CHAPTER 2

MATERIALS AND EXPERIMENTAL DETAILS

2.1 General

2.1.1 Heterocyclic compounds

Heterocyclic compounds have played an important role in medicinal chemistry serving as key templates central to the development of numerous therapeutic agents. Among many five member heterocycles studied, pyrazolines, flavones and chromones have been identified as active core structure in antibacterial, hypotensive, antiflametry, muscarinic agonists etc.. Several therapeutically interesting biological activities of certain flavonoids have been reported including anti-cancer, anti-HIV and antioxidant properties.

Natural chalcones have been found mainly as petal pigments and also occur in leaf, fruit and root of variety of trees and plants' Chalcones containing plants such as Angelica, Glycyrrhiza piper and ruscus species have been used as medicine in Asia, Africa, South America. Natural chalcones were not isolated until 1910. Several pure chalcones were approved for chemical use since then. The chalcones class of compounds is known for their anti-infective especially antifungal, antibacterial activities since a long time. The word chalcone is derived from Greek word chalcos meaning bronze. It exists in two isomeric form, cis and trans. Trans isomer is regarded thermodynamically favorable.

Flavones and isoflavones play a prominent role in cancer prevention since these compounds are found in numerous plants that are associated with reduced cancer rates. The bioavailability of flavones and isoflavones has been shown to be influenced by their chemical form in foods, their hydrophobicity, susceptibility to degradation, the microbial flora of the consumer, and the food matrix. Many mechanisms of action have been identified for isoflavone/flavone prevention of cancer, including estrogenic/antiestrogenic activity, antiproliferation, induction of cell-cycle arrest and apoptosis, prevention of oxidation, induction of detoxification enzymes, regulation of the host immune system, and changes in cellular signaling. It is expected that some combination of these mechanisms will be found to be responsible for cancer prevention by these compounds.
2.1.2 Solvents

The polarity, dipole moment, polarizability and hydrogen bonding of a solvent determines what type of compounds it is able to dissolve and with what other solvents or liquid compounds it is miscible.

2.1.2.1 Methanol (ME)

Methanol is also known as methyl alcohol, wood alcohol, wood naphtha or wood spirit. It boils at 64.96°C.

It is produced naturally in the anaerobic metabolism of any varieties of bacteria and is ubiquitous in the environment. The modern method of preparation of methanol is based on the combination of carbon monoxide and hydrogen in presence of catalyst at elevated temperature and pressure.

Methanol can be manufactured from any hydrocarbon source like naphtha, oil, coal wood, biomass, LPG etc.. The naphtha fraction of crude oil distillation is used as raw material in many older facilities for the manufacture of it.

- It is the simplest alcohol and is a light, volatile, hygroscopic, violent poison, colorless, readily miscible in water at room temperature.
- It is a polar, flammable liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol. Because of its toxic properties, it is frequently used as a denaturant additive for ethanol manufactured for industrial uses as well as in polyacrylamide gel electrophoresis.
- It is used as - a fuel in camping and boating stove; for producing bio-diesel via trans esterification reaction; mixture of methanol and water is injected into high performance diesel engines for an increase of power and a decrease in exhaust gas temperature; as a solvent for many polymers and also used in the paint and varnish industry; in a separation of saturated and unsaturated hydrocarbon and in pharmaceutical synthesis.
- In some waste water treatment plants, a small amount of methanol is added to water treatment to provide a food source of carbon for the denitrifying bacteria which convert nitrate to nitrogen to reduce the denitrification of sensitive aquifers.

2.1.2.2 Dimethyl sulfoxide (DMSO)

It was first synthesized in 1866 by the Russian scientist Alexander Zaytsev
who reported his findings in 1867. Dimethyl sulfoxide is a by-product of kraft pulping, which produces DMSO as a side product. Oxidation of dimethylsulfide with oxygen or nitrogen dioxide gives DMSO.

- It is a colorless liquid having boiling point 189°C and freezing point 18.5°C, so at room temperature, it is a solid, which has limitation to use in some chemical processes because of its high boiling point, it evaporates slowly at normal atmospheric pressure. It has high dielectric constant and relative permittivity.
- It is an important polar aprotic solvent which is less toxic than other members of this class such as DMF that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. Reactions conducted in DMSO are often diluted with water to precipitate or phase-separate products. In its deuterated form (DMSO-d$_6$), it is a useful but expensive solvent for NMR spectroscopy, again due to its ability to dissolve a wide range of analytes, its own simple spectrum, and its suitability for high-temperature NMR spectroscopic studies.
- It penetrates the skin very readily, giving it the unusual property of being secreted onto the surface of the tongue after contact with the skin and causing garlic like taste in the mouth.
- It is used as a solvent for chemical reactions involving salts; in manufacturing processes to produce microelectronic devices; as an extractant in biochemistry and cell biology; to strip photo resist in TFT-LCD 'flat panel' displays and advanced packaging applications; in biopreservation especially stem cell banking i.e. added to cell media to prevent cell death during the freezing process; as cryoprotectant and veterinary medicine as a liniment for horses; in PCR to inhibit secondary structures in the DNA template or the DNA primers; as a topical anesthetic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory and an antioxidant, antifungal; an effective paint stripper being safer than many of the others such as nitromethane and dichloromethane.
- Because it is only weakly acidic, it tolerates relatively strong bases and as such has been extensively used in the study of carbanions. A set of non-aqueous pKa values for thousands of organic compounds have been
determined in DMSO solution.

2.1.2.3 Dimethylformamide

It can be synthesized from methyl formate and dimethylamine or by reaction of dimethylamine with carbon monoxide.

- It is colourless liquid miscible with water and the majority of organic liquids. The density of it is very similar to that of water at 20°C. In pure state, it itself associate through dipole-dipole interaction. It is odorless in pure form whereas technical grade or degraded it often has a fishy smell due to impurity of dimethylamine.

- It is a polar aprotic common solvent with a high boiling point, large dipole moment and relatively high dielectric constant.

- It especially at elevated temperature is not stable in the presence of strong bases like sodium hydroxide or strong acids such as hydrochloric acid or sulfuric acid and is hydrolyzed back into formic acid and dimethylamine.

- It is biologically important and also very good solvent which is widely used in polymer science for the production of acrylic fibers and plastic as well as in peptide coupling for pharmaceuticals, in the development and production of pesticides.

- Binary liquid mixtures of it can be broadly classified into simple mixtures and associated mixtures. Simple mixtures are defined as those in which the nominal components are identical with the actual species in the pure liquids as well as in the mixtures. The associated mixtures are defined as those in which there is an evidence for the association of at least one of the components either with each other (self association) or with those of another component. It is possible to approach the description of such mixtures in terms of the properties of the components in a formal thermodynamic manner or with respect to the molecular interactions, such as dipole-interactions, hydrogen bonding, and coordinative bond formation.

2.1.3 Density and specific gravity

Mass is a physical property which all objects possess, but objects of the same size can have different masses and weights. This difference is
characterized by density.

Density is defined as the ratio of an object's mass to its volume \( d = \frac{m}{v} \), since it is rare to find two different substances with identical densities; density is of value in helping to identify materials. All liquids can be defined by their density. Just like all measurements in science, liquids are compared to standard, e.g. pure water, which are one g/cm\(^3\). Where g is the mass of water and cm\(^3\) is the volume of water. Density is an important fundamental property of liquids and gases. Density is a useful means of displaying the mass in a liquid. The density of any substance is the mass of the material divided by the volume it occupies.

Specific gravity is often used as a measure of the change in density. The specific gravity is a comparison of the density of the liquid compared to the density of pure water at a specific temperature. The specific gravity of a substance is defined as the ratio of the density of the substance to the density of water (1 g/cm\(^3\)).

2.1.4 Viscosity

The viscosity of a fluid is an important property in the analysis of liquid behavior and fluid motion near solid boundaries. The viscosity is the fluid resistance to shear or flow and is a measure of the adhesive/cohesive or frictional fluid property. The resistance is caused by intermolecular friction exerted when layers of fluids attempt to slide by one another.

Formally, viscosity is represented by the symbol \( \eta \) (eta) and is the ratio of the shearing stress to the velocity gradient in a fluid. A liquid with high viscosity is thick and flows slowly and liquid with low viscosity is thin and flows quickly. Different liquids have different viscosities.

The Poise represents absolute viscosity, the tangential force per unit area of either of two horizontal planes at unit distance apart, the space between being filled with the substance. A liquid with an absolute viscosity of one Poise requires a force of one dyne to maintain a velocity differential of one centimeter per second over a surface one centimeter square. When the ratio of shearing stress to the rate of shear is constant, as is the case with water and thin motor oils, the fluid is called a Newtonian fluid. In the case of non-Newtonian fluids, the ratio varies with the shearing stress, and viscosities of such fluids are called apparent viscosities.

The SI unit of viscosity is the pascal second (Pas) which has no special
name. Despite its self-proclaimed title as an international system, the International System of Units has had very little international impact on viscosity. The pascal second is rarely used in scientific and technical publications today. The most common unit of viscosity is the dyne second per square centimeter (dyne s/cm\(^2\)) which is given the name poise (P) after the French physiologist Jean Louis Poiseuille (1799-1869). Ten poise equal one pascal second (Pa.s) making the centipoise (cP) and millipascal second (mPa.s) identical.

### 2.2 Synthesis

#### 2.2.1 Synthesis of chalcones

Aqueous KOH (0.02 mol) was added to the suspension of 2-hydroxyacetophenone (0.01 mol) and p-chlorobenzaldehyde (0.01 mol) in ethanol. The reaction mixture was stirred at room temperature for overnight. The reaction mixture was then poured onto ice cold water and acidified with HCl (1M). The solid obtained was filtered and crystallized from ethanol to get pure chalcone 1.

![Molecular Formula](image)

**Molecular Formula** = C\(_{15}\)H\(_{11}\)ClO\(_2\)

**Formula Weight** = 258.70

**Composition** = C(69.64%) H(4.29%) Cl(13.70%) O(12.37%)

**M+** = 258.04 m/z

Same procedure was followed to synthesize Chalcone 2 from m-nitrobenzaldehyde.

#### 2.2.2 Synthesis of Flavones

**Chalcone 1** (0.002 mol) was dissolved in DMSO (20 ml) and a crystal of iodine was added to it. The mixture was refluxed 30-45 min. The solid obtained (F1) after dilution with excess of water was filtered, washed with aqueous 20%
sodium thiosulphate till the product become colorless and further purified by column chromatography using hexane:ethylacetate (80:20 v/v) as an eluent.

2-(4-chlorophenyl)-4H-chromen-4-one

\[ \text{Molecular Formula} = \text{C}_{15}\text{H}_9\text{ClO}_2 \\
\text{Formula Weight} = 256.68 \\
\text{m.p.} = 185-187^\circ\text{C} \\
\text{Composition} = \text{C}(70.19\%) \text{ H}(3.53\%) \text{ Cl}(13.81\%) \text{ O}(12.47\%) \\
\text{M+} = 256.02 \text{ m/z} \]

Above experimental procedure was followed to prepare the flavone (F2) using Chalcone 2.

2-(3-nitrophenyl)-4H-chromen-4-one

\[ \text{Molecular Formula} = \text{C}_{15}\text{H}_9\text{NO}_4 \\
\text{Formula Weight} = 267.24 \\
\text{m.p.} = 282-284^\circ\text{C} \\
\text{Composition} = \text{C}(67.42\%) \text{ H}(3.39\%) \text{ N}(5.24\%) \text{ O}(23.95\%) \\
\text{M+} = 267.05 \text{ m/z} \]

2.2.3 **Synthesis of Pyrazolines**

Chalcone 1 (0.002 mol) was dissolved in ethanol (10 ml). To this reaction mixture, hydrazine hydrate (0.006 mol) was added. The reaction mixture was heated under mild reflux for 2.5 hrs. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured onto ice
cold water. The white solid obtained was filtered off and crystallized from ethanol to obtain pure pyrazoline (P₁).

![chemical structure of 2-[5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-3-yl]phenol]

P₁

Molecular Formula = C₁₅H₁₃ClN₂O
Formula Weight = 272.73
m.p. = 122-124°C
Composition = C(66.06%) H(4.80%) Cl(13.00%) N(10.27%) O(5.87%)
M+ = 272.07 m/z

Same procedure was used to prepare P₂ using Chalcone 2.

![chemical structure of 2-[5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl]phenol]

P₂

Molecular Formula = C₁₅H₁₃N₃O₃
Formula Weight = 283.28
m.p. = 110-112°C
Composition = C(63.60%) H(4.63%) N(14.83%) O(16.94%)
M+ = 283.09 m/z

2.2.4 Synthesis of Chlorochromones

Chalcone 1 (0.001mol) was dissolved in minimum quantity of DMSO (5-6ml) Then 2g of anhydrous CuCl₂ was added and reaction mixture was reflux for 3hrs. This reaction mixture was kept overnight. Further, the reaction mass was quenched into crushed ice and left for 1 hr. A white solid was obtained which was filtered & washed with three times by water and 1:1 HCl till the colour of the mother liquor was colorless. The solid product (CL₁) was purified by recrystallisation from ethanol.

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3-chloro-2-(4-chlorophenyl)-4H-chromen-4-one

![Molecular structure of CL1]

Molecular Formula $= C_{15}H_{8}Cl_{2}O_{2}$
Formula Weight $= 291.13$
m.p. $= 130-132^\circ C$
Composition $= C(61.88\%)$ H$(2.77\%)$ Cl$(24.36\%)$ O$(10.99\%)$
M+ $= 289.99$ m/z

Above experimental procedure was followed to prepare CL2 using Chalcone 2.

3-chloro-2-(3-nitrophenyl)-4H-chromen-4-one

![Molecular structure of CL2]

Molecular Formula $= C_{15}H_{8}ClNO_{4}$
Formula Weight $= 301.68$
m.p. $= 121-123^\circ C$
Composition $= C(59.72\%)$ H$(2.67\%)$ Cl$(11.75\%)$ N$(4.64\%)$ O$(21.21\%)$
M+ $= 301.01$ m/z

2.3 Preparation of binary mixtures and solutions containing solute

Even though the purity of substance is not a crucial factor in measurements of density, it is very important for viscosity measurements. ME, DMSO and DMF were of standard grade (SRL) with purity near to 99% and used as such.

Binary liquid mixtures of DMSO and DMF with ME($x_1$) of compositions 0 – 100 mass % as well as $x_1 = 0.1$ to 0.9 were prepared by mixing a known mass of each liquid in an airtight stoppered bottle. The masses were recorded on a digital balance (SHIMADZU AUX 220) to an accuracy of $\pm 1 \times 10^{-5}$ g. No attempt was
made to monitor the relative humidity of the air to which the liquids were exposed for a short period of time during preparation. The mole fraction of each component was calculated. The estimated error in mole fraction was $< 1 \times 10^{-4}$. Care was taken to avoid contamination during mixing. Solutions containing 0.001 to 0.01m heterocyclics ($F_1$, $P_1$, $Cl_1$, $F_2$, $P_2$ and $Cl_2$) in binary mixtures (as a solvent) were also prepared by usual method.

### 2.4 Density measurements [1-11]

Densities of liquids/solutions were measured by weighing a definite volume of the liquid in specific gravity bottle or single stem pycnometer having a volume about of 10 c.c..

Pycnometer was first cleaned by the chromate cleaning mixtures and washed several times with tap water and finally by distilled water and with little acetone or methanol and drained to dry to remove obstructions in the capillary. This enabled a smooth flow of liquid without drops sticking behind then dried it by passing a stream of dry and warm air from hot blower. Distilled water was kept standing in balance room for at least one hour so that it attains the room temperature of the balance room.

First weighed the empty pycnometer using 0.01 mg electronic balance and then filled the bottle with air free distilled water and inserted the stopper into its mouth so that small amount of water flows out the capillary. Its outer surface was carefully wiped by means of blotting paper or filter paper to ensure that outer surface is completely dried. The filled pycknometer was weighed after allowing them to stand for a short time to take the temperature of the balance case. The weight of water was then found from difference in weight. From the known density of water at room temperature and the weight of the water taken in the pycknometer, corresponding volume of water was calculated.

Pycnometer was cleaned and dried as discussed above. It was then filled with experimental liquids. Masses of liquids under investigation were obtained and the corresponding densities thus determined.

### 2.5 Viscosity measurements by capillary flow method [1-11]

The time required when liquid flow through capillary under specified condition can be used to determine the viscosity of the liquid. This method is based on Poiseuille’s principle.
In the present study, this method was employed to determine the viscosity of fluid at various temperatures. The usual form of this simple, yet accurate, apparatus known as Ostwald viscometer was used for comparing viscosities of different liquids is shown in Fig. 2.1.

It consists of U tube with two bulbs, the left hand limb of U tube is essentially a pipette with two defining marks ‘A’ and ‘B’ and capillary resistance ‘C’ through the liquid contained in bulb ‘D’ flows under gravity back into the ‘E’ in the right hand limb. A definite volume of liquid was introduced into larger bulb using calibrated pipette. The quantity of liquid should be adjusted so that when it is forced by applying pressure into the left hand limb up to the mark A, then the meniscus in the right hand limb stands at the bottom of the bulb ‘E’. On releasing the liquid the meniscus falls from A to B before the liquid stand at the same level in both the limbs. By applying a pressure to the right hand tube the liquid is forced up into the left hand limb above the mark A and then allowed to fall back through the capillary under a pressure due its own weight. Viscometer suspended in water containing large beaker was always kept in vertical position. A piece of rubber tubing, cleaned internally to remove dust, was attached to the tube left hand limb and used when sucking the liquid into the left hand limb.

The time of flow of the liquid from the mark A to B was noted by a stop watch with an accuracy of 0.01 s. The flow time measurement was repeated a number of times (usually 3-4 times). It is usually sufficient to compare the viscosity of liquid with that of water by measuring the time taken for equal volumes of two liquids to flow through same capillary under pressure due to their own weights. The densities of both liquids must be known. The absolute viscosity of the liquid can then be obtained knowing the viscosity of the standard liquid. The viscometer was calibrated with triple distilled water at room temperature (vary with seasons) using the relation:

$$\eta = \rho \left( AT - B/t \right)$$

where A and B are the viscometer constants and t is the time of flow. All flow times were greater than 100s.

The force driving the liquid through the capillary in Ostwald viscometer is equal to \( \rho_1 gh \) where ‘h’ is mean difference of level of liquid in the two limbs of the tube, ‘\( \rho_1 \)’ is the density of the liquid and ‘g’ is gravitational constant. The
resistance of flow depends on the dimensions of the capillary which are constant and on the viscosity of the liquid. If now, the same volume of a second liquid of known viscosity is introduced in the tube, the mean difference of level of the two liquid surfaces will also be h, so that the driving force is now \( \rho_1gh \). Thus, the driving force is proportional to their viscosities. Since the rate of flow is proportional to force/resistance, the times of outflow \( (t_1 \text{ and } t_2) \) for the same volume of the two liquids are in the inverse ratio i.e.

\[
\frac{t_1}{t_2} = \frac{(\eta_1/\rho_1)}{(\eta_2/\rho_2)} \text{ OR } \frac{\eta_1}{\eta_2} = \frac{(\rho_1/t_1)}{(\rho_2/t_2)}
\]

Thus, if the absolute viscosity of one liquid is known, that of the given liquid can be determined.

Since the rate of flow through a capillary tube depends on ‘r’ (internal radius of capillary) can vary from 0.2 to 2.0 mm, Ostwald viscometer can be made to cover a range of \( 10^4 \) in viscosities. A small error may arise in these measurements due to the change of volume of the liquid owing to expansion. But this may be neglected provided that during the out flow period, the lower meniscus lies inside the bulb ‘E’ so that the change of level is small. The estimated error of viscosity measurement was \( \pm 0.1 \) or \( 0.2\% \). The uncertainties in dynamic viscosities were of the order \( \pm 0.003 \text{ m.Pas} \). The difference reading did not deviate from the mean by more than \( 0.2 \text{ s} \). Fig. 2.2 is the photograph of experimental set up for calibration of pycnometer and viscometer at different temperatures.

Experimental densities and viscosities of solvents were compared with those reported in the literature. From the observation of Table 2.1, it could be said that, our experimental values matched very well with those of literature.

### 2.6 UV measurements

UV Spectra of above solvent systems and solutions were recorded on a UV 2400 PC in the wavelength range 200-400 nm. The scan speed was fast and sampling interval was about 2.0. The UV measurements are reported directly in nm, and the corresponding range in \( \text{cm}^{-1} \).

On passing electromagnetic radiation in the UV regions through a compound with multiple bonds, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of compound. Ultraviolet spectrum recorded the
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wavelength of maximum absorption ($\lambda_{\text{max}}$).

2.7 IR measurements

FTIR spectra of experimental solvent systems and solutions were recorded on a FTIR spectrometer (Model: SIMADZU 8400S PC) by using KBr pellet in the region 400-4000 cm\(^{-1}\) with 4.0 cm\(^{-1}\) resolution. The transmission values were read in steps of 5%. The spectrometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded. The FTIR – 8400S relies on an interferometer to perform infrared measurement and a personal computer to control the interferometer and process the data.

Selected stretching frequencies of solvents and solutes used in this work are listed in Tables 2.2 – 2.4.

2.8 Optimization of geometries using Gaussian Package

Geometry optimizations of heterocyclic compounds, pure solvents and their 1:1 and 1:1:1 complexes were carried out using the DFT/B3LYP method with medium size 6-31G (d) basis set available in G03(W) series of programs [32]. All optimized geometries were viewed through GaussView 4.1 software.

Figs. 2.3-2.5 include optimized geometries of solvents and solutes under investigation.


2.9 References


Table 2.1 Comparison of experimental data of $\rho$ and $\eta$ of solvents with literature at different temperatures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp. K</th>
<th>$\rho$</th>
<th></th>
<th></th>
<th>$\eta$</th>
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</thead>
<tbody>
<tr>
<td>ME</td>
<td>298.15</td>
<td>0.7863</td>
<td>0.7863$^a$, 0.7864$^b$, 0.7866$^c$</td>
<td>0.547</td>
<td>0.549$^d$, 0.551$^b$</td>
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<td>303.15</td>
<td>0.7820</td>
<td>0.7820$^d$, 0.7819$^e$, 0.7816$^f$</td>
<td>0.513</td>
<td>0.516$^g$, 0.515$^f$</td>
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<td></td>
<td>308.15</td>
<td>0.7769</td>
<td>0.7771$^h$, 0.7770$^a$</td>
<td>0.472</td>
<td>0.469$^k$, 0.479$^k$</td>
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<tr>
<td>DMSO</td>
<td>298.15</td>
<td>1.0956</td>
<td>1.0953$^a$, 1.0959$^b$, 1.0956$^i$, 1.0957$^h$, 1.0958$^m$</td>
<td>1.994</td>
<td>1.991$^b$, 1.991$^i$, 1.996$^f$, 1.996$^m$, 1.996$^n$</td>
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<td></td>
<td>303.15</td>
<td>1.0885</td>
<td>1.0853$^h$, 1.0896$^o$</td>
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<td>1.654$^b$, 1.798$^o$</td>
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<td></td>
<td>308.15</td>
<td>1.0854</td>
<td>1.0853$^h$, 1.0855$^i$, 1.0855$^o$, 0.856$^p$</td>
<td>1.650</td>
<td>1.654$^b$, 1.644$^i$, 1.654$^o$, 1.645$^p$</td>
<td></td>
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<tr>
<td>DMF</td>
<td>298.15</td>
<td>0.9444</td>
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<td></td>
<td>303.15</td>
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<td>308.15</td>
<td>0.9351</td>
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<td>0.709</td>
<td>0.707$^a$, 0.707$^i$</td>
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$^a$Ref.12, $^b$Ref.13, $^c$Ref.14, $^d$Ref. 15, $^e$Ref.16, $^f$Ref.17, $^g$Ref.18, $^h$Ref.19, $^i$Ref.20, $^j$Ref.21, $^k$Ref.22, $^l$Ref.23, $^m$Ref.24, $^n$Ref.25, $^o$Ref.26, $^p$Ref.27, $^q$Ref.28, $^r$Ref.29, $^s$Ref.30, $^t$Ref.31.
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Table 2.2 Selected neat IR frequencies of solvents

<table>
<thead>
<tr>
<th>ME</th>
<th>DMSO</th>
<th>DMF</th>
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<tbody>
<tr>
<td>O-H</td>
<td>3570, 3450</td>
<td>S=O</td>
</tr>
<tr>
<td>C-H</td>
<td>2833.00</td>
<td>C-H</td>
</tr>
<tr>
<td>C-H</td>
<td>2945.40</td>
<td>--</td>
</tr>
<tr>
<td>C-O</td>
<td>1030.02</td>
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</tr>
</tbody>
</table>

Table 2.3 IR stretching frequencies of F₁, P₁ and CL₁

<table>
<thead>
<tr>
<th>F₁</th>
<th>P₁</th>
<th>CL₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>ν</td>
<td>Group</td>
</tr>
<tr>
<td>C-H</td>
<td>3074</td>
<td>N-H</td>
</tr>
<tr>
<td>C-H</td>
<td>3173, 32261</td>
<td>O-H</td>
</tr>
<tr>
<td>C=O</td>
<td>1632</td>
<td>C=N</td>
</tr>
<tr>
<td>C=C</td>
<td>1478, 1411</td>
<td>C=C</td>
</tr>
<tr>
<td>C-Cl</td>
<td>761</td>
<td>C-Cl</td>
</tr>
</tbody>
</table>

Table 2.4 Neat IR frequencies of F₂, P₂ and CL₂.

<table>
<thead>
<tr>
<th>F₂</th>
<th>P₂</th>
<th>CL₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>ν</td>
<td>Group</td>
</tr>
<tr>
<td>C-H</td>
<td>3064, 3005</td>
<td>N-H</td>
</tr>
<tr>
<td>C=O</td>
<td>1640</td>
<td>O-H</td>
</tr>
<tr>
<td>C=C</td>
<td>1601, 1431</td>
<td>C=N</td>
</tr>
<tr>
<td>N=O</td>
<td>1339, 1516</td>
<td>C=C</td>
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<tr>
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<td>N=O</td>
</tr>
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Fig. 2.1 An Ostwald Viscometer
Fig. 2.2 Experimental setup for calibration of pycnometer and viscometer
Fig. 2.3 Optimized geometries of DMSO and DMF using B3LYP/6-31G (d) basis set
Fig. 2.4 Minimum energy structures of $F_1$, $F_2$ and $P_1$ by DFT method using B3LYP /6-31G(d) basis set
Chapter 2  

*Materials and experimental details*

2-\{5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl\}phenol

\[ \text{P}_2 \]

3-chloro-2-(4-chlorophenyl)-4H-chromen-4-one

\[ \text{CL}_1 \]

3-chloro-2-(3-nitrophenyl)-4H-chromen-4-one

\[ \text{CL}_2 \]

*Fig 2.5.* DFT optimized geometries of \( \text{P}_2 \), \( \text{CL}_1 \) and \( \text{CL}_2 \) by using B3LYP/6-31G(d) basis set