Error Analysis of the Oscillating Cup Method for Viscosity Measurements of Molten Salts

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The errors in viscosity measurements by the oscillating cup method were calculated as a function of the limit of accuracy imposed by the uncertainty in determining the constants of the oscillating system R, I, T_0, δ_0 and the limit of precision resulting from errors in determining the experimental parameters δ, T, h, ρ.

Thus, by evaluating the fractional error of each of the parameters and implicitly its distinct contribution to the total standard error, it was established that the “meniscus error” Δh, which is difficult to be controlled or avoided, represents the major source of imprecision of oscillating cup viscometers.

Key words: Viscosity; Molten Salts; Oscillating Cup Viscometer; Error Analysis.

1. Introduction

The reliability of viscosity measurements with an oscillating cup viscometer depends on the errors resulting from determining either of the constants of the oscillating system: R (the inner radius of the cup), I (the moment of inertia of the whole oscillating system), T_0 and δ_0 (the period of oscillation and the logarithmic decrement in the atmosphere), or of the experimental parameters: δ (the logarithmic decrement of the amplitude), T (the oscillating period of the filled cup), h (the height of the liquid column including the meniscus effect, Δh).

In the following, the discussion is focussed on the cylindrical oscillating cup viscometer method, which is claimed to be a very accurate method [1 – 4]. A typical cylindrical cup, with flat bottom and a lid, is illustrated in Fig. 1 together with the specific parameters R, h and Δh. More details on all parameters, the employed viscometer and the experimental procedure, are given in [4].

The present approach aims at establishing the specific contribution of all types of error mentioned above and at determining the range of variation over which the experimental viscosity data are the most reliable.

Such an error analysis is of real interest, especially as the viscosity data obtained by this method

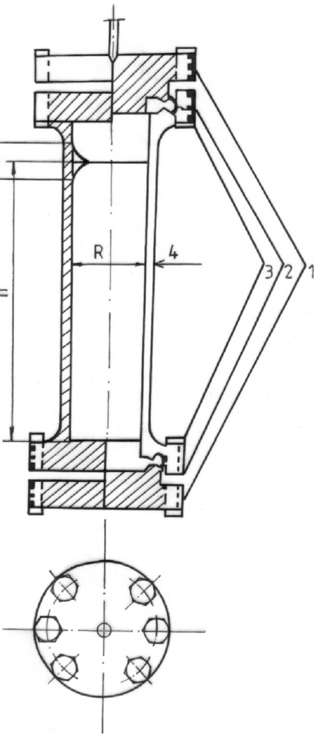

Fig. 1. Cylindrical cup: 1, lid; 2, platinum ring seals; 3, screws M6; 4, cylindrical cup; R, inner radius of the cup; h, height of the liquid; Δh, meniscus’s effect (both possibilities).

for molten KNO_3 and NaCl [1 – 4] differ within 2 – 8% with respect to those data obtained by other methods as part of the so-called "Molten Salts Standard Program" [5]. In fact this international program attempted to establish the "calibration quality data" for viscosity, and molten KNO_3 and NaCl were selected as "standard salts" for high temperature.

2. Working Equations

Based on the theoretical analysis of the oscillating body viscometer given by Kestin and Newell [6], several rigorous solutions or approximate working equations have been proposed for the oscillating cup viscometer. For the long size cylindrical cup, the general solution was given by Beckwith and Newell [7].

Presently, the absolute viscosity is calculated from the polynomial equation, as derived by Brockner et al. [8],

$$\frac{\pi\rho h R^4}{kI}[A(p-\Delta q)x^{-1} - Bx^{-2} + Cqx^{-3}] = 2\left(\Delta - \frac{\Delta_0}{\omega}\right), \tag{1}$$

which was adapted for carrying out the intended error analysis. Thus, by reordering all terms, multiplying them by x^3 and dividing them by m, the following more adequate formula is obtained:

$$x^3 - \left(4+\frac{R}{h}\right)\left(p - \frac{\delta}{4\pi\rho}\right)mx^2 + \left(6+\frac{16R}{\pi h}\right)mx - \left(\frac{3}{2}+\frac{9R}{h}\right)\frac{m}{2p} = 0, \tag{2}$$

where

$$m = \frac{\pi^2 \rho h R^4 T_0}{I(\delta T - \delta_0 T_0)}. \tag{3}$$

All symbols in (2) and (3) are already defined in Section 1, except for ρ which stands for the density of the melt and p and x which are given as

$$p = \frac{1}{\sqrt{2\left(\delta + \sqrt{1+\delta^2}\right)}}, \tag{4}$$

$$x = R\sqrt{\frac{2\pi\rho}{\eta T}}. \tag{5}$$

The viscosity is computed by solving (2) for x. Using a numerical method, the real positive roots are obtained and the viscosity η is expressed in Pa · s according to

$$\eta = \frac{1}{cx^2}, \tag{6}$$

where

$$c = \frac{T}{2\pi\rho R^2}. \tag{7}$$

3. Error Analysis

The fractional uncertainty of the measured viscosity is expressed as the sum of the derivatives of (6) with respect to the variables x and c:

$$\ln\eta = \ln c - 2\ln x, \tag{8}$$

$$\frac{\mathrm{d}\eta}{\eta} = -\frac{\mathrm{d}c}{c} - 2\left(\frac{\mathrm{d}x}{x}\right). \tag{9}$$

If the fractional uncertainty $\left(\frac{\mathrm{d}x}{x}\right)$ in the root x is also determined by summing up the derivatives of (2) with respect to x and m, this can be expressed as

$$\frac{\mathrm{d}x}{x} = \left[\frac{\left(4+\frac{R}{h}\right)\left(p-\frac{\delta}{4\pi p}\right)x^2 - \left(6+\frac{16R}{\pi h}\right) + \frac{\frac{3}{2}+\frac{9R}{h}}{2p}}{\frac{3x^3}{m} - 2\left(4+\frac{R}{h}\right)\left(p-\frac{\delta}{4\pi p}\right)x^2 + \left(6+\frac{16R}{\pi h}\right)x}\right] \cdot \left(\frac{\mathrm{d}m}{m}\right) = K\left(\frac{\mathrm{d}m}{m}\right). \tag{10}$$

Accordingly, (9) may be reformulated as follows:

$$\frac{\mathrm{d}\eta}{\eta} = -\frac{\mathrm{d}c}{c} - 2K\left(\frac{\mathrm{d}m}{m}\right), \tag{11}$$

where the fractional uncertainties $\left(\frac{\mathrm{d}c}{c}\right)$ in c and $\left(\frac{\mathrm{d}m}{m}\right)$ in m, calculated by summing up the derivatives of (7) and (3), are given as

$$\frac{\mathrm{d}c}{c} = \frac{\mathrm{d}T}{T} - \frac{\mathrm{d}p}{p} - 2\left(\frac{\mathrm{d}R}{R}\right) \tag{12}$$

and

$$\frac{\mathrm{d}m}{m} = \frac{\mathrm{d}\rho}{\rho} + \frac{\mathrm{d}h}{h} + 4\left(\frac{\mathrm{d}R}{R}\right) + \frac{\delta_0 T}{\Delta T_0 - \delta_0 T}\left(\frac{\mathrm{d}T}{T}\right) - \frac{\delta_0 T}{\Delta T_0 - \delta_0 T}\left(\frac{\mathrm{d}T_0}{T_0}\right) - \frac{\delta T_0}{\Delta T_0 - \delta_0 T}\left(\frac{\mathrm{d}\delta}{\delta}\right) - \frac{\mathrm{d}I}{I}. \tag{13}$$

If instead of the derivative symbol (d) the finite difference (Δ) is used, and taking into account that the absolute value of the relative error of a quantity equals the sum of the relative errors of the component terms, then on the basis of (9) – (13) the following equation for the absolute value of the relative error in the viscosity is obtained:

$$\begin{aligned}|\varepsilon_\eta| &= \left|\frac{\Delta\eta}{\eta}\right| \\ &= 2\left\{|4K-1|\left|\frac{\Delta R}{R}\right| + |K|\left|\frac{\Delta I}{I}\right| + \frac{|K|\delta_0 T}{\delta T_0 - \delta_0 T}\left|\frac{\Delta T_0}{T_0}\right|\right\} \\ &\quad + \left\{|2K-1|\left|\frac{\Delta\rho}{\rho}\right| + \left(1 + \frac{2|K|\delta_0 T}{\delta T_0 - \delta_0 T}\right)\left|\frac{\Delta T}{T}\right|\right. \\ &\quad \left. + 2|K|\left|\frac{\Delta h}{h}\right| + \frac{2|K|\delta T_0}{\delta T_0 - \delta_0 T}\left|\frac{\Delta\delta}{\delta}\right|\right\}. \end{aligned} \tag{14}$$

The absolute value of the relative error in the viscosity $|\varepsilon_\eta|$ can now be split into two terms: the limit of accuracy imposed by the uncertainty in determining the constants of the oscillating system and the limit of precision resulting from errors in determining the experimental parameters. Accordingly

$$|\varepsilon_\eta| = |Accuracy| + |Precision|, \tag{15}$$

where the $|Accuracy|$ is given by the first term in the big bracket on the right-hand side of (14) and the $|Precision|$ by the second term.

The error analysis of a single measurement as given by (14) and (15) is useful to understand what to do to obtain realistic viscosity data. However, any approach of an error analysis usually relies on the statistical analysis of the experimental data obtained in a single or in many experiments. Consequently, the quantities of (14) are now obtained by averaging the nQ measured values, and the "obtained average value" is expressed as $\bar{Q} = \frac{1}{n}\sum_{i=1}^{n} Q_i$.

On the other hand, if the Q values are normally distributed around the real value Q_0 with the uncertainty $|\Delta Q|$, then the expected standard deviation of $\bar{Q}$ is given as

$$\varepsilon_\eta^{(\mathrm{s})} = \left[\frac{1}{n_Q}\left|\frac{\Delta\bar{Q}}{Q}\right|^2\right]^{\frac{1}{2}}. \tag{16}$$

The above analysis does not apply to the errors in R or h, because the uncertainties ΔR and Δh originate in the measurement of different diameters and heights of the liquid column, and consequently they express an intrinsic fluctuation in "the shape" and "the filling in" of the cup which cannot be improved by the number of measurements.

Table 1. The uncertainty limits for various parameters.

	Experimental data	Uncertainty limits
Constants of the oscillating system	$R_{(298)} = 1.000$ cm	$\Delta R = \pm 3 \cdot 10^{-4}$ cm
	$I_{(298)} = 1165.13$ g cm^2	$\Delta I = \pm 5.9 \cdot 10^{-1}$ g cm^2
	$T_{0(298)} = 2.149615$ s	$\Delta T_0 = \pm 1 \cdot 10^{-6}$ s
Experimental parameters	δ	$\Delta\delta = \pm 5 \cdot 10^{-4}$
	T	$\Delta T = \pm 1 \cdot 10^{-3}$ s
	h	$\Delta h = \pm 1.5 \cdot 10^{-2}$ cm
	ρ	$\Delta\rho = 1.8 \cdot 10^{-4}$ g cm^{-2}

On the basis of all the above statements, the standard error may be defined as

$$\varepsilon_\eta^{(\mathrm{s})} = \left[\left(Accuracy^{(\mathrm{s})}\right)^2 + \left(Precision^{(\mathrm{s})}\right)^2\right]^{\frac{1}{2}} \tag{17}$$

with

$$\begin{aligned}|Accuracy^{(\mathrm{s})}| &= \left\{4\left[(4K-1)^2\left(\frac{\Delta R}{R}\right)^2 + K^2\left(\frac{\Delta I}{I}\right)^2\right.\right. \\ &\quad \left.\left. + \frac{K^2}{n_{T_0}}\left(\frac{\delta_0 T}{\delta T_0 - \delta_0 T}\right)^2\left(\frac{\Delta T_0}{T_0}\right)^2\right]\right\}^{\frac{1}{2}}, \end{aligned} \tag{18}$$

$$\begin{aligned}|Precision^{(\mathrm{s})}| &= \left[(2K-1)^2\left(\frac{\Delta\rho}{\rho}\right)\right. \\ &\quad + \frac{1}{n_T}\left(1 + \frac{2|K|\delta_0 T}{\delta T_0 - \delta_0 T}\right)^2\left(\frac{\Delta T}{T}\right) + 4K^2\left(\frac{\Delta h}{h}\right)^2 \\ &\quad \left. + \frac{4K^2}{n_\delta}\left(\frac{\delta T_0}{\delta T_0 - \delta_0 T}\right)^2\left(\frac{\Delta\delta}{\delta}\right)^2\right]^{\frac{1}{2}}. \end{aligned} \tag{19}$$

4. Discussion

The quantitative evaluation of the standard errors, as discussed above, was performed on the basis of the authors' own $\eta_{\mathrm{KNO_3}}$ and η_{NaCl} experimental data [4]. The characteristic constants of the oscillating system and the experimental parameters of interest, along with their uncertainty limits, are listed in Table 1.

Regarding the standard errors together with the corresponding fractional errors, calculated according to (17) – (19) they are summarized in Table 2. Because the estimated values of $\frac{\Delta\delta_0}{\delta_0}$ and $\frac{\Delta T_0}{T_0}$ are too small to alter the overall standard error, their contribution to the standard accuracy was neglected. In fact δ_0 and T_0

Table 2. Standard error, accuracy and precision for the viscosity of molten KNO_3 and NaCl.

Salt	T, K	$\varepsilon_\eta{}^{(s)}$, %	*Accuracy*$^{(s)}$, % according to (18)			*Precision*$^{(s)}$, % according to (19)				
			Total	Fractional error		Total	Fractional error			
				$c_1\left(\frac{\Delta R}{R}\right)^2$	$c_2\left(\frac{\Delta I}{I}\right)^2$		$c_3\left(\frac{\Delta \delta}{\delta}\right)^2$	$c_4\left(\frac{\Delta T}{T}\right)^2$	$c_5\left(\frac{\Delta \rho}{\rho}\right)^2$	$c_6\left(\frac{\Delta h}{h}\right)^2$
KNO_3	649.9	±0.39	±0.21	0.0316	0.0148	±0.33	0.00029	0.00001	0.0144	0.0948
	710.4	±0.39	±0.21	0.0316	0.0148	±0.32	0.00029	0.00001	0.0144	0.0936
	719.6	±0.39	±0.21	0.0313	0.0146	±0.32	0.00029	0.00001	0.0144	0.0924
NaCl	1151.5	±0.37	±0.20	0.0282	0.0125	±0.31	0.00025	0.00001	0.0121	0.0858
	1168.6	±0.37	±0.20	0.0282	0.0215	±0.31	0.00025	0.00001	0.0121	0.0852
	1183	±0.37	±0.20	0.0275	0.0125	±0.31	0.00026	0.00001	0.0121	0.0846

Table 3. Standard errors resulting from varying the parameters ΔR, ΔI, Δh.

Varying parameter		$\varepsilon_\eta{}^{(s)}$, %	*Accuracy*$^{(s)}$, %	*Precision*$^{(s)}$, %
$\Delta R =$	±1 μm	±0.33	±0.13	±0.31
	±2.5 μm	±0.37	±0.20	±0.31
	±5 μm	±0.48	±0.37	±0.31
$\Delta I =$	±0.57 g cm^2	±0.37	±0.20	±0.31
	±1.14 g cm^2	±0.41	±0.29	±0.31
	±2.28 g cm^2	±0.54	±0.45	±0.31
$\Delta h =$	±0.0142622 cm	±0.37	±0.20	±0.31
	±0.0292448 cm	±0.63	±0.20	±0.60
	±0.060948 cm	±1.21	±0.20	±1.20

were initially evaluated [4] to obtain the best possible values.

If the data in Table 2 are examined, one can immediately ascertain that the uncertainty in the characteristic constants of the viscometer, R and I, and in the experimental parameters, ρ and h, have an essential contribution to the corresponding maximum uncertainties, so that increasing the number of δ and T measurements ends up in no important improvement.

Since according to the above establishments a discussion on the reliability of any experiment should necessarily focus on the estimated uncertainties of the parameters R, I and h, Table 3 summarizes the standard errors resulting from varying their values within some arbitrary assigned limits. The discussion is arbitraryly focussed on an NaCl melt at 1168 K and may be extended to any other molten salt.

The analysis of data in Table 3 demonstrates beyond any doubt, that the main contribution to the standard error is given by the standard precision resulting from Δh. It is worth mentioning that the η_{KNO_3} and η_{NaCl} data employed in this analysis were obtained in the so-called "full-up cup", experimental conditions so as to avoid the Δh effect [4]. Consequently, most probably the Δh variation in Table 3 originates only in the variation of R and ρ as a function of the temperature. In fact, according to the data in Table 2, the density of the melt which is not an intrinsic parameter of the oscillating cup viscometer contributes significantly to decreasing the precision of the experimental data. At the same time, the standard precision is getting indirectly dependent on the constancy of the working temperature.

5. Conclusions

On the basis of the new error analysis it is established that the "meniscus error", Δh, is the major source of imprecision of oscillating cup viscometers. Moreover it is very difficult to control or avoid the meniscus variation of any molten salt.

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