Investigating the relationship between volume contraction and carbon chain length in alcohols

Introduction:

Volume contraction is a phenomenon where the total volume of a mixture is less than that of its original constituent fluids. Alcohols and water both have hydrogen atoms bonded to oxygen atoms causing the hydrogen to acquire a significant positive net dipole moment due to a large electronegativity difference between hydrogen and oxygen. This principle causes hydrogen bonding which allows for a strong dipole-dipole attraction between molecules. Hydrogen bonding doesn't limit itself to alike particles, so hydrogen bonds can exist between water and the alcohol molecules. Pure liquid water exists as a cluster of up to 30 water molecules held through hydrogen bonds, forming a loose structure, whereas pure alcohol is similar but exists in smaller clusters. When water and alcohols are mixed, they form hydrogen bonds between themselves. This leads to the disruption of the loose structure of water, leaving the molecules to collapse and become packed closer together and in turn cause a macroscopic decrease in volume and increase in density of the mixture.

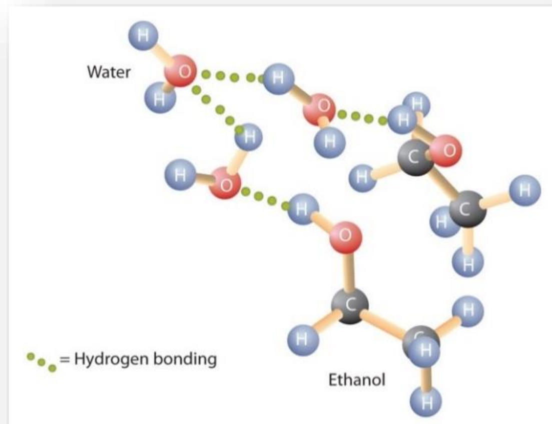


Figure 1. Hydrogen bonds between water and ethanol molecules

This phenomenon, in practice, has vital applications in real life scenarios: storage of alcohols, winemaking, pharmaceutical dosage forms, and more. However, one of the applications of this phenomenon takes a large significance in my life: alcohol and its absorption in the blood stream through alcoholic beverages and medicines. This volume contraction may have vital consequences in health with links to congestive heart failure to pulmonary heart disease[2]. With alcohol taking the life of my grandfather, I have come to take sincere interest in how alcohols of different chain length affect volume contraction, if at all. Further, as drawing comparisons between the different compounds in the homologous series of alcohol has not been explored for volume contraction, this investigation is especially intriguing. While it may not be possible for me to explore alcohol volume contraction for blood, this experiment can be done with water, laying the foundation for future research into volume contraction for blood. Thus, the focus of my experiment can be stated with the research question: **How does a change in alcohol carbon chain length affect the volume contraction in a mixture with water?**

Hypothesis:

Based on the properties of alcohols and the principles of volume contraction, I predict that with an increase in carbon chain length of alcohol there will be a decrease in the volume contraction experienced. Even though there are hydrogen bonds present at the O-H group of the alcohol, when the length of the carbon chain increases, there is a greater portion of the non-polar hydrocarbon chain in the molecule. The hydrocarbon part of the molecule does not allow hydrogen bonding, leaving only

[1] https://saylordotorg.github.io/text_the-basics-of-general-organic-and-biological-chemistry/s17-03-physical-properties-of-alcohol.html
[2] https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/volume-contraction

Van der Waals forces between the water molecules and hydrocarbon part of the molecule. Since Van der Waals forces are much weaker than hydrogen bonds between molecules, the mixture is not as closely packed as compared to a molecule with a smaller portion of the hydrocarbon chain. However, as the carbon chain length of alcohol increases, the solubility in water also decreases, meaning that alcohols with carbon chain lengths of 3 and above don't completely dissolve in water at room temperatures[3]. Hence, my investigation will be limited to methanol, ethanol, and propanol as all three are fully miscible in water. In my experiment, I predict that the volume contraction of an alcohol will rise as the fraction of water in the solution is increased till a certain point. However, after that point, as the fraction of water in the alcohol solution becomes closer to pure water, the volume contraction will decrease. Further, I anticipate a negative linear correlation between the volume contraction and the carbon chain length of an alcohol for a water to alcohol molar ratio.

Variables:

A) Independent variable: Molar fraction of the alcohol in the mixture (mol Alcohol/mol Solution). Molar fractions of 0.2, 0.4, 0.6, and 0.8 of the alcohol was used. This experiment was repeated for 4 alcohols: methanol, ethanol, and propanol.

B) Dependent variable: Volume contraction per mole of the mixture (cm^3/mol)

C) Controlled variables:

1) Temperature:
   a) Reason: Volume contraction of an alcohol-water mixture is dependent on the temperature because when temperature rises the solution performs thermal expansion, and when temperature drops the solution performs thermal contraction.
   b) Method: To keep the value of temperature constant, the entire experiment was conducted in an air-conditioned room with a fixed temperature of 25°C.

2) Water:
   a) Reason: Different types of water (such as tap water, pure water and distilled water) may have certain and distinct effects on the volume contraction as the solution is not of the same molecular composition, so it is important to use water of the same type throughout the experiment.
   b) Method: To obtain consistent and accurate results, purified water was used from the same water purifier throughout the experiment.

3) Number of moles in solution:
   a) Reason: The total number of moles of water plus alcohol are required to be the same. This is because the amount of volume contraction is directly related to the moles in the solution. (2 mol solution of alcohol and water has more volume contraction than a 1 mol solution)

[3] https://www.britannica.com/science/alcohol/Physical-properties-of-alcohols

b) Method: The total moles of every solution was 5 moles. This was done by determining the number of moles of water and alcohol using weight of each liquid and its molecular formula using equation:

$$2 = \frac{water\ weight}{water\ molecular\ mass} + \frac{alcohol\ weight}{alcohol\ molecular\ formula}.$$

4) Wind and Humidity:
   a) Reason: Evaporation of the solution may make the volume contraction higher than it actually is.
   b) Method: The entire experiment was conducted in a closed room, where liquids were covered with a lid. When the liquids were to be mixed, a burette with a small radius was used to reduce the exposed surface area of the solution to minimize evaporation when mixing.

Apparatus and Materials

Apparatus	Properties	Quantity
Container Flask	Measurements up to 100.0cm^3 0.1cm^3 increments	2
Burette	Measurements up to 100.0cm^3 0.1cm^3 increments	1
Lid	Radius: 2cm	2
Stirring Rod	Hydrophobic coating Length: 20cm	1
Funnel	-	1
Digital Weighing Scale	0.01g increments	1
Pipette	10cm^3 capacity	2

Table 1. Apparatus and properties

Material	Properties
Water	Relatively Purified
Methanol	99% concentration
Ethanol	99% concentration
Propanol	99% concentration
Food Coloring	Red and Green

Table 2. Materials and properties

Method:

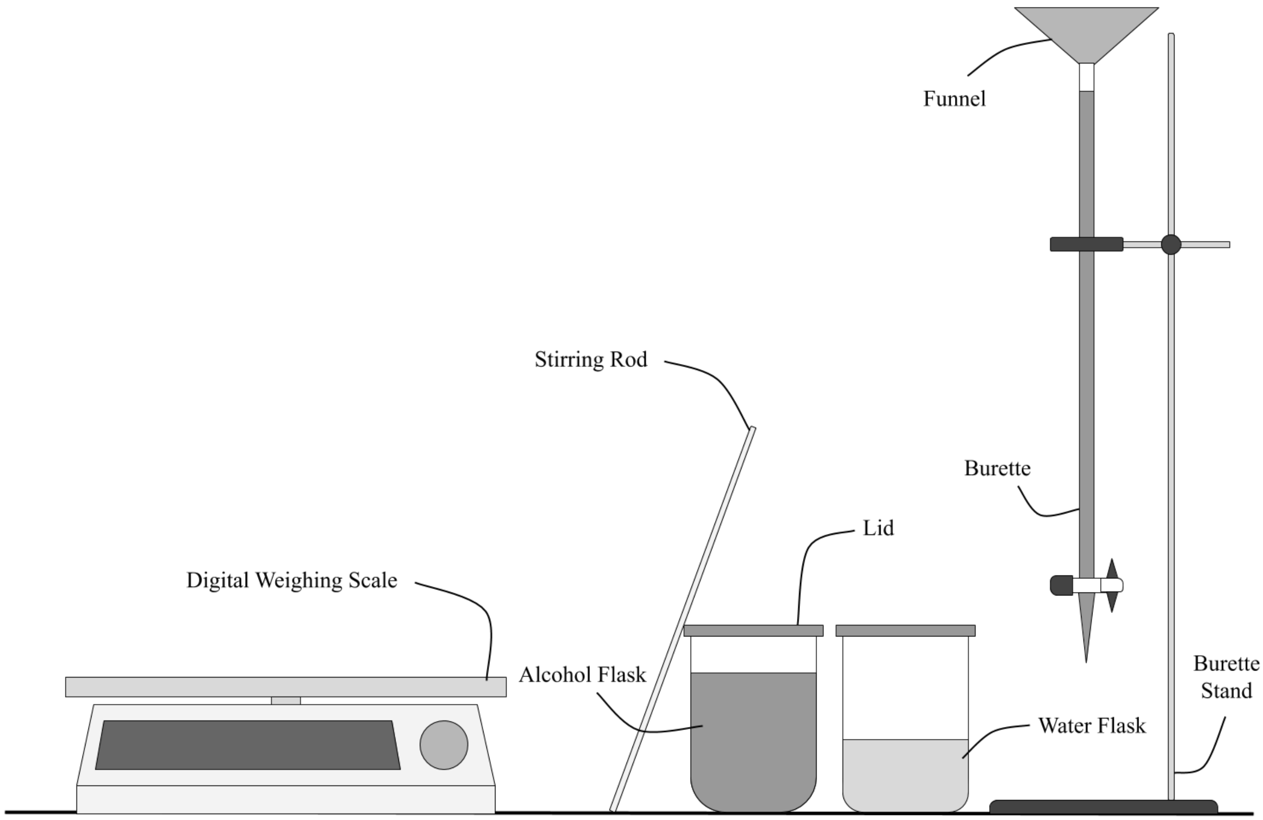


Figure 2. Experimental Setup

Procedure:

Preparation:

1) Using the digital weighing scale, weigh the mass of one of the empty container flasks.
2) Calculate the mass of 1 mol of water by using the formula:
$$moles \times molecular\ massof\ water = 1 \times 18.02.$$
3) Using a pipette, add water to the first flask until it weighs the mass of an empty flask + the calculated mass of water required.
4) Record the volume of water inside the first flask.
5) Add a few drops of green food coloring inside the first flask.
6) Calculate the mass of 4.5 mol of water by using the formula:
$$moles \times molecular\ mass\ of\ alcohol = 4 \times 32.04.$$
7) Using a pipette, add methanol to the second flask until it weighs the mass of an empty flask + the calculated mass of methanol required.
8) Record the volume of methanol inside the second flask.
9) Add a few drops of red food coloring inside the second flask.

Experiment:

10) Using a funnel, pour the water in the first flask into the burette.
11) Using a funnel, pour the methanol in the second flask into the burette.
12) Using a stirring rod, stir the solution until there is the same blue color present across the entire burette with no inconsistencies.
13) Record the volume of the solution present inside the burette.
14) Repeat steps 2 through 13 three times.
15) Repeat steps 2 through 14 by changing the moles of water to alcohol as follows: 2:3, 3:2, 4:1.
16) Repeat steps 2 through 15 replacing methanol with ethanol, and propanol.

Risk assessment

Hazard	Control Measures
Safety: Methanol, ethanol, and propanol are highly flammable.	Eliminate ignition sources like flames, hot surfaces and sparks. Keep storage areas cool and dry. Perform experiment in a well-ventilated room. Have fire extinguishing equipment available.
Safety: Methanol, ethanol, and propanol are toxic and are harmful when inhaled and in contact with skin and eyes.	Wear safety goggles and gloves when adding alcohol to the flask and when pouring the methanol into the burette. Continue to wear safety goggles until the alcohol is disposed of.
Safety: Glassware is utilized throughout the procedure and experiment which can be broken easily. Broken glass is a physical hazard.	All glassware must be handled carefully at all times. If the glassware is broken, a dustpan and brush must be used to clean up shards of broken glass. Broken glassware must be disposed to a bin for glass.
Safety: Accidental spillage of methanol, ethanol, and propanol is extremely dangerous.	Call trained response staff. Remove all ignition sources. Attempt to contain the spillage as to prevent it from reaching the sewers. Absorb the solution into a non-combustible absorbent material like earth or sand, then containerize for disposal.
Environmental: Disposal of methanol, ethanol, and propanol solution to a sewage system or an open water body can be very dangerous.	The solution should be absorbed into a non-combustible absorbent material like earth or sand, then must be containerized for disposal to hazardous waste container.
Ethical: None	As there are no living organisms endangered or used in this experiment, there are no ethical concerns that can be identified.

Table 3. Experiment risk assessment

Quality of Data

→ Throughout the day of data collection, temperature in the room often fluctuated between 24°C and 26°C, even though the AC was left on, when measured through a thermometer. The experiment was halted until the temperature restabilized. However, this could still have led to errors.

→ Even though, the stirring rod had a hydrophobic layering over it, after mixing the solution, some water drops were seen on the stirring rod when removed from the burette. Though unnoticeable, this can artificially increase the amount of volume contraction observed in the experiment.

→ When the flasks were used to fill the burette, the full amount of alcohol and solution weren't transferred to the burette, and a few water droplets remained in the flasks. Thus, the amount of volume contraction is systematically increased.

→ The digital weighing scale was not entirely accurate as when an empty beaker was placed on it, the digital weighing scale fluctuated between 67.03g and 67.11g without coming to a halt. This means there may have been something wrong with the weighing scale, however no amendments could be made because the laboratory was only partially open due to COVID-19 quarantining measures, and no other additional apparatus could be accessed. Hence, as the volume uncertainty of the water and alcohol would increase due to random uncertainties, I take multiple readings of the volume of the water and alcohol flasks, getting a more accurate average.

Data Collection and Analysis

In this section, to optimize spacing in graphs and tables, water will be referred to with 'W,' alcohol will to referred to with 'A' and the mixed solution will be referred to with 'S.'

W : A mol	Volume of W ($V_W \pm 0.1$) cm^3	Volume of A ($V_A \pm 0.1$) cm^3	Volume of S ($V_S \pm 0.1$) cm^3	Mean Volume of W V_W cm^3	Mean Volume of A V_A cm^3	Mean Volume of S V_S cm^3
Methanol						
1:4	17.9	161.8	174.5	18.0 ± 0.2	161.8 ± 0.2	174.5 ± 0.1
	18.0	161.9	174.5			
	18.0	161.8	174.5			
2:3	36.2	121.4	151.2	36.1 ± 0.2	121.4 ± 0.1	151.1 ± 0.2
	36.1	121.4	151.1			
	36.0	121.4	151.0			
3:2	54.2	80.9	129.1	54.1 ± 0.2	80.9 ± 0.1	129.1 ± 0.2
	54.0	80.9	129.0			
	54.0	80.9	129.1			
4:1	72.2	40.5	108.7	72.2 ± 0.1	40.5 ± 0.2	108.6 ± 0.2
	72.2	40.4	108.5			
	72.2	40.5	108.5			

Table continued on the next page…

W : A mol	Volume of W (V_W ± 0.1) cm^3	Volume of A (V_A ± 0.1) cm^3	Volume of S (V_S ± 0.1) cm^3	Mean Volume of W V_W cm^3	Mean Volume of A V_A cm^3	Mean Volume of S V_S cm^3
Ethanol						
1:4	18.2	233.7	246.9	18.1 ± 0.2	233.7 ± 0.1	246.9 ± 0.2
	18.0	233.7	246.8			
	18.1	233.7	247.0			
2:3	36.1	175.3	205.4	36.0 ± 0.2	175.2 ± 0.2	205.4 ± 0.1
	36.0	175.1	205.4			
	36.0	175.1	205.4			
3:2	54.0	116.8	165.6	54.0 ± 0.1	116.8 ± 0.2	165.6 ± 0.2
	54.0	116.7	165.5			
	54.0	116.8	165.6			
4:1	72.1	58.5	126.9	72.1 ± 0.2	58.4 ± 0.2	126.9 ± 0.1
	72.1	58.3	126.9			
	72.0	58.4	126.9			
Propanol						
1:4	17.9	299.4	312.8	18.0 ± 0.2	299.4 ± 0.1	313.1 ± 0.2
	18.1	299.4	312.7			
	17.9	299.4	312.7			
2:3	36.1	224.5	255.2	36.1 ± 0.2	224.5 ± 0.2	255.4 ± 0.2
	36.2	224.5	255.0			
	36.1	224.4	255.1			
3:2	54.1	149.8	198.7	54.0 ± 0.2	149.7 ± 0.2	199.1 ± 0.2
	54.1	149.7	198.7			
	53.9	149.6	198.8			
4:1	72.0	74.8	143.2	72.0 ± 0.1	74.8 ± 0.2	143.8 ± 0.2
	72.0	74.8	143.4			
	72.0	74.9	143.3			

Table 4. Volume of W and Volume of A ratio that gives Volume S

Calculations for table 4:

The mean volume of W, A, and S was calculated using the formula:

$$\frac{V_1 + V_2 + V_3}{3}$$

The uncertainty of the mean volume of W, A, and S was calculated using the formula:

$$\frac{V_{max} - V_{min}}{2} + V_{uncertainity}$$

Sample calculation of mean volume for V_W = 1:4 (W : A mol)

$$\text{Average} = \frac{18.2+18.0+18.1}{3} \approx 18.1 \text{ cm}^3 \text{ (1 decimal places)}$$

$$\text{Uncertainty} = \frac{18.2-18.0}{2} + 0.1 = 0.2 \text{ cm}^3 \text{ (1 decimal places)}$$

Here, 0.1 is added due to the uncertainty in the measurement of the volume in the flask.

W : A mol	Volume Contraction V_C cm^3		
	Methanol	Ethanol	Propanol
1:4	5.3 ± 0.5	4.9 ± 0.5	4.3 ± 0.5
2:3	6.4 ± 0.5	5.8 ± 0.5	5.2 ± 0.6
3:2	5.9 ± 0.5	5.2 ± 0.5	4.6 ± 0.6
4:1	4.1 ± 0.5	3.6 ± 0.5	3.0 ± 0.5

Table 5. Volume Contraction of Methanol, Ethanol, and Propanol depending on W : A ratio

Calculations for table 4:

To find the volume contraction of methanol, ethanol, and propanol, we must find the total volume before mixing and subtract that with the new volume of the solution. We can find the total volume by adding V_W and V_A to find the volume contraction we can subtract V_S:

$$V_W + V_A - V_S$$

The uncertainty of the volume contraction was calculated using the formula:

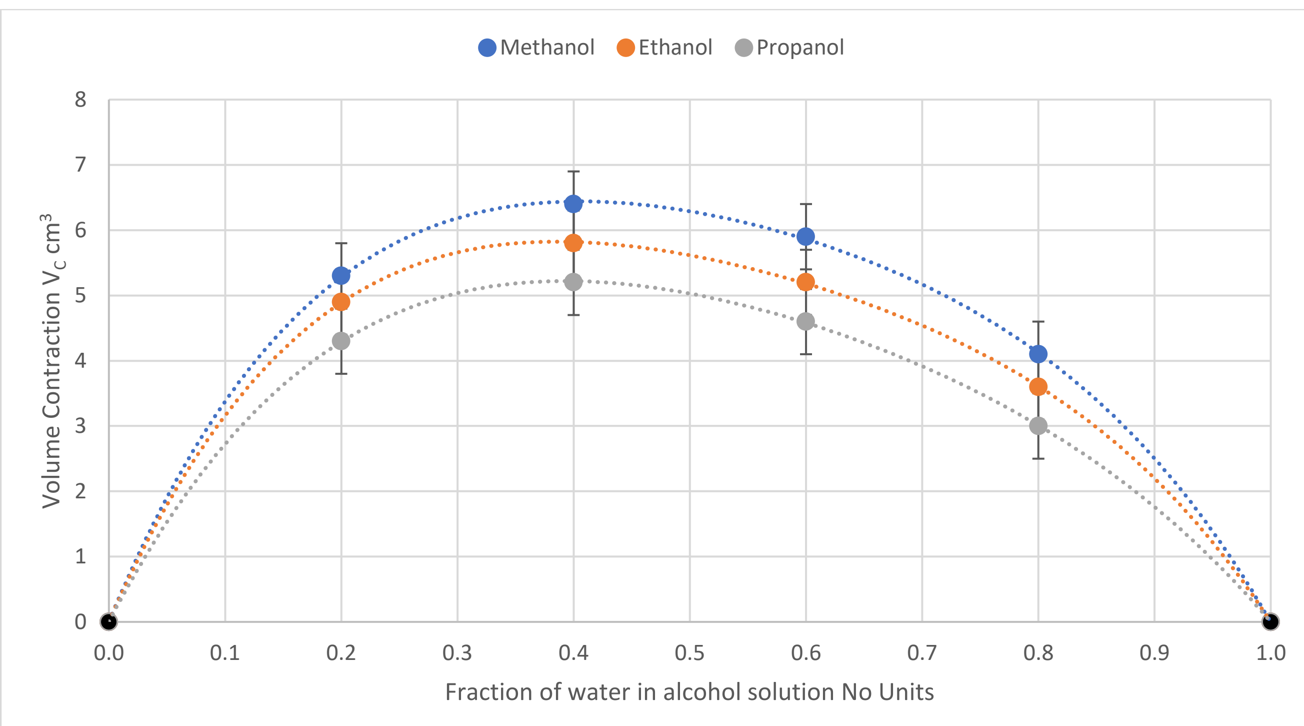
$$V_W\ uncertainity + V_A\ uncertainity + V_S\ uncertainity$$

Sample calculation of volume contraction for Methanol with 1:4 (W : A mol)

$$V_C = 18 + 161.8 - 174.7 \approx 5.1\ \text{cm}^3\ \text{(1 decimal places)}$$

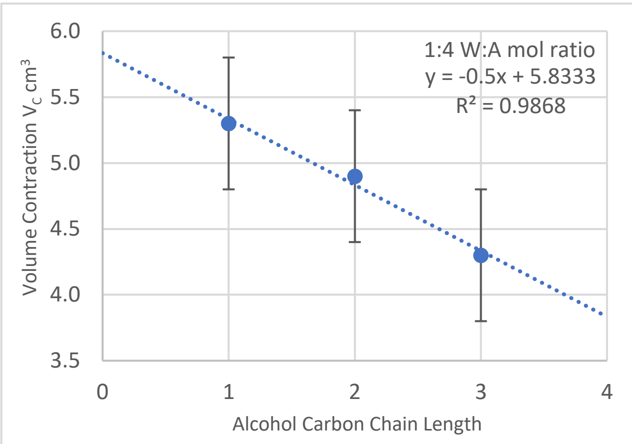
$$\text{Uncertainty} = 0.2 + 0.2 + 0.1 = 0.5\ \text{cm}^3\ \text{(1 decimal places)}$$

Graphical Analysis

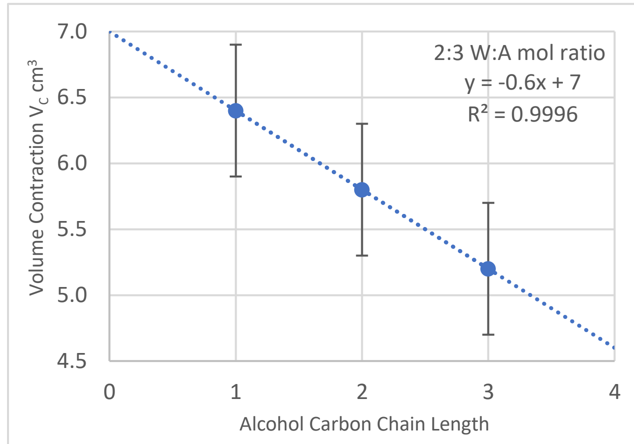


Graph 1. Volume Contraction of Methanol, Ethanol, and Propanol depending on W : A ratio

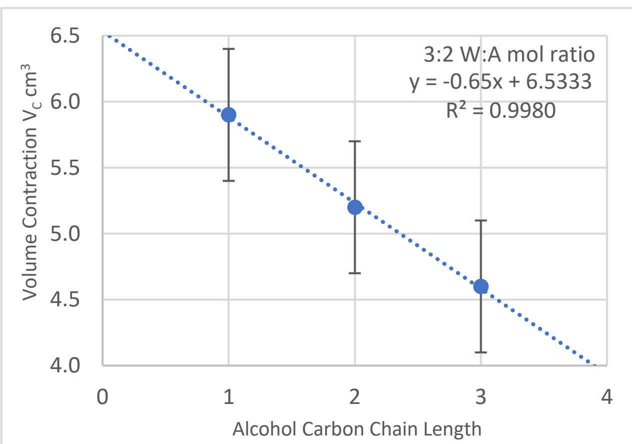
From the data collected and plotted, the graph suggests that as the fraction of water in the alcohol solution increases, the volume contraction increases up until the fraction of water reaches its maxima at a 2:3 water alcohol ratio. After that point, volume contraction gradually decreases to 0. This is consistent with my hypothesis, as this phenomenon occurs in all three alcohols.



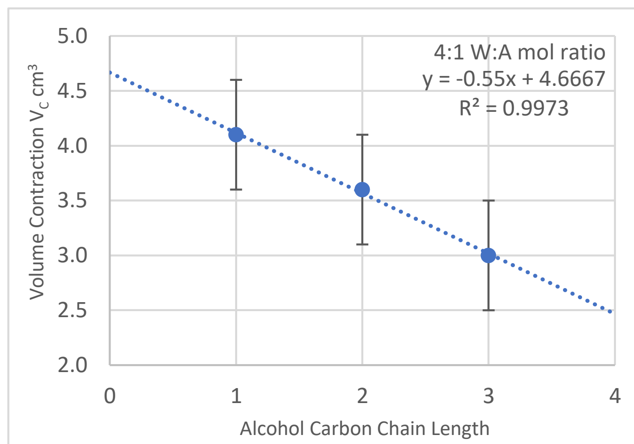
Graph 2. A carbon chain length vs V_C (1:4) W : A mol ratio



Graph 3. A carbon chain length vs V_C (2:3) W : A mol ratio



Graph 4. A carbon chain length vs V_C (3:2) W : A mol ratio



Graph 5. A carbon chain length vs V_C (4:1) W : A mol ratio

In graph 2, 3, 4, and 5, we can see that every ratio tested for yielded a negative linear relationship. Further, the line of best fit (LOBF), intersects all 3 error bars in all four graphs, proving that there is low systematic error.

Range of R^2	Strength of Correlation
Below 0.49	Weak
0.50 to 0.69	Moderate
0.70 to 0.89	Strong
0.90 to 1.00	Very strong

Table 6. R^2 and its corresponding strength of relationship

The value of R^2, the square of the correlation coefficient, if the different ratios range from 09868 to 0.9996. Here, R^2 evaluated the strength of the relationship between the two variables—the alcohol carbon chain length and volume contraction. This value can be assed using table 6, where we can infer that the experiment provided data that has a very strong strength of correlation, and thus a considerably low systematic error.

Conclusion

Collecting, processing, and analyzing the data, we can see that the results seem to validate the initial hypothesis. The fraction of water in the alcohol solution did increase the amount of volume contraction, up until 40% of the solution consisted of water and 60% of the solution consisted of alcohol, as supported by table 5 and graph 1 for all alcohols tested. Further, the volume contraction did decrease to zero as it became pure water. Here, a smooth curved line could be made with the data available for all three alcohols in the experiment, further strengthening the results. To confirm that there would be "a negative linear correlation between volume contraction and the carbon chain length of a alcohol," the data was then manipulated to be represented in graph 2, 3, 4, 5, showing that as the carbon chain length of a alcohol increases, the volume contraction decreases for all ratios that were tested. Further, the graphs demonstrate that the LOBF was linear and had a negative correlation proving the hypothesis. An unexpected result, that was not stated in the hypothesis, that was also observed, which was the fact that the gradient of the volume contraction vs carbon chain length of an alcohol was different in the case of each ratio tested.

On one hand, the experiment was observed to demonstrate a high degree of accuracy, which can be attributed to the very high R^2 value and the fact that all trendlines intersected every single error bar. This can highlight the fact that there was very little systematic error present within the experiment, revealing that the experiment was well designed and successful. On the other hand, however, the precision of the experiment can be seen to be low for table 5, and graph 1, 2, 3, 4, 5. This can be attributed to the fact that the values of volume contraction were very low, and that the burette and flasks proved to have a large measurement uncertainty which added up when calculating the volume contraction. This uncertainty was highest in the case of propanol for ratio 4:1 [$\frac{0.5}{3.0} = 16.7\%$], and lowest in the case of methanol for ratio 2:3 [$\frac{0.5}{6.4} = 7.8\%$], showing that all values had a tremendous amount of random uncertainty. There are many factors that can play into the high amount of random uncertainty, like the faulty weighing scale or the measurement scale of the burette and flasks. These factors will be explored further in the evaluation.

Evaluation

Strengths of the experiment

This experiment exhibits very low systematic error, showing that the experiment designed was largely accurate and effective. The experimental setup prioritized to account for the most minute precautions and variables that would have affected the results. This included the use of a burette as the container for mixing both solutions which would leave a small exposed surface area that would lead to minimal evaporation; This was reinforced by the lids on the container flasks. Further, temperature was regularly checked throughout the experiment, making sure that it remained 25°C, otherwise the experiment was halted. A hydrophobic stirring rod was also used to reduce the solution being removed from the burette. Lastly, a large number of readings and trials were taken to produce the most accurate values and substantially lower the systematic errors during the experiment.

Weaknesses of the experiment

Source of error & effects	Significance & evidence	Possible improvements
Systematic errors affecting accuracy		
Solution droplets on stirring rod: The stirring rod often picked up a few droplets of the solution.	Moderate significance: - The solution droplets artificially increase the volume contraction. However, the droplets amount to little.	Use a sealable flask which allows shaking, enabling for no amount of solution to be removed from the container.
Solution droplets in flasks: When the burette was filled with the liquids, a few drops of water and alcohol remained in their respective flasks.	Moderate significance: - This, again, increases the volume contraction in the experiment as there is less solution to begin with.	Coat the flasks with hydrophobic coating, which would minimize the amount of liquid that remains in the flask when emptied.
Temperature of room: The temperature often fluctuated by 1°C. Even though experiment was halted every time it did, there may have been instances in between checks where temperature was not 25°C	Low significance: - 1°C has minimal effects on the volume expansion of water and alcohol and thus is almost negligible.	Utilize a small room that is well insulated and has an effective AC system that stabilizes quickly. This reduces the chances of temperature fluctuation
Evaporation: When the solution in the burette was mixed, the solution was exposed to the open air and the air currents produced by the AC.	Low significance: - The surface area exposed and the time the lid was opened is very less time to expect any noticeable evaporation.	Use a sealable flask which allows for shaking. Rather than exposing solution while mixing, the solution can be mixed by shaking.
Random errors affecting precision		
Weighing scale: The weighing scale was used to get the volume of alcohol and water in molar mass, however, the weigh scale was giving inaccurate readings, so multiple readings were taken to average.	High significance: - The weight effected the volume measured by up to $\frac{0.1}{3.0} = 3.4\%$ in the case of propanol (4:1), which accounts for $\frac{3.4}{16.7} = 20\%$ of the total uncertainty.	Make use of a weighing that provides accurate values to 3 decimal places, giving much more precise results.
Flask and Burette uncertainty: The measurement uncertainty of the flask and burette used was $0.1cm^3$.	High significance: - The uncertainty of the flask and burette, which, through calculations, compounded and resulted in up to $\frac{0.4}{3.0} = 13.4\%$ uncertainty in the case of propanol (4:1), which accounts for $\frac{13.4}{16.7} =$ 80% of the total uncertainty.	Perform the experiment with 10 times the number of moles of water and alcohol, which will lead this uncertainty to only amount to $\frac{0.4}{30.0} = 1.3\%$ in the case of propanol (4:1).

Table 7. Weaknesses and limitations effecting results and its improvements

Further research suggestions

To further research in this underrepresented field of chemistry, volume contraction should be charted for numerous more liquids that are more connected to health to gain a better understand of how alcohol truly affects our body. These liquids could be blood, or compounds like hydrochloric acid and glucose. This would more closely align to my initial inquiry of research.

Bibliography

[1] https://saylordotorg.github.io/text_the-basics-of-general-organic-and-biological-chemistry/s17-03-physical-properties-of-alcohol.html

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[3] https://www.britannica.com/science/alcohol/Physical-properties-of-alcohols