Viscosity of Potassium Nitrate

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The viscosity of KNO_3 in the temperature range 340° to 500° C. has been determined using a capillary viscometer calibrated with 0.5M aqueous KCl solution at room temperature. The temperature dependence of the viscosity was found to be slightly lower than the commonly accepted value. The new value is in agreement with earlier determinations with capillary viscometers, but significantly different from the reported results obtained with oscillating sphere viscometers.

POTASSIUM nitrate is often used as a standard for the calibration of viscometers for use at high temperature (*1, 3*) since it is a stable material and Dantuma (*2*) determined the viscosity very carefully by an absolute method (oscillating sphere). The viscosity of KNO_3 had been investigated earlier by several groups including Goodwin and Mailey (*6*) (capillary), Lorenz and Kalmus (*8*) (capillary), and Fawsitt (*5*) (oscillating disk). None of the earlier sets of data agreed exactly with Dantuma's or with each other, but the differences were not large and the viscosity of KNO_3 has been generally accepted as well established, with Dantuma's values being the most reliable.

In the course of an investigation of capillary viscometers and the corrections to be applied in calculating the data (*4*), the temperature dependence of the viscosity of KNO_3 was determined many times in the temperature range from 340° to about 500° C. Initially it was presumed that Dantuma's data were exact and any deviations from his values were due to errors in the techniques or calculations used. However, as the precision of our determinations improved, it became obvious that there was a small, but nearly constant, difference between the temperature dependence as measured in our apparatus and that found by Dantuma. Therefore, the viscosity of KNO_3 was redetermined by calibration of the viscometers, with 0.5*M* aqueous KCl solution as the calibration liquid. In the calculation of the data, the authors' applied the results of an investigation into the correct calculation of data from capillary viscometers (*4*).

EXPERIMENTAL

Materials. Reagent grade KNO_3 was purified by drying under vacuum at 100° C. for at least two hours, followed by heating slowly until molten while still under vacuum. The molten salt was filtered through a fritted glass filter of medium porosity. At the start and conclusion of a viscosity measurement experiment, a sample of the salt was removed and analyzed. Emission spectroscopy was used to analyze the material for possible contamination. The samples were also checked for alkalinity, which would indicate loss of nitrate ion, by hydrolysis and subsequent evaporation of the HNO_3, but they were consistently neutral. Reagent grade KCl was used to make up the 0.5*M* aqueous solution. These solutions were analyzed for chloride ion at the end of each viscosity determination.

Apparatus and Procedure. Two different capillary viscometers were used in this work. The viscometers, auxiliary equipment, and possible errors, both random and systematic, are discussed in detail in another paper (*4*).

Viscometer I had concentric reservoirs and a vertical capillary; it was constructed entirely of platinum except for the outer reservoir which was nickel with a Vycor glass liner. A resistance furnace—with noninductive, spiral windings—was used as the heat source with this viscometer.

Viscometer II had identical borosilicate glass reservoirs connected by a horizontal borosilicate glass capillary. It was maintained at constant temperature by a thermostatically controlled bath. A bath of molten alkali nitrates was used in the range from 340° to 500° C.; a water bath was used for the room temperature work.

Both viscometers used electrical probes (platinum) with a relay system and an electric clock to measure the time required to transfer a fixed volume of liquid under a known pressure. The constant pressure used to drive the liquid through the capillary was provided by a large reservoir pressured with high purity helium which had been dried by passing it through a column of molecular sieves. The pressure was measured with a mercury manometer.

Method of Calculation. The viscosities were calculated by fitting the data from 15 to 20 pressure-time points to the relation

$$P' = \frac{A\eta}{t} \qquad (1)$$

where A is a constant, η is the viscosity, t is the time, and P' is corrected pressure as discussed below. The constant, A, is a function of the viscometer dimensions (equal to $8LV/\pi R^4$, where V is the volume of liquid transferred, and L and R are the length and radius of the capillary). However, A is not temperature dependent in viscometers, such as the authors', where the applicable dimensions involve the same material since the ratio, LV/R^4, is not changed by a linear expansion.

P' is the pressure after correction for the effect of the changing hydrostatic head and for the pressure lost as kinetic energy of the effluent liquid. As has been shown previously (*4*), with changing kinematic viscosities, it is necessary to use a calculation that includes the interaction between the hydrostatic head and kinetic energy effects. This type of correction is obtained by defining P' as follows:

$$P' = \frac{C}{Z_0 - Z + \ln \dfrac{Z_0 - 1}{Z - 1}} \qquad (2)$$

where

$$Z = \left[1 + m\rho\left(\frac{R^2}{4L\eta}\right)^2 (P_0 - C)\right]^{1/2} \qquad (3)$$

and

$$Z_0 = \left[1 + m\rho\left(\frac{R^2}{4L\eta}\right)^2 (P_0)\right]^{1/2} \qquad (4)$$

In the above equations, C is the total change in hydrostatic pressure, ln is the natural logarithm, ρ is the density, and

R and L are the radius and length of the capillary. P_0 is the algebraic sum of the applied pressure and the initial hydrostatic pressure. m is a factor which adjusts the kinetic energy correction for such factors as the loss of energy at the capillary entrance; it has been shown to be constant within experimental error over a wide range of flow rates (*4*).

The viscosity must be known to calculate P', and therefore Equations 1 and 2 must be solved by a series of approximations. This was done using an electronic computer. The constants were determined by fitting the data from the calibration runs to Equations 1 and 2 rather than by direct measurement of R and L.

Since the viscometers had electric probes, the calibration fluid had to be conductive and we used 0.5M aqueous KCl at room temperature. Kaminsky's data (*7*) for 0.5M aqueous KCl was represented by the equation, with η in centipoises and T in degrees K,

$$\log \eta_{\text{KCl}} = -2.7584 + \frac{807.3}{T} \qquad (5)$$

for convenience in our calculations.

RESULTS AND DISCUSSION

Two determinations of the absolute viscosity of KNO_3 and its temperature dependence were made with viscometer I and one with viscometer II. These results are given in Table I and are shown graphically as a plot of log viscosity *vs.* the reciprocal of the absolute temperature in Figure 1. The results confirmed our earlier findings that the temperature dependence is slightly less than that found by Dantuma.

In the authors' experiments, the temperature dependence is determined more accurately than the absolute viscosity since an error in the value of the calibration constant—A in Equation 1—will give a correct temperature dependence but a percentage-wise constant error in the absolute viscosity. Also, our greatest possibility for error was probably in the temperature measurement for the aqueous KCl calibration experiments. With the Pt viscometer, which was designed specifically for high temperature studies, it was difficult to ascertain the temperature of the aqueous KCl, at the capillary, closer than ±1° C. In these experiments, an error of 1° C. in the temperature of the aqueous KCl would result in an error of about 2% in the calibration constant, and therefore in the absolute viscosity measurement. This effect may explain the small amount of scatter observable in Figure 1.

To compare present results with those of previous investigators, the following equation was used

$$\log \eta = a + \frac{b}{T} \qquad (6)$$

Table I. Viscosity of KNO_3

Temp., ° C.	Viscosity, C. P.
Calibration A, Viscometer I	
492.	1.4596
487	1.5031
344	2.8624
343	2.8642
Calibration B, Viscometer II	
473.1	1.5608
439.7	1.7804
407.1	2.0500
368.0	2.4936
Calibration C, Viscometer I	
482	1.4923
462	1.6104
440	1.7305
423	1.8624
404	2.0151
394	2.1263
379	2.2750
359	2.5278
353	2.6192
344	2.7770

Table II. Comparison of Different Results on the Temperature Dependence of KNO_3

(as $\log \eta = a + b/T$)[a]

Data Source	a	b
Lorenz and Kalmus	−0.9838	884.81
Goodwin and Mailey	−1.0056	887.20
This paper	−1.0275	908.32
Murgulescu and Zuca	−1.0856	943.11
Dantuma	−1.1121	963.93

[a] The data from each investigation were fitted to this equation by determining a and b by a least squares technique.

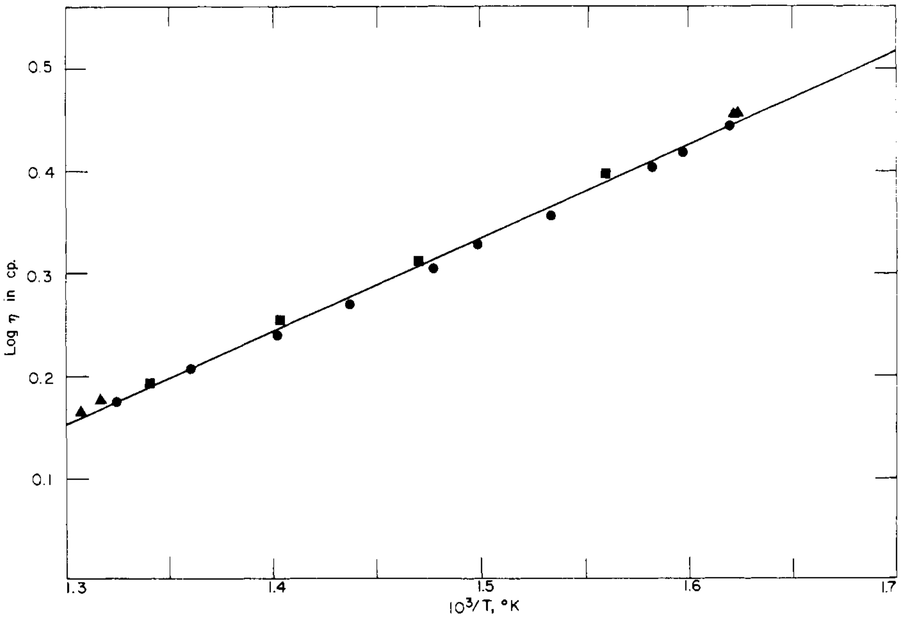

Figure 1. Log η for KNO_3 as a function of the reciprocal of the absolute temperature

Calibration A, Viscometer I. Calibration B, Viscometer II. Calibration C, Viscometer I.

where T is the absolute temperature and a and b are constants. The constants for Equation 6 were determined to fit the authors' data, and those from each of the previous investigations, by a least squares calculation. These results are shown in Table II.

Goodwin and Mailey gave only smoothed data from a linear plot of fluidity as a function of temperature, and Lorenz and Kalmus gave only data from a smoothed curve. To obtain an idea of how well Goodwin and Mailey's smoothed data represented their experimental values, we calculated Dantuma's data and our data for Calibration C (with 10 points well distributed over the temperature range investigated) as

$$1/\eta = a + bT \qquad (7)$$

This relation gave a better fit to the authors' data than did Equation 6. The fit with Dantuma's data was about the same for the two relations. From this, we presume that Goodwin and Mailey's actual data are well represented by the smoothed data they reported.

The methods and calculations used by each group were reviewed in an attempt to determine their probable reliability and to provide a better basis for comparison of the previous results with each other and with ours. Fawsitt used a rather crude oscillating disk viscometer before the theory of this type of apparatus was well understood. His results are probably the least reliable and were omitted from consideration.

Goodwin and Mailey and Lorenz and Kalmus used capillary viscometers and considered most, but not all, of the necessary corrections to the data. For example, the effect of surface tension was ignored in both investigations, and Lorenz and Kalmus used a linear (rather than time) average hydrostatic head correction. Despite these criticisms, the results obtained by these two groups should be reliable within a few per cent.

Dantuma's work has been considered to be as good as any viscosity determination on fused salts. KNO_3 was originally chosen as a calibration material because the authors found no grounds for criticism when they reviewed Dantuma's work, and assumed his values to be exact within 1%. Murgulescu and Zuca (*9*) used essentially a duplicate of Dantuma's apparatus. They determined the viscosity of KNO_3 to check their results against Dantuma's and, therefore, gave viscosity values at only four temperatures (357° to 413° C.).

The five values of the temperature dependence listed in Table II fall into two groups. The three values determined with capillary viscometers agree within experimental error and the values determined with oscillating sphere viscometers also agree with each other, but not with the first group.

The review and analysis of the techniques used by the earlier investigators yielded no explanation for the discrepancy between the results obtained with capillary viscometers and those obtained by Dantuma or Murgulescu and Zuca. The neglect of some small corrections could easily account for the earlier capillary viscometer results giving a slightly lower temperature dependence than we found, but these errors could not account for the temperature dependence being 6 to 7 % too low.

In conclusion, it is not possible to judge which results are more correct since either type of determination could be in error because of some unrecognized effect. However, the authors' results should best represent those to be expected in the calibration of capillary-type instruments.

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Isobaric Ternary Vapor-Liquid Equilibria System

Acetone–Carbon Tetrachloride–Benzene

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PRECISE DETERMINATION of the vapor-liquid equilibrium data is essential if the distillation and the contacting equipment designed using this experimental data are to operate to the predicted specifications. The need for reliable vapor-liquid equilibrium data is further increasing with the development of extractive and azeotropic distillation processes as potential methods of separating close-boiling mixtures. The present investigation on this system was carried out to obtain reliable vapor-liquid equilibrium data, to correlate the data so obtained, to see to what extent the ternary effect is a contributing factor in the evaluation of ternary vapor-liquid equilibria, and to see whether benzene could be used as a third component in the separation of azeotropic mixtures of acetone and carbon tetrachloride.

CHEMICALS USED

Acetone, Baker Analyzed; carbon tetrachloride, British Drug House Ltd, London—0.0015% nonvolatile matter, 0.0025% absorbed oxygen, 0.0005% carbon disulfide, 0.02% water; and benzene, Veb Berline, Germany, were used in the present investigation after further purification. Acetone was treated with fused anhydrous calcium chloride to remove traces of moisture and subjected to fractional distillation in a laboratory glass fractionating column. Product boiling at 56.1° C. at 760 ± 1 mm. of Hg pressure was collected and used. Carbon tetrachloride and benzene were also subjected

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