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A relationship between the mole fractions and the absolute viscosities of blended lubricating oils

Ernest Reginald Epperson

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A RELATIONSHIP BETWEEN THE MOLE FRACTIONS AND THE
ABSOLUTE VISCOSITIES OF BLENDED
LUBRICATING OILS

BY

ERNEST REGINALD EPPERSON

born

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
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Rolla, Missouri
1932

Approved by ...................

Professor of Organic Chemistry
ACKNOWLEDGMENTS

The writer wishes to express his sincere appreciation to Dr. H.L. Dunlap for suggesting this problem, and for his helpful collaboration in its development.

Thanks are due to the Shell Petroleum Corporation and to the Standard Oil Refinery of Wood River, Illinois for furnishing oils for this investigation.
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A RELATIONSHIP BETWEEN THE MOLE FRACTIONS AND THE
ABSOLUTE VISCOSITIES OF BLENDED
LUBRICATING OILS

Introduction

The viscosity of binary liquid mixtures has been a subject of much investigation, but most of the work has been done with mixtures of substances other than lubricating oils. Lubricating engineers have found viscosity to be the most important property of a good lubricant, though up to the present time no one has succeeded in deducing a satisfactory expression by which the viscosity of a blended lubricant may be calculated from a knowledge of the physical properties of its components.

This investigation has been an attempt to find a relationship between the absolute viscosity of a blended lubricating oil and the viscosities and relative numbers of molecules of its components.
Historical Considerations

Viscosity may be defined as the internal frictional resistance offered by a fluid to change of shape or to relative motion of its parts. Absolute viscosity is the force in dynes necessary to move a surface of one square centimeter past an equal parallel surface one centimeter distant with a velocity of one centimeter per second, the space being filled with the fluid whose absolute viscosity is sought. Absolute viscosity is expressed in poises, (one dyne-second per square centimeter = 1 poise). The reciprocal of absolute viscosity is fluidity.

Many determinations of the viscosities of liquid mixtures have been made in the endeavor to discover a mathematical expression connecting the viscosity of a mixture with the relative amounts and viscosities of its components. The fundamental difficulty in drawing any definite conclusions from the available data is the fact that the law of "ideal" mixtures is not known.
Einstein reasoned that there should be a linear increase in viscosity with concentration, a result which does not agree with observation except at very low concentrations.

Bingham, reasoning from the analogy between electrical resistance and viscous resistance, deduced the theory that fluidity and not viscosity should be additive,

\[ \frac{1}{n} = \frac{X}{n_1} + \frac{(1 - X)}{n_2} \]

where \( n \) is the blend viscosity, \( n_1 \) and \( n_2 \) the viscosities of the respective components, and \( X \) is the concentration of one of the components expressed as a volume fraction. Lees had, however, previously tested this equation and concluded that it was unsatisfactory when the concentration was expressed as a volume fraction. Drucker and Kassel suggested the same equation with weight-composition units.

---

2 - Am. Chem. J. 35:195 (1906)
3 - Phil. Mag. (6), 1:123 (1901)
4 - Z. Physik. Chem. 76:367 (1911)
Arrhenius proposed a purely empirical formula, \( \log n = X \log n_1 + (1 - X) \log n_2 \), in which the logarithms of the viscosities are assumed to be additive. Reyer found that the logarithmic formula holds fairly well when \( X \) is expressed as a volume percent and one liquid is present to the extent of ninety percent or more. Kendall pointed out that, by expressing the concentration as a molar fraction, viscosities calculated by the use of Arrhenius' equation fell into much closer agreement with experimental data.

Kendall and Monroe tested all the formulas which had been proposed on 84 presumably chemically indifferent and non-associated liquid mixtures. When the viscosities were plotted against the percentage composition, the curves were, in general, found to be sagged with no suggestion of agreement with any of the proposed formulae. Kendall and Monroe then, left with a

1 - Z. Physik. Chem. 1:285 (1887)
2 - Z. Physik. Chem. 2:744 (1888)
3 - J. Am. Chem. Soc. 39:1787 (1917)
J. Am. Chem. Soc. 42:1776 (1920)
clear field, proposed the equation

$$n_3^\frac{1}{3} = Xn_1^\frac{1}{3} + (1 - X)n_2^\frac{1}{3}.$$ 

Viscosities calculated by means of this equation were found to be in close agreement with those determined experimentally. The maximum divergence from the experimental data was only 3.8 percent for the system benzene - benzyl benzoate. Some of the other systems investigated gave less satisfactory results. However, the above cube root formula has been found to represent the viscosities of approximately "ideal" mixtures better than any other.

Molecular Weights of Lubricating Oils

--------------------

Little work has been done on the determination of the mean molecular weights of lubricating oils. In 1923 Wilson and Wylie published a paper on the "Vapor Tension of Solvents". In their investigations they determined the mean molecular weights of a number of hydrocarbon lubricants by means of the Beckmann cryoscopic method, benzene being used as the solvent. This paper was criticised by C.F. Mabrey, who declared benzene

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1 - J. Ind. Eng. Chem. 15:801 (1923)
was unsatisfactory as a solvent for oils of high molecular weight. He recommended stearic acid for this purpose.

In a paper on "Nitrobenzene as a Solvent for Cryoscopic Work", Roberts and Bury, showed that the freezing point of nitrobenzene altered on standing; this was found to be due to water absorption. A.H. Steed used anhydrous sodium sulphate to dehydrate the nitrobenzene used as a solvent in his work on the determination of the mean molecular weights of light petroleum fractions.

In September 1931, Gullick published a paper on "The Determination of Mean Molecular Weights of Lubricating Oils by Improved Cryoscopic Methods". One method employed a platinum resistance thermometer and the other a mercurial thermometer. Both benzene and nitrobenzene were used as solvents, anhydrous sodium sulphate being used as a dehydrating agent. Molecular weights at increasing concentrations

1 - J. Chem. Soc. 123:2037 (1923)
2 - J. Inst. Petr. Tech. 16:798 (1930)
3 - J. Inst. Petr. Tech. 17:541 (1931)
were determined and "molar weight"-depression curves were plotted. Extrapolation of these curves to zero concentration gave what was called the true molecular weight. The curves were linear but not horizontal; the cause of the sloping was discussed and attributed to association rather than mixed crystal formation.
EXPERIMENTAL PART

Materials Used

Four closely cut fractions of mid-continent lubricating oil were furnished by the Shell Petroleum Corporation and two by the Standard Oil Company of Wood River, Illinois. Four samples of Pennsylvania oil were obtained from a commercial sample of Quaker State oil by fractionation under reduced pressure.

The benzene was Baker's Analyzed chemically pure and thiophene free. It was recrystallized, dried, and stored over fused calcium chloride.

The nitrobenzene was of the C.P. grade. It was recrystallized and stored in a bottle one-fourth full of fused calcium chloride.

The ethylene bromide was a German brand. It was washed with a dilute solution of sodium carbonate, then with water, dried and stored in a bottle containing fused calcium chloride.

The acetone was of a presumably pure grade. To purify it, it was precipitated as the crystalline compound, \((\text{CH}_3)_2\text{C(OH)SO}_3\text{Na}\), by shaking with a saturated solution of sodium bisulphite. The precipitated compound was filtered
off, dried, and distilled with a sodium carbonate solution. The purified acetone was dehydrated over fused calcium chloride and distilled, the distillate being collected in fractions having a boiling point range of 0.2°C.

The ethyl acetate was U.S.P. grade. It was diluted with a large volume of water and distilled from a water bath until all of the ester had distilled. The ester was separated from the water, dehydrated over fused calcium chloride and redistilled, the distillate being collected in fractions having a boiling point range of 0.2°C.

Apparatus Used

The equipment used in the cryoscopic determinations of mean molecular weight was the regular Beckmann freezing point apparatus, with the addition of a mechanical stirrer and equipment for keeping the solvent under a slight

   Beckmann, Z. Physik. Chem. 7:323 (1891)
   Beckmann, Z. Physik. Chem.15:656 (1894)
   Beckmann, Z. Physik. Chem.44:183 (1903)
pressure with dried compressed air. The air was
dried by passing through sulphuric acid and
fused calcium chloride. (See Fig. 1).

In the ebullioscopic determinations of
molecular weight the McCoy apparatus was
employed.

Viscosities were determined by means of a
Sayblot Standard Universal Viscosimeter. The
oil bath was heated by a 500 watt immersion
heater.

Standard A.P.I. hydrometers, manufactured by
the Tagliabue Manufacturing Company, were used to
determine the gravities of the various fractions
and blends.

In the fractionation of the Pennsylvania
oils under reduced pressure, the apparatus used
was very similar to that described in the U.S.
Bureau of Mines Bulletin No. 207 for the
"Analytical Distillation of Petroleum and its
Products.

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1 - Am. Chem. Jour. 23:353 (1900)
EXPERIMENTAL PROCEDURE

Cryoscopic Determinations of Molecular Weight

The freezing bath of the Beckmann apparatus was filled with a freezing mixture and maintained at a temperature slightly below the freezing point of the solvent. The Beckmann thermometer was adjusted till, at the freezing point of the solvent, the top of the mercury column was about the middle of the scale. The freezing point tube was weighed, about 25 cc. of the solvent was introduced, and it was again rapidly weighed. The thermometer and stirrer were inserted into the tube so that the bulb of the thermometer was completely immersed in the solvent. The compressed air tube was attached, and a very slow current of air was passed through the drying train. The speed of the air current was controlled by observing the rate of bubbling in the sulphuric acid tubes.

The freezing point of the solvent was then determined. In doing this, an approximate determination was first made by placing the freezing point tube directly in the cooling bath, so that the temperature fell comparatively
rapidly. When the solid began to separate, the tube was quickly placed in the air mantle in the cooling bath; it was stirred slowly and the temperature was read when it became constant. The tube was then withdrawn from the mantle and the solvent was melted by means of the hand. The tube was again placed directly in the cooling bath and the temperature allowed to fall to within about half-a-degree of the freezing point as determined above; the tube was then quickly placed in the air mantle and the temperature was allowed to fall, stirring slowly all the while. When the temperature had fallen to about 0.2° below the previously determined approximate freezing point, it was stirred vigorously. When the temperature started to rise it was stirred more slowly and, with the aid of a lens, temperature readings were taken every few seconds, the thermometer being tapped with the finger each time before reading. The highest temperature reached was recorded. The solid particles of solvent were again melted and the freezing point redetermined in the manner just described. At least three concordant readings of
freezing point were obtained for each sample of solvent, the mean being taken as the true freezing point.

A weighed amount of substance, the molecular weight of which was to be determined, was introduced into the solvent through the side tube of the apparatus. A sufficient amount of the solute was used to give a freezing point depression of 0.2 to 0.3 degree. After the substance had dissolved the freezing point of the solution was determined in exactly the same manner as described for the pure solvent. The molecular weight of the substance was calculated by means of the formula

\[ M = \frac{K}{d \cdot W} \]

where \( K \) is a constant depending only on the solvent employed, \( W \) is the weight of the solvent, \( w \) the weight of the solute, and \( d \) the freezing point depression. The value of \( K \) was determined experimentally for each solvent by the use of a compound of known molecular weight. Naphthalene was used for this purpose.
Ebullioscopic Determinations of Molecular Weight

A McCoy boiling point apparatus equipped with condensers and an electric heater was used for this part of the investigation.

About 50 cc of pure solvent was placed in the outer jacket of the apparatus. A few pieces of porous tile were added to insure steady ebullition. 12 to 15 cc of the solvent was placed in the graduated inner tube, and the apparatus was assembled, the condensers adjusted, and the heating was started. The side tube leading to the reflux condenser was closed causing the vapors from the boiling solvent to pass into the inner tube and to heat the solvent therein. The rate of boiling in the outer tube was adjusted so that the solvent in the inner tube boiled slowly but regularly, a very slow distillation into the condenser taking place.

When the thermometer registered a constant temperature, the reading was recorded as the boiling point of the pure solvent. The stop cock between the outer tube and the reflux condenser was then opened and the heating was interrupted. A weighed amount of substance, the molecular
weight of which was to be determined, was introduced into the inner tube, and the above method of procedure was repeated until a constant boiling point was obtained. After reading the boiling temperature of the solution, the stop cock was again opened and the boiling stopped. The thermometer was carefully raised out of the solution and the volume of the latter was read.

After replacing the thermometer a fresh determination of the boiling point was made exactly as explained above. Owing to the condensation in the inner tube of a certain quantity of the solvent vapor, the concentration of the solution, and consequently the boiling point, showed a change in each successive determination. Thus a series of boiling points was obtained corresponding to different concentrations, from which the molecular weight was calculated by means of the formula,

\[ M = \frac{w}{K - \frac{e}{V}} \]

where \( K \) is a constant depending upon the solvent employed, \( w \) is the weight of the substance taken, \( e \) the elevation of the boiling point and \( V \) is the volume of the solution.
Compounding of the Blends

Eight series of blends were prepared in which the oils were compounded on the basis of their mean molecular weights. Each series consisted of blends containing approximately 20, 40, 60, and 80 mole percents of each of the two components. In preparing the blends, which were about 250 cc each in volume, the component oils were weighed on a large balance to the nearest tenth of a gram. The mixtures were then heated to approximately 250°F. and agitated ten minutes with a high speed electric stirrer.

Viscosity Determinations

The viscosities of all the fractions and blends of oil were determined by the regular A.S.T.M. method, by means of the Saybolt Standard Universal Viscosimeter. The Saybolt viscosities were converted to absolute viscosities by means of the Herschel equation,

1 - Cross, Handbook of Petroleum, Asphalt and Natural Gas.
2 - Herschel, U.S.B.S. Technologic Paper No. 112
\[
\frac{n}{D} = 0.00220 \frac{t^{1.80}}{t},
\]

where \( n \) is the absolute viscosity in poises, \( t \) is the Saybolt viscosity in seconds, and \( D \) is the density in grams per cubic centimeter.

DATA

The results of the molecular weight determinations and tests on the original oil samples are shown in tables one and two. Each of the values of molecular weight and viscosity were checked by three or more independent determinations. The values in the tables represent averages.

Tables 3 to 10 show the composition, density, and viscosity of each of the blended oils. Plates 9 to 16 represent the composition expressed in mole percent plotted as abscissa and the absolute viscosity as ordinate. Plates 1 to 8 represent the composition expressed in the same manner plotted as abscissa and the cube root of the absolute viscosity as ordinate. The latter relationship was suggested by the formula of Kendall and Monroe for "ideal" mixtures.
<table>
<thead>
<tr>
<th>Name of Oil</th>
<th>Designation Letter</th>
<th>Density in Grams per cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 200 Golden Neutral</td>
<td>A</td>
<td>0.9203</td>
</tr>
<tr>
<td>Shell 850 Golden Neutral</td>
<td>B</td>
<td>0.9283</td>
</tr>
<tr>
<td>Shell Golden Stock</td>
<td>C</td>
<td>0.9056</td>
</tr>
<tr>
<td>Shell &quot;H&quot; Bright Stock</td>
<td>D</td>
<td>0.9161</td>
</tr>
<tr>
<td>Standard No. 1</td>
<td>E</td>
<td>0.9015</td>
</tr>
<tr>
<td>Standard No. 2</td>
<td>F</td>
<td>0.9209</td>
</tr>
<tr>
<td>Pennsylvania No. 1</td>
<td>G</td>
<td>0.8689</td>
</tr>
<tr>
<td>Pennsylvania No. 2</td>
<td>H</td>
<td>0.8727</td>
</tr>
<tr>
<td>Pennsylvania No. 3</td>
<td>I</td>
<td>0.8775</td>
</tr>
<tr>
<td>Pennsylvania No. 4</td>
<td>J</td>
<td>0.8969</td>
</tr>
</tbody>
</table>
Table II

Results of tests and Determinations on Original Oil Samples

<table>
<thead>
<tr>
<th>Mean Molecular Weight Oil</th>
<th>Absolute Viscosity, $n^2$</th>
<th>Saybolt Viscosity in Sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_4$</td>
<td>$C_6H_4NO_2$</td>
<td>$C_6H_4Br_2$</td>
</tr>
<tr>
<td>A</td>
<td>360</td>
<td>362</td>
</tr>
<tr>
<td>B</td>
<td>468</td>
<td>465</td>
</tr>
<tr>
<td>C</td>
<td>578</td>
<td>583</td>
</tr>
<tr>
<td>D</td>
<td>678</td>
<td>---</td>
</tr>
<tr>
<td>E</td>
<td>427</td>
<td>427</td>
</tr>
<tr>
<td>F</td>
<td>701</td>
<td>---</td>
</tr>
<tr>
<td>G</td>
<td>425</td>
<td>431</td>
</tr>
<tr>
<td>H</td>
<td>460</td>
<td>468</td>
</tr>
<tr>
<td>I</td>
<td>511</td>
<td>510</td>
</tr>
<tr>
<td>J</td>
<td>824</td>
<td>---</td>
</tr>
</tbody>
</table>
### TABLE III

Blends of Shell 200 Golden Neutral with Shell "H" Bright Stock

<table>
<thead>
<tr>
<th>Blend Composition No.</th>
<th>by Weight, Grams</th>
<th>Composition in Mole Percents</th>
<th>Density Absolute Grams per cc</th>
<th>Viscosity ( n_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.4 A</td>
<td>34.7 A</td>
<td>0.9170</td>
<td>0.2154</td>
</tr>
<tr>
<td></td>
<td>152.9 D</td>
<td>65.3 D</td>
<td></td>
<td>0.598</td>
</tr>
<tr>
<td>2</td>
<td>100.8 A</td>
<td>61.4 A</td>
<td>0.9180</td>
<td>0.1540</td>
</tr>
<tr>
<td></td>
<td>118.9 D</td>
<td>38.6 D</td>
<td></td>
<td>0.513</td>
</tr>
<tr>
<td>3</td>
<td>153.0 A</td>
<td>77.3 A</td>
<td>0.9188</td>
<td>0.1010</td>
</tr>
<tr>
<td></td>
<td>83.7 D</td>
<td>22.7 D</td>
<td></td>
<td>0.465</td>
</tr>
<tr>
<td>4</td>
<td>189.3 A</td>
<td>92.1 A</td>
<td>0.9198</td>
<td>0.0707</td>
</tr>
<tr>
<td></td>
<td>30.1 D</td>
<td>7.9 D</td>
<td></td>
<td>0.413</td>
</tr>
<tr>
<td>6</td>
<td>22.1 A</td>
<td>16.3 A</td>
<td>0.9165</td>
<td>0.2704</td>
</tr>
<tr>
<td></td>
<td>200.3 D</td>
<td>83.2 D</td>
<td></td>
<td>0.647</td>
</tr>
<tr>
<td>Blend No.</td>
<td>Composition by Weight, Grams</td>
<td>Composition in Mole Percents</td>
<td>Density Grams per cc</td>
<td>Absolute Viscosity $n_3$</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>----------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>5</td>
<td>71.1 A</td>
<td>41.4 A</td>
<td>0.9099</td>
<td>0.1166, 0.490</td>
</tr>
<tr>
<td></td>
<td>161.8 C</td>
<td>58.6 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>54.3 A</td>
<td>21.6 A</td>
<td>0.9076</td>
<td>0.1416, 0.520</td>
</tr>
<tr>
<td></td>
<td>199.6 C</td>
<td>78.4 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>107.1 A</td>
<td>57.9 A</td>
<td>0.9118</td>
<td>0.1003, 0.465</td>
</tr>
<tr>
<td></td>
<td>129.3 C</td>
<td>42.1 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>139.0 A</td>
<td>72.7 A</td>
<td>0.9103</td>
<td>0.0853, 0.440</td>
</tr>
<tr>
<td></td>
<td>84.3 C</td>
<td>27.3 C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE IV**

Blends of Shell 200 Golden Neutral with Shell Golden Stock
### TABLE V

Blends of Shell 850 Golden Neutral with Shell "W" Bright Stock

<table>
<thead>
<tr>
<th>Blend No.</th>
<th>Composition by Weight, Grams</th>
<th>Composition in Mole Grams</th>
<th>Density, in Percents per cc</th>
<th>Absolute Viscosity, nS</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>34.0 B, 187.0 D</td>
<td>20.8 B, 79.2 D</td>
<td>0.9181</td>
<td>0.2840</td>
<td>0.657</td>
</tr>
<tr>
<td>11</td>
<td>66.0 B, 156.0 D</td>
<td>37.6 B, 62.4 D</td>
<td>0.9199</td>
<td>0.2484</td>
<td>0.629</td>
</tr>
<tr>
<td>12</td>
<td>109.3 B, 98.2 D</td>
<td>61.8 B, 38.2 D</td>
<td>0.9230</td>
<td>0.1973</td>
<td>0.582</td>
</tr>
<tr>
<td>13</td>
<td>142.9 B, 92.3 D</td>
<td>69.0 B, 31.0 D</td>
<td>0.9240</td>
<td>0.1845</td>
<td>0.568</td>
</tr>
</tbody>
</table>
### TABLE VI

Blends of Standard No. 1 with Standard No. 2

<table>
<thead>
<tr>
<th>Blend No.</th>
<th>Composition by Weight, Grams</th>
<th>Composition in Mole Percents</th>
<th>Density Absolute in grams per cc</th>
<th>Viscosity n³</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>32.5 E</td>
<td>22.7 E</td>
<td>0.9180</td>
<td>0.2792</td>
</tr>
<tr>
<td></td>
<td>180.4 F</td>
<td>77.3 F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>58.0 E</td>
<td>38.9 E</td>
<td>0.9155</td>
<td>0.2235</td>
</tr>
<tr>
<td></td>
<td>149.5 F</td>
<td>61.1 F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>98.4 E</td>
<td>57.3 E</td>
<td>0.9121</td>
<td>0.1711</td>
</tr>
<tr>
<td></td>
<td>120.6 F</td>
<td>42.7 F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>133.5 E</td>
<td>72.6 E</td>
<td>0.9084</td>
<td>0.1303</td>
</tr>
<tr>
<td></td>
<td>82.8 F</td>
<td>27.4 F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blend No.</td>
<td>Blend Composition</td>
<td>Composition by Weight</td>
<td>Composition in Mole Percents</td>
<td>Density Grams</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------------</td>
<td>------------------------</td>
<td>----------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>18</td>
<td>23.1 C</td>
<td>21.2 G</td>
<td>0.3934</td>
<td>0.2573</td>
</tr>
<tr>
<td></td>
<td>165.5 J</td>
<td>78.8 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>56.2 C</td>
<td>40.8 G</td>
<td>0.8888</td>
<td>0.1942</td>
</tr>
<tr>
<td></td>
<td>76.1 J</td>
<td>59.2 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>65.4 C</td>
<td>74.5 G</td>
<td>0.8796</td>
<td>0.0990</td>
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<tr>
<td></td>
<td>45.5 J</td>
<td>25.5 J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>46.0 C</td>
<td>55.3 G</td>
<td>0.8860</td>
<td>0.1512</td>
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<tr>
<td></td>
<td>72.2 J</td>
<td>44.7 J</td>
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</table>

**TABLE VII**

Blends of Pennsylvania No. 1 and Pennsylvania No. 4
<table>
<thead>
<tr>
<th>Blend No.</th>
<th>Blend Composition by Weight, in Grams</th>
<th>Composition in Mole Percents</th>
<th>Density Grams per cc</th>
<th>Absolute Viscosity n₁</th>
<th>n²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>23.5 A 191.5 F</td>
<td>19.5 A 80.5 F</td>
<td>0.9208</td>
<td>0.3004</td>
<td>0.676</td>
</tr>
<tr>
<td>21</td>
<td>50.0 A 167.4 F</td>
<td>36.8 A 63.2 F</td>
<td>0.9207</td>
<td>0.2376</td>
<td>0.620</td>
</tr>
<tr>
<td>22</td>
<td>76.5 A 145.5 F</td>
<td>50.7 A 49.3 F</td>
<td>0.9206</td>
<td>0.1360</td>
<td>0.570</td>
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<tr>
<td>23</td>
<td>123.3 A 106.8 F</td>
<td>69.4 A 30.6 F</td>
<td>0.9204</td>
<td>0.1250</td>
<td>0.500</td>
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<tr>
<td>24</td>
<td>167.8 A 58.0 F</td>
<td>85.0 A 15.0 F</td>
<td>0.9203</td>
<td>0.0388</td>
<td>0.446</td>
</tr>
</tbody>
</table>
### TABLE IX

Blends of Standard No. 1 with Shell "H"

**Bright Stock**

<table>
<thead>
<tr>
<th>Blend</th>
<th>Composition No.</th>
<th>Composition by Weight</th>
<th>Composition in Mole</th>
<th>Density</th>
<th>Absolute Viscosity</th>
<th>n_{3}</th>
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<tbody>
<tr>
<td>25</td>
<td>32.7 E</td>
<td>21.0 E</td>
<td>79.0 D</td>
<td>0.9139</td>
<td>0.2655</td>
<td>0.642</td>
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<tr>
<td></td>
<td>192.4 D</td>
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<td></td>
<td></td>
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<tr>
<td>26</td>
<td>64.3 E</td>
<td>38.0 E</td>
<td>62.0 D</td>
<td>0.9118</td>
<td>0.2097</td>
<td>0.595</td>
</tr>
<tr>
<td></td>
<td>165.3 D</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>27</td>
<td>101.5 E</td>
<td>57.2 E</td>
<td>42.8 D</td>
<td>0.9091</td>
<td>0.1544</td>
<td>0.537</td>
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<tr>
<td></td>
<td>120.6 D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>155.1 E</td>
<td>72.3 E</td>
<td>27.7 D</td>
<td>0.9068</td>
<td>0.1210</td>
<td>0.495</td>
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<tr>
<td></td>
<td>81.9 D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blend Composition</td>
<td>Composition in Mole</td>
<td>Grams</td>
<td>Density</td>
<td>Absolute Viscosity</td>
<td>$n_3^n$</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------</td>
<td>-------</td>
<td>---------</td>
<td>-------------------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>by Weight, Grams</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>17.0 G 20.2 G</td>
<td>106.5 D 79.8 D</td>
<td>0.9094</td>
<td>0.2349</td>
<td>0.617</td>
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<tr>
<td>32</td>
<td>39.0 G 45.0 G</td>
<td>82.1 D 57.0 D</td>
<td>0.9004</td>
<td>0.1603</td>
<td>0.543</td>
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<tr>
<td>33</td>
<td>57.2 G 53.3 G</td>
<td>65.2 D 41.7 D</td>
<td>0.8934</td>
<td>0.1280</td>
<td>0.501</td>
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<tr>
<td>34</td>
<td>84.9 G 77.5 G</td>
<td>39.1 D 25.5 D</td>
<td>0.8832</td>
<td>0.0878</td>
<td>0.445</td>
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</tr>
</tbody>
</table>

TABLE X

Blends of Pennsylvania No. 1 with Shell "H" Bright Stock
Plate I

Blends of Shell 200 Golden Neutral with Shell "H" Bright Stock

Mole Percent Shell "H" Bright Stock

The Root of Absolute Viscosity
Plate II

Blends of Shell 200 Golden Neutral with Shell Golden Stock

Mole Percent Shell Golden Stock
Plate III

Blends of Shell 850 Golden Neutral with Shell "M" Bright Stock

Chlor Sulf 20 Absolute Paraffinity

0.4

0.5

0.6

0.7

0.8

0.9

1.0

Male Percent Shell "M" Bright Stock
Plots IV

Blends of Standard No. 1 with Standard No. 2

Graph showing the relationship between the cube root of absolute viscosity and mole percent Standard No. 2.
Plate V

Blends of Pennsylvania No. 1 with Pennsylvania No. 4

Mole Percent Pennsylvania No. 4
Blends of Shell 200 Golden Neutral with Standard No. 2
Plate VII

Blends of Standard No. 1 with Shell "H" Bright Stock
Plate VIII

Blends of Pennsylvania No. 1 with
Shell "H" Bright Stock

Mole Percent Shell "H" Bright Stock
Plate IX

Blends of Shell 200 Golden Neutral
with Shell "H" Bright Stock
Plate X

Blends of Shell 200 Golden Neutral with Shell Golden Stock

Mole Percent Shell Golden Stock

Absolute Viscosity in Poise

0.04
0.08
0.12
0.16
Plate XI

Blends of Shell 850 Golden Neutral with Shell "K" Bright Stock

Mole Percent Shell "K" Bright Stock

Absolute Viscosity in poises
Plate XIII

Blends of Standard No. 1 with
Standard No. 2

Absolute viscosity in poises

Mole Percent Standard No. 2
Plate XIII

Blends of Pennsylvania No. 1 with Pennsylvania No. 4

Abscissa: Viscosity in Poises

Ordinate: Molé Percent Penn. No. 4
Plate XIV

Blends of Shell 200 Golden Neutral with Standard No. 2

Absorbance Increase in Percent

Mole Percent Standard No. 2
Plate XIV

Blends of Standard No. 1 with Shell "N" Bright Stock

Absolute Viscosity in Pond. 68

Mole Percent "N" Bright Stock
Plate XVI

Blends of Pennsylvania No. 1 with Shell "Z" Bright Stock
DISCUSSION OF RESULTS

The ebullioscopic method was found to be unsatisfactory for the determination of the mean molecular weights of lubricating oils. The boiling point of the pure solvent was not constant but showed a gradual increase as the distillation proceeded. The molecular weights determined by this method were therefore erratic and inconsistent. Acetone, benzene and ethyl acetate were the solvents employed.

The cryoscopic method, on the other hand, gave very satisfactory results. Examination of table 2 shows that the molecular weights determined by means of the three different solvents are in very close agreement. Benzene, nitrobenzene, and ethylene bromide were employed as solvents. Benzene and nitrobenzene have been employed for such determinations by other investigators. But there is no record in the literature of ethylene bromide having been used for the determination of the molecular weights of lubricants. During the determination, the solvent was kept under a slight pressure of dried compressed air to prevent
the absorption of moisture from the atmosphere. Dried air was used in preference to the anhydrous sodium sulphate employed by Steed and Gullick.

The viscosities of all the oils were determined at 210°F., since at lower temperatures the time of efflux was increased to such an extent that for some of the oils it was impossible to maintain the oil bath at a constant temperature throughout the run. Viscosities of a few of the oils were determined at 100°F. and were found to vary in the same order as when determined at 210°F.

The close accordance between the molecular weights as determined by means of three different solvents tends to preclude any evidence of association between the molecules of solute and those of the solvent or any lack of complete solubility at the temperature of the freezing point of the solvent. It also shows that ethylene bromide is a suitable solvent for cryoscopic determination of the molecular weights of hydrocarbon lubricants. Three of the heavier oils, though soluble in both benzene and ethylene bromide, were not completely soluble in nitrobenzene. It was therefore impossible to determine their
molecular weights by means of this solvent.

Both van't Hoff and Raoult have emphasized the fact that the formulas derived for the determination of molecular weights in solution depend upon assumptions which are valid only for dilute solutions. Yet in Gullick's determinations of the mean molecular weights of lubricating oils, he ran several determinations at increasing concentrations on the same sample of solvent. He then plotted the freezing point depression against the apparent molecular weight at each concentration and extrapolated his curve to zero concentration to obtain the true molecular weight. He admits that, "the possible extrapolation errors are so considerable that a considerable tolerance in the molecular weight at zero concentration must be allowed in all cases". In this investigation low concentrations of solute were used for all molecular weight determinations. Extrapolations are therefore unnecessary and the results are less questionable than if determined by the extrapolation of curves plotted from doubtful data.

Examination of plates 9 to 16 shows that the

1 - Jour. Inst. Petr. Tech. 17:541 (1931)
absolute viscosity of a blended lubricant is not a simple linear function of the viscosities and relative numbers of molecules of its components. However, when the cube root of the absolute viscosity is plotted against composition, the experimental data is in relatively close accordance with Kendall and Monroes' formula for "ideal" mixtures.

SUMMARY AND SUGGESTIONS

The mean molecular weights of ten fractions of lubricating oil have been determined by the cryoscopic method and checked by means of three different solvents, namely, benzene, nitrobenzene, and ethylene bromide.

Ethylene bromide has been found to be a suitable solvent for the cryoscopic determination of the mean molecular weights of hydrocarbon lubricants.

Viscosity determinations on 34 binary blends prepared from these fractions have been found to be in close accordance with the viscosity values calculated from Kendall and Monroes' formula for "ideal" mixtures.
This relationship should be of practical value in the blending of lubricants to meet viscosity specifications. At the present time, blending for viscosity is merely a matter of trial and error. The proportions of the components to be used are determined by experiment, separate experiments being required for each type of oil and each value of blend viscosity.

By means of the cube root formula of Kendall and Monroe, the viscosity of a blended lubricant of any composition could be calculated from the mean molecular weights and the absolute viscosities of its components. The calculated value of viscosity would be sufficiently accurate for blending purposes, and the trial and error method could be discarded.
Figure 1
McCoy Boiling Point Apparatus

Figure 2
Beckmann Freezing Point Apparatus with Air Drying Train
Figure 3
Saybolt Standard Universal Viscosimeter with Accessories

Figure 4
Vacuum Distillation Apparatus
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