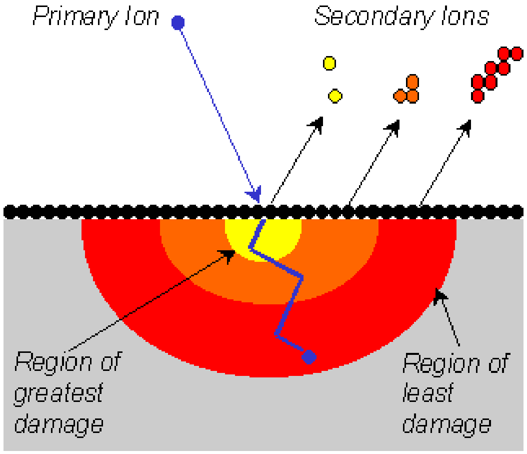
TOF-SIMS is a mass spectroscopy technique which separates molecules by comparing the speeds through which they travel through a drift chamber. As seen in figure 1b this technique uses a primary ion beam to bombard the surface of a sample and cause it to emit secondary ions from its surface. These secondary ions are then accelerated into a drift region by giving all of the ions the same kinetic energy after exposing them to an electric field with energy qV. By the energy relation

$$qV = \tfrac{1}{2}mv^2 \tag{1}$$

it can be seen that the more massive a molecule is, the more slowly it will move through the drift chamber. Thus, the time that it takes for the emitted ions to travel through the drift region to a detector can be used in order to determine the mass of the molecules [3]. It is very important that the drift region be kept at vacuum because any particles in the drift region could interact with the ions emitted from the sample and thus affect the travel time of the ions, destroying the measurement of their mass. Thus, in choosing a solvent, or matrix, in which the molecules being detected by TOF-SIMS reside it is important to choose one that can bring molecules to its surface and does not outgas into the drift chamber. This can be a difficult task because liquids usually vaporize in vacuum, and transporting ions so that they concentrate at a specific spot on the surface of the matrix can be difficult in solids.



(a)



(b)

Figure 1

Figure 2

Figure 1: (a) an example of a TOF-SIMS apparatus (b) Diagram of the surface of a sample being analyzed by a TOF-SIMS apparatus

2.2 Room Temperature Ionic Liquids

Room temperature ionic liquids (RTILs) are a class of ionic solvents which exist in the liquid phase at room temperature. RTILs can be composed of many combinations of ionic molecules, and can thus be customized to exhibit certain specific characteristics [4]. Importantly for their role in TOF-SIMS, many RTILs have negligible vapor pressures and are highly stable, thus providing a perfect matrix for TOF-SIMS since they are liquids that do not outgas.

2.2.1 [BMIM][PF_6]

The RTIL [BMIM][PF_6] or 1-butyl-3-methylimidazolium hexafluorophosphate is made up of a positive $[C_8H_{15}N_2]^+$ ion associated with a negative $[PF_6]^-$ ion. The $[BMIM]^+$ ion consists of a single butyl chain connected to the nitrogen at position one of an imidazole ring with a CH_3 connected to the nitrogen at position three (see figure 2a). The charge on this ion may be found on the ring [5]. Although this ion is rather large, it is planar. The $[PF_6]^-$ ion on the other hand is octahedral and thus it has a relatively larger overall volume with its charge evenly distributed around this volume [6].

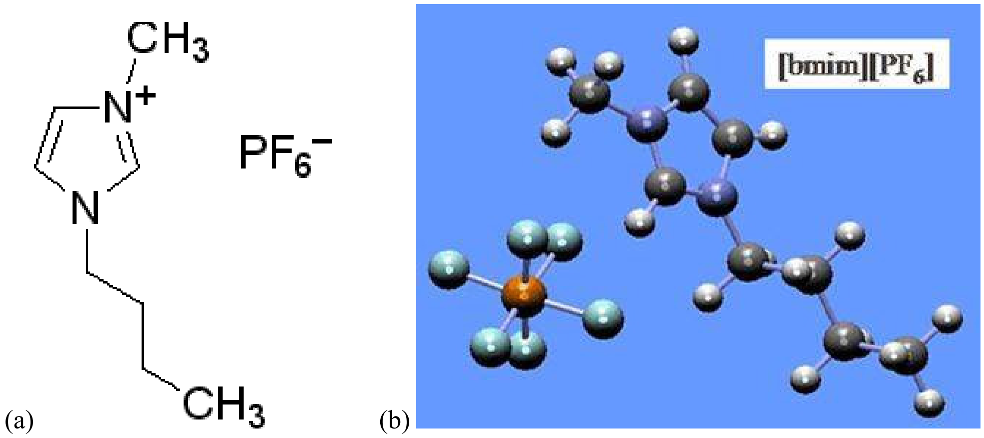


Figure 2: (a) Chemical makeup of [BMIM][PF_6] (b) Ball and stick diagram of [BMIM][PF_6]

2.3 Transport

When an electric field is placed across a solution, molecules tend to be transported by one of two methods, electrophoresis or electroosmosis.

2.3.1 Electrophoresis

Electrophoresis refers to the movement of ions of the solute through a stationary solvent. This occurs when a charged solute moves through a neutral solvent in the presence of an applied electric field. Usually, the solvent is rigid, as in gel electrophoresis, in order to prevent the solvent itself from moving. The movement of the charged solute molecule arises from the Lorentz force by the equation:

$$\mathbf{F_L} = q\mathbf{E} \tag{2}$$

and a frictional force:

$$\mathbf{F_F} = -6\pi\eta r\mathbf{v} \tag{3}$$

where η is the viscosity of the solution, r is the radius of the solute particle, and **v** is the electrophoretic velocity of the solute molecule. Equating the forces in equations 2 and 3, it can be seen that the velocity of the charged solute molecule is proportional to its charge and the electric field, with the constant of proportionality, known as the electrophoretic mobility, described by [7]:

$$\mu_e = |\mathbf{v}|/|\mathbf{E}| = q / (6\pi\eta r) \tag{4}$$

The charged molecules move in the direction the charge they carry would move in an electric field.

2.3.2 Electroosmosis

As opposed to electrophoresis where a molecule moves according to the effect of the electric field on its charge, in electroosmosis the transport of charged solute molecules occurs as a result of being dragged by solvent molecules moving as a result of the applied electric field. In the literature electroosmosis is generally described as an electroosmotic flow being cancelled by an electrophoretic flow at the walls of a capillary [8]. In the case of an RTIL solution, a better understanding of electroosmotic motion would be to describe the test molecules as being dragged through the solution by charged RTIL molecules moving electrophoretically, a process known as ion pairing. Ion pairing can be thought of as creating a single charged molecule consisting of multiple, possibly oppositely charged molecules whose electrostatic attractions between each other cause temporary bonding between them.

2.4 Chemical Dyes

The transport properties of an RTIL solvent may be easily investigated using, charged indicator dyes as solutes because the motion of these molecules may be investigated visually as well as through the application of absorption measurements. The charged indicator dyes bromophenol blue and crystal violet are good solute candidates for an RTIL-dye solution because their colors remain the same over large pH ranges and also because they are charged molecules.

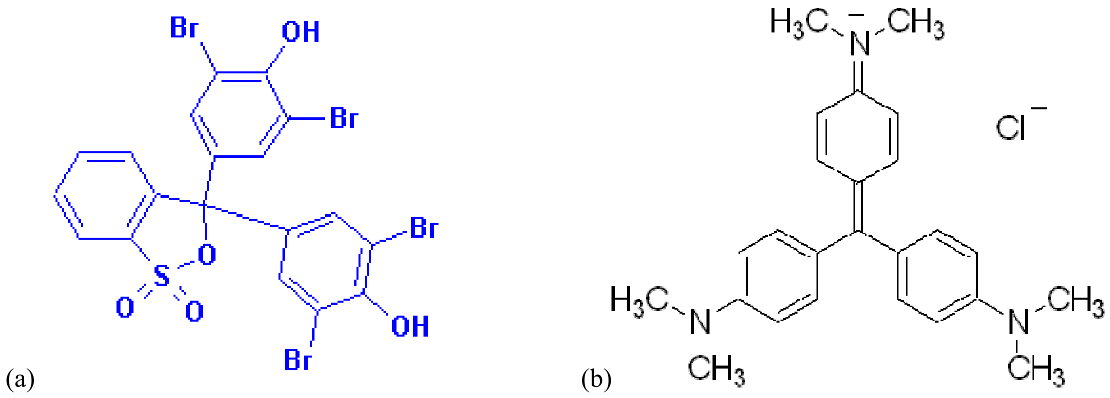


Figure 3: (a) Chemical form of bromophenol blue (b) Chemical from of crystal violet

2.4.1 Bromophenol Blue

Bromophenol blue, or tetrabromophenolsulfonephthalein ($C_{19}H_{10}Br_4O_5S$), is a pH indicator dye which appears blue at pH values above 4.6 and changes to yellow in solutions at pH values below 3.0. This color change occurs as a result of electron confinement, where the addition of a hydrogen ion in a more acidic solution causes the causes more blue light to be absorbed and the molecule to appear yellow [9][10]. Bromophenol blue is a good candidate for use as a solute in an RTIL-dye solution because, in addition to its bright color in solution, it also has a net negative charge which can be found on the SO_3 group seen in figure 3a. This negative charge allows the dye to be influenced by an applied electric field and thus to display electrically induced transport properties, moving towards a positive charge.

2.4.2 Crystal Violet

Crystal violet, or methyl violet 10B ($C_{25}H_{30}N_3Cl$), is another good candidate for use as a solute in an RTIL-dye solution. Crystal violet appears deep purple at pH values above 2.0 and changes to yellow in solutions at pH values below 0.1 as a result of a similar form of electron confinement, so it is also easy to see in solution. Contrary to bromophenol blue, crystal violet has a net positive charge which comes from its doubly-bonded nitrogen (see figure 3b). In the presence of an electric field crystal violet would be expected to display opposite electrically induced transport properties to those of bromophenol blue dye and migrate towards a negative charge.

2.5 Chemical Modification of Dye

The apparent movement of color in RTIL-dye solutions exposed to an electric field does not necessarily imply that the dye molecules themselves are moving. The colors reflected by pH indicator dyes depend on the structure of the dyes and thus may change over specific pH ranges as well as a result of chemical modification of the dyes. It can thus be difficult to determine whether these dyes are moving under the influence of an electric field or whether they are in fact being chemically modified to produce color changes. One method for determining which process is occurring would be to look at the amount of light absorption at various points in the RTIL-dye solution. The intensity of light passing through a solution varies according to a form of Beer's Law [11]:

$$I(x) = I_0 e^{-\alpha x} \quad (5)$$

where I_0 is the intensity of the light before passing through the material, x is the depth of the material, and α is the absorption coefficient of the material, equal to:

$$\alpha = n\sigma \tag{6}$$

where n is the number density of the material in solution and σ represents the materials' absorption cross-section. The amount of absorption can be found by modifying this relation to give:

$$\alpha x = n\sigma x = -\ln(I(x) / I_0) \tag{7}$$

If the dye were not being moved, but simply being modified to create the clear region, it would be expected that the amount of light absorption would remain the same in the vicinity of the positive electrode because the dye in this region would remain unchanged, while the dye near the negative electrode would be modified. Also, in this situation, the amount of total dye would be decreased, so the amount of absorption over the entire volume of the solution would decrease compared to the total absorption of the original RTIL-dye solution. Conversely, if the dye were in fact being moved from the negative electrode to the positive electrode it would be expected that the amount of light absorption would increase from the negative electrode to the positive electrode, with the amount of absorption at the positive electrode being greater than in the original RTIL-dye solution that existed before the application of the electric field because of the increased density of dye in this area. Taking into account the total amount of absorption throughout the entire solution, which can be obtained by integrating the absorption measurements obtained throughout the area of the solution perpendicular to the laser beam,

$$\int(\alpha x)dy = \sum(-\ln(I(x)/I_0)) \tag{8}$$

the case for moving dye would conserve the amount of dye and thus absorption in the solution.

3 Transport

In order to investigate the transport properties in an RTIL-dye solution exposed to an electric field, a circuit was created with two copper electrodes connected across a 1.5cm diameter drop of the solution being tested on a microscope slide. This created a voltage difference and thus a current across the solution. Measuring the voltage across a resistor in series with the solution and applying Ohm's Law allowed this current to be determined. The movement of color in the solution gave insight into the possible forms of movement of the dye molecules in the solution.

3.1 Transport of Dye in Water

A solution consisting of indicator dye mixed with de-ionized water at a concentration of .0.5mg dye to 1mL de-ionized water was tested in order to investigate how the movement of the indicator dye was affected by its net charge. The de-ionized water had no net charge ensuring that the movement of the dye was a result of only the charge on the solute molecules and not any charge effects of the solvent. Solutions were prepared using the indicator dyes bromophenol blue, which had a net negative charge, and crystal violet, which had a net positive charge.

3.2 Transport of Dye in [BMIM][PF_6]

In order to investigate the transport properties of the RTIL [BMIM][PF_6], the process of the previous section was repeated using [BMIM][PF_6] as a solvent, replacing water, along with the same indicator dyes, bromophenol blue and crystal violet as solute ions in the same .5mg dye to 1mL RTIL solution. Any variation from the results of the de-ionized water-dye tests would be as a result of the effects of the charged $[BMIM]^+$ and $[PF_6]^-$ ions.

3.3 Results

The de-ionized water-dye solutions appeared to behave primarily electrophoretically with the dyes moving in the directions expected by the applied electric field, bromophenol blue towards the positive electrode and crystal violet towards the negative electrode. With an applied voltage of 4V this migration took about a half an hour to complete, i.e. for the dye to migrate from being distributed uniformly throughout the solution to being concentrated around the proper electrode.

Unexpected results arose in the $[BMIM][PF_6]$-dye solution tests with the color migrating towards the positive electrode in all cases regardless of the charge on the dye. The bromophenol blue ions moved towards the positive electrode, as expected based on their net charge. However, the positively charged crystal violet ions also seemed to migrate towards the positive electrode in a direction opposite that expected if the RTIL were a neutral solvent. This different behavior suggests that if it was in fact transport of the dye occurring in the presence of the electric field, it would be the ions of the RTIL dictating the movement of the crystal violet ions rather than crystal violet's intrinsic electric charge.

Another odd property of the indicator dyes' apparent motion in the RTIL is that rather than simply moving completely from the direction of the negative electrode towards the positive electrode, the dyes tended to follow odd flow patterns and changed color to yellow in the vicinity of the positive electrode. This suggests that there is possibly chemistry going on in the solution in addition to transport both at the electrodes as well as between the dye and the ions of the RTIL. It is more likely however, that the pH of the solution is getting driven lower near the positive electrode than throughout the rest of the solution, and causing the indicator dye to change from its purple or blue state to its yellow state. This is the believed process because when an electric field is applied to pure RTIL it picks up a very slight white cloudy color on a small portion of its area, but for the most part it remains perfectly clear. Nowhere does any yellow appear.

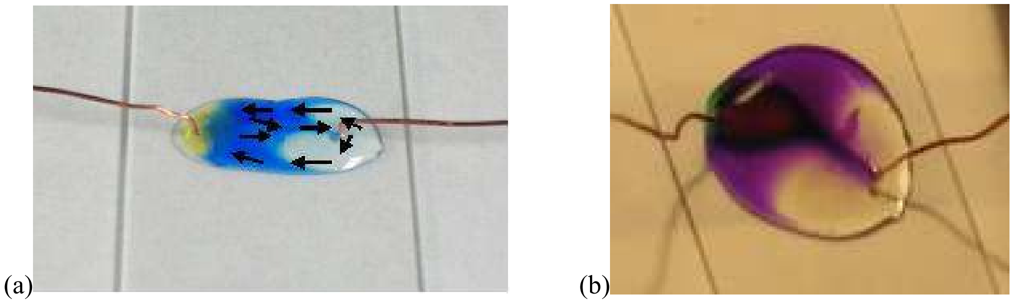


Figure 4: (a) Movement of bromophenol blue dye in a solution of [BMIM][PF_6]. The positive electrode is on the left and the negative electrode is on the right. (b) Movement of crystal violet dye in a solution of [BMIM][PF_6]. The electrodes are arranged in the same positions as in figure 4a.

3.2.1 Electroosmosis vs. Electrophoresis

The big question involving transport was whether the movement of the dye was dominated by electrophoresis or electroosmosis. In the various tests it seemed that the rate and direction of migration of the dye through the solution was relatively unaffected by the type of dye being used. This presents strong evidence supporting the hypothesis that electroosmosis is dominating the transport process because it suggests that the ions of the RTIL are moving in the field and are dragging the dye ions along with it. The direction of the dye migration agrees with this hypothesis because the dye moves in the direction of the more bulky, slower-moving, $[PF_6]^-$ ion where the charge is evenly distributed over its surface rather than the planar $[BMIM]^+$ ion which is able to move more easily through the solution and has its charge confined to a ring closer to the interior of the ion. These properties suggest that the dye ions will be more readily associated with the $[PF_6]^-$ ions, which are the ones moving towards the positive electrode.

3.2.2 Conductivity

The conductivity of $[BMIM][PF_6]$ is another factor that affects the rate at which the dye molecules move through the solution. The conductivity was found using the equations:

$$\mathbf{J} = n q \mathbf{v} = \rho \mathbf{v} = \sigma \mathbf{E} \tag{9}$$

$$\mathbf{F} = q\mathbf{E} = \eta r v \tag{10}$$

$$n = N / (M/A) = 2.90 \times 10^{27}/m^3 \tag{11}$$

to solve for the conductivity, which can be shown to equal.

$$\sigma = (nq^2) / (\eta r) \tag{12}$$

The conductivity of $[BMIM][PF_6]$ is found to be 0.079S/m in comparison with the known value for the conductivity of $[BMIM][PF_6]$ of 0.14S/m. This gives a decent approximation as it is within an order of magnitude of the expected value, with the error most likely occurring as a result of the estimation of the molecular radius of the RTIL [5].

4 Absorption

The setup for the absorption measurement used the same transport setup as for the water-dye and RTIL-dye transport tests, with the only differences being that a 1,000Ω resistor was used, the RTIL-dye solution was made less concentrated in order to allow more light to pass through the solution, and the RTIL-dye solution was placed in a trough made by cutting a cuvette in half along the long axis and sticking the lid on the open end. Crystal violet dye was used for the absorption measurements because it was the dye that moved contrary to expectation based on its charge and also because its color stayed constant over a larger pH range than bromophenol blue's color did. A mixture of .1mg crystal violet per one mL $[BMIM][PF_6]$ was created by taking a 0.5mg/mL mixture and mixing it with four times as much pure RTIL. The cuvette allowed more of the [BMIM][PF_6]-crystal violet solution to be used than in the tests performed on slides and forced the [BMIM][PF_6]-crystal violet solution to take a specific repeatable shape. This more uniform shape allowed absorption measurements to be taken at standard points along the long axis of the cuvette going from one end to the other, so that an accurate idea of the change in absorption with position could be determined.

4.1 Absorption of Laser Light

There were three different optical setups that were attempted for measuring the absorption through the [BMIM][PF_6]-crystal violet solution with each subsequent setup giving an improvement in accuracy of measurement over the previous setups. In all three setups the beam of a helium-neon (He-Ne) laser was reflected off of mirrors and sent through the [BMIM]][PF_6]-crystal violet solution before its intensity was measured.

4.1.1 Two-Beam Setup

The first setup constructed split the beam of the He-Ne laser using a mirror whose silvering increased with position acting as a 50-50 beam-splitter. The two beams were then directed so that they were traveling parallel to each other separated by approximately 4cm. After being reflected by multiple mirrors, the beams were directed so that one passed through the RTIL-dye solution near the negative electrode and one passed through near the positive electrode. The idea was that one beam would pass through what would be the clear region around the negative electrode after transport and the other would pass through the region around the positive electrode, which was the one being used to determine whether the dye was being modified or moved. After passing through the RTIL-dye solution the laser light from each beam was directed to a separate photodiode. The outputs of the two photodiodes were sent to an oscilloscope in order to observe the voltages created by the intensity of the two beams. In order to ensure that the photodiodes were not being saturated and thus giving inaccurate data filters were placed in the paths of the two beams in order to filter out enough light, so that the measured voltage would drop linearly with respect to the intensity passing thorough the RTIL-dye solution. It was also necessary to ensure that the voltage near the negative electrode remained linear when the solution became clear in this region during the test.

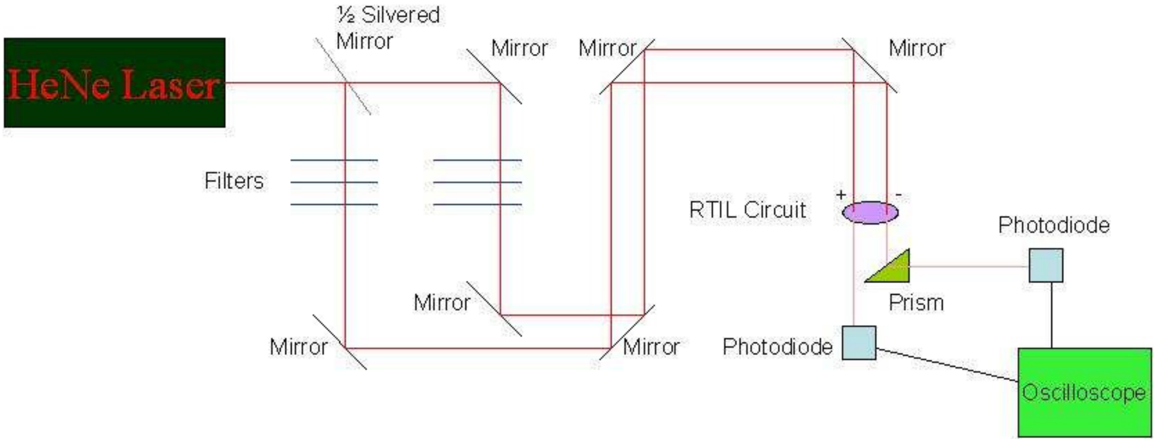


Figure 5: Original two beam setup for the absorption measurement

This setup with two beams and two photodiodes proved insufficient for the needs of the experiment because it only measured the absorption at randomly determined points rather than uniformly throughout the solution. Also, it was very difficult to get any voltage reading near the positive electrode and also keep the voltage reading near the negative electrode linear throughout the entire range from the purple of the RTIL-dye solution to the clear resulting after the test.

4.1.2 One-Beam Setup

The second absorption setup kept the optics of the first setup in place, but only used one of the split beams for measuring the intensity through the [BMIM][PF_6]-crystal violet solution. The absorption was measured by moving the trough through the laser beam starting with the laser beam passing through the center of the narrow dimension of the trough near the negative electrode and moving towards the positive electrode keeping it in the center of the trough in the narrow dimension for all measurements in order to minimize reflection and refraction due to meniscus effects. The voltage incident on the photodiode created by the laser light was measured at 2.5mm intervals along the length of the trough as determined by moving the trough by hand through the laser beam following ticks on an index card placed next to the trough as a guide.

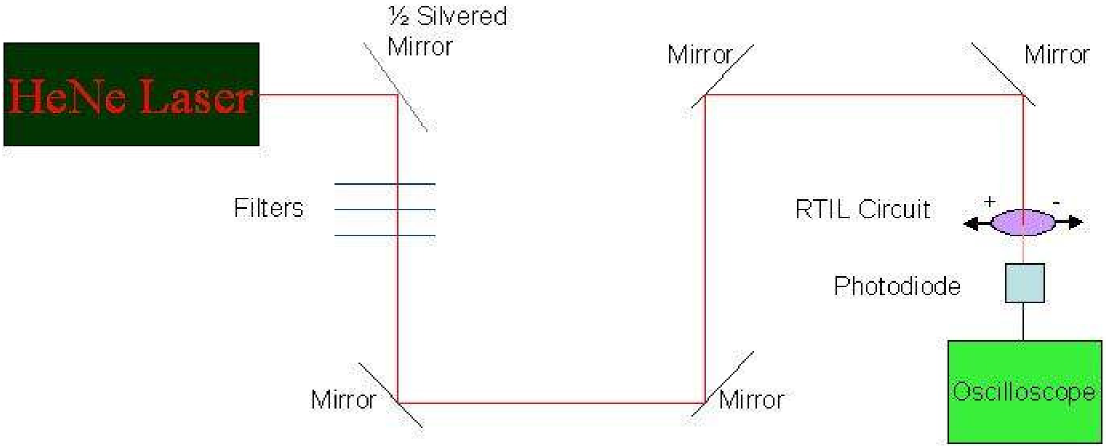


Figure 6: One beam moving trough absorption setup

As with the first setup, the photodiode in the second setup had to be tested for linearity in the clear region in order to ensure that accurate data could be obtained and the photodiode was not being saturated. Filters had to be placed in front of the laser beam in order to ensure that this linearity was obtained when light passed through the empty trough. This linearity was tested by measuring the voltage on the oscilloscope both with and without the light being blocked by a 50% filter. The ratio of the voltages was then compared with the readings of a power meter for the amount of power coming from the laser both with and without the 50% filter in place. The linearity test with light passing through the empty trough gave an upper limit for the amount of light that would reach the photodiode and ensured that any oscilloscope reading with a lower voltage than this value would be in the linear region.

The voltage read from the laser light passing through the trough also served as an initial value for comparison with outputs from the tests with RTIL solutions in the trough. In order to determine the amount of reflection by the RTIL in the trough the absorption of a 1mL solution of RTIL with no dye added to it was measured. The absorption of a solution of RTIL mixed with 0.1mg/mL dye was also measured in order to determine how much more light the RTIL-dye solution absorbed than the RTIL solution without added dye.

The electrodes were put in place at the two ends of the trough after all of the other measurements had been taken and a current was allowed to run through the [BMIM][PF_6]-crystal violet solution until a clear region had been created near the negative electrode and absorption measurements could be taken.

This absorption setup offered an improvement over the two beam setup in that it was able to measure the absorption throughout the length of the trough rather than at arbitrary points at the edges of the trough near the electrodes, however it still suffered multiple deficiencies which prevented it from taking accurate absorption measurements. First, moving the trough by hand disturbed the dye slightly and introduced a good deal of error in the position measurements for the trough. These variations in position prevented accurate absorption data to be collected at each position. Also, the lens on which the trough was resting was just set in place, not secured, and thus also possibly moved slightly during measurements, introducing more error into the data. The biggest deficiency in this setup was that the area of the light collection portion of the photodiode was too small to collect all of the light, which was diverging after emerging from the bottom of the [BMIM][PF_6]-crystal violet filled trough.

4.1.3 Power Meter Setup

The third optical setup constructed addressed all of the problems of the previous two subsections and also added a few more improvements to the setup. The lens on which the trough was placed was secured in a lens holder and the trough fit perfectly in this lens holder lengthwise, holding it in place in one dimension. Index cards were attached to the two sides of the lens holder in order to secure the trough in place along the other dimension and also to block unwanted light not passing through the trough from getting detected. To allow for more accurate movement of the trough, the lens holder on which the trough rested was attached to a micrometer allowing the translation of the trough through the laser beam to be measured precisely. The silvered mirror was removed from the setup, so that the maximum power of the beam passed through the trough, giving a greater range of light intensities to be measured. Also, a light power meter was inserted in place of the photodiode, allowing for all of the light passing through the trough to be collected and also for a more accurate value of the intensity to be recorded than the oscilloscope allowed. The power meter was found to be in the linear region without any filtering of the laser beam being necessary, removing another complication from the setup.

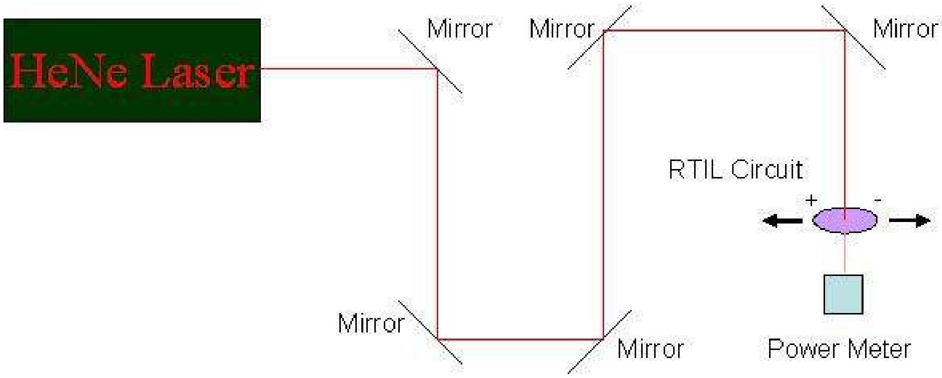


Figure 7: One beam, micrometer translated, secured trough setup

Once these improvements to the setup had been put in place the test proceeded as in the previous setup, with the only difference being that each micrometer unit corresponded to 0.1in, so absorption measurements were taken every .05in between the electrodes rather than every 2.50mm. Also, in order to correct for possible meniscus effects and to obtain a larger sample of data in the [BMIM][PF_6] solution, a second round of tests were conducted in which absorption measurements were taken at points off center from the long axis of the trough.

4.2 Trough Center Data and Results

4.2.1 Base Intensity Measurements

Two tests were carried out using the power meter setup for measuring the absorption characteristics of a [BMIM][PF_6]-crystal violet solution exposed to the electric field created by introducing a voltage of 6.25V across the solution for one hour and two hours respectively. The base value for the intensity of light passing through the setup was found by passing the empty trough through the laser beam through the whole range of position measurements four times and recording the measured intensity every ½ division. The data can be seen in figure 8 where it can be seen that there is very little variation between the intensity values between tests, but the intensity values of the individual points on the trough are a little more varied. These variations can be attributed to randomly spaced imperfections in the trough caused by small scratches or splotches, along with other imperfections in the trough. The average value of the laser power passing through the trough was 0.2030mW ± 0.0038mW.

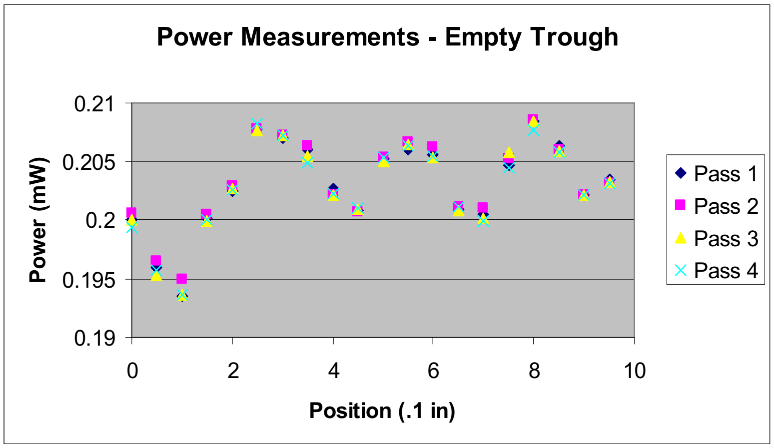


Figure 8: Power measurements for the laser light passing through the empty trough

The power of the light passing through 1mL of [BMIM][PF$_6$] with no dye added to it provided another basis for measurement because this liquid exposed the laser light to the meniscus effects that it would pass through in all of the tests of RTIL-dye solutions, but with very little absorption occurring. The effects of reflection and absorption bye the dye can be seen in figure 9. The variation among power values across different trials is slightly larger for this test, although the overall structure of the data arrangement is the same, inspiring confidence in the measured values. The average power for this test was 0.189mW ± 0.0029mW, which is 93.1% of the average power values for the light passing through just the trough. This is within the 10% necessary for the assumption that most of the light is being lost from reflection off the additional surface rather than through absorption. The plot thus serves as a non-absorbing basis with which to compare the RTIL-dye solutions which will absorb.

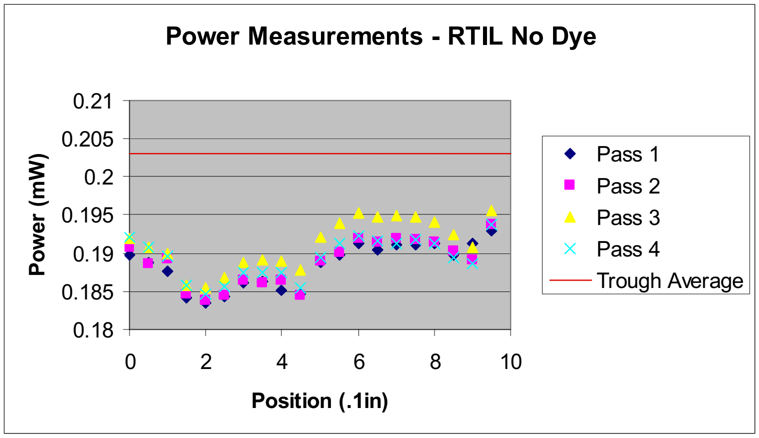


Figure 9: Power measurements for the laser light passing through a solution of RTIL with no added dye

4.2.2 RTIL-Dye Intensity Measurements

The intensity data for the two [BMIM][PF_6] solutions before the application of the electric field are shown in figures 10a and 10b. Rather than the intensities varying randomly around an average value as would be expected, the intensities for both samples decreased as the location of the laser was moved from the positive electrode towards the negative electrode. Not including the first series of data points from the 2 hour test, which may have varied as a result of variations in laser power or as a result of the solution not settling into its final resting position in the trough before data measurements began being taken, the intensity values of the solutions seemed to vary in much the same ways. The best possible explanation of these similar decreases in the measured intensity is that the solution took a shape such that meniscus effects caused the path length of the laser light through the solution to vary slightly at different points along the solution causing the drop in the intensity measurements. As a means for comparison with the after transport intensity relations, the average values for the two solutions were found to be 0.0710mW± 0.0040mW for the one hour tests and 0.0664mW ± 0.0033mW for the two hour test, values within 10% of each other.

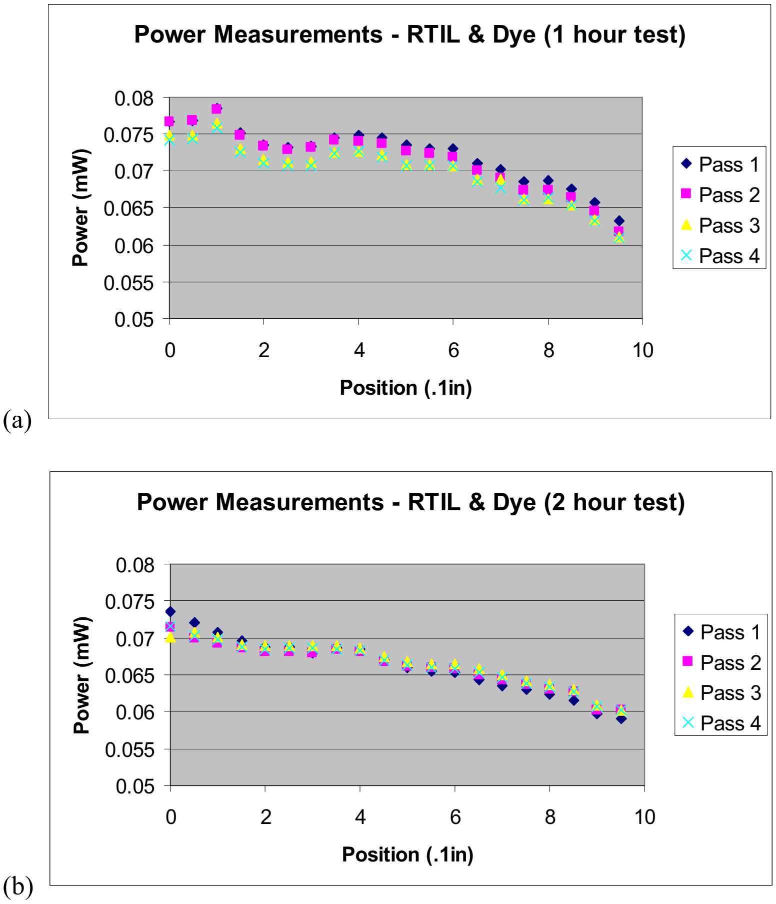
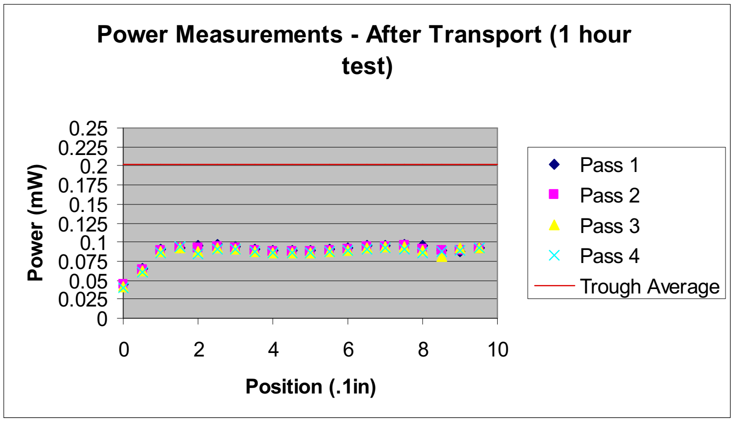


Figure 10: Power measurements for the laser light passing through solutions of 0.1mg crystal-violet/1mL [BMIM][PF_6] before applying the electric field for (a) 1hour and (b) 2 hours

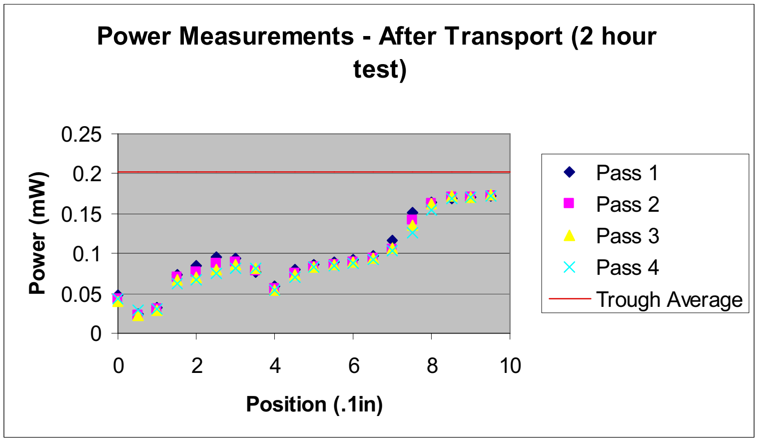
4.2.3 After Transport Intensity Measurements

The measured intensity values throughout the length of the solution after the application of an electric field for one and two hours respectively are shown in figures 11a and 11b. Interestingly these two data sets give very different plots. This variation may be a result of the properties of the solution after transport. After an hour the color hadn't been greatly modified visually; a yellow, purple, green region had appeared at the positive electrode, but the dye appeared uniformly distributed throughout the rest of the solution. This visual seems consistent with the plot in figure 11a in which an increased level of absorption was found when the laser was passing through the yellow region and a relatively constant, slightly decreased level was found throughout the rest of the solution.

After two hours there was much more variation in the color of the solution, with the yellow, green, purple region covering over half of the length of the trough, followed by a purple region, which whose absorption appeared to decrease moving towards the negative electrode, and finally a large clear region surrounding the negative electrode. This observation agrees with the plot in figure 11b.



(a)



(b)

Figure 11: Power measurements for the laser light passing through solutions of 0.1mg crystal-violet/1mL [BMIM][PF_6] after application of the electric field for (a) 1hour and (b) 2 hours

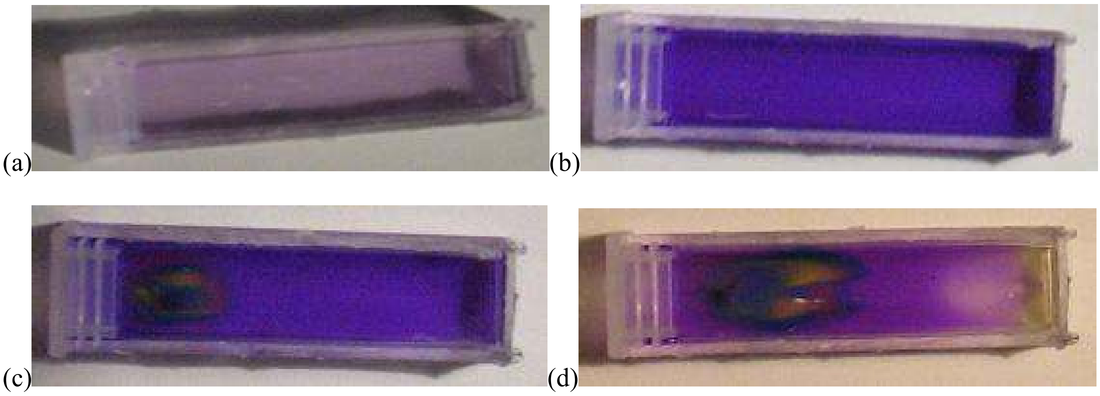


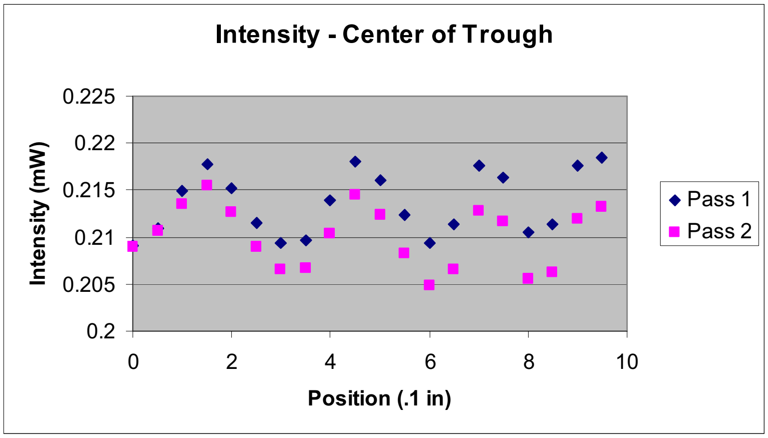
Figure 12: (a) [BMIM][PF_6] solution with no dye added, (b) .1mg/1mL [BMIM][PF_6]-crystal violet solution, [BMIM][PF_6]-crystal violet solution after the application of an electric field for (c) 1 hour and (d) 2 hours. The positive electrode was placed on the left side of the trough in both figures and the negative electrode was placed on the right side.

4.3 Transverse Data and Results

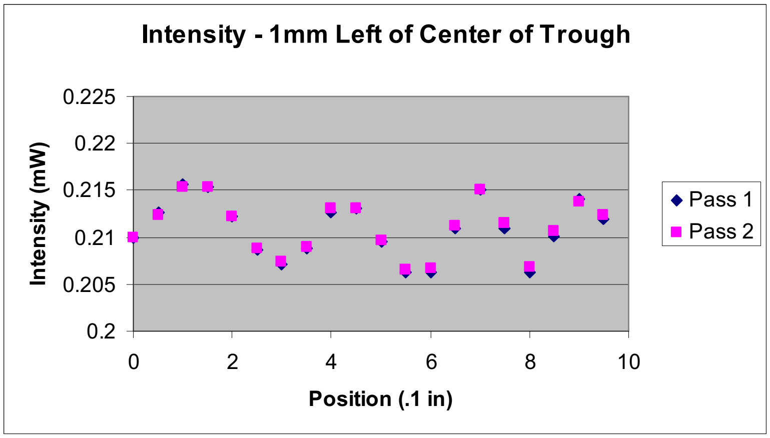
The large regions of color change in the two hour test, and to a lesser extent the one hour test, along with the consistently decreasing intensity levels in the solution of [BMIM][PF_6] and crystal violet suggest inadequacies in the two tests conducted. The yellow and green regions present in the dye after transport do not absorb He-Ne laser light in the same fashion as the purple regions and so does not give useful information about how much dye is present in these regions. Better data would be found by running a shorter test in order to ensure that more of the dye remains purple giving a larger sample area for investigation. The change in height of the dye as a result of menicus effects, which seems to be present in the [BMIM][PF_6]-crystal violet solution before the application of the electric field also suggests the need for sampling a larger area of the solution. By measuring the absorption of laser light at points parallel to those taken along the center of the trough more data is available for analysis and a better picture of the effect of small height variations on the amount of absorption can be obtained. Implementing these improvements, a third test was conducted measuring the absorption through the center axis of the trough along with points 1mm and 2mm to either side of the center and applying the voltage for only thirty minutes. All other conditions and variables in this test were identical to those of the previous two tests.

4.3.1 Base Intensity Measurements

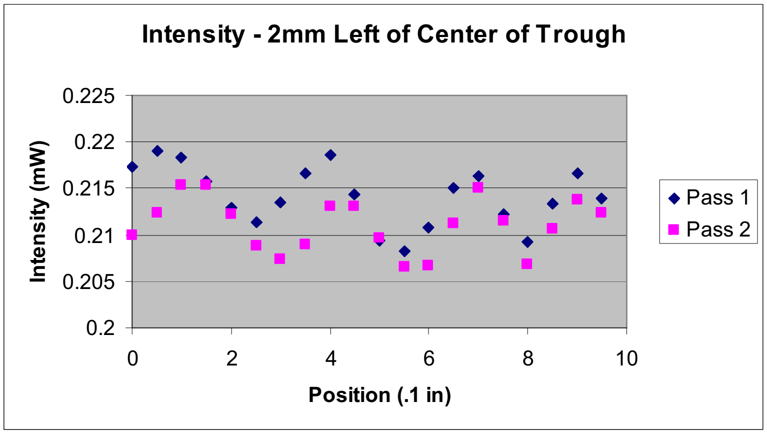
As expected figures 13(a-f) show that the intensity of laser light passing through the empty trough is relatively constant with respect to the position compared to the center of the trough with an average value over all of the measurements of 0.2129mW ± 0.0035. The perceived oscillatory behavior of the data can be attributed to random imperfections in the trough affecting the reflection and absorption of light by the bottom of the trough. The amount of light lost when RTIL is added to the trough as a result of reflection and absorption is shown in figure 14. The lower levels of reflection and absorption in this test than in the previous two is a result of the fact that the RTIL in this test is completely pure, while the RTIL being used in the previous two tests was contaminated with a low level of crystal violet dye. Figure 14 shows that the least amount of light is lost to reflection and absorption at the points to the right of the center, followed by the center, then the left and the further right which had similar vales, and finally by the further left. These intensities show that the laser light wasn't passing through the center axis exactly. The large intensity variations at the points further left of center suggests that more light is being reflected or absorbed at the edge of the trough, most likely as a result of reflection off of its side or the RTIL's greater height at this point as a result of meniscus effects. For the other points there did not seem to be any variation in the amount of light lost along the length of the axis as expected.


Intensity - Center of Trough
0.225
0.22
0.215
0.21
0.205
0.2
Intensity (mW)
0
2
4
6
8
10
Position (.1 in)
◆ Pass 1
■ Pass 2

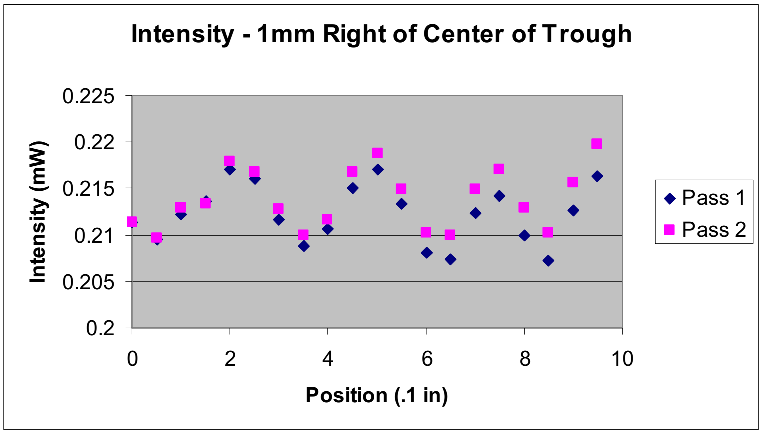
(a)


Intensity - 1mm Left of Center of Trough
0.225
0.22
0.215
0.21
0.205
0.2
Intensity (mW)
0
2
4
6
8
10
Position (.1 in)
◆ Pass 1
■ Pass 2

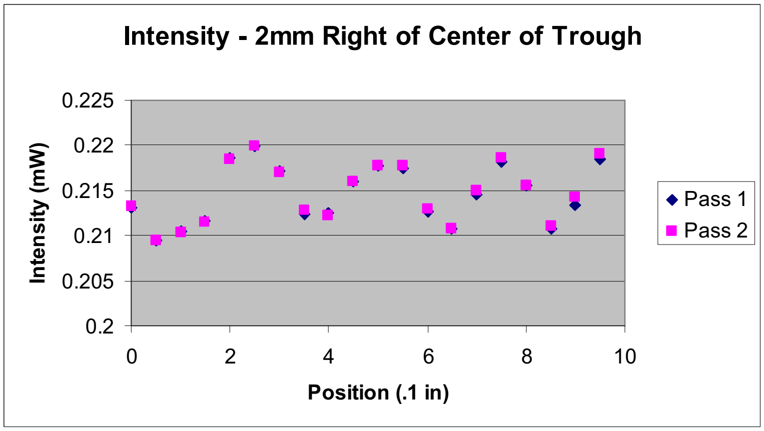
(b)


Intensity - 2mm Left of Center of Trough
0.225
0.22
0.215
0.21
0.205
0.2
Intensity (mW)
0
2
4
6
8
10
Position (.1 in)
◆ Pass 1
■ Pass 2

(c)



(d)



(e)

Figure 13: Power measurements for the laser light passing through (a) the center, (b) 1mm left of the center, (c) 2mm left of the center, (d) 1mm right of the center, (e) 3mm right of the center of the empty trough

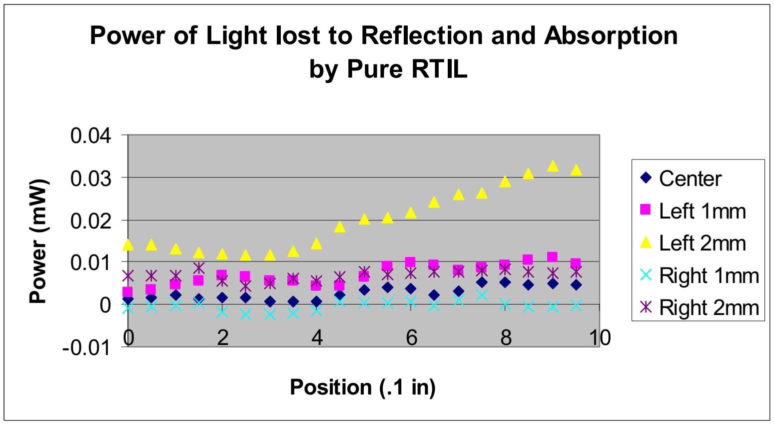


Figure 14: Average difference between the intensity of light passing through the empty trough and through pure RTIL at the various distances from the center axis

4.3.2 RTIL-Dye Intensity Measurements

The average power of the light that is absorbed by the solution of [BMIM][PF_6] and crystal violet is shown in figure 15. This solution shows different structure than the pure RTIL. Again, slightly higher levels of absorption were seen at the sets of points off center because they were closer to the edges. Also, all of the sets of points showed variation along the length of the trough exposing the changes in the height of the dye. The amount of absorption increases as the position values increase from 0.50in to 0.95in as expected if the height of the solution were at a minimum at the center and a maximum at this end. There is more variation in the meniscus effects between points 0in to 5in because this was the end of the trough at which the lid of the cuvette was located and thus the shape of the solution was less uniform. It is unexpected that the variation along the length of the trough is greater than the variation between points along the shorter dimension of the trough. A possible explanation for this effect is that the sides constraining the shorter dimension of the trough had grooves in the making it difficult for the dye to move up the sides and leveling out the dye more in this dimension.

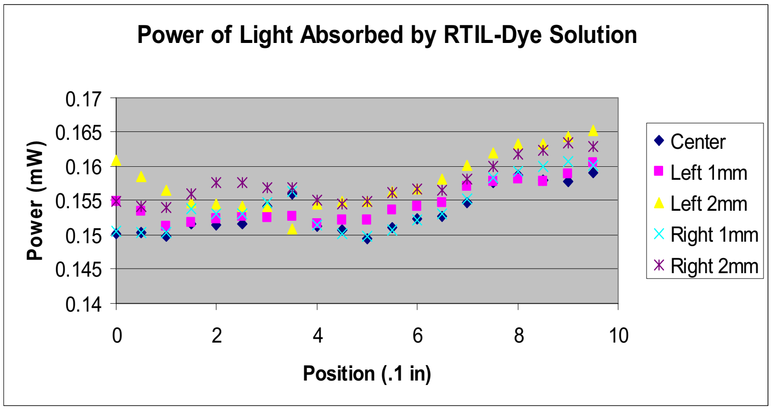


Figure 15: Average power of laser light absorbed by the solution of RTIL and dye at the various distances from the center axis

4.3.3 After Transport Intensity Measurements

The intensity of light absorbed by the [BMIM][PF_6]-crystal solution after 30 minutes of exposure to an electric field can be seen in figure 16. The differences in intensity of light absorbed along the axes parallel to the center of the trough again suggest that there is a meniscus present in the solution, with the lowest point being at the center of the trough and the highest points at the edges.

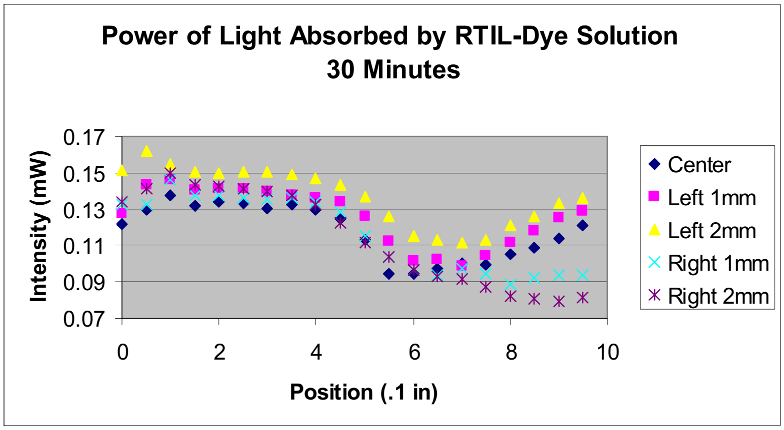
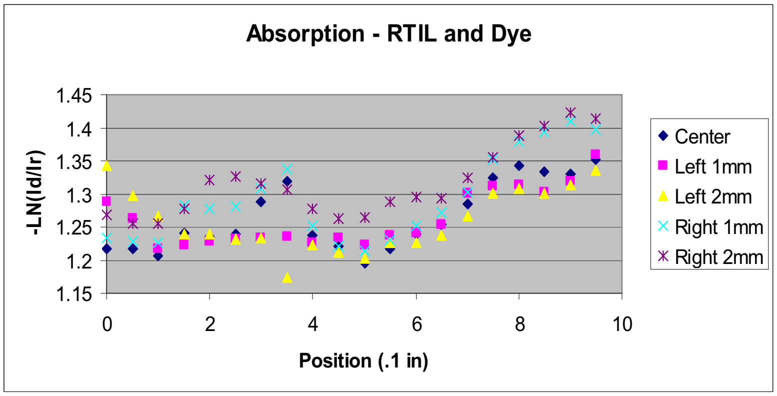


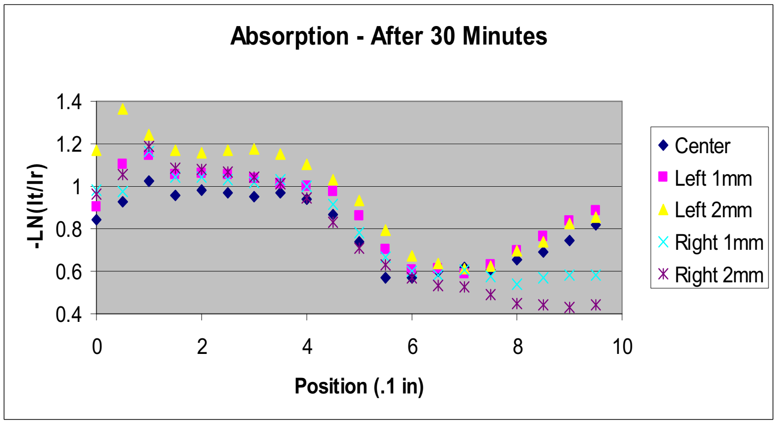
Figure 16: Average power of laser light absorbed by the solution of RTIL and dye at the various distances from the center axis after applying an electric field for 30 minutes

4.3.4 Absorption Levels

The absorption levels of the [BMIM][PF_6] solutions both before and after the application of a 6.25V to the solution are displayed in figures 17(a, b). These levels were found using equation 7, which relates the measured intensity of light passing through the RTIL solution with dye to the intensity passing through the solution of RTIL without dye. Looking at the absorption values in the figures it can be seen that the absorption values are lower before transport than they were after transport, especially as expected in the region near the negative electrode where the solution would become clear if the voltage were allowed to run long enough. The decrease in absorption that can be seen at positions 0mm-0.1in after the application of the electric field can be attributed to the presence of a small green and yellow region in the solution. At the other end of the dye, the large difference between the points to the right and far right of center can be attributed to the fact that the solution had turned clear in this part of the trough, but not on the other side of center. The increase in absorption at these positions at the center, left, and far left are likely a result of the meniscus effects that were seen in the solution present before the application of the field. The interesting region it the region present at positions .3-.7in in all of the tests because it shows that there is a linear decrease in the absorption in this region going from the side of the negative electrode to that of the positive electrode.



(a)



(b)

Figure 17: Absorption by RTIL and dye found using equation 7 comparing the intensity of light passing through the RTIL-dye solution to the intensity of light passing through pure RTIL at the various distances from the center axis (a) before and (b) after applying an electric field for 30 minutes

Table 1 shows the calculated amounts of total absorption found in the two samples both before and after exposing the sample to the electric field. It can be seen from the table that after applying an electric field for 30 minutes the total amount of absorption was only 66.07% of its original value. This strongly suggests that the dye was being modified rather than simply moved.

Sample	Total Absorption $\sum(-\ln(I_{Sample}/I_{No\ Dye}))$
[BMIM][PF_6]-crystal violet original state	128
[BMIM][PF_6]-crystal violet After 30 minutes	84

Table 1: Total absorption values for the pre and post-electric field [BMIM][PF_6] solutions as found using by summing the absorption values at each position along the length of the trough.

4.3.5 Absorption Coefficient and Dye Density

The amount of absorption in the [BMIM][PF_6]-crystal violet solutions before the application of the electric field can be found using equation 7, where the calculated depth of the liquid in the trough of .26cm gives an average absorption coefficient of 499.99m^{-1} ± 25.50m^{-1} for the original solution. From equation 6 and the known value of the crystal violet concentration in this solution of $1.48x10^{23}$ molecules/m^3, an approximate value for the absorption cross-section of crystal violet at 633nm was found to equal $3.39x10^{-21}m^2$ ± $1.39x10^{-22}m^2$. This value is on the same order of magnitude as and falls between the absorption cross-sections in solutions of crystal violet and water and crystal violet and glycerol, $2.87x10^{-21}m^{-1}$ and $7.92x10^{-21}m^{-1}$ respectively. The calculated absorption cross-section value was then used in order to determine the changes in density with position that occurred in the solutions that existed after the tests.

5 Conclusions

Room temperature ionic liquids offer a promising solution to the problem of solvent outgassing and transport to the surface for use in TOF-SIMS. This research has investigated the underlying electrically induced properties which occur in solutions of the RTIL [BMIM][PF_6] and the indicator dyes bromophenol blue and crystal violet. In solutions of de-ionized water and bromophenol blue and of de-ionized water and crystal violet the dyes moved to the electrodes which were opposite their charge, suggesting that they were moving electrophoretically. In solutions of [BMIM][PF_6] and the indicator dyes bromophenol blue and crystal violet the color in the solution seemed to move away from the negative electrode regardless of the charge of the indicator dye.

By comparing the amount of absorption by a solution of [BMIM][PF_6] and crystal violet both before and after the application of an electric field it was seen that in thirty minutes the amount of absorption had decreased throughout the entire area of the solution and total absorption in the solution had dropped by approximately one-third. This shows that rather than the dye moving through the solution electroosmotically, it was actually being destroyed. Consistent with the dye being destroyed at the negative electrode, the amount of absorption increased linearly in the middle of the trough, from the side closest to the negative electrode to the side closest to the positive electrode. Also, by the end of the test, the area surrounding the negative electrode was beginning to become clear.

Further investigation is necessary in order to gain a better understanding of the electrochemical mechanisms which cause the modification of the crystal violet, so that the possibility of creating an RTIL-solute solution that is not destroyed by an electric field can be evaluated. Possible areas of research towards finding an RTIL-solute solution in which transport for TOF-SIMS is possible would be to try using different solute molecules or different RTILs, hoping to find ones with different structures which will not be affected by the application of an electric field. A further possibility would be to induce an electric field in the RTIL-solute solution, removing the need for physical leads to be placed in the solution and preventing electrons from modifying the structure of the solution.

6 Acknowledgements

I would like to thank Dr. William Cooke for his help serving as my advisor for this project and providing the necessary help with all aspects of the project. I would also like to thank Erik Spahr for his help getting me familiarized with the electrically induced transport tests as well as with the initial design and setup of the two-beam optical setup for the absorption measurements. In addition, I would like to thank Pete Harris for his aid in the lab with any questions I had during the absorption measurements and lastly I'd like to thank Drs. Pike and Rice from the Chemistry department for their aid in understanding the electrochemistry occurring in the [BMIM][PF_6] solution.

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