

Transport Properties and Chemical Kinetics

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Experiment 17

Viscosity of Liquids Part I: Low Viscosities

Objective To measure and analyze the viscosities of ideal (toluene/*p*-xylene) and nonideal (methanol/water) binary solutions and their components; to determine the activation energy to viscous flow.

Introduction From a phenomenological point of view, we can say that the viscosity of a fluid is its resistance to flow. Viscosity measurements are often carried out for either of two main reasons. Viscosity is a quantitative property of a fluid and although a particular sample might be highly complex, such as a blend of various resins or polymers, its viscosity serves to represent a physical property of that system. Viscosity therefore can be used as an empirical index in quality-control applications concerning, for example, oils and resins, latex paints, or chocolate mousse. Another motivation for measuring viscosity is to determine a fundamental and intrinsic property of a liquid (as a solvent medium): the rate of mass transport, or diffusion, within the medium. In this application, for example, viscosity data can provide important information about chemical reaction kinetics. In this experiment, the fluid will be either a pure liquid or a mixture of liquids.

Considered macroscopically, viscosity is a frictional force that arises from the directed motion of molecules past each other in the liquid state. From a microscopic viewpoint, viscosity reflects the energetics of molecular association in the liquid state because in order for a liquid to flow, a force must be applied to overcome the attractive forces between the molecules. These forces are appreciable; they are manifest, for example, as latent heat of vaporization and surface tension. The mathematical treatment of viscosity is best introduced by looking at Figure 1.

A liquid is presumed to be flowing smoothly in the x -direction. Imagine that the liquid is composed of sheets of infinitesimal cross section dA that are oriented in the x - y plane, and that each sheet flows tangentially to its surface area, in the positive x -direction. If a given sheet is kept at a velocity v_x such that it exceeds the velocity of an adjacent sheet by an amount dv_x and the adjacent sheet is displaced by a distance dz the force required (per unit area) to maintain the motion of the given sheet, df_x , is given by

$$\frac{df_x}{dA} = \eta \left(\frac{\partial v_x}{\partial z} \right)_z \quad (1)$$

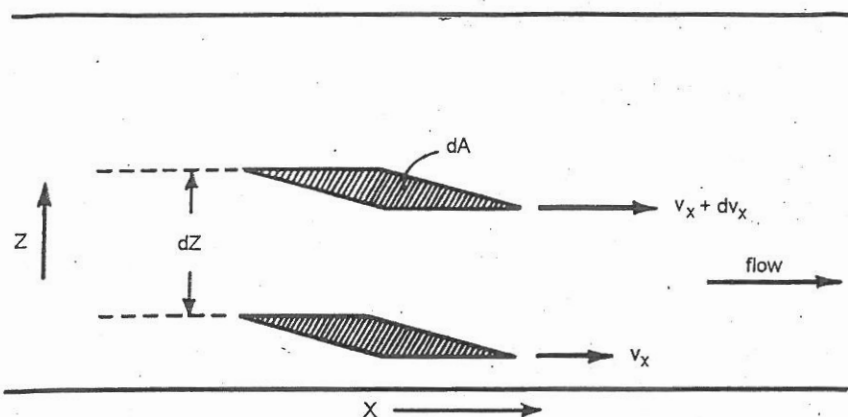


Figure 1. In viscous flow, a sheet of fluid having cross-sectional area dA is subjected to a force that causes it to move faster by an amount dV than an equivalent, adjacent sheet separated by a distance dz . The planes of the sheets are normal to the flow direction.

The partial derivative, $(\partial v_x / \partial z)_z$, is the tangential velocity gradient, and η , the proportionality constant between f_x and this gradient, is now defined as the *viscosity coefficient*. From equation (1), it can be seen that the SI dimensions of the viscosity coefficient are $\text{kg m}^{-1} \text{s}^{-1}$. Equation (1) is called Newton's law of viscous flow. Fluids that behave according to (1) are called Newtonian fluids and are said to undergo *laminar* flow. Cases of nonlaminar, or non-Newtonian flow (at ordinary temperatures and pressures) are unusual but not uncommon (e.g., "silly putty"). Materials whose viscosity decreases at high shear rates (e.g., paints that "thin out" as they are applied with a brush but then stiffen when quiescent) are examples of non-Newtonian fluids.

With respect to this experiment, a useful application of equation (1) to the case of mass transport through a circular tube of small internal diameter was derived by Poiseuille (1844):

$$\frac{dV}{dt} = \frac{\pi r^4 \Delta P}{8\eta L}, \quad (2)$$

where dV/dt is the volume flow rate of the liquid emerging from the tube, and r and L are, respectively, the radius and length of the tube. ΔP is the pressure difference across the ends of the tube and is the driving force for the bulk flow. Equation (2) assumes that the flow rate is slow and uniform. The viscosity coefficient, η , is called the *poise* in recognition of Poiseuille, and has cgs units. Thus one poise, P, is $1 \text{ g cm}^{-1} \text{s}^{-1}$ (or dyne s). For many common liquids at room temperature, viscosities are about 0.002 to 0.04 P. For convenience, the centipoise (10^{-2} P), cP, is often used to report viscosity. In SI units, the viscosity coefficient is $\text{kg m}^{-1} \text{s}^{-1}$ (or Pa s). $10^3 \text{ Pa s} = 1 \text{ cP}$.

Mixtures

From the way viscosity is defined, it follows that a mobile liquid is one that has a relatively low viscosity. Another useful parameter that applies to fluid mobility is *fluidity*, F , which is simply the reciprocal of the viscosity coefficient:

$$F = \frac{1}{\eta} \quad (3)$$

One particular advantage to the use of fluidity is that the fluidities of mixed solutions of nonassociating liquids are often found (empirically) to be additive. Thus for a binary solution of liquids A and B , each pure liquid having fluidities F_A° and F_B° , respectively, the fluidity of a mixture containing mole fractions x_A and x_B may be approximated as

$$F \approx x_A F_A^\circ + x_B F_B^\circ, \quad (4)$$

i.e., a mole fraction-weighted linear combination of the pure liquid fluidities. The viscosity of the mixture is

$$F \approx \frac{1}{x_A/\eta_A^\circ + x_B/\eta_B^\circ} \quad (5)$$

and is obviously not linear in the composition variable, x_A (or x_B). Another approach for expressing the viscosity of a mixture is the following, proposed by Kendall (1913). For a binary solution,

$$\ln \eta = x_A \ln \eta_A^\circ + x_B \ln \eta_B^\circ \quad (6)$$

In this context, an *ideal solution* can be defined as one in which the interaction energies between the constituents are the same as those between the pure components. More specifically, it is assumed that in such a mixture the intermolecular interactions between identical molecules (e.g., A - A and B - B) are equal to those between different molecules (A - B). The failure of component fluidities to be additive in the mixed state arises, then, either from the formation of association complexes between the components or from the destruction of such complexes that may be present in the pure component(s) after the pure components are mixed. Under these circumstances equations (5) and (6) would not be valid.

Temperature Dependence of Viscosity

It is found that over a reasonably wide temperature range, the viscosity of a pure liquid increases exponentially with the inverse absolute temperature. This relationship was first expressed

quantitatively by Arrhenius (1912):*

$$\eta = A \exp\left(\frac{E_{\eta}}{RT}\right), \quad (7)$$

where A is a constant for a given liquid, and E_{η} is sometimes called the activation energy to viscous flow of the liquid. Several theories have been proposed to rationalize equation (7). Simply viewed, however, an energy barrier must be surmounted in order for a molecule to "squeeze" by its neighbors if it is to undergo transport in the bulk medium. In so doing the transported molecule is overcoming intermolecular attractive forces. A plot of $\ln \eta$ vs. $1/T$ (sometimes called an Arrhenius plot) should, according to (7), be linear and have a slope equal to E_{η}/R .

Experimental Method The apparatus used in this experiment is called an Ostwald viscometer and is shown in Figure 2. Its design reflects the application of Poiseuille's law in that the liquid whose viscosity is being measured flows through a uniform capillary tube. In principle, the viscosity of a fluid could be measured absolutely using equation (2) if its flow rate was determined and the physical dimensions of the viscometer were known. However, it is more practical to calibrate a given viscometer with a liquid of known viscosity. The wisdom of this empirical approach can be appreciated by noting that, from Poiseuille's law, the viscosity depends on r^4 ; thus the error in measuring the capillary radius enters fourfold into the measured viscosity.

Operationally, the experiment consists of measuring the time required for a given volume of liquid to flow through the viscometer capillary. The driving pressure that forces the liquid through the capillary is provided by gravity; hence, the difference in driving force between the measured and calibrating liquids is accounted for through the respective densities of these liquids. The Ostwald viscometer is designed to keep the separation of the upper and lower levels of the flowing liquid as constant as possible. This is accomplished by the spherical bulbs on the feed and receive ends of the apparatus. The volume of liquid that flows through the viscometer is determined by the positions of two lines that are inscribed on either side of the feed bulb. These lines are called fiducial (fixed reference) marks. The experiment, then, consists of measuring the time required for the liquid meniscus to pass between the upper and lower fiducial marks of the viscometer.

We can readily integrate Poiseuille's law [equation (2)] and then express the viscosity as

$$\eta = \frac{\pi r^4 P t}{8 V L}, \quad (8)$$

*Arrhenius is also associated with a similar equation that expresses the temperature dependence of a rate constant (see Experiment 21).

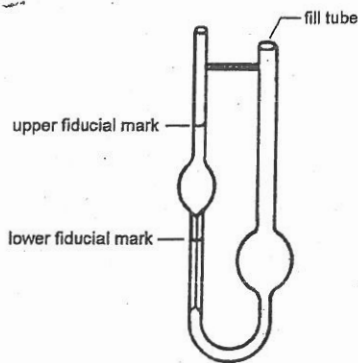


Figure 2. Ostwald viscometer.

where t is the elapsed time and V is the volume of liquid passing through the viscometer. The latter is constant for a given viscometer. Because the hydrostatic pressure, P , is proportional to the liquid density, ρ (the height is the same for both liquids), and the physical characteristics of the viscometer can be lumped into a constant, $k = r^4/8V$, the expression for viscosity becomes simply

$$\eta = k\rho t. \quad (9)$$

Thus if you measure the flow time, t , for a liquid having a density ρ you can determine its viscosity relative to that of some reference liquid, i.e.,

$$\eta = \frac{\eta_r \rho t}{\rho_r t_r}, \quad (10)$$

where η_r , ρ_r , and t_r are the viscosity, density, and flow time of the *reference* liquid, usually water. It is important that you carry out the set of measurements at a known and controlled temperature; hence, the η_r value pertains to this temperature.

Safety Precautions

- ☐ Safety goggles must be worn.
- ☐ This experiment requires the use of flammable materials. There should be no open flames in the laboratory. Fire extinguishers must be accessible at all times.
- ☐ **Methanol** and **toluene** are used in this experiment. These liquids must not come in contact with the skin. Gloves should be worn and eye protection **MUST** be used when handling these materials.
- ☐ The laboratory must be properly ventilated.

Procedure

Ostwald Viscometer

1. Suspend the viscometer in one of the constant-temperature baths using a clamp around a rubber sleeve attached to the viscometer. Make sure that the viscometer capillary is vertical and is below the surface of the water; see Figure 2. Adjust the temperature of the bath to 25.0°C by adding, if necessary, small amounts of crushed ice. Pipet 5 mL of distilled water into the viscometer. (Make all subsequent measurements using this volume of liquid and the same viscometer.) By placing the pipet bulb on the extended portion of the viscometer, and by gently squeezing the bulb, you should be able to push the liquid level up above the upper fiducial mark on the viscometer. Allow the water to run back down and start the electric timer exactly as the meniscus passes the upper fiducial mark. Stop the timer just as the meniscus passes the lower fiducial mark; record the elapsed time. Using the pipet bulb, bring the water back to the upper part of the viscometer and repeat the measurement. Do this until two or three measurements agree to within about 0.2 s.
2. Remove the viscometer from the bath. Clean and dry the viscometer by running a few milliliters of clean acetone through it using a pipet. Drain the acetone from the viscometer and carefully attach a suction tube from the aspirator to the viscometer. Aspirate for about a minute until the acetone has completely evaporated.
3. Prepare and label solutions of water and methanol that are 20, 40, 60, and 80% by volume methanol. Using the dried viscometer, determine the flow times of each of the methanol/water solutions at 25°C. Repeat each measurement until the flow times agree within about 0.2 s. After completing the measurement of one solution, rinse the viscometer with a few milliliters of the next solution to be studied. Complete the series by measuring the flow time for pure methanol.
4. Remove the viscometer from the bath. After draining the methanol, aspirate and reassemble the viscometer in the bath. Measure the flow times of a series of toluene/*p*-xylene solutions that are 0, 20, 40, 60, 80, and 100% by volume. Follow the procedure in step 3.
5. Remove the viscometer from the bath, clean it with acetone and aspirate. Suspend the viscometer in a water-filled 2-L beaker that is placed on a hot plate. Make sure the viscometer is fully immersed in the water. Add 5 mL of *p*-xylene and determine the flow time for a bath temperature of about 25°C. The exact temperature is not important as long as it is known to $\pm 0.5^\circ\text{C}$. Measure the flow times at higher temperatures, roughly every 10° up to about 65°C. Make sure that the temperature is constant and that the viscometer has had time to equilibrate to a new temperature. A 1000-W immersion heater can be used to accelerate the heating of the bath water; it must be disconnected well before the desired temperature is reached to avoid overshooting.

Data Analysis

1. Enter your run times for each set of experiments into a spreadsheet. Using equation (10) and the values of ρ , and η , transform these data into viscosities. Relevant data are presented in the appendix. Also transform the data to obtain the fluidity of each methanol/water and toluene/*p*-xylene mixture; compare these values with the fluidity calculated from equation (4).
2. Test the validity of equations (4) and (6) for the two binary systems studied.
3. Plot $\ln \eta$ vs. $1/T$ and determine the activation energy (and its standard deviation) for viscous flow for *p*-xylene.
4. Comment on the "ideality" of the two solutions.

Questions and Further Thoughts

1. Using a propagation-of-errors technique as applied to Poiseuille's law [equation (2)], show that the relative error in the capillary radius, ϵ_r/r , enters fourfold into the relative error of the viscosity.
2. Is it possible to have a homogeneous binary liquid solution whose viscosity is higher (or lower) than that of either of the two component liquids? What conclusions would you draw about the nature of intermolecular interactions in such a mixture?
3. In the case(s) in question 2, comment on the nature of the intermolecular forces of each pure liquid relative to the mixture.

Further Readings

- R. A. Alberty and R. J. Silbey, *Physical Chemistry*, 2d ed., pp. 710–713, Wiley (New York), 1997.
 P. W. Atkins, *Physical Chemistry*, 5th ed., pp. 833–834, W. H. Freeman (New York), 1994.
 I. N. Levine, *Physical Chemistry*, 4th ed., pp. 457–465, McGraw-Hill (New York), 1995.
 J. H. Noggle, *Physical Chemistry*, 3d ed., pp. 478–481, HarperCollins (New York), 1996.

Appendix

Table 1. Density of *p*-Xylene

$T (^{\circ}\text{C})$	$D (\text{g mL}^{-1})$	$T (^{\circ}\text{C})$	$D (\text{g mL}^{-1})$
20	0.879	45	0.839
25	0.857	50	0.834
30	0.852	55	0.830
35	0.848	60	0.825
40	0.943		