Properties of aliphatic and aromatic aldehydes under high pressure: Viscosity and compressibility measurements.

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PROPERTIES OF ALIPHATIC AND AROMATIC ALDEHYDES UNDER HIGH PRESSURE: VISCOSITY AND COMPRESSIBILITY MEASUREMENTS

BY

PRADIP MITRA CHAUDHURI

THESIS

Submitted to the Faculty of Graduate Studies Through the Department of Chemical Engineering in Partial Fulfilment of the Requirements for the Degree of Master of Applied Science at University of Windsor

Windsor, Ontario
1967
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ABSTRACT

Studies of the effect of pressure on the physical properties of the aliphatic and the aromatic aldehydes at pressures from 0 to 20,000 p.s.i.g. at room temperature were made in a newly designed, compact, easy to operate high pressure apparatus. Seven aliphatic and three aromatic aldehydes were examined in this work. The properties investigated were viscosity and specific volume.

An equation of state and an empirical viscosity-pressure correlation for liquids have been developed. These can be used with a confidence level of more than 95%.

The proposed equation of state is

$$ P = r(B(V))^q $$

where

$$ B(V) = \left\{ \left( \frac{V_o}{V} \right)^4 - \left( \frac{V_o}{V} \right)^2 \right\} $$

and $r$ and $q$ are empirical constants and $V_o$ is volume at atmospheric pressure.

The viscosity-pressure correlation is

$$ \eta = \eta_o \exp mP $$

where

$$ m = b \exp a\alpha $$

The symbol $\alpha$ represents the number of carbon atoms.

It was found that Thodos' correlation for the prediction of viscosity failed in the case of aldehydes and so a new generalized equa-
tion has been developed which is

$$(n-n_o)\xi = (e\rho_R)^{a'+b'M}$$

where

$$\xi = \frac{T^{1/6}}{M^{1/2} \rho_c^{2/3}}$$

$$\rho_R = \rho/\rho_c$$ and

$a'$ and $b'$ are constants.
ACKNOWLEDGEMENT

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I. INTRODUCTION

The design of chemical engineering appliances demands the availability of physical property data of a wide variety of substances. Measurement of such properties is not always possible, and therefore a sufficiently accurate theoretical prediction is necessary.

For liquids, the scope of theory is definitely limited, at the same time, because of wide gaps in the availability of literature data, formulation of a reliable semi-empirical correlation is rather difficult.

It was felt that the development of versatile equipment for simultaneous measurements of several physical properties with relative ease is needed in this era of greatest technological advancement. It was an objective of this project to make sufficient data available to formulate semi-empirical correlations for the prediction of physical properties of liquid aldehydes at higher pressures.

The properties investigated were viscosity and compressibility. Efforts were also made to measure electrical conductivity simultaneously. Measurements of these properties were undertaken by numerous investigators in the last few years for various organic compounds. But no work has so far been reported for aldehydes, which are organic compounds with characteristic -CHO groups.

It may be interesting to note that an attempt was also made to detect possible reversible or irreversible pressure-induced transitions of aldehydes to polyaldehydes (7,14,15,40) by noting the sudden changes in the physical properties like volume. However, it was observed that the present experimental conditions were not sufficient to bring about polymeric transformations of aldehydes.
II. LITERATURE REVIEW

A. Liquid Viscosity Data

The effect of temperature and pressure on the viscosity of liquids has been studied intensively for many years because of the importance of the data both to the engineering and to the fundamental study of the liquid state. A complete review of viscosity literature to 1950 can be found in Bridgman's book (8) and his survey article (9). Since then the published works have been concerned almost exclusively with organic compounds.

Viscosity data for organic halides, hydrocarbons and alcohols were reported by Bridgman for pressures up to about 30 kb (10). Above this pressure almost all liquids that have been studied become solid. The viscosity of all substances, with the exception of water, increases with pressure at constant temperature.

Amongst various researchers, Griest et al (19) and Lowitz et al (36) have studied various complicated high molecular weight organic compounds purely from the academic point of view and deduced interesting conclusions. For example, they found that the more complex the molecule, the more marked is the effect of pressure on the viscosity.

Boelhower and Toneman (5) have studied the pressure dependence of viscosity for several high molecular weight substituted hydrocarbons and a few polymers up to a pressure of 1400 bars.
Babb et al (2) obtained rough viscosity-pressure data for several hydrocarbons up to 10 kb at room temperature. The work of Sage and co-workers (13, 44, 41) is also primarily based on hydrocarbons and is noteworthy. Recently Huang et al (25) have done some valuable work on methane and propane for pressures up to 5000 p.s.i. and at temperatures from -170°C to 0°C.

No work appears to have so far been done on either aromatic or aliphatic aldehydes to establish their viscosity or density behaviour with pressure.

B. Viscosity Measurement

Most high pressure measurements have been made by modifying the rolling ball type viscometer, first used by Flowers (17), or falling cylinder viscometer, used by Lawaczeck (31). Bridgman (11) was the first to adopt Lawaczeck's falling body apparatus for viscosity-measurements at higher pressures. His timing device was a simple combination of a small synchronous 60 cycles motor with an ordinary clock movement, started and stopped with appropriate relays. Hersey et al (25) used a rolling ball viscometer to a pressure of 4 kb. Later workers have mostly chose either of the above two types of apparatus with modifications in timing devices.

Jobling et al (28) took a fall cylinder containing a magnet which induced a transient current in the coil wound around the fall tube. The transient current was recorded by an oscillograph and a movie camera which gave the fall time.

Heiks et al (23) used a plummet containing radio active cobalt 60 along with external coincident ionization chambers to facilitate precise
time measurement. Carmichael et al (13) utilized a thyraton circuit which
operated a chronograph, as a function of the position of the ball. Rabb
et al (2) used a lab-scaler as a timing device which produced square waves
between fall time.

C. Compressibility Measurement

In order to employ density corrections on the measured viscosity,
knowledge of compressibility is essential. Nonetheless, almost all of the
previous workers, including Bridgman, did not attempt to determine density
concurrently with viscosity in the same equipment. Very recently (1966)
Huang et al (25) measured viscosity and density concurrently. However, their
presentation fails to clarify the experimental procedure utilized by them.

D. Liquid Correlations

Because of the anomalous nature of the liquids, generalized co­
rrelations for predicting their properties are difficult to establish.

The growing importance of high pressure physical properties of
liquids has led many workers (29,32,50,49,16,45,46) to develop reduced
correlations, which seem to be rather promising. One of the most discussed
equations is due to Thodos and co-workers (29), which is

\[(n-n_o)\xi = (23.13 \exp 1.079 \rho_R^{-25}) \times 10^{-5} \]  

(II-1)

where

\[\xi = \frac{T_c^{1/6}}{\{M^{1/2} \times p_c^{2/3}\}}\]

\[\rho_R = \frac{\rho}{\rho_c}\]

and \(n_o\) is the viscosity at atmospheric pressure. All the other terms have
usual significance, given under nomenclature at the end of this thesis.
III. GENERAL THEORY

The viscosity behaviour of liquids is quite different from that of gases. Moreover, the mechanism of momentum transfer in liquids is not completely understood. The present work is not primarily concerned with the basic theory of viscosity behaviour of liquids but rather with the measurement and correlation of such data.

The main interest of this project is the development of a simple but accurate high pressure apparatus of the falling weight-piston displacement type. It is desirable to indicate the theory behind such equipment.

A. Theory of the Falling Weight Viscometer

Lawaczeck (31) and later Heinze (24) have studied in detail the theory behind the falling weight viscometers. According to Lawaczeck, there are three distinct resistances to the fall of the plummet through the liquid. These can be enumerated as:

(i) The resistance which results from the liquid flowing through the plummet and the fall tube

(ii) A viscous drag resulting from relative movement of the two cylindrical walls

(iii) A head resistance caused by the formation of stream lines.

The effect of head resistance can be lowered to a negligible value by using a long plummet and a very small clearance between the plummet and the fall tube.
The following equation was proposed by Lawaczeck for calculating absolute viscosity.

\[ \eta = \frac{t(\sigma - \rho)}{S} \left\{ \frac{\delta^3 d}{3(d+2\delta)^2 + 4\delta^2} \right\} \]  

(III-1)

After a little simplification the above equation was used by Heinze (24) and later Jobling (28) for absolute viscosity measurement up to a pressure of about 420 atmospheres.

The simplified form is as follows:

\[ \eta = \frac{(\sigma - \rho)(a-b)^3}{6Sb} \]  

(III-2)

\[ \eta = \kappa(\sigma - \rho)t \]  

(III-3)

where

\[ \kappa = \frac{(a-b)^3}{6S} \]

= instrument constant.

The expression for Reynolds number is as follows:

\[ \frac{D_s p}{\eta} \]  

(III-4)

where

\[ D_e = 4R_H \]

and \( S \) is the flight length of the plummet.

Again,

\[ D_e = \frac{4(\pi D^2/4 - \pi d^2/4)}{\pi D + \pi d} \]

\[ = D - d \]

\[ = 2b - d . \]
Diagramatic Representation of the Dimensional Terms Used in Eqn. III-1

FIGURE 1.
Hence
\[ D_e = 2(a-b) \]
\[ = 26 \]

B. Reduced State Viscosity

Following Abas-Zade's (29) proposed correlation between residual thermal conductivity and density of liquids, Thodos and co-workers have tried to find a similar correlation for residual viscosity with fairly reasonable success. They proposed that the residual viscosity, \( \eta - \eta_o \), of a substance can be dimensionally related to its critical properties, in which case,
\[ \eta - \eta_o = \alpha T^a \rho^b \frac{v^c}{T^d} M^e N^f. \quad (III-6) \]

Upon dimensional analysis, the values of the exponents are found to be
\[ a = d \]
\[ d = d \]
\[ b = 1/2 - d \]
\[ e = 1/2 \]
\[ c = -1/6 - d - f \]
\[ f = f. \]

Using these exponents equation (III-6) can be written as
\[ (\eta - \eta_o)T = \beta Z^m c^p R^n. \quad (III-7) \]

Thodos and co-workers have found that in the range \( 0.3 \leq \rho R \leq 2.0 \), the following relationship fairly accurately represents the data available in the literature.
\[ (\eta - \eta_o)T = (23.13 \exp 1.079 \rho R - 25) \times 10^{-5} \quad (III-8) \]
Later in this thesis, the comparison of this equation with present data will be made to check the validity of this equation.

C. The Equation of State

Bridgman (8) tried various P-V-T relations for a large number of liquids he studied. Beside his polynomial equation, he found a very simple relation between pressure and volume to be approximately true for liquids up to even 9 Mb.

\[ \Delta V = -b \ln P + C \]  

(III-9)

For twelve liquids, the constants in the above equation were established to be:

\[ \Delta V = -0.1 \ln P + 0.602 \]  

(III-10)

The equation (III-9) can also be extracted from the Tait equation (4) which has the form,

\[ V_0 - V = c' \ln \left( \frac{B + P}{B + P_0} \right) \]  

(III-11)

where \( B \) and \( c' \) are constants.

Surprisingly Khoubesserian (30), and later Sood (48), both apparently ignorant of Bridgman's well-known equation, found the same to be valid for solids at pressures up to 23 kb. Khoubesserian studied organic polymers whereas Sood studied inorganic hydrates. These researchers used the following form of Bridgman's equation,

\[ - \frac{\Delta V}{V_0} = a + b \ln P \]  

(III-12)
In the present case, however, though Bridgman's equation was found to hold only approximately, a better correlation is called for.

Griest et al (19) tried to adopt the semi-empirical equation,

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

(III-13)

to their viscosity-pressure data. The above equation can be written as

\[ \log\left( \frac{\eta}{\eta_0} \right) = \frac{(B - B_0)}{(2.303RT)} \]  

(III-14)

where \( \eta \) and \( B \) refer to the values at elevated pressures. They suggested the following relation of \( B \) with specific volume:

\[ B(v) = \frac{b'}{v^l} - \frac{a'}{v^2} \]  

(III-15)

where

\[ b' = a'v_0^2 \]

and \( a' \) is a constant. This follows from the Lennard-Jones intermolecular potential function (33), which is

\[ \phi = C_1 r^{-6} + C_2 r^{-12} \]  

(III-16)

The above considerations resulted in the following equation:

\[ \ln \left( \frac{\eta}{\eta_0} \right) = \frac{K}{T} \left\{ \left( \frac{v^l}{v_0^l} \right) - \left( \frac{v_0^2}{v^2} \right) \right\} \]  

(III-17)

\[ = \frac{K}{T} B(V) \]

The equation (III-17) fitted the data of Griest et al in an excellent manner.

Now, in the present case, a semi-empirical equation

\[ \eta = Q \exp SP \quad (S=\text{constant}) \]  

(III-18)
i.e.

\[ \ln \left( \frac{\eta}{\eta_0} \right) = S(P - P_0) \]  

(III-19)
has been found to fit the experimental data for aldehydes rather well and hence it has been expected that a linear correlation should exist between pressure and volume function \( B(V) \). Equating equations (III-19) and (III-17) the pressure volume relationship can be presented as

\[
P = P_o + K'(\frac{V_o}{V})^4 - (\frac{V_o}{V})^2 \quad \text{(III-20)}
\]
or

\[
P = P_o + K'B'(V) \quad \text{(III-21)}
\]

Where

\[
K' = \frac{K}{ST},
\]

and

\[
B'(V) = (\frac{V_o}{V})^4 - (\frac{V_o}{V})^2.
\]

Now if the reference pressure \( P_o \ll P \), one can write

\[
P = K' B'(V) \quad \text{(III-22)}
\]

which is the proposed equation of state for liquids. The constant \( K' \) is expected to depend on the temperature and on the nature of the liquid concerned.

It will be found in the later part of the thesis that the above equation of state agrees well with the experimental results.
IV. EQUIPMENT AND PROCEDURE

As indicated in Chapter II, the most widely used viscometer was that of Lawaczeck, adopted by Bridgman for higher pressures. Previous workers generally used piezometers (6) for compressibility measurements.

Whereas viscosity and specific volume used to be measured by separate instruments, the present equipment was designed to measure them in a combined apparatus and is referred to as visco-compressibility meter (Fig. 2). A detailed description of the equipment follows.

A. Pressure Generation and Measurement

Pressure was generated in the equipment by a hydraulic pump, manually operated. The pump was obtained from Black-Hawk Industrial Products Co., Wisconsin. The rated pressure of the pump was 40,000 p.s.i., with usable oil volume of 30.7 cu. in.

The oil pressure was measured by a Heise Bourdon gauge. The gauge could read up to a maximum pressure of 20,000 p.s.i., and had graduations of 5 p.s.i.

B. The Viscometer

This consisted of 1) a fall tube, 2) plummet, 3) a pair of electrical connectors and 4) a pair of plugs, and are described below.

1. Fall Tube

The length and the internal diameter of the fall tube was
A = Viscometer          P = Plugs
B = Compressibilitymeter  T = T-Joints
C = High Pressure Gauge  V = Valves

FIGURE 2. Details of Visco-compressibilitymeter Assembly
152.5294 cm. and 0.4710 ± 0.00385 cm. respectively. The material of construction was stainless steel, type 304 (Fig. 3).

2. Plummet

The design of plummet was based on experience gathered during test runs with steel balls and solid steel cylinders of arbitrary dimensions. Essentially the type of plummet used was a thin hollow steel cylinder of a uniform outside diameter of 0.43688 cm. having smooth rounded forced-fitted caps at both ends (Fig. 3). The body of the plummet was carefully polished by usual methods and finally with chamois leather to give it a smooth glassy finish. Bridgman (1926) used sinkers with three small projecting lugs as guides to keep the cylinder coaxial during its fall, and also to maintain electrical contact with the wall of the tube as a necessary feature of his timing device. Eventually the lugs introduced some errors in absolute measurements and were omitted in the present case. Instead, modified electrical contacts were used.

Moreover, it was found with the help of a stethoscope that the plummet did not contact the wall and it was therefore assumed that the plummet landed coaxially without the aid of the lugs.

The optimum clearance between the plummet and the fall tube was determined by the range of viscosity studied. A compromise between the length of the plummet and the clearance was made.

3. Electrical Contacts

Electrical contacts were constructed to get electrical signals at the top and at the bottom of the travel of the plummet. They were made out of hollow, very thin walled stainless steel tubes and were designed.
A. Fall Tube

Details of the Fall Tube and a Fall Cylinder

B. Fall Cylinder

1½” N.T.P., 19 threads per inch

3/16”

9/16”

FIGURE 3.
so as not to hinder smooth passage of liquids into the viscometer. The bottom connector is shown in Figure 4. It has a positive and a negative pole. The negative pole was connected to the viscometer wall by an ordinary phosphor bronze spring. The positive part was kept electrically insulated from the rest of the viscometer and was connected to the inner steel cylinder of the lower plug (Fig. 5), through hair pin shaped phosphor bronze spring. The tip of the connector was made very smooth and slightly concave in order to make a seat for the plummet and to facilitate good connection at both positive and negative ends.

4. Plugs

The viscometer tube was closed at the top end by a plug through a reducer coupling. The bottom end ran into a narrow pressure tube through another reducer which went into one leg of a T-joint. One of the other two legs went to another T-joint which was connected to a secondary pump and the compressibility meter (Fig. 2). The last of the three legs was closed by a plug through which a copper wire ran into the main tube of the viscometer. The electrical connections required that the wire passing through the metal plug be insulated from it. This created a problem of leakage. A specially designed plug was therefore used.

The sectional elevation of the plug is shown in Figure 5. A hole of 3/32" diameter runs through the base of the plug which widens a little above the lower end of the collar where a paper base polyphenol disc with 1/64" diameter hole at the centre sits and supports a solid cylinder insulated from the rest of the plug by Teflon packing.

Paper base polyphenol has a compressive strength of 36,000 p.s.i.
Details of the Connector

- **Teflon Ring**
- **Phosphor Bronze Spring Connecting the Tube Wall**
- **Stainless Steel Connector Tube**
- **Phosphor Bronze Spring Connecting Wire to the Connector Tube Wall**
- **Teflon Insulation insulating the Connector from the rest of the Viscometer**
- **Teflon Spaghetti to Protect and Insulate the Copper Wire**
- **Copper Connecting Wire**

FIGURE 4.
Sectional Elevation of a Plug

FIGURE 5.

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as shown in tests conducted prior to use. The copper wire which runs through the plug was soldered to the groove at both ends of the steel cylinder. The wire was insulated with a Teflon spaghetti which also had the purpose of protecting the wire from corrosive liquids.

C. High Pressure Fittings

All the fittings and tubings used were standard, made of 304 stainless steel and supplied by Autoclave Engineers, Erie, P.A., U.S.A. They were all rated for use up to a pressure of 30,000 p.s.i. The high pressure tubings used for connecting viscometer and the compressibility meter with the pumps and the gauge had an I.D. of 0.083" and an O.D. of 0.25".

D. Compressibility Meter

This consisted of a 16" long, 9/16" O.D., 1/4" I.D., stainless steel (type 316) tube with cap-collar-gland assembly at both ends. Inside the tube there was an AMPCO piston-ALNICO magnet assembly soldered together. The piston had two circular grooves for rubber 'O' rings to prevent mixing of oil and the liquid samples. After every run the 'O' rings had to be replaced because of corrosion and erosion of the rings.

Outside the compressibility meter tube there was a magnet-pointer assembly. This was fitted on a pivot in a rectangular plexiglass box with slots which could slide back and forth along a graduated scale on the tube. The pointer used to indicate the positions of the piston to 1/10 th of a millimeter rode on an ALNICO magnet. The magnet was magnetized along the length and had a sharp pointed nose.
E. Electrical Circuits

The pulse network designed for operating the counter during the flight of the plummet is very simple, containing a 0.1 μF capacitor and a 1 kΩ resistor in series with a 9 volts D.C. power supply. The electronic counter to which pulses were fed for measurement of time interval was from Hewlett-Packard company. The time constant of the circuit was of the order of micro-seconds. The electrical setup is shown in Figure 6.

F. Source of Chemicals

Materials used in the experiments were all white label A.C.S grade highest purity organic aldehydes supplied by Fisher Scientific Company. Some of the chemicals were supplied by Eastman Kodak Company.

G. Loading the Equipment

As most of the aldehyde vapours are very harmful to the respiratory system, extreme precautions were taken during the loading of the equipment.

The secondary pump which was used to inject liquids into the visco-compressibility meter was first filled to its usable volume in a fume closet. Then the pump was quickly joined to the liquid entrance line. All the joints of the apparatus were kept loose at this moment. The piston of the compressibility meter which separates the high pressure oil and the organic liquids was brought to the sample end of the compressibility meter and the valve V₁ (Fig. 2) adjacent to the gauge was tightly closed. The sample liquid was then pumped into the apparatus from the secondary pump and was allowed to flow out of the viscometer through its top for about two minutes. All the joints which were kept loose during liquid
Details of the Electrical Connectors and Accessories

A. Magnets  F. 1kΩ Resistor
B. Viscometer  G. Electronic Counter
C. Plummet  H. 0.1μF Capacitor
D. Connector  I. A.C.Power Supply
E. Plug  J. D.C. Power Supply

FIGURE 6.

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Injection to eliminate air pockets were tightened slightly. The main pump was opened to the atmosphere and the valve $V_1$ was also opened so as to facilitate injection of liquid into the compressibility meter. When this was done, liquid entrance valve from the secondary pump was closed tightly.

The main pump was then closed from atmosphere and a pressure of 2,000 p.s.i. was built up in the apparatus. Next all the reducer and T-joints were well tightened, the pressure was brought back to atmosphere and the experiment was started. The whole loading operation took about 25 to 30 minutes.

Polyvinyl disposable rubber gloves and a respirator mask was used when handling liquids. The cartridge used in the respirator could absorb up to about 0.1% of organic vapour by volume. In the case of extremely poisonous liquids at pressures higher than 10,000 p.s.i. a plastic shield was used to protect the face.

H. Test Runs

Before starting the actual experiment with the aldehydes, several test runs were made with various liquids of known viscosity to examine the accuracy of the instrument. Plummets of different dimensions (diameters ranging from 0.130" to 0.180" and lengths ranging from 0.5" to 4.5") were tried to find the optimum plummet size for the range of viscosity expected. It was discovered that plummets with smaller clearances and larger lengths gave more accurate results than plummets of larger clearances and smaller lengths. Finally a plummet was chosen for the experimental purpose which had 1" length and 0.172" diameter (i.e. clearance of 0.006") and which gave the best results among the ten plummets tried.
FIGURE 7. Details of the Bomb Used to Replace the Secondary Pump in Special Cases
Test run data of benzene and carbon tetrachloride agree to three significant figures with data of Jobling and Lawrence (28) and also with that of Smithsonian values (47). Extreme care was necessary in measuring the necessary dimensions of the apparatus.

In case of highly volatile and poisonous liquids, the secondary pump was actually replaced by a stainless steel and aluminum bomb (Fig. 7) which was specially designed for working with liquids (aromatic aldehydes) that are oxidized by atmospheric oxygen.
V. DATA REDUCTION AND RESULTS

Processing and analysis of data was carried out on an IBM 1620 II computer. A Calcomp 656 plotter was used for making initial plots.

A.1. Treatment of Viscosity Data

The time interval between the start and the stop of the plummet was noted by an electronic counter. For each pressure at least 10 flight times were recorded and the average value was used for calculation of viscosity.

A.2. Viscosity-Pressure Correlation

Regression analysis of the viscosity pressure data gave an excellent correlation of the form

\[ \ln \left( \frac{\eta}{\eta_0} \right) = \ln P \]

i.e.

\[ \eta = \eta_0 \exp mP \]  \hspace{1cm} (V-1)

where \( m \) is a constant dependent on the nature of the substance and the temperature and \( P \) is given in p.s.i.

The values of the constants and the coefficients of correlation for all the compounds are given in the Table-I. The average value of the coefficient of correlation shows a level of significance of 5%, that is a confidence level of 95% (39).

B.1. Treatment of Compression Data

168122

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<table>
<thead>
<tr>
<th>Compounds</th>
<th>Formula</th>
<th>m (1/p.s.i.)</th>
<th>Coeff. of Correlation</th>
<th>Room Temp.</th>
<th>No. of C-Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>CH₃CHO</td>
<td>0.1957x10⁻⁴</td>
<td>0.9950</td>
<td>71.6°F</td>
<td>2</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>CH₃CH₂CHO</td>
<td>0.2883x10⁻⁴</td>
<td>0.9965</td>
<td>74.3°F</td>
<td>3</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>CH₃(CH₂)₂CHO</td>
<td>0.2671x10⁻⁴</td>
<td>0.9980</td>
<td>84.0°F</td>
<td>n</td>
</tr>
<tr>
<td>Iso-Butyraldehyde</td>
<td>(CH₃)₂CHCHO</td>
<td>0.2769x10⁻⁴</td>
<td>0.9962</td>
<td>82.8°F</td>
<td>1</td>
</tr>
<tr>
<td>Iso-Valeraldehyde</td>
<td>(CH₃)₂CHCH₂CHO</td>
<td>0.3053x10⁻⁴</td>
<td>0.9984</td>
<td>81.0</td>
<td>1-5</td>
</tr>
<tr>
<td>Heptaldehyde</td>
<td>CH₃(CH₂)₅CHO</td>
<td>0.3682x10⁻⁴</td>
<td>0.9998</td>
<td>71.1</td>
<td>7</td>
</tr>
<tr>
<td>Caprylic Aldehyde</td>
<td>CH₃(CH₂)₆CHO</td>
<td>0.4757x10⁻⁴</td>
<td>0.9999</td>
<td>69.3</td>
<td>8</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>C₆H₅CHO</td>
<td>0.3494x10⁻⁴</td>
<td>0.9999</td>
<td>71.7</td>
<td>7</td>
</tr>
<tr>
<td>Anisaldehyde</td>
<td>CH₃OC₆H₄CHO</td>
<td>0.6008x10⁻⁴</td>
<td>0.9951</td>
<td>76.7</td>
<td>8</td>
</tr>
<tr>
<td>Trans-Cinnamaldehyde</td>
<td>C₆H₅CHCHO</td>
<td>0.7489x10⁻⁴</td>
<td>0.9990</td>
<td>84.3</td>
<td>9</td>
</tr>
</tbody>
</table>
Linear compression obtained from the compressibility meter was converted into volume compression by multiplying it with a factor of 0.31653. This corresponds to the volume of each centimeter displacement of the piston in the compressibility meter.

B.2. Pressure-Volume Correlation

The pressure volume data was also analyzed by computer by the method of least mean squares which resulted in a virtually perfect correlation of the following form.

\[ \ln P = \ln r + q \ln B(V) \]

or

\[ P = r(B(V))^q \] \hspace{1cm} (V-2)

In equation (V-2) \( r \) and \( q \) are constants and \( B(V) \) is a volume function given by

\[ B(V) = \left\{ \left( \frac{V_o}{V} \right)^4 - \left( \frac{V_o}{V} \right)^2 \right\} \] \hspace{1cm} (V-3)

Results of statistical analysis for both aliphatic and aromatic compounds are given in Table-II. The average coefficient of correlation shows a level of significance above 95%.

C.1. Critical Properties

The critical properties were estimated by methods involving the least quoted errors. It may be pointed out that Thodos' methods for calculating critical constants gave greater percentage errors than those used and enumerated in Table-III.

The constants \( \theta, \phi, \psi \) in Table-3 are calculated from the structure of the organic compound by a building block method (h2). Table-IV shows all
<table>
<thead>
<tr>
<th>Compounds</th>
<th>a</th>
<th>ln r</th>
<th>Coeff. of Correlation</th>
<th>- mean ln(B(V))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>1.0587</td>
<td>10.9950</td>
<td>0.9998</td>
<td>1.7792</td>
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<tr>
<td>Propionaldehyde</td>
<td>1.0249</td>
<td>11.1993</td>
<td>0.9999</td>
<td>2.0372</td>
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<tr>
<td>Butyraldehyde</td>
<td>1.0790</td>
<td>11.2589</td>
<td>0.9999</td>
<td>1.9903</td>
</tr>
<tr>
<td>Iso-Butyraldehyde</td>
<td>1.0576</td>
<td>11.1304</td>
<td>0.9950</td>
<td>1.9089</td>
</tr>
<tr>
<td>Iso-Valeraldehyde</td>
<td>1.2234</td>
<td>11.3932</td>
<td>0.9994</td>
<td>1.8651</td>
</tr>
<tr>
<td>Heptaldehyde</td>
<td>1.0474</td>
<td>11.4762</td>
<td>0.9998</td>
<td>2.2579</td>
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<tr>
<td>Caprylic Aldehyde</td>
<td>1.0516</td>
<td>11.5505</td>
<td>0.9999</td>
<td>2.3194</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.0669</td>
<td>11.9274</td>
<td>0.9999</td>
<td>2.6394</td>
</tr>
<tr>
<td>Anisaldehyde</td>
<td>1.0319</td>
<td>12.0487</td>
<td>0.9999</td>
<td>2.8466</td>
</tr>
<tr>
<td>Trans-Cinnamaldehyde</td>
<td>1.1719</td>
<td>12.2186</td>
<td>0.9999</td>
<td>2.6515</td>
</tr>
<tr>
<td>Property</td>
<td>Method</td>
<td>Formula</td>
<td>Quoted Errors</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------</td>
<td>------------------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>$T_c$ (Critical Temperature)</td>
<td>Reidel-Guldberg</td>
<td>$T_c = T_b / \theta$</td>
<td>1.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 0.574 + \Delta T$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_c$ (Critical Pressure)</td>
<td>Lynderson</td>
<td>$P_c = \frac{M}{(\phi + 0.37)^2}$</td>
<td>3.1%</td>
<td></td>
</tr>
<tr>
<td>$V_c$ (Critical volume)</td>
<td>Lynderson</td>
<td>$V_c = \text{Base value} + \psi$</td>
<td>2.1%</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_c$ ($^\circ$K)</th>
<th>$T_b$ ($^\circ$K)</th>
<th>$P_c$ (Atmos)</th>
<th>$V_c$ (cc/gmole)</th>
<th>$\rho_c$ (gms/cc)</th>
<th>$M$ (Mol.Wt.)</th>
<th>$\frac{Z_c}{P_c V_c / RT_c}$</th>
<th>$\frac{1}{6 \frac{1}{M_c^{2/3}}} \Xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>462.516</td>
<td>294.16</td>
<td>54.747</td>
<td>168</td>
<td>0.2622</td>
<td>44.05</td>
<td>0.2423</td>
<td>0.0291</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>493.804</td>
<td>321.96</td>
<td>46.542</td>
<td>223</td>
<td>0.2604</td>
<td>58.08</td>
<td>0.2561</td>
<td>0.0285</td>
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<tr>
<td>Butyraldehyde</td>
<td>522.246</td>
<td>348.86</td>
<td>39.502</td>
<td>278</td>
<td>0.2594</td>
<td>72.10</td>
<td>0.2563</td>
<td>0.0288</td>
</tr>
<tr>
<td>Iso-Butyraldehyde</td>
<td>506.256</td>
<td>366.66</td>
<td>40.516</td>
<td>274</td>
<td>0.2631</td>
<td>72.10</td>
<td>0.2672</td>
<td>0.0282</td>
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<tr>
<td>Iso-Valeraldehyde</td>
<td>536.946</td>
<td>365.66</td>
<td>35.347</td>
<td>329</td>
<td>0.2618</td>
<td>86.13</td>
<td>0.2639</td>
<td>0.0285</td>
</tr>
<tr>
<td>Heptaldehyde</td>
<td>597.989</td>
<td>428.16</td>
<td>27.653</td>
<td>443</td>
<td>0.2577</td>
<td>114.18</td>
<td>0.2497</td>
<td>0.0297</td>
</tr>
<tr>
<td>Caprylic Aldehyde</td>
<td>596.393</td>
<td>436.56</td>
<td>25.124</td>
<td>498</td>
<td>0.2574</td>
<td>128.21</td>
<td>0.2557</td>
<td>0.0299</td>
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<tr>
<td>Benzaldehyde</td>
<td>648.510</td>
<td>452.66</td>
<td>41.766</td>
<td>334</td>
<td>0.3177</td>
<td>106.12</td>
<td>0.2621</td>
<td>0.0373</td>
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<tr>
<td>Anisaldehyde</td>
<td>720.443</td>
<td>520.16</td>
<td>34.692</td>
<td>408</td>
<td>0.3337</td>
<td>136.14</td>
<td>0.2394</td>
<td>0.0213</td>
</tr>
<tr>
<td>TransCinnamalde-</td>
<td>720.000</td>
<td>524.16</td>
<td>33.370</td>
<td>424</td>
<td>0.3117</td>
<td>132.15</td>
<td>0.2395</td>
<td>0.0251</td>
</tr>
<tr>
<td>-de</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
the necessary critical and other constants used in the following section.

C.2. Residual Viscosity-Density Correlation

The residual viscosity and reduced density values were calculated from the estimated values of critical constants given in Table-IV. An attempt was made to find the constants of Thodos' Dimensional equation (Ch. III) in light of data available for aldehydes. The exponent of the compressibility factor was assumed to be unity.

\[(n-n_o)_{\xi} = \beta Z_c \rho_R^n \quad \text{(V-4)}\]

Combining \(\beta Z_c\) into one constant \(k\),

\[(n-n_o)_{\xi} = k \rho_R^n \quad \text{(V-5)}\]

The equation (V-5) was tested statistically using data of all the compounds together to obtain results given in Table-V. The correlation factor indicates a very poor confidence level.

The generalized equation can be presented as

\[\ln (n-n_o)_{\xi} = n \ln \rho_R + \ln k \quad \text{(V-6)}\]

or

\[\ln (n-n_o)_{\xi} = 32.9375 \ln \rho_R - 48.5658\]

i.e.

\[(n-n_o)_{\xi} = \exp \{32.9375 \ln \rho_R - 48.5658\} \quad \text{(V-7)}\]

Data of individual compounds treated separately gave a confidence level below 95%. Results can be found in Table-VI.

D.1. Temperature Correction for Density

As the temperature variation is small, from 69 to 84°F, a linear
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>32.9375</td>
</tr>
<tr>
<td>ln k</td>
<td>-4.5658</td>
</tr>
<tr>
<td>Coefficient of Correlation</td>
<td>0.8056</td>
</tr>
<tr>
<td>Mean ln $\rho_R$</td>
<td>1.19916</td>
</tr>
<tr>
<td>Mean ln $(n-n_0)\xi$</td>
<td>-9.0685</td>
</tr>
<tr>
<td>Compounds</td>
<td>n</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>17.1747</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>29.9416</td>
</tr>
<tr>
<td>n-Butyaldehyde</td>
<td>23.6049</td>
</tr>
<tr>
<td>Iso-Butyaldehyde</td>
<td>23.2746</td>
</tr>
<tr>
<td>Iso-Valeraldehyde</td>
<td>24.0456</td>
</tr>
<tr>
<td>Heptaldehyde</td>
<td>32.3859</td>
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<tr>
<td>Caprylic Aldehyde</td>
<td>36.2566</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>46.2594</td>
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<tr>
<td>Anisaldehyde</td>
<td>60.7911</td>
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<tr>
<td>Trans-Cinnemaldehyde</td>
<td>59.3451</td>
</tr>
<tr>
<td>Compounds</td>
<td>A</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Acetaldehyde *</td>
<td>0.7271x10^{-2}</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.0099x10^{-2}</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>0.0153x10^{-2}</td>
</tr>
<tr>
<td>Iso-Butyraldehyde</td>
<td>0.0449x10^{-2}</td>
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<tr>
<td>Iso-Valeraldehyde †</td>
<td>0.0449x10^{-2}</td>
</tr>
<tr>
<td>Heptaldehyde</td>
<td>0.7472x10^{-2}</td>
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<td>0.4399x10^{-2}</td>
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<td>Benzaldehyde</td>
<td>1.1031x10^{-2}</td>
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<tr>
<td>Anisaldehyde</td>
<td>0.0619x10^{-2}</td>
</tr>
<tr>
<td>Trans-Cinnamaldehyde</td>
<td>0.0171x10^{-2}</td>
</tr>
</tbody>
</table>

* Values calculated from Thorp et al formula (27) \( n = \frac{A}{(B+t)^n} \), where \( A=15652.8 \), \( B=286.11 \), \( n'=2.7550 \), \( t \) is in °C.

† Values assumed to be very close to Iso-Butyraldehyde.
FIGURE 8. Density versus Temperature Plot
FIGURE 9. In $\eta$ versus $1/T$ For Aldehydes
relation between density and temperature was assumed.

\[ \rho = C + DT \quad (V-8) \]

The constants were evaluated from atmospheric density data (Fig. 8) obtained with Sergant's modified Sprengle density meter at three different temperatures. Such a type of density meter is used for volatile substances. The values of C and D are given in Table-VII.

D.2. Temperature correction of Viscosity

The well known exponential correlation was used to account for the temperature variation of viscosity. Atmospheric viscosity at three different temperatures was obtained by using a Hoepppler viscometer.

\[ \eta = A \exp \frac{B}{T} \quad (V-9) \]

The estimated values of the constants are given in Table-VII. It was assumed that the constants A, B, C, and D are independent of pressure. Graphical presentation of data can be found in Figure 9.
VI. DISCUSSION OF RESULTS

As indicated previously both aliphatic and aromatic groups of aldehydes were studied for volume and viscosity changes with pressure from 0 to 20,000 p.s.i.g. Combined results of both the groups were presented in the previous chapter and will be discussed here separately.

It should be pointed out that all graphs presented in this chapter represent the average of several runs. Since the experiments were carried out at room temperature which used to vary within ±5°F, an average temperature had been noted during each run.

The effect of temperature on viscosity and density at higher pressures was assumed to be the same as that at atmospheric pressure. This was a reasonable, though not perfectly accurate assumption.

In some cases it was observed that viscosity and compressibility of the liquids was time dependent at higher pressures, possibly because of certain changes in molecular structure. In those cases an average flight time was calculated and recorded. Error due to this effect was well below 2%.

The Reynolds number during the experiments never exceeded 72 and fell in a range of 0.05 to 72.00 in contrast to Heiks et al.'s average value of 100 (22). Hence in the present case, the assumption that the plummet was at its terminal velocity immediately after it's release from the top of the viscometer may be assumed valid.
Data were noted for both ascending and descending pressures but only ascending pressure data are reported. Difference in ascending and descending pressure data indicate the marked hysterisis of the Bourdon pressure gauge used in the experiment. An example of such hysterisis can be found in Figure 18. In case of doubtful results, experiments were repeated.

A. Aliphatic Aldehydes

Seven members (C₂-C₈) of the aliphatic aldehyde homologue were studied at pressures up to 20,000 p.s.i.g. The results will be discussed under viscosity and volume heads as follows.

1. Viscosity-Pressure Correlation

Viscosity of all substances with the exception of water (8) increases with pressure at constant temperature. Unlike most of the other physical properties its rate of change increases as the pressure increases. Figure 10 shows the effect of pressure on viscosity of aliphatic aldehydes.

It is to be noted that greater the chain length of the compound, the greater is the rate of change of viscosity with pressure. The convexity towards the pressure axis of C₃ to C₅ compounds is very small, in fact C₄ compounds (both normal- and iso-) has almost linear isotherms, whereas C₇ and C₈ compounds have marked convexity towards the pressure axis.

It should be pointed out that whereas the boiling point of acetaldehyde is 21°C, its viscosity measurements were carried out at a temperature of 22°C. This may have some influence on the viscosity-pressure relation which appears to be fairly linear in Figure 10 but is not actually so in a very enlarged scale given in Figure 11. Here one may note a marked
$C_2$ = Acetaldehyde  
$C_3$ = Propionaldehyde  
$i-C_4$ = Iso Butyraldehyde  
$n-C_4$ = Normal Butyraldehyde  
$i-C_5$ = Iso Valeraldehyde  
$C_7$ = Heptaldehyde  
$C_8$ = Caprylic Aldehyde
FIGURE 11. Viscosity of Acetaldehyde versus Pressure at Room Temperature
concauity of the curve towards the pressure axis.

However, on a semi-log paper, a plot of all compounds shows a linear relation between \( \log \eta \) and \( P \). This was also indicated by Hamann (20) in 1957 as an approximate general rule for all liquids (Fig. 12).

The correlation is

\[
\ln \left( \frac{\eta}{\eta_0} \right) = mP.
\]

or

\[
\eta = \eta_0 \exp mP
\]

values of \( m \) were calculated and given in Table-I, chapter V. The correlation factors indicate a confidence level of 95% which is reasonably good.

The isobaric variation of viscosity with number of carbon atoms may be found in Figure 13. It has been found that log of the constant \( m \) of the equation (VI-1) varies linearly with pressure (Fig. 14). Hence one can replace the constant \( m \) in the above equation by the expression

\[
m = b \exp \alpha a
\]

where \( a \) is the number of carbon atoms, \( a \) and \( b \) are empirical constants.

2. Pressure-Volume Correlation

Isothermal linear compression of aliphatic aldehydes is plotted against pressure in Figure 15. The nature of the curve depends on the chain length of the compound concerned. As expected, the liquids become less compressible as the pressure increases.

The usual procedure of presenting the compressibility data is through a plot of \(-\Delta V/V_0 \times 100 \) versus \( P \), as in Figure 16. The nature of
In Order of Increasing Slope,
1) $c_2$
2) $c_3$
3) $n-C_4$
4) $i-C_4$
5) $i-C_5$
6) $c$
7) $C_8$

FIGURE 12. Semi-log plot of $\eta/\eta_o$ versus Pressure
FIGURE 15. Compression Diagram of Aliphatic Aldehydes

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FIGURE 16. Compressibility Diagram for Aliphatic Aldehydes at Room Temperature
the compressibility curves is similar to that of the compression curves
given in Figure 15, for obvious reasons.

As the theory suggests (Chapter III, Section c), there should
be a linear relation between the volume function B(V) and the applied gauge
pressure. In practice it was found that the relationship, though not exactly
linear, is nonetheless very close to the same. The plot of ln B(V) versus
lnP is shown in Figure 17.

The correlation can be given as

\[ P = r \{B(V)\}^q \]  \hspace{1cm} (VI-3)

where \( r \) and \( q \) are constants and

\[ B(V) = \{(V_o/V)^h-(V_o/V)^2\} \]

The average value of the constant \( q \) for all the aliphatic compounds is about
1.05. The constant \( r \) was found to be dependent on the nature of the sub­
tance and the temperature. Correlation factors found in Chapter V shows
a confidence level well above 95%.

B. Aromatic Aldehydes

Comments on the general nature of the aromatic aldehydes are di­
fficult to make as only a few of them were studied. The main difficulty
associated in experimenting with them was their slow oxidation in the pre­
sence of iron or copper. Later, for this reason, a nitrogen atmosphere was
used above the bomb. The nitrogen pressure also helped in the injection of
the liquid into the sample line (Fig. 7).

The oxidation of benzaldehyde was prevented by addition of 0.001%
FIGURE 17. $B(V)$ versus $P$ at Room Temperature
(Aliphatic)

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of hydroquinone. It was observed that this minute amount of hydroquinone had no observable effect on the viscosity of benzaldehyde.

A marked change in the nature of salicylaldehyde was noted after the experiment and so its viscosity data cannot be considered completely reliable. Trans-Cinnamaldehyde demonstrated a very slow change into cinnamic acid, probably increasing its viscosity.

1. Viscosity-Pressure Correlation

Because of their structural complexity (cf. Sec. 2 below) pressure effect on viscosity of the aromatic aldehyde is much more pronounced than that on the viscosity of their aliphatic counterparts. Figure 18 shows the effects of both ascending and descending pressure on the viscosity of benzaldehyde. The effect of gauge pressure on the viscosity of anisaldehyde and trans-cinnamaldehyde can be found in Figure 19.

The exponential behaviour of the viscosity with pressure was also found to be true for aromatic aldehydes. Correlation factors for these are even better (Chapter V). A plot of log viscosity against pressure can be found in Figure 20.

2. Pressure-Volume Correlation

The benzene ring in the structure of the aromatic aldehydes probably imparts resistance and stability towards the application of pressure. Compression and volume changes in these cases are less pronounced as the compression and compressibility curves in Figures 21 and 22 flatten out comparatively quickly.

The equation of state which had an excellent fit with the aliphatic
FIGURE 18. Gauge Hysteresis in Viscosity Measurement of Benzaldehyde
FIGURE 19. \( \eta \) versus \( P \) at Room Temperature
(Aromatic Aldehydes)
In order of increasing slope, -

1) \( \text{C}_6\text{H}_5\text{CHO} \)
2) \( 4\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO} \)
3) \( \text{C}_6\text{H}_5\text{CH=CHCHO} \)

**Figure 20.** Log Viscosity versus Pressure at Room Temperature
FIGURE 21. Compression Diagram for Aromatic Aldehydes
FIGURE 22. Compressibility Diagram of Aromatic Aldehydes at Room Temperature

\[ \Delta = \text{C}_6\text{H}_5\text{CHO} \]
\[ \bullet = 4-\text{CH}_3\text{OC}_6\text{H}_4\text{CHO} \]
\[ \square = \text{C}_6\text{H}_5\text{CH}=\text{CHCHO} \]
FIGURE 23. B(V) versus Pressure for Aromatic Aldehydes

- △ = C₆H₅CHO
- □ = 4-CH₃OC₆H₄CHO
- ○ = C₆H₅CH=CHO

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P-V data was found to hold for aromatic aldehydes as well. The statistical fit of data is excellent. A plot of B(V)-P on a log-log scale is given in Figure 23. Slopes of the curve appear to be dependent on the nature of the compounds.

C. Reduced Property Correlation

The theory of Thodos and co-workers suggests an excellent correlation between residual viscosity and reduced density. The values of \((n-n_0)\xi\) and \(\rho_R\) were calculated for all compounds and plotted on a log-log scale which resulted in a straight line with reasonable scatter (Fig. 24). The equation of the straight line may be given by

\[
(n-n_0)\xi = \exp (32.9375 \ln \rho_R - 48.5658)
\]

which is comparable to Thodos' correlation

\[
(n-n_0)\xi = (23.13 \exp 1.079 \rho_R - 25) \times 10^{-5}
\]

Both these equations were used to predict viscosity of different aldehydes and the values compared with the experiment. Both of the above equations seem to be very poor in predicting viscosity values of aldehydes.

However, it may be suggested here, that inclusion of another variable, like molecular weight may improve the situation for a generalized correlation. We had

\[
(n-n_0)\xi = k \rho_R^p
\]

Now, Figure 25 suggests that \(n\) is a linear function of molecular weight \(M\). So we can write

\[
n = a_1 + b_1 M.
\]
FIGURE 24. Residual Viscosity Diagram

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FIGURE 26. n versus \(-\ln k\) for Aliphatic and Aromatic Compounds

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The values of $a_1$ and $b_1$ for aliphatic aldehydes are 16 and 2.2 respectively. Again, Figure 26 shows, $k$ is an exponentially decreasing function of $n$ which in turn is a function of molecular weight $M$. Therefore,

$$n = m' \ln k + C$$

or

$$k = \exp(C-n)/m'$$

Values of $C$ and $m'$ can be found from Figure 24 to be 4.5 and 0.757 respectively. Hence,

$$k = \exp(15.2 - 2.9M).$$

Which gives

$$(n-n_0)k = \exp(15.2 - 2.9M) x \rho_R^{16 + 2.2M}$$

or

$$(n-n_0)k = (\epsilon \rho)a' + b'M$$

The values of $a'$ and $b'$ should of course be verified experimentally for other compounds.
VII. CONCLUSIONS

The visco-compressibility meter designed and developed in this project may be found useful in industry. The main advantage of this instrument is that the density which is essential for viscosity measurement can be readily obtained in the same apparatus.

The three equations

i) Pressure-Volume

ii) Viscosity-Pressure

iii) Residual Viscosity-Density

developed in this work seem to be promising for liquids and can be safely used in the design of chemical engineering appliances within the range of pressure studied.

Thodos' equation for predicting liquid viscosity was found to be incorrect for aldehydes.

Though low molecular weight aldehydes were expected to undergo polymeric transformations (either reversible or irreversible), and thus show sudden change in viscosity or volume (18), it was noted that the experimental conditions were not suitable to bring about any observable transition.

It was felt that by a more careful design it would be possible to measure the change in the electrical resistance of a liquid with pressure in conjunction with viscosity and volume measurements.
As measurements of any physical property requires careful and accurate control of all the variables involved, in any future extension of this work temperature should be controlled very accurately. This would demand a separate chamber with accurate heating and refrigeration units. If a jacket is desired, a better plummet lifting device is essential.

The equipment should be redesigned for higher pressures to detect transitions beyond the present pressure range. This requires a dead weight gauge as the usual Bourdon gauge has its inherent hysteresis.

Experiments should be carried out with aldehyde-water mixtures because there is tendency of aldehydes to polymerize by the reaction:

\[ \text{H}_2\text{O} + n \text{R-CHO} \rightarrow \text{HO(CHR-O)}_n \text{H.} \]  

(Pressure)

Study of this reaction with different aldehydes may turn out to be extremely interesting.
VIII. NOMENCLATURE

A, B, C, D, = Constants of equation (V-8) and (V-9)
B(V) = Volume Function, \( (V_o / V)^4 - (V_o / V)^2 \)
D = Diameter, cm.
K = Constant of equation (III-17)
M = Molecular Weight
\( N_{Re} \) = Reynolds Number
P = Pressure, p.s.i.g.
R = Radius, cm.
S = Flight distance in equation (III-4), cm.
T = Temperature, °K
V = Volume, cc.
Z = Compressibility Factor
a, b = Constant in equation (VI-2)
k = Constant in equation (V-6)
l = Length of the plummet, cm.
m = Constant in equation (VI-2)
n = Constant in equation (V-5)
q, r = Constant in equation (V-2)
v = Specific Volume, cc./gm.

Subscripts

c = Critical
e = Equivalent
\( o \) = Under atmospheric Condition

\( R \) = Reduced

**Greek Letters**

\( \alpha \) = Number of Carbon Atoms in equation (VI-2)

\( \theta \) = Constant in Reidel-Guldberg equation

\( \delta \) = Clearence between the plummet and fall tube, cm.

\( \phi, \psi \) = Constants of Lynderson's equations

\( \xi \) = Constant of Thodos equation, \( T_c^{1/6}/(M^{1/2} \times P^{2/3}) \)

\( \eta \) = Viscosity, cp.

\( \rho \) = Density, gms./cc.

\( \kappa \) = Constant of equation (III-3)

\( \sigma \) = Sp. Gr. of plummet
IX. BIBLIOGRAPHY


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X. APPENDIX

I. For a ready reference to the reader pressure and viscosity units and conversion factors are given below which have been used throughout this thesis.

\[ 1 \text{ bar} = 10^6 \text{ dynes/sq. cm.} \]
\[ = 0.987 \text{ atms.} \]
\[ = 1.019 \text{ kg/sq. cm.} \]
\[ = 14.406 \text{ p.s.i.} \]

\[ 1 \text{ kilo bar} = 1000 \text{ bars} \]

\[ (\text{kb}) \]

\[ 1 \text{ poise} = 1 \text{ gm./cm. sec.} \]

\[ 1 \text{ cp.} = 0.672 \times 10^{-3} \text{ lbs./ft. sec.} \]
\[ = 1/1488 \text{ lbs./ft. sec.} \]
\[ = 2.42 \text{ lbs./ft. hrs.} \]
\[ = 0.001 \text{ kg./meter.sec.} \]

\[ 1 \text{ Stoke} = 1 \text{ sq. cm./sec.} \]

II. For the convenience of the future workers the sequence of operation of the electronic counter by the make and break R-C circuit is given in the following page.
To counter Stop or Start with Stop/Start in common position.

Start Control Set to
+ Slope
- 8 Volts

Stop Control Set to
- Slope
+ 8 Volts
III. The original experimental data is available on computer cards from the Department of Chemical Engineering, University of Windsor, Windsor, Ontario, Canada.
V I T A

Born in a small town near Darjeeling, Mr. Pradip Mitra Chaudhuri completed High School in Calcutta in 1958. Receiving Intermediate Science education in Saint Xavier's College, Mr. Chaudhuri joined Jadavpur University, where he obtained the B.Ch.E. degree in 1964 convocation. Presently (1967, Spring) Mr. Chaudhuri is a candidate for the M.A.Sc. degree at the University of Windsor, Canada.