Goals and Resources

**Goal:** The viscosity of three simple liquids is given over an extended temperature range. Each data set is analyzed in order to determine the activation energy ($E_a$) for viscous flow of the given liquid.

**Prerequisites:** The tasks associated with this assignment can be carried out with an introductory level knowledge of chemistry.

**Resources you will need:** This exercise should be carried out within a software environment that is capable of data manipulation and which can generate a best-fit line for an x-y data set. You will also be graphing the data along with the fitted function.

Viscosity ($\eta$) is a fluid property which indicates how resistant that fluid is to flow. Highly viscous liquids, like motor oil or molasses, take much longer to flow from their container than a relatively low viscosity liquid, like benzene or diethyl ether. To quantify viscosity, we will imagine our bulk fluid as consisting of a number of very thin layers. In order for the fluid to flow, a force will be required to slide these layers relative to one another. The amount of force ($f$) required is assumed to be directly proportional to the area ($A$) of the layers in contact with one another and the velocity difference ($V$) between the layers. Furthermore, the force is inversely proportional to the distance ($d$) between the layers. Viscosity ($\eta$) can then be introduced as a constant of proportionality, yielding a force equation of the form

\[
f = \eta \frac{A V}{d}
\]

Dimensional analysis of Equation \ref{1} give SI Units for viscosity of $(kg \cdot m^{-1} \cdot s^{-1})$. However, the unit that is typically employed in practice is called the 'poise' (P), where

\[
1 \text{ P} = 1 \text{ gram} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}.
\]

Liquid viscosities are usually reported in centipoise, $(cP)$, and gas viscosity are reported in micropoise, $(\mu P)$.

What factors determine whether a given fluid has a high (or low) viscosity? Certainly the strength of intermolecular attractions has an influence; nitro-benzene has a much higher viscosity than regular benzene because the former is capable of dipole-dipole attractions which are considerably stronger than the dispersion forces of attraction present in bulk benzene. Other factors can contribute, such as the size and shape of molecules. For example, long chain molecules like polymers are capable of becoming entangled with each other which causes friction between the hypothetical layers of the fluid which translates into a large viscosity.

A number of experimental methods are available for measuring viscosity. Many are based upon measuring the amount of time ($t$) it takes for a given amount of fluid to flow through a thin glass tube or to drain from a vessel that has a small opening in the bottom. An equivalent measurement is carried on a fluid of known viscosity. The unknown viscosity is then calculated using the expression

\[
\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}
\]

where $(\rho)$ represents the density of each fluid (which is usually measured separately).
Viscosity varies with temperature, generally becoming smaller as temperature is elevated. This trend occurs because the increased kinetic motion at higher temperatures promotes the breaking of intermolecular bonds between adjacent layers. A considerable amount of research has been carried out in an attempt to understand the exact nature of the temperature variation of viscosity. One relatively simple model assumes that the viscosity obeys an ‘Arrhenius-like’ equation of the form

\[ \eta = A \exp \left( \frac{E_a}{RT} \right) \]

where \(A\) and \(E_a\) are constants for a given fluid. \(A\) is called the pre-exponential factor and \(E_a\) can be interpreted as the activation energy for viscous flow. Note that this expression is nearly identical to the Arrhenius equation that describes the temperature variation of the rate constant (\(k\)) of a chemical reaction, except equation (3) does not have a negative sign in the exponential which causes the viscosity to get smaller with increasing temperature.

Equation \ref{3} can be written in the logarithmic form

\[ \ln \eta = \ln A + \left( \frac{E_a}{R} \right) \frac{1}{T} \]

If a fluid obeys Equation \ref{4}, then a plot of viscosity versus reciprocal absolute temperature should be linear and the slope can be used to determine the activation energy for viscous flow.

In this assignment, the viscosities of three liquids are given over a certain temperature range. Each data set is analyzed in order to investigate whether the liquid obeys the simple Arrhenius model and to determine the activation energies for viscous flow for these liquids.

### Experimental Data

The following table presents viscosity data for water, ethanol, and diethyl ether over specific temperature ranges. The data were obtained from the CRC Handbook of Chemistry and Physics.

<table>
<thead>
<tr>
<th>Water</th>
<th>Ethanol</th>
<th>Diethyl ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>η (cP)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>20</td>
<td>1.002</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0.7975</td>
<td>10</td>
</tr>
<tr>
<td>40</td>
<td>0.6529</td>
<td>20</td>
</tr>
<tr>
<td>50</td>
<td>0.5468</td>
<td>30</td>
</tr>
<tr>
<td>60</td>
<td>0.4665</td>
<td>40</td>
</tr>
<tr>
<td>70</td>
<td>0.4042</td>
<td>50</td>
</tr>
<tr>
<td>80</td>
<td>0.3547</td>
<td>60</td>
</tr>
</tbody>
</table>
Exercise

1. Inspect the table and note the relative values of viscosity for each liquid at a given temperature. Comment on why the viscosity of diethyl ether is considerably lower than the other two liquids. What reason(s) can be postulated for why the viscosity of ethanol is higher than that of water.

2. Enter the data into an appropriate software environment and, for each liquid, plot the data in the form implied by Equation \(\text{ref}(4)\). Determine the best-fit line for each data set, and plot the original data along with each best-fit line. Does Equation \(\text{ref}(4)\) accurately represent the temperature variation of viscosity for these liquids (note any discrepancies between your data and the best-fit line)? Does the model work better for any one of these liquids than it does for another?

3. Report the activation energy for viscous flow \((E_a)\) for each liquid in units of kJ/mol and also rank them from smallest to largest. What is the value of \((E_a)\) relative to ambient thermal kinetic energy (given by \((Ek = RT)\))?

4. Consult the literature (an internet source will do) and find an approximate strength for a typical (O-H ... O) hydrogen-bond. Compare the literature value to the \((E_a)\) values obtained for water and ethanol. Are they of similar magnitude? What reasons can you postulate for any discrepancy that you may observe between the \((E_a)\) values and a typical hydrogen-bond strength?