



Determination of the Viscosity, Fluidity, and Solution Ideality of Methanol/Water and Toluene/p-Xylene Mixtures (of Variable Concentrations)

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Running Title: *Viscosity of Binary Solutions*

INTRODUCTION

The viscosity of a liquid, an intrinsic physical property that is quantifiable, is analogous to the flow resistances that are studied in the context of fluid mechanics. That is to say, in a practical context, the viscosity of a liquid is essentially its ability to resist flow through an apparatus. As a quantifiable property of a system, viscosity is commonly used to determine the quality (stickiness, thickness, etc.) of a given solution compared to another, such as commercial resins, oils, paints, etc. The viscosity of a solution is also important as it provides important information regarding the kinetics or reactions in the context of the diffusion of the reagents and products of a reaction in solution (the medium); invaluable information to physical chemist and material scientist.

On a macroscopic level, the idea of viscosity can be interpreted as the frictional force between molecules as they move across each other via the flow of the liquid. The attractive intermolecular forces between the molecules that comprise the liquid must be overcome in order for the liquid to flow.

In this experiment, we measure the viscosities of binary solutions as they flow through a circular tube of small internal diameter, specifically an Ostwald viscometer. The flow of the solution through the capillary tube diameter follows Poiseuille's law (eq. 1), which describes the volume flow rate based on the physical dimensions of the viscometer, the solution's density (expressed as a pressure difference, as the hydrostatic pressure is proportional to the liquid density), and

its viscosity. We also determine the fluidity of these mixtures, which are simply the reciprocal of the viscosity (eq. 2). We use the fluidities of the mixtures to determine the solution ideality. A solution mixture comprised of liquids that do not associate (or relatively weakly associate) is said to be ideal. The fluidity of an ideal mixture is additive (eq. 3), as the interaction energies of each of the constituents of the solution are independent and thus constant compared to the components in a pure solution. In contrast, a non-ideal solution has components that do strongly associate via intermolecular forces, and thus the fluidity of the solutions is more complicated than the simple additive nature of ideal solutions. The association of the constituents via strong intermolecular forces cause the fluidity of the overall mixed solution to be dependent on the interaction energies of each of the constituents alone, as well as the interaction energies of the constituents together. The method of solution ideality determination will be reviewed in detail in the discussion section.

METHODOLOGY

The viscosity of each mixture was determined using an Ostwald viscometer by measuring the flow times. A series of concentrations were mixed at a ratio of 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0 for mixtures of water/methanol and toluene/p-xylene. The Ostwald viscometer was suspended in a ring stand and maintained at room temperature (25 °C). 10 mL of each solution was then placed in the viscometer (with solution washes in between each

change in mixture) and several flow time trials were video recorded. These videos were then analyzed to determine the flow times of each trial by measuring the time it took the solution to pass each mark in the viscometer (time between frames allowed precision up to one-hundredth of a second). Measurements were taken until the flow times agreed to within 0.5 seconds.

RESULTS AND DISCUSSION

Several flow time trials were performed until the measurements agreed within 0.5 seconds (or at most four trials) for each solution mixture and tabulated as such.

Methanol %	Trial 1	Trial 2	Trial 3	Trial 4	Avg.
0	11.5	11.69	11.81	11.59	11.65
20	15.97	16.12	16.36	16.49	16.24
40	18.81	19.15	19.47	19.51	19.24
60	18.56	18.68	19.09	19.01	18.84
80	15.19	15.53	15.53	15.56	15.45
100	9.66	9.84	9.94	10	9.86

TABLE 1. Flow Time Measurements (seconds) for Mixtures of Methanol and Water

Toluene %	Trial 1	Trial 2	Trial 3	Trial 4	Avg.
0	9.88	9.86	9.99	9.92	9.91
20	9.89	9.81	9.77	9.78	9.81
40	9.47	9.57	9.47	9.5	9.50
60	9.5	9.66	9.69	9.33	9.55
80	9.66	9.66	9.73	9.75	9.70
100	9.31	9.28	9.35	9.34	9.32

TABLE 2. Flow Time Measurements (seconds) for Mixtures of Toluene and p-Xylene

These flow times were then used with the reference values of the viscosities of pure water and pure p-Xylene, and the densities of each mixture (found in the appendix) with the equation for viscosity (relative to the reference liquids – eq. 4) that was derived from the integrated form of Poiseuille’s law (eq. 5), to find the experimental viscosities of each mixture. These experimental viscosities were then transformed into the experimental fluidities with (eq. 2).

Methanol %	Experimental Viscosity (Pa·s) – (eq. 4)	Experimental Fluidity ($\text{Pa}^{-1} \cdot \text{s}^{-1}$) – (eq. 2)
0	0.00089	1123.60
20	0.00120	827.687
40	0.00139	718.578
60	0.00131	762.094
80	0.00102	982.983
100	0.00060	1679.32

TABLE 3. Experimental Viscosities and Fluidities for Mixtures of Methanol and Water

Toluene %	Experimental Viscosity (Pa·s) – (eq. 4)	Experimental Fluidity ($\text{Pa}^{-1} \cdot \text{s}^{-1}$) – (eq. 2)
0	0.00061	1652.89
20	0.00060	1667.79
40	0.00059	1720.19
60	0.00058	1712.54
80	0.00066	1507.88
100	0.00057	1749.80

TABLE 4. Experimental Viscosities and Fluidities for Mixtures of Toluene and p-Xylene

The mole fractions of each of the constituent liquids were then calculated using simple stoichiometric equations and the densities, molar masses, and volumes of each of the constituents. These mole fractions were then used with the fluidities of the pure constituents and (eq. 3) to determine the theoretical fluidities (associated with ideal mixtures). The percent differences between these theoretical fluidities and the experimental fluidities (from tables 3 and 4), were determined to quantify the agreement between the experimental fluidities from (eq. 4) and the theoretical fluidities from (eq. 3), which allows us to determine the ideality of the mixtures.

Methanol %	Experimental Fluidity	Theoretical Fluidity	Percent Difference
0	1123.60	1123.60	0
20	827.687	1152.86	39.3
40	718.578	1196.68	66.5
60	762.094	1269.47	66.6
80	982.983	1414.20	43.9
100	1679.32	1841.62	9.66

TABLE 5. Comparison Between Experimental and Theoretical Fluidities of Methanol/Water Mixtures

Toluene %	Experimental Fluidity	Theoretical Fluidity	Percent Difference
0	1652.89	1652.89	0
20	1667.79	1652.89	0.89
40	1720.19	1652.89	3.91
60	1712.54	1652.89	3.48
80	1507.88	1652.89	9.62
100	1749.80	1652.89	5.54

TABLE 6. Comparison Between Experimental and Theoretical Fluidities of Toluene/p-Xylene Mixtures

In addition to the ideality determinations by comparing the fluidities from equations 2 (from eq. 4 viscosities) and 3, we also found the natural logarithm of the binary solution's viscosity using equation 6 and by taking the natural logarithm of the experimental viscosities (from eq. 4), comparing the two to provide further evidence of a solution's ideality.

Methanol %	Experimental $\ln \eta$	Theoretical $\ln \eta$	Percent Difference
0	-7.024	-7.024	~0
20	-6.719	-7.044	4.85
40	-6.577	-7.075	7.56
60	-6.636	-7.125	7.36
80	-6.891	-7.224	4.84
100	-7.426	-7.518	1.24

TABLE 7. Comparison Between Experimental and Theoretical $\ln \eta$ Values of Methanol/Water Mixtures

Toluene %	Experimental $\ln \eta$	Theoretical $\ln \eta$	Percent Difference
0	-7.410	-7.410	0
20	-7.419	-7.410	0.12
40	-7.450	-7.410	0.54
60	-7.446	-7.410	0.48
80	-7.318	-7.410	1.25
100	-7.467	-7.410	0.76

TABLE 8. Comparison Between Experimental and Theoretical $\ln \eta$ Values of Toluene/p-Xylene Mixtures

As seen in tables 5, 6, 7, and 8, we observe that the large percent difference for the water/methanol mixtures indicate that the experimental and theoretical fluidities and $\ln \eta$ values do not agree, and thus the mixture is non-ideal. In contrast, the relatively small percent

differences for the toluene/p-xylene mixtures indicate that the experimental and theoretical fluidities and $\ln \eta$ values do generally agree, and thus the mixture is ideal, as equations 3 and 6 are valid (for this ideal mixture).

A possible explanation for these determined idealities could be based on the intermolecular forces that exist between the components of each mixture. For the methanol and water mixture, both molecules are highly polar due to the presence of the electronegative oxygen and can participate in hydrogen bonding interactions, which are strong intermolecular forces. In contrast, toluene and p-xylene are relatively non-polar molecules (methyl substituted benzene rings), and the aromatic benzene ring moiety of each are planar allowing for only weak van der Waals interactions – they do not strongly associate. As discussed in the introduction section, these differences in component association determine the ideality of the binary solutions.

A possible source of experimental error in this experiment come from the delayed reaction times inherent in a person pressing a stopwatch, which was reduced by using the video frame analysis discussed in the methodology section. In addition, there is also error introduced in the data analysis due to fluctuations in the room's temperature, as the reference viscosities and mixture densities are temperature dependent.

QUESTIONS & FURTHER THOUGHTS

Poiseuille's law (eq. 1) describing the flow time (and thus the viscosity through the integrated form, eq. 5) is based on the capillary's radius to the fourth power. As an exponential function, the propagation-of-errors results in a relative error times the exponent, in this case, four-fold for the viscosity. This is derived as such:

$$\eta = \frac{\pi r^4 P t}{8 V L} \Rightarrow \eta = C r^4$$

We see that the viscosity can be expressed as a constant times the radius to the fourth power. We

can then take the natural logarithm of both sides to get

$$\ln \eta = \ln C + 4 \ln r$$

We can then take the derivative, resulting in

$$\frac{d\eta}{\eta} = 4 \frac{dr}{r} \Rightarrow \frac{\epsilon_{\eta}}{\eta} = 4 \frac{\epsilon_r}{r}$$

Thus we see that the relative error from the capillary radius enters fourfold into the relative error of the viscosity.

It would be possible to have a homogeneous binary liquid solution whose viscosity is higher (or lower) than that of the two component liquids. This is seen in cases where the intermolecular force of attraction between the two components are stronger than that of each of the pure components, which results in a higher viscosity, or resistance to flow. In contrast, if the intermolecular force of attraction between the two components are weaker than compared to solutions of each pure component, then the viscosity would be lower. As we saw in this experiment, the former was observed in the water/methanol mixtures, as each had a higher viscosity than its individual components (refer to table 3). We can conclude that the intermolecular forces between the molecules in the mixture are stronger (and thus resulting in a greater viscosity) than the intermolecular forces of each individual pure components.

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APPENDIX – EQUATIONS

All calculated values from the discussion and result section were determined using the following equations.

$$\frac{dV}{dt} = \frac{\pi r^4 \Delta P}{8\eta L} \quad \text{eq. 1}$$

Poiseuille’s Law, where dV/dt is the volume flow rate of the liquid emerging from the tube, r and L are, respectively the radius and length of the tube in the Ostwald viscometer, ΔP is the pressure difference, and η is the viscosity coefficient.

$$F = 1/\eta \quad \text{eq. 2}$$

The fluidity F , of a solution based on its viscosity.

$$F \approx x_A F_A + x_B F_B \quad \text{eq. 3}$$

The fluidity of a solution based on the component fluidities and the mole fractions x .

$$\eta = \frac{\eta_r \rho t}{\rho_r t_r} \quad \text{eq. 4}$$

The experimental viscosity based on the mixture’s density ρ and flow time t relative to a reference liquid.

$$\eta = \frac{\pi r^4 P t}{8 V L} \quad \text{eq. 5}$$

The integrated form of Poiseuille’s law.

$$\ln \eta = x_A \ln \eta_A + x_B \ln \eta_B \quad \text{eq. 6}$$

The natural logarithm of the binary solution’s viscosity.

APPENDIX – REFERENCE VALUES

Reference Values (at 25°C)

	Viscosity (Pa · s)	Fluidity (Pa ⁻¹ · s ⁻¹)	Density (g/mL)	Mol. Wt. (g/mol)
<i>Water</i>	0.00089	1123.60	0.997	18.01
<i>Methanol</i>	0.00054	1841.62	0.792	32.04
<i>Toluene</i>	0.00061	1652.89	0.867	92.14
<i>p-Xylene</i>	0.00061	1652.89	0.857	106.2

Density of Methanol/Water Mixtures (at 25°C)

Methanol Volume %	Density (g/mL)
0	0.997
20	0.971
40	0.944
60	0.909
80	0.859
100	0.788

Density of Toluene/p-Xylene Mixtures (at 25°C)

Toluene Volume %	Density (g/mL)
0	0.857
20	0.858
40	0.859
60	0.859
80	0.960
100	0.861