Viscosity of the Vanadium Pentoxide–Potassium Sulfate Eutectic

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The viscosity of the vanadium pentoxide–potassium sulfate eutectic mixture (37 mole % vanadium pentoxide) was determined using a falling-ball viscometer equipped with field coils at two different levels to determine the rate of fall. The viscosity at 461°, 505°, and 586° C. is 63.5, 41.8, and 18.0 cp., respectively, and has an activation energy of 13 kcal.

THE VISCOSITY of the 37 mole % V_2O_5-63 mole % K_2SO_4 eutectic mixture (*1*) was determined as a function of temperature in the range of 460° to 600° C. In an associated investigation, possible catalytic effects of this melt system for the gas phase partial oxidation of *o*-xylene (*7*) were studied in a bubble reactor. For interpretation of the rsults of that study, it was important to have a knowledge of the viscosity of the melt at various reaction temperatures. The present study was limited in scope, but the results may be of some general interest since little is known about the viscosity characteristics of melts containing a nonionic.

EXPERIMENTAL

The apparatus is shown in Figure 1. A borosilicate glass test tube 45.5 mm. I.D. × 400 mm. long was placed in a well-insulated furnace, in which heat was supplied by two coils of Chromel wire wrapped circumferentially around the spiral serrated Alundum core, with each coil connected to a Variac. Several thermocouples were installed along the outside surface of the tube. Two field coils, 10.22 cm. apart and each with three turns in series, were wrapped around the outside surface of the test tube. A high frequency current (about 60 second^{-1}) was passed through the coils, and the signals were displayed on a Dual Beam 502 Tektronic oscilloscope screen. The normal signal pattern was distorted when a steel ball-bearing fell through the plane of the coils. Time exposure photographs were taken of the signals appearing on the oscilloscope screen, and the distance between successive distortions was measured. Detailed information on the electronic circuitry is reported elsewhere (*2*). A recent paper (*6*), published after the completion of this work, describes a similar type of apparatus including details of design and operation.

Union Carbide Nuclear Co. donated the vanadium pentoxide. The analysis, provided by the supplier, was:
V_2O_5, 99.6%; Fe_2O_3, 0.01%; CaO, nil; MgO, nil; K_2O, 0.13%; Na_2O, 0.03%; SiO_2, 0.05%; Nitrogen, 0.001%.

The potassium sulfate was Baker Company's reagent grade.

ANALYTICAL

The steady-state velocity of a solid sphere falling in an undisturbed, infinite fluid medium at Reynolds number less than about 2 is given by Stokes' law:

$$V = \frac{gD^2(\rho_s - \rho)}{18\mu} \qquad (1)$$

For the instantaneous velocity as a function of the vertical distance traversed by the sphere, Ladenburg (*5*) established the following correction by which the right-hand side of Equation 1 should be divided.

$$f_h = 1 + 3.3\, r/h \qquad \text{for } h \gg r \qquad (2)$$

Hunter (*4*), from experiments with fluids having viscosities of 4 poises (glycerol) and 700 poises (glucose), recommended division by the following for the wall correction:

$$f_w = \left(1 - \frac{r}{R}\right)^{-2.25} \qquad \text{for } \frac{r}{R} < 0.35 \qquad (3)$$

This expression also agrees with that given by Ladenburg for the wall correction for values of $r/R < 0.1$. In this investigation, r/R ranged from 0.07 to 0.105.

When studying the behavior of geometrical shapes in a fluid medium, it is common practice to correlate the drag coefficient —the ratio of the net gravitational force to the inertial force— as a function of the Reynolds number. For spheres, the drag coefficient is given by

$$C^* = \frac{4gD(\rho_s - \rho)}{3\rho V^3} \qquad (4)$$

Relations between the drag coefficient and the Reynolds number have been experimentally established by a variety of other studies (*3*). In the Stokes' law region $C = 24/N_{Re}$. For higher Reynolds numbers, between about 2 and 500, in the so-called intermediate region, the relationship is approximately:

$$C = 18.5/Re^{0.6} \qquad (5)$$

RESULTS

To check the apparatus, 13 runs were made with a lubricating oil (supplied by Texaco, Inc.) which exhibited a large change in viscosity with temperature and whose properties were available from the manufacturer. Steel ball bearings of 1/8, 5/32, and 3/16 inch diameter were dropped, one at a time, into the oil at various constant temperatures from 25° to 112° C. This covered a viscosity range of from 0.2 to 80 poises and Reynolds numbers of about 0.04 to 300. A Reynolds number of 2 corresponded to an oil temperature of about 52° C.; below this temperature, the laminar (Stokes' law) regime was encountered and above it, the intermediate regime.

For each run, the experimental drag coefficient as calculated by Equation 4 was compared with the value predicted by $C = 24/N_{Re}$ or Equation 5 using the known value of the oil viscosity at the run temperature. Nine runs were made in the laminar region, covering Reynolds numbers of 0.04 to 0.3. The height correction factor was calculated to vary in different runs from 1.016 to 1.024 and the wall correction factor from 1.777 to 1.285. Applying these factors, the per cent average deviation between observed and predicted drag coefficients, $[(C^*/f_h \cdot f_w \cdot C) - 1]\,100$, was 0.5%.

Four calibration runs were made in the intermediate regime, covering Reynolds numbers of 31 to 158. The wall correction factor would be expected to be small in this regime. Neglecting height and wall corrections, the average deviation between observed and predicted drag coefficients, $[(C^*/C) - 1]\,100$, was 3%, with no significant trend with Reynolds number.

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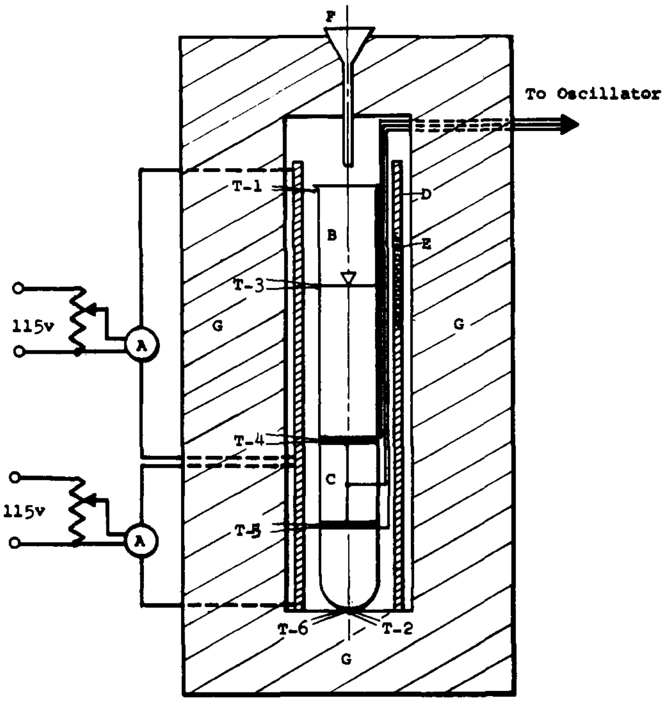

Figure 1. Apparatus (drawing not to scale)
A. Ammeter
B. 45.5 mm.I.D. × 400 mm. borosilicate glass test tube
C. Oscillator coils, 3 turns each
D. Alundum core
E. Chromel A resistor wire
F. Borosilicate glass funnel
G. Insulation

Experimental data with the eutectic melt were all obtained in the intermediate regime. Hence, the viscosities were calculated from Equations 4 and 5 using a proportionality constant in Equation 5 of 19.1 instead of 18.5, based on these calibration runs.

The average density for the V_2O_5–K_2SO_4 eutectic mixture was found to vary less than 2% over the temperature range of 470° to 600° C. so a constant value of 2.25 grams per cc. was used. The density of the spheres was obtained by weighing them carefully on an analytical balance and measuring the diameter with a caliper. Balance readings were accurate to within ± 0.0001 gram and diameter to within ± 0.001 inch. The density of the melt was determined by measuring carefully the volume of a known weight of melt mixture in the test tube.

After falling through the melt, the steel spheres resting on the bottom of the test tube slowly reacted with the melt over a period of many hours, ultimately forming a solidified mass. Reaction during the brief period of fall is presumably insignificant, and the data reported were obtained during the initial period before diffusion of iron compounds upward had an opportunity to alter the viscosity of the melt. Borosilicate glass spheres packed with iron filings were also tried, but their apparent density was too close to that of the melt to yield significant results. A fresh eutectic melt was prepared for each temperature studied.

A total of about 10 runs was made at each of three temperatures, using spheres of three different diameters. If the velocity of fall were too great or mechanical vibration interfered with the signal, it was difficult to read the peaks precisely. For each temperature, the run which gave the most precise measure of the time of fall was chosen to calculate the viscosity at that temperature. Accordingly, the melt viscosity at 461°, 505°, and 586° C. was determined to be 63.5, 41.8, and 18.0 cp., respectively. The experimental results are displayed in Figure 2 and show a linear relationship between viscosity and the reciprocal of the absolute temperature. Published data for pure V_2O_5 (*8*) are also shown. The two straight lines are remarkably parallel. The V_2O_5–K_2O_4 eutectic melt viscosity may be represented by:

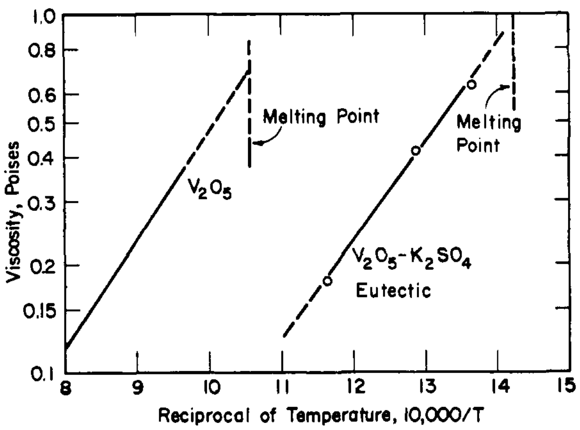

Figure 2. Effect of temperature on viscosity of melts of pure V_2O_5 and V_2O_5–K_2SO_4 eutectic

$$\ln \mu = -9.13 + 6390/T \qquad (6)$$

where μ is in poises. The activation energy for the viscosity of the V_2O_5–K_2SO_4 mixture is 13 kcal., essentially equal to the value of 13.2 kcal. reported for pure V_2O_5 (*8*).

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NOMENCLATURE

C = drag coefficient predicted by previous studies
C^* = drag coefficient as experimentally measured, calculated by Equation 4
D = diameter of sphere, cm.
f_h = velocity correction for height
f_w = velocity correction for wall effect
g = local acceleration of gravity, 981 cm./sec.^{2}
h = vertical distance below top surface of melt, cm.
r = radius of sphere, cm.
R = radius of container, cm.
N_{Re} = Reynolds number
T = temperature, °K.
V = velocity of sphere, cm./sec.
ρ_s = density of melt, gram/cc.
ρ = density of sphere, gram/cc.
μ = viscosity of melt, poises

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