## Related topics

Liquid, Newtonian liquid, Stokes law, fluidity, dynamic and kinematic viscosity, viscosity measurements.

## Principle and task

Due to internal friction among their particles, liquids and gases have different viscosities. The viscosity, a function of the substance's structure and its temperature, can be experimentally determined, for example, by measuring the rate of fall of a ball in a tube filled with the liquid to be investigated.

## Equipment

Falling ball viscometer
Thermometer, 24..+51C, f. 18220.00
Immersion thermostat A100
18220.00

Accessory set for A100
Bath for thermostat, Makrolon
Retort stand, h 750 mm
Right angle clamp
Universal clamp with joint
Pyknometer, calibrated, 25 ml
Volumetric flask 100 ml, IGJ12/21
Glass beaker, tall, 150 ml
Glass beaker, short, 250 ml
Pasteur pipettes, 250 pcs
Rubber caps, 10 pcs

| Hose clip, diam. $8-12 \mathrm{~mm}$ | 40996.01 | 6 |
| :--- | :--- | :--- |
| Rubber tubing, i.d. 7 mm | 39282.00 | 6 |
| Stopwatch, digital, $1 / 100$ sec. | 03071.01 | 1 |
| Laboratory balance, data outp. 620 g | 45023.93 | 1 |
| Wash bottle, plastic, 500 ml | 33931.00 | 2 |
| Methanol | 500 ml | 30142.50 |
| Water, distilled | 5 l | 31246.81 |

## Problems

Measure the viscosity

1. of methanol-water mixtures of various composition at a constant temperature,
2. of water as a function of the temperature and
3. of methanol as a function of temperature.

From the temperature dependence of the viscosity, calculate the energy barriers for the displaceability of water and methanol.

## Set-up and procedure

Perform the experimental set-up according to Fig. 1. Connect the falling ball viscometer to the pump connection unit of the thermostat with rubber tubing (secure the tubing connections with hose clips!). Fill the bath of the circulating thermostat with

Fig. 1: Experimental set up: Viscosity measurements with the falling ball viscometer.

distilled or demineralised water to avoid furring. Connect the cooling coil of the thermostat to the water supply line with tubing (secure the tubing connections with hose clips!).

In addition, prepare the falling ball viscometer according to its operating instructions; calibrate it; and for each experiment fill it with the liquid to be investigated (water, methanol or metha-nol-water mixtures according to Tab. 1) in such a manner that it is bubble-free.

Ball number 1, which is made of borosilicate glass, is appropriate for investigations in the given viscosity range. Its characteristic data can be obtained from the enclosed test certificate. After the ball has been placed in the gravity tube, first allow the viscometer to equilibrate to the selected working temperature $T$ for approximately 10 minutes before determining 3 to 5 falling times $t$. Calculate the arithmetic mean of the measured values in each case.

A constant working temperature of 298 K is recommended for the viscosity measurements in methanol- water mixtures (Problem a).
Conduct the investigations on the temperature dependence of the viscosity of pure liquids (Problems b and c) in steps of 5 K in the temperature range between 293 K and 323 K . Parallel to this, determine the density of the respective liquids, which is required for the calculations. To do this, weigh the clean and dry pycnometer; fill it with the liquid to be investigated; fix it to the retort stand, and equilibrate it in the thermostatic water bath for approximately 15 minutes. Subsequent to bubble-free closure with the accompanying stopper and a quick external drying, reweigh the filled pycnometer. From the mass difference of the two weighings and the volume of the pycnometer, determine the density of the liquid. Rinse the gravity tube and the pycnometer thoroughly with the next liquid to be investigated each time before it is refilled.

Tab. 1: Literature values for the density $\rho$ and the dynamic viscosity $\eta$ of methanol-water mixtures of different compositions at constant temperature ( $T=298.15 \mathrm{~K}$ )

| $m\left(\mathrm{CH}_{3} \mathrm{OH}\right)$ <br> $/ \mathrm{g}$ | $\mathrm{m}\left(\mathrm{H}_{2} \mathrm{O}\right)$ <br> $/ \mathrm{g}$ | $\rho$ <br> $/ \mathrm{g} \cdot \mathrm{cm}^{-3}$ | $\eta$ <br> $/ \mathrm{mPa} \cdot \mathrm{s}$ |
| :---: | :---: | :---: | :---: |
| 0 | 100 | 0.9970 | 0.897 |
| 10 | 90 | 0.9804 | 1.178 |
| 20 | 80 | 0.9649 | 1.419 |
| 30 | 70 | 0.9492 | 1.581 |
| 40 | 60 | 09316 | 1.671 |
| 50 | 50 | 0.9122 | 1.577 |
| 60 | 40 | 0.8910 | 1.427 |
| 70 | 30 | 0.8675 | 1.234 |
| 80 | 20 | 0.8424 | 1.025 |
| 90 | 10 | 0.8158 | 0.788 |
| 100 | 0 | 0.7867 | 0.557 |

Tab. 2: Literature values for the density $\rho$ and the dynamic viscosity $\eta$ of water and methanol at different temperatures

| T / K | Water |  | Methanol |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $\stackrel{\rho}{/ \mathrm{g} \cdot \mathrm{~cm}^{-3}}$ | $\stackrel{\eta}{/ \mathrm{mPa} \cdot \mathrm{~s}}$ | $\stackrel{\rho}{\mathrm{g} \cdot \mathrm{~cm}^{-3}}$ | $\stackrel{\eta}{/ \mathrm{mPa} \cdot \mathrm{~s}}$ |
| 293.15 | 0.9982 | 1.002 | 0.7915 | 0.608 |
| 398.15 | 0.9970 | 0.897 | 0.7868 | 0.557 |
| 303.15 | 0.9956 | 0.797 | 0.7819 | 0.529 |
| 308.15 | 0.9940 | 0.726 | 0.7774 | 0487 |
| 313.15 | 0.9922 | 0.653 | 0.7729 | 0.458 |
| 218.15 | 0.9902 | 0.597 | 0.7690 | 0.425 |
| 323.15 | 0.9880 | 0.548 | 0.7650 | 0.396 |

## Note

The measurements are time consuming and take approximately 10 hours when painstakingly performed. It is therefore appropriate to divide the experiment according to the three given problems or to have them performed optionally. Another possibility is to have the complete experiment carried out on two laboratory days.

## Theory and evaluation

The dynamic viscosity $\eta$ of a liquid (1) is defined by the force $F$ which is required to move two parallel layers of liquid both having the area $A$ and separated by $d x$ with the velocity $d \omega$ with respect to each other.

$$
\begin{equation*}
\eta=\frac{F}{A \frac{d \omega}{d \omega}} \tag{1}
\end{equation*}
$$

By relating the dynamic viscosity to the density $\rho$ of the liquid, one obtains the kinematic viscosity $v(2)$; the reciprocal of the dynamic viscosity is designated as fluidity $\varphi(3)$.

$$
\begin{align*}
& v=\frac{\eta}{\rho}  \tag{2}\\
& \varphi=\frac{1}{\eta} \tag{3}
\end{align*}
$$

A spherical particle with a radius $r$ moves in a liquid under the influence of a force $F$ and the viscosity $\varphi$ with a constant velocity $\omega$.

$$
\begin{equation*}
\omega=\frac{F}{6 \pi \eta r} \tag{4}
\end{equation*}
$$

(Stokes Law)
For the fall of a sphere in the gravitational field of the earth the motive force Fis equal to the product of the acceleration of gravity $g$ and the effective mass $m$, which can be expressed as the density difference between the sphere $\left(\rho_{1}\right)$ and the liquid $\left(\rho_{2}\right)$.

Fig. 2: Dependence of the viscosity $\eta$ of the methanol-water system on the composition described by the mass traction $w$ at constant temperature ( $T=298 \mathrm{~K}$ ).


$$
\begin{equation*}
F=m^{\prime} g=\frac{4}{3} \pi r^{3} g\left(\rho_{1}-\rho_{2}\right) \tag{5}
\end{equation*}
$$

The correlation (6) for the calculation of the viscosity, which is derived from (4) and (5), is only considered as the limit law for expanded media (the radius can be neglected with respect to that of the gravity tube); otherwise, the relationship can be approximated by corrections (Ladenburg Correction).

$$
\begin{equation*}
\eta=\frac{2 g r^{2}\left(\rho_{1}-\rho_{2}\right)}{g \omega} \tag{6}
\end{equation*}
$$

For commercial falling ball viscometers with sets of calibrated spheres, the constants in equation (6) are combined with the apparative factors to form the spherical constant $K$; this makes the calculations much simpler:

$$
\begin{equation*}
\eta=K t\left(\rho_{1}-\rho_{2}\right) \tag{7}
\end{equation*}
$$

( $t=$ rate of fall of the sphere for a measuring distance of $s=100 \mathrm{~mm}$ )

The density $\rho_{2}$ of the liquid at temperature $T$ which is contained in eqn. (7), can be calculated using the relationship

$$
\begin{equation*}
\rho_{2}=\frac{m}{V} \tag{8}
\end{equation*}
$$

( $m=$ mass of the liquid; $V=$ volume of the pycnometer)
using the experimentally determined pycnometer data or alternatively that obtained from Tables 1 and 2.

The viscosity is a function of the structure of the system and the temperature. The alteration in the measured viscosity in

Fig. 3: Dependence of the viscosity $\eta$ of the methanol water system on the composition described by the mole fraction x at constant temperature ( $T=298 \mathrm{~K}$ ).

which the composition of methanol-water mixtures are expressed as the mass fraction $w$ (9.1) or the mole fraction x (9.2) is an expression of the non-ideal behaviour of the liquids. It correlates to additional mixing phenomena such as mixing volume (volume contraction) and mixing enthalpy.

$$
\begin{equation*}
w_{1}=\frac{m_{1}}{m_{1}+m_{2}} \tag{9.1}
\end{equation*}
$$

( $w_{\mathrm{i}}=$ mass fraction, $r n_{\mathrm{i}}=$ mass of the substance i )

$$
\begin{equation*}
x_{1}=\frac{n_{1}}{n_{1}+n_{2}}=\frac{\frac{m_{1}}{M_{1}}}{\frac{m_{1}}{M_{1}}+\frac{m_{2}}{M_{2}}} \tag{9.2}
\end{equation*}
$$

( $w_{i}=$ mole fraction, $n_{i}$ quantity of substance, $m_{i}=$ mass of the substance $i, M_{i}=$ molar mass of substance i)

For many liquids the reduction of the viscosity with temperature is described by an empirically determined exponential function (10).

$$
\begin{equation*}
\frac{1}{\eta}=\varphi=C e^{-\frac{E}{R T}} \tag{10}
\end{equation*}
$$

( $R=8.31441 \mathrm{~J} \cdot \mathrm{~K}^{-1} \cdot \mathrm{~mol}^{-1}$, universal gas constant)
In this relationship which is analogous to the Arrhenius equation, $C$ represents a system-dependent constant; $E$ is an expression of the molar energy which is required to overcome the internal friction. This activation energy can be determined from the slope obtained by the linear relation (10.1) between In $\eta$ and $1 / T$ (Fig. 4).

$$
\begin{equation*}
\ln \eta=\frac{E}{R} \cdot \frac{1}{T}-\ln C . \tag{10.1}
\end{equation*}
$$

## LEP

## Data and results

The experimentally determined viscosities are presented graphically in the Figures 2 to 4 as a function of the composition of the methanol-water mixtures or of the temperature.
The following values are determined for the slopes of the linear relationships between In $\eta$ and 1/T, which are obtained by linear regression analysis:
$\Delta(\ln \eta) / \Delta(1 / T)=1.799 \cdot 10^{3} \mathrm{~K}\left(\mathrm{H}_{2} \mathrm{O}\right)$ and
$\Delta(\ln \eta) / \Delta(1 / T)=1.134 \cdot 10^{3} \mathrm{~K}\left(\mathrm{CH}_{3} \mathrm{OH}\right)$.
Substituting these values in Eq. (10.1), the corresponding energy barriers are obtained
$E=14.8 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\left(\mathrm{H}_{2} \mathrm{O}\right)$ and $E=9.4 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\left(\mathrm{CH}_{3} \mathrm{OH}\right)$.
The energy barriers, which are obtained by using the literature values for $\eta$ (given in Table 2), are $E=15.9 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$ and $E=11.1 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$.

Fig. 4: Temperature dependence of the dynamic viscosity $\eta$ of water (o) and methanol ( + ), respectively.


