Viscosity of Polar Vapor Mixtures

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THE VISCOSITY of the vapors of many pure organic compounds and simple binary mixtures has been measured and reported in the literature. Among these, there have, however, been few studies to determine the viscosity of binary mixtures of so-called polar molecules.

The experimental values for the viscosity of mixtures of superheated aliphatic alcohol vapors are reported here for several reasons.

Mixtures of alcohol vapors are often encountered in chemical plant operations, and viscosity data are important in determining the mass, momentum, and heat transfer characteristics of such systems.

Relatively little information is available on the transport theory of mixtures of two highly polar vapors.

Correlation methods acceptable for estimating the viscosity of binary nonpolar vapor mixtures have not been adequately tested for polar vapor mixtures.

Viscosities were determined at constant temperature and at pressures near atmospheric by measuring the pressure drop occurring upon flowing the alcohol mixture through a capillary tube. The viscosity, μ, was related to the pressure drop in the capillary tube with a modified version of the Poiseuille equation corrected for gas compressibility and end effects:

$$\mu = \frac{10^6 \pi r^4 M (P_1^2 - P_2^2)}{16\, L\, w\, R\, T\, z} - \frac{mw}{8\pi L} \qquad (1)$$

where

r = integrated fourth-power average radius of the capillary bore
M = molecular weight of the vapor mixture
$(P_1 - P_2)$ = pressure drop in the capillary
L = length of capillary
w = mass flow rate
R = gas constant
T = absolute temperature
z = compressibility factor
m = $\frac{\text{radius of tube}}{\text{radius of vena contracta at the inlet}}$

APPARATUS AND PROCEDURE

The apparatus is shown in Figure 1. The capillary viscometer is a modification of one used for the measurement of the viscosity of water and hydrogen peroxide vapors (3).

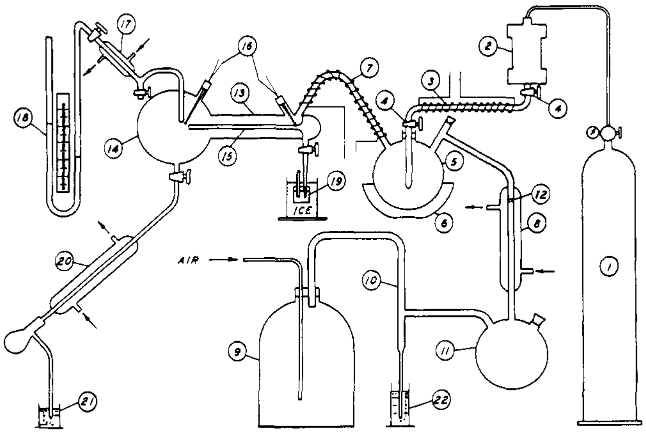

Figure 1. Viscosity Apparatus

The binary liquid mixture was placed in the feed container, 2, which consisted of a 5-inch stainless steel pipe, 5-1/2 inches long, threaded and closed at the ends with two stainless steel caps. A hole in the top was connected to a copper tube leading from a nitrogen-filled cylinder. Nitrogen gas was used to establish a pressure of about 30 p.s.i.g. in the feed container. The bottom of the feed container was connected to the liquid vaporizing tube, 3. This was a 1/4-inch copper tube, 42 inches long, wrapped with Chromel-A heating wire and asbestos tape. Needle valves, 4, were placed at both ends of the liquid vaporizing tube for better control of the flow rate. The downstream end of the liquid vaporizing tube was connected to a flattened copper nozzle. This nozzle extended about 5 inches down into a 2-liter, 3-necked surge chamber, 5, which was heated by an electric heating mantle, 6. The vapor entered the middle neck through the vaporizing tube and flowed out of the second neck to the superheater, 7, and part of the vapor went to the pressure regulating system through the interface condenser, 8. To maintain the pressure difference in the capillary tube, 15, compressed air was used, feeding from a large surge tank, 9, through a borosilicate glass connecting tube, 10. One branch of the connecting tube led into the excess air cylinder containing water, and the other to a 1-liter condensate collector, 11, which in turn was connected to the 2-liter borosilicate glass flask by the interface condenser. The air-vapor interphase, 12, was easily visible, and was kept in the upper quarter of the condensing tube.

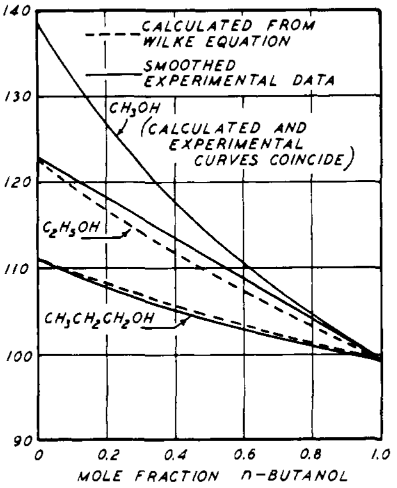

Figure 2. Experimental and calculated viscosities of vapor mixtures with 1-butanol at 150°

The superheater, 7, was simply a borosilicate glass tube wrapped with Chromel heating wire and asbestos insulation. From the superheater, the vapor entered the viscometer, 13, described by Satterfield and others (3). It was a Tru-Bore capillary tube surrounded by an outer tube 4 cm. in diameter, closed on one end by a large sphere, 14, of about 2-liter volume. The length of the capillary, 15, was 28.53 ± 0.04 cm. The temperature of the vapor was measured at the two ends of the capillary tube by Chromel-Alumel thermocouples, 16. The upper part of the sphere was connected to the manometer, 18. Any vapor entering this section was condensed in the manometer knock-back condenser, 17, and taken out through a condenser stopcock. The viscometer was also wrapped with heating wire and asbestos tape to maintain the desired temperature. The sample was collected in a weighing bottle, 19, partially submerged in an ice-water bath. The sample bottle was fitted with a rubber stopper, through which two tubes led from the bottle, one to the end of the capillary, and the other, a 3-inch length of 3 mm.-glass tube, was open to the atmosphere to enable the pressure at the downstream end of the capillary to remain at atmospheric pressure. The bottle of the sphere, 14, was connected to the main product condenser, 20.

Any air leaking through the interphase condenser could be noted by gas flow into the sample bottle. Such gas leakage was evident at times when the equipment was being heated in preparation of a test run, but was never evident after the system was operating in steady state.

EXPERIMENTAL RESULTS

Viscosity measurements were made with different mixture compositions at 150° C. and at atmospheric pressure. Viscosities for the systems of methanol-1-butanol, ethanol-1-butanol, and 1-propanol-1-butanol are plotted on Figure 2 as a function of the mole fraction of 1-butanol. The viscosity of the system ethanol-1-propanol is shown in Figure 3. Viscosities of 1-butanol as a function of temperature had not been previously reported and were measured in this work. The variation in viscosity of 1-butanol with temperature at atmospheric pressure is shown in Figure 4 from 120° to 200° C.

DISCUSSION OF RESULTS

An error analysis indicates that the standard deviation of the calculated viscosity is about 1 centipoise, with most of the error contributed by a random manometer pressure fluctuation. The precision limits at the 95% confidence level is about ±2 centipoises or about ±2% of the measured viscosities. The chemicals used in this investigation were obtained from the Eastman Kodak Co., rated with a purity of A.

Correction Factor. In Equation 1, the correction term for end effects is approximated by the correction term $(mw/8\pi L)$. Defining this term as K, it may be estimated or determined from calibration runs using a vapor whose viscosity is well known. In these experiments, calibration runs were made using water vapor between 170° and 240° C. at atmospheric pressure. The results indicated that the correction factor could well be estimated, assuming that the value of m(radius of tube/radius of vena contracta at the inlet) is inity; and in all cases, with the very small mass flow rates used in this work, the value of K was small compared to the other term in Equation 1. For example, with a value of unity for m, the value of viscosity is reduced between 0.7 to 2% by inclusion of the correction factor. As the uncertainty in m is no greater than 10%, no large error was introduced by assuming m to be unity.

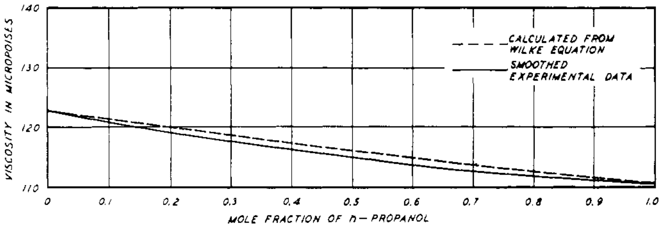

Figure 3. Experimental and calculated viscosities of ethanol-1-propanol vapor mixtures at 150° C. and 1 atm.

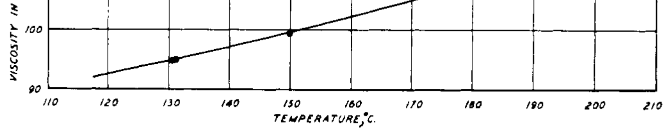

Figure 4. Viscosity of 1-butanol vapor as a function of temperature at 1 atm.

Viscosity of Pure Components. Viscosities of the pure components were measured in this investigation at 150° C. and compared with literature data. For methanol, the experimentally measured viscosity was 138.5 micropoises, which is in good agreement with 140.8 micropoises at 153.9° C. as reported in the literature (*2*). The measured viscosity of ethanol at 150° C. was 122.9 micropoises, compared to the reported 123.2 micropoises (*2*). The viscosity of 1-propanol was measured at 110.7 micropoises, in good agreement with 110.5 micropoises (*1, 2*). The experimental values of the viscosity of pure 1-butanol vapor are shown in Figure 4.

Estimation of the Viscosity of Binary Vapor Mixtures. The viscosity of mixtures of binary vapors may be estimated by a method proposed by Wilke (*4*), whereby

$$\mu_{\text{mixt.}} = \frac{\mu_1}{1 + \left(\frac{y_2}{y_1}\right)\Phi_{12}} + \frac{\mu_2}{1 + \left(\frac{y_1}{y_2}\right)\Phi_{21}} \qquad (2)$$

where

$\mu_{\text{mixt.}}$ = viscosity of mixture at low pressure
μ_1, μ_2 = viscosities of pure components
y_1, y_2 = mole fractions of components

$$\Phi_{12} = \frac{\left[1 + \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{1/4}\right]^2}{2\sqrt{2}\left(1 + \frac{M_1}{M_2}\right)^{1/2}}$$

$$\Phi_{21} = \frac{\left[1 + \left(\frac{\mu_2}{\mu_1}\right)^{1/2}\left(\frac{M_1}{M_2}\right)^{1/4}\right]^2}{2\sqrt{2}\left(1 + \frac{M_2}{M_1}\right)^{1/2}}$$

where

M_1, M_2 = molecular weight of the components

Wilke compared results obtained from his equation with data on 17 binary systems, and reported an average deviation of less than 1%. For the four systems investigated in this work, values of mixture viscosities from Wilke's equation are also plotted in Figures 2 and 3. Agreement is good, and the maximum discrepancy is less than 3%. The good agreement may be in part due to the similar polarities of the alcohols. Viscosity data for polar systems with different polarities would be of value in testing the Wilke equation further.

Wilke's equation may be used to estimate the viscosity of binary vapor mixtures of aliphatic alcohols within 2 to 3%.

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