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| Experiment 2 – Partial Molar Volumes |
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| Max Shi – I pledge my honor that I have abided by the Stevens Honor System.  11-15-2021 |

# Abstract

This experiment examines the concept of partial molar volume of components of a binary solution with the example of a methanol-water solution. The densities of solutions with varying concentrations of methanol and water were measured with a densometer, and the molalities of the components combined with this density measurement were used to calculate an apparent molar volume of methanol. A regression was used to obtain functions for the partial molar volumes of both methanol and water over the experimental range of molalities. A trend was identified in the 1-5 molal methanol range, where the partial molar volumes reversed the overall trend seen in the data – this was explained with a discussion of intramolecular forces.

# Introduction

In this experiment, the concept of partial molar volume will be explored with binary solutions of different concentrations of methanol and water. When two solutions of different compounds are mixed, their total volume is not necessarily the sum of the two volumes of the solutions added. In solution, two different molecules can interact, increasing or decreasing the total volume of the solution depending on attractive or repulsive forces, and how well the molecules pack together.

Partial molar volume is defined as:

Equation : Definition of Partial Molar Volume

Essentially, this equation is representing the change in volume as the amount of moles of the molecule change. Thus, to obtain the total volume, we add two terms together with the change in moles. As volume is a state function, and the path from one point to another point does not matter, this equation can be written as seen below:

Equation : Expression of Total Volume with Partial Volumes

Deriving an equation for the partial molar volumes of these two solutions requires a few substitutions. By redefining this equation with the volume of pure water and substituting a term for the “apparent molar volume” of methanol, equation 3 is obtained.

Equation : Expression of Apparent Molar Volume of Methanol

Substituting V for the total volume of methanol and water over the density of this binary solution, and assuming 1 kilogram of pure water is in the solution, yields the following term for phi.

Equation : Calculation of Apparent Molar Volume of Methanol

Where d0 is the density of pure water, d is the density of the solution, and m is the molality of methanol. Differentiating equation 3 with respect to methanol and substituting into equation 1 yields the following expression for the partial molar volume of methanol in water.

Equation : Expression for Partial Molar Volume of Methanol

Rearrangement of the result of equation 2 also yields the following equation for the partial molar volume of pure water in methanol.

Equation : Expression of Partial Molar Volume of Water

In this experiment, the densities of different water-methanol solutions will be calculated along with the molality of methanol, such that an equation for phi can be established. Thus, an expression for the partial molar volumes of both water and methanol can also be derived.

# Experimental

In this experiment, to find an equation for phi, the density of many different binary solutions must be calculated, and the equation can be estimated. Thus, 14 solutions as seen below will be prepared, and the mass of the smaller mole fraction in the solution will be measured to calculate the mole fraction of both components, which is needed for molality. The weight of the solution will also be measured after both components have been combined. Finally, the density of each solution will be measured with a densometer. Each solution will be saved in a test-tube in case a trial needs to be repeated. After each trial, the densometer will be rinsed 3 times with DI water. All waste will go into the organic waste tank.

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| --- | --- |
| Water, mL | Methanol, mL |
| 50 | 0 |
| 45 | 1 |
| 45 | 2 |
| 30 | 2 |
| 25 | 3 |
| 30 | 5 |
| 20 | 5 |
| 25 | 10 |
| 18 | 10 |
| 15 | 15 |
| 10 | 15 |
| 6 | 20 |
| 3 | 25 |
| 0 | 30 |

Figure : Volumes of Components of Experimental Binary Solutions

# Results

During the experiment, along with the density of each solution, the masses of the methanol and combined solution were also recorded, such that the mass of both methanol and pure water were known. These data points are in the table below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Volume of Water (mL)** | **Volume of Methanol (mL)** | **Mass of Water (g)** | **Mass of Methanol (g)** | **Density (g/cm^3)** |
| 50 | 0 | 50.148 | 0 | 0.999 |
| 45 | 1 | 44.923 | 0.787 | 0.9958 |
| 45 | 2 | 45.044 | 1.606 | 0.9927 |
| 30 | 2 | 30.493 | 1.607 | 0.9904 |
| 25 | 3 | 25.209 | 2.401 | 0.9842 |
| 30 | 5 | 30.032 | 4.038 | 0.9785 |
| 20 | 5 | 20.046 | 4.044 | 0.9712 |
| 25 | 10 | 24.911 | 8.149 | 0.9579 |
| 18 | 10 | 17.948 | 8.142 | 0.9478 |
| 15 | 15 | 14.575 | 12.305 | 0.9237 |
| 10 | 15 | 9.89 | 12.31 | 0.9046 |
| 6 | 20 | 5.826 | 16.054 | 0.8671 |
| 3 | 25 | 2.584 | 20.266 | 0.8250 |
| 0 | 30 | 0 | 24.179 | 0.7921 |

Figure : Experimental Data of Measurements from Experimental Solutions

Using these masses, the molality of methanol in the solutions was calculated and substituted into equation 4 along with the measured densities to obtain values for phi, also known as the apparent molar volume. The plot is shown below.

Figure : Plot of Apparent Molar Volume against Molality of Methanol

These points have characteristics of an inverse function as well as a polynomial, so combining those with an added constant in a regression yields the following equation and derivative, with the following plot:

Equation : Regression Equation and Derivative for Apparent Molar Volume

Figure : Plot of Apparent Molar Volume against Molality of Methanol with Regression

Finally, substituting this equation and derivative for equations 5 and 6 to recover partial molar volumes, and plotting molality against these partial molar volumes yields the following plot.

Figure : Plot of Partial Molar Volumes against Molality of Methanol

# Discussion

While examining the measured values of densities of the different solutions, there is a trend for the density to go down as the concentration of methanol goes up, approaching the density of pure methanol as the solution is mostly methanol. This trend seems to be consistent with the measured and actual values of the partial molar volume of water and methanol, which are 1.000 and 0.7914 g/mL, respectively. It also makes sense that as the solution is composed more of one component, the density approaches the density of that pure component in a sense of weighted average. However, be examining partial molar volumes through the calculations around the apparent molar volume of methanol, the data highlights a discrepancy that suggests the density cannot be calculated with a simple weighted average.

After calculating the partial molar volumes of each component of the solution, an interesting trend was the decrease of partial molar volume of methanol before increasing, and an increase in partial molar volume of water before ultimately decreasing, both around the 1-5 molal methanol range. At this molality, there is a large excess of water, and a relatively small amount of methanol. However, this trend can be explained when considering the interactions between small amounts of methanol with large excesses of water. As more methanol is added to the solution, some methanol molecules are able to interact with water molecules instead of water molecules interacting with each other. This causes methanol to disrupt the packing of the water molecules, which increases the partial molar volume of water, as they cannot pack in the most efficient manner. Methanol, on the other hand, being bulkier than water, uses water to take up more of the unused space that would result from pure methanol, while fitting into the unused space of water. Thus, the partial molar volume of methanol would decrease over this range.

Also noticeable is the same effect seen with large concentrations of methanol compared to water. The partial molar volume of methanol becomes greater than the molar volume of pure methanol, as the water has now disrupted the interactions between methanol molecules. Furthermore, because water is a much smaller molecule than methanol, it can fit better in the unused space leftover from methanol-methanol interactions, thus drastically lowering its partial molar volume to 12.76 mL/mol.

# Appendix

1. Full experimental datasheet and plots 