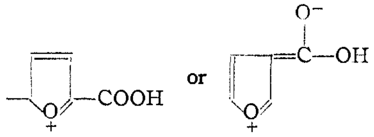

found in the 3-acid. On the other hand, the fact that the furanacetic acids also show similar differences may indicate that the inductive effect of the furan ring when substituted in the 2-position is greater than when substituted in the 3-position.

An examination of Table III shows that there is little influence of conjugation on the rate of hydrogenation over platinum catalyst. All four acids have the same rate constants within a factor of approximately two, while the activation energies are essentially within the experimental error. (It is estimated that the error in activation energies for the esterification reactions is ±200 calories, while for the hydrogenations the error is of the order of ±500 calories.) This indicates that the resonance between the groups is destroyed when the acids are adsorbed by the platinum. This is probably caused by destruction of the resonance of the furan ring itself, since the carboxyl group is presumably not influenced by the course of the reaction.

Acknowledgment.—The authors are indebted to the Office of Naval Research for financial support which made this research possible.

KNOXVILLE, TENNESSEE RECEIVED APRIL 6, 1951

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Rate of Rise of Liquids in Fine Vertical Capillaries

BY JOSEPH R. LIGENZA[1] AND RICHARD B. BERNSTEIN

The rates of ascent of several liquids in two vertical fine capillary tubes have been measured. By the use of tubes of radii 0.002 to 0.005 cm., in which the rate of rise is quite slow for most liquids, precise data are readily obtained. The small velocity makes possible a simplification of the differential equation of motion, resulting in a simple solution suitable for direct comparison with experiment. The data could be represented by this expression over the entire ascent. For the initial portion of the rise in short, fine vertically mounted capillaries, the equation reduces to the approximation $h^2 = R\gamma t/4\eta$, suggesting a rapid and simple method for the estimation of the viscosity of micro quantities of liquids.

Introduction

Although considerable theoretical work on the problem of the rate of capillary rise has been carried out, few precise experimental data are available to allow critical evaluation of the theoretical results.[2-7] Those data in the literature were obtained for only a few liquids, using rather large bore capillaries, of radii 0.01 to 0.04 cm. With tubes of this size the initial rate of rise is very rapid, requiring special techniques for the measurements, which were not of high precision. This paper is concerned with the rise of various liquids in fine capillaries, of radii 0.002 to 0.005 cm. The use of fine tubes has the advantage that the heights travelled by the liquid are much greater, and that the rate of ascent is slow enough for precision measurement. In addition, the slow rate of rise makes possible an appreciable simplification of the differential equation of motion, without sacrifice of rigor. The solution is in a form suitable for direct comparison with experiment.

An exact treatment of the rise of a liquid in a vertical capillary under the influence of its surface tension would be very difficult. Neither the hydrodynamic problem of accelerated flow nor the physico-chemical problem of the rate of wetting is well understood. With the usual assumptions that Poiseuille's law obtains for the non-stationary state, and that wetting is very rapid, the differential equation of motion is

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\pi R^2[\rho h + \rho_a(l - h)]\frac{\mathrm{d}h}{\mathrm{d}t}\right\} = 2\pi R\gamma\cos\theta - 8\pi\frac{\mathrm{d}h}{\mathrm{d}t}[\eta h + \eta_a(l - h)] - \pi R^2 gh(\rho - \rho_a) - \frac{1}{4}\pi R^2\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}\right)^2 \quad (1)$$

where h is the height of the column of liquid at time t, R and l are the radius and length of the capillary, η and η_a the viscosity of the liquid and of air, respectively, ρ and ρ_a the density of liquid and air, while γ is the surface tension (liquid–air) and θ the contact angle, assumed constant. The term on the left is the rate of change of the momentum of the contents of the capillary; the terms on the right are, respectively, forces due to surface tension, viscous resistance, gravity, and the "end-drag effect" of Brittin.[5b]

Equation 1 is not amenable to explicit solution. However, for a tube of *sufficiently small* radius, the rate of rise may be slow enough so that the rate of change of momentum and end-drag terms are negligible with respect to the others. The solution for this simplified case of Equation 1 is then

$$t = \frac{8}{R^2\rho g}\left\{[(\eta - \eta_a)h_\infty + \eta_a l]\ln\left(\frac{h_\infty}{h_\infty - h}\right) - (\eta - \eta_a)h\right\} \quad (2)$$

where $h_\infty = 2\gamma\cos\theta/R\rho g$.

For convenience, the final height, h_∞, (an experimentally measurable quantity), has been introduced into the equation; also, $(\rho - \rho_a)$ has been approximated by ρ.

Equation 2 is equivalent to the result of Washburn,[3] reduced to zero hydrostatic head. How-

---

[1] Department of Chemistry, Columbia University, New York, N. Y.

[2] E. J. LeGrand and W. A. Rense, *J. Appl. Phys.*, **15**, 456 (1944).

[3] E. W. Washburn, *Phys. Rev.*, **17**, 273 (1921).

[4] C. H. Bosanquet, *Phil. Mag.*, **6**, 525 (1923).

[5] (a) G. Pickett, *J. Appl. Phys.*, **15**, 623 (1944); (b) W. E. Brittin, *ibid.*, **17**, 37 (1946).

[6] J. M. Bell and F. K. Cameron, *J. Phys. Chem.*, **10**, 658 (1906).

[7] R. L. Peek and D. A. McLean, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 85 (1934).

ever, this result has been shown here specifically for the case of a *fine* capillary tube, where the momentum term and the end-drag effect are expected to be negligibly small.[8]

Experimental

Two Pyrex fine bore capillary tubes were used in this investigation. They were mounted vertically, and thermostated. One centimeter marks were scratched on the capillaries and calibrated with a cathetometer (±0.002 cm.).

The radii of the capillaries were determined at the conclusion of the experiments, by breaking up the tubes into short lengths which were measured end-wise under a microscope. The change in radius of Tube I and II with length was plotted. The estimated uncertainty in the measured values was ±0.15 micron, corresponding to ±0.6% and 0.4% for Tubes I and II, respectively. Straight lines through the data indicated a total change in radius over the working range of less than 2%, so that the use of the "mean radii" of 23.9 and 41.3 microns would introduce a probable error of less than 1%. The tubes were 21.3 and 56.5 cm. in length, respectively.

The seven liquids used were C.P., distilled before use. The specific gravity and viscosity of each was determined at three temperatures near 25°. Deviations from literature values were <0.5% in density and <2% in viscosity, with the exception of the particular sample of carbon tetrachloride where the viscosity was approximately 25% different. The surface tension of each liquid at one temperature was determined by capillary rise in Tube II. The final height was approached from both directions and was read with a precision of ±0.01 cm. The surface tension was calculated using the radius taken from the appropriate graph, and assuming zero contact angle. Deviations from literature were <2%. The ranges of physical properties encompassed with these liquids at 25° were: density 0.68–1.6 g./cc., surface tension 20–36 dynes/cm., and viscosity 4.0–33.0 millipoises.

The tubes were cleaned with 1:1 nitric acid, allowed to stand for 10 minutes; after washing with distilled water for 15 minutes, the tube was dried by slowly drawing air through for 10 minutes. The liquid was placed in a small vessel raised until the surface was in contact with the opening of the capillary. A slight pressure of dry air was applied to the top of the tube so that slow bubble formation would result. This pressure was then relieved and the bubble of air collapsed gradually. At the instant the liquid entered the tube the time measurement was begun. For the liquids of high viscosity the rate of rise was slow enough to allow measurement by stopwatch. For the liquids of lower viscosity, stopwatch timing was not sufficiently accurate. An Esterline–Angus a.c. operated Graphic Milliameter Model A.W. operated at maximum chart speed was used; a tapping key was provided to make rapid contact in a circuit consisting of a dry cell, resistor and the recording milliameter. As the liquid entered the tube the key was tapped; at the same time a stopwatch was started. The key was tapped as the liquid level reached each of the calibrated 1-cm. marks along the capillary. As the liquid approached its final height, h_∞, and its rate of ascent became inconveniently slow, a final pip was impressed on the chart; simultaneously the watch was stopped. The total chart length was measured, and the calibration coefficient of the chart drive checked for each run. The drive was found to be very uniform when no tension was applied to the paper; the value of the reciprocal chart speed used was 0.1970 ± 0.0002 sec./mm. Accuracy in time measurement was ±0.2 sec.

Each kinetic experiment was repeated 3–5 times, cleaning the tube between each run. The average deviation in the time required to reach a given height was less than ±1% except toward the end of the ascent, where the average deviations rose to about ±2%.

Results

A portion of the experimental kinetic results carried out at temperatures near 25° is presented in Figs. 1–3. The experimental points are indicated by circles, while the solid lines are the theoretical curves obtained from Eq. 2. The observed values of η, ρ, γ and l were used in the calculations. The viscosity of air was taken to be 0.18 millipoise. A constant mean value of R and h_∞ was used throughout. The theoretical curves computed in this way are in good agreement with the experimental data. Results for chloroform and data at other temperatures are not included; the results are comparable, however.

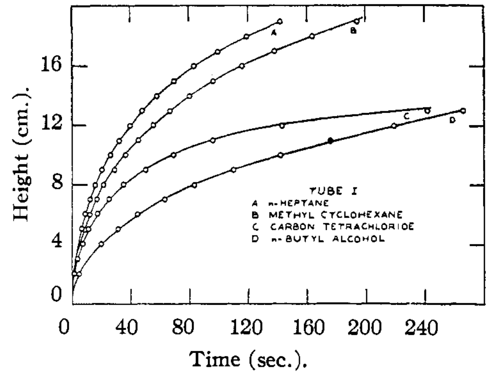

Fig. 1.—Agreement of theory with experiment. Circles are experimental points. Solid curves are theoretical.

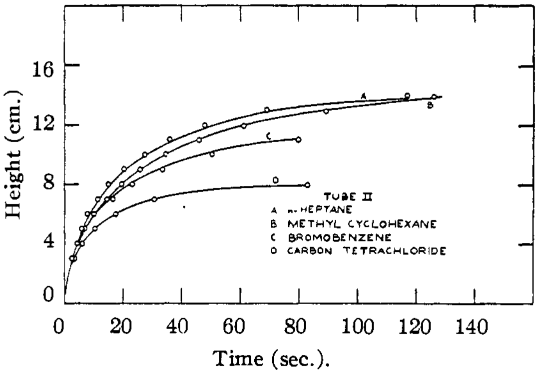

Fig. 2.—Agreement of theory with experiment. Circles are experimental points. Solid curves are theoretical.

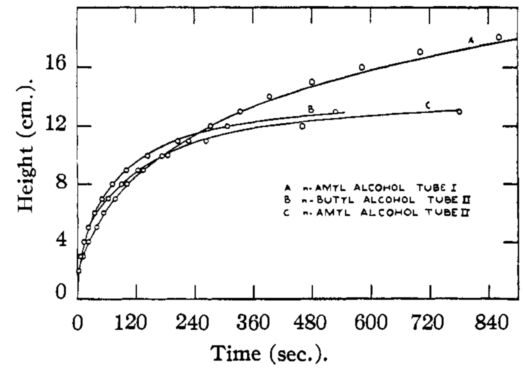

Fig. 3.—Agreement of theory with experiment. Circles are experimental points. Solid curves are theoretical.

---

(8) The validity of these assumptions was tested directly by graphical differentiation of the observed data for carbon tetrachloride in Tube I, one of the least favorable cases. The numerical values of the momentum term and the end-drag term were less than 0.1% of the larger of the terms due to density or surface tension, over the entire range for which kinetic data were obtained. A similar attempt using the data of ref. 2 was not entirely successful due to the scatter in the data; however, approximate values for the momentum term in the initial portion of the ascent were obtained which were in considerable excess of 1% of the largest of the other terms.

Discussion

The results of this investigation indicate that the rise of a liquid in a fine vertical capillary may be accurately represented by the solution to the differential equation of motion in which the rate of change of the momentum of the contents of the capillary is assumed to be negligible. It also appears that here the end-drag effect is negligible. The data support the validity of the viscous drag term, the form of which results from the assumption of Poiseuille flow in the accelerated state. In addition, the rate of wetting and the rate of assumption of constant (zero) contact angle are apparently sufficiently rapid compared with the rate of ascent that they need not be considered. Thus considerable simplifications in both the experimental and theoretical treatment of the general problem result from the use of fine capillaries.

It may prove possible to utilize the results and techniques described in this paper for the estimation of the viscosity of small quantities of liquids. For a fairly short capillary where $\eta_a l \ll (\eta - \eta_a)h_\infty$, and where $\eta \gg \eta_a$, Eq. 2 reduces to the following equation for the viscosity

$$\eta = \frac{R^2 \rho g t}{8h_\infty}\left[\ln\left(\frac{h_\infty}{h_\infty - h}\right) - \frac{h}{h_\infty}\right]^{-1} \qquad (3)$$

For the *initial* portion of the ascent, Eq. 3 may be approximated by expansion to yield the result

$$\eta = \frac{R^2 \rho g h_\infty}{8}\left(\frac{t}{h^2}\right) = \frac{R\gamma}{4}\left(\frac{t}{h^2}\right) \qquad (4)$$

Thus, a plot of h^2 *vs.* t should be linear, with a slope $\gamma R/4\eta$. This is very similar to the result for a horizontal tube.[7]

It was found that the data plotted in this way did give straight lines in the initial portion of the ascent; however, the extent and accuracy of the data in the early rise was insufficient for a precise determination of the viscosity from the kinetic data. A rapid approximate micro viscosity determination suggests itself, however, using very fine tubes; the time required for a liquid to rise to a given height is proportional to viscosity divided by surface tension. Calibration with known liquids would make possible rapid relative measurements of viscosity.

CHICAGO 16, ILL. RECEIVED APRIL 20, 1951

[CONTRIBUTION NO. 415 FROM THE DEPARTMENT OF CHEMISTRY, KANSAS EXPERIMENT STATION, KANSAS STATE COLLEGE]

The Decomposition of Formic Acid at Low Temperatures[1]

BY H. N. BARHAM AND LOUIS WATTS CLARK

The purpose of the present work was to study the rate of the non-catalyzed decomposition of pure formic acid at low temperatures, and to determine the effects of water upon the rate of decomposition. The formic acid used possessed a purity of 99.9%. Calculated specific reaction velocity constants and temperature coefficients for the non-catalyzed reaction are descriptive of the stability of formic acid at various temperatures. Constants in the Arrhenius and Eyring equations also were calculated.

It is well known that only a few simple unimolecular reactions have been the subject of kinetic investigations. One that has received considerable attention is the decomposition of formic acid in the liquid phase, yielding water and carbon monoxide, in the presence of various catalysts.[2,3] While kinetic data of much value relative to the catalyzed decomposition of formic acid have been obtained, the decomposition of formic acid alone has not been studied. Reasons for this may have been (1) the difficulty of obtaining formic acid of high purity, and (2) the exceedingly slow rate of decomposition of formic acid at low temperatures. Although the rate of the non-catalyzed decomposition of liquid formic acid is quite slow, it was observed by the authors that the amounts of gas evolved with time from a 100-ml. sample of the dry acid between 40° and 100° were sufficiently large to be measured with accuracy. Using formic acid which was nearly 100% water-free, in a modified form of the apparatus designed by Walton,[4] the authors determined: (1) the influence of water on the rate of decomposition of the acid at two different temperatures, and (2) the rate of decomposition of the dry acid at nine different temperatures between 40° and 100°. These data then were used to calculate the temperature coefficients of the reaction, the stability of formic acid, and the thermodynamic constants in the Arrhenius[5] and Eyring[6] equations.

Experimental

Purification of Formic Acid.—Reagent formic acid of 96.0% purity was further dried by standing over Anhydrone for several days, then distilled at 30° under 20 mm. pressure. The product thus obtained tested 99.9% pure formic acid by titration with standard base using a weight buret, and showed the following physical properties: n^{20}_D 1.3710; d^4_{20} 1.2200; freezing point 8.1°.

Apparatus.—The apparatus used in studying the rate of decomposition of formic acid was patterned after that of Walton, with the following modifications: (1) a mercury sealed stirrer was substituted for the shaker; (2) a cold water condenser was attached to the reaction flask; (3) a tube of Ascarite was inserted between the condenser and the water-jacketed buret; (4) all sections of the apparatus were connected by standard taper joints; and (5) an electrically heated, thermostatically controlled oil-bath was used in lieu of a water-bath.

Gas Analysis.—Analysis in an Orsat apparatus confirmed the observation of Branch[7] that the only gas produced by the decomposition of formic acid was carbon monoxide.

Effect of Water.—At a temperature of 98.6° the initial rate of evolution of carbon monoxide by a 122-g. sample of formic acid was found to be over 100 ml. per hour. However, the rate gradually decreased with time, reaching after

---

(1) From the Ph.D. Thesis of Louis Watts Clark, Kansas State College, May, 1950.

(2) Walton and Stark, *J. Phys. Chem.*, **34**, 359 (1930).

(3) (a) Schierz, THIS JOURNAL, **45**, 447 (1923); (b) Schierz, *ibid.*, **45**, 455 (1923); (c) Schierz and Ward, *ibid.*, **50**, 3240 (1928).

(4) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

(5) Arrhenius, *ibid.*, **4**, 226 (1889).

(6) Wynne-Jones and Eyring, *J. Phys. Chem.*, **3**, 492 (1935).

(7) Branch, THIS JOURNAL, **37**, 2316 (1915).