Experimental

Materials and experimental techniques used for the determinations of various parameters like densities, viscosities and conductance in aqueous solutions have been summarized in this chapter. These thermodynamic and transport properties of aqueous solutions of drugs and vitamins are useful for the elucidation of various interactions taking place in the solutions. The theoretical background and determination of uncertainties of the various physicochemical properties have also been given.

3.1 Materials

The sources, grades and mass fraction purity of the chemicals used in the present study are listed in the Table 3.1.

Table 3.1 Sources and Grades of the Chemicals Used

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Source</th>
<th>Grade</th>
<th>Mass Fraction Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphanilamide</td>
<td>C₆H₈N₂O₂S</td>
<td>Spectrochem</td>
<td>AR</td>
<td>0.99</td>
</tr>
<tr>
<td>Sulphanilic acid</td>
<td>C₆H₇NO₃S</td>
<td>Spectrochem</td>
<td>,,</td>
<td>0.99</td>
</tr>
<tr>
<td>Sulphosalicylic acid dihydrate</td>
<td>C₇H₆O₆S • 2H₂O</td>
<td>SRL</td>
<td>,,</td>
<td>0.995</td>
</tr>
<tr>
<td>L-ascorbic acid</td>
<td>C₆H₈O₆</td>
<td>,,</td>
<td>,,</td>
<td>0.99</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>C₆NH₂O₂</td>
<td>,,</td>
<td>,,</td>
<td>0.99</td>
</tr>
<tr>
<td>Thiamine hydrochloride</td>
<td>C₁₂H₁₇N₄OS • HCl</td>
<td>,,</td>
<td>,,</td>
<td>0.98</td>
</tr>
<tr>
<td>Pyridoxine hydrochloride</td>
<td>C₈H₁₁NO₃ • HCl</td>
<td>,,</td>
<td>,,</td>
<td>0.98</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>,,</td>
<td>,,</td>
<td>0.99</td>
</tr>
<tr>
<td>Magnesium Chloride hexahydrate</td>
<td>MgCl₂ • 6H₂O</td>
<td>,,</td>
<td>,,</td>
<td>0.995</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>NaC₁₂H₂₅SO₄</td>
<td>,,</td>
<td>,,</td>
<td>0.99</td>
</tr>
</tbody>
</table>
All chemicals (Table 3.1) were of highest purity grade (AR) and were used without further purification. However, these were dried in vacuum desiccator before use.

Conductivity water was prepared by distilling deionised water first over acidic potassium permanganate and then over alkaline potassium permanganate. The doubly distilled water was degassed before use by boiling for 5-10 minutes. The specific conductivity of the water used for studies was less than $1.3 \times 10^{-6} \Omega^{-1}\cdot cm^{-1}$.

### 3.2 Experimental Techniques

The density, viscosity, and conductance of solutions were measured using density meter, Ubbelohde type capillary viscometer and digital conductivity meter, respectively.

#### 3.2.1 Measurement of Density

To measure the density of the liquids numerous instruments are available. Most of the data on density of liquids have been collected by the use of magnetic float density cell, differential hydrostatic balance, pycnometer and vibrating-tube digital density meter. The vibrating-tube digital density meter (Model: DMA 60/602 Anton Paar, Austria) was used for density measurements and the schematic diagram for this is shown in the Figure 3.1.

**a) Principle**

The vibrating-tube digital density meter is based on the law of time-lapse measurement of oscillations of vibrating U-shaped sample tube. The usual frequency of the oscillator is influenced by the mass and therefore, by the density of the liquid filled in the U-tube.\(^1,2\) The oscillation device is a hollow glass and is electronically excited, in an undamped fashion. The oscillations are produced in perpendicular direction to a plane passing through the inlet and outlet opening of the sample tube. The volume of the sample affects the natural frequency of the oscillating device. Therefore it is necessary to fill the oscillating sample tube at least past its nodal points, which are fixed and not oscillating.

The mathematical relation between sample density and natural frequency or period can be derived as given below.
Figure 3.1: Schematic Diagram of the Digital Density Meter (DMA 60/602).
Consider an equivalent system consisting of a hollow body with the mass $M$, which is suspended on a spring with a spring constant $C$. Its volume $V$ is assumed to be filled by a sample of the density $d$.

The natural frequency of such a system is thus given by equation (3.1):

$$f = \frac{1}{2\pi} \sqrt{\frac{C}{M + Vd}}$$  \hspace{1cm} (3.1)

Therefore, time period of oscillation $\Gamma$ is as:

$$\Gamma = 2\pi \sqrt{\frac{M + Vd}{C}}$$  \hspace{1cm} (3.2)

By squaring and simplifying the expression:

$$\Gamma^2 = \frac{4\pi^2 M}{C} + \frac{4\pi^2 Vd}{C}$$  \hspace{1cm} (3.3)

On substituting $A = \frac{4\pi^2 V}{C}$ and $B = \frac{4\pi^2 M}{C}$ into equation (3.3), it becomes,

$$\Gamma^2 = A.d + B$$  \hspace{1cm} (3.4)

where $A$ and $B$ are the constants of the oscillator having the contribution from the spring constant of oscillator, empty oscillator’s mass and the volume of the sample which participate in the oscillations. These are instrument’s constants for each individual oscillator and can be determined by time calibration measurements with sample of known density e.g. dry air and distilled water.

Therefore following relation can be used for the density difference of the samples:

$$d_1 - d_2 = K (\Gamma_1^2 - \Gamma_2^2)$$  \hspace{1cm} (3.5)

where $K = 1/A$

$d_1$ and $d_2$, and $\Gamma_1$ and $\Gamma_2$ are densities and time periods of samples 1 and 2, respectively. Thus,

$$d_1 = d_2 + K (\Gamma_1^2 - \Gamma_2^2)$$  \hspace{1cm} (3.6)
To obtain a precision of \( \pm 10^{-n} \) in determining densities, it is required to measure a time lapse at least \( 10^{n+1} \) times a chosen unit of time. If the resonance period of the oscillator, which is of the order 2-5 ms, is chosen as the time unit, then 5-6 hours measurement time would be mandatory. Since this is impractical, the total time lapse is measured by independent means in small but correctly defined units for a preset number of oscillations of the sample holder. For reasons defined by electronic circulatory, the smallest time unit which can be measured is 10 \( \mu \)s. Thus precision of \( \pm 1 \cdot 10^{-3} \) kg m\(^{-3}\) in density measurements is achieved by measuring the time lapse in the range of 10 to 100 s.

b) DMA 602 density measuring cell

Density measuring cell DMA 602 is enclosed separately with oscillator counter mass and thermostat connectors. It consists of a U-shaped borosilicate oscillator sample tube fused into a dual wall glass cylinder. The space between the U-shaped sample tube and the inner wall of the dual-wall cylinder is packed with gas of high thermal conductivity to easily establish thermal equilibrium of the sample inside the oscillator with the thermostat liquid which flows through the dual wall cylinder around the sample tube. A supplementary shorter capillary tube inside the inner space of the dual wall cylinder determines temperature by means of a temperature sensor. This capillary tube of about 2 mm inside diameter has a very thin wall thickness of about 0.2 mm to assure good heat transfer. The rest of the instrument consists of the electronic excitation system for the oscillation and the electronics, which guarantee an interface – free transmission of the period signal to the processing unit.

Air pump with a sintered glass filter for drying the sample tube as well as the sample tube lighting system have also been provided in the density meter.

c) DMA 60 electronic processing unit

Analog signal created in synchronism with the oscillating sample tube in the density measuring cell, is transmitted into the electronic processing unit DMA 60. This signal is enhanced and demonstrated digitally through the light emitting diodes. Details of its working are described elsewhere.\(^1,2\)
d) Temperature bath

The temperature of the water flowing through the density meter cell has been controlled by a constant temperature cum circulator bath (Model MC 31A Julabo/Germany). It is equipped with cooling and heating arrangement simultaneously. Temperature was controlled within ± 0.01 K. The lengths of the water circulating tubes were kept minimum and were insulated properly to avoid any heat loss.

e) Experimental procedure for density measurements

Initial start time of about 30 minutes was given to the instrument. The sample tube was washed several times with deionised water and then with double distilled water and dried. The liquid in question was injected continuously into the lower opening of the U-shaped vibrating-tube, until the excess liquid flows out of the upper opening. The tube was filled slowly to wet properly the walls and care has been taken that no micro bubbles are present. Solution was injected into the U-tube by disposable, polyethylene syringe having volume 2 cm$^3$ and after filling the sample tube completely its openings were closed with teflon stoppers. Then the light was switched off and start point was pressed on the DMA 60 processing unit. After observing few read out cycles, a constant $I^*$ was noted. In this way the mean of three constant readings was taken as the final value.

Instrument constant, $K$, was calculated after measuring the $I^*$ values for dry air and double distilled degassed water in the U-tube, which were taken as standards. The density of dry air $\rho_{T,P}$ in g·cm$^{-3}$, at a temperature, $t$ °C and atmospheric pressure, $P$ torr was calculated by using the following equation:

$$\rho_{T,P} = [0.0012390/1 + 0.00367 I^*] \cdot [P/760]$$

(3.7)

Kell’s data$^4$ for air free pure water was taken for densities. The density meter was tested by measuring the densities of the aqueous solutions of sodium chloride of different concentrations and temperatures. The present results agree well with the literature values within the combined uncertainties of 0.1%.$^5$-$^8$
3.2.2 Measurement of Viscosity

A variety of viscometers are available commercially, but many factors are considered for choosing a better one. These include magnitude of viscosity to be measured, whether the liquid or solution is elastic, whether they are transparent or opaque and the temperature dependence of viscosity. There are three basic types of viscometers: capillary, rotational and moving body. In the present work the viscosities of the solutions have been measured by Ubbelohde type capillary viscometer as described below.

a) Ubbelohde type capillary viscometer

The viscosity of the Newtonian type liquids is measured accurately with capillary viscometer. It is actually the measurement of flow time. This is the time necessary for a certain quantity of the sample liquid to flow through a capillary tube with defined width and length. The Ubbelohde type capillary viscometer used in the present case is attached with the Automatic Viscosity Measuring Unit SCHOTT AVS 350 as shown in Figure 3.2. It can measure the flow time within 0.01 s. The final efflux time contain the average of at least six readings. The working of the viscometer was checked by measuring the viscosities of aqueous solutions of glycine at 298.15 K and it agrees well with the literature values. The viscosities for water at different temperatures were taken from the literature. The measured viscosity has an uncertainty $\pm 0.002 \text{ mPa}\cdot\text{s}$.

b) Functional principles of the unit

The Viscosity Measuring Unit AVS 350 has been utilized to measure the flow time in capillary viscometer. It is equipped with two sensors to measure the level of liquid whose viscosity is to be measured. The liquid is drawn inside the viscometer by an automated pump upto measuring levels $M_2$ and $M_1$. The pump pressure is controlled automatically by the Viscosity Measuring Unit AVS 350.

c) Measuring principles

For optoelectronic sensing of the meniscus of the liquid in the viscometer, a measuring stand AVS/S (anodized aluminium) is mandatory. The LED in the upper
part of the measuring stand produce light in the near infrared range, which is transmitted in the course of a glass fiber cable to the measuring levels. The light beam passes through the viscometer and arrives at the input end of another light guide cable which executes the light to a receiver in the upper part of the measuring stand. When the sample liquid meniscus exceed through the measuring level, the light beam is darkened briefly by the optical lens effect of the meniscus and afterward intensified for a concise period. This fluctuation of the light beam fabricates a signal, which can be estimated precisely.

Figure 3.2: SCHOTT AVS 350 with JULABO Temperature Bath.

d) Temperature conditioning of sample

The viscometer filled with liquid sample is suspended in Julabo MC, constant temperature Immersion Circulator, which was kept at the desired temperature within ± 0.01 K. Measurements were made only after an equilibrium time of approximately 15 minutes.

e) Design of the viscometer

Ubbelohde type capillary viscometer employed in the present study is shown in Figure 3.3. The viscometer essentially consists of the capillary tube (1), venting tube (2) and the filling tube (3), reservoir (4), the capillary (7) with the measuring bulb (8), the pre-run bulb (9) and the reference level vessel (5). Above and below the
measuring bulb (8) are the timing marks $M_1$ and $M_2$. These marks not only define the flow through volume of the sample, but also the mean hydrostatic head ($h$). The capillary (7) ends in the upper part of the reference level vessel (5). The sample runs down from the capillary (7) as a thin film on the inner surface of the reference level vessel (5).

**Figure 3.3: Ubbelohde Capillary Viscometer from SCHOTT-GERÄTE**
f) Calibration of the viscometer

The viscometer was standardized by using deionised, doubly distilled and degassed water. The flow time of water between reference marks $M_1$ and $M_2$ was noted with the help of AVS 350 at different temperatures. The flow times were fitted to the equation (3.8):

$$\eta = \rho \{a\tau - b/\tau\}$$  \hspace{1cm} (3.8)

where $a$ and $b$ are constants of the viscometer, $\rho$ is the density and $\tau$ is the flow time for water. The values of $\eta$ and $\rho$ have been taken from literature.

g) Cleaning of viscometer

Before the start of the measurement of viscosity of liquid sample, the viscometer was cleaned properly with labolene (AR) using the ultrasonicator for 15 minutes and subsequently it was rinsed with dry acetone and then dried steadily. It was kept under dust free environment before it was put to use for automatic measurement of viscosity.

h) Filling of viscometer

About 15ml of the fresh sample was transferred through the filling tube (3) into the reservoir (4) of the viscometer. Filling capacity is indicated by etched marks on reservoir (4).

3.2.4 Measurement of Conductance

A digital conductivity meter (Model: Systronics-306) (Figure 3.4) was employed at fixed frequency of 50 Hz, to measure the specific conductance of solutions. A dip type cell with double walled glass jacket to circulate the thermostated water was used for all the measurements. The capacity of the conductivity cell was about 100 mL. An automated thermostate bath (Model: MV 25 F Julabo/Germany) was used for maintaining the temperature with uncertainty $\pm 0.01K$. It is to be noted that the constant reading of conductance have been recorded.
3.3 Theoretical Background of Measured Properties

3.3.1 Partial molar volume

The partial molar volume of a solute $\bar{V}_2$ may be visualized by considering a large reservoir of solution, so that with the addition of one mole of solute, the concentration remains the same. The change in volume of solution upon addition of one mole solute to this large reservoir, is the partial molar volume when the absolute temperature, $T$, pressure, $P$, and the number of moles of the other components if present remain unchanged.

Mathematically, the partial molar volume of a solute can be represented as:

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \ldots \quad (3.9)$$

The total volume of solutions, $V$ can be given by equation (3.10):

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (3.10)$$

where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes and $n_1$ and $n_2$ are the number of moles of solvent and solute respectively. $\bar{V}_2$, is generally determined from the apparent molar volume, $V_{2,\phi}$ which may be defined by the equation as follows:
\[ V_{2,\phi} = \frac{V - n_1 \bar{V}_1^o}{n_2} \quad T, P \text{ constant} \quad (3.11) \]

or

\[ V = n_2 V_{2,\phi} + n_1 \bar{V}_1^o \quad (3.12) \]

where \( \bar{V}_1^o \) is molar volume of pure water under identical conditions of \( T \) and \( P \).

The relationship between \( V_{2,\phi} \) and \( \bar{V}_2 \) can be obtained by using the equations (3.9) and (3.12):

\[
\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} = V_{2,\phi} + n_2 \left[ \left( \frac{\partial V_{2,\phi}}{\partial n_2} \right)_{T,P,n_1} \right] \quad (3.13)
\]

and

\[
\bar{V}_1 = \frac{V - n_2 \bar{V}_2}{n_1} = \frac{1}{n_1} \left[ n_1 \bar{V}_1^o - n_2 \left( \frac{\partial V_{2,\phi}}{\partial n_2} \right)_{T,P,n_1} \right] \quad (3.14)
\]

In terms of the experimentally measured densities, \( d_o \) and \( d \) of solvent and solution, and the molar masses, \( M_1 \) and \( M_2 \) of solvent and the solute, the \( V_{2,\phi} \) is given by following equation:

\[
V_{2,\phi} = \frac{1}{n_2} \left( \frac{n_1 M_1 + n_2 M_2}{d} - n_1 \bar{V}_1^o \right) \quad (3.15)
\]

when the molal concentration is used \( n_2 = m \), the molality of the solution and \( n_1 \) is equal to number of moles of water in 1000 g, then \( V_{2,\phi} \) becomes:

\[
V_{2,\phi} = \frac{1}{m} \left( \frac{1000 + mM_2}{d} - \frac{1000}{d_o} \right) \quad (3.16)
\]

or

\[
V_{2,\phi} = \frac{M_2}{d} \left[ \left( d - d_o \right) \times \frac{1000}{mdd_o} \right] \quad (3.17)
\]

When the molar concentration is used, \( n_2 = c \), the molarity, then \( V_{2,\phi} \) becomes:
\[ V_{2,\phi} = \frac{M_2}{d} - \frac{1000(d_o - d)}{cd_o} \]  \hspace{1cm} (3.18)

To obtain reliable values of apparent molar volumes, \( V_{2,\phi} \) and partial molar volumes, \( V_2^o \) at infinite dilution, it is necessary to measure the densities with great precision. At infinite dilution, the apparent molar volume and the partial molar volume become equal \( (V_2^\infty = V_2^o) \).

The extrapolation of apparent molar volume to infinite dilution has been made by the following equations: 1) Masson equation,\(^{13}\) 2) Redlich-Meyer equation\(^{14}\) and 3) Owen-Brinkley equation\(^{15}\).

Masson\(^{14}\) found that \( V_{2,\phi} \) of electrolyte varies linearly with square root of their molar concentrations, \( c \) by the linear equation as:

\[ V_{2,\phi} = V_2^o + b_v \sqrt{c} \]  \hspace{1cm} (3.19)

where \( b_v \) is the experimental slope.

Redlich and Rosenfeld\(^{16}\) on the basis of Debye-Huckel limiting law predicted a constant slope for a given ionic charge.

On this basis Redlich and Meyer\(^{14}\) suggested the following extrapolation function:

\[ V_{2,\phi} = V_2^o + S_v \sqrt{c} + b_v c \]  \hspace{1cm} (3.20)

known as Debye – Huckel limiting slope which depends upon the valency of the solute and not on its nature and is given by the equation:

\[ S_v = k w^{3/2} \]  \hspace{1cm} (3.21)

where \( k \) is the limiting slope and \( w \) is the valency factor. Valency factor is defined by the following equation:

\[ w = 0.5 \sum v_i z_i^2 \]  \hspace{1cm} (3.22)

where \( v_i \) and \( z_i \) are the number and charge of each ion constituting the electrolyte.
Redlich – Meyer\textsuperscript{14} developed the following polynomial equation for the limiting slope $k$ in terms of temperature $t$ in °C between 0 and 70 °C:

$$k = 1.4447 + 1.6799 \times 10^{-2} t - 8.4055 \times 10^{-6} t^2 + 5.5153 \times 10^{-7} t^3$$  \hspace{1cm} (3.23)

The values for Debye–Huckel limiting slope $S_v$ for electrolytes at the temperature of interest can be calculated by using equations (3.21) to (3.23).

Equation (3.20) can be rearranged in the form of linear equation as follows:

$$V_{2,\phi} - S_v \sqrt{m} = V_{2}^o + b_v m$$  \hspace{1cm} (3.24)

Owen-Brinkley’s equation\textsuperscript{15} can be used in the extrapolation and to represent concentration dependence of $V_{2,\phi}$ as:

$$V_{2,\phi} = V_{2}^o + S_v \theta (K_a) \sqrt{c} + W_v \theta (K_a) c + \frac{1}{2} K_v c$$  \hspace{1cm} (3.25)

The ideal method to determine $V_{2}^o$ value is to make the measurements for very dilute solutions, where the deviation from limiting law is very small.

In the case of non-electrolytes and zwitter ionic solutes, $V_{2,\phi}$ versus molality, $m$ plots are linear and $V_{2}^o$ values are obtained by least square fitting of the following equation:

$$V_{2,\phi} = V_{2}^o + b_v m$$  \hspace{1cm} (3.26)

In the present study the equations (3.24 and 3.26) have been used to obtain $V_{2}^o$ or $\overline{V}_{2}^o$ values. In case of negligible concentration dependence of $V_{2,\phi}$, the $\overline{V}_{2}^o$ values have been determined by taking average of all the data points.

3.3.2 Viscosity

Viscosity is the quantity that describes a fluid’s resistance to flow. Viscosity is the ratio of the shearing stress to the shearing rate or velocity gradient in a fluid, which is constant and is independent of the shear rate. This is true for only Newtonian or ideal solutions, whereas non-Newtonian fluids are not independent of shear rate. Relative viscosity, $\eta_r$, may be defined by the relation, $\eta_r = \eta / \eta_o$, where $\eta$ and $\eta_o$ are viscosities of the solution and solvent, respectively.
Development of Jones Dole equation

Arrhenius\textsuperscript{17} gave the following relationship between the relative viscosity and concentration, $c$ for moderately dilute solutions:

$$\eta_r = A^c$$

(3.27)

where $A$ is a constant for given salt and temperature. Various workers have shown negative curvature for the salt solutions instead of straight at lower concentrations and at low temperature. Rabionovich\textsuperscript{18} have concluded that depolymerization of water molecules must be responsible for negative viscosity.

Inspired by the special behaviour of salts, Jones and Dole\textsuperscript{19} concluded that there must be some effect which is of relatively greater importance and is responsible for curvature in viscosity vs concentration plots, and this effect always tend to increase whether the overall effect of addition of salt is to increase or decrease the viscosity. The decrease in viscosity was attributed to interionic forces.

Earlier Debye and Huckel observed that the effect of interionic forces in opposing the motion of ions is proportional to the square root of the concentration in very dilute solutions. Thus they gave the equation:

$$\phi = \frac{1}{\eta} = 1 + A\sqrt{c} + Bc$$

(3.28)

where $\phi$ is the fluidity and $A$ and $B$ are constants, where $A$ has negative value for the strong electrolytes, which tend to stiffen the solution or decrease the fluidity and zero for the non-electrolytes. The $B$ has positive value for the liquids with high fluidity and negative for those with low fluidity.

Later Jones and Talley\textsuperscript{20} measured the viscosities of urea and sucrose solutions and further confirmed that the values of $A$ for non-electrolytes like urea and sucrose is zero and the equation reduced to:

$$\phi = 1 + B.c$$

(3.29)

This equation was extended to represent the data of solutes in the form:

$$\eta_r = \frac{\eta}{\eta_o} = 1 + B.c$$

(3.30)
where $B$ is viscosity $B$-coefficient, $c$ is the molarity.

The Jones-Dole\(^9\) expression for electrolytes is as follows:

$$\eta_r = 1 + Ac^{1/2} + Bc$$  \hspace{1cm} (3.31)

Some electrolytes require an additional term in the square of the concentration at accessible concentrations:

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2$$  \hspace{1cm} (3.32)

with $A$, $B$, and $D$ being coefficients depending on the solute, the solvent, and the temperature. For most salts the term in the square of the concentration is unimportant at $c < 0.5$ mol dm\(^{-3}\), but its inclusion makes the empirical expression (3.32) valid at substantially higher concentrations.

Equation (3.31) has been used in the present work.

**Preparation of Solutions**

All the solutions were made on mass basis using a Mettler balance having an accuracy of $\pm$ 0.01 mg. The standard joint flasks (50 cm\(^3\)) were used for the preparations of solutions. The flasks were cleaned with freshly prepared chromic acid, followed by washing with deionized water and then after rinsing with dry acetone these were dried in oven. The mass of the dry and clean flasks were determined with solute and solvent to find the solutions of requisite molality as follows:

- Mass of empty flask $= W_1$ g
- Mass of empty flask + solute $= W_2$ g
- Mass of empty flask + solute + solvent $= W_3$ g
- Mass of solute $= (W_2 - W_1)$  $= 'a'$ g
- Mass of solvent $= (W_3 - W_2)$  $= 'b'$ g

Molality ($m$) = (1000 $\times$ 'a')/ (Molecular weight of solute $\times$ 'b') mol·kg\(^{-1}\).

**3.4 Estimation of Uncertainties**

**a) Uncertainty in $V_{2\phi}$**

The uncertainty in $V_{2\phi}$ may arise from (i) density and (ii) molality measurements.
(i) **Uncertainty in density measurements**

Density has been calculated as follows:

\[ d_f = d_2 + K (\Gamma_1^2 - \Gamma_2^2) \]  
\[ (3.33) \]

The uncertainty in density ‘\(d_2\)’ determination may arise due to uncertainties in calibration constant \(K\) and \(\Gamma\) values.

By rearranging the equation (3.33)

\[ K = \frac{d_1 - d_2}{\Gamma_1^2 - \Gamma_2^2} \]  
\[ (3.34) \]

where densities \(d_1\) and \(d_2\) are constant (taken from literature) and time periods \(\Gamma_1\) and \(\Gamma_2\) are experimentally determined quantities for water and dry air, respectively.

Uncertainty in ‘\(K\)’ due to uncertainty in \(\Gamma\):

\[ \text{in } \Gamma_1 = U_1 = \frac{((d_1 - d_2)2 \Gamma_1 (\Gamma_1^2 - \Gamma_2^2)^2)}{\Gamma_1^2 - \Gamma_2^2} \cdot d \Gamma_1 \]  
\[ (3.35) \]

\[ \text{in } \Gamma_2 = U_1 = \frac{((d_1 - d_2)2 \Gamma_2 (\Gamma_1^2 - \Gamma_2^2)^2)}{\Gamma_1^2 - \Gamma_2^2} \cdot d \Gamma_2 \]  
\[ (3.36) \]

Total uncertainty in \(K\):

\[ \text{Total uncertainty in } K = \sqrt{U_1^2 + U_2^2} \]

For \(d\Gamma_1 = d\Gamma_2 = 1 \times 10^{-6}\), the estimated uncertainty in ‘\(K\)’ comes out to be \(4.54 \times 10^{-7}\).

From equation (3.5),

Uncertainty in ‘\(d_2\)’ due to uncertainty,

\[ \text{in } \Gamma_1 = U_1 = 2K \Gamma_1 \cdot d\Gamma_1 \]  
\[ (3.37) \]

\[ \text{in } \Gamma_2 = U_2 = 2K \Gamma_2 \cdot d\Gamma_2 \]  
\[ (3.38) \]

\[ \text{in } K = U_3 = (\Gamma_1^2 - \Gamma_2^2) \cdot dK \]  
\[ (3.39) \]

Estimated uncertainty in ‘\(d_2\)’ due to uncertainty in temperature (0.01 \(K\)) is 0.0000003 = \(U_4\).

Thus the uncertainty in density measurement

\[ U_d = \sqrt{U_1^2 + U_2^2 + U_3^2 + U_4^2} \]  
\[ (3.40) \]

\[ = 2.18 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3} \]
(ii) **Uncertainty in molality**

Molality \( m \) of a solution has been calculated using the relation:

\[
m = \frac{\text{Weight of solute (} W_2 \text{) x 1000}}{[\text{Weight of solvent (} W_1 \text{) x molecular weight of solute (} M_2 \text{)}]}
\]  

\[ (3.41) \]

\( M_2 \) is constant, so uncertainty in ‘\( m \)’ may arise from the uncertainty in \( W_2 \) and \( W_1 \), which can be estimated as follows:

Uncertainty in ‘\( m \)’ due to uncertainty

in \( W_2 = U_1 = \frac{1000 \times dW_2}{M_2 \times W_1} \)  

\[ (3.42) \]

\[ = 2.83 \times 10^{-6} \]

in \( W_1 = U_2 = \frac{1000 \times W_2 \times dW_1}{M_2 \times W_1^2} \)  

\[ (3.43) \]

\[ = 2.20 \times 10^{-8} \]

Total uncertainty in ‘\( m \)’ \( U_m = \sqrt{U_1^2 + U_2^2} \) comes out to be 2.83 \( \times 10^{-6} \) mol \( \cdot \) kg\(^{-1} \).

Uncertainty in \( V_{2,\phi} \)’ due to uncertainty,

in \( m = U_m = \left[ \left( \frac{1000}{d_0 \times m^2} \right) - \left( \frac{1000}{d \times m^2} \right) \right] dm \)  

\[ (3.44) \]

\[ = 4.61 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \]

in \( d = U_d = \left[ \frac{1000}{m \times d^2} + \frac{M_2}{d^2} \right] dd \)  

\[ (3.45) \]

\[ = 0.05 \text{ cm}^3 \cdot \text{mol}^{-1} \]

Total uncertainty in \( V_{2,\phi} \)

\[
U(V_{2,\phi}) = \sqrt{U_m^2 + U_d^2}
\]  

\[ (3.46) \]

Estimated uncertainty in ‘\( V_{2,\phi} \)’ comes out to be 0.05 cm\(^3\) \cdot mol\(^{-1}\).
b) Uncertainty in viscosity

The uncertainty in viscosity $\eta$ may arise due to uncertainty in (i) constants $a$ and $b$ of the equation (3.8) i.e. $\eta = d \cdot \{a\tau - b/\tau\}$, (ii) measured efflux time and (iii) density.

Uncertainty in ‘$a$’ due to uncertainty in $\tau$ = $U_a = \{(\eta/d\tau^2) + (2b/\tau^3)\} \cdot d\tau$ (3.48)

$= 4.962 \times 10^{-6}$

Uncertainty in ‘$b$’ due to uncertainty $\tau$ = $U_b = \{2a\tau - \eta/d\} \cdot d\tau$ (3.48)

$= 0.202$

Uncertainties in ‘$\eta$’ due to uncertainty in $a = U_1 = \tau \cdot d \cdot da$ (3.49)

$= 1.00 \times 10^{-3}$

in $b = U_2 = (d / \tau) \cdot db$ (3.50)

$= 1.00 \times 10^{-3}$

in $\tau = U_3 = \{(ad \cdot d\tau) + (bd / \tau^2)\} \cdot d\tau = d\tau \{(ad + bd / \tau^2)\}$ (3.51)

$= 1.28 \times 10^{-4}$

in $d = U_4 = \{(a\tau \cdot dd) - (b / \tau)\} \cdot dd = dd (a\tau - b / \tau)$ (3.52)

$= 2.28 \times 10^{-8}$

Thus the total uncertainty in viscosity, $U_\eta = \sqrt{U_1^2 + U_2^2 + U_3^2 + U_4^2}$ comes out to be 0.002 mPa·s.
References:

16. O. Redlich, P. Z. Rosenfeld, Electrochem., 1931, 37, 705.