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Precise viscosity measurements of Newtonian liquids with $\nu < 1\ \mathrm{mm^2/s}$ for the selection of suitable standards

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Abstract: The application of long capillary Ubbelohde viscometers in the determination of low viscosities is described. Corrections and measurement uncertainties are discussed. Viscosity and density data are given for 18 Newtonian liquids of commercially available purity, with viscosities below about 1 mm²/s. For several liquids the commonly used purity specifications were found to be sufficient to qualify these liquids as viscosity standards, which can be used for viscometer calibration.

Key words: Long capillary viscometer, viscometer calibration, Newtonian liquid, viscosity standard

1. Introduction

Practical viscometry is based on the internationally accepted value of 1.0038 mm²/s [1] for the kinematic viscosity of water at 20 °C and atmospheric pressure. Starting with this reference liquid the unit of kinematic viscosity is realized using glass capillary viscometers and standard liquids [2], generally mineral oils. This method usually yields an accuracy of 0.2% to 0.3%. The main problem in relating viscosity measurements to the water base is due to some unusual properties of water with respect to surface tension and wetting. Once this basic calibration has been achieved using suitable viscometers [3], the most important problem which remains – especially for measurements below 1 mm²/s – is the kinetic energy correction [4, 5]. The equations that are commonly used for calculating this correction [6, 7] give satisfactory results above the viscosity of water, but fail in the lower viscosity range down to 0.3 mm²/s [8]. It is for this reason that, for example, standard methods for the determination of the viscosity of dilute polymer solutions [9], commonly used in production and quality control, do not give reproducible results when applied to systems with a low viscosity solvent like methylene chloride. Deviations of several percent may be observed between results obtained from identical samples with different viscometers [10].

It therefore seems necessary to improve the accuracy of viscosity determinations in the range below 1 mm²/s and to provide a method of viscometer calibration that can be applied with relatively little experimental effort.

2. Experimental details

Basic calibrations with water were carried out using Cannon master viscometers [3], since the influence of surface tension on this type of viscometers has been studied [11]. For precise measurements of lower viscosities down to 0.3 mm²/s these viscometers are, however, less suitable because the kinetic energy correction becomes too large in this range. Ubbelohde-type suspended level viscometers specially designed to show extremely low kinetic energy corrections were therefore used. All the dimensions of these viscometers were chosen according to DIN 51 562 (part 1) except for the capillary length, which was 400 mm instead of 90 mm, and one capillary diameter, which was chosen to be 0.24 mm (type 1). The other type of viscometer (type 2) with an 0.36 mm capillary diameter corresponds to standard size 0. The viscometers were placed in frames equipped with a photoelectric device for the automatic measurement of the flow time. Viscometer constants were determined by comparison with the Cannon

Table 1. Characteristic data of the long capillary Ubbelohde viscometers. L – Capillary length, V – volume of measuring bulb, R – capillary radius, K – viscometer constant

Type	L mm	V ml	R mm	K mm^2/s^2
1	400	5.7	0.12	0.00019
2	400	5.7	0.18	0.00070

master viscometers using standard oils with viscosities above 1 mm^2/s. The characteristics of the long capillary Ubbelohde viscometers are listed in table 1.

All measurements were undertaken in a 230 l temperature controlled stirred water bath. The temperature was measured by means of platinum resistance thermometers connected to an automatic A.C. bridge with a resolution of 0.1 mK. Temperature deviations from the nominal value were registered by a recorder.

The determination of density, necessary for the calculation of the dynamic viscosity, was carried out using 50 ml Reischauer pycnometers.

3. Corrections and measurement uncertainties

3.1 *Kinetic energy correction*

The determination of viscosity with capillary viscometers is based on the Hagen-Poiseuille law, which if the liquid flows through the capillary under gravity, can be written as

$$\nu = \frac{\eta}{\varrho} = \frac{\pi R^4 g\, h_m}{8\, VL} \cdot t = K \cdot t\,. \tag{1}$$

ν is the kinematic and η the dynamic viscosity and ϱ is the density of the liquid. V is the volume of liquid which flows during the flow time t through the capillary with radius R and length L under the influence of acceleration due to gravity g. The average value of the pressure head in the viscometer during the measurement is denoted by h_m. All the constants can be gathered together into a viscometer constant K. The kinetic energy correction [4, 5] accounts for the fact that part of the hydrostatic pressure $\varrho \cdot g \cdot h_m$ is necessary to accelerate the liquid as it enters the capillary and build up the parabolic velocity profile. At the outlet of the capillary the kinetic energy is partially dissipated. These effects are usually taken into account by a correction Δt_H to the observed value of the flow time t_g according to

$$\nu = K \cdot (t_g - \Delta t_H)\,. \tag{2}$$

This kinetic energy correction Δt_H can be expressed as [4, 5]

$$\Delta t_H = \frac{m \cdot V}{8\, \pi\, LK\, t_g}\,. \tag{3}$$

In this equation, m is a dimensionless parameter depending on the Reynolds number Re of the capillary flow and the geometry of the capillary ends, especially the capillary outlet [6, 7, 12]. For viscometers with a square-cut capillary outlet it is usual to assume complete dissipation of kinetic energy and so take $m = 1$. If the capillary ends are trumpet-shaped, it is usual [7, 13, 14] to use $m = 0.037 \cdot \sqrt{Re}$, which was obtained in an early experimental investigation [6]. This leads to

$$\Delta t_H = \frac{E}{K\, t_g^2}\,; \qquad E = \frac{0.00166 \cdot V^{3/2}}{L \cdot (2RK)^{1/2}}\,. \tag{4}$$

However, as a result of viscometer calibrations carried out over many years at the Physikalisch-Technische Bundesanstalt, it has been found that for Ubbelohde viscometers with trumpet-shaped capillary ends the value of $m = 0.32$ gives better results than eq. (4) if the Reynolds number is lower than about 50.

All viscometers used in this work were made with trumpet-shaped capillary ends. For type 1 viscometers (0.24 mm capillary diameter) the difference between the two methods of calculating Δt_H can be seen in figure 1. For comparison, the correction based on $m = 1$ is also shown. The difference between the assumptions $m \sim \sqrt{Re}$ and $m = 0.32$ is very small over the range of viscosities considered here. The correction Δt_H itself is also rather small and does not exceed 0.04% of the flow time. In further calculations, $m = 0.32$ is used for these viscometers. As an estimate of the maximum uncertainty which may be caused by this method of calculating the kinetic energy correction we allow an error of 100% in the correction.

For type 2 viscometers (0.36 mm capillary diameter) the kinetic energy correction was determined experimentally according to eq. (5) using several low viscosity liquids for which the viscosity was determined using type 1 viscometers.

$$\Delta t_H = t_g - \frac{\nu}{K}\,. \tag{5}$$

Figure 2 shows such a calibration curve. The theoretical correction according to eq. (4), which differs from the experimental values by up to 0.15%, is also shown.

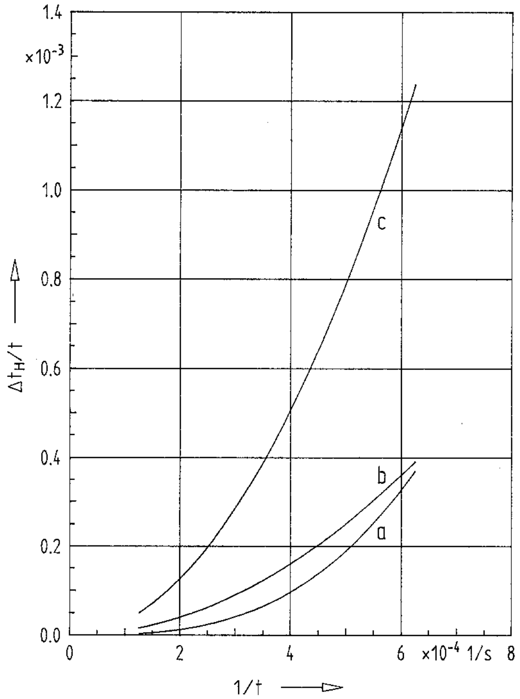

Fig. 1. Ratio of the kinetic energy correction Δt_H to the flow time t for type 1 viscometers as a function of $1/t$ in the viscosity range between 1.5 mm²/s and 0.3 mm²/s: a) $m = 0.037 \cdot \sqrt{Re}$, b) $m = 0.32$, c) $m = 1$

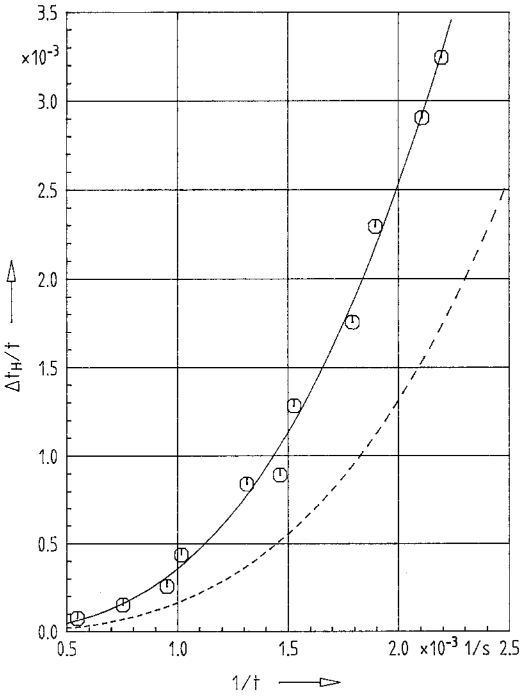

Fig. 2. Experimentally determined kinetic energy correction Δt_H divided by the flow time t for a type 2 viscometer as a function of $1/t$ in the viscosity range between 1.5 mm²/s and 0.3 mm²/s. The dashed line corresponds to the correction based on $m = 0.037 \sqrt{Re}$

3.2 *Buoyancy correction*

The buoyancy of the liquid column produced by the ambient air leads to a correction of the pressure head by a factor $(1 - \varrho_{air}/\varrho)$ where ϱ_{air} is the density of ambient air and ϱ is the density of the liquid. In many applications, liquids are measured with a density close to that of the standard oil ϱ_0 (≈ 0.8 g/cm³) used to determine the viscometer constant. Therefore the buoyancy correction is usually included in the viscometer constant K_0 as

$$K_0 = \frac{\pi R^4 g \cdot h_m}{8 V L} \cdot \left(1 - \frac{\varrho_{air}}{\varrho}\right), \tag{6}$$

and no correction is applied. If, however, liquids are measured with a density ϱ significantly different from ϱ_0, the effect of the air buoyancy has to be considered and eq. (2) must be modified to

$$\nu = K_0 \cdot \left[1 - \left(\frac{\varrho_{air}}{\varrho} - \frac{\varrho_{air}}{\varrho_0}\right)\right] \cdot (t_g - \Delta t_H) \,. \tag{7}$$

Neglecting this correction in determining the viscosity of tetrachlorethylene ($\varrho = 1.6$ g/cm³), for example, causes an error in the viscosity of 0.07%.

The accuracy of this correction is limited by the fact that especially in the case of liquids with high vapour pressures, a mixture of air and vapour exists in the viscometer. The density of this mixture is difficult to determine and so in this work $\varrho_{air} = 1.2 \cdot 10^{-3}$ g/cm³ is used for calculating the air column correction and the influence of vapour pressure is included in the uncertainty considerations. Assuming that in the worst case the saturation pressure is reached, the density ϱ_D of the air-vapour mixture can be calculated. The maximum contribution to the relative uncertainty of the viscosity determination is then given by $(\varrho_D - \varrho_{air})/\varrho$. For the liquids investigated here, values up to 0.15% (for diethyl ether at 20 °C) were obtained.

3.3 *Surface tension*

Ubbelohde viscometers are designed so that the influence of the surface tension σ in the measuring bulb is almost completely compensated by the appropriate curvature of the suspended level. For both practical and theoretical reasons, however, complete compensation of surface tension effects is not achieved in standard Ubbelohde viscometers [15–17]. The remaining influence of surface tension also varies with each viscometer, since some parts of these instruments are handmade. The effect on the viscosity determination is usually less than 0.1% but values up to 0.3% have also been observed. In principle, the influence of surface tension could be calculated [15, 16] if the geometry and, in particular, the curvature of the measuring bulb and the suspended level were known. These data are, however, difficult to obtain. Therefore a correction factor $\varkappa$ which accounts for the remaining surface tension effect and which can be experimentally determined is defined as follows:

$$\nu = K_0 \cdot (t_g - \Delta t_H) \cdot \left[1 - \left(\frac{\varrho_{air}}{\varrho} - \frac{\varrho_{air}}{\varrho_0}\right)\right] \cdot \left[1 - \varkappa \cdot \left(\frac{\sigma_0}{\varrho_0} - \frac{\sigma}{\varrho}\right)\right] . \tag{8}$$

In this equation σ_0/ϱ_0 is an arbitrary reference value for the ratio of surface tension to density. It may be useful to choose the values for the standard oil that has been used to determine K_0 as a reference.

An easy method of determining $\varkappa$ is to measure the flow times for two liquids having the same kinematic viscosity but different values of σ/ϱ. Assuming that the kinetic energy correction is the same for both liquids, Δt_H can be eliminated from eq. (8) thus allowing $\varkappa$ to be calculated. The accuracy of this method increases with an increasing difference in σ/ϱ for the two liquids. Though the use of water would allow very large differences in σ/ϱ, this liquid was disregarded because of its peculiar wetting properties and its sensitivity to surfactants. Thus a search was made to find pairs of liquids which are insensitive against surfactants and with different values of σ/ϱ, which arise mainly from differences in ϱ.

Measurements with Cannon master viscometers for which the influence of the surface tension is knwon [3, 11] showed that trichloroethylene at 20 °C and anhydrous acetone at 24.63 °C have the same viscosity of $0.3850\ \mathrm{mm^2/s}$ but σ/ϱ-values of $19.5\ \mathrm{cm^3/s^2}$ and $29\ \mathrm{cm^3/s^2}$, respectively. Toluene at 20 °C and chlorobenzene at 25.83 °C are a similar pair of liquids with a viscosity of $0.678\ \mathrm{mm^2/s}$ and σ/ϱ-values of $32.9\ \mathrm{cm^3/s^2}$ and $29.6\ \mathrm{cm^3/s^2}$.

The correction factors $\varkappa$ determined for the long capillary Ubbelohde viscometers were between $-0.3 \cdot 10^{-4}\ \mathrm{s^2/cm^3}$ and $-0.6 \cdot 10^{-4}\ \mathrm{s^2/cm^3}$ for type 1 and between $-0.6 \cdot 10^{-4}\ \mathrm{s^2/cm^3}$ and $-1.2 \cdot 10^{-4}\ \mathrm{s^2/cm^3}$ for type 2 viscometers. A negative value of $\varkappa$ indicates a traction opposite to gravity. Most viscometers behave like this and therefore qualitatively agree with theoretical predictions [17]. On the other hand, positive $\varkappa$ values were also occasionally found.

This method of correcting for surface tension effects has also been tested with special *U*-tube viscometers with a significantly greater surface tension influence. The results indicate that more than 90% of the surface tension effects are corrected in this way. However, there may be an influence due to the different wetting behaviour of different liquids that is not taken into account. Furthermore, only literature data were used for the surface tension values. It is therefore assumed that the correction may neglect up to 50% of the prevailing surface tension effect, thus contributing up to 0.03% to the uncertainty of the viscosity determination for liquids investigated in this work.

3.4 Temperature

During viscosity measurements the temperature of the water-bath did not deviate from the average value by more than 2 mK. The average temperature itself differed by less than 1 mK from the nominal temperature. Temperature gradients along the viscometer were less than 2 mK. Considering, in addition, the uncertainty of the thermometer calibration, the total uncertainty of the temperature measurement is less than 5 mK, thus contributing not more than 0.01% to the uncertainty of the viscosity determination for the liquids tested.

3.5 Flow time and random uncertainty

No systematic errors in the determination of the flow time are considered, since the same timing device was used for both the viscosity measurements and the viscometer calibration.

At least two, but usually three viscometers were used when measuring the viscosity of a liquid. Each viscometer was filled at least twice with a fresh test sample and the flow time was measured at least four times. The maximum deviation of a single flow time from the average for this test sample was usually less than 0.01%. The average flow times determined with different samples in the same viscometer also usually differed by less than 0.01% from the average of all test samples. The difference between the viscosities determined with different viscometers was typically 0.01% to 0.02%. In only a few cases were values up to 0.04% observed. In order to estimate an upper limit for the random uncertainty, the maximum deviation of the viscosity determined with a single test sample from the average of all measurements with all viscometers was calculated, resulting in contributions of 0.01% to 0.04% to the uncertainty of the viscosity determination.

3.6 Viscometer constant and density determination

The viscometer constant of the long capillary Ubbelohde viscometers is known to an uncertainty of 0.1% referred to the viscosity of water. Density measurements were performed with a maximum error of 0.015%.

4. Measurements and results

For 18 high purity liquids commercially available for various purposes (spectrophotometry, analysis, etc.), the kinematic viscosity and the density were determined at 20 °C and 25 °C (in general). With few exceptions, measurements were carried out on samples from two different suppliers in order to discover whether the commonly used purity specifications would be sufficient to qualify these liquids as viscosity standards. The results are listed in table 2. Literature data [18] for the surface tension-density ratio as well as the relative uncertainty $\Delta \nu/\nu$ of the viscosity values are included. The minimum purity of the samples and their intended application as specified by the suppliers are also listed.

For all liquids recommended as viscosity standards (denoted by (+) in table 2) the relative difference in viscosity between samples from different suppliers and generally with different specifications was not more than 0.06%. Considering, in addition, the uncertainty of the measurements, it can be concluded that for these

Table 2. Results of viscosity measurements on low viscosity liquids investigated for their use as viscosity standards. ν – kinematic viscosity, ϱ – density, σ/ϱ – ratio of surface tension to density, T – temperature, and $\Delta\nu/\nu$ – maximum relative uncertainty for the viscosity data.

List of suppliers:
A – E. Merck, Labor- und Industriechemikalien, Darmstadt (FRG)
B – J. T. Baker, Chemicals B.V., Deventer (The Netherlands)
C – C. Roth K.G., Chemische Fabrik, Karlsruhe (FRG)
D – Community Bureau of Reference, Brussels (Belgium)
E – EGA-Chemie, Steinheim (FRG)

Material	Minimum purity (%)	Supplier	T (°C)	ν (mm²/s)	ϱ (g/cm³)	$\frac{\sigma}{\varrho}$ (*) (cm³/s²)	$\frac{\Delta\nu}{\nu}$ $\cdot 10^{-3}$	Remarks
Carbon disulfide	99.9	A (d)	25.00	0.28113	1.2596 (*)	25.1	2.8	
Methylenechloride (+)	99.5	A (a)	20.00	0.32738	1.3256	21.1	3.0	0.002% Amylen
	99	B (c)	20.00	0.32724				
	99.5	A (a)	25.00	0.31418	1.3164	20.6	3.0	
Diethyl ether	99.5	A (a)	20.00	0.32691	0.7136	23.9	3.8	
Chloroform (&)	99	A (d)	20.00	0.38055	1.4776	18.4	2.7	< 0.8% C_2H_5OH
	99	B (d)	20.00	0.38103				0.8% C_2H_5OH
		A (dp)	20.00	0.37988				< 0.005% C_2H_5OH
	99	A (d)	25.00	0.36393	1.4681	18.1	2.7	
Trichloroethylene (+)	99.5	A (a)	20.00	0.38503	1.4639	19.7	2.2	
	99.6	B (i)	20.00	0.38502				
	99.5	A (a)	25.00	0.36928	1.4555	19.5	2.6	
Acetone (&)	99.5	A (a)	20.00	0.40068	0.7902	29.7	1.9	0.07% H_2O
	99.5	C (a)	20.00	0.40210				
	99.7	C (b)	20.00	0.40150				
		C (bp)	20.00	0.40000				< 0.01% H_2O
	99.5	A (a)	24.82	0.38499		29.2	1.9	
	99.5	A (a)	25.00	0.38439	0.7844	29.2	1.9	
n-Hexane (&)	99	A (a)	20.00	0.46856	0.6595	27.9	2.5	
	95	A (k)	20.00	0.47123				
	99	A (a)	25.00	0.44896	0.6550	27.3	2.9	
	95	A (k)	25.00	0.45110				
Methyl ethyl ketone (&)	99.7	A (c)	20.00	0.49326	0.8050	30.3	2.0	analysis data see text
	99.7	B (e)	20.00	0.49431				
	99.7	A (c)	25.00	0.47106	0.7998	29.9	2.0	
Tetrachloroethylene (+)	99.7	A (f)	20.00	0.55235	1.6228	19.8	1.9	
	99.5	B (a)	20.00	0.55248				
	99.7	A (f)	25.00	0.52574	1.6144	19.4	1.9	
Tetrachloromethane (+)	99.8	A (a)	20.00	0.61102	1.5941	16.8	2.5	
	99.5	B (d)	20.00	0.61086				
	99.8	A (a)	25.00	0.57145	1.5843	16.5	2.4	

Table 2 (continued)

Material	Minimum purity (%)	Supplier	T (°C)	ν (mm^2/s)	ϱ (g/cm^3)	$\frac{\sigma}{\varrho}$ (*) (cm^3/s^2)	$\frac{\Delta\nu}{\nu} \cdot 10^{-3}$	Remarks
Toluene (+)	99.5	A (a)	20.00	0.67774	0.8669	32.9	1.8	0.027% H_2O
	(x)	B (h)	20.00	0.67790				< 0.03% H_2O
	99.5	A (a)	25.00	0.64037	0.8622	32.4	1.8	
Chlorobenzene (+)	99	A (g)	20.00	0.72518	1.1065	30.1	1.4	
	99	B (g)	20.00	0.72509				
	99	A (g)	25.00	0.68461	1.1010	29.7	1.4	
	99	A (g)	25.83	0.67807		29.6		
	99	B (g)	25.83	0.67795				
	99	A (g)	27.00	0.66968				
Benzene (+)	99.7	A (a)	20.00	0.73952	0.8791	32.8	2.1	
	99	B (c)	20.00	0.73920				
	99.7	A (a)	25.00	0.69068	0.8737	32.3	2.0	
2,2,4-Trimethylpentane (&) (iso-Octane)	(x)	D (l)	20.00	0.72918	0.6918	27.2	1.9	
	99	B (c)	20.00	0.72856				
	(x)	B (h)	20.00	0.69208				
	(x)	D (l)	25.00	0.69201	0.6877	26.8	1.9	
o-Xylene	98	A (g)	20.00	0.91434	0.8787	33.8	1.5	
	99.4	B (e)	20.00	0.92132				
	98	A (g)	25.00	0.85758	0.8745	33.4	1.6	
1,1,2,2-Tetrachloroethane		E (p)	20.00	1.1006	1.6025 (*)	22.2	2.2	analysis data see text
		E (p)	25.00	1.0157	1.5942 (*)	21.9	2.2	
Cyclohexane (+)	99.7	A (b)	20.00	1.2585	0.7786	31.7	2.1	
	99	B (c)	20.00	1.2577				
	99.7	A (b)	25.00	1.1603	0.7739	31.2	2.1	
n-Undecane (+)	99.5	A (a)	20.00	1.5862	0.7402	33.4	1.5	
	99	B (x)	20.00	1.5861				
	99.5	A (a)	25.00	1.4675	0.7365	32.9	1.5	

(*) literature data [18], (x) not specified, (a) for analysis, (b) for chromatography, (c) for gas chromatography, (d) for spectroscopy, (e) for UV spectroscopy, (f) for IR, NMR spectroscopy, (g) for synthesis, (h) for organic residue analysis, (i) MOS quality, (k) for residue analysis, (l) standard liquid for flash point determination, (p) after additional purification (see text), (+) recommended as viscosity standard, (&) recommended as viscosity standard with restrictions (see text)

liquids the common purity specification is sufficient to characterize the viscosity to within 0.3% to 0.4%, referred to the viscosity of water.

Carbon disulfide was only investigated at 25 °C in order to study the kinetic energy correction at extremely low kinematic viscosities. A single sample was tested. Since this liquid is highly toxic, it should only be used as a standard liquid in special cases.

The methylene chloride, trichloroethylene and tetrachloroethylene contained small amounts of stabilizers. However, these did not significantly effect the viscosity as shown by the methylene chloride, which had the same viscosity after distillation as when the stabilizer was present.

No measurements were performed on diethyl ether at 25 °C because of the high vapour pressure (boiling point 34.5 °C). The kinematic viscosity is very close to that of methylene chloride and the surface tension-density ratio is not very different. Therefore, provided only the kinematic viscosity is of interest, it is not usually necessary to use diethyl ether as a standard liquid.

Chloroform usually contains 0.5% to 1.0% ethanol as a stabilizer. As this amount of stabilizer changes the viscosity, a sample of chloroform was purified by a 1 µm molecular sieve and subsequent distillation. The remaining mass fraction of ethanol was less than 0.005% and at 20 °C a viscosity value of 0.37988 mm^2/s was obtained. By adding ethanol to this purified sample the increase in viscosity as a function of the ethanol content was investigated. The results are given in figure 3. Only when the ethanol content of a chloroform sample is known can it be used as a viscosity standard.

The problem with acetone is its miscibility with water and the sentivity of the viscosity to a change in the water content. Though the hygroscopicity of acetone is less pronounced than that, for example, of ethanol or glycerol varying water contents may be observed in samples of otherwise the same quality. Differences in the viscosity as observed in samples intended for different purposes (see table 2) must be attributed to the differing water content. Because of this, the viscosity of freshly distilled acetone containing less than 0.01% (mass fraction) water was measured as well as the viscosity increase due to increasing water content. The results are

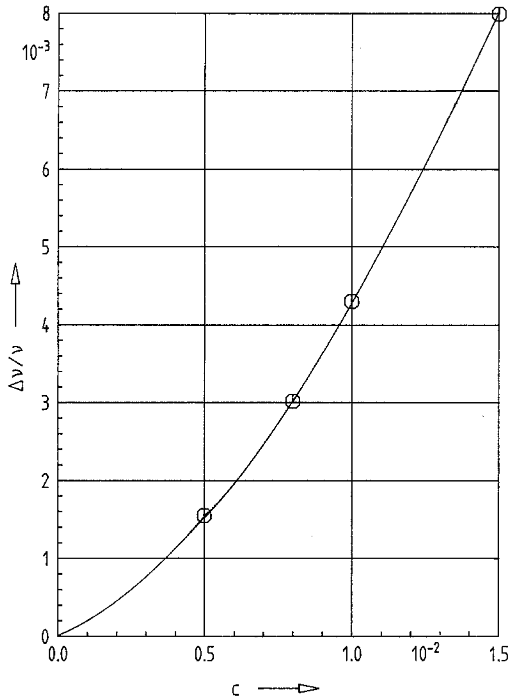

Fig. 3. Relative viscosity increase of chloroform $\Delta\nu/\nu$ at 20 °C as a function of the mass fraction c of ethanol in the sample

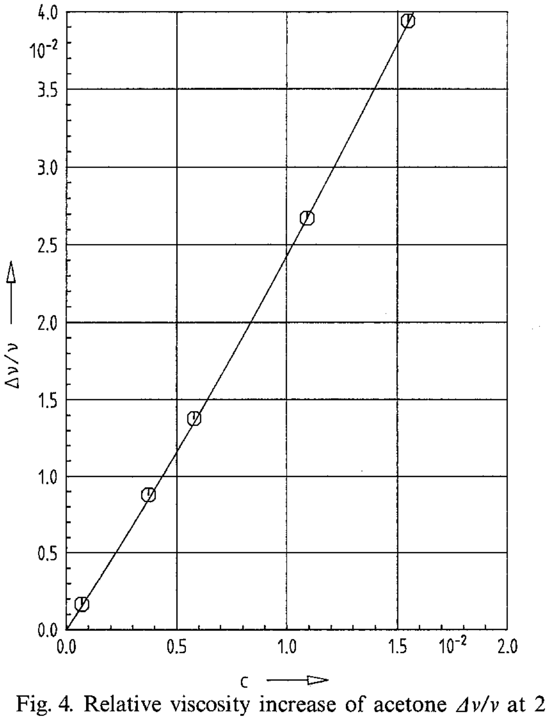

Fig. 4. Relative viscosity increase of acetone $\Delta\nu/\nu$ at 20 °C as a function of the mass fraction c of water in the sample

shown in figure 4. It should be noted that the rate of viscosity increase is about five times larger than for the chloroform-ethanol system. For a water content up to 0.5% the viscosity is given by $0.4000 \cdot (1 + 0.0238 \cdot c)$ mm^2/s where c is the mass fraction of water (in %). If acetone is to be used as a viscosity standard either a freshly dried and distilled sample must be used, or the actual water content must be known.

Since only one sample of high purity n-hexane has been tested it is not possible to decide whether the viscosity value obtained from this sample is representative of n-hexane with the specification "for analysis". The situation is similar for o-xylene.

The observed difference of 0.21% in the viscosity of different methyl ethyl ketone samples must be attributed to the 0.2% (mass fraction) ethyl acetate, 0.1% 4-methylpentanone-2, 0.06% water and 0.1% unidentified impurities found in the sample from supplier B, whereas the material supplied by A contained 0.04% water and less than 0.05% of other impurities.

Three different samples of 2,2,4-trimethylpentane (isooctane) were measured. The two samples intended for flash point calibration and for gas chromatography differed in viscosity by only 0.09%. However, it is possible that lower alcanes, which were probably responsible for the low viscosity of the sample specified "for organic residue analysis", may have influenced the viscosity.

1,1,2,2-tetrachloroethane was chosen in order to provide a liquid with a low σ/ϱ ratio at a viscosity close to 1 mm^2/s. This liquid was not available in highly pure form and was therefore distilled at 50 °C and a pressure of 25 mbar. Gas chromatographic analysis showed a 0.5% mass fraction of remaining impurities including 0.03% water. Since this liquid is highly toxic, it should only be used for viscosimetric purposes in special cases.

5. Application in viscometer calibration

Long capillary viscometers such as those used in this work are not suitable for normal laboratory use, since they require large temperature control baths and special care in handling. On the other hand, standard-type Ubbelohde viscometers require individual determination of the kinetic energy correction and the influence of surface tension when used for low viscosity measurements [8]. Carrying out this calibration by direct comparison with long capillary viscometers or using certified standard liquids would be relatively expensive in comparison with the price (and the lifetime in routine laboratory work) of a glass viscometer. In comparison, the liquids proposed here for use as viscosity standards provide an easy means of calibrating capillary viscometers for low viscosity measurements. As far as surface tension is concerned, the liquids can be roughly divided into two groups with σ/ϱ values of about 20 cm^3/s^2 and about 30 cm^3/s^2. In many applications it may be sufficient for the calibration liquids and the liquid under test to belong to the same σ/ϱ group. The influence of surface tension is

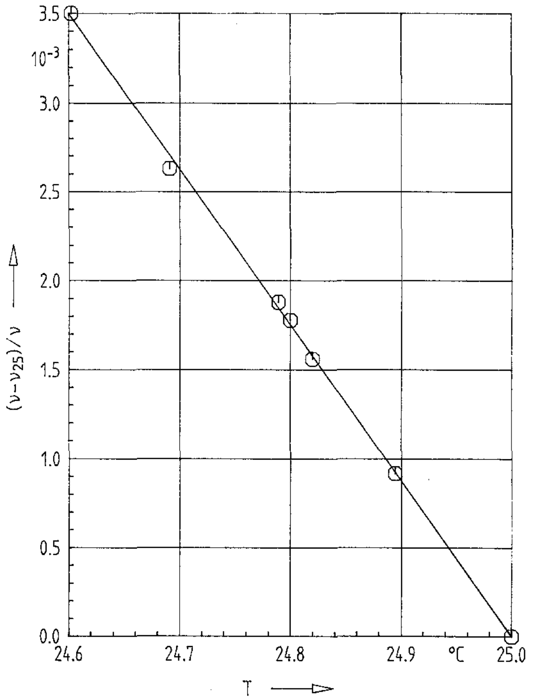

Fig. 5. Temperature dependence of the kinematic viscosity of acetone between 24.6 °C and 25 °C

then included in the individual kinetic energy correction and no further surface tension correction has to be applied. If, however, the viscometer shows a pronounced surface tension influence, or if the liquid under test differs significantly in σ/ϱ from the calibration liquids, the correction factor $\varkappa$ should be determined according to the procedure described in section 3.3. Acetone and trichloroethylene should be given preference for this purpose because of the relatively large difference in σ/ϱ. In order to enable $\varkappa$ to be determined when anhydrous acetone is not available but the water content is known, the temperature dependence of the kinematic viscosity of acetone between 24.6 °C and 25 °C is shown in figure 5. The relative change in viscosity is $8.75 \cdot 10^{-3}/°C$. Combining this result with the data shown in figure 4, the temperature that should be selected to obtain a viscosity of 0.3850 mm^2/s (the same as for trichloroethylene at 20 °C) for a sample of acetone with a water content of c_1 (mass fraction in %) is given by $(24.63 + 2.72 \cdot c_1)$ °C. This relation is valid up to a water content of 0.2%.

An application of this calibration procedure for determining the dilute solution viscosity of polymers is given in [10].

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References

1. ISO technical report 3666 (1977)
2. IUPAC Recommendation (1980) Recommended reference materials for realization of physicochemical properties, section viscosity, Pure & Appl Chem 52:2393
3. ASTM D2162 (1973) Basic calibration of master viscometers and viscosity oil standards
4. Erk S (1929) Z techn Phys 10:452
5. Muschelknautz E, Heckenbach M (1980) In: Hengstenberg J, Sturm B, Winkler O (eds) Messen, Steuern und Regeln in der chemischen Technik, vol 2, p 431, Springer, Berlin Heidelberg New York
6. Cannon MR, Manning RE, Bell JD (1960) Anal Chem 32:355
7. DIN 53012 (1981) Kapillarviskosimetrie newtonscher Flüssigkeiten, Fehlerquellen und Korrektionen
8. Bauer H, Meerlender G (1982) Rheol Acta 21:499
9. ISO recommendation R 1628 (1970) Directives for the standardization of methods for the determination of the dilute solution viscosity of polymers
10. Meerlender G, Bauer H, in preparation
11. Swindells JE, Hardy RC, Cottington RL (1954) J Res Nat Bur Stand 52:105
12. Weber W, Fritz W (1963) Rheol Acta 3:34
13. DIN 51562 (1983) Messung der kinematischen Viskosität mit dem Ubbelohde-Viskosimeter
14. ISO 3105 (1976) Glass capillary kinematic viscometers – specification and operating instructions
15. Peter S, Wagner E (1958) Z Phys Chem (Neue Folge) 17:184
16. Einfeldt J, Sändig R, Schmelzer N (1979) Exper Technik Physik 27:271
17. Wedlake GD, Vera HJ, Ratcliff GA (1979) Rev Sci Instrum 50:93
18. Beilsteins Handbuch d. organischen Chemie, 3. u. 4. E.W. Springer, Berlin Heidelberg New York

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