# The Effect of Solvent and Solute Polarity on the Thermodynamic Stabilization of Solute Molecules by Solvent Molecules

Lareine Jeng

December 17, 2010

The Cooper Union

Ch 160 C.1

Principles of Physical Chemistry

## ABSTRACT

Several factors affect how much energy is required for a solute to dissolve in a solvent. The dipole moment, polar surface area (PSA), and volume of a solute have a weak negative correlation to the amount of energy required for them to dissolve. The dielectric constant of a solvent has a modest positive correlation with solvation energy. None of these factors alone can be used to predict the solvation energy of the solute in a given solvent because the correlations are not strong enough. However, if each of these factors is known, a reasonable estimate of the solvation energy can be made. Using the least squares method, a linear function to predict the solvation energy as the function of the dipole moment, PSA, and volume of a solute, and the dielectric constant of the solvent was derived. The function was found to be:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = 2.791617\mathbf{p} - 0.66416A - 0.22056V + 0.183546\varepsilon$$

where ΔHsolv is the solvation energy in kilojoules per mole; **p** is the dipole moment of the solute in debye; A is the polar surface area of the solute in square angstrom units; V is the volume of the solute in cubic angstrom units; ε is the dielectric constant of the solvent.

## INTRODUCTION

Solutes tend to dissolve easily in solvents with like polarity. For instance, a non-polar solute, such as oil, is immiscible in a polar solvent, such as water because their polarities are different. The polarity of a solute is linked to its dipole moment. The higher the dipole moment of a solute is, the more polar it is. Dipole moment is a measure of how unevenly distributed the charges of a molecule are. The polarity of a solvent is linked to its dielectric constant. The higher its dielectric constant is, the more polar the solvent is. Dielectric charge is a measure of how high the permittivity of a substance is and how well it can polarize and hold charges. The more easily a solute can dissolve in a solvent, the less energy is required for it to dissolve. This energy is called the solvation energy, or the enthalpy of solvation. Therefore, a solute will require little energy to dissolve in a solvent if the dipole moment of the solute is like the dielectric charge of the solvent.

There are other factors besides polarity that affect the amount of energy required to dissolve a solute in a solvent. A solvent with a high PSA or a high volume would require less energy to dissolve. However, the volume of a solvent has very little to do with how easily the solute can dissolve.

## PROCEDURE

Benzene ($C_6H_6$) was constructed using SPARTAN. The molecular structure of benzene is shown in **Appendix I**. The energy of the molecule was minimized. The properties of benzene in a vacuum were calculated using Density Functional Theory with 6-316*. A screenshot of all the settings used is shown in **Figure 1**.

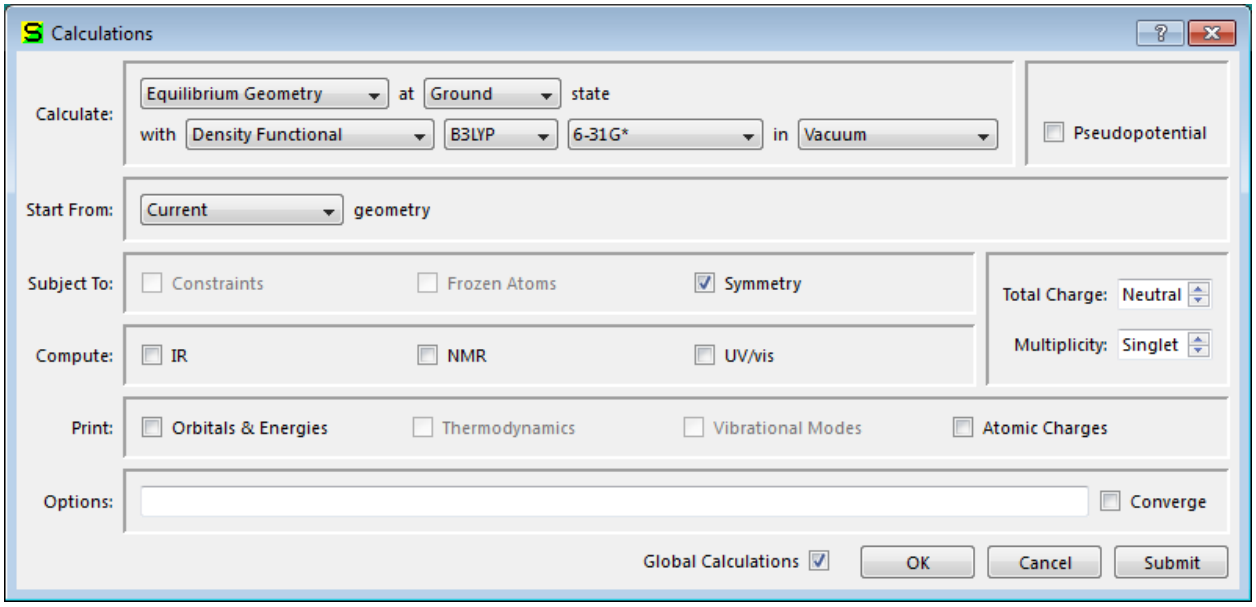



**Figure 1.** Summary of settings used to calculate properties of a solute in a vacuum.

When the calculation finished running, the energy, dipole moment, polar surface area (PSA), and volume of benzene in a vacuum were viewed by selecting **Display**, and then clicking on **Properties**, and this data was recorded.

The same procedure for calculating the properties of benzene in a vacuum was repeated for the same molecule in water, acetone, ethanol, and tetrahydrafuran (THF) by changing the dropbox selection shown in **Figure 2**.

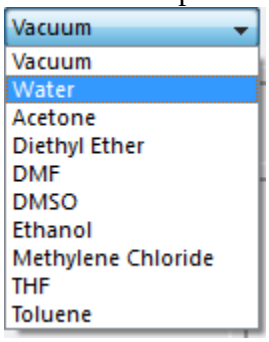



**Figure 2.** This dropbox allows the user to select from a list of solvents.

The same procedure for calculating the properties for benzene in these five solvents was repeated for calculating the properties of fluorobenzene, nitrobenzene, toluene, and phenol in the same set of

solvents. The molecular structures of fluorobenzene, nitrobenzene, toluene, and phenol can be found in **Appendix I**. The same set of data that was recorded for benzene in these solvents was recorded for the other four solutes in each of these solvents.

The dielectric constants of a vacuum, acetone, ethanol, THF, and water were found[1] and recorded.

The solvation energy in Hartree atomic units (au) for each solution was calculated by subtracting the energy of the solute in a vacuum from the energy of the solute in a particular solvent. This value was then converted into kJ/mol by multiplying by $2625.4996\frac{\text{kJ}}{\text{mol} \cdot \text{au}}$.

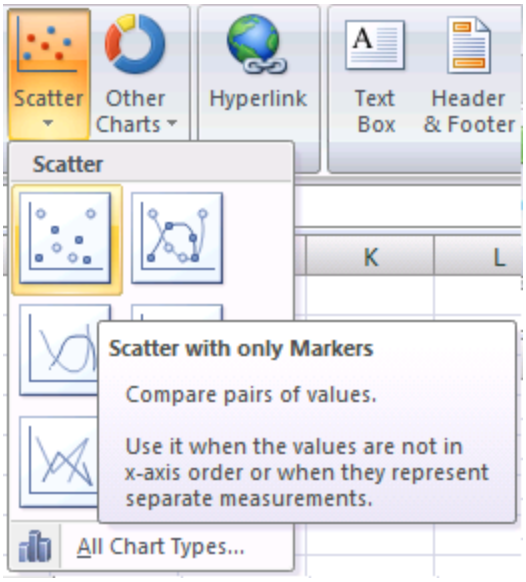



**Figure 3.** A scatter plot with only markers was used to plot the data.

The dipole moment of each solute in water was plotted against its solvation energy in water in Microsoft Excel using the **Scatter with only Markers** option as shown in **Figure 3**. A linear trendline was added to the plot, and the equation and R-squared value of the trendline were shown. The full options selected for the trendline are shown in **Figure 4**.

The dipole moments of each solute in ethanol, acetone, and THF were plotted against the solvation energies in a similar manner, and the trendlines were added. Using the same method, the PSA and volumes of solution, except for the solutes in a vacuum, were plotted, and the corresponding trendlines were added. Using the same method again, the dielectric constant of each solvent was plotted against the solvation energy of each solution, and the trendlines were added once more.

From a rough examination of the $R^2$-values displayed on the graphs, it was easily detected that most of the $R^2$-values are too low to be useful. However, although the correlations are weak, they are all fairly consistent in slope.

A formula to estimate the solvation energy as a function of the dipole moment, PSA and volume of the solute, and the dielectric constant of the solvent was sought.

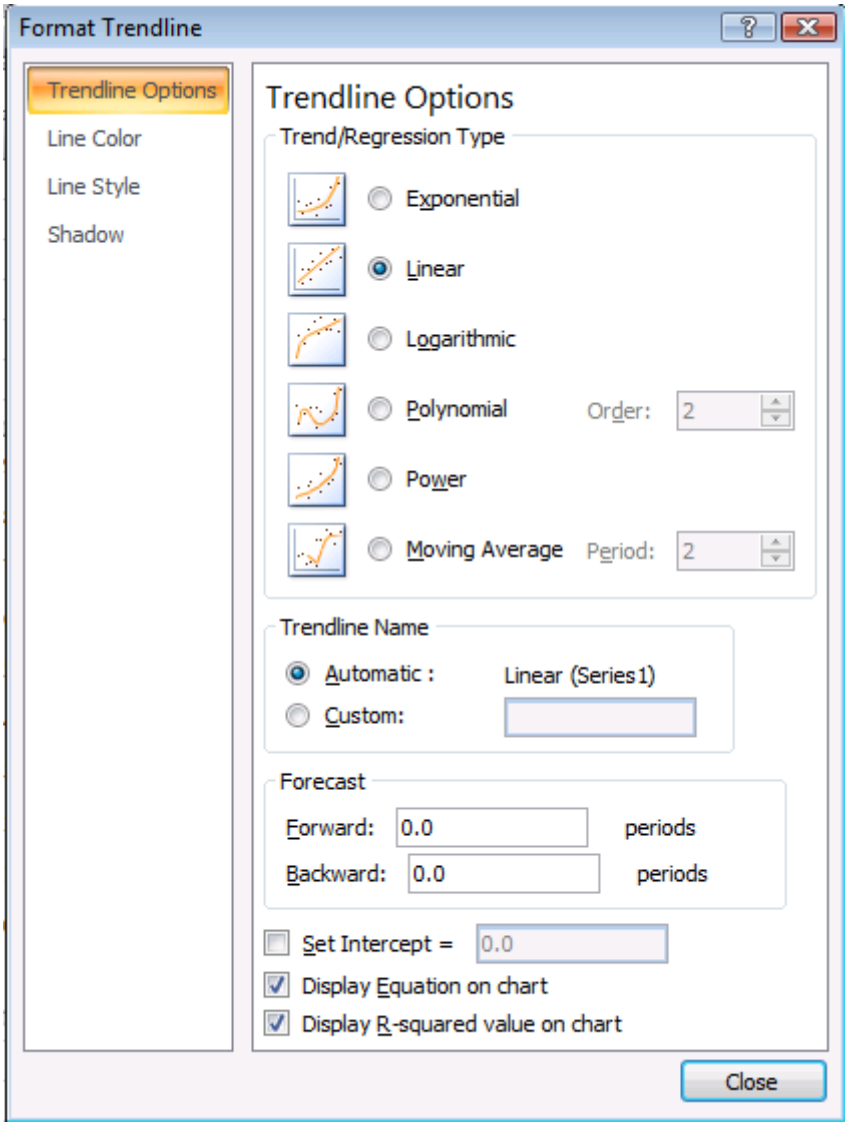



**Figure 4.** These trendline settings were used for all of the plots.

A table was constructed displaying each solution, except the vacuum as a solvent. The dipole moment, PSA and volume of the solute; the dielectric constant of the solvent; and the solvation energy calculated by SPARTAN were included in the table for each solution. Because all the correlations between each factor and the solvation energy are linear, the formula to estimate the solvation energy would also be a linear one, so it would take the form of:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = W\mathbf{p} + XA + YV + Z\varepsilon$$

where ΔHsolv is the solvation energy in kilojoules per mole; **p** is the dipole moment of the solute in debye; A is the polar surface area of the solute in square angstrom units; V is the volume of the solute in cubic angstrom units; ε is the dielectric constant of the solvent; and W, X, Y, and Z are constants.

The constants were determined using the least squares method. The constants W, X, Y, and Z were inserted on the same spreadsheet as the table in cells B23, B24, B25, and B26 respectively. Their values were at first set to arbitrary numbers. Two additional columns titled "$\Delta H_{solv}$ by Regression (kJ/mol)" and "Absolute Error Squared," respectively, were added to the table. The column displaying the solvation energies calculated by SPARTAN was renamed "$\Delta H_{solv}$ by SPARTAN (kJ/mol)." $\Delta H_{solv}$ by Regression (kJ/mol)" will show the solvation energy calculated by the regression formula. The formula was entered in each of the cells in that column, with W, X, Y, and Z as arbitrary constants. This function was entered into the column "Absolute Error Squared":

$$(H_{solv} \text{ by SPARTAN} - H_{solv} \text{ by Regression})^2$$

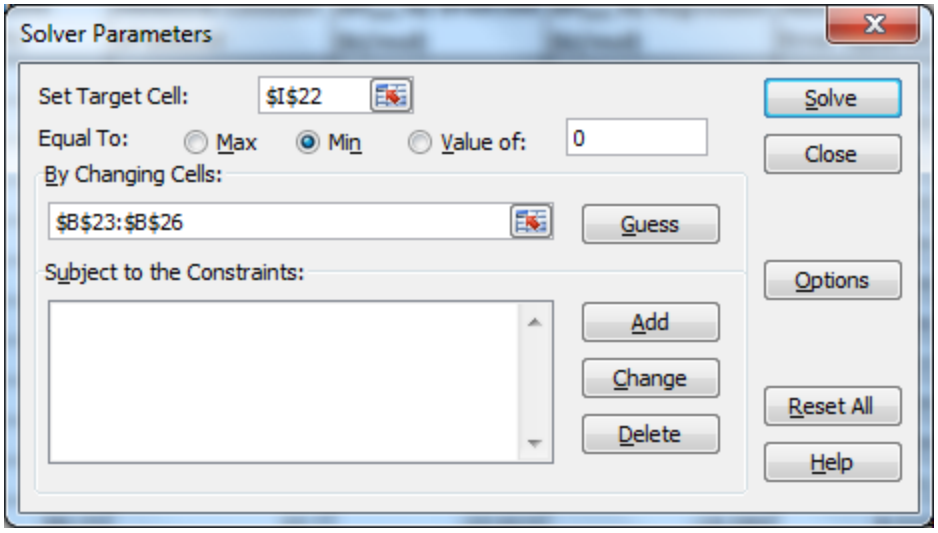



**Figure 5.** These are the settings applied to Solver to minimize the sum of the squares of the error. I22 is the cell containing this sum and B23:B26 are the cells containing the constants that can be changed.

The sum of this column was calculated below the column in cell I22. This sum was minimized by changing constants W, X, Y, and Z using the Solver add-in. If already activated, this tool can be found in

the **Data** ribbon in Excel. The settings used in Solver are shown in **Figure 5**, and Solver was executed by clicking the **Solve** button.

The numerical values for W, X, Y, and Z can be viewed on the spreadsheet after Solver calculated their values. These values were then plugged into the original equation:

$$\Delta H_{solv} = \Delta H_{solv}\,(p, A, V, \varepsilon) = W\mathbf{p} + XA + YV + Z\varepsilon$$

## RESULTS

**Spreadsheet 1** shows the energy, dipole moment, PSA, and volume of each solvent in each solute. The dielectric constants of the solvents in this spreadsheet were found in literature. The solvation energies for each solution were calculated by subtracting the energy of the solute in a vacuum from its energy in the given solvent. This value was converted from Hartree atomic units to kilojoules per mole.

The plots with trendlines of the dipole moments, PSAs, volumes, and dielectric constants vs. the solvation energies can be found in Appendix II.

**Table 1** shows the R-squared values for the plots of the dipole moments, PSAs, and volumes for each solution against the solvation energies.

**Table 1.** R-squared values for the plots of the dipole moments, PSAs, and volumes of each solvent against the solvation energies.

| Variable | Solvent | $R^2$ |
|---|---|---|
| Dipole moment | Acetone | 0.5348 |
| Dipole moment | Ethanol | 0.4689 |
| Dipole moment | THF | 0.4975 |
| Dipole moment | Water | 0.4142 |
| PSA | Acetone | 0.8870 |
| PSA | Ethanol | 0.8302 |
| PSA | THF | 0.8646 |
| PSA | Water | 0.7802 |
| Volume | Acetone | 0.3380 |
| Volume | Ethanol | 0.2059 |
| Volume | THF | 0.3189 |
| Volume | Water | 0.1101 |

PSA has a consistently higher R-squared value than dipole moment does, which has a consistently higher R-squared value than volume does. Water not only consistently has the lowest R-squared value of all the solvents, but it is also an outlier.

**Table 2** shows the R-squared values for the plots of the dielectric constants of each solvent containing each solute against the solvation energies. The dielectric constants have a consistently higher R-squared value than the dipole moments, PSAs, and volumes.

**Table 2.** R-squared values for the plots of the dielectric constants of each solvent against the solvation energies.

| Solute | $R^2$ |
|---|---|
| Benzene | 0.9416 |
| Fluorobenzene | 0.9035 |
| Nitrobenzene | 0.8756 |
| Toluene | 0.9398 |
| Phenol | 0.7405 |

All of these variables – dipole moment, PSA, volume, and dielectric constant – were combined to form a linear function to estimate the solvation energy. This function was found to be:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = 2.791617\mathbf{p} - 0.66416A - 0.22056V + 0.183546\varepsilon$$

## DISCUSSION

The solvation energy of a solute in a solvent is equal to the difference between the total energy of the solute in the solvent and the total energy of the solute in a vacuum. The solvents in order of increasing average solvation energy are: acetone, ethanol, THF, and water. Generally, the average solvation energy increases as the dielectric constant of the solvent increases. The only exception found was THF, which has a dielectric constant of only 7.52 but a mean solvation energy of -23.0 kJ/mol.

There is a weak negative correlation (mean $R^2 = 0.4789$) between the dipole moment of the solute and the solvation energy. There is a modest negative correlation (mean $R^2 = 0.8405$) between the PSA of the solute and the solvation energy. There is almost no correlation (mean $R^2 = 0.2432$) between the volume of the solute and the solvation energy. These correlations are valid for all of the solvents assessed with the exception of the vacuum. There is a modest-strong positive correlation (mean $R^2 = 0.8802$) between the dielectric constant of the solvent and the solvation energy, and this correlation is valid for all solutes assessed.

Water may have a significantly lower correlation than the other solvents for all the variables because it is an unusual substance.[2] Aside from this, water also has several chemical and physical properties that are much different from those of other substances.

None of the variables examined had a high enough $R^2$-value for the solvation energy to be predicted just by any one variable. However, the solvation energy can be estimated by using the function as stated in the **Results**:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = 2.791617\mathbf{p} - 0.66416A - 0.22056V + 0.183546\varepsilon$$

This equation can predict the solvation energy of a solution moderately well, with a mean percentage error of 22.21%. Solutions water as the solvent have a significantly higher percentage

error than solutions in other solvents. The mean percentage error for water solutions is 61.37%, while the mean percentage error for other solutions is only 9.15%. Without water, this function is much more accurate and may be reliable. However, this function should not be used to predict solvation energies for aqueous solutions. If water is removed from the solvents, this function can be adjusted to be even more accurate:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = 2.62334\mathbf{p} - 0.61327A - 0.18458V + 0.07431\varepsilon$$

This adjusted function, excluding water as a solvent, returns a mean percentage error of a mere 5.45%.

Strangely, although the dipole moment of the solute has a negative correlation with the solvation energy, solvation energy estimated by the equation is a function of the dipole moment multiplied by a positive constant.

## CONCLUSION

The solvation energy of a solution is affected by several factors. The variables that impact the solvation energy, in increasing order of their impact, are volume, dipole moment, PSA, and dielectric constant. The first three have a negative correlation with solvation energy, while the last has a positive correlation with it. The solvation energy calculated using Density Functional B3LYP 6-31G* can be predicted using a linear function derived by the least squares method:

$$\Delta H_{solv} = \Delta H_{solv}(p, A, V, \varepsilon) = 2.791617\mathbf{p} - 0.66416A - 0.22056V + 0.183546\varepsilon$$

where ΔHsolv is the solvation energy in kilojoules per mole; **p** is the dipole moment of the solute in debye; A is the polar surface area of the solute in square angstrom units; V is the volume of the solute in cubic angstrom units; and ε is the dielectric constant of the solvent.

Polar solutes dissolve better in polar solvents, and non-polar solutes dissolve better in non-polar solvents. Solutes with low dipole moments are classified as non-polar and those with high dipole moments are classified as polar. Solvents with low dielectric constants are classified as non-polar and those with high dielectric constants are classified as polar. Therefore, solutes with low dipole moments dissolve require less energy to dissolve in solvents with low dielectric constants and vice versa.[1]

## REFERENCES

[1] "Solvents." *University of Southern Maine*.

<http://usm.maine.edu/~newton/Chy251_253/Lectures/Solvents/Solvents.html>.

[2] "Water Properties: Water Science for Schools: Physical and Chemical Water Properties."

*USGS Georgia Water Science Center - Home Page*.

<http://ga.water.usgs.gov/edu/waterproperties.html>.

# APPENDIX I – MOLECULAR STRUCTURES OF SOLUTES

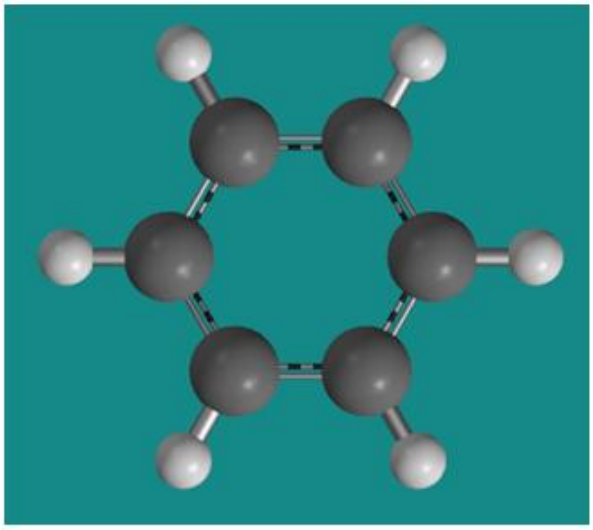


Figure 6. Benzene.

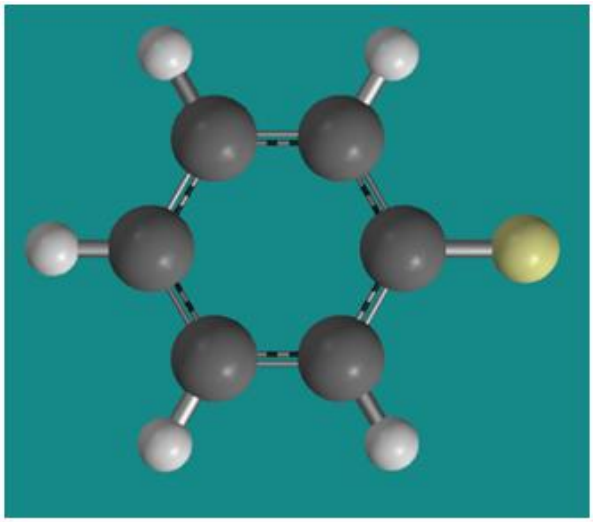


Figure 7. Fluorobenzene.

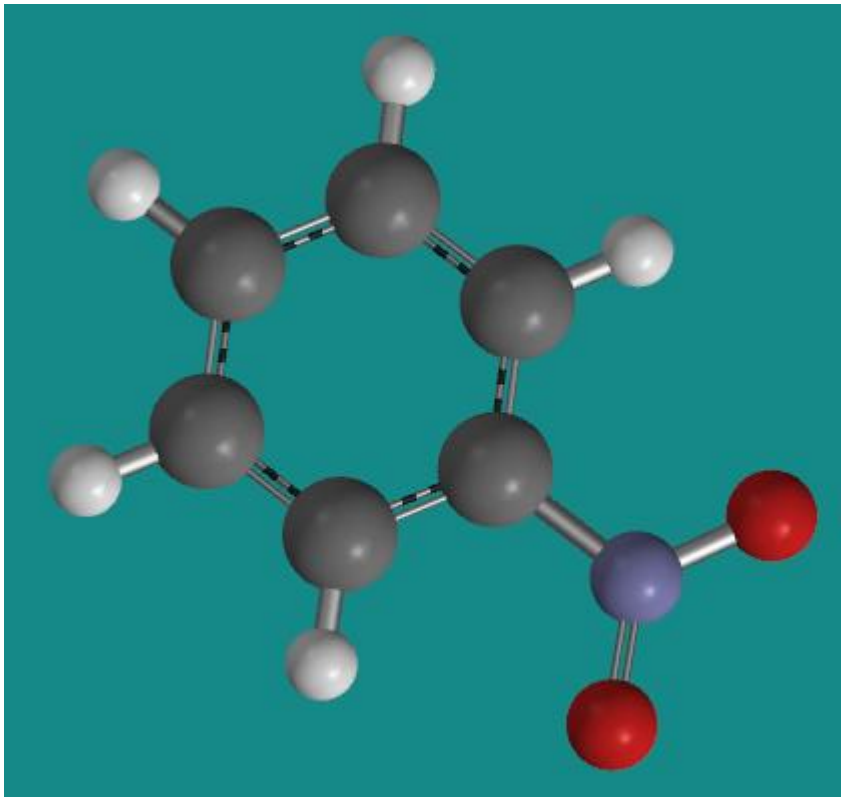


**Figure 6.** Nitrobenzene.

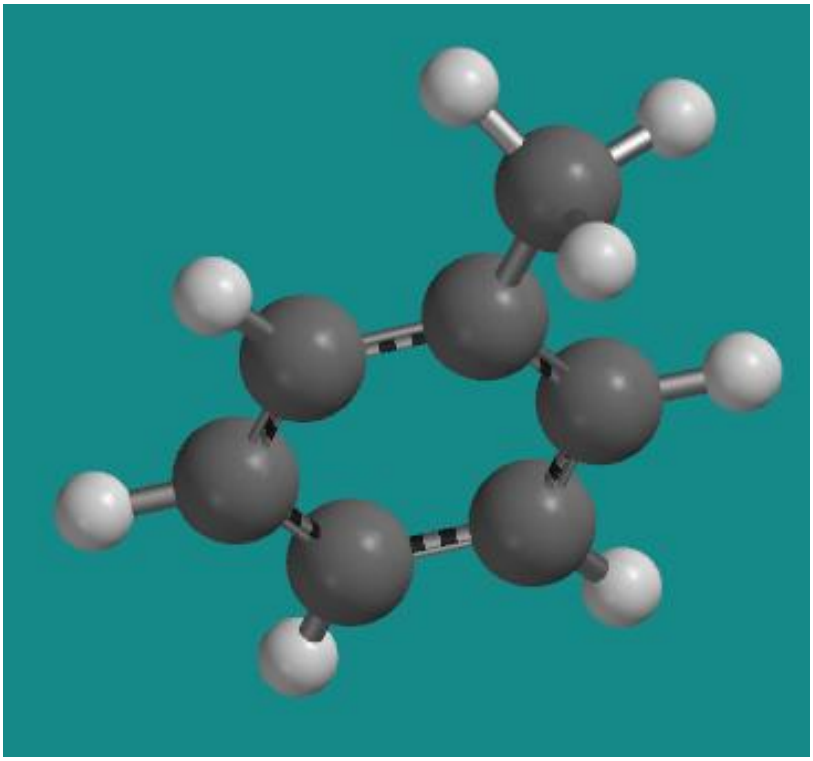


**Figure 7.** Toluene.

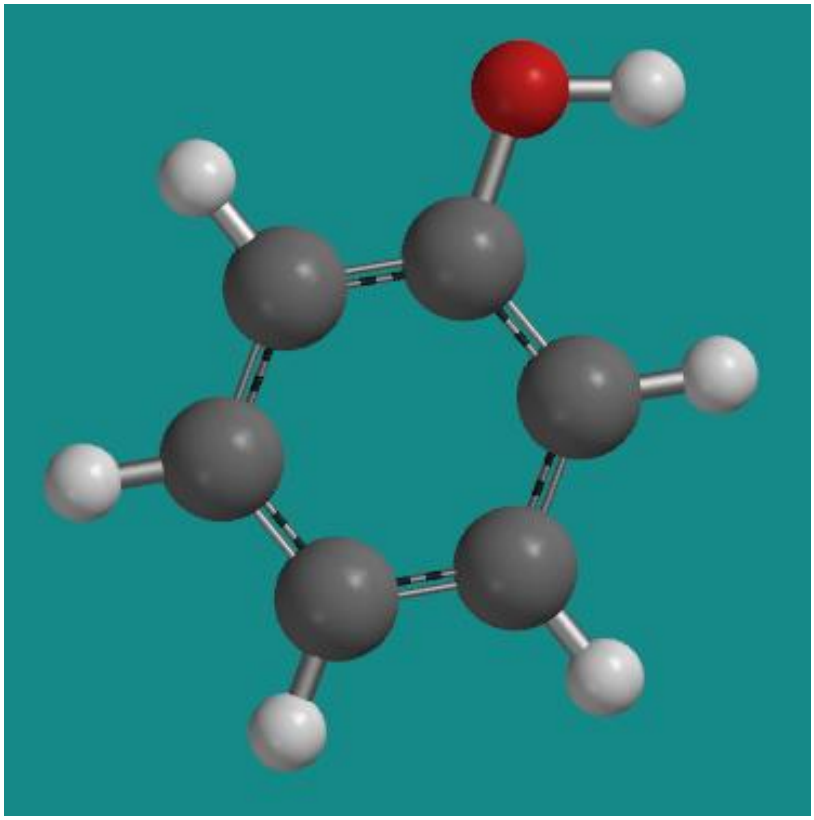
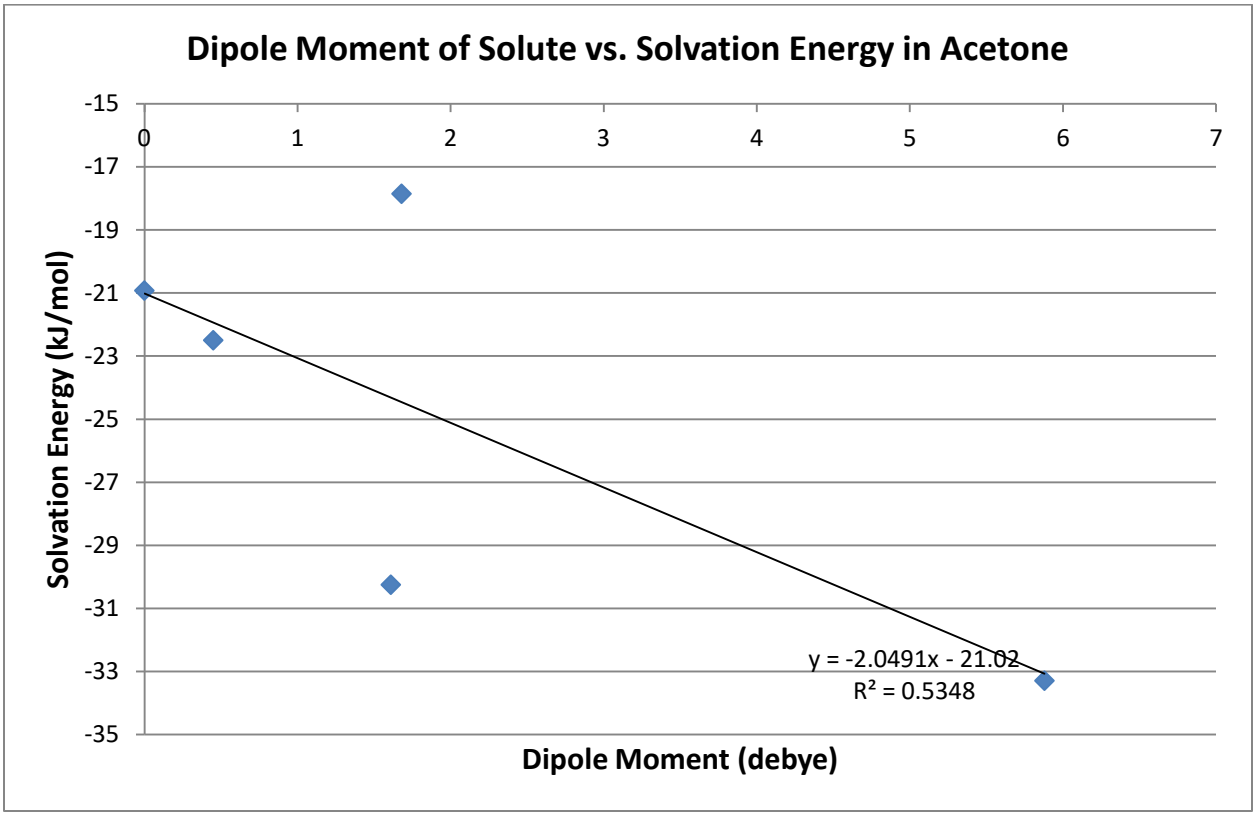
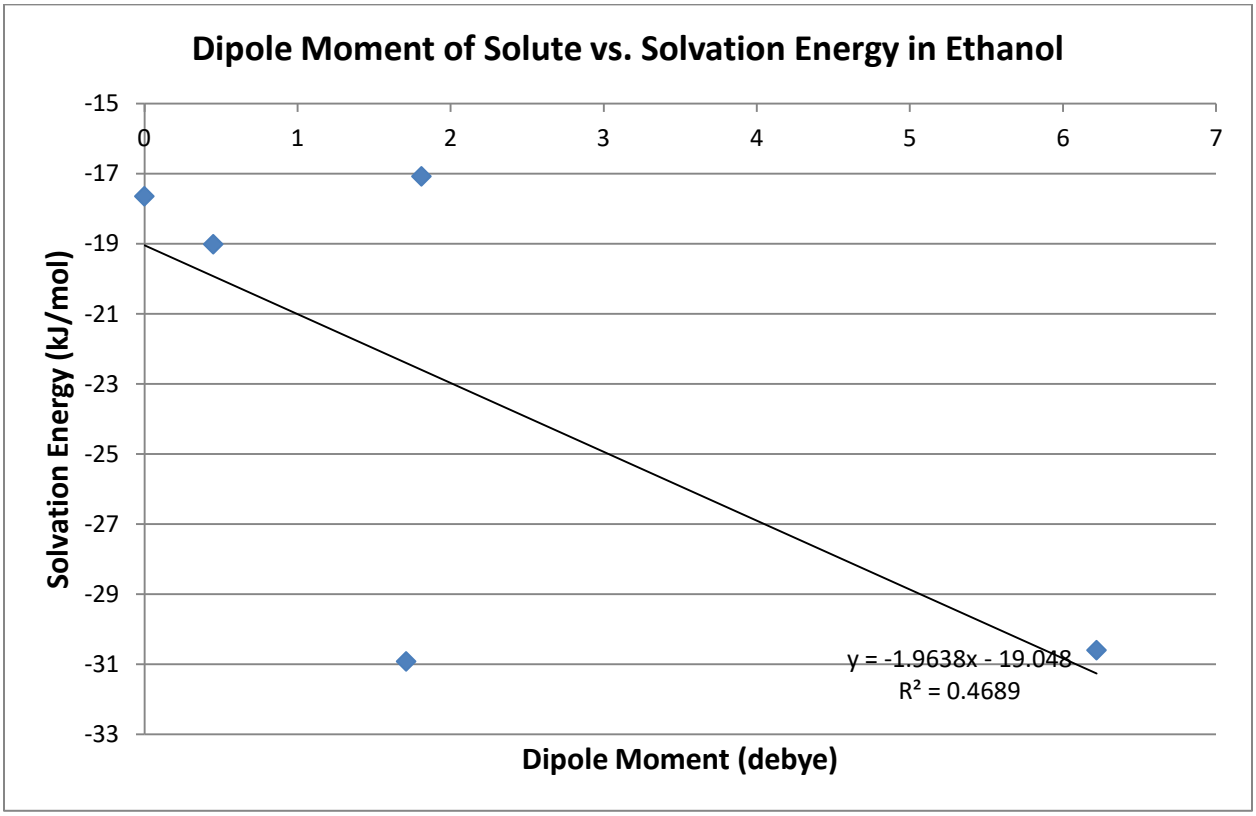
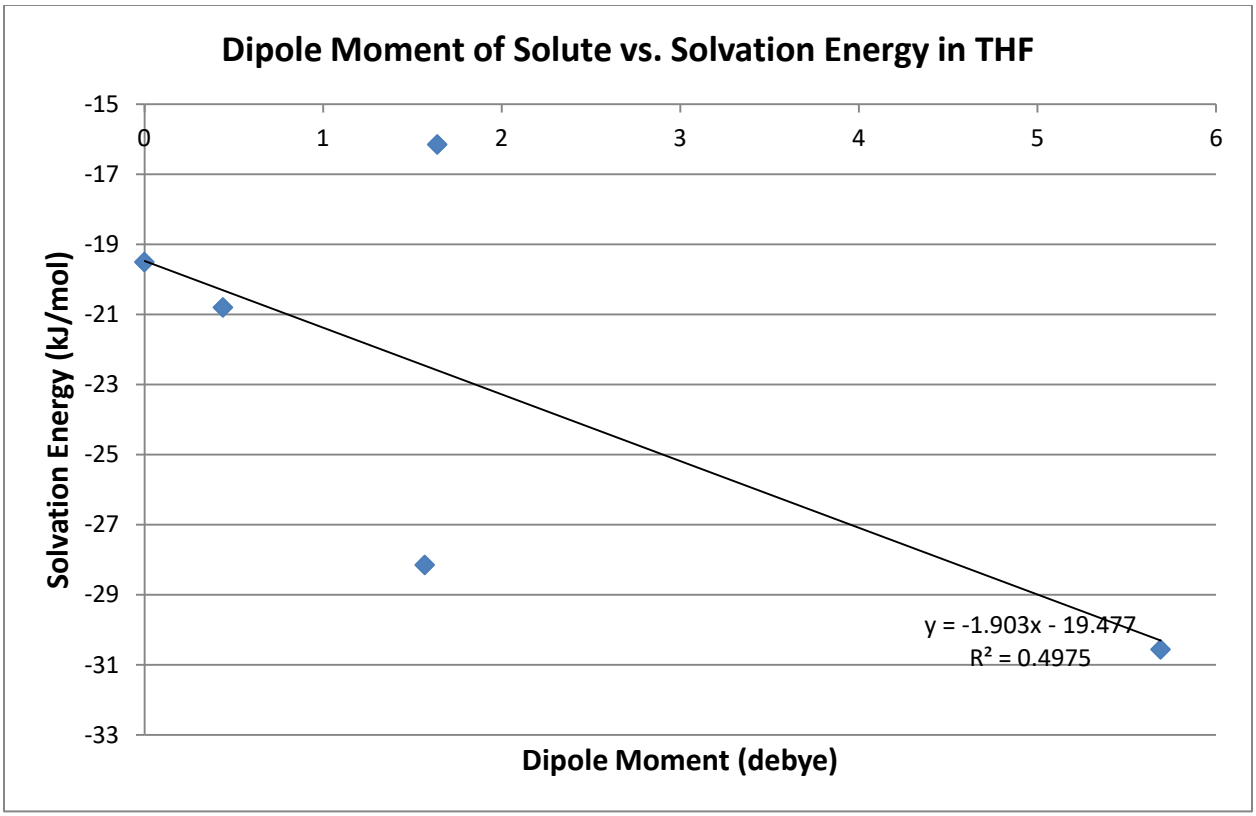


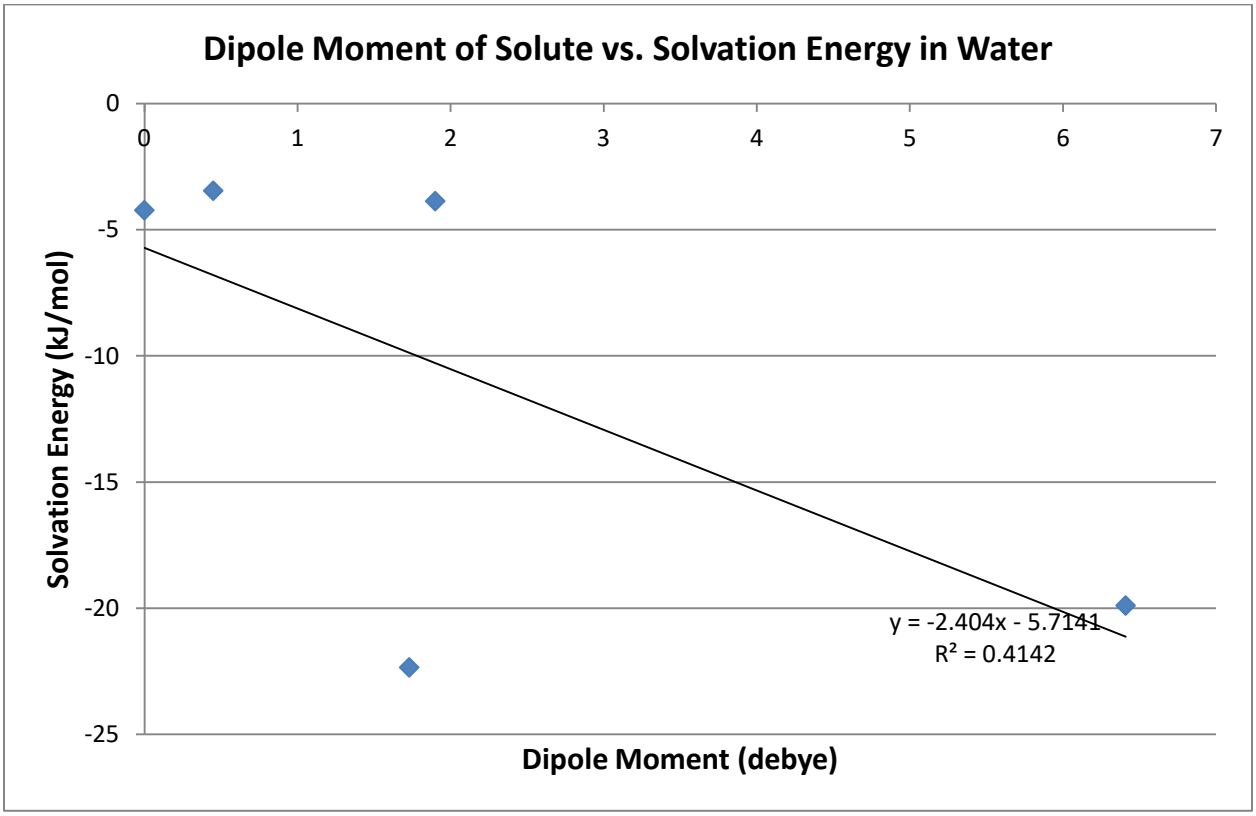
**Figure 8.** Phenol.

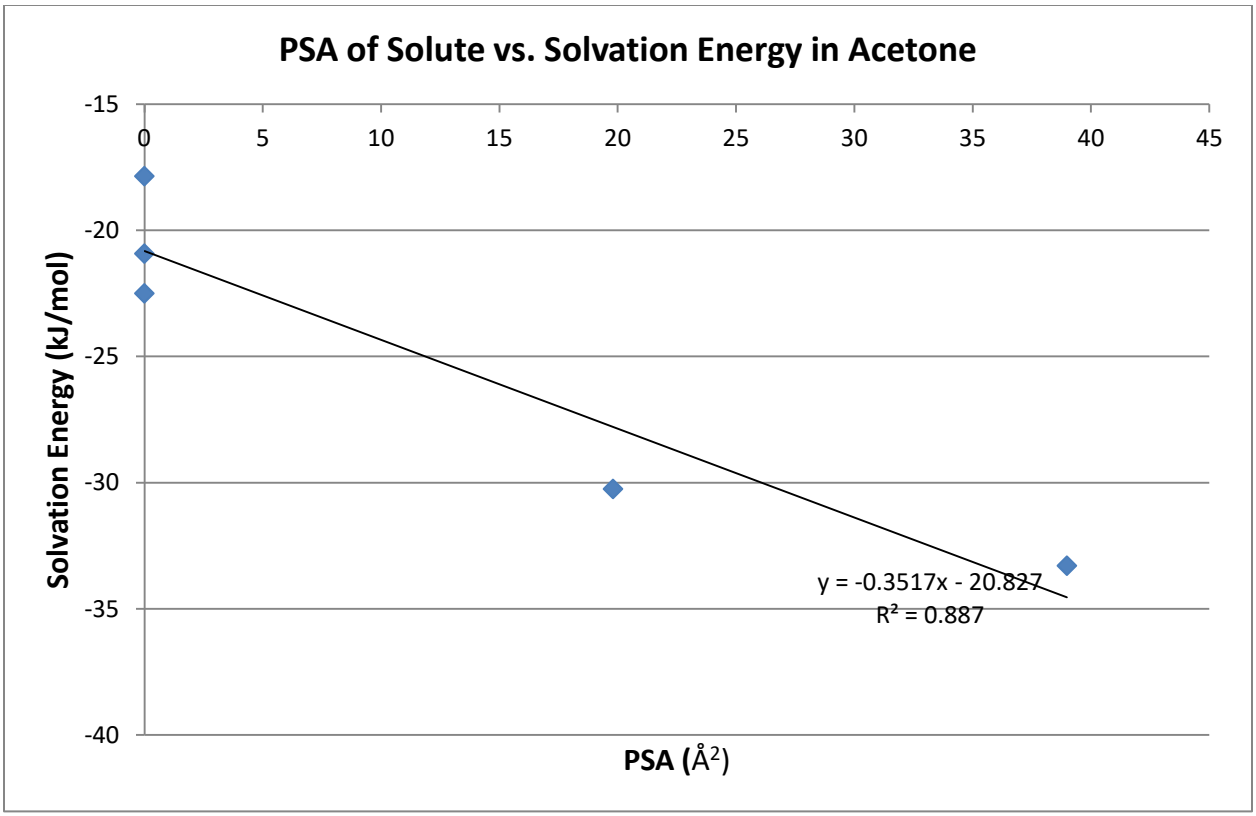
## APPENDIX II - PLOTS

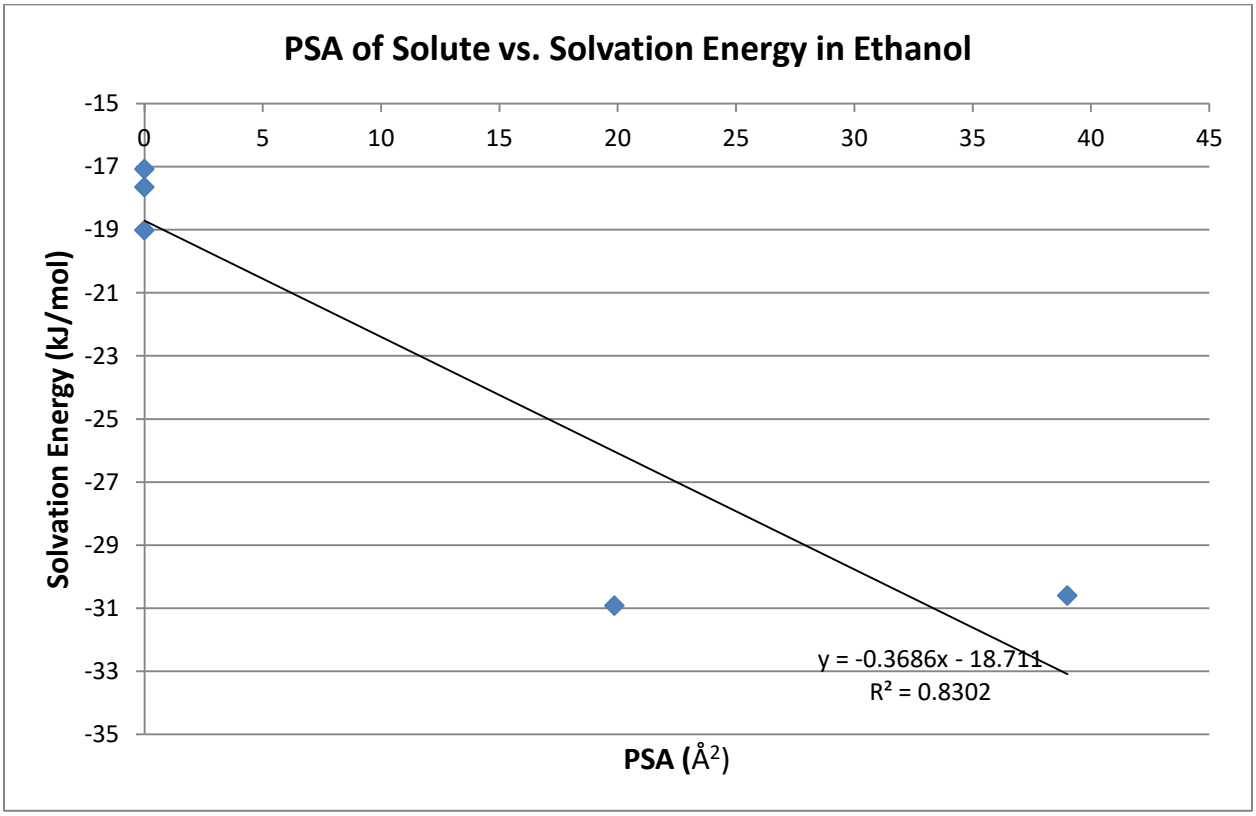


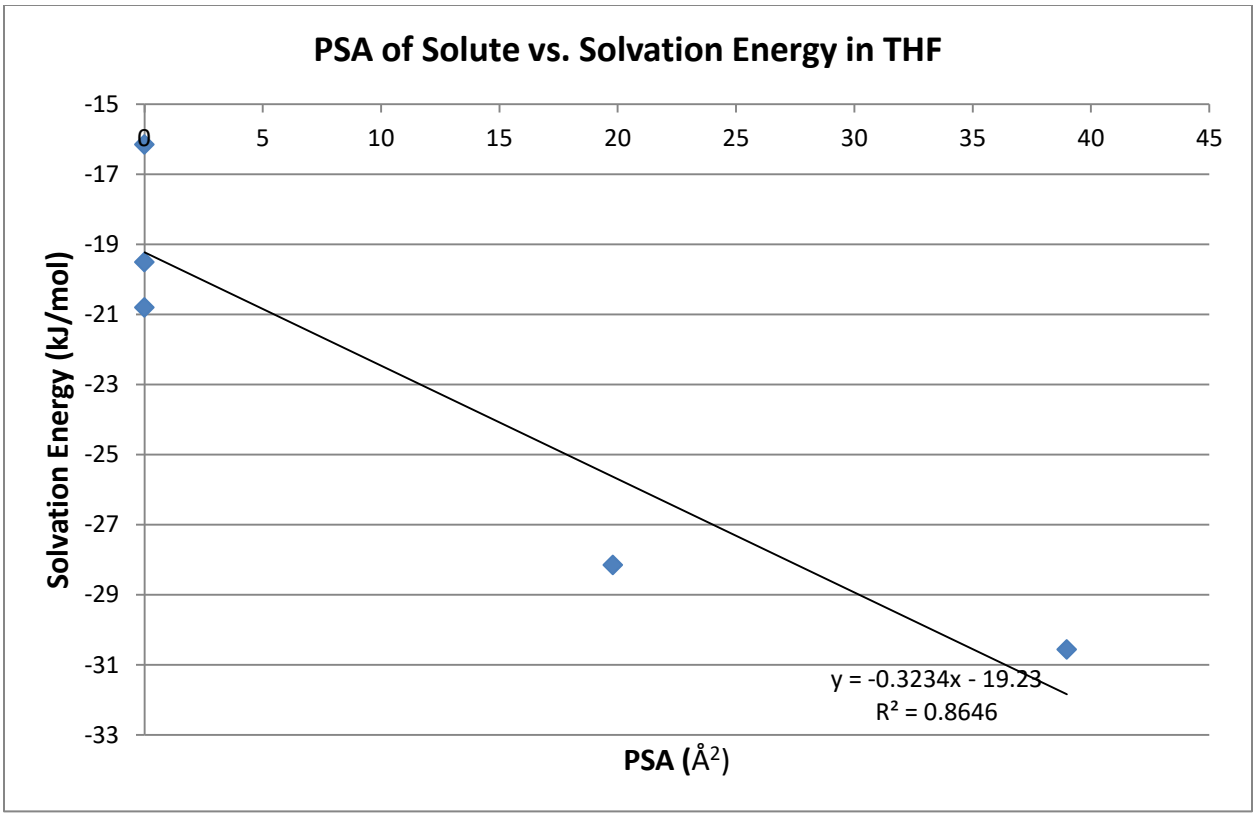



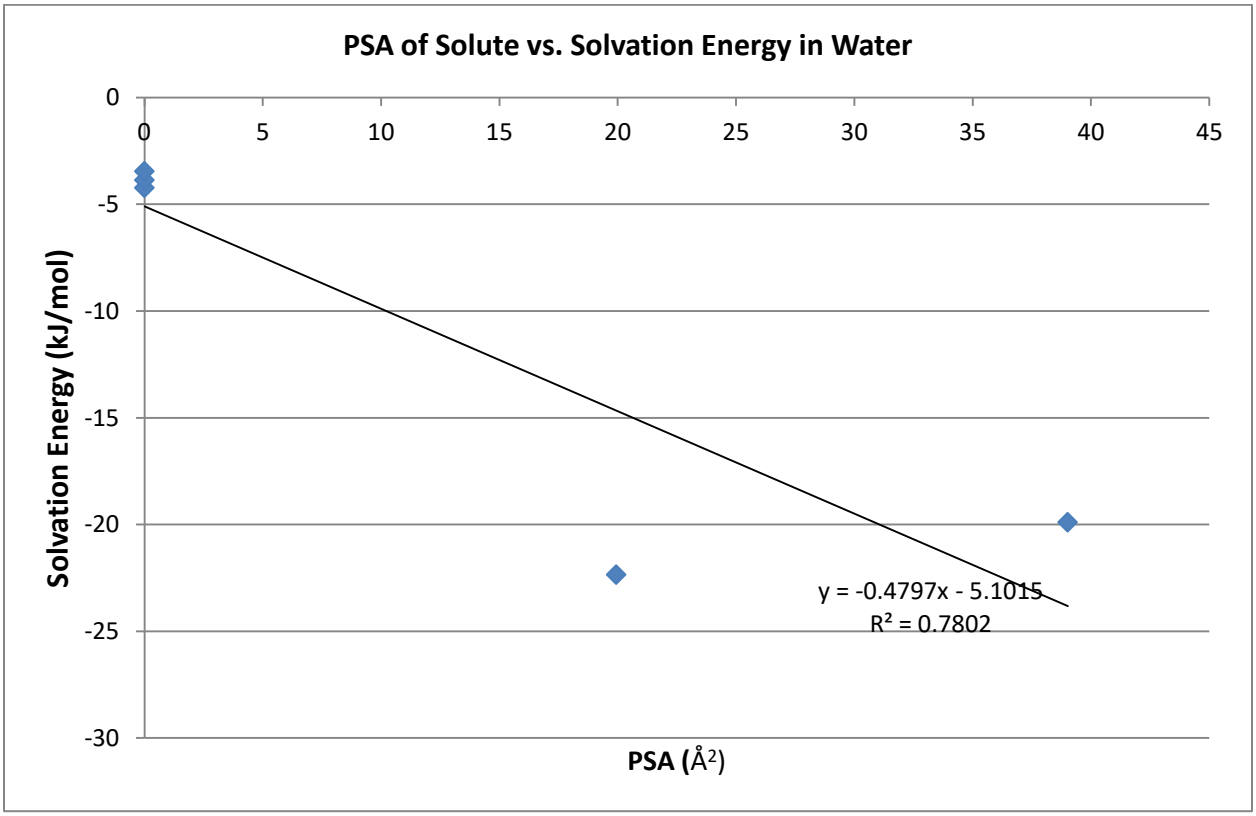

Dipole Moment of Solute vs. Solvation Energy in THF
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
0
1
2
3
4
5
6
y = -1.903x - 19.477
R² = 0.4975
Dipole Moment (debye)

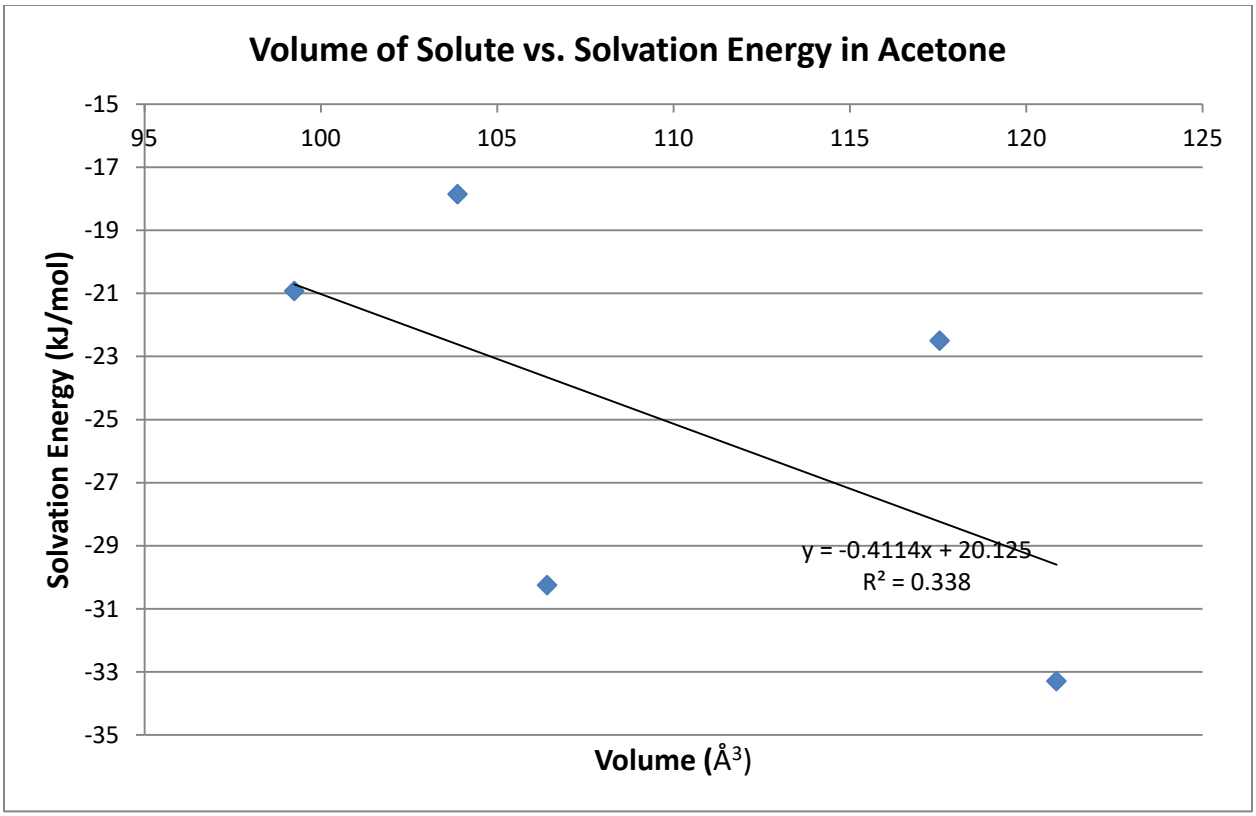

Dipole Moment of Solute vs. Solvation Energy in Water
Solvation Energy (kJ/mol)
0
-5
-10
-15
-20
-25
0
1
2
3
4
5
6
7
y = -2.404x - 5.7141
R² = 0.4142
Dipole Moment (debye)

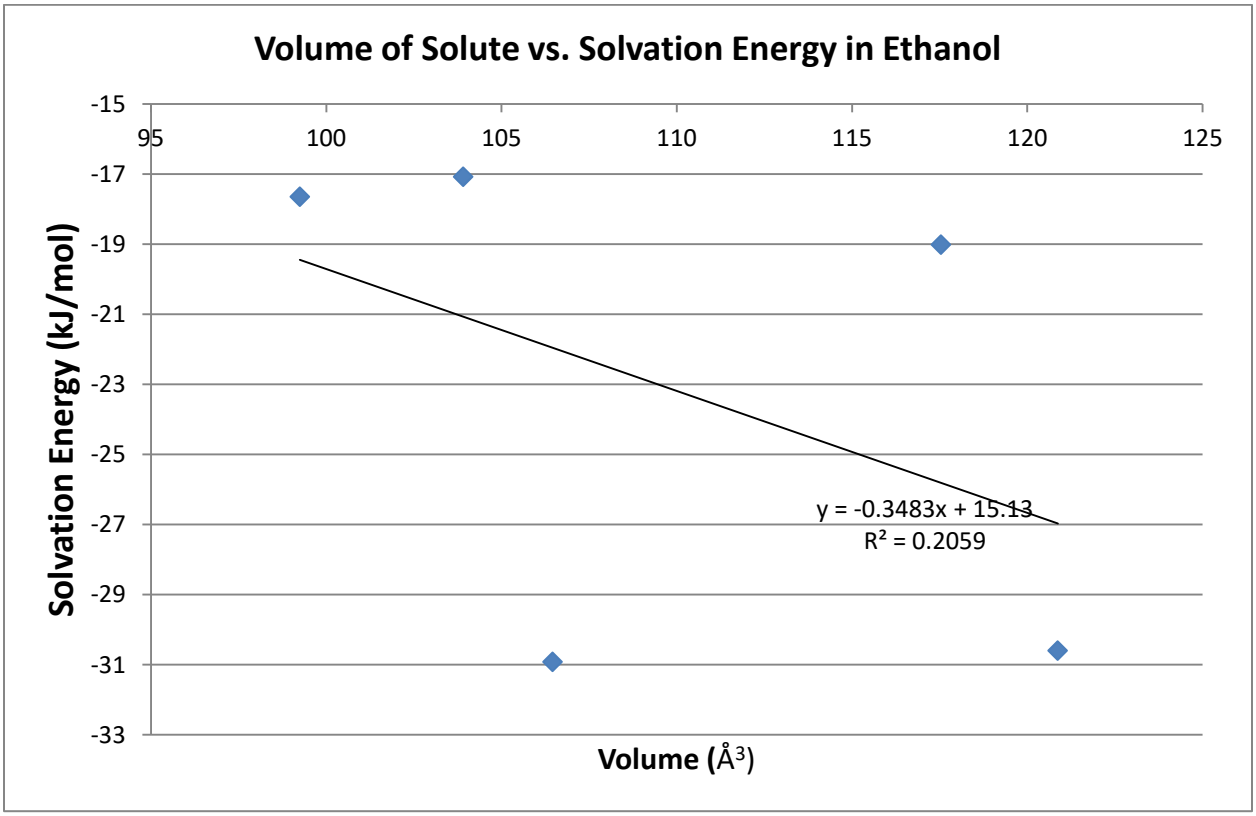

PSA of Solute vs. Solvation Energy in Acetone
Solvation Energy (kJ/mol)
-15
-20
-25
-30
-35
-40
0
5
10
15
20
25
30
35
40
45
y = -0.3517x - 20.827
R² = 0.887
PSA (Å²)

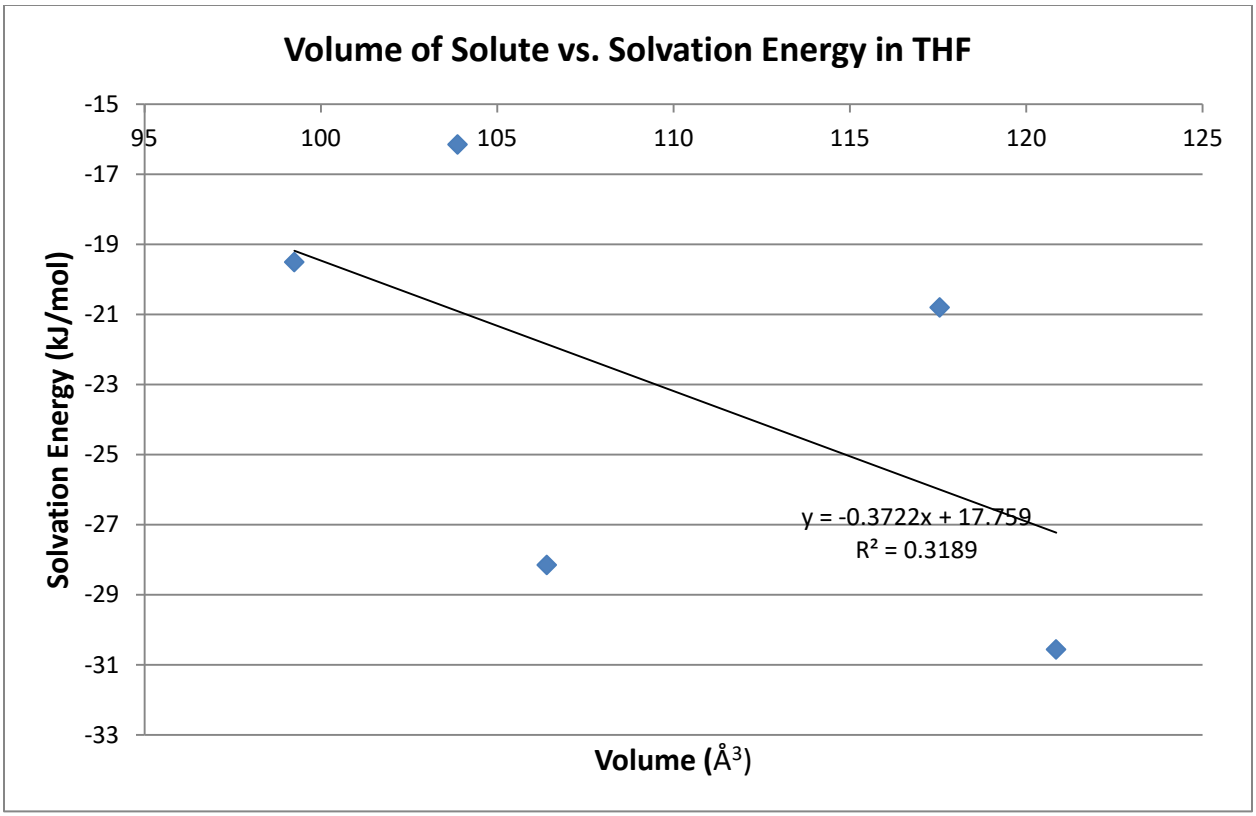

PSA of Solute vs. Solvation Energy in Ethanol
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
-35
0
5
10
15
20
25
30
35
40
45
y = -0.3686x - 18.711
R² = 0.8302
PSA (Å²)

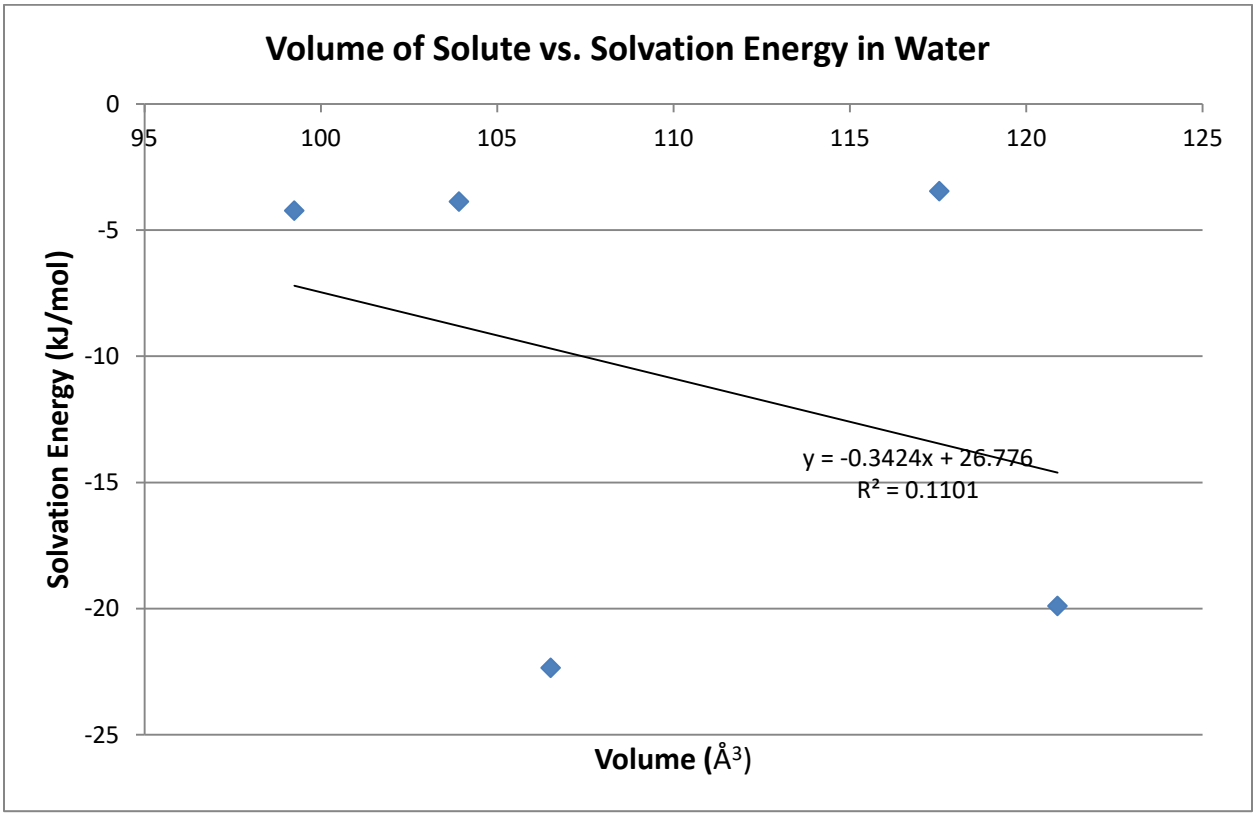

PSA of Solute vs. Solvation Energy in THF
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
0
5
10
15
20
25
30
35
40
45
y = -0.3234x - 19.23
R² = 0.8646
PSA (Å²)

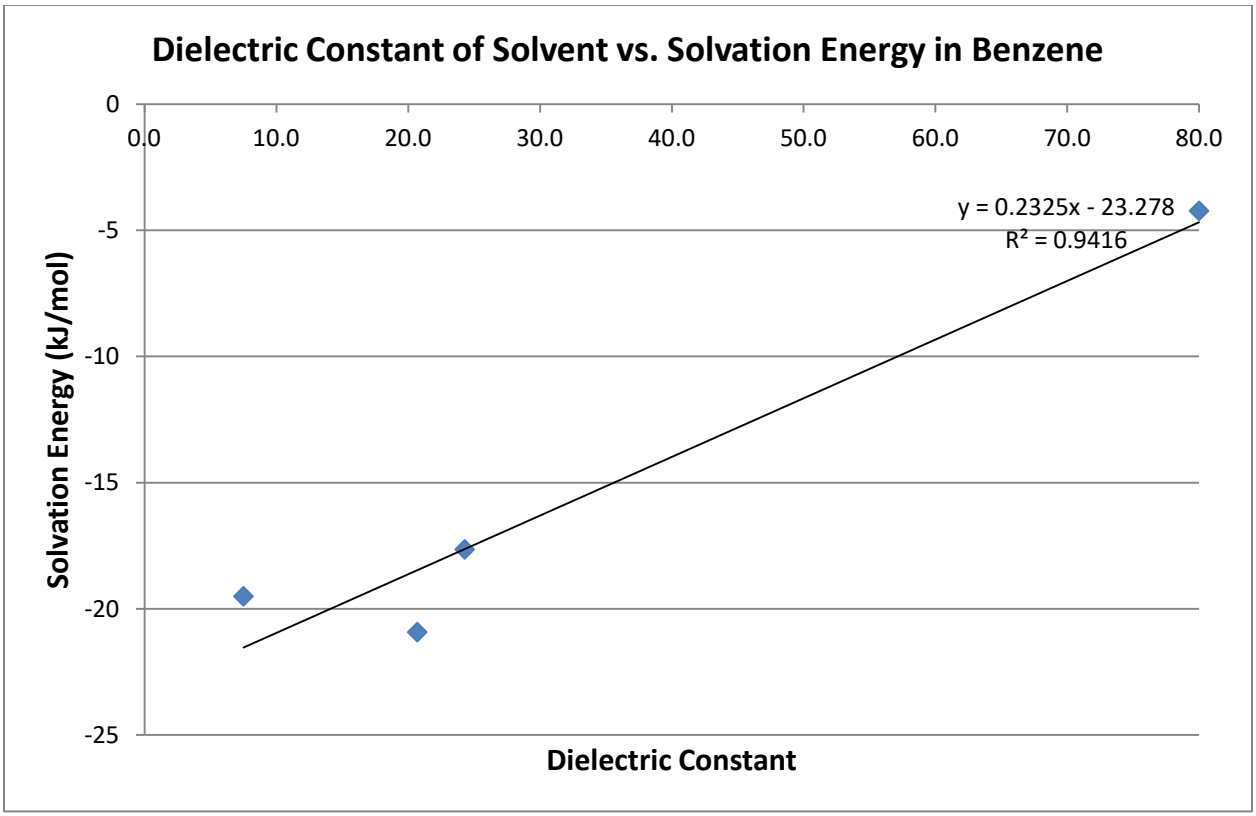

PSA of Solute vs. Solvation Energy in Water
Solvation Energy (kJ/mol)
0
-5
-10
-15
-20
-25
-30
0
5
10
15
20
25
30
35
40
45
y = -0.4797x - 5.1015
R² = 0.7802
PSA (Å²)

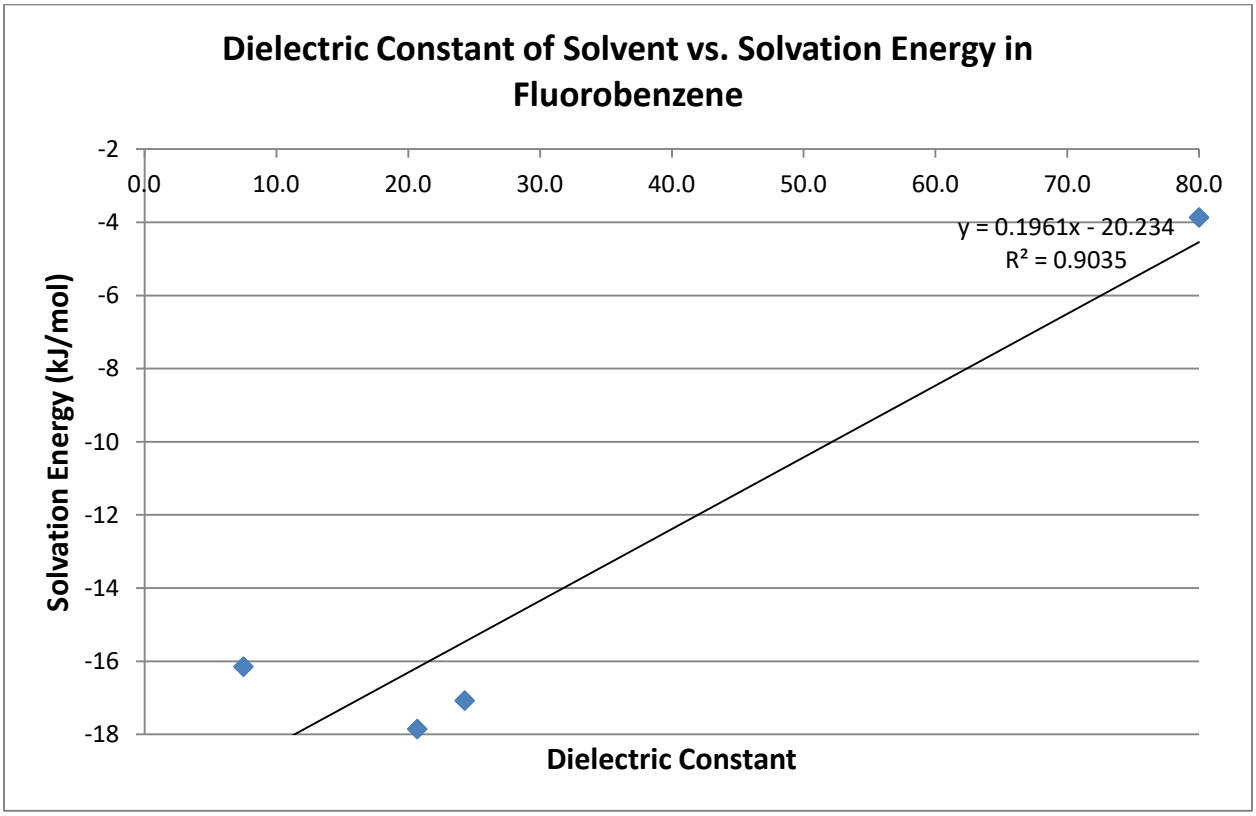

Volume of Solute vs. Solvation Energy in Acetone
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
-35
95
100
105
110
115
120
125
y = -0.4114x + 20.125
R² = 0.338
Volume (Å³)

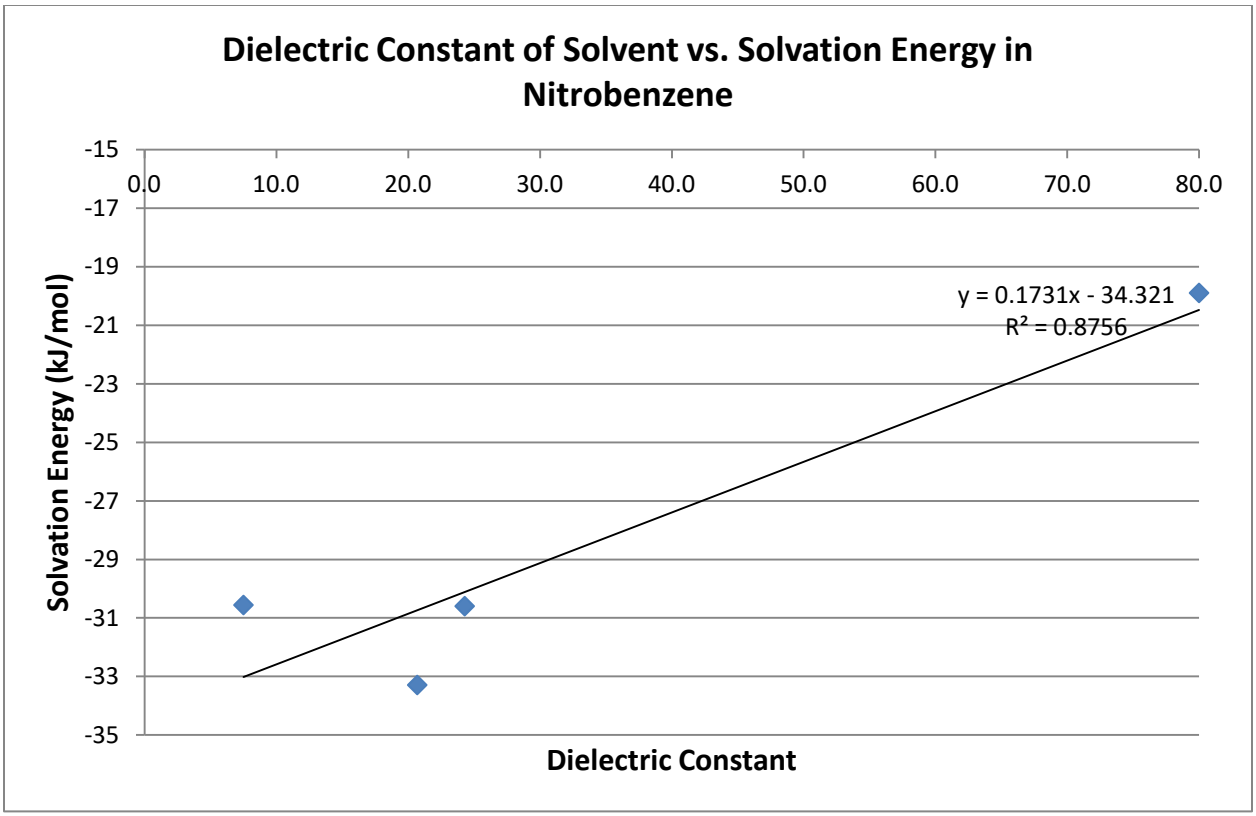

Volume of Solute vs. Solvation Energy in Ethanol
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
95
100
105
110
115
120
125
y = -0.3483x + 15.13
R² = 0.2059
Volume (Å³)

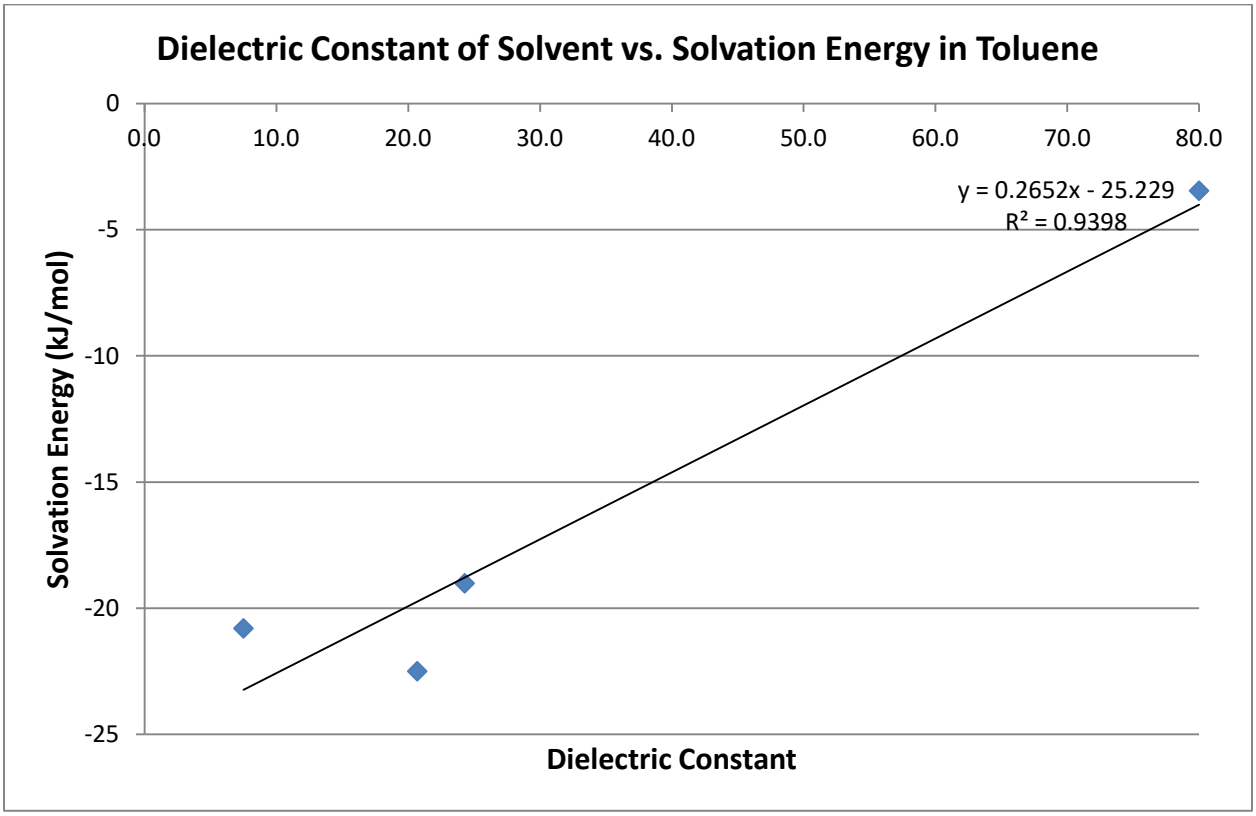

Volume of Solute vs. Solvation Energy in THF
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
95
100
105
110
115
120
125
y = -0.3722x + 17.759
R² = 0.3189
Volume (Å³)

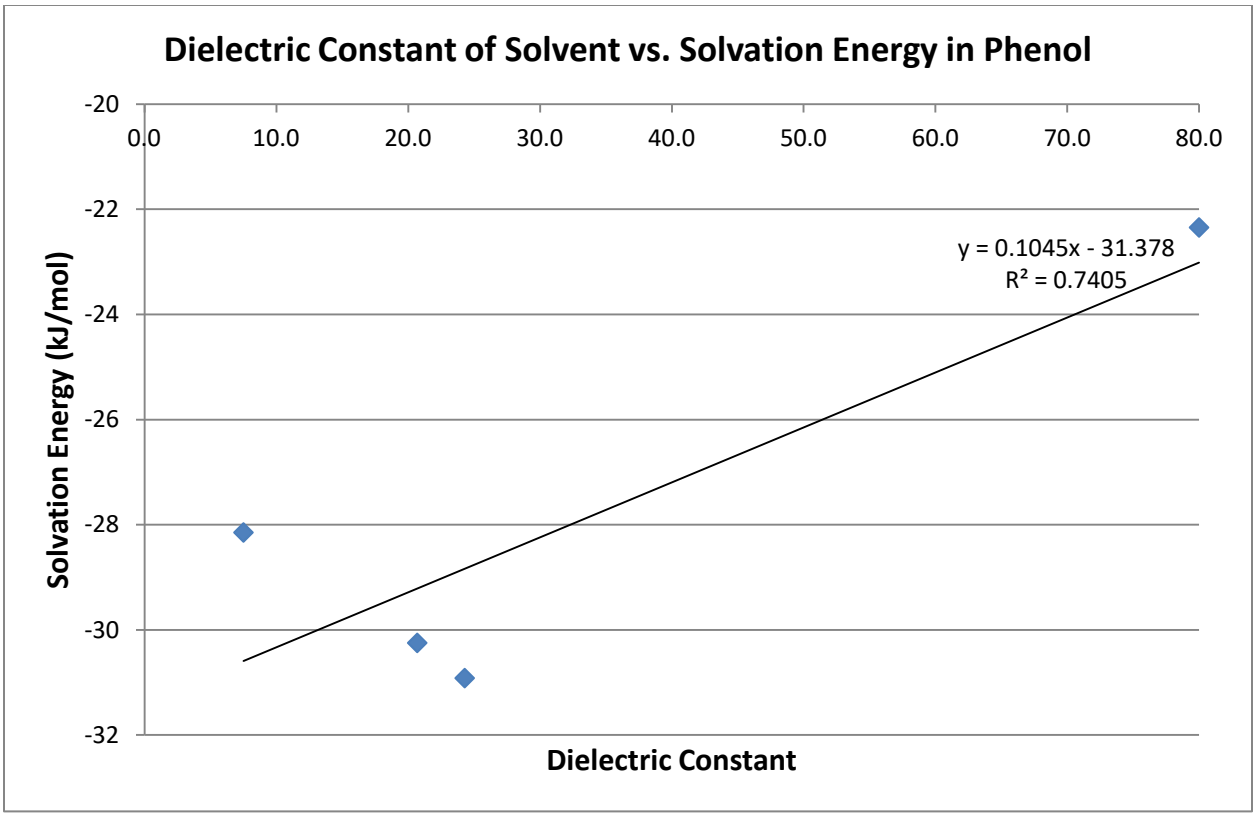

Volume of Solute vs. Solvation Energy in Water
Solvation Energy (kJ/mol)
0
-5
-10
-15
-20
-25
95
100
105
110
115
120
125
y = -0.3424x + 26.776
R² = 0.1101
Volume (Å³)


Dielectric Constant of Solvent vs. Solvation Energy in Benzene
0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
-5
-10
-15
-20
-25
y = 0.2325x - 23.278
R² = 0.9416
Solvation Energy (kJ/mol)
Dielectric Constant


Dielectric Constant of Solvent vs. Solvation Energy in Fluorobenzene
-2
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
-4
-6
-8
-10
-12
-14
-16
-18
y = 0.1961x - 20.234
R² = 0.9035
Solvation Energy (kJ/mol)
Dielectric Constant


Dielectric Constant of Solvent vs. Solvation Energy in Nitrobenzene
Solvation Energy (kJ/mol)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
-35
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
y = 0.1731x - 34.321
R² = 0.8756
Dielectric Constant


Dielectric Constant of Solvent vs. Solvation Energy in Toluene
Solvation Energy (kJ/mol)
0
-5
-10
-15
-20
-25
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
y = 0.2652x - 25.229
R² = 0.9398
Dielectric Constant


Dielectric Constant of Solvent vs. Solvation Energy in Phenol
-20
-22
-24
-26
-28
-30
-32
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
Solvation Energy (kJ/mol)
Dielectric Constant
y = 0.1045x - 31.378
R² = 0.7405