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The Temperature and Composition of the Density, Refractive Index and Viscosity of Dioxande and Methyl-Alcohol. The Temperature Coefficients of Density, Refractive Index and Viscosity of the Pure Solvents.

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THE TEMPERATURE AND COMPOSITION COEFFICIENTS OF THE DENSITY
REFRACTIVE INDEX AND VISCOSITY OF DIOXANE AND METHYL ALCOHOL

THE TEMPERATURE COEFFICIENTS OF DENSITY REFRACTIVE INDEX AND
VISCOSITY OF THE PURE SOLVENTS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
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Doctor of Philosophy

in

The Department of Chemistry

By

Frank Lykins Padgitt
A. B., Southwest Missouri State Teachers College, 1935
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ABSTRACT

In this investigation the densities, refractive indexes, and viscosities of methyl alcohol-dioxane mixtures were measured over a complete range of compositions and at several temperatures. The densities, refractive indexes, and viscosities of the pure substances were measured at several temperatures.

Great care was exercised in purifying the materials, preparing the mixtures, controlling the temperatures, and choosing the type of apparatus used so as to eliminate as far as possible any errors. Precision calculations gave an average deviation of plus or minus two in the fifth decimal place in densities, plus or minus two in the fourth decimal place of refractive indexes, and a minimum of two parts in eighteen hundred in the viscosities.

Composition coefficient equations for density and refractive index of methyl alcohol-dioxane mixtures and temperature coefficient equations for the densities, refractive indexes and viscosities of the pure substances and their mixtures were derived by the method of least squares. A satisfactory equation for the composition coefficient of viscosity was difficult to formulate, and the one finally selected from Bingham (7) was not as satisfactory as could be desired.
The constants for the composition and temperature coefficient equations were tabulated along with numbers for plotting deviations of the calculated from the observed functions so that corrections can always be applied to computed values to make them agree with those observed. This makes possible the use of these substances and their mixtures as media in conductance, electromotive force, and kinetic measurements in which it is desired to use a controlled viscosity or density.

Comparison of the observed values of the densities, refractive indexes, and viscosities of the pure substances were made with values of the same properties recorded in the literature. In many cases our values of density were in agreement with recorded values, while in other instances rather wide variations were noted. It was pointed out that the use of various investigators of the same method of purification of a substance does not always guarantee that they will obtain the same value for its density.

Observed and recorded values of refractive indexes were in satisfactory agreement for both methyl alcohol and dioxane.

The table for comparison of our experimentally observed viscosities for methyl alcohol and dioxane with those observed by other investigators graphically
illustrates the uncertainties of knowledge concerning this property. No one seems to know when a correct value for this function is actually obtained, although recently probable sources of error are being recognized, and design of apparatus and methods of experimental procedure are being developed to minimize these errors.

At twenty-five degrees our experimental viscosities of methyl alcohol do agree with those of several other observers, while our values for dioxane closely parallel those of Geddes throughout the temperature range investigated. As in the case of densities the same method of purification of the substances yielded wide variations in observed viscosities. Altogether the whole field of viscosity needs investigation by both the best experimentalists and the best theoreticists.
INTRODUCTION

The interest in measurements on conductance, electromotive force, thermodynamic properties of solutes, and reaction rates in mixed solvents has increased very rapidly during the last decade. Among the properties of the solvent which are pertinent to such measurements are the density, viscosity and dielectric constant. Investigations are now appearing in the literature where a controlled dielectric constant is shown to have a very important effect on thermodynamic and kinetic measurements in solution (3, 29, 60, 61).

The effect of viscosity on conductance is well established by its occurrence in Onsager's equation (46) while the interest shown in the relationship between viscosities and reaction rates is illustrated by the work of Flory (22). Macleod (47) in his attempts to correlate viscosities and free space of liquids, states that often the densities are not known accurately enough to permit conclusive comparison of data and theory.

The data on these physical properties of pure solvents are fairly extensive, but woefully meager for their mixtures. Akerlof and co-workers (1, 2) and Wyman and co-workers (64, 65) have made, over fairly wide
temperature ranges, complete investigations of the dielectric constants of several binary mixtures, one component of which is water.

Fuoss and Kraus (23, 24, 42) have developed extensively the theory of conductance in solvents of low dielectric constant, but were hampered somewhat by lack of accurate viscosity data for the solvents used. The authors wanted to investigate these theories in media where it would be possible to control either dielectric constant or viscosity at will, and both as far as possible. Before such measurements could be made, however, these physical properties of a solvent pair would have to be determined over a wide range both of temperature and of concentration. Since the dielectric constants of methyl alcohol-dioxane mixtures have been determined over some range of temperature and composition (6), and since this solvent pair can be used to produce low controlled dielectric constants, it was determined to measure the density, viscosity, and refractive index at several temperatures of methyl alcohol-dioxane and their mixtures.
REVIEW OF THE LITERATURE

Density:

Though several methods of determining densities are in common use (54), a survey of the literature made it apparent that for purposes of this paper a pyknometer such as the one described by Hartley and Barrett (32) and commonly known as a Sprengle type would be most satisfactory. These authors have shown that the buoyancy of air must not be neglected in the calculations, and Wade and Merriman (63) and Guy Barr (5) have discussed in detail the various corrections necessary for accurate determination of density. Hartley and Barrett (32) have developed a formula which is simple and at the same time accurate to \( \pm 5 \) units in the sixth decimal place using about 25 ml. of liquid. The derivation is as follows:

\[
\text{if } W_p \text{ is the true weight of the empty pyknometer in vacuum,}
\]

\[
W_c \text{ is the true weight of the counterpoise in a vacuum,}
\]

\[
V_p \text{ is the volume of liquid in the pyknometer when filled to the mark,}
\]

\[
V_{pg} \text{ volume of the glass of the pyknometer,}
\]

\[
V_c \text{ external volume of the counterpoise,}
\]
$W_1$ is the apparent weight in air of the empty pyknometer (corrected for air displaced by the brass weights) when weighed against the counterpoise.

$W_2$ is the apparent weight in air of the pyknometer full of water (corrected for air displaced by the brass weights) when weighed against the counterpoise.

$W_3$ is the apparent weight in air of the pyknometer full of liquid (corrected for air displaced by the brass weights) when weighed against the counterpoise.

$D_1$, $D_2$, $D_3$ are the densities of air at these successive weighings, $d_w$ is the density of water, $d_l$ is the density of the liquid at the temperature of the experiment referred to water at 4°.

Then:

$$W_1 = W_p - D_1 V_p - (W_e - D_1 V_e)$$  \hspace{1cm} (1)

$$W_2 = W_p + d_w V_p - D_2 (V_p + V_e) - (W_e - D_2 V_e)$$  \hspace{1cm} (2)

$$W_3 = W_p + d_l V_p - D_3 (V_p + V_e) - (W_e - D_3 V_e)$$  \hspace{1cm} (3)

If

$$V_e = V_p + V_p$$

$$W_1 = W_p - W_e + D_1 (V_e - V_p)$$  \hspace{1cm} (4)

$$W_2 = W_p + d_w V_p - W_e$$  \hspace{1cm} (5)

$$W_3 = W_p + d_l V_p - W_e$$  \hspace{1cm} (6)

Dividing (6) by (5)

$$d_l = d_w \frac{W_3 - W_p + W_e}{W_2 - W_p + W_e} = d_w \frac{W_3 - (W_p - W_e)}{W_2 - (W_p - W_e)}$$  \hspace{1cm} (7)

Substitute (4) in (3)

$$d_l = d_w \frac{W_3 - W_1 + D_1 (V_e - V_p)}{W_2 - W_1 + D_1 (V_e - V_p)}$$  \hspace{1cm} (8)

The formula requires the use of a counterpoise whose external volume is made equal to the sum of the volume of the glass of the pyknometer and the liquid it holds when full. They
have shown that if this adjustment is made within 0.5 ml. the buoyancy error is about two units in the sixth decimal place. They have further shown that if the density of the liquid varies much from that of water, that is, falls outside the limits 2.0 and 0.85, the density of air at the time of weighing cannot be neglected. Ewart and Raikes (21) have made use of the reduced form (Eq. 7). This formula requires only the determination of the apparent weight of the pyknometer full of liquid \( W_2 \) and may be used when the accuracy of the measurements need only be in the fifth decimal place.

In regard to the methods of weighing necessary to insure sufficient accuracy in a research of this type, the interesting work of Manley and Oxon (48) should be cited. This paper deals with some of the lesser known factors affecting the accuracy of the balance and stresses in particular the necessity of allowing the beam to become properly fatigued by allowing it to oscillate for about ten minutes before making the final adjustment of the rider.

**Refractive Index:**

The refractometer is one of the most universally used instruments in scientific investigations. Most common of these instruments is the Abbe type. Based on exact optical laws, the Abbe refractometer is so simple to operate that it needs no extended review. Excellent discussions of
this instrument may be found in Livingston (44), Reilly and Rae (55) and technical literature published by Bausch and Lomb (53). Refractive indexes can be measured over a range of 1.5000 to 1.7000 with an accuracy of two units in the fourth place. The Abbe type needs no source of monochromatic light, and the refractive index may be read directly from the scale which is calibrated for the sodium D line. Only a few drops of the liquid are needed and the temperature can be accurately controlled. These considerations, together with the fact that it requires only a few seconds to make a reading, make it an extremely useful instrument.

Viscosity:

The determination of viscosity from the flow of liquids in capillary tubes has been the subject of much research. Poiseuille (52) in 1842 made the first studies of liquid flow in capillary tubing. By about 1860 the methods of measurement and formula used in calculation were about the same as today. The formula is:

$$\eta = \frac{mg^rR^4t}{8Vl} - \frac{mdV}{8\pi lt}$$

where $\eta$ = coefficient of viscosity
$g$ = gravitational constant
$p$ = pressure
$R$ = radius of the capillary
$t$ = time
$V$ = volume of efflux
$m$ = Hagenbach factor or kinetic energy coefficient
$d$ = density

The work of Thorpe and Rodgers (62) done in 1893 remains one of the classical pieces of research on viscometry.
Modern work has been largely devoted to elimination of experimental error rather than to any fundamental change in the theory. Thus Reynolds (56) experimenting with factors which govern the change of linear flow to turbulent flow has shown that if the mean velocity of efflux exceeds a certain critical velocity, the flow is probably turbid and the law of Poiseuille is not valid. Bingham (7) gives detailed discussions of the factors involved in selecting the proper dimensions of the viscometer, that is, radius, length of capillary, volume of efflux, etc., for liquids of any given fluidity.

Jones and Talley (41) have developed a very accurate electrical method for the automatic measurements of the time of efflux.

With all these advances in technique, certain questions of theory such as the value of the Ragenbach factor, m, (31) in the kinetic energy correction are still the subject of much doubt. Bingham (7, pp.17-29) gives a comprehensive discussion of this factor. Values have been found which range from 0 to 1.12 and though Riemann (57) gave a value for methyl alcohol of 1.124, the better practice is to make the dimensions of the viscometer such that the kinetic energy constant is small in comparison with that of the larger term. A relatively large error in the value of m will, therefore, exert only a small influence on the main term of the viscosity equation.
Couette (16, 17) also suggests a correction which has to do with the friction of the liquid near the end of the capillary. He concludes that in effect it amounts to a slight alteration in the length of the tube, is constant and approximately three times the diameter of the tube. This correction is eliminated in the determination of relative viscosities.

The question of drainage errors has been dealt with in a very interesting research by Jones and Stauffer (40). They concluded that incomplete drainage was not a serious source of error in determination of the viscosity of aqueous solutions relative to pure water. Cannon and Fenske (13) have confirmed this conclusion.

Contrary to the opinion of earlier investigators, Jones and Fournwalt (39) have shown that the surface tension of the liquid has an unexpectedly large influence on the viscosity. In a highly mathematical treatment of the subject, they have shown how to calculate the magnitude of this error. It is appreciable in all viscometers of the type where the upper bulb varies in diameter from that of the lower bulb. That it is negligible for upper and lower bulbs of the same size has been shown by these authors as well as Cannon and Fenske (13).

Apparently modern viscometry is tending toward the use of the Ostwald type of viscometer. Jones and Talley (41) and Jones and Fournwalt (39) have obtained especially high
precision with this instrument. The latter paper and the one of Cannon and Fenske (13) have excellent discussions of the magnitude of the errors involved and methods of keeping them at a minimum.
The 1, 4 dioxane used in this work was manufactured by the Eastman Kodak Company. Three grades were used:

1. P 2144 - 1, 4 Dioxane, practical, $1.11 per kg.
2. 2144X - 1, 4 Dioxane, histological, $2.00 per kg.
3. £144 - 1, 4 Dioxane, $2.75 per kg.

All were carefully purified by the methods described by Hess and Frahm (35). The practical and histological grades were refluxed for a day with 100 ml. of normal HCl per liter of dioxane. At the same time a slow current of air was drawn through the condenser to sweep out any acetaldehyde originally present as an impurity and any formed by hydrolysis of ethylene acetal. Oxford (51) reports that technical grades of dioxane contain considerable amounts of both of these impurities. The dioxane was now treated with solid KOH and the aqueous layer which settled out was separated in a separatory funnel. After two or three treatments in this manner, the dioxane was refluxed over metallic sodium until the bright luster of the sodium indicated that there was no more chemical reaction. It was then carefully distilled through a fractionating column 115 cm. long and fitted with an efficient still head of the total condensation partial take off type. The initial boiling points were always low,
usually below 90°, whereas the boiling point of dioxane is 101.31°C. Usually 15 to 20 per cent of the dioxane would distill over before the boiling point reached 101.3°C. The next portion, about 60 per cent boiling within a range of two hundredths of a degree, was collected. This fraction was further purified by fractional recrystallization in an ice bath. In order to protect the dioxane from moisture in the air, glass stoppered flasks equipped with calcium chloride drying tubes were used. Recrystallization was repeated until no further increase in the density was observed. This would often take as many as six or eight recrystallizations. In the case of the best grade of dioxane, the HCl treatment was omitted since Hess and Frahm (35) have stated that refluxing over metallic sodium was sufficient if the impurities were present in small amounts. The same distillation procedure was followed. It was quite noticeable, however, that the initial boiling point was considerably higher than in the case of the other two and as much as 80 per cent would distill over within two hundredths of a degree boiling point range. Usually four or five recrystallizations of this product were sufficient to bring it to the correct density. After this final treatment, the dioxane was stored over metallic sodium, from which it was distilled as needed. It may be pointed out that the densities of the three grades of dioxane, after distillation but before recrystallization, were not the same nor could they be made
to agree by repeated rectification. All three grades, however, gave the same density after recrystallization. It is our opinion that because of better yields it is more economical to use the dioxane listed as No. 2144 at $2.75 per kilogram than the cheaper grades.

The methyl alcohol used in this investigation was manufactured by Eimer and Amend and contained not more than 0.005 per cent aldehydes and acetone. It was further purified by the method of Lund and Bjerrum (45). One hundred grams of magnesium turnings, and 1 g. of iodine per liter of C. P. methyl alcohol was refluxed until the iodine disappeared. Four liters of C. P. methyl alcohol were then added and refluxed for about half an hour. The alcohol was then distilled through the fractionation column previously described, and the middle 80 per cent fraction, which distilled over within 0.02°, was collected.

This procedure was repeated and the final product stored over magnesium methylate, prepared as above and distilled off immediately before use. No difficulty was ever experienced in obtaining the same density with different batches.

The solutions were made up by weight just before use and kept in 250 cc. pyrex bottles. The solvents and solutions were never poured from bottle to bottle but always pumped by means of pressure from dry air. Every precaution was taken in all the experimental stages to prevent absorption of
moisture from the air.

Two constant temperature baths were used and the temperature held to \(0.005^\circ\). The thermometers and weights were checked against standards calibrated by the Bureau of Standards. The calibration of the weights included the correction for the buoyancy of air, using for the density the average value of 0.0012 g. per ml.

Following the technique of Hartley and Barrett (52), three pyknometers were prepared and adjusted so that the external volume of all three agreed within 0.5 ml. One of these was used as a counterpoise. At least two determinations were made using different pyknometers. If the average deviation of the mean was greater than 0.00001, more determinations were made in order to keep it within this figure. On the pure liquids many more measurements were made than were required to give this precision.

Temperature control for the measurement of refractive index was accomplished by pumping water from the thermostats through the prisms of the Abbe refractometer. In each determination several independent readings on different samples of liquid were observed and the average taken as the correct value.

The dimensions of the Ostwald viscometer were made to conform with the recommendations of Bingham (7), Jones and Fornwalt (39), and Cannon and Fenske (13), and were as follows:
Volume of efflux \( V = 8.09 \, \text{ml.} \)
Loading volume \( v = 11.34 \, \text{ml.} \)
Fluid head \( H = 24.59 \, \text{cm.} \)
Length of capillary \( l = 29.7 \, \text{cm.} \)
Radius of capillary \( R = 0.02805 \pm 0.00003 \, \text{cm.} \)
Radius of upper and lower bulb \( r = 0.7 \, \text{cm.} \)

That flow in the viscometer was not turbulent may be shown by the criteria of Reynolds (56). That is

\[
\frac{V}{\pi R^2 t} \text{ must be } \frac{1000 \gamma}{Rd}
\]

where \( t \) is seconds and the other symbols are given above.

For the extreme case of methyl alcohol at 50°, we have from equation (10)

\[
\frac{8.09}{3.142 \times 0.02805^2 \times 181.4} \text{ is less than } \frac{1000 \times 0.003913}{0.02805 \times 0.73266}
\]

\[
\text{or } 18.1 \text{ is less than } 183.
\]

The condition of Bingham (7) that the kinetic energy term be small in comparison with main term of viscosity in the equation

\[
\gamma = \frac{gHdR^4t}{8Vl} - \frac{mdV}{8\pi lt}
\]

where \( g \) is the gravitational constant, \( d \) the density, and \( m \) the kinetic energy coefficient is also satisfied, as shown by dividing the kinetic energy term by the main term. For the extreme case of methyl alcohol at 50°, the kinetic energy correction is about 1.6 per cent. A small error in the kinetic energy coefficient will, therefore, have a negligible influence on the main term.

Surface tension effects, as suggested by Jones and
Fornwalt (39), and Cannon and Fenske (13), have been eliminated as far as possible by making the diameter of the upper and lower bulbs the same.

Combining the constants in equation (11) it may be written

$$\eta = \frac{CdHt - C_1d}{t}$$

where \( C = \frac{\pi gR^4}{8\nu l} \) and \( C_1 = \frac{mV}{8\nu l} \)

When determining relative viscosities the equations may be combined thus:

$$\frac{\eta}{\eta'} = \frac{CdHt - C_1d/t}{C'd'H't' - C_1d'/t'}$$

where the \( \eta' \), \( d' \), \( H' \) and \( t' \) are the values for the reference liquid. Dividing the numerator of equation (13) by the denominator, we obtain

$$\frac{\eta}{\eta'} = \frac{d'Ht}{d'H't'} + \frac{C_1dHt}{CH'2d't'^3} - \frac{C_1d}{CH'd't't}$$

Then

$$\gamma = \frac{\eta'd'Ht}{d'H't'} + \frac{\eta'C_1d}{\eta'}\left(\frac{tH}{H't'^2} - \frac{1}{t}\right)$$

Or

$$\eta = \frac{\eta'd'Ht}{d'H't'} + \frac{C_1d}{t}\left(\frac{t^2}{t'^2} - 1\right)$$

The second term is the kinetic energy correction and since it is small and \( H \) and \( H' \) do not differ greatly, their ratio is taken as unity in this term. In our experimental procedure, \( H \) and \( H' \) are not constant since our viscometer was
always filled at 30°, and the fluid head is different at other
temperatures.

We have modified equation (16) in the following
manner to take care of the change in fluid head at tem­
peratures other than 30°. Let

\[ H_{30} = \text{fluid head at 30°} \]
\[ H = \text{fluid head at temperature } t \]
\[ \nu_{30} = \text{density of the fluid at 30°} \]
\[ d = \text{density of the fluid at temperature } t \]

then

\[ V = \frac{\nu_{30}d_{30}}{d} \quad (17) \]

and

\[ \Delta V = V - \nu_{30} = \frac{\nu_{30}d_{30}}{d} - \nu_{30} \quad (18) \]

\[ h = \frac{\Delta V}{t} = \frac{\nu_{30}}{t} \left( \frac{d_{30}}{d} - 1 \right) \]
\[ = k\left( \frac{d_{30}}{d} - 1 \right) \quad (20) \]

but \[ H = H_{30} - h \quad (21) \]

therefore from equations (16), (20) and (21), we obtain

\[ \eta = \frac{\gamma'\, dt}{dt} \left[ \frac{h_{30} - k\left( \frac{d_{30}}{d} - 1 \right)}{h'_{30} - k\left( \frac{d'}{d} - 1 \right)} \right] + C_1 d \left( \frac{t^2}{t^2} - 1 \right) \]

Each recorded value of viscosity represents the mean
of at least two measurements made upon separate samples. If
the difference in the observed efflux time was more than two
tenths of a second other observations were made until the
average deviation was of this order of precision. Two tenths
of a second represents a minimum of two parts in eighteen
hundred. This minimum precision occurs for methyl alcohol at
50° since this is the lowest viscosity measured.
DISCUSSION OF DATA

In Tables I, II, and III are given the measured values of densities, refractive indexes, and viscosities, respectively, of methyl alcohol-dioxane mixtures at various temperatures and compositions together with the densities, refractive indexes, and viscosities of the pure substances at various temperatures. The small number in parenthesis to the right of each value is the quantity to be added algebraically to the value calculated from the composition coefficient equation in order to make this calculated value agree with the one observed. These composition coefficient equations were derived by the method of least squares, and will be given later.

Densities and refractive indexes as a function of composition are represented by the general parabolic equation

\[ f(m) = a + bm + cm^2 + dm^3 + em^4 \]  

(23)

where \( m \) is the weight per cent. Tables IV and V contain the constants to be inserted in the above equation when representing densities and refractive indexes, respectively. These constants are to be incorporated in the equation along with the sign as indicated in the table. The mean percentage deviation between the calculated and observed quantities, although small, as shown in the last column in Table IV is
still greater than the measured precision. The deviation is always in the fifth place of measured density and values calculated from the equation are good for most purposes. However, if more accurate densities are desired the calculated values can be corrected by preparing a deviation graph from the numbers given in parentheses in Table I. An example of such graph is given in Figure 1.

The mean percentage deviation represented in the last column of Table V for the difference between calculated and observed values of refractive index are somewhat beyond the experimental accuracy and, therefore, calculated values of this function require no correction. For purposes of comparison a deviation graph of refractive index has also been included in Figure 1.

It is extremely difficult to represent viscosity as a function of concentration. It may be pointed out that no such empirical equation appears in the International Critical Tables. Many forms of equations were tried and rejected because of the wide variation between calculated and observed viscosities. Numerous additive relationships have been proposed for the function \( f(\gamma) \) but none have proven generally acceptable. For our purposes Bingham’s formula \((7)\) was adopted as being the most satisfactory. This equation can be written

\[
\frac{1}{\gamma} = \frac{\nu_{1\%}}{\gamma_{1\%}} + \frac{\nu_{2\%}}{\gamma_{2\%}} + \frac{K(\nu_{1\%} - \nu_{1\%})}{\gamma_{2\%}}
\]  

(24)
where $\eta_1$ and $\eta_2$ are the viscosities, $V_1$ and $V_2$ the volume per cents, $W_1$ and $W_2$ the weight per cents of the pure components, and $K$ is a constant at a given temperature. Table IV contains $K$ at various temperatures to be used in the above equation.

The mean percentage deviations recorded in this table between calculated and observed values appear at first sight to be quite large. When it is remembered, however, that percentage deviations of one to three per cent are considered good by many investigators (see Bingham (7) page 169) is evident that our calculated and observed values are in surprisingly good agreement. Furthermore, viscosities calculated from this equation are superior in accuracy to those obtained by graphical means. Calculated values, sensibly in agreement with observed values, can be obtained from equation (24) and deviation plots prepared from the numbers given in parentheses in Table III. An example of such a plot is also included in Figure 1.

Using these methods, we have prepared tables for the densities, refractive indexes, and viscosities at even percentage compositions. These values are tabulated in Tables VII, VIII, and IX, respectively. The number in parenthesis will be explained later.

The temperature coefficients of density, refractive index, and viscosity of methyl alcohol-dioxane mixtures and of the pure substances may be represented by the following
general formula

\[ f(t) = a + bt + ct^2 + \ldots \ldots. \quad (25) \]

Using the data of Tables VII, VIII, and IX, the constants for the temperature coefficient equations of densities, refractive indexes, and viscosities were calculated by the method of least squares and are tabulated in Tables X, XI, and XII. These constants are to be incorporated, along with the indicated signs, in the above general equation.

In the last column of Table X are given the mean percentage deviations between the densities calculated by the temperature coefficient equations and the data tabulated in Table VII. These percentage deviations show that the equations reproduce the data within a maximum of five units in the fifth decimal place. If greater accuracy is required, the calculated values must be corrected by deviation graphs which can be prepared from the numbers given in parentheses in Table VII. These numbers, as before, are the quantities which must be added algebraically to the calculated values to make them agree with the data of Table VII.

The percentage deviation of the values calculated by means of the temperature coefficient equations of refractive index from those tabulated in Table VIII show excellent agreement; consequently, no further correction is necessary.

As indicated by the mean percentage deviations in the
last column of Table XII, we have succeeded in formulating an equation for the temperature coefficients of viscosities which, although not as good as could be desired, is superior to the composition coefficient equation in the accuracy with which it will reproduce our data. More accurate viscosities can be obtained by correcting the values calculated by the temperature coefficient equations using deviation graphs obtained from the numbers given in parentheses in Table IX. Even without corrections, our temperature coefficient equations give calculated viscosities as acceptable as many other like equations now recorded in the literature. For example, alcohols in general show a much larger mean percentage deviation than our value of 0.07 for methyl alcohol (see Bingham (7) pages 135-36).

Tables XIII, XIV, and XV contain comparisons of the values obtained in this investigation with those found in the literature for the densities, refractive indexes, and viscosities, respectively, of methyl alcohol and dioxane. In the temperature range from 10° to 25°, our values of the densities of methyl alcohol are somewhat lower than those given in the International Critical Tables. However, from 30° to 50° the agreement is all that can be desired. At 25°, where the greatest number of comparisons can be made, our value is almost identical with that of Lund and Bjerrun (45), and of Jones and Fornwalt (39). Although Lund and Bjerrun, Jones and Fornwalt, and the authors of this paper purified
their methyl alcohol by the same procedure, it should be pointed out that this is not the sole reason for the agreement noted since other investigators, using like methods, have not obtained the same density. The measured density of this paper is in perfect agreement with the average of the entire group. It will be noticed that the International Critical Table value at the temperature is the highest of any of the recorded values.

The densities of dioxane for any temperature show a wider divergence than those of methyl alcohol. The probable explanation for the variation of the observed densities is due to the difficulty of obtaining pure dioxane. Even among authors who use the same method of purification there is a relatively wide range of observed density. For example, Meisenheimer and Dorner, Horvorka, Schaefer and Dreisbach, Hess and Frahm, and the authors used similar methods of purification including recrystallization yet obtained 1.0296, 1.03318, 1.03378, and 1.03359, respectively, for the density of dioxane. This is a further indication that the method of purification of a substance does not always insure agreement in observed values of the physical constants. The other values recorded at 20° are consistently lower than those of Hess and Frahm and of the authors. At other temperatures, similar variations are observed in the data of various investigators.

The refractive indexes for both methyl alcohol and
dioxane obtained in this investigation agree well with the observations of other investigators as is shown in Table XIV.

It is evident from Table XV that the viscosities of both methyl alcohol and dioxane vary widely, even at the same temperatures. At 25° the value for methyl alcohol recorded in this paper agrees very well with the values recorded by Jones and Fornwalt, Ewart and Raikes, Goldschmidt and Aarflot, and Dunstan, Thole and Benson. In the temperature range from 20° to 50°, the viscosities of dioxane observed by the authors closely parallel those of Geddes. The wide variation in viscosity for the same substances at the same temperature strongly emphasizes the difficulties involved in its measurement.
TABLE I

Measured densities of methyl alcohol-dioxane mixtures at various temperatures and compositions: measured densities of the pure substances at various temperatures.

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>10.04°</th>
<th>20.00°</th>
<th>30.00°</th>
<th>40.00°</th>
<th>50.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.04451 (0)</td>
<td>1.03382 (0)</td>
<td>1.02227 (0)</td>
<td>1.01071 (0)</td>
<td>0.99949 (0)</td>
</tr>
<tr>
<td>9.362</td>
<td>1.01381 (-2)</td>
<td>1.00294 (-6)</td>
<td>0.99540 (-3)</td>
<td>0.98401 (-5)</td>
<td>0.96941 (-3)</td>
</tr>
<tr>
<td>10.635</td>
<td>0.98998 (+2)</td>
<td>0.97934 (+6)</td>
<td>0.96621 (-2)</td>
<td>0.95523 (+7)</td>
<td>0.94630 (+3)</td>
</tr>
<tr>
<td>19.231</td>
<td>0.96012 (+2)</td>
<td>0.94978 (+6)</td>
<td>0.93848 (0)</td>
<td>0.92773 (+2)</td>
<td>0.91474 (+6)</td>
</tr>
<tr>
<td>20.010</td>
<td>0.93345 (-10)</td>
<td>0.92302 (-3)</td>
<td>0.91283 (+2)</td>
<td>0.90224 (-4)</td>
<td>0.89142 (+6)</td>
</tr>
<tr>
<td>30.410</td>
<td>0.91091 (+2)</td>
<td>0.90087 (-6)</td>
<td>0.88888 (+4)</td>
<td>0.87850 (+4)</td>
<td>0.86970 (-9)</td>
</tr>
<tr>
<td>30.587</td>
<td>0.88664 (+3)</td>
<td>0.87677 (-4)</td>
<td>0.85629 (-9)</td>
<td>0.84614 (-8)</td>
<td>0.84614 (-8)</td>
</tr>
<tr>
<td>40.782</td>
<td>0.86442 (+3)</td>
<td>0.85467 (-1)</td>
<td>0.83452 (-4)</td>
<td>0.82460 (+1)</td>
<td>0.82460 (+1)</td>
</tr>
<tr>
<td>40.925</td>
<td>0.84076 (-2)</td>
<td>0.83121 (+5)</td>
<td>0.82273 (-2)</td>
<td>0.81149 (-3)</td>
<td>0.80168 (+7)</td>
</tr>
<tr>
<td>60.206</td>
<td>0.81977 (-4)</td>
<td>0.81040 (+5)</td>
<td>0.80174 (-2)</td>
<td>0.79098 (+4)</td>
<td>0.78131 (+4)</td>
</tr>
<tr>
<td>60.624</td>
<td>0.80512 (+1)</td>
<td>0.79125 (-7)</td>
<td>0.78187 (+4)</td>
<td>0.77233 (-4)</td>
<td>0.76269 (-6)</td>
</tr>
</tbody>
</table>
**TABLE II**

Measured refractive indexes of methyl alcohol-dioxane mixtures at various temperatures and compositions: measured refractive indexes of the pure substances at various temperatures.

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.4223 (0)</td>
<td>1.4178 (+2)</td>
<td>1.4133 (-1)</td>
<td>1.4088 (0)</td>
</tr>
<tr>
<td>9.362</td>
<td>1.4101 (-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.535</td>
<td></td>
<td>1.4073 (+1)</td>
<td>1.4028 (-1)</td>
<td>1.3970 (+1)</td>
</tr>
<tr>
<td>19.231</td>
<td>1.4008 (-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.010</td>
<td></td>
<td>1.3962 (+2)</td>
<td>1.3915 (+1)</td>
<td>1.3876 (-2)</td>
</tr>
<tr>
<td>30.410</td>
<td>1.3895 (+1)</td>
<td>1.3854 (0)</td>
<td>1.3805 (-1)</td>
<td>1.3763 (+1)</td>
</tr>
<tr>
<td>30.587</td>
<td></td>
<td>1.3854 (0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.782</td>
<td>1.3792 (0)</td>
<td>1.3754 (0)</td>
<td>1.3708 (0)</td>
<td>1.3664 (+2)</td>
</tr>
<tr>
<td>40.925</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.975</td>
<td>1.3706 (0)</td>
<td>1.3660 (-1)</td>
<td>1.3616 (+1)</td>
<td>1.3576 (-2)</td>
</tr>
<tr>
<td>50.695</td>
<td></td>
<td></td>
<td>1.3563 (+3)</td>
<td></td>
</tr>
<tr>
<td>60.206</td>
<td>1.3613 (0)</td>
<td>1.3573 (+3)</td>
<td>1.3533 (+2)</td>
<td>1.3489 (+1)</td>
</tr>
<tr>
<td>60.624</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.785</td>
<td>1.3526 (-1)</td>
<td>1.3482 (0)</td>
<td>1.3443 (+1)</td>
<td>1.3404 (-2)</td>
</tr>
<tr>
<td>69.931</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70.353</td>
<td>1.3478 (0)</td>
<td>1.3438 (+1)</td>
<td>1.3398 (+3)</td>
<td>1.3358 (-3)</td>
</tr>
<tr>
<td>80.058</td>
<td></td>
<td></td>
<td>1.3358 (+3)</td>
<td></td>
</tr>
<tr>
<td>80.566</td>
<td>1.3360 (+1)</td>
<td></td>
<td>1.3323 (+1)</td>
<td>1.3283 (+3)</td>
</tr>
<tr>
<td>90.119</td>
<td></td>
<td></td>
<td></td>
<td>1.3253 (+2)</td>
</tr>
<tr>
<td>90.669</td>
<td>1.3383 (+1)</td>
<td></td>
<td>1.3297 (+2)</td>
<td>1.3240 (-2)</td>
</tr>
<tr>
<td>100.000</td>
<td>1.3283 (-1)</td>
<td>1.3249 (+3)</td>
<td>1.3207 (+3)</td>
<td>1.3168 (+1)</td>
</tr>
</tbody>
</table>
**TABLE III**

Measured viscosities of methyl alcohol-dioxane mixtures at various temperatures and compositions: measured viscosities of the pure substances at various temperatures.*Calculated

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>10.04°</th>
<th>20.00°</th>
<th>30.00°</th>
<th>40.00°</th>
<th>50.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.015941*(0)</td>
<td>0.013133 (0)</td>
<td>0.011040 (0)</td>
<td>0.009421 (0)</td>
<td>0.008190 (0)</td>
</tr>
<tr>
<td>9.392</td>
<td>0.011809 (-253)</td>
<td>0.009992 (-140)</td>
<td>0.008759 (-116)</td>
<td>0.007572 (-84)</td>
<td>0.006508 (-80)</td>
</tr>
<tr>
<td>10.855</td>
<td>0.010169 (-125)</td>
<td>0.008686 (-49)</td>
<td>0.007425 (-24)</td>
<td>0.006436 (-43)</td>
<td>0.005742 (-56)</td>
</tr>
<tr>
<td>19.231</td>
<td>0.008882 (-6)</td>
<td>0.007639 (+36)</td>
<td>0.006573 (-8)</td>
<td>0.005763 (-4)</td>
<td>0.005093 (-28)</td>
</tr>
<tr>
<td>20.010</td>
<td>0.008111 (+46)</td>
<td>0.006972 (+47)</td>
<td>0.006056 (+26)</td>
<td>0.005294 (+14)</td>
<td>0.004701 (+3)</td>
</tr>
<tr>
<td>30.410</td>
<td>0.007612 (+42)</td>
<td>0.006579 (+53)</td>
<td>0.005694 (+33)</td>
<td>0.004990 (+26)</td>
<td>0.004449 (+10)</td>
</tr>
<tr>
<td>30.586</td>
<td>0.007242 (+47)</td>
<td>0.006268 (+53)</td>
<td>0.005455 (+48)</td>
<td>0.004782 (+32)</td>
<td>0.004249 (+21)</td>
</tr>
<tr>
<td>40.782</td>
<td>0.007005 (+42)</td>
<td>0.006069 (+48)</td>
<td>0.005288 (+46)</td>
<td>0.004627 (+23)</td>
<td>0.004107 (+18)</td>
</tr>
<tr>
<td>40.925</td>
<td>0.006887 (+42)</td>
<td>0.005935 (+35)</td>
<td>0.005172 (+36)</td>
<td>0.004520 (+25)</td>
<td>0.004003 (+15)</td>
</tr>
<tr>
<td>49.975</td>
<td>0.006787 (+21)</td>
<td>0.005837 (+29)</td>
<td>0.005105 (+21)</td>
<td>0.004460 (+13)</td>
<td>0.003949 (+15)</td>
</tr>
<tr>
<td>50.695</td>
<td>0.006783 (0)</td>
<td>0.005838 (0)</td>
<td>0.005080 (0)</td>
<td>0.004438 (0)</td>
<td>0.003913 (0)</td>
</tr>
</tbody>
</table>
TABLE IV

Constants for equations derived by the method of least squares for the composition coefficients of the densities of methyl alcohol-dioxane mixtures. The mean percentage deviation of calculated densities made by these equations.

\[ d_4^t = a + bm + cm^2 + dm^3 + em^4 \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( b \times 10^3 )</th>
<th>( c \times 10^6 )</th>
<th>( d \times 10^9 )</th>
<th>( e \times 10^{12} )</th>
<th>Mean percentage deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.04</td>
<td>+1.04451</td>
<td>-2.9460</td>
<td>+5.814</td>
<td>-7.07</td>
<td>-4.6</td>
</tr>
<tr>
<td>20.00</td>
<td>+1.03362</td>
<td>-2.9524</td>
<td>+7.122</td>
<td>-28.48</td>
<td>+102.1</td>
</tr>
<tr>
<td>30.00</td>
<td>+1.02227</td>
<td>-2.9262</td>
<td>+6.629</td>
<td>-18.52</td>
<td>+44.4</td>
</tr>
<tr>
<td>40.00</td>
<td>+1.01071</td>
<td>-2.9147</td>
<td>+7.631</td>
<td>-39.84</td>
<td>+166.7</td>
</tr>
<tr>
<td>50.00</td>
<td>+0.99349</td>
<td>-2.9016</td>
<td>+7.645</td>
<td>-37.45</td>
<td>+144.2</td>
</tr>
</tbody>
</table>
TABLE V

Constants for the equations derived by the method of least squares for the composition coefficients of the refractive indexes of methyl alcohol-dioxane mixtures. The mean percentage deviation of the calculated refractive indexes made by these equations.

\[ n_D^t = a + bm + cm^2 + dm^3 + em^4 \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>a</th>
<th>b $\times 10^3$</th>
<th>c $\times 10^6$</th>
<th>d $\times 10^9$</th>
<th>e $\times 10^{11}$</th>
<th>Mean percentage deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.00</td>
<td>+1.4223</td>
<td>-1.128</td>
<td>+4.40</td>
<td>-34.1</td>
<td>+15.5</td>
<td>+.004</td>
</tr>
<tr>
<td>30.00</td>
<td>+1.4176</td>
<td>-1.129</td>
<td>+2.75</td>
<td>-13.3</td>
<td>+5.8</td>
<td>+.009</td>
</tr>
<tr>
<td>40.00</td>
<td>+1.4134</td>
<td>-1.167</td>
<td>+3.63</td>
<td>-19.7</td>
<td>+6.6</td>
<td>+.012</td>
</tr>
<tr>
<td>50.00</td>
<td>+1.4083</td>
<td>-1.140</td>
<td>+2.17</td>
<td>+8.3</td>
<td>-8.1</td>
<td>+.011</td>
</tr>
</tbody>
</table>
TABLE VI

Constants for the equations for the composition coefficients of the viscosities of methyl alcohol-dioxane mixtures. The mean percentage deviation of calculated viscosities made by these equations.

\[
\frac{1}{\eta} = \frac{v_{1\%}}{\eta_1} + \frac{v_{2\%}}{\eta_2} + K(v_{1\%} - v_{1\%})
\]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>10.04(^\circ)</th>
<th>20.00(^\circ)</th>
<th>30.00(^\circ)</th>
<th>40.00(^\circ)</th>
<th>50.00(^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>327.1</td>
<td>354.8</td>
<td>377.5</td>
<td>403.9</td>
<td>409.3</td>
</tr>
<tr>
<td>Mean percentage deviation</td>
<td>±0.60</td>
<td>±0.60</td>
<td>±0.55</td>
<td>±0.48</td>
<td>±0.43</td>
</tr>
</tbody>
</table>
**TABLE VII**

Densities of methyl alcohol, dioxane and their mixtures calculated by the temperature coefficient equations and their deviation graphs to even percentage composition at various temperatures.

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>10.04°</th>
<th>20.00°</th>
<th>30.00°</th>
<th>40.00°</th>
<th>50.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.04451 (0)</td>
<td>1.03362 (-3)</td>
<td>1.02227 (+3)</td>
<td>1.01071 (-2)</td>
<td>0.99949 (+1)</td>
</tr>
<tr>
<td>10.000</td>
<td>1.01560 (+2)</td>
<td>1.00472 (-4)</td>
<td>0.99362 (+7)</td>
<td>0.98223 (-3)</td>
<td>0.97116 (+3)</td>
</tr>
<tr>
<td>20.000</td>
<td>0.98788 (0)</td>
<td>0.97727 (+2)</td>
<td>0.96624 (-4)</td>
<td>0.95525 (+2)</td>
<td>0.94427 (-1)</td>
</tr>
<tr>
<td>30.000</td>
<td>0.96119 (-2)</td>
<td>0.95083 (+2)</td>
<td>0.93999 (-5)</td>
<td>0.92922 (+3)</td>
<td>0.91849 (-1)</td>
</tr>
<tr>
<td>40.000</td>
<td>0.93541 (0)</td>
<td>0.92533 (+2)</td>
<td>0.91477 (-1)</td>
<td>0.90417 (+2)</td>
<td>0.89369 (+1)</td>
</tr>
<tr>
<td>50.000</td>
<td>0.91085 (0)</td>
<td>0.90083 (-1)</td>
<td>0.89053 (-2)</td>
<td>0.88015 (+3)</td>
<td>0.86964 (-1)</td>
</tr>
<tr>
<td>60.000</td>
<td>0.88712 (0)</td>
<td>0.87724 (-3)</td>
<td>0.86711 (+3)</td>
<td>0.85675 (-3)</td>
<td>0.84660 (0)</td>
</tr>
<tr>
<td>70.000</td>
<td>0.86427 (+3)</td>
<td>0.85451 (-6)</td>
<td>0.84463 (+9)</td>
<td>0.83435 (-7)</td>
<td>0.82445 (+2)</td>
</tr>
<tr>
<td>80.000</td>
<td>0.84220 (+1)</td>
<td>0.83265 (-4)</td>
<td>0.82290 (+5)</td>
<td>0.81287 (-4)</td>
<td>0.80306 (+1)</td>
</tr>
<tr>
<td>90.000</td>
<td>0.82096 (0)</td>
<td>0.81157 (-4)</td>
<td>0.80198 (+5)</td>
<td>0.79213 (-4)</td>
<td>0.78246 (+2)</td>
</tr>
<tr>
<td>100.000</td>
<td>0.79052 (+1)</td>
<td>0.79127 (+1)</td>
<td>0.79127 (+2)</td>
<td>0.77233 (0)</td>
<td>0.76269 (0)</td>
</tr>
</tbody>
</table>
TABLE VIII

Refractive indexes of methyl alcohol, dioxane and their mixtures calculated by the composition coefficient equations for even percentage composition at various temperatures.

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>20.00°</th>
<th>30.00°</th>
<th>40.00°</th>
<th>50.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.4223 (0)</td>
<td>1.4178 (0)</td>
<td>1.4133 (0)</td>
<td>1.4088 (0)</td>
</tr>
<tr>
<td>10.000</td>
<td>1.4107 (-1)</td>
<td>1.4067 (+2)</td>
<td>1.4019 (-3)</td>
<td>1.3977 (0)</td>
</tr>
<tr>
<td>20.000</td>
<td>1.3999 (0)</td>
<td>1.3962 (0)</td>
<td>1.3917 (-1)</td>
<td>1.3868 (0)</td>
</tr>
<tr>
<td>30.000</td>
<td>1.3899 (0)</td>
<td>1.3854 (-2)</td>
<td>1.3812 (0)</td>
<td>1.3768 (+2)</td>
</tr>
<tr>
<td>40.000</td>
<td>1.3800 (-1)</td>
<td>1.3760 (+1)</td>
<td>1.3715 (-1)</td>
<td>1.3672 (+1)</td>
</tr>
<tr>
<td>50.000</td>
<td>1.3705 (0)</td>
<td>1.3666 (0)</td>
<td>1.3623 (0)</td>
<td>1.3575 (-1)</td>
</tr>
<tr>
<td>60.000</td>
<td>1.3614 (0)</td>
<td>1.3580 (+3)</td>
<td>1.3534 (-1)</td>
<td>1.3491 (+3)</td>
</tr>
<tr>
<td>70.000</td>
<td>1.3526 (-1)</td>
<td>1.3489 (+1)</td>
<td>1.3446 (-1)</td>
<td>1.3404 (0)</td>
</tr>
<tr>
<td>80.000</td>
<td>1.3443 (-1)</td>
<td>1.3406 (+1)</td>
<td>1.3364 (-1)</td>
<td>1.3323 (0)</td>
</tr>
<tr>
<td>90.000</td>
<td>1.3364 (0)</td>
<td>1.3324 (0)</td>
<td>1.3284 (0)</td>
<td>1.3244 (0)</td>
</tr>
<tr>
<td>100.000</td>
<td>1.3288 (0)</td>
<td>1.3249 (+1)</td>
<td>1.3207 (-1)</td>
<td>1.3168 (0)</td>
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</tbody>
</table>
TABLE IX

Viscosities of methyl alcohol, dioxane and their mixtures calculated by the temperature coefficient equations and their deviation graphs to even percentage composition at various temperatures.

<table>
<thead>
<tr>
<th>Per cent by wt. of MeOH</th>
<th>10.00°</th>
<th>20.00°</th>
<th>30.00°</th>
<th>40.00°</th>
<th>50.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.015941 (0)</td>
<td>0.013134 (-1)</td>
<td>0.011040 (+18)</td>
<td>0.009422 (-7)</td>
<td>0.008190 (+4)</td>
</tr>
<tr>
<td>10.000</td>
<td>0.011903 (-16)</td>
<td>0.010101 (+24)</td>
<td>0.008642 (+2)</td>
<td>0.007485 (-12)</td>
<td>0.006579 (+7)</td>
</tr>
<tr>
<td>20.000</td>
<td>0.010017 (-12)</td>
<td>0.008587 (+11)</td>
<td>0.007421 (+12)</td>
<td>0.006437 (-23)</td>
<td>0.005686 (+6)</td>
</tr>
<tr>
<td>30.000</td>
<td>0.008898 (-15)</td>
<td>0.007670 (+28)</td>
<td>0.006612 (-9)</td>
<td>0.005785 (-7)</td>
<td>0.005113 (+4)</td>
</tr>
<tr>
<td>40.000</td>
<td>0.008147 (-12)</td>
<td>0.007021 (+11)</td>
<td>0.006092 (+7)</td>
<td>0.005324 (-16)</td>
<td>0.004732 (+5)</td>
</tr>
<tr>
<td>50.000</td>
<td>0.007600 (-10)</td>
<td>0.006577 (+14)</td>
<td>0.005717 (+3)</td>
<td>0.005009 (-10)</td>
<td>0.004448 (+4)</td>
</tr>
<tr>
<td>60.000</td>
<td>0.007240 (-8)</td>
<td>0.006272 (+8)</td>
<td>0.005469 (+8)</td>
<td>0.004786 (-13)</td>
<td>0.004253 (+4)</td>
</tr>
<tr>
<td>70.000</td>
<td>0.006998 (-7)</td>
<td>0.006067 (+7)</td>
<td>0.005292 (+9)</td>
<td>0.004626 (-13)</td>
<td>0.004106 (+4)</td>
</tr>
<tr>
<td>80.000</td>
<td>0.006849 (-7)</td>
<td>0.005941 (+9)</td>
<td>0.005173 (-5)</td>
<td>0.004525 (-9)</td>
<td>0.004008 (+4)</td>
</tr>
<tr>
<td>90.000</td>
<td>0.006736 (-11)</td>
<td>0.005878 (+13)</td>
<td>0.005107 (-1)</td>
<td>0.004451 (-14)</td>
<td>0.003951 (+5)</td>
</tr>
<tr>
<td>100.000</td>
<td>0.006783 (-4)</td>
<td>0.005858 (+7)</td>
<td>0.005031 (+2)</td>
<td>0.004433 (-4)</td>
<td>0.003913 (+2)</td>
</tr>
</tbody>
</table>
#TABLE X

Constants for the equations derived by the method of least squares for the temperature coefficients of the densities of methyl alcohol-dioxane mixtures and for the pure substances: mean percentage deviation of the calculated densities made by these equations.

\[ d_4 = a + bt + ct^2 + dt^3 \]

<table>
<thead>
<tr>
<th>Per cent</th>
<th>(a \times 10^4)</th>
<th>(b \times 10^4)</th>
<th>(c \times 10^6)</th>
<th>(d \times 10^8)</th>
<th>Mean percentage deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>+1.05459</td>
<td>-9.477</td>
<td>-6.244</td>
<td>+6.314</td>
<td>†.0020</td>
</tr>
<tr>
<td>10.000</td>
<td>+1.02592</td>
<td>-9.917</td>
<td>-4.148</td>
<td>+4.144</td>
<td>†.0038</td>
</tr>
<tr>
<td>20.000</td>
<td>+0.99815</td>
<td>-9.906</td>
<td>-3.349</td>
<td>+3.232</td>
<td>†.0018</td>
</tr>
<tr>
<td>30.000</td>
<td>+0.97111</td>
<td>-9.515</td>
<td>-4.012</td>
<td>+3.991</td>
<td>†.0028</td>
</tr>
<tr>
<td>40.000</td>
<td>+0.94491</td>
<td>-9.040</td>
<td>-4.746</td>
<td>+4.670</td>
<td>†.0013</td>
</tr>
<tr>
<td>50.000</td>
<td>+0.92054</td>
<td>-9.445</td>
<td>-2.422</td>
<td>+1.917</td>
<td>†.0016</td>
</tr>
<tr>
<td>60.000</td>
<td>+0.89649</td>
<td>-9.004</td>
<td>-3.746</td>
<td>+3.597</td>
<td>†.0021</td>
</tr>
<tr>
<td>70.000</td>
<td>+0.87346</td>
<td>-8.819</td>
<td>-3.900</td>
<td>+3.854</td>
<td>†.0060</td>
</tr>
<tr>
<td>80.000</td>
<td>+0.85127</td>
<td>-8.723</td>
<td>-3.512</td>
<td>+3.358</td>
<td>†.0036</td>
</tr>
<tr>
<td>90.000</td>
<td>+0.82993</td>
<td>-3.656</td>
<td>-3.109</td>
<td>+2.861</td>
<td>†.0037</td>
</tr>
<tr>
<td>100.000</td>
<td>+0.30974</td>
<td>-9.130</td>
<td>-5.586</td>
<td>---</td>
<td>†.0013</td>
</tr>
</tbody>
</table>
TABLE XI

Constants for the equations derived by the method of least squares for the temperature coefficients of the refractive indexes of methyl alcohol-dioxane mixtures and for the pure substances: mean percentage deviation of the calculated refractive indexes made by these equations.

\[ n_D = a + bt + ct^2 \]

<table>
<thead>
<tr>
<th>Per cent</th>
<th>( a )</th>
<th>( b \times 10^4 )</th>
<th>( c \times 10^7 )</th>
<th>Mean percentage deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>+1.4313</td>
<td>-4.50</td>
<td>-</td>
<td>+.0028</td>
</tr>
<tr>
<td>10.000</td>
<td>+1.4190</td>
<td>-4.03</td>
<td>-5.0</td>
<td>+.0086</td>
</tr>
<tr>
<td>20.000</td>
<td>+1.4057</td>
<td>-2.28</td>
<td>-30.0</td>
<td>+.0015</td>
</tr>
<tr>
<td>30.000</td>
<td>+1.3980</td>
<td>-3.86</td>
<td>-7.5</td>
<td>+.0072</td>
</tr>
<tr>
<td>40.000</td>
<td>+1.3879</td>
<td>-3.77</td>
<td>-7.5</td>
<td>+.0014</td>
</tr>
<tr>
<td>50.000</td>
<td>+1.3769</td>
<td>-2.76</td>
<td>-22.5</td>
<td>+.0014</td>
</tr>
<tr>
<td>60.000</td>
<td>+1.3675</td>
<td>-2.58</td>
<td>-23.0</td>
<td>+.0013</td>
</tr>
<tr>
<td>70.000</td>
<td>+1.3596</td>
<td>-3.22</td>
<td>-12.5</td>
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</tr>
<tr>
<td>80.000</td>
<td>+1.3514</td>
<td>-3.32</td>
<td>-10.0</td>
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<tr>
<td>90.000</td>
<td>+1.3444</td>
<td>-4.00</td>
<td>-</td>
<td>+.0000</td>
</tr>
<tr>
<td>100.000</td>
<td>+1.3368</td>
<td>-4.00</td>
<td>-</td>
<td>+.0038</td>
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</tbody>
</table>
TABLE XII

Constants for the equations derived by the method of least squares for the temperature coefficients of the viscosities of methyl alcohol-dioxane mixtures and for the pure substances: mean percentage deviation of the calculated viscosities made by these equations.

\[ \eta = a + bt + ct^2 \]

<table>
<thead>
<tr>
<th>Per cent</th>
<th>a</th>
<th>b</th>
<th>s</th>
<th>Mean percentage deviation</th>
</tr>
</thead>
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<td>0.003727</td>
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<td>10.000</td>
<td>69.59</td>
<td>1.3686</td>
<td>0.005643</td>
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<td>1.4794</td>
<td>0.007192</td>
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<tr>
<td>30.000</td>
<td>94.88</td>
<td>1.6582</td>
<td>0.007202</td>
<td>+.16</td>
</tr>
<tr>
<td>40.000</td>
<td>103.58</td>
<td>1.8232</td>
<td>0.006729</td>
<td>+.16</td>
</tr>
<tr>
<td>50.000</td>
<td>111.86</td>
<td>1.8671</td>
<td>0.007918</td>
<td>+.14</td>
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<tr>
<td>60.000</td>
<td>117.38</td>
<td>1.9134</td>
<td>0.008722</td>
<td>+.15</td>
</tr>
<tr>
<td>70.000</td>
<td>122.31</td>
<td>1.9378</td>
<td>0.009841</td>
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<tr>
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<td>125.11</td>
<td>1.9596</td>
<td>0.010646</td>
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</tr>
<tr>
<td>90.000</td>
<td>125.68</td>
<td>2.0318</td>
<td>0.010448</td>
<td>+.17</td>
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<tr>
<td>100.000</td>
<td>125.88</td>
<td>2.0232</td>
<td>0.011457</td>
<td>+.06</td>
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</table>
TABLE XIII

Comparison of the values obtained in this investigation with those found in the literature for the densities of methyl alcohol and dioxane.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Density of MeOH</th>
<th>Density of Dioxane</th>
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<tr>
<td>This paper</td>
<td>0.80052</td>
<td>1.03361 ± 1.10 x 10⁻⁵</td>
</tr>
<tr>
<td>Intern. Crit. Tab. III: p. 27</td>
<td>0.80066</td>
<td>1.03375 ± 1.10 x 10⁻⁵</td>
</tr>
<tr>
<td>McKelvy and Simpson</td>
<td>0.78658</td>
<td>1.0336</td>
</tr>
<tr>
<td>Ewart and Raikes</td>
<td></td>
<td>1.0330</td>
</tr>
<tr>
<td>Lund and Bjerrum</td>
<td></td>
<td>1.0335</td>
</tr>
<tr>
<td>Butler, Thompson and Maclennan</td>
<td></td>
<td>1.0332</td>
</tr>
<tr>
<td>Cornish, Archibald, Murphy and Evans</td>
<td></td>
<td>1.03326 ± 4 x 10⁻⁵</td>
</tr>
<tr>
<td>Jones and Fornwalt</td>
<td></td>
<td>1.03318</td>
</tr>
<tr>
<td>Golse</td>
<td>0.7912</td>
<td>1.02761</td>
</tr>
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</table>
Comparison of the values obtained in this investigation with those found in the literature of the refractive indexes of methyl alcohol and dioxane. Values calculated by equation.

<table>
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<tr>
<th>Reference</th>
<th>14.5°</th>
<th>15°</th>
<th>17.5°</th>
<th>20°</th>
<th>20.5°</th>
<th>25°</th>
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</thead>
<tbody>
<tr>
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<td>1.3310</td>
<td>1.3308</td>
<td>1.3298</td>
<td>1.3289</td>
<td>1.3286</td>
<td>1.3283</td>
</tr>
<tr>
<td>(38) Intra. Crit. Tab. VII: p. 79</td>
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<td></td>
<td>1.3289</td>
<td></td>
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<tr>
<td>(38) Intra. Crit. Tab. VII: p. 79</td>
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<td></td>
<td>1.32663</td>
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<tr>
<td>(19) Doroszewskii</td>
<td></td>
<td>1.33057</td>
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</tr>
<tr>
<td>(38) Intra. Crit. Tab. VII: p. 79</td>
<td></td>
<td></td>
<td>1.32979</td>
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<td></td>
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</tr>
<tr>
<td>(26) Getman and Gibbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.32875</td>
<td></td>
</tr>
<tr>
<td>(28) Golse</td>
<td></td>
<td></td>
<td></td>
<td>1.3290</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10) Bruhl and Schroder</td>
<td>1.33118</td>
<td></td>
<td></td>
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<tr>
<td>(43) Landolt and Jahn</td>
<td></td>
<td>1.3290</td>
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</tbody>
</table>

Refractive Index of Dioxane

<table>
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<th>Reference</th>
<th>1.4223</th>
<th>1.4202</th>
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<tr>
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<td></td>
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<tr>
<td>(36) Hopkins, Yerger and Lynch</td>
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<tr>
<td>(35) Hess and Frahm</td>
<td>1.42225</td>
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<tr>
<td>(37) Hovorka, Schaefer and Dreisbach</td>
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</tbody>
</table>
TABLE XV

Comparison of the values obtained in this investigation with those found in the literature of the viscosities of methyl alcohol and dioxane.

Viscosity of MeOH

<table>
<thead>
<tr>
<th>Reference</th>
<th>10°</th>
<th>20°</th>
<th>25°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
</tr>
</thead>
<tbody>
<tr>
<td>This paper</td>
<td>0.006783</td>
<td>0.005858</td>
<td>0.005445</td>
<td>0.005080</td>
<td>0.004438</td>
<td>0.003919</td>
</tr>
<tr>
<td>(39) Jones and Fornwalt</td>
<td>0.005445</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(21) Ewart and Raikes</td>
<td>0.00545</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(27) Goldschmidt and Aarflot</td>
<td>0.00544</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18) Dunstan, Thole and Benson</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.00546</td>
</tr>
<tr>
<td>(62) Thorpe and Rodger</td>
<td>0.00690</td>
<td>0.00593</td>
<td>0.00553</td>
<td>0.00515</td>
<td>0.00449</td>
<td>0.00395</td>
</tr>
<tr>
<td>(15) Conrad and Hall</td>
<td>0.00552</td>
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<tr>
<td>(9) Bingham, White</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Thomas and Caldwell</td>
<td>0.007037</td>
<td>0.006382</td>
<td>0.005482</td>
<td>0.005720</td>
<td>0.005013</td>
<td>0.004296</td>
</tr>
<tr>
<td></td>
<td>0.006540</td>
<td>0.006353</td>
<td>0.005411</td>
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<td>0.004060</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.007158</td>
<td>0.006072</td>
<td>0.005385</td>
<td>0.004843</td>
<td>0.004063</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.006859</td>
<td>0.006135</td>
<td>0.005149</td>
<td>0.004509</td>
<td>0.003959</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.005903</td>
<td>0.005316</td>
<td>0.004598</td>
<td>0.004111</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.006203</td>
<td>0.005126</td>
<td>0.004470</td>
<td>0.003942</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.005865</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Viscosity of Dioxane

<table>
<thead>
<tr>
<th>Reference</th>
<th>10°</th>
<th>20°</th>
<th>25°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
</tr>
</thead>
<tbody>
<tr>
<td>This paper</td>
<td>0.013133</td>
<td>0.011996</td>
<td>0.011039</td>
<td>0.009421</td>
<td>0.008190</td>
<td></td>
</tr>
<tr>
<td>(36) Hopkins, Yerger and Lynch</td>
<td>0.011840</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(33) Herz and Lorentz</td>
<td>0.01255</td>
<td>0.01063</td>
<td>0.00917</td>
<td>0.00778</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25) Geddes</td>
<td>0.013075</td>
<td>0.011969</td>
<td>0.010998</td>
<td>0.009415</td>
<td>0.008158</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1.- Deviation curves of composition coefficient equations
The densities, refractive indexes and viscosities of mixtures of methyl alcohol and dioxane were measured over a complete range of composition and at several temperatures. The densities, refractive indexes and viscosities of the pure substances were measured at several temperatures.

The composition coefficient equations for the densities, refractive indexes, and viscosities are given and the constants of these equations tabulated along with the numbers for plotting deviation graphs so that computed values agreeing with observed values may be obtained.

Temperature coefficient equations for densities, refractive indexes, and viscosities of the pure substances and their mixtures are derived and the constants of these equations are given, together with the numbers for plotting the deviation curves of calculated from observed values.

Comparison of our experimentally observed values of densities, refractive indexes and viscosities of pure methyl alcohol and pure dioxane is made with the values of these properties of the pure substances recorded in the literature.
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VITA

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EXAMINATION AND THESIS REPORT

Candidate: Frank Lykins Padgitt

Major Field: Physical Chemistry

Title of Thesis: The Temperature and Composition Coefficients of the Density, Refractive Index, and Viscosity of Methyl Alcohol-Dioxane Mixtures. The Temperature Coefficients of the Density, Refractive Index, and Viscosity of the Pure Solvents.

Approved:

Edward L. \\
Major Professor and Chairman

Charles W. Pipkin \\
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