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Surface-Tension Effects in Suspended-Level Capillary Viscometers

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The results of an experimental study of surface-tension effects in kinematic capillary viscometers of the suspended-level type are presented. These results are deduced from a comparison with measurements obtained with a special Ostwald viscometer in which surface-tension effects are negligibly small. It is shown that surface-tension effects in suspended-level viscometers are sensitive to the shape of the capillary exit. Recommendations how to minimize these effects are discussed.

KEY WORDS: capillary viscometers; Ostwald viscometer; surface tension; Ubbelohde viscometer; viscosity.

1. INTRODUCTION

The viscosity of liquids at atmospheric pressure is usually measured with so-called kinematic capillary viscometers in which the liquid is allowed to flow under the action of gravity [1–3]. Such viscometers are preferred in practice because of their ease of handling, versatility, and high reproducibility.

Two important types of kinematic capillary viscometers are shown schematically in Fig. 1, namely, an Ostwald viscometer (Fig. 1a) and an Ubbelohde viscometer (Fig. 1b) [4]. An Ostwald viscometer is filled with a known amount of liquid. To operate the viscometer, pressure is applied to the left tube or suction to the right tube to cause the liquid to rise in the right tube to a position slightly above m_1. The pressure or suction is then released and the time is observed for the meniscus to pass from mark m_1

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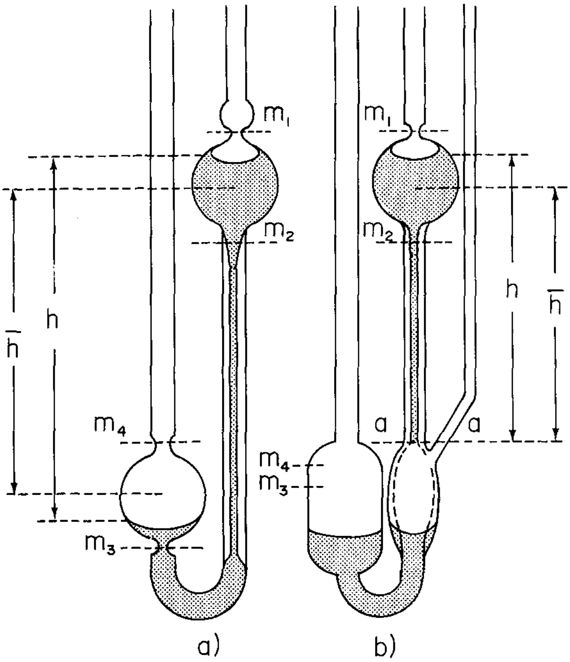

Fig. 1. (a) Ostwald viscometer. (b) Suspended-level viscometer or Ubbelohde viscometer.

to m_2. A complication with the Ostwald viscometer is that the hydrostatic driving head h, or its average value $\bar{h}$, depends on the volume of the liquid in the viscometer which therefore must be known. Moreover, to obtain accurate results the lower meniscus should be at mark m_3 when the upper meniscus is at mark m_1, so that the two menisci in the two identical bulbs have the same surface areas at all instants during a measurement. This means that the volume of the liquid has to be carefully adjusted, a tedious procedure which needs to be repeated at different temperatures. Viscometers of the Ubbelohde type shown in Fig. 1b are therefore preferred in practice. In the latter the "suspended" exit cross section is always at the same level a–a. The driving head is independent of the amount of liquid in the viscometer and the effective working volume of the liquid becomes equal to the volume of the upper bulb between the two timing marks m_1 and m_2. Ubbelohde viscometers are also known as suspended-level viscometers.

The essential element in all kinematic capillary viscometers is a capillary in which Poiseuille flow is developed over most of its height. However, in spite of the high reproducibility, capillary-viscometer measurements may suffer from several sources of error depending on the specific instrument used [3] and several corrections may need to be applied [4]. The theory of capillary viscometers has undergone a slow evolution from Poiseuille [5] through Hagenbach [6] to Erk [7]. More recently, improved theories have been presented by Cannon et al. [8] and by Kestin et al. [9]. The thrust of this development was to take into account the flow in the initial length of the capillary, where the radial velocity distribution in the liquid changes from a nearly square profile to its asymptotic parabolic form. There exists now general agreement on how to deal with these inlet-length effects [10].

Nevertheless, when the viscosity of a particular liquid is measured with different capillary viscometers one may find, as shown in the present paper, a spread of viscosity values significantly larger than the reproducibility obtainable with a single instrument; such a spread can be attributed to surface-tension effects. Surface-tension effects in kinematic capillary viscometers have been considered by several investigators [1, 4, 11–14]. An accurate theoretical analysis of such surface-tension effects is complicated [12–14] and there does not appear to exist a simple procedure of calibrating for surface-tension effects, at least not when liquids with widely different densities and surface tensions are considered. Hence, it is imperative to assure that any surface-tension effects are small by choosing an appropriately designed capillary viscometer. In fact, a major motivation of Ubbelohde in introducing suspended-level viscometers was the idea that the presence of the suspended level could compensate for the surface-tension effects due to the meniscus in the upper bulb. [15, 16]. However, as most recently pointed out by Wedlake et al. [14], this goal cannot be rigorously achieved.

As already realized by Ubbelohde originally, the importance of any surface-tension effects in suspended-level viscometers will depend on the shape of the capillary exit. We have made an experimental study of the magnitude of these surface-tension effects. We have done this by measuring the viscosity of some suitably chosen liquids with a variety of suspended-level viscometers and by comparing these results with those obtained with a special Ostwald viscometer in which surface-tension effects have been made negligibly small.

2. WORKING EQUATIONS

Poiseuille flow in a capillary with length L and radius R is described by the equation [17]

$$Q=\frac{dV}{dt}=\frac{\pi R^4 \Delta P}{8L\eta} \tag{1}$$

where $Q = dV/dt$ is the volume flow rate, ΔP the pressure drop across the capillary, and η the viscosity of the liquid. As mentioned in Section 1, one must consider a correction due to deviations from Poiseuille flow near the inlet of the capillary. A theoretical analysis shows that as a consequence the pressure drop ΔP in Eq. (1) should be replaced with

$$\Delta P = \rho g h + \Delta P_{\mathrm{k}} \tag{2}$$

where $\rho g h$ is the gravitational pressure drop associated with the driving head h, g being the gravitational acceleration constant and ρ the density of the liquid, and where [9]

$$\Delta P_{\mathrm{k}} = -m \frac{\rho Q^2}{\pi^2 R^4} \tag{3}$$

The coefficient m turns out to be a function of the Reynolds number $\mathrm{Re} = \rho \bar{u} R/\eta$, where $\bar{u}$ is the average velocity of the liquid. The dependence of m on Re for very small values of the Reynolds number is not well known, but there exists agreement that m reaches a constant value between 1.1 and 1.2 for Reynolds numbers larger than about 10, but much smaller than those causing transition to turbulence [8, 9]. We refer to the correction given by Eq. (3) as the "inlet" correction. Replacing the driving head h by its average value $\bar{h}$ and the flow rate Q by its average value $\bar{Q} = V/\tau$, where V is the working volume of the liquid and τ the efflux time, one deduces from Eqs. (1)–(3) for the kinematic viscosity $\nu = \eta/\rho$:

$$\nu = C\tau[1 - D/\tau^2] \tag{4}$$

with

$$C = \pi R^4 g\bar{h}/8LV, \qquad D = mV^2/\pi^2 R^4 g\bar{h} \tag{5}$$

The driving head h and, hence, the flow rate Q are not constant in practice. This problem is dealt with by treating C and D as effective constants, whose values are determined by calibrating the viscometer with the aid of reference liquids with known kinematic viscosities [4, 9, 18].

As mentioned in Section 1, an accurate assessment of surface-tension effects in capillary viscometers is difficult [12–14]. A crude estimate, often suggested, is obtained as follows. The experimentally observed driving head h_{expt} will not be equal to the gravitational driving head h, but will be modified as a consequence of the capillary rise of the two menisci. A simple formula for the capillary rise of a liquid meniscus in a capillary with radius R under the assumption of complete wetting is [19]

$$\Delta h = \frac{2\sigma}{\rho g R} \tag{6}$$

where σ is the surface tension of the liquid. In an Ostwald-like viscometer the upper meniscus yields a positive contribution and the lower meniscus a negative contribution to h_{expt}, so that

$$\bar{h}_{\text{expt}} = \bar{h}[1 - S\sigma\rho^{-1}] \tag{7}$$

with

$$S = \frac{2}{g\bar{h}}\left(\frac{1}{R_{\text{l}}} - \frac{1}{R_{\text{u}}}\right) \tag{8}$$

where R_{l} and R_{u} are the average radii of the lower and upper surfaces. Substitution of Eq. (7) into Eqs. (4) and (5) yields the modified working equation

$$v = C\tau \frac{1 - D\tau^{-2}}{1 - S\sigma\rho^{-1}} \tag{9}$$

with

$$C = \pi R^4 g\bar{h}_{\text{expt}}/8LV \tag{10}$$

We note that the effect of any capillary rise on the term $D\tau^2$ does not need to be considered, since it would yield a correction to a correction.

The factor $[1 - S\sigma/\rho]^{-1}$ in Eq. (9) has the form of the surface-tension correction commonly recommended [3, 10, 20, 21]. However, there are many problems with this estimate. First, the radius R in Eq. (6) is, strictly speaking, the radius of curvature of the meniscus, and only for very small capillaries can R be identified with the radius of the capillary. For the actual conditions in the bulbs of the viscometers the capillary rise cannot be taken as proportional to σ and inversely proportional to R [22, 23]. Second, Eq. (6) applies only to a cylindrical capillary, and not to surfaces in bulbs or cones where the walls are not perpendicular to the horizontal surface [11, 23]. Furthermore, the radii R_{l} and R_{u} are not constant during a measurement. Finally, Eq. (6) applies to a static surface and not to a moving surface as in the case of the suspended level. The next best attempt to deal with surface-tension effects is to retain the working equation (9) but to treat the coefficient S as an effective constant to be determined by calibration, even in the case of suspended-level viscometers for which $\bar{h}_{\text{expt}}$ in Eq. (10) is an instrumental constant [4]. This is the procedure which was used by Bauer and Meerlander [24] and it is also the procedure adopted in this publication. However, as pointed out by Wedlake et al. [14], the coefficient S depends in reality on the properties of the liquid including the surface tension. Hence, there is no theoretical justification for Eq. (9). We can only hope that Eq. (9) will account empirically for surface-tension effects when they are small.

With a given capillary viscometer, two liquids, A and B, will yield efflux times τ_A and τ_B, respectively. From the working equation (9) it follows that for a given viscometer

$$\frac{\nu_B}{\nu_A} = \frac{\tau_B}{\tau_A} C_k^{BA} C_\sigma^{BA} \tag{11}$$

where

$$C_k^{BA} = \frac{1 - D\tau_B^{-2}}{1 - D\tau_A^{-2}} \tag{12}$$

is the relative inlet correction and where the factor

$$C_\sigma^{BA} = \frac{1 - S\sigma_A \rho_A^{-1}}{1 - S\sigma_B \rho_B^{-1}} \tag{13}$$

accounts for the relative surface-tension effects. We have performed measurements both with an Ostwald viscometer and with a variety of Ubbelohde viscometers. From Eq. (11) we have

$$\left(\frac{\nu_B}{\nu_A}\right)_{\text{Ost}} = \frac{\tau_B}{\tau_A} C_k^{BA} C_\sigma^{BA} \tag{14}$$

and

$$\left(\frac{\nu_B}{\nu_A}\right)_{\text{Ub}} = \frac{\tilde{\tau}_B}{\tilde{\tau}_A} \tilde{C}_k^{BA} \tilde{C}_\sigma^{BA} \tag{15}$$

where we use the tilde to refer to efflux times and correction factors associated with an Ubbelohde viscometer.

We have selected two liquids, A and B, with similar kinematic viscosities $\nu_A \simeq \nu_B$, but with widely different values of σ/ρ. With $\tau_A \simeq \tau_B$ and $\tilde{\tau}_A \simeq \tilde{\tau}_B$, the relative inlet-correction factors C_k^{BA} and $\tilde{C}_k^{BA}$ reduce to unity. Furthermore, our Ostwald viscometer is constructed so as to make surface-tension corrections negligibly small, i.e., $C_\sigma^{BA} = 1$. Noting that ν_B/ν_A should be independent of the viscometer, we have

$$\tilde{C}_\sigma^{BA} = \frac{\tau_B}{\tau_A} \frac{\tilde{\tau}_A}{\tilde{\tau}_B} \tag{16}$$

From Eq. (13) it then follows that, for the Ubbelohde viscometers under consideration,

$$S = \frac{1 - \tilde{C}_{\sigma}^{\mathrm{BA}}}{\sigma_{\mathrm{A}} \rho_{\mathrm{A}}^{-1} - \tilde{C}_{\sigma}^{\mathrm{BA}} \sigma_{\mathrm{B}} \rho_{\mathrm{B}}^{-1}} \tag{17}$$

Equations (16) and (17) enable us to determine the surface-tension corrections for Ubbelohde viscometers by comparing the efflux times $\tilde{\tau}_{\mathrm{A}}$ and $\tilde{\tau}_{\mathrm{B}}$ with the efflux times τ_{A} and τ_{B} observed with a suitably designed Ostwald viscometer in which surface-tension effects have been made small.

3. EXPERIMENTS

We have investigated the presence of surface-tension effects in five Ubbelohde viscometers designated Ub1, Ub2, etc. For this purpose we compared the efflux times observed in these Ubbelohde viscometers with the efflux times observed in a specially designed Ostwald viscometer in which surface-tension effects have been made negligibly small. The geometrical features and dimensions of the Ostwald viscometer and of the five Ubbelohde viscometers are given in Table I. The Ubbelohde viscometers constructed for this work differed in the shape of the capillary exit. Ub1, Ub4, and Ub5 had a sudden enlargement at the capillary exit, Ub2 had a gradual opening, and Ub3 had a trumpet-like exit, because we suspected that a trumpet-like exit, recommended by Caw and Wylie [25], may lead to serious surface-tension effects. These different exit shapes are shown in Fig. 2.

The Ostwald viscometer, designated Ost, had upper and lower bulbs of identical size and shape. As a consequence, first-order surface-tension effects are absent, since $R_{\mathrm{u}} = R_{\mathrm{l}}$ in Eq. (8). Nevertheless, Ostwald viscometers do have secondary surface-tension effects [11], since the

Table I. Geometric Constants and Features of the Viscometers

	Ost	Ub1	Ub2	Ub3	Ub4	Ub5
R (cm)	0.020	0.020	0.020	0.020	0.0225	0.015
L (cm)	44.2	39.0	39.0	34.0	37.7	39.4
$\bar{h}$ (cm)	47.0	41.7	42.0	40.0	46.0	41.3
V (cm^3)	11.3	11.3	12.5	11.5	15.4	5.2
Exit shape[a]		Sudden opening	Gradual	Trumpet-like	Sudden opening	Sudden opening

[a] See Fig. 2.

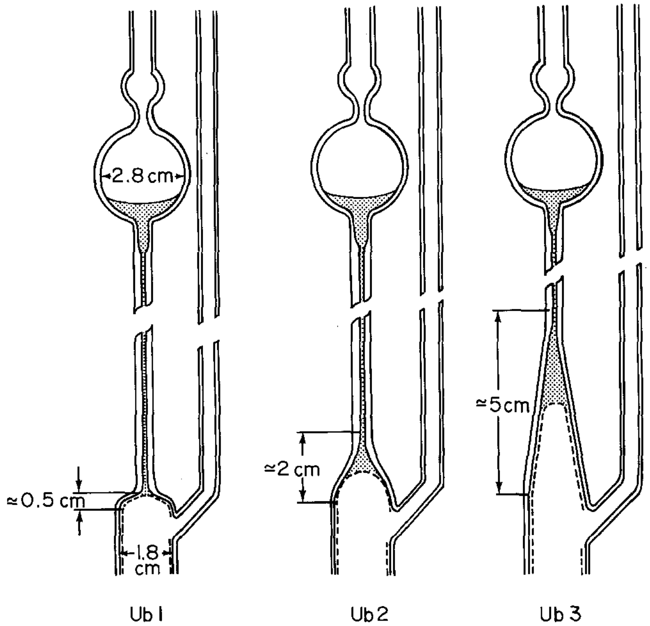

Fig. 2. Capillary exit shape of the viscometers. Ub4 is similar to Ub1 but has a larger bulb; Ub5 is similar to Ub1 but has a smaller bulb.

menisci in the upper and lower bulbs have different shapes as schematically indicated in Fig. 1a. In practice we make these secondary surface-tension effects negligible by using an Ostwald viscometer with large bulbs ($V = 11\ \mathrm{cm}^3$) and a long capillary ($L = 44\ \mathrm{cm}$).

All viscometers were firmly attached to a common frame in a thermostatic bath containing about $70\ \mathrm{dm}^3$ of water. The temperature was controlled to within 0.01 °C and it was measured by means of calibrated mercury thermometers graduated in 0.01 °C. The experiments were performed at five different temperatures, namely, 20.00, 25.00, 30.00, 40.00, and 60.000 °C. Efflux times were measured with mechanical timers graduated in 0.1 s, calibrated against a broadcasting-station time signal.

For the reasons mentioned in Section 2 we want to use two liquids A and B with comparable flow times τ_A and τ_B but with widely different values of σ/ρ. We achieved this goal by selecting nitrobenzene (liquid B), whose surface tension is low, and aqueous solutions of $CaCl_2$, whose surface tension is high. The composition of the $CaCl_2$ solutions (approximately 2.3 M) was adjusted by trial and error so as to obtain, at each working temperature, efflux times close to those obtained for nitrobenzene. The density of these liquids was measured with a pycnometer of 50-cm^3 capacity. The surface tension of the $CaCl_2$ solutions was measured with the capillary-rise method; for nitrobenzene the surface tension was calculated from an equation recommended by Riddik and Toops [26]. In the experiments we also tried to determine the kinematic viscosity of nitrobenzene and the $CaCl_2$ solutions relative to the kinematic viscosity of water at the same temperature. For water, designated liquid 0, we adopted the viscosities recommended by Swindells et al. [27], Coe and Godfrey [28], and Hardy and Cottington [29] and the densities recommended by Kell and Whalley [30], while the surface tensions were taken from the Handbook of Chemistry and Physics [31]. The values obtained for those auxiliary properties are listed in Table II.

The experimental efflux times observed for these liquids in the various viscometers are presented in Table III. Each efflux time was obtained as the average from at least three runs with a mean deviation of 0.1 to 0.2 s. It should perhaps be mentioned that Ub5 gave somewhat erratic efflux times, probably due to the small size of the capillary radius of this viscometer. Ub4 had the largest capillary radius and worked therefore at higher Reynolds numbers.

It is seen that the efflux times τ_A and τ_B do not differ by more than a few percent. From the experimental efflux times τ_A and τ_B we have calculated the relative inlet correction factor $C_k^{BA} = (1 - D\tau_B^{-2})/(1 - D\tau_A^{-2})$; for this purpose we estimated D from Eq. (5), adopting the usual value

Table II. Property Values for Nitrobenzene (Liquid B), $CaCl_2$ Solutions (Liquid A), and Water (Liquid 0) at the Experimental Working Temperatures

	20.00°C	25.00°C	30.00°C	40.00°C	60.00°C
(Nitrobenzene)					
(liquid B)					
σ ($g \cdot s^{-2}$)	42.59	42.00	41.41	40.24	37.88
ρ ($g \cdot cm^{-3}$)	1.2035	1.1985	1.1936	1.1837	1.1640
σ/ρ ($cm^3 \cdot s^{-2}$)	35.39	35.04	34.70	33.99	32.54
$CaCl_2$ solutions					
(liquid A)					
σ($g \cdot s^{-2}$)	82.4	81.6	81.5	81.0	75.7
ρ ($g \cdot cm^{-3}$)	1.1894	1.1872	1.1928	1.1949	1.1957
σ/ρ ($cm^3 \cdot s^{-2}$)	69.3	68.7	68.3	67.8	63.3
Water					
(liquid 0)					
σ ($g \cdot s^{-2}$)	72.75	71.97	71.18	69.56	66.18
ρ ($g \cdot cm^{-3}$)	0.99820	0.99705	0.99565	0.99222	0.98320
σ/ρ ($cm^3 \cdot s^{-2}$)	72.89	72.18	71.49	70.11	67.31
ν ($cm^2 \cdot s^{-1}$)	0.010038	0.008929	0.008010	0.006582	0.004745

Table III. Experimental Efflux Times (s) of Liquids A, B, and 0

Temp. (°C)	Liquid	Ost	Ub1	Ub2	Ub3	Ub4	Ub5
20	O	1729.3	1721.9	1880.5	1608.3	1476.0	2510.8
	A	2946.7	2934.7	3203.7	2747.7	2512.9	4283.1
	B	2893.8	2882.4	3157.4	2752.6	2472.4	4213.7
25	O	1538.1	1531.6	1672.6	1430.9	1312.9	2234.1
	A	2651.9	2640.9	2883.2	2473.4	2261.6	3854.1
	B	2654.5	2641.9	2894.7	2524.9	2265.0	3863.7
30	O	1379.6	1373.7	1500.5	1283.8	1177.8	2004.9
	A	2480.6	2471.2	2699.0	2312.6	2117.9	3603.9
	B	2444.7	2433.6	2666.3	2325.9	2086.3	3558.2
40	O	1133.6	1128.9	1233.2	1055.5	968.1	1647.6
	A	2129.4	2120.3	2317.1	1985.6	1817.8	3093.5
	B	2102.7	2092.7	2292.7	2001.5	1794.0	3060.6
60	O	817.4	814.3	889.5	762.0	699.1	1188.2
	A	1612.3	1604.6	1754.7	1505.2	1377.0	2342.1
	B	1621.8	1614.6	1769.3	1545.7	1384.3	2361.9

$m = 1.12$. Because we made sure that all viscometers had a long capillary, the inlet-correction factor $C_{\rm k}^{\rm BA}$ was equal to unity within a few parts in 10^5 for all viscometers at all working temperatures. In most cases $C_{\rm k}^{\rm BA}$ was actually equal to unity within 1×10^{-5}; exceptions were Ub4 at 30 and 40°C, where $C_{\rm k}^{\rm BA} = 0.99998$, and Ub3 at 60°C, where $C_{\rm k}^{\rm BA} = 1.00005$. We conclude that the inlet correction is, indeed, negligibly small for all our viscometers at all temperatures.

Having verified that $C_{\rm k}^{\rm BA}$ is equal to unity for both the Ostwald and the Ubbelohde viscometers, we calculated the relative surface-tension correction factor $\tilde{C}_\sigma^{\rm BA}$ and the corresponding surface-tension parameter S for the Ubbelohde viscometers from Eqs. (16) and (17). The results obtained for these quantities are presented in Tables IV and V.

From these experimental results we draw the following conclusions.

(a) For Ub1 and Ub4, which have a sudden opening, the average surface-tension parameter $|\bar{S}|$ is zero within experimental accuracy ($|\bar{S}| < 1 \times 10^{-5}\ {\rm s}^2 \cdot {\rm cm}^{-3}$). From Table IV we see that for these two viscometers the surface-tension correction is less than 0.1% at all temperatures, except for Ub4 at 20°C, where the correction is 0.2%.

(b) Ub5 has a more significant surface-tension parameter $S \simeq 6 \times 10^{-5}\ {\rm s}^2 \cdot {\rm cm}^{-3}$ in spite of the fact that Ub5 has a sudden

Table IV. Relative Surface-Tension Correction $C_\sigma^{\mathrm{BA}} = \tau_{\mathrm{B}}\tilde{\tau}_{\mathrm{A}}/\tau_{\mathrm{A}}\tilde{\tau}_{\mathrm{B}}$ for the Ubbelohde viscometers[a]

Temperature (°C)	Ub1	Ub2	Ub3	Ub4	Ub5
20	0.9999	0.9964	0.9803	0.9981	0.9982
25	1.0006	0.9970	0.9806	0.9995	0.9985
30	1.0008	0.9976	0.9799	1.0005	0.9982
40	1.0005	0.9980	0.9796	1.0006	0.9981
60	0.9997	0.9977	0.9795	1.0006	0.9975

[a] $\tilde{\tau}_{\mathrm{A}}$ and $\tilde{\tau}_{\mathrm{B}}$ refer to the Ubbelohde viscometers; τ_{B} and τ_{B} refer to the Ostwald viscometer.

opening as well. We think that the finite surface-tension correction, amounting to about 0.2%, is due to the smaller working volume of this viscometer.

(c) In Ub2 surface-tension effects are also definitely present. The value $S = 8 \times 10^{-5}\ \mathrm{s}^2 \cdot \mathrm{cm}^{-3}$ leads to a relative surface-tension correction of about 0.3%. Ub2 is similar to Ub1 and Ub4 except for the gradual opening of the capillary exit.

(d) In Ub3, which has a trumpet-like opening, the surface-tension parameter $S \simeq 60 \times 10^{-5}\ \mathrm{s}^2 \cdot \mathrm{cm}^{-3}$, leading to relative surface-tension corrections as large as 2%.

Evidently the exit shape of the capillary plays an important role in relation to the surface-tension effect. With a sudden opening the surface-tension effects can be made negligibly small provided the working volume is suitably large. The surface-tension effects become more significant when a gradual opening is used and they become really large for an Ubbelohde viscometer with a trumpet-like exit. We note that for all Ubbelohde

Table V. Values of the Surface-Tension Parameter S ($\mathrm{s}^2 \cdot \mathrm{cm}^{-3}$) for the Ubbelohde Viscometers

Temp. (°C)	Ub1	Ub2	Ub3	Ub4	Ub5
20	0.4×10^{-5}	10.5×10^{-5}	57×20^{-5}	5.5×10^{-5}	5.2×10^{-5}
25	-1.8×10^{-5}	8.9×10^{-5}	57×10^{-5}	1.5×10^{-5}	4.5×10^{-5}
30	-2.2×10^{-5}	7.1×10^{-5}	59×10^{-5}	-1.3×10^{-5}	5.3×10^{-5}
40	-1.5×10^{-5}	6.0×10^{-5}	59×10^{-5}	-1.7×10^{-5}	5.7×10^{-5}
60	1.1×10^{-5}	7.5×10^{-5}	65×10^{-5}	-1.9×10^{-5}	8.2×10^{-5}
Mean	-0.8×10^{-5}	8.0×10^{-5}	59×10^{-5}	0.4×10^{-5}	5.8×10^{-5}

viscometers the relative surface-tension correction is more important than the inlet correction.

As the next step we deduce the kinematic viscosities ν_A and ν_B of the two liquids relative to the kinematic viscosity ν_0 of liquid water as determined from the efflux times observed with the various viscometers. The results thus obtained for nitrobenzene (liquid B) are presented in Table VI. For each temperature and for each viscometer we give the values obtained for ν_B/ν_0 without and with the surface-tension correction. If we neglect the surface-tension correction, ν_B/ν_0 would be given by $\nu_B/\nu_0 = \tau_B/\tau_0$ since $C_k^{BO} \simeq 1$ [cf. Eq. (11)]; the values obtained for ν_B/ν_0 yield a spread of 0.6%; specifically the value τ_B/τ_0 obtained with Ub3 is 2% larger than the values obtained with either Ost or Ub1. However, if the values of τ_B/τ_0 are multiplied with the surface-tension correction factor C_σ^{BO}, the spread disappears, i.e., the spread becomes within the experimental precision of about 0.05%. The corresponding values obtained for the $CaCl_2$ solutions are presented in Table VII. Again, the same tendency is found, i.e., any spread in the apparent kinematic-viscosity ratio disappears after including the surface-tension correction factor C_σ^{AO}. The only difference is that the magnitude of the surface-tension effects is smaller, since σ/ρ for the $CaCl_2$ solution is close to σ_0/ρ_0 of water.

We remark that Bauer and Meerlander [24] have also used Ubbelohde viscometers with long capillaries in an attempt to obtain

Table VI. Apparent Kinematic-Viscosity Ratios With and Without a Correction for Surface-Tension Effects[a]

Temp. (°C)	ν_B/ν_O	Ost	Ub1	Ub2	Ub3	Ub4	Ub5	Mean value	Percentage mean deviation
20	τ_B/τ_O	1.6734	1.6740	1.6790	1.7115	1.6751	1.6782	1.6819	0.60
	$(\tau_B/\tau_O)\,C_\sigma^{BO}$	1.6734	1.6745	1.6739	1.6728	1.6748	1.6745	1.6740	0.04
25	τ_B/τ_O	1.7258	1.7249	1.7307	1.7646	1.7252	1.7294	1.7334	0.60
	$(\tau_B/\tau_O)\,C_\sigma^{BO}$	1.7258	1.7254	1.7255	1.7251	1.7249	1.7257	1.7254	0.02
30	τ_B/τ_O	1.7720	1.7716	1.7769	1.8117	1.7714	1.7748	1.7797	0.60
	$(\tau_B/\tau_O)\,C_\sigma^{BO}$	1.7720	1.7721	1.7717	1.7716	1.7711	1.7710	1.7716	0.02
40	τ_B/τ_O	1.8549	1.8538	1.8591	1.8963	1.8531	1.8576	1.8625	0.61
	$(\tau_B/\tau_O)\,C_\sigma^{BO}$	1.8549	1.8543	1.8537	1.8551	1.8528	1.8537	1.8541	0.04
60	τ_B/τ_O	1.9841	1.9828	1.9891	2.0285	1.9801	1.9878	1.9921	0.61
	$(\tau_B/\tau_0)\,C_\sigma^{BO}$	1.9841	1.9834	1.9836	1.9861	1.9798	1.9838	1.9835	0.06

[a] Liquid B, nitrobenzene; liquid O, water.

Table VII. Apparent Kinematic-Viscosity Ratios with and Without a Correction for Surface-Tension Effects[a]

Temp. (°C)	ν_A/ν_O	Ost	Ub1	Ub2	Ub3	Ub4	Ub5	Mean value	Percentage mean deviation
20	τ_A/τ_O	1.7040	1.7043	1.7036	1.7084	1.7025	1.7059	1.7048	0.09
	$(\tau_A/\tau_O)\,C_\sigma^{AO}$	1.7040	1.7043	1.7031	1.7046	1.7039	1.7055	1.7042	0.03
25	τ_A/τ_O	1.7241	1.7243	1.7238	1.7286	1.7226	1.7251	1.7248	0.08
	$(\tau_A/\tau_O)\,C_\sigma^{AO}$	1.7241	1.7243	1.7233	1.7249	1.7226	1.7248	1.7240	0.04
30	τ_A/τ_O	1.7981	1.7989	1.7987	1.8014	1.7982	1.7975	1.7988	0.05
	$(\tau_A/\tau_O)\,C_\sigma^{AO}$	1.7981	1.7989	1.7982	1.7979	1.7982	1.7972	1.7981	0.02
40	τ_A/τ_O	1.8784	1.8782	1.8789	1.8812	1.8777	1.8776	1.8787	0.05
	$(\tau_A/\tau_O)\,C_\sigma^{AO}$	1.8784	1.8782	1.8785	1.8785	1.8777	1.8780	1.8782	0.02
60	τ_A/τ_O	1.9725	1.9705	1.9727	1.9753	1.9697	1.9711	1.9720	0.08
	$(\tau_A/\tau_O)\,C_\sigma^{AO}$	1.9725	1.9706	1.9721	1.9705	1.9697	1.9706	1.9710	0.05

[a] Liquid A, $CaCl_2$ solutions; liquid O, water.

accurate experimental viscosities for a number of liquids. Our surface-tension parameter S is to be compared with the parameter κ in the working equation used by Bauer and Meerlander. While Bauer and Meerlander found mostly negative values of S for their Ubbelohde viscometers, we find for our viscometers values of S that are positive.

4. APPLICATIONS

In this paper we have adopted Eq. (9) as the working equation

$$\nu = C\tau \frac{1 - D\tau^{-2}}{1 - S\sigma\rho^{-1}} \qquad (18)$$

With the surface-tension parameter S determined from the experiments described in the previous section, the viscometer constants C and D can be determined from a calibration with a reference liquid for which we use liquid water. Our viscometers can then be used to obtain accurate viscosities for some other liquids.

As an example we have measured the viscosity of aqueous solutions of NaCl at various concentrations. The measurements were made with the Ostwald viscometer and with Ub1 and Ub3. For Ost and Ub1 the surface-tension effects were shown to be negligibly small and the results obtained with Ost and Ub1 were presented in a previous publication [32]. For comparison we have also measured the viscosity of these NaCl solutions with Ub3. As an illustrative example we compare in Table VIII the results obtained for the NaCl solutions with Ost, Ub1, and Ub3 at 50°C. For Ub3 we present both the apparent kinematic viscosity obtained without taking and that obtained taking into account the surface-tension correction factor. The viscosities obtained with Ost and Ub1 are again in excellent agreement, confirming that in these viscometers surface-tension effects are negligibly small. However, without the surface-tension correction, Ub3 yields apparent kinematic viscosities which differ from those obtained with Ost and Ub1; these differences increase with increasing values of σ/ρ, reaching a maximum value of 0.4%. After applying the surface-tension correction these differences become smaller than 0.1%.

We have also used Ub1 to measure the viscosity of liquid toluene from 25 to 75°C [33] and of *trans*-decalin from 25 to 135°C [34]. The results presented in this paper confirm that these measurements are free from surface-tension effects.

We repeat that the form of the surface-tension correction in the working equation (18) does not have a satisfactory theoretical foundation. Hence, it can be used only when the surface-tension corrections are small. For instance, the data in Table VIII confirm the applicability of the empirical surface-tension correction only for values up to 0.4%. In a previous paper [33] we noted the existence of a 0.45% difference between the value of the kinematic viscosity ν found by us with Ub1 for toluene at 25°C and

Table VIII. Kinematic Viscosity ν Obtained for Aqueous Solutions of NaCl at 50°C with Ost, Ub1, and Ub3

	Ost,	Ub1		Ub3[a]		Ub3[b]	
Concentration $(\mathrm{mol \cdot kg^{-1}})$	ν $(\mathrm{mm^2 \cdot s^{-1}})$	ν $(\mathrm{mm^2 \cdot s^{-1}})$	δ^c (%)	ν $(\mathrm{mm^2 \cdot s^{-1}})$	δ^c (%)	ν $(\mathrm{mm^2 \cdot s^{-1}})$	δ^c (%)
0.01719	0.5541_0	0.5543_9	0.05	0.5545_7	0.08	0.5544_6	0.06
0.05351	0.5557_3	0.5559_5	0.04	0.5561_9	0.08	0.5560_5	0.06
0.17230	0.5603_9	0.5607_6	0.06	0.5611_1	0.13	0.5609_0	0.09
0.55893	0.5754_7	0.5957_8	0.05	0.5761_3	0.11	0.5756_9	0.04
1.13947	0.5988_8	0.5992_4	0.06	0.5999_2	0.17	0.5991_4	0.04
2.35546	0.6558_1	0.6564_0	0.09	0.6574_9	0.23	0.6560_4	0.03
3.87979	0.7443_1	0.7448_9	0.08	0.7472_3	0.39	0.7449_1	0.08
5.45241	0.8589_4	0.8599_2	0.11	0.8624_9	0.41	0.8592_6	0.04

[a] Without correction for surface-tension effect.

[b] With correction for surface-tension effect.

[c] Difference with ν from the Ostwald viscometer.

the value found by Bauer and Meerlander [24]. It is possible that this difference is still due in part to a surface-tension effect in spite of the fact that Bauer and Meerlander tried to correct for it.

5. DISCUSSION

We have made a comparative study of the viscosity of liquids as measured with a number of different viscometers. We have demonstrated that it is possible to obtain an accuracy of better than 0.1% when the viscosity of liquids is measured with kinematic capillary viscometers, but only when an assessment is made of the presence of surface-tension effects. Surface-tension effects can be made negligibly small in the case of an Ostwald viscometer with identical upper and lower bulbs that are sufficiently large and with a driving head $\bar{h}$ that is sufficiently long. In Ubbelohde viscometers surface-tension effects can be reduced to negligible values by selection of an adequate exit shape and employing sufficiently large values of the working volume V and the driving head $\bar{h}$ (Ub1 and Ub4). Gradual openings or trumpet-like exits lead to significant surface-tension effects in the case of Ubbelohde viscometers (Ub2 and Ub3). With a trumpet-like exit we have found that surface-tension effects can become as large as 2%.

The bulbs should be small enough to reduce the inlet correction ($B = mV/8\pi L$), but not so small as to make surface-tension effects noticeable (Ub5). A value V of 10 to 12 cm^3 proved to be convenient.

Small capillary diameters cause the flow rate to decrease to conveniently low Reynolds numbers ($\text{Re} < 50$). Very small bores, however, cause efflux times to be erratic due to small dust particles. Careful filtration of the liquids is an essential requirement.

The capillary length L and the mean driving head $\bar{h}$ should be as large as possible in order to obtain a small inlet correction ($B = mV/8\pi L$) and to reduce the surface-tension effect [cf. Eq. (9)]. Thermostat considerations restrict these values to at most about 40 cm.

Ubbelohde viscometers are clearly preferable for routine work. However, when very high accuracy is required, Ostwald viscometers with large identical bulbs and long driving heads should be considered.

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