A study of the density and viscosity of water and ethanol binary mixtures under high pressure.

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A STUDY OF THE DENSITY AND VISCOSITY OF WATER AND ETHANOL BINARY MIXTURES UNDER HIGH PRESSURE

A 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 the University of Windsor

By

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Windsor, Ontario, Canada
1973
(c) Makoto Yusa 1973
ABSTRACT

Compression and viscosity under high pressure have been measured by the falling cylinder method for viscosity and the piston displacement method for compression. The apparatus measures both properties concurrently thus making the experimental method unique.

The system chosen is water-ethanol binary liquid mixtures, for which very few references are available.

The experimental results were subjected to analysis such as, error estimation, comparison to other reported data and degree of fit to the existing equations of state. The errors involved in the compression measurement are estimated as ±1.2 % and high pressure viscosity measurements are estimated to have ±1.3 % error.

For this particular system, the equations of state by Chaudhuri and Tait were found to fit very well.

The viscosity of water-ethanol mixtures was observed to exhibit both minima, maxima with changes in composition.
ACKNOWLEDGEMENT

For the rigorous and sincere advice given by Dr. R. A. Stager and Dr. G. P. Mathur throughout the period of work, Mr. G. Ryan for his assistance in modifying the equipment, and for the financial support given by National Research Council of Canada, for all, the author would like to express his great appreciation.

Also for the continuous encouragement given by author’s parents Mr. and Mrs. M. Yusa, the author is very much grateful.
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I. INTRODUCTION

The measurement of physical properties such as viscosity, compression of the liquid becomes significant when one sets out to design a fluid handling equipment in which the fluid experiences temperature and pressure changes, and one discovers how difficult it is to obtain appropriate data from the literature. Viscosity and compression data also give some indication of how the fluid molecules interact with each other thus leading to an understanding of the liquid structure under these conditions.

The present work is concerned with the refinement of the equipment developed by Chaudhuri et al.*, for faster and more reliable measurements, with an increased temperature range. In this work, both viscosity and compression are measured concurrently, a significant advantage over previously reported techniques.

The system chosen was a binary mixture of ethanol and water for which very limited literature data are available, especially under the high pressures to be attained in this study. The measurement of viscosity at high pressures requires reference values at atmospheric pressure over the same temperature range. Such measurements also require the
density of the system at atmospheric pressure.

Thus, subsequent chapters will deal with the measurement of density and viscosity at atmospheric pressure at selected temperatures as a preliminary step to the high pressure viscosity and compression measurement. The data obtained were subjected to analyses such as the comparison of various equations of state. Also, verification of the observed data has been done for both viscosity and compression by comparing to other reported data.
II. LITERATURE SURVEY

Among the many available sources of literature, several references are pertinent to the present work.\textsuperscript{23, 56, 65, 73}

1. Compression Data for the Binary Liquid Mixture

There are several references for compression data on pure water and pure ethanol but very little is known for the binary liquid mixture. Moesveld\textsuperscript{46} and Gibson\textsuperscript{25} measured compression of the aqueous solutions of ethanol and methanol respectively. Richard and Chadwell\textsuperscript{53} reported the data on aqueous solutions of ether and methyl acetate. Measurements of Newitt and Weale\textsuperscript{67} were on the compression of water- n-propyl alcohol, acetone and pyridine using a piezometer similar to the one used by Bridgman\textsuperscript{12}. It is noteworthy that these authors only measured compression at 1000 atm and temperature of 25°C and 30°C because of the limited capability of the apparatus.

Hamann\textsuperscript{27}, using the same type of the apparatus as Stutchbury\textsuperscript{61}, measured the compression of ten organic components each of them mixed with water to make binary mixture. Hamann's conditions were 1000 atm and 30°C. The latest report was by Smith\textsuperscript{57} on the water-acetone system, with pressures up to 35,000 psi and a temperature range of from 25 to 45°C.
2. The Viscosity of Liquid mixtures Under High Pressure

Much of the viscosity data are reported for pure substances, and relatively few references report the viscosity of liquid mixtures. This may be because of the complicated nature of mixture behavior and the subsequent difficulties in interpreting mixture data. Several workers have attempted to satisfy this lack of data by the prediction of the liquid mixture viscosity based on the data of the pure substances. In an early work of Dow, modification of the existing Arrhenius equation (sometimes called Kendall, etc.) to the form

\[ \eta = \eta_1^{x} \eta_2^{1-x} \]

resulted in following equations which depended upon pressure and temperature. If there is no change in concentration with pressure and temperature, it was suggested that above equation can be written as

\[ \ln \eta = x \ln \eta_1 + (1-x) \ln \eta_2 \]

and

\[ \frac{1}{\eta} \frac{d\eta}{dp} = \frac{x}{\eta_1 dp} + \frac{1-x}{\eta_2 dp} \]

also

\[ \frac{1}{T_1} \frac{dT}{dT} \approx \frac{x}{\eta_1 dT} + \frac{1-x}{\eta_2 dT} \]
where \( x \): a fraction of component 1.

\( \eta_1, \eta_2 \) are viscosity of component 1 and 2 respectively.

These equations imply that the viscosity of the binary liquid mixture may be predicted from the viscosity of pure components.

In 1952 Tamura and Kurata assumed that the relaxation time for each molecule collision was proportional to the probability of collision and by assuming small volume changes, on mixing, reported the following equation for a binary mixture.

\[
\eta_{\text{mix}} = x_1 \eta_1 \eta_2^{1/2} + x_2 \eta_2 \eta_1^{1/2} + 2(x_1 x_2 V_1 V_2) \eta_{12}^{1/2}
\]

where \( x_1, x_2 \): mole fraction of components

\( \eta_1, \eta_2 \): viscosity of pure substances at low pressure

\( \eta_{12} \): viscosity of interacting substances

\( V_1, V_2 \): volume fractions of components

Equation 5 is a one constant equation in which \( \eta_{12} \) is determined empirically at each temperature.

In the case of Raman (1968), the combination of the Katti's equation and Eyring's equation resulted in the following equation.

\[
\ln(\eta_{SV}) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 W_{\text{visc}} / RT
\]
where $x_1, x_2$ : fraction of the components

$V_1, V_2$ : volume of pure substances

$V_S$ : total volume

$n_1, n_2, n_s$ : viscosity of components 1, 2 and their mixture

$R$ : gas constant

$T$ : absolute temperature

$W_{visc}$ : the interaction energy between the components which is an empirical constant (from equimolar mixtures)

A similar type of equation was also given by Jun Su Behng\textsuperscript{36} in 1970.

Other workers have continued to measure the viscosity of mixtures at high pressures. Abaszade\textsuperscript{1} in 1971 reported the viscosity of ethanol-water mixtures by the capillary method combined with a quartz micrometer for various compositions at pressure of up to 1,200 kg/cm\(^2\) and temperature of 50\textdegree, 100\textdegree, and 200\textdegreeC. Agaev\textsuperscript{3}, also in 1971, reported the results of water-ethanol mixture studies using the same type of apparatus as Abaszade over the same pressure range and temperatures of 0\textdegree and 30\textdegreeC. These two papers are the only papers directly related to the fluids studied in the present work.
3. Viscosity Data for Ethanol, Water and their Binary Mixture at Atmospheric Pressure

In many cases, when the viscosity is measured at atmospheric pressure, water is used as a reference liquid and this is undoubtedly one of the reasons why so much work has been reported on water even in recent years. Somewhat less time has been spent on ethanol properties.

Starting from the well known Poiseuille's experiment (1846) on water-ethanol system, many measurements have been made and these data are contained, for instance, in the International Critical Tables and Physico Chemical Constants by Timmerman. Some of the references for water-ethanol system are indicated below.

### TABLE 1

<table>
<thead>
<tr>
<th>Workers</th>
<th>Measured temperature</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traube</td>
<td>20°-60°C</td>
<td>1895</td>
</tr>
<tr>
<td>Varenne &amp; Godefroy</td>
<td>25°C</td>
<td>1903</td>
</tr>
<tr>
<td>Dunstan &amp; Tbole</td>
<td>20, 25, 30°C</td>
<td>1904</td>
</tr>
<tr>
<td>Dunstan</td>
<td>25°C</td>
<td>1908</td>
</tr>
<tr>
<td>Bingham-White &amp; Thomas-Cadwell</td>
<td>25, 30, 35, 40, and 80°C</td>
<td>1913</td>
</tr>
<tr>
<td>Kikuchi &amp; Oikawa</td>
<td>15-60°C, 5°C intervals</td>
<td>1967</td>
</tr>
</tbody>
</table>
4. Summary of References on the Viscosity and Compression Data for Pure Water, Pure Ethanol and Their Mixtures Under Pressure

Among numerous references for the viscosity and compression on water and ethanol, following table indicates some of the work done in this field.

<table>
<thead>
<tr>
<th>Workers</th>
<th>Substance</th>
<th>Measured Property</th>
<th>Pressure</th>
<th>Temp.</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warburg</td>
<td>water</td>
<td>viscosity</td>
<td>150kg/cm²</td>
<td>20°C</td>
<td>1884</td>
</tr>
<tr>
<td>Roentgen</td>
<td>water</td>
<td>viscosity</td>
<td>~20atm</td>
<td>5-11°C</td>
<td>1884</td>
</tr>
<tr>
<td>Amagat</td>
<td>water</td>
<td>PVT</td>
<td>~1000 bar</td>
<td></td>
<td>1893</td>
</tr>
<tr>
<td>Hauser</td>
<td>water</td>
<td>viscosity</td>
<td>400kg/cm²</td>
<td>0-100°C</td>
<td>1901</td>
</tr>
<tr>
<td>Parsons</td>
<td>water</td>
<td>PV</td>
<td>4kbar</td>
<td>4°C</td>
<td>1911</td>
</tr>
<tr>
<td>Faust</td>
<td>ethanol</td>
<td>viscosity</td>
<td>3k kg/cm²</td>
<td></td>
<td>1914</td>
</tr>
<tr>
<td>Moesveld</td>
<td>water</td>
<td>PV</td>
<td>500,1000,</td>
<td>25°C</td>
<td>1922</td>
</tr>
<tr>
<td></td>
<td>ethanol</td>
<td></td>
<td>1500 atm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridgman</td>
<td>water</td>
<td>viscosity</td>
<td>12kbar</td>
<td>30,75°C</td>
<td>1925</td>
</tr>
<tr>
<td>Adams</td>
<td>water</td>
<td>PV</td>
<td>1kbar</td>
<td>25°C</td>
<td>1931</td>
</tr>
<tr>
<td>Tamman</td>
<td>water</td>
<td>PVT</td>
<td>~3.5kg/cm²</td>
<td>20-650°C</td>
<td>1932</td>
</tr>
<tr>
<td></td>
<td>ethanol</td>
<td></td>
<td></td>
<td>20-400°C</td>
<td></td>
</tr>
<tr>
<td>Yeat-Smith</td>
<td>water</td>
<td>PVT</td>
<td>~350bar</td>
<td>30-450°C</td>
<td>1933-35</td>
</tr>
</tbody>
</table>
Table 2 continues

<table>
<thead>
<tr>
<th>Workers</th>
<th>Substance Measured property</th>
<th>Pressure</th>
<th>Temp.</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibson</td>
<td>water PVT</td>
<td>1kbar</td>
<td>~100°C</td>
<td>1935</td>
</tr>
<tr>
<td>Bridgman</td>
<td>water ethanol PVT</td>
<td>50kbar</td>
<td>25, 75, 125, 175°C</td>
<td>1942</td>
</tr>
<tr>
<td>Newitt &amp; Weale</td>
<td>water ethanol PV</td>
<td>1k atm</td>
<td>25°C</td>
<td>1951</td>
</tr>
<tr>
<td>Stychbury</td>
<td>water alcohol PV</td>
<td>1k atm</td>
<td>30°C</td>
<td>1956</td>
</tr>
<tr>
<td>Kell &amp; Whalley</td>
<td>water PVT</td>
<td>5-1026 bar</td>
<td>0-150°C</td>
<td>1965</td>
</tr>
<tr>
<td>Bett &amp; Kappi</td>
<td>water viscosity</td>
<td>~10 k kg/cm²</td>
<td>2.2-100°C</td>
<td>1965</td>
</tr>
<tr>
<td>Horne &amp; Johnson</td>
<td>water viscosity</td>
<td>~2 k kg/cm²</td>
<td>2-8°C</td>
<td>1966</td>
</tr>
<tr>
<td>Pearce &amp; Strauss</td>
<td>water PV</td>
<td>1.5kbar</td>
<td>25°C</td>
<td>1967</td>
</tr>
<tr>
<td>Stanley &amp; Batton</td>
<td>water viscosity</td>
<td>~1.5 k kg/cm²</td>
<td>2-30°C</td>
<td>1968</td>
</tr>
<tr>
<td>Miller &amp; Curry</td>
<td>water PVT</td>
<td>~50 atm</td>
<td>2-55°C</td>
<td>1969</td>
</tr>
<tr>
<td>Hamann &amp; Smith</td>
<td>water ethanol PV</td>
<td>1k atm</td>
<td>30°C</td>
<td>1971</td>
</tr>
<tr>
<td>Agaev</td>
<td>water ethanol viscosity</td>
<td>~1200 kg/cm²</td>
<td>0-30°C</td>
<td>1971</td>
</tr>
<tr>
<td>Abaszade</td>
<td>water ethanol viscosity</td>
<td>~1200 kg/cm²</td>
<td>50-200°C</td>
<td>1971</td>
</tr>
<tr>
<td>Smith</td>
<td>water PVT viscosity</td>
<td>~35 k psi</td>
<td>25-45°C</td>
<td>1972</td>
</tr>
</tbody>
</table>

* indicates the data includes the mixtures of water and ethanol.
III. THEORETICAL BACKGROUND

1. Viscosity Measurement by the Falling Cylinder Method

The theory for the falling cylinder type viscometer was first studied by Lawaczeck,\textsuperscript{1} Heinze,\textsuperscript{30} and has since been mentioned by Jobling,\textsuperscript{35} Chaudhuri\textsuperscript{16} et al. When given the dimensions of the system as in Fig. 1, Lawaczeck's equation for the calculation of viscosity is,

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

where \( \eta \) : viscosity
\( S \) : flight distance
\( \sigma \) : density of the falling cylinder
\( \rho \) : density of the fluid
\( \delta \) : clearance between the falling cylinder and outside tube
\( D \) : inside diameter of outside tube
\( d \) : diameter of the falling cylinder
\( t \) : flight time
\( g \) : acceleration due to gravity

Equation 7 was later modified by Jobling and expressed as
\[ h = \frac{(0 - \rho)(a-b)^3}{6 \rho b} \times gt \]

where \( a = D/2 \)
\( b = d/2 \)

Equations 7 and 8 can be written in the form

\[ h = K (\sigma - \rho) t \]

where \( K \) is an instrument constant to be determined with respect to a reference state. This equation has been used extensively for the various viscometers in which gravity causes an object (or the fluid itself) to fall.

It should be noted that although equation 9, follows from equations 7 and 8, it is not restricted by the limitations imposed in the derivation of these basic equations; it is an empirical equation.

2. Viscosity Data Correlation

The viscosity changes with both pressure and temperature and there have been many attempts to correlate the effects of the two variables.
For the effect of temperature, there is, among many equations, a well known equation often called as Andrade's equation or Arrhenius' equation in the form

\[ n = A e^{-\frac{B}{T}} \]

or \[ \ln n = \ln A + \frac{B}{T} \]

where \( A \) and \( B \) are constants.

The effect of pressure on viscosity have been examined by several people. One equation of note is that of Griest which has the following form:

\[ \ln n = A + B \left[ \frac{v_0}{V} - \left( \frac{v}{V} \right)^2 \right] \]

where \( A \) and \( B \) are constants, \( v_0 \) and \( v \) are specific volume at reference pressure \( p_0 \) and at pressure \( p \).

Another equation, which has been reported by Chaudhuri et al. states

\[ n = n_0 \exp(mP) \]

or \[ \ln \frac{n}{n_0} = A + mP \]

where \( A \) and \( m \) are constants.
3. Correlation of Compression Data

Among the numerous equations of state for liquids, Tait, Hudleston and Bridgman's equation are still used frequently.

Chaudhuri proposed an equation based on the Lennard-Jones intermolecular potential function which he expressed as,

\[ P = \frac{A}{[B(v)]^q} \]

where \( B(v) = \left( \frac{v_0}{v} \right)^n - \left( \frac{v_0}{v} \right)^2 \)

\( v_0, v \) : specific volume at reference pressure \( P_0 \) and at pressure \( P \) respectively

and \( A, q \) are constants

This equation was tested by Chaudhuri for aliphatic and aromatic aldehydes and water against that of Hudleston in 1968. The results were very good, especially for water. The equation was further verified by Rungta for butylaldehyde. Several other attempts by Liew and Smith also confirmed the usefulness of the equation.

The data obtained in this work have been correlated by the following equations of state.
1. Bridgman (1952)¹

\[ V_0 - V = A + B \ln P \]

where \( V_0, V \): volume at reference pressure \( P_0 \) and at pressure \( P \).

\( A, B \): constants

2. Hudleston (1932)³

\[ \ln \left( \frac{V^{2/3} P}{(V_0^{1/3} - V^{1/3})} \right) = A + B(V_0^{1/3} - V^{1/3}) \]

where \( V_0, V \): volume at reference pressure \( P_0 \) and at pressure \( P \)

3. Tait (1838)⁶² - Original form from Hayward (1967)²⁹

\[ \frac{V_0}{P} = A + m P \]

where \( A, m \) are constants and \( V_0, V \) are volume at reference pressure \( P_0 \) and at pressure \( P \).

4. Chaudhuri (1967)¹⁶

\[ P = A \left[ B(v) \right]^q \]

where \( B(v) = \left( \frac{v_0}{v} \right) - \left( \frac{V_0}{V} \right)^2 \)

\( v_0, V \): specific volume at reference pressure \( P_0 \) and at pressure \( P \)

\( A, q \): constants
5. \[ P = A [ B(v) ] \]

This is a simplified form of equation 13, obtained by letting \( q = 1 \).

6. \[ \Gamma = A + M [ B(v) ] \]

where \( B(v) \) is the same as Chaudhuri's and \( A, M \) are constants.

To arrive at equation 19, the equation 20 from Griest and the equation 21, an empirical equation of viscosity were used as follows.

\[
\ln \left( \frac{\eta}{\eta_0} \right) = \frac{K}{T} [ B(v) ]
\]

20

and \( \ln \left( \frac{\eta}{\eta_0} \right) = \ln A + m P \)

21

Combination of above two equations leads to

\[
\ln A + m P = \frac{K}{T} [ B(v) ]
\]

22

and

\[
\ln A = \frac{-1}{m} \ln A + \frac{K}{m T} [ B(v) ]
\]

23

or \( P = A + \beta M [ B(v) ] \)

24

where \( A \) and \( M \) are new constants.
IV. EXPERIMENTAL SET UP

The experimental work consists of two major parts, one on the properties at atmospheric pressure and the other at high pressure. Both parts are interrelated since high pressure values of viscosity and density are relative to atmospheric pressure measurements which in turn relate to chosen standards. Further relationships exist since in order to measure viscosity at high pressure the compression value is required. The diagram given below demonstrates above relationships.

![Diagram]

**Fig. 2** Block diagram of the experimental constituents and their interrelationship
1. Atmospheric Pressure System

1.1 Pycnometer

Figure 3 is a diagram of the pycnometer used. This model was modified from a design by Ward or Weissberger, and its unique features lie in:

a. a low evaporation rate of the sample solution

b. no laborious adjustment of volume such as filling the liquid exactly to the zero point

c. continuous density measurement at different temperatures.

The position of the meniscus was obtained by use of a cathetometer equipped with a graticule which allowed readings within ±0.04 mm.

1.2 Viscometer

A Cannon–Fenske type viscometer as shown in Fig. 4 was used. A type No. 50/A (ASTM Spec. D-2515 equivalent) was used exclusively.

1.3 Temperature Control

A constant temperature water bath 1.5 feet in diameter and 1.0 foot in height was used. This bath allowed control of the sample temperature to within ±0.1°C over the range of 25 to 55°C.
Fig. 3
Double capillary
Pycnometer

Fig. 4
Cannan-Fenske
Viscometer
2. High Pressure System

The measurement of compression and viscosity under pressure was carried out in a specially designed apparatus, which is shown schematically in Fig. 5.

The system consists of a low pressure hydraulic pump which energizes an intensifier thus producing hydraulic pressures up to 50,000 psi. The pressurized fluid contacts a magnetic piston in the compression meter which separates the sample under study from hydraulic system. Compression measurements were taken by locating this piston by means of magnetic reed switch. Viscosity was obtained by measuring the time of fall of a cylinder between two reed switches.

2.1 Pressure generation

The high pressures used in this work are generated in two stages. First, a hand operated hydraulic pump supplies up to 5,000 psi to an intensifier. This intensifier then produces the required pressure of up to 50,000 psi.
Fig. 5 Schematic diagram of the entire high pressure viscosity and compression measuring system.
2.2 Measurement

2.2.1 Viscometer

The viscometer consists of the following components:

a. A fall tube which is made of 316 stainless steel having an OD = 9/16 inches (nominal), ID = 3/16 inches (nominal) and a measured length of 57.56 inches. This tube has a rated pressure of 50,000 psi (supplied from American Instruments Co.).

b. A falling cylinder is fabricated from Alnico 5 having a density of 7.251 g/cm³ (supplied from Storch Products Co.). The cylinder is 0.171 inches in diameter and 1.246 inches in length. Its surface is highly polished.

c. A magnetic ring made of Alnico 5 with an OD of 1.0 inch, an ID of 0.6 inch and a depth of 1.5 inches is used to raise the falling cylinder after each drop.

2.2.2 Compression meter

The compression meter consists of:

a. Tubing of 316 stainless steel with nominal dimensions of OD = 3/16, ID = 1/16 inch and a length of 61 inches. The tubing was obtained from American Instruments Co.
and had a rated pressure of 65,000 psi.

b. A rubber piston made from a Chloroprene O-ring and formed into a truncated core, having nominal dimensions of $D_{\text{max}} = 1/10$ inch, $D_{\text{min}} = 1/15$ inch and the length of 0.15 inches. This piston is attached to the magnet by an epoxy adhesive.

2.3 Temperature control

The temperature control bath is a commercially available unit (Lab-line Instruments Co.) having a capacity of nine gallons, a heating capacity of 1 kW and a pumping capacity of three gallons per minute. This bath was connected to the water tank through rubber hoses. Temperature variation in the tank did not exceed ± 0.5°C at a given temperature.

2.4 Detecting devices

2.4.1 Viscometer

The time of fall is measured using the following devices:

In order to measure the time interval of the falling cylinder, two dry reed switches as in Fig. 6 were used (General Electric). The switches were encased in the shrinkable Teflon tubing to prevent wetting lead wires.
**Fig. 6** Details of switch setting

**Fig. 7** Electric circuit of the viscosity switching system
To allow close contact with the viscometer, very thin (0.015 inch) tubing was used.

The system starts counting as the magnetic cylinder activates the top switch when it passes by and terminates counting when it passes the bottom switch. A switching circuit was designed to sharpen the on-off switch signals. It is shown in Fig. 7. A model 361A-R/M27 Electronic counter manufactured by Transistor Specialties Inc. was used exclusively for the above purpose.

2.4.2 Compression meter

To determine the location of the rubber piston, a small magnet was attached to it. It was located by the following device.

![Diagram of compression detecting system]

Fig. 8 Compression detecting system
The small magnet inside the compression measuring tube rotates the floating magnet contained in plexiglas holder, which in turn activates the reed switch on the extreme left in the fig. 8. The displaced length of the piston was calculated from the number of revolutions of the threaded rod supporting the plexiglas holder.

2.4.3 High pressure gauge

A Heise solid front-B with a rated pressure of 100,000 psi with 100 psi graduations was used to measure the pressure of the fluid in the system.
V. EXPERIMENTAL PROCEDURE

1. Viscosity and Density Measurement at Atmospheric Pressure

The following flow diagram summarizes the entire procedure for the measurements of viscosity and density:

\[
\begin{align*}
\text{Pycnometer} & \quad \downarrow & \quad \text{Viscometer} \\
\downarrow & \quad \text{Cleaning} & \downarrow \quad \text{9.0 cc} \\
\text{Little above} & \quad \downarrow & \quad \text{Filling} \\
\text{point} & \quad \downarrow & \quad \text{Start measurement} \\
\downarrow & \quad \text{Read both} & \quad \text{Measure 5 times} \\
\text{capillary heights} & \quad \text{at each occasion} & \text{before} \\
\text{weigh before} & \quad \text{and after} & \text{and after} \\
\end{align*}
\]

Fig. 9 Process of measuring viscosity, density at atmospheric pressure
2. Compression and Viscosity Measurement Under High Pressure

A flow diagram for the compression and viscosity measurement under pressure is shown below.

- Clean the system
- Assemble
- Fill with liquid
- Pressure generation
- Read pressure
- Water bath
- Control temperature
- Attach rubber piston to small magnet
- Prepare sample liquid
- Compression measurement
- Viscosity measurement 5 times
- Go to higher pressure of up to 40,000 psi
- Go to lower pressure, check hysterisis
- Calculate compression and viscosity

Fig. 10 Process of compression and viscosity measurement under pressure
There are several points in this process which require clarification.

2.1 Filling

The small tube is difficult to fill without entrapping air inside. To avoid this a plastic tube which has a slightly larger diameter is mounted over the tube, then the liquid is poured into the plastic tube and the whole assembly is rocked back and forth occasionally draining the liquid from the other end. Finally the bottom end is plugged with the rubber piston. The filling of the entire system is completed by means of a syringe attached to a spaghetti tube made of Teflon.

2.2 Compression measurement

Prior to collecting the data, the zero point for compression measurement is determined by repeatedly pressurizing to 10,000 psi and releasing the system.

2.3 Waiting period

After reaching the required pressure a waiting period of 10 to 15 minutes is required to avoid erroneous readings on compression measurement. As for the viscosity measurement at least a one minute waiting period after raising the falling cylinder is made. This is a procedure recommended by Horne and Johnson who performed similar measurements.
2.4 Limit of the compression measurement

Due to the high compression rate of ethanol the system reached its limit at about 30,000 psi, whereas water could be studied up to 50,000 psi.

3 Specimen

Distilled water from a still manufactured by Baumstead Sybron Corp. was used throughout the experiment. A preliminary experiment showed the difference of the density between the ordinary distilled water and deaerated water was very small and fell within experimental error.

As for ethanol, commercially available absolute alcohol was obtained. Specifications are as follows.

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specifications on absolute ethanol</td>
</tr>
<tr>
<td>Manuf.</td>
</tr>
<tr>
<td>Ethanol content by volume</td>
</tr>
<tr>
<td>Water content by volume</td>
</tr>
<tr>
<td>Specific gravity 60°F/60°F</td>
</tr>
<tr>
<td>Non volatile matter /100cc</td>
</tr>
<tr>
<td>Benzene g/cc</td>
</tr>
<tr>
<td>Distillation range</td>
</tr>
</tbody>
</table>
VI. ANALYSIS OF DATA

1. Estimation of Errors

There are various ways of estimating errors in the experimental results. A common method of estimating errors in dependent variables depends on developing the total differential and then substituting the errors in each of the dependent variables. However, this method can be quite complicated unless the functional relationship is simple.

Another more practical method involves the calculation of the maximum, minimum and mean values of the dependent variables by appropriate direct substitution of the maximum, minimum and mean values of the dependent variables into the function. This method requires no differentiation. These two methods are used in this section extensively whenever the need arises.

1.1 Density measurement by pycnometer

Details of density measurements by various pycnometers are described by Weissberger.72
The biggest correction to the pycnometer requires the determination of the volume which changes with temperature. The lower bulb represents the greatest portion of the volume. Using the reference value of pure water at each temperature up to 55°C, the volume of the bulb was measured.

The average values were,

**TABLE 4**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Average volume of the bulb</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>16.519 cm$^3$</td>
</tr>
<tr>
<td>35°C</td>
<td>16.519 cm$^3$</td>
</tr>
<tr>
<td>45°C</td>
<td>16.523 cm$^3$</td>
</tr>
<tr>
<td>55°C</td>
<td>16.521 cm$^3$</td>
</tr>
<tr>
<td>Ave.</td>
<td>16.520 cm$^3$</td>
</tr>
</tbody>
</table>

with a deviation of ±0.002 cm$^3$

Thus, the percentage deviation is,

$$\frac{0.002 \times 100}{16.520} = 0.012 \%$$

The volume of the capillary section was measured at all temperature-ranges. It was found that the deviations fall within the range of bulb volume deviation.
1.2 Viscosity measurement at atmospheric pressure

1.2.1 Viscometer

In the use of the Cannon-Fenske viscometer following experimental conditions were applied.

- Number of data taken at one time: 5
- Minimum efflux time: 200 sec
- Time left in the bath prior to measurement: 15 min.
- Amount of liquid used at one time: 9.0 cc
- Temperature change of the bath during the measurement: ±0.1°C
- Maximum time deviation: ±0.5 sec

Thus, time deviation involved in the measurement is at a maximum

\[ ±0.5 \times 100 / 200 = ±0.25 \%

1.2.2 Viscosity calculation

The viscosity, measured by capillary type viscometer, is calculated in the following way:

The applicable equation is

\[ \eta = \frac{mV}{\rho 8(1+nr)V} \frac{mV}{8\pi(1+nr)t} \]
where \( \eta \) : viscosity
\( \rho \) : density
\( r \) : radius of capillary tube
\( g \) : acceleration due to gravity
\( h \) : mean height of the liquid
\( t \) : efflux time
\( V \) : total efflux volume
\( l \) : capillary length
\( n, m \) : constants

The two terms on the right hand side of the equation can be simplified by the use of two constants.

\[
C_1 = \frac{\pi r^4 g h}{8(1+nr)V} \quad \text{and} \quad C_2 = \frac{m V}{8\pi(1+nr)}
\]

and then equation 25 becomes

\[
\frac{\eta}{\rho} = C_1 \frac{1}{t} - C_2 \frac{1}{t}
\]

Thus using two liquids of known viscosity and density, \( C_1 \) and \( C_2 \) can be determined from equations

\[
\eta_1 = C_1 \rho_1 t_1 - C_2 \rho_1/t_1
\]

\[
\eta_2 = C_1 \rho_2 t_2 - C_2 \rho_2/t_2
\]
and \( C_{11} = C_{21} \), \( C_{12} = C_{22} \) if one viscometer is used.

From these two constants and measured density, an unknown \( n \) can be found from

\[
\eta = C_1 \rho t - C_2 \rho / t
\]

The reference liquids used were pure water and absolute ethanol.

Now, the total error involved in the calculation of the viscosity at atmospheric pressure may be obtained by differentiating the above equation after rearranging the equation as

\[
\eta = \rho (C_1 t - C_2 / t)
\]

\[
\frac{d\eta}{\eta} = \frac{d\rho}{\rho} - \frac{(1 + \frac{C_2}{C_1 t})}{(1 - \frac{C_2}{C_1 t^2})} dt + \frac{dC_1}{C_1} - \frac{dC_2}{C_2 \left( \frac{t}{C_2} - \frac{1}{C_1 t} \right)}
\]

\[
\frac{dC_1}{C_1} + \frac{dC_2}{C_2 \left( \frac{t}{C_2} - \frac{1}{C_1 t} \right)}
\]

30
For the given values of

\[ C_1 = 0.00393 \]

\[ C_2 = 22.254 \]

\[ t = 200 \]

and from previous results

\[ \frac{dr}{p} \times 100 = \pm 0.01 \% \]

\[ \frac{dt}{t} \times 100 = \pm 0.25 \% \]

\[ \frac{dC_1}{C_1} \times 100 = \pm 0.18 \% \]

\[ \frac{dC_2}{C_2} \times 100 = \pm 0.29 \% \]

Hence \[ \frac{dn}{n} \times 100 = \pm 0.37 \% \]

This is the maximum error.
1.3 Compression measurement

1.3.1 Principle of compression calculation

Calculation of the compression from the experimental results may be made according to the following analysis.

The system change by pressure at certain given temperature is described in the Fig. 11.

![Schematic diagram of the system](image)

**Fig. 11 Schematic diagram of the system**

The total volume of the system at 0 psig and at pressure p psig can be expressed as,

\[
V_{OT} = (L^S_{OT} - r_0)A^S_{OT} - V_{OTM} + V^b_{OT} - V_{OTN} \tag{31}
\]

\[
V = (L^S_{OT} - r)A^S_{C_2} - V_{OTM} + V^b_{C_2} - V_{PTN} \tag{32}
\]
where

\[ C_1 = \frac{L^s_{PT}}{L^s_{0T}} \]
\[ C_2 = \left( \frac{d^s_{PT}}{d^s_{0T}} \right)^2 \]
\[ C_3 = \frac{L^b_{PT} d^{b2}}{L^b_{0T} d^{b2}} \]

and

\[ V : \text{total volume of the system} \]
\[ L : \text{total length of the tube} \]
\[ A : \text{area of the tube} \]
\[ l : \text{displaced length in the small tube} \]
\[ d : \text{diameter of the tube} \]

subscripts and superscripts are

0 : 0 psig
p : p psig
s : small tube
b : big tube
T : temperature °C
M : magnetic piston
N : falling cylinder and stopper

The effect of pressure and temperature on the internal dimensions of the test vessel is estimated by use of the theory of elasticity. Appendix 4 gives details on the method used in obtaining the values of the correction factors \( C_1, C_2 \) and \( C_3 \).

Now, compression is by definition

\[ k = \frac{\Delta V}{V_{0T}} = \frac{V_{0T} - V_{pT}}{V_{0T}} \]
Substituting \( V_{0T} \) and \( V_{pT} \) with previously obtained values and assuming that the size of the piston, falling cylinder and stopper do not change with pressure,

\[
k = \frac{\Delta V}{V_{OT}} = \frac{L_s^{0T}(1-C_1C_2) + (rC_2-r_0) + \frac{V_b}{V_{0T}(1-C_3)}}{A_s^{0T}}
\]

\[
(L_s^{0T} - r_0) = \frac{V_{OTM} + V_{OTN}}{A_s^{0T}} + \frac{V_{b}}{A_s^{0T}}
\]

1.3.2 Error estimation for compression values

Actual value of \( V_{OTM} \) and \( V_{OTN} \) are

\[
V_{OTM} = 0.049
\]

\[
V_{OTN} = 0.450 + 0.815 = 1.265
\]

and \( V_{OTM} + V_{OTN} = 1.314 \text{ cm}^3 \)

\( L_s^{0,25} \) and \( L_b^{0,25} \) have been measured to 1/100 inch which represents a deviation of ±0.02 \%. Likewise, \( V_s^{0,25} \) and \( V_b^{0,25} \) have been measured by the use of a mercury displacement method and the obtained percent deviations are

\[
\frac{\Delta V_s^{0,25}}{V_s^{0,25}} = ±0.07 \% \quad \text{and} \quad \frac{\Delta V_b^{0,25}}{V_b^{0,25}} = ±0.04 \%
\]
The precision of locating the piston for compression measurement as was described before is up to half revolution of the rotor which is

\[
\frac{1}{11 \times 2} = 0.05 \text{ inch, that is}
\]

\[
\frac{0.05}{25} \times 100 = 0.20 \%
\]

Summarizing all results:

\[ V_{0,25}^S : \pm 0.07 \% \]
\[ V_{0,25}^b : \pm 0.04 \% \]
\[ L_{0,25}^s : \pm 0.02 \% \]
\[ r \quad : \pm 0.20 \% \]

From above results, estimation of error for the calculated compression can now be obtained. To do this it is first necessary to select a typical run which is the representative of the entire series of runs.

The case chosen is that of pure water at 25°C and two pressures, 14,900 psig and 40,400 psig. These two pressures are chosen to estimate errors in the middle and highest pressure range. Relevant values for the calculation are,
\[ L_{0.25}^s = 152.075 \pm 0.013 \text{ cm} \]
\[ V_{0.25}^h = 25.379 \pm 0.010 \text{ cm}^3 \]
\[ A_{0.25}^s = 0.0346 \pm 2.4 \times 10^{-5} \text{ cm}^2 \]
\[ V_{OTM} + V_{OTN} = 1.314 \text{ cm}^3 \]
\[ r_0 = 39.960 \pm 0.127 \text{ cm} \]

Of which all values are used for both calculations, and pressure variable terms are

\[
\begin{align*}
14,400 \text{ psig} & \quad 40,400 \text{ psig} \\
76.502 \pm 0.127 \text{ cm} & \quad 121.311 \pm 0.127 \text{ cm} \\
0.9999 & \quad 0.9999 \\
1.0034 & \quad 1.0091 \\
1.0034 & \quad 1.0091
\end{align*}
\]

The results are

\[
\begin{align*}
14,400 \text{ psig} & \quad \pm 0.90 \% \\
40,400 \text{ psig} & \quad \pm 1.21 \%
\end{align*}
\]
1.4 Viscosity measurement at high pressure.

Estimation of the error involved in the viscosity measurement under pressure can be made from the equation

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

Error involved in \( K \), \( \sigma - \rho \) and \( t \) are needed for the calculation of error in \( \eta \).

1.4.1 Instrument constant \( K \)

The estimated error in \( K \) is found from the data at atmospheric pressure with the equation

\[ K = \frac{\eta}{(\sigma - \rho) t} \]

Based on this equation, by the use of maximum and minimum method, estimated percent deviation of \( K \) is found for pure water at two different temperatures. With following given values, percent deviations were obtained.

\[
\begin{array}{ccc}
25^\circ C & 55^\circ C \\
\eta &=& 0.894 \pm 0.002 \\
t &=& 26.47 \pm 0.05 \\
\rho &=& 0.997 \pm 0.002 \\
\sigma &=& 7.251 \text{ (Assumed to be constant)} \\
0.507 \pm 0.002 \\
15.71 \pm 0.05 \\
0.986 \pm 0.002 \\
\end{array}
\]
and calculated percent deviations are at 25°C ±0.51 % and at 55°C ±0.87 %.

1.4.2 Density difference (σ-ρ) and time t

The remaining two terms (σ-ρ), and t have been estimated to have following error. First for (σ-ρ) term σ is assumed to be constant and only the ρ term which is found from compression measurement, may contribute to the error. This liquid density change is comparable to the overall error in compression that reached to ±1.2 % as was described before. Using the density of water as a typical value the overall error is calculated as.

\[
\text{Percent deviation} = \left\{ 1 - \frac{σ-ρ(1±0.012)}{σ-ρ} \right\} \times 100 = \frac{1.2ρ}{σ-ρ}
\]

Substituting σ = 7.251 and ρ = 0.997 to above equation gives the result of ±0.19 %.

Now for time t, maximum deviation was ±0.05 sec and minimum observed time was 16 sec which gives percentage deviation of ±0.31 %.

Based on these values, the error in the viscosity of water at 55°C, 0 psig is calculated as ±1.25 %, which is the maximum possible error.
1.5 Summary of the estimated errors in this work

The results of the error analyses are:

- Density measurement by pycnometer: ±0.01%
- Viscosity measurement by Cannon-Fenske viscometer: ±0.37%
- Compression measurement: ±1.20%
- Viscosity measurement at high pressure: ±1.25%
2. Discussion and Presentation of Results

The experimental results on compression and viscosity are first discussed by comparison to existing literature values to demonstrate external consistency. Then the experimental data are presented as functions of temperature, pressure and composition.

2.1 Density data

2.1.1 Standard values

The densities of water as obtained from the International Critical Tables\(^4\) and listed below were used as references in calibrating the pycnometer.

TABLE 5
Density of water at 1 atm.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Density g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.99707</td>
</tr>
<tr>
<td>35</td>
<td>0.99406</td>
</tr>
<tr>
<td>45</td>
<td>0.99020</td>
</tr>
<tr>
<td>55</td>
<td>0.98570</td>
</tr>
</tbody>
</table>
2.1.2 The density of mixtures at atmospheric pressure

The experimental values at atmospheric pressure are tabulated in Appendix 2. A comparison of these values with the data of Perry is presented in Fig 12.

It is clear from this figure that all experimental data fall within ±0.3% of the Perry's data.

It should also be observed that the deviations are not truly random but seem to appear as a set of matching pairs. One possible explanation for this pattern may be that the measured compositions are in error. However, since the mixtures were precisely prepared by weight with an estimated maximum error in composition of ±0.1% this postulate does not appear valid.

2.1.3 Density of water at high pressure

Among many available sources, the data of Kel1 & Whalley have been chosen for comparison. Although their data are only for pressures up to 1000 atm., Fig 13 still allows a comparison and indicates very good agreement between this work and that of Kel1 & Whalley.
Fig. 13  Density vs Pressure for Pure Water
2.2 Compression data as a function of temperature, pressure and composition

2.2.1 Comparison of the compression data

Comparison of the data with that of Moesveld is shown in Fig. 14 at a temperature of 25°C and a pressure of 1000 atm. This figure shows a good agreement of both data except at higher ethanol fractions, where experimental values are higher than that of Moesveld.

The experimental values are also compared to that of Namann and Stutchbury in Fig. 15 at a temperature of 30°C and at 1000 atm. To compare with these two data experimental values were interpolated from the data at 25°C and 35°C.

It is shown that a slight discrepancy at higher ethanol compositions exists. The experimental values are again higher as is observed in Fig. 15, and at low compositions all three data show considerable differences.

2.2.2 Experimental results

The numerical values of density and compression are tabulated in Appendix 2.

In figures 16 to 19, the relation between compression and composition at various temperatures and pressures is shown. The peculiar phenomenon observed in these figures is that regardless of applied pressure and temperature
Fig. 14 Compression vs Composition
At 1000 atm
Fig. 15 Compression vs Composition
At 1000 Atm

30°C

- Author (interpolated)
- Stutchbury
- Hamann & Smith

COMPRESSION \times 10^2

ETOH Mol%
Fig. 16 Compression vs Composition at 25°C
Fig. 17. Compression vs Composition At 35°C
Fig. 18 Compression vs Composition At 45°C
there is a minimum in compression at about 5-10 mol\% ethanol. This phenomenon is also reported for many other binary systems involving water with chemicals such as 1,4-dioxane, acetone and propanol.

Newitt and Weale correlated this phenomenon with other properties. For instance, at similar concentrations there exists a maximum velocity of ultrasonic waves, and the partial molar volume of ethanol in water, calculated from specific volume exhibits a minimum at a similar concentration. Newitt and Weale tabulated the details of compositions in which minimum or maximum values were observed. These are listed in Table 6.

TABLE 6
Compositions at which minimum or maximum occur in various properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Composition</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression minimum at 25°C, 1000 atm</td>
<td>9 mol% Ethanol</td>
<td></td>
</tr>
<tr>
<td>Maximum ultrasonic velocity at 25°C</td>
<td>11 mol%</td>
<td></td>
</tr>
<tr>
<td>Minimum partial molar volume at 25°C</td>
<td>7 mol%</td>
<td></td>
</tr>
</tbody>
</table>

The author's work indicates there appears to be a minimum around 5 to 10 mol\% ethanol.

Hamann and Smith also refer to this phenomenon and roughly relate this to the excess volume.
The reasoning of Pearce and Strauss on the compression minimum after observing the water-dioxane system is that water contains more hydrogen bonds per unit volume than any other substance, and the introduction of solute molecules must inevitably reduce the hydrogen bonding in the system.

2.3 Viscosity data

2.3.1 Standard values and experimental values of viscosity at atmospheric pressure

The viscosity of pure water and pure ethanol as obtained from I.C.T. and Bingham respectively are listed in Table 7.

<table>
<thead>
<tr>
<th>T°C</th>
<th>Water (I.C.T.)</th>
<th>Ethanol (Bingham)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.8949 cp</td>
<td>1.0995 cp</td>
</tr>
<tr>
<td>35</td>
<td>0.7208</td>
<td>0.9135</td>
</tr>
<tr>
<td>45</td>
<td>0.5970</td>
<td>0.7660</td>
</tr>
<tr>
<td>55</td>
<td>0.5072</td>
<td>0.6451</td>
</tr>
</tbody>
</table>
2.3.2 The viscosity of mixtures at atmospheric pressure

A comparison of mixture viscosity data to two other works were made.

Fig. 20 compares Bingham's data to the present work and Fig. 21 presents a comparison with the work of Kikuchi and Oikawa.

These two data sets appear to be the only ones covering a wide range of temperatures and compositions. The figures show good agreement between our experimental values and the references except, for slight differences at higher temperatures.

2.3.3 Comparison of data at high pressure

The only comparable viscosity measurement done at high pressure for this system is that of Abaszade, et al. The result of a comparison is shown in Fig. 22. At lower pressure the agreement of both data seems very good, however, differences develop with increasing pressure.

2.3.4 Experimental results

Figures 23 to 26 show the change of viscosity for the system with pressure and temperature at various compositions. The data indicate the viscosity of mixtures are higher than those of the pure components. A single maximum in viscosity is exhibited. This feature has been reported by many
workers since early in the century.\textsuperscript{51}

At high pressures the maximum still remains but is observed to gradually shift to higher ethanol fractions.

It is well known that the viscosity of pure water exhibits a minimum at a pressure of about 15,000psi. This anomalous behavior disappears at a temperature of approximately 35\degree to 40\degree C. This has been reported by Cohen\textsuperscript{18} and subsequently observed by many others such as Horne and Johnson.\textsuperscript{19} The present work also shows this phenomenon (Fig. 27a).

This exhibition of minimum has been explained\textsuperscript{19} as a breaking down of the so-called "clusters" of water molecules held together by hydrogen bond.\textsuperscript{10}

The viscosity behavior with respect to pressure at all compositions appears quite regular except at 55\degree C. At 55\degree C the anomalous behavior becomes more noticeable as the ethanol fraction increases (Fig. 27d-k). There are minima, maxima and sometimes just points of inflection at 55\degree C.

Most of these occur at pressures beyond the range of Abaszade's observations and no external confirmation is possible.

The structure of water-alcohol mixtures has been investigated by several people. Lawrence et al. stated that water and ethanol form water-centered aggregates in which four alcohol molecules are hydrogen bonded to one water molecule. Lawrence quoted from other sources that the water
molecule is not in the center of the aggregate but there exist the combination of four ethanol molecules and one water molecule, which is called as 4A/W aggregate.
Fig. 20  Viscosity vs Composition at 1 atm

Data of Author and Bingham
Fig. 21  Viscosity vs Composition at 1 atm

Data of Author and Kikuchi
Fig. 22 Viscosity vs Composition
Comparison of Author and Abaszade's Data At 50°C
Fig. 23  Viscosity vs Composition at various pressures at 25°C
Fig. 24  Viscosity vs Composition at various pressures at 35°C
Figure 25. Viscosity vs Composition at various pressures at 45°C.
Fig. 25  Viscosity vs Composition at Various pressures at 55°C
Fig. 27 Viscosity vs Pressure with various Compositions
VII. CORRELATION OF DATA

1. P-V-T Relations

Six equations of state were tested by first expressing them in the linear form, and finding the correlation coefficients for their linearity. The values calculated indicate that on the basis of correlation coefficients alone, all six equations fit the data well.

The correlation coefficient is not a sufficient quantitative measure of fit. Therefore, using the calculated constants, volumes at different temperatures and pressures were estimated. The procedure involved considerable trial and error.

The estimated volume was finally compared to the experimental volume and the comparison was expressed as a standard deviation expressing how closely the estimated value are to the experimental value. This comparison is shown in Table 8.

Interpretation of table 8 can be done in many ways. For instance, if the sum of the standard deviations for all data points is taken as a criterion, the order from smallest to largest deviation is,
<table>
<thead>
<tr>
<th>ETHOH MOLT</th>
<th>RPIDC</th>
<th>TAIT</th>
<th>CHAUD</th>
<th>EQU.5</th>
<th>EQU.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
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Total: 0.74396 0.11288 0.27785 1.45183 1.66891
1. Tait
2. Chaudhuri
3. Bridgman
4. Eqn.5
5. Eqn.6

That is, the equation of Tait fits best for this particular system. Estimation of volumes from Hudleston's equation of state by trial and error failed due to the peculiar nature of the equation. The indications are that the equation does not fit the data as well as other equations of state.

Chaudhuri's equation gives almost the same fit as Tait's. Eqn.5 and Eqn.6 are useful if one wishes to calculate actual values without the aid of a computer, though they are not as good as Chaudhuri's equation.

2. Correlation of Viscosity Data

Figure 28 shows the relation between temperature and viscosity for atmospheric pressure, 15,000 psig and 30,000 psig respectively. The figure plots \( \ln \eta \) vs \( 1/T \) to test the well known relationship

\[
\eta = A e^{B/T}
\]
Fig. 28: $\ln \eta$ vs $1/T$ at atmospheric pressure
FIG. 28: IN. N. V. I/I

Pressure = 15000 psi
Graphically the line of best correlation is obtained for each composition, though some of the lines are merely short line segments linking the same composition for easy visualization.

In this figure, the slope represents $B$ in the equation and $A$ the intercept if the line is straight.

The effect of pressure on viscosity has been investigated by many people without much success partly because of its complex nature. For the water-ethanol system the viscosity-pressure curves appear to contain maxima and minima which makes any correlations difficult.

However, two equations, equation 11 and 12, are subjected to investigation as to their fit by means of calculating the correlation coefficients.

Results were as expected. Pure water, 5 mol% and 10 mol% ethanol solutions did not indicate correlation at all, though much better results were obtained at higher compositions. Results also showed that these two equations gave almost the same degree of fit to the data.
VIII. CONCLUSIONS

By the use of the falling cylinder method the viscosities of water-ethanol binary mixtures were measured at atmospheric pressure and under high pressure.

The system originally designed by Chaudhuri et al is also capable of measuring the compression concurrently.

This study, therefore, measured viscosity and compression on water-ethanol system and the results are compared to those previously reported. The literature survey revealed that for this system very few data actually exist.

The estimation of error for the entire system showed that the viscosity and compression measurement involve 1.25 % and 1.20 % error respectively.

For compression (or density) results, the equations of state by Chaudhuri, Tait, Hudleston, Bridgman and two other equations of state based on Lennard-Jones potential function were tested and results were expressed in terms of standard deviations.

The Chaudhuri and Tait equations were found to fit this particular system very well.
A compression minimum at some composition, also reported by other workers, was observed in this work. This is thought to be the effect of structure change by the change of composition.

Correlation of viscosity to temperature, pressure and density were considered. Because of the abnormal behavior of viscosity with composition and pressure change, none of the equations fit very well.

No satisfactory explanation is presently available for the existence of these minima and maxima.
APPENDIX 1

Gauge Calibration

Prior to the experiment it was necessary to determine the accuracy of the Heise pressure gauge using a Budenberg dead weight tester.

The average of three measurements are shown in the Fig. 1, as the deviation from standard. This figure indicates that the deviation of the gauge readings over the range covered is within the minimum graduation of the gauge. Pressure can thus be read with an accuracy of ±50 psia.
### Experimental Data

1. **Specific Volume at Various Compositions and Temperatures at 1 Atm**

#### Specific Volume cm³/g

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(a) Values obtained from I.C.T. and used as the reference.
### Experimental Values: Density, Compression and Viscosity

![Table of experimental values with columns for Mole, P x 10^-3, Dg/cm³, k, and n cP.](image-url)

### Notes
- The table includes data for various concentrations of ethanol (EtOH) and their corresponding properties.
- Each row represents a different concentration, with columns indicating the concentration, density, and other physical properties.
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APPENDIX 3

Statistical Equations

1. Correlation coefficient

Correlation analysis in statistics is the method to determine the fit between variables assuming the dispersion of each variable is in normal distribution.

Take the case of two variables \( x \) and \( y \), and express the sum of squares for \( x, y \) and \( xy \) as,

\[
S(xx) = \sum(x_i - \bar{x})^2
\]

\[
S(yy) = \sum(y_i - \bar{y})^2
\]

\[
S(xy) = \sum(x_i - \bar{x})(y_i - \bar{y})
\]

Then the correlation coefficient can be expressed as,

\[
r = \frac{S(xy)}{\sqrt{S(xx) S(yy)}}
\]

where \( r \) is the ratio of the sum of products and variation of \( x \) and \( y \). Equation 4 can also be expressed as
\[ r = \frac{n \Sigma xy - \Sigma x \Sigma y}{\sqrt{[n \Sigma x^2 - (\Sigma x)^2][n \Sigma y^2 - (\Sigma y)^2]}} \]

Equation 5 was used in this work.

2. Standard deviation

One of the fundamental properties in statistical analysis is the standard deviation, which expresses the degree of dispersion quantitatively. The equation is of the form

\[ s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n}} \]

This value, however, is the sample standard deviation which is normally a smaller value than the true value. Thus a better estimation is obtained if the equation is divided by \((n-1)\) instead of \(n\).

\[ \sqrt{V} = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{(n-1)}} \]

where \(V\) is called variance
APPENDIX 4

Tube Size Correction by Temperature and Pressure

According to the "Theory of Elasticity" by Timoshenko and Goodier, the radial displacement $u$ and the normal stress components in $r$ and $z$ directions are written as,

$$u = \frac{1+v}{1+v} \frac{\alpha}{r} \int_0^r Trdr + C_1 \frac{r}{r}, \frac{C_2}{r} - \frac{vr}{E} C_3$$  \hspace{1cm} (1)$$

$$\sigma_r = -\frac{\alpha E}{1-v} \frac{1}{r^2} \int_0^r Trdr + \frac{E}{1+v} \left( \frac{C_1}{1-2v} - \frac{C_2}{r^2} \right)$$  \hspace{1cm} (2)$$

$$\tau_z = -\frac{\alpha E T}{1-v} + \frac{2\alpha E}{(1+v)(1-2v)} C_1 + C_3 = 0$$  \hspace{1cm} (3)$$

Since $T$ = constant through thickness, let $T$ = $\Delta T$ (measured temperature), thus

$$\int_0^r \frac{Trdr}{a} = \Delta T \int_0^r \frac{rdr}{a} = \frac{\Delta T}{2} (r^2 - a^2)$$

from (2) \hspace{1cm} C_3 = \frac{\alpha E \Delta T}{1-v} - \frac{2\alpha E}{(1+v)(1-2v)} C_1$$  \hspace{1cm} (4)
and from equation 2,

\[ \sigma_r = -\frac{\alpha E \Delta T}{1 - \nu} \left( \frac{r^2 - a^2}{2r^2} \right) + \frac{E}{1 + \nu} \left( \frac{C_1 - C_2}{r^2} \right) \]

B.C. \( \sigma = -\pi \) at \( r = a \)

\[ -\pi = -\frac{\alpha E \Delta T}{1 - \nu} \left( \frac{a^2}{2a^2} \right) + \frac{E}{1 + \nu} \left( \frac{C_1 - C_2}{a^2} \right) \]

and \( \frac{C_1}{1 - 2\nu} - \frac{C_2}{a^2} = \frac{\pi (1 + \nu)}{E} \)

B.C. \( \sigma_r = 0' \) at \( r = b \)

\[ 0 = -\frac{\alpha E \Delta T}{1 - \nu} \left( \frac{b^2 - a^2}{2b^2} \right) + \frac{E}{1 + \nu} \left( \frac{C_1 - C_2}{b^2} \right) \]

and \( \frac{C_1}{1 - 2\nu} - \frac{C_2}{b^2} = \frac{1 + \nu \Delta T}{1 - \nu} \left( \frac{b^2 - a^2}{2b^2} \right) \)

Subtracting \( a \) from \( b \) gives the value \( C_2 \) as,

\[ C_2 = \frac{a^2 b^2}{b^2 - a^2} \left[ \frac{1 + \nu \Delta T}{1 - \nu} + \frac{\pi (1 + \nu)}{E} \right] \]
Substituting \( C_2 \) into equation a gives

\[
C_1 = (1-2\nu) \left( \frac{C_2}{a^2} - \frac{P(1+\nu)}{E} \right)
\]

Thus,

\[
\Delta d = 2u = 2[C_1a + \frac{C_2}{a} - \frac{\nu a C_3}{E}]
\]

General form of the stress-strain relation in the \( z \) direction is

\[
\varepsilon_z = \alpha T - \frac{1}{E} \left[ \sigma_z - \nu(\sigma_r + \sigma_\theta) \right]
\]

and if \( \sigma_z = 0 \)

\[
\varepsilon_z = \alpha (\Delta T) - \frac{\nu}{E} (\sigma_r + \sigma_\theta)
\]

where

\[
\sigma_\theta = \frac{\alpha E}{1-\nu} \left( \frac{\Delta T}{2r^2} \right) (r^2 - a^2) - \frac{\alpha E (\Delta T)}{1-\nu}
\]

\[
+ \frac{E}{1+\nu} \left( \frac{C_1}{1-2\nu} + \frac{C_2}{r^2} \right)
\]

now \( \sigma_r + \sigma_\theta = \frac{-\alpha E (\Delta T)}{1-\nu} + \frac{2E}{1-\nu} \left( \frac{C_1}{1-2\nu} + \frac{C_2}{r^2} \right) \)
and
\[ e_z = \alpha(\Delta T) + \frac{v\alpha(\Delta T)}{1-v} - \frac{2v}{1-v} \frac{c_l}{1-2v} \]

\[ e_z = \frac{\partial w}{\partial l} \]

\[ w = e_z l = \Delta l \]

thus,
\[ \Delta l = 1 \left[ \frac{\alpha(\Delta T)}{1-v} - \frac{2v}{1-v} \frac{c_l}{1-2v} \right] \]

\[ \frac{1}{1-v} \left[ \alpha(\Delta T) - \frac{2vc_l}{1-2v} \right] \]

where
- \( a \): inside diameter of the tube
- \( b \): outside diameter of the tube
- \( E \): Young's modulus
- \( r \): radius
- \( u \): radial displacement
- \( \Delta d = 2u \)
- \( \Delta l = w \): longitudinal displacement
- \( P \): pressure
- \( T \): temperature
- \( \alpha \): coefficient of thermal expansion
- \( \varepsilon \): unit elongation
- \( v \): Poisson ratio
- \( \sigma \): normal stress component

Subscripts are:
- \( r, \theta, z \): radial, tangential and axial direction
APPENDIX 5

Effect of Pressure on Instrument Constant K

One of the problems encountered in the course of determining the viscosity at high pressure is the evaluation of K in the equation

$$\eta = K(\sigma - \beta) t$$

In this work the standard viscosity used is the value obtained from reference sources while (\sigma - \beta) t and t term are measured values at atmospheric pressure.

Once K is obtained for a particular mixture the high pressure viscosity calculations use this value as long as the liquid compositions and temperature are the same.

The high pressure viscosities are thus calculated from equation 1, assuming K is a constant, independent of pressure for the particular temperature and mixture composition.

But is not K a function of P and if so by how much? An analysis of this problem follows.
The theory of the falling cylinder viscometer leads to the equation of the form

\[ \eta = \frac{(0-\delta)(a-b)^3g}{6Sb} \]

where the symbols are in part defined by Fig. 1.

Equation 2 can be rewritten as

\[ \eta = K(\delta-\rho)t \]

such that

\[ K = \frac{(a-b)^3g}{6Sb} \]

if we assume that:

1. falling cylinder diameter does not change
2. and the system is at a constant temperature

then, it is clear from equation 4 that factors affecting the change in \( K \) are \( a \) and \( S \). And knowing the variation of \( a \) and \( S \), it is possible to estimate the variation of \( K \).

Calculation of the change in \( a \) and \( S \) is done by the method explained in Appendix 4.
The given conditions used for the calculations are,

- Pressure inside the tube: 40,000 psig
- Inside diameter: 0.1851 inch
- Outside diameter: 0.5590 inch
- Tube length: 42 inches
- Young's modulus: \(2.80 \times 10^7\) psi
- Poisson ratio: 1/3

and the results are,

\[ \Delta R = 8.354 \times 10^{-6}\text{ inch} \]
\[ \Delta l = -9.852 \times 10^{-3}\text{ inch} \]

Now how much effect do these variations have on the value of \(K\)? At pressure 0 and at \(P\) psig, equation 4 can be written as

\[ K = \frac{q(a-b)^3}{6 S b} \quad \text{and} \quad K_p = \frac{q(a_p-b_p)^3}{6 S_p b_p} \quad \text{(5)} \]

Where subscript \(P\) indicates values at pressure \(P\).

It follows that

\[ \frac{K_p}{K} = \left( \frac{a_p - b_p}{a - b} \right)^3 \quad \text{(6)} \]
where
\[
\frac{b_p}{b} = 1.0 \text{ (by assumption)}
\]
\[
a/b = 1.0818, \quad a_p/b_p = 1.0867
\]
\[
S/S_p = 1.0002346
\]
leading to
\[
\frac{K_p}{K} = 1.1901
\]
\[
K = 3.40 \times 10^{-3}
\]
That is, theoretical calculation shows a 19% increase in \( K \) at pressure 40,000 psig.

Experimentally obtained \( K \) values (atmospheric pressure) are listed in the following table 1. The overall average value of \( K \) is \( 6.25 \times 10^{-3} \) and the deviation of \( \pm 20 \%

The following conclusions may be drawn from above considerations:

1. Effect of pressure on \( K \) may be significant according to the theoretical formula (equation 4).

2. However, the theoretical formula does not predict \( K \) sufficiently as \( K \) varies with temperature and composition, in contradiction to the equation.

3. The best procedure to account for possible variations in \( K \) with pressure would be to calibrate against standard values at high pressure. At present, however, these values are not available.
### TABLE 1

Instrument constants at different temperatures
and compositions

\[ K = X \times 10^3 \]

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X. BIBLIOGRAPHY

5. Andrade, E.N. da C., Phil Mag, 17, 497 (1934); 17, 698 (1934)
6. Arrhenius, S., Zeits f Phys-Chemie, 1, 285 (1887)
7. A.S.T.M. Method D-445 (1952)
17. Chemical Abstracts, Vol 54 to 76 (1972), Am Chem Soc, Columbus, Ohio
18. Cohen, R., Ann Phys, 45, 666 (1892)
20. Dow, R.B., Physics, 6, 71 (1935)
23. The Engineering Index 1960 - 1972, Engineering Index Inc, New York
24. Faust, O., Phys Chem, 86, 479 (1914)
28. Hauser, L., Ann Phys., 5, 597 (1901); Quoted from A. Zeitlin
30. Heinze, Dissertation, Berlin (1925)
34. International Critical Tables of Numerical Data, V, 10, 11, 12, (1929)
41. Lawaczeck, F., Z Ver Deut Ing, 63, 677 (1919)

43. Lennard-Jones, J.E., A.F. Devonshire, Proc Roy Soc London (A) 163, 53 (1937); (A) 165, 111 (1938)


46. Moesveld, Z Physikal Chem, 105, 450 (1923)

47. Newitt, D.M., K.E. Weales, J Chem Soc, 3092 (1951)


51. Poiseuille, J.L.H., Mem de l'Inst de Paris, 9, 433 (1846)

52. Raman, C.V., Nature, 3, 532 (1923); 3, 600 (1923)

53. Richards, T.W., H.M. Chadwell, J Am Chem Soc, 47, 2296 (1925)

54. Roentgen, Wied Ann, 222, 518 (1884)


56. Science Citation Index, Institute for Scientific information, Phil Peh, up to 1972


60. Statistical Analysis in Chemistry and the Chemical Industry, by Bennet, F.

61. Stutchbury, J.E., Aust J Chem, 9, 536 (1956)

63. Tammann, G., Z. Phys. Chem., 11, 676 (1893); 17, 620, 767 (1895)


65. Theoretical Chemical Engineering Abstracts


68. Traube, J., Ber., 19, 871 (1886); quoted from Ishikawa, "Theory of Binary Liquid Mixture.", Maruzen, Tokyo

70. Warburg, S., Wied. Ann., 22, 518 (1884)

71. Ward, A., L. Brooks, Analyst 73, 158 (1948)


XI. NOTATIONS

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<th>A</th>
<th>Area of tube</th>
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<td>C</td>
<td>Correction factor or Constant</td>
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<tr>
<td>D</td>
<td>Diameter of tube</td>
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<tr>
<td>E</td>
<td>Young's modulus</td>
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<tr>
<td>K</td>
<td>Instrument constant</td>
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<tr>
<td>L</td>
<td>Length of tube</td>
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<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>S</td>
<td>Flight length of falling cylinder</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>V</td>
<td>Volume fraction of components or Variance in statistics</td>
</tr>
<tr>
<td>V</td>
<td>Total or partial volume</td>
</tr>
<tr>
<td>W</td>
<td>The interaction energy between the components which is an empirical constant</td>
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</tbody>
</table>

| a       | Diameter or radius of tube    |
| b       | Diameter or radius of tube    |
| d       | Diameter of tube              |
| g       | Acceleration due to gravity   |
| h       | Mean height of the liquid     |
| k       | Compression                   |
| l       | Capillary length              |
m  Constant
n  Number of sample or constant
p  Pressure
k  Standard deviation
t  Time (of fall or efflux)
u  Radial displacement
v  Specific volume
w  Displaced length
x  Fraction of component
y  Fraction of component
α  Coefficient of thermal expansion
δ  Clearance between the falling cylinder and outside tube
ε  Unit elongation
η  Viscosity
ν  Poisson ratio
ρ  Density of the fluid
γ  Density of the falling cylinder or normal stress component

Subscript and superscript
1,2  Component 1 and 2
0,p  Pressure at atmospheric and at pressure P
s,b  Small and big tube
T  Temperature
m  Magnetic piston
N  Falling cylinder and stopper
r,θ,z  Designation of polar coordinate Radiial, Tangential and Axial
VITA AUCTORIS

1939 Born in Tokyo, Japan

1963 Received the Bachelor of Engineering in Industrial Chemistry at CHUO University, Tokyo, Japan

1973 Presently a candidate for the degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada