

## **Oscillating-Cup Viscometry Over an Extended Viscosity and Temperature Range<sup>1</sup>**

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The viscosity of some ZrF<sub>4</sub>-based melts is presented and it is demonstrated that it is possible to perform reliable viscosity studies of these highly corrosive melts. Graphite crucibles have been utilized and corrections for the meniscus and the penetration into the crucible have been performed. A general discussion of oscillating-cup viscometry is given and it is shown that the present setup can be used for determination of viscosities in the range from 0.05 to above 500 mPa · s.

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**KEY WORDS:** hydrocarbons; molten salts; oils; viscosity; ZrF<sub>4</sub>.

### **1. INTRODUCTION**

The use of damped free oscillating cylinders for the determination of viscosity is an absolute method and calibration against standards is hence not necessary. High accuracy has been obtained by the use of an oscillating solid cylinder immersed in the liquid [1, 2] or a hollow cylindrical cup containing the liquid [3, 4]. The method is based on measurements of the damping of the oscillation as well as the change in the period due to friction exerted by the viscous fluid.

The mathematical procedure applied in the calculation of the viscosity is developed by Kestin and Newell [5] and Beckwith and Newell [6]. Grouvel and Kestin [7] have provided a review of the exact theory of the oscillating cup, and the exact solution was programmed on the computer to generate accurate values of the damping and period of the oscillation

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that would be encountered if measurements were performed under a variety of conditions.

Use of a solid cylinder is restricted to low-viscous fluids, as the damping in high-viscous fluids will easily be too high for reliable studies. A similar restriction does not apply to the use of a hollow cup. A hollow cup can also be made from materials like graphite, which opens up the possibility of measuring viscosities up to 2000°C.

The present paper gives viscosities of the highly corrosive  $ZrF_4$ -based melts. It also demonstrates the possibility of determining viscosities in the range 0.05 to 500 mPa · s.

## 2. EXPERIMENTS

### 2.1. Apparatus

The oscillating-cup viscometer has been described in detail by Tørklep and Øye [8]. The electronic and computer facilities have been changed and improved since the viscometer was developed, and these modifications have

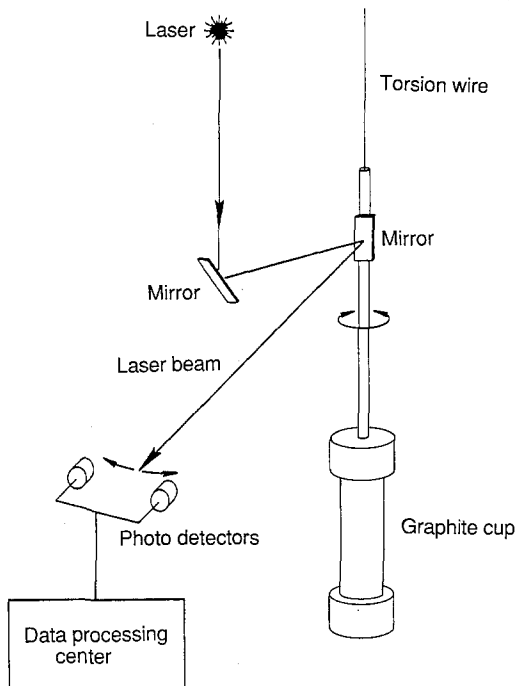
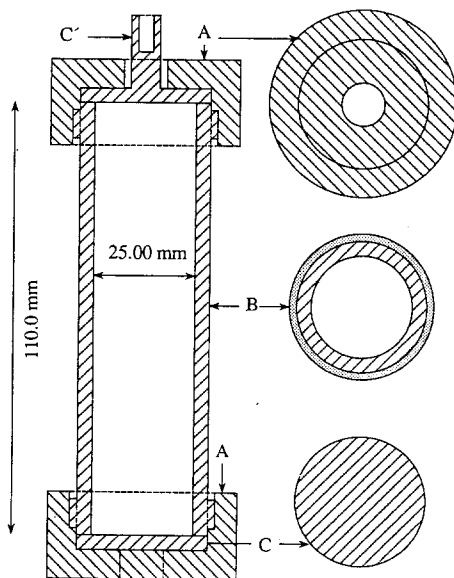


Fig. 1. Schematic arrangement of the viscometer.

been described by Berstad et al. [2]. A schematic arrangement of the viscometer is shown in Fig. 1. The experimental setup can basically be described as an oscillating cup containing the fluid under investigation. The cup could be a closed, fully filled cup or an open cup. The cup is attached to a torsion pendulum suspended from a torsion wire ( $\phi = 0.8$  mm, 92% Pt/8% W). A microprocessor-controlled initiator starts the oscillation of the pendulum. The oscillations are monitored by means of two fixed photodiodes placed in the path of a laser beam reflected from a mirror attached to the pendulum. The photodiodes are connected to an Apple IIe microcomputer, and the time intervals between each time the laser beam passes one of the detectors are recorded.

Two different cups were used in the present study. The cup shown in Fig. 2 ( $25.00 \pm 0.01$ -mm inner diameter, 110.0-mm internal length) was made of graphite (Graph-I-Tite G, Carborundum Co., USA). This cup was used for the measurements on the corrosive zirconium fluoride based melts. The nickel cup which is described by Brockner et al. [3] was used in the measurement of the viscosity of two synthetic oils.



**Fig. 2.** The graphite oscillating cup. (A) Outward lids with threads; (B) main cylindrical segments with threads on both ends; (C) bottom main lid; (C') upper main lid with threads for connection to the torsion pendulum.

**Table I.** Chemicals Used in the Viscosity Measurements

Chemical	Quality	Manufacturer
ZrF <sub>4</sub>	Window grade	BDH, England
BaF <sub>2</sub>	Fiber grade	BDH, England
LaF <sub>3</sub>	Fiber grade	BDH, England
NaF	p.a. 99.5%	E. Merck AG, Germany
Diffusion pump fluid 704		Dow Corning Inc., USA
Batch: XZ 2041505		
Brookfield standard viscosity Oil 490 cP		Brookfield Engineering Labs. Inc, MA, USA
N <sub>2</sub>	99.99%	Norsk Hydro, Norway

The temperature of the synthetic oils was measured using a platinum resistance thermometer which was calibrated against the melting point of water.

The furnace used for the high-temperature measurements has been described previously [8]. The temperature in the furnace was measured with a Pt/Pt10% Rh thermocouple placed 0.5 cm below the bottom of the cup. The thermocouple was calibrated against the melting points of pure Sn and Ag. The vertical temperature-gradient cup was controlled by a specially designed shunting unit [8]. A temperature gradient of 1–2°C over the cup, the upper part being hottest, was established to avoid thermal convection in the melt and condensation of fluorides above the liquid surface. For studies of the synthetic oils a double-walled thermostat was used.

The replacement of N<sub>2</sub> by the melt during the measurements requires a correction term which is calculated from Eq. (9). Density and viscosity data for N<sub>2</sub> are used. A further correction is required as the weight of the fluid sample will stretch the torsion wire [2]. The load coefficient ( $0.181 \times 10^{-5} \text{ cm}^2$ ) of the torsion wire used in this procedure is taken from previous studies with the same torsion wire.

The chemicals used in the measurements of the viscosity are listed in Table I.

## 2.2. Procedure

Preliminary experiments for each cup were performed at various temperatures to determine the period and damping of the empty cup in N<sub>2</sub>. The damping and period of the empty cups were fitted to a second- and third-order polynomial as functions of the temperature. The moments of inertia of the empty cups were measured using a procedure given by Berstad et al. [2].

Table II. Measured Damping and Reduced Period and Calculated Viscosity and Dimensionless Radius for Several Different Liquids at Various Temperatures

Liquid	Temp. (°C)	Damping $\Delta$	Reduced period $T/T_0$	Viscosity (mPa · s)		Dimension- less radius
				Real part	Imaginary part	
BaZr <sub>2</sub> F <sub>10</sub>	572.8	0.0978156	1.0241400		47.147	7.427
	588.4	0.0931407	1.0220632		39.208	8.125
	593.5	0.0921911	1.0214570		37.522	8.299
	617.0	0.0854684	1.0191634		29.295	9.358
	617.5	0.0854269	1.0189894		29.163	9.378
	659.5	0.0756664	1.0160391		20.295	11.17
	699.6	0.0679808	1.0138854		15.027	12.90
	741.5	0.0617330	1.0122574		11.589	14.59
	784.6	0.0565818	1.0109691		9.218	16.24
826.7	0.0526196	1.0098012		7.604	17.76	
Dow Corning diffusion pump oil	9.3	0.0242295	1.018957	103.4	104.5	2.355
	9.7	0.0245931	1.018918	101.6	102.6	2.376
	13.3	0.0306886	1.018044	75.26	75.67	2.762
	16.5	0.0345608	1.017260	61.76	62.05	3.046
	21.7	0.0393421	1.015783	45.91	15.81	3.533
	29.8	0.0423507	1.013425	30.64	25.36	4.311
	38.0	0.0416070	1.011428	21.56	21.21	5.162
	42.1	0.0402480	1.010404	17.67	17.41	5.687
	50.5	0.0379081	1.009157	13.46	13.28	6.487
	64.1	0.0340883	1.007618	9.106	8.992	7.835
	77.3	0.0308539	1.006559	6.634	6.535	9.138
Brookfield standard oil 490 cP	20.1	0.0042429	1.018003	446.7	523.2	0.997
	26.7	0.0048079	1.017995	417.5	459.2	1.061
	28.6	0.0049782	1.017991	402.9	442.8	1.080
	31.5	0.0053485	1.017992	404.1	411.0	1.119
	32.4	0.0053910	1.017990	397.6	407.5	1.124
	50.5	0.0073582	1.017939	294.2	293.0	1.314
	98.1	0.0143266	1.017615	143.7	139.9	1.858
	123.0	0.0188886	1.017259	102.5	100.2	2.169
	146.5	0.0234737	1.016760	76.47	74.93	2.478
0.5AlCl <sub>3</sub> -0.4NaCl- 0.1LiCl [11]	110.2	0.0413971	1.0083311		6.128	12.01
	120.0	0.0393042	1.007795		5.343	12.83
	136.8	0.0361646	1.007018		4.306	14.23
	151.9	0.0339251	1.006490		3.659	15.39
	165.7	0.0320238	1.006060		3.167	16.48
	180.4	0.0303835	1.005692		2.777	17.54
	200.0	0.0283916	1.005277		2.351	18.98
	220.4	0.0267447	1.004929		2.030	20.32
	240.1	0.0254188	1.004647		1.792	21.53
	260.7	0.0240509	1.004373		1.567	22.91
	282.7	0.0230078	1.004132		1.406	24.07
	302.9	0.0220129	1.003955		1.262	25.28

Table II. (Continued)

Liquid	Temp. (°C)	Damping $\Delta$	Reduced period $T/T_0$	Viscosity (mPa · s)		Dimension- less radius
				Real part	Imaginary part	
<i>n</i> -Tetradecane [4]	19.8	0.0194684	1.003909		2.313	41.96
	40.6	0.0163881	1.003161		1.549	50.81
	60.1	0.0142456	1.002633		1.135	58.87
	80.3	0.0125203	1.002284		0.860	67.02
	124.0	0.0098849	1.001775		0.529	83.80
	151.0	0.0087369	1.001554		0.414	93.58
84.7 mol% methane, 15.3 mol% <i>n</i> -decane [10]	19.93	0.0009906	1.000052		0.1100	172.4
	26.26	0.0009581	1.000044		0.1043	175.7
	34.97	0.0009391	0.999979		0.1003	179.0
	43.52	0.0009001	1.000030		0.0937	183.4
	61.82	0.0008306	1.000019		0.0822	192.3
	80.95	0.0007642	1.000005		0.0728	199.5
	102.25	0.0006791	0.999993		0.0619	208.0
	126.16	0.0006201	0.999976		0.0546	214.8
	150.51	0.0005935	0.999970		0.0511	219.3

Weighed amounts of crushed fluorides were transferred to the graphite cup in a glovebox under  $N_2$  atmosphere. The closed cup was attached to the pendulum and the furnace evacuated to  $\sim 10^{-4}$  Torr and refilled with  $N_2$  before heating the assembly. The viscosity measurements were carried out in a stream of  $N_2$ . To achieve steady state in the viscometer, the experiments were performed no less than 3–4 h after the temperature was altered. Temperature changes were less than  $0.1^\circ\text{C}$  during the time required for the five measurements carried out at each temperature. The cup was finally weighed to determine the weight loss after each experiment. The density of the fluoride melt has been measured in the author's laboratory and is found to be

$$\rho = 4.718 - 1.245 \times 10^{-3} t \text{ (g} \cdot \text{cm}^{-3}\text{)}$$

where  $t$  is given in  $^\circ\text{C}$ . For the synthetic oil studies the nickel cup was carefully filled with weighed amounts to avoid formation of bubbles. The cup was filled up to a liquid level of only about 10–11 cm. The exact liquid height was calculated from the density of the oils given by the manufacturers.

### 3. CALCULATION OF THE VISCOSITY

The mathematical procedure applied in the calculation of the viscosity has been developed by Kestin and Newell [5] and Beckwith and Newell [6]. The exact theory of the oscillating cup is briefly recapitulated in the following section.

The fundamental equation for a damped harmonic oscillation is given by

$$\alpha(t) = \alpha_0 \exp(-\Delta\omega t) \sin(\omega t) \quad (1)$$

and the second-order differential equation describing the oscillation as a function of the dimensionless time  $\tau$ , equal to  $\omega_0 t$ , is given by

$$I\omega_0^2 \left[ \frac{d^2\alpha}{d\tau^2}(\tau) + 2\Delta_0 \frac{d\alpha}{d\tau}(\tau) + (1 + \Delta_0^2) \alpha(\tau) \right] = M(\tau) \quad (2)$$

where

$\alpha$  = angular deflection

$\alpha_0$  = constant

$\omega = 2\pi/T$

$\omega_0 = 2\pi/T_0$

$T$  = period

$T_0$  = period of the empty cup

$\Delta$  = decrement

$\Delta_0$  = decrement of the empty cup

$M(\tau)$  = torque friction

$I$  = total moment of inertia of oscillating mechanical systems

The torque friction can be expressed as

$$M(\tau) = \rho v \int_{\Sigma} r \frac{\partial V}{\partial n} \mathbf{n} \, d\sigma \quad (3)$$

where  $\Sigma$  denotes the wetted boundary surface,  $\partial V/\partial n$  is the velocity gradient along the normal  $\mathbf{n}$  to the boundary, and  $t$  is the distance from the axis of rotation.  $v$  is the kinematic viscosity ( $v = \eta/\rho$ ), where  $\rho$  is the density

of the fluid. The solution of the differential Eq. (2) in the Laplace plane is given by

$$(S + A_0)^2 + 1 + D(S) = 0 \quad (4)$$

where  $D(S)$  is the Laplace transform of the friction torque  $M(\tau)$ , and the complex frequency of the oscillation is defined by

$$S = T_0/T(-A \pm i) \quad (5)$$

The mathematical solution of Eqs. (2) and (4) describes exactly the Laplace transform  $D(S)$  of the torque friction  $M(\tau)$ . Kestin and Newell [5] gave exact solutions of  $D(S)$  for a hollow cylinder. One of them is

$$D(S) = S^2 \frac{I'}{I} \left( 1 - 8S \sum_{j=1}^{\infty} \left[ \frac{1 - \tanh S_{\mu_j} z_0}{S_{\mu_j} z_0} \right] \frac{1}{\mu_j^2 S_{\mu_j}^2} \right) \quad (6)$$

Here  $\mu_j$  denotes the  $j$ th zero of the Bessel function  $J_1$ .  $S_{\mu_j}$  is defined by

$$S_{\mu_j}^2 = \mu_j^2 / \zeta_0^2 + S \quad (7)$$

where  $\zeta_0 = R/(v/\omega_0)^{1/2}$  and  $z_0 = z/(v/\omega_0)^{1/2}$  are dimensionless length variables for the cup radius and liquid height, respectively, reduced by the boundary layer thickness  $(v/\omega_0)^{1/2}$ .  $I'$  represents the moment of inertia of the fluid inside the cup,

$$I' = \frac{1}{2} \rho z R^4 \quad (8)$$

Equation (4) can now be written explicitly as follows:

$$(S + A_0)^2 + 1 + S^2 \frac{I'}{I} \left( 1 - 8S \sum_{j=1}^{\infty} \left[ \frac{1 - \tanh S_{\mu_j} z_0}{S_{\mu_j} \zeta_0} \right] \frac{1}{\mu_j^2 S_{\mu_j}^2} \right) = 0 \quad (9)$$

Beckwith and Newell [6] have provided an approximate solution of the Laplace transform  $D(s)$  for a hollow cylinder when  $\zeta_0$  and  $z_0 \gg 1$ :

$$D(S) = S^2 \frac{I'}{I} \left( \frac{4}{S^{1/2} \zeta_0} - \frac{6}{S \zeta_0^2} + \frac{3}{2S^{3/2} \zeta_0^3} + \frac{3}{2S^2 \zeta_0^4} \right. \\ \left. + \frac{1}{S^{1/2} z_0} - \frac{16}{\pi S \zeta_0 z_0} - \frac{9}{S^{3/2} \zeta_0 z_0} - \frac{8}{S^2 \zeta_0 z_0} - \frac{\exp[-2S^{1/2} z_0]}{2S^{1/2} z_0} \right) \quad (10)$$

This approximate solution neglecting the exponential term when  $\zeta_0$  and  $z_0 > 10$  has been introduced in the working equations applied in previous studies in the authors' laboratory [1-4, 10, 11].



The exact solution Eq. (9) constitutes two equations. The real and imaginary part must both be equal to zero. These two relations formally allow the calculation of the values of  $\rho$  and  $\eta$  from the values of  $T$  and  $\Delta$ , together with the values of  $T_0$  and  $\Delta_0$  of the empty cup. In addition, the moment of inertia  $I$  of the empty cup as well as  $R$  has to be known.

The liquid height  $z$  in the cup must also be known in order to calculate the viscosity and density. However, a partially filled cup is used in the present work, and the liquid height can be obtained only by knowing the liquid density.

Since the density of the studied liquid has to be known when a partially filled cup is used, the real and imaginary parts of Eq. (9) are now two independent equations from which the viscosity can be calculated. For the same measurement, they should yield the same value for the viscosity. For our previous determination of water viscosity [2], which was carried out with extreme care, the two values differed only by 0.01% as pointed out by Tørklep [11] in this issue.

The real and imaginary part of Eq. (9) can be calculated with the aid of a computer program by iterative methods. It turns out that the viscosity obtained from the real part is sensitive to the values of  $T/T_0$  and, to a lesser degree, to the value of  $\Delta$ . Similarly, the viscosity obtained from the imaginary part is sensitive to  $\Delta$  and, to a smaller degree, to  $T/T_0$  [7].

A computer program written in FORTRAN given by Grouvel [12] was used for the iterative solution of both the real and the imaginary part of Eq. (9). The program was slightly modified from the original version given by Grouvel. The Bessel function  $J_1$  in Eq. (9) is replaced by a subroutine allowing the summation to  $j=200$ :

$$J_{1,j} = \beta \left( 1 - \frac{3x}{8} + \frac{3x^2}{128} - \frac{1179x^3}{5120} + \frac{1951209x^4}{1146880} + \dots \right) \quad (11)$$

where  $\beta = (j + 1/4)\pi$  and  $x = \beta^{-2}$ . The modified version of the program also included the polynomials describing the period and the damping of the empty cup and the density of the studied liquid as a function of the temperature.

Figure 3 shows the approximate solution [4, 10] and the exact solution [9] of the viscosity equation for the measurements on the Dow Corning diffusion-pump fluid. Corresponding viscosities obtained by the use of an oscillating solid cylinder are also shown in the figure. The values are given as functions of the dimensionless radius  $\zeta_0$ . For viscosities lower than 15 mPa · s and  $\zeta_0 > 5.5$ , the approximate and exact solution gives the same value for both the imaginary and the real part. The imaginary part of the approximate solution deviates at higher viscosities, while the

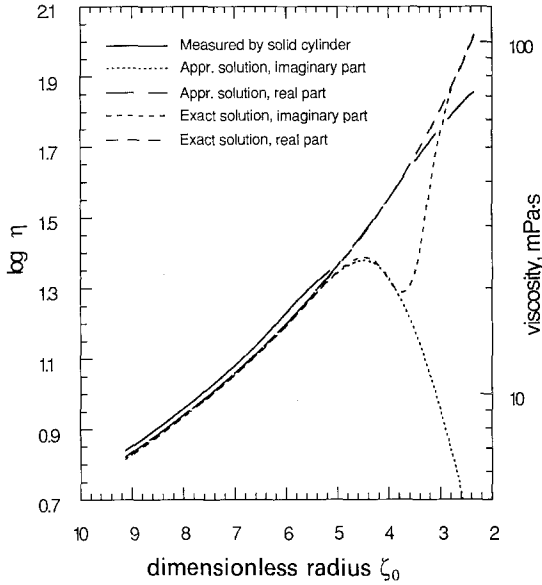


Fig. 3. Viscosity (in mPa·s) of the Dow Corning diffusion pump fluid.

approximate real solution does not deviate until above 30 mPa·s and  $\zeta_0 < 4.2$ . The real part of the exact solution gives correct answers over the whole intermediate region between the “large” and the “small” cup regions defined by  $2 < \zeta_0 < 7$ . The exact imaginary solution deviates as expected in the region when the damping is insensitive to the viscosity (see later) but becomes equal to the real part solution for viscosities above 75 mPa·s and  $\zeta_0 < 2.5$ .

Viscosity determination of elevated temperatures must take into account the thermal expansion of the crucible. The thermal expansion  $a$  of the empty cup is directly measured by the temperature  $t$  (°C) dependence of the period  $T_0$  and is given by

$$a = (l_0 + \Delta l)/l_0 = T_0/T_{00} \quad (12)$$

where  $l_0$  denotes the length at room temperature and  $T_{00}$  is the period at room temperature. The thermal expansion influences several of the parameters in Eq. (9). The radius  $r_t$ , the liquid level  $z_t$ , and the moment of inertia  $I_t$  of the empty cup at temperature  $t$  were calculated in the modified program by the following equations:

$$r_t = ar_0 \quad (13)$$

$$z_t = \frac{m}{\rho_t \pi \cdot r_t^2} \quad (14)$$

$$I_t = a^2 I_0 \quad (15)$$

where  $I_0$  is the moment of inertia of the cup at room temperature,  $r_0$  the radius at room temperature, and  $m$  the mass of the liquid sample being studied.

#### 4. VISCOSITY OF ZrF<sub>4</sub>-BASED MELTS

In the study of the highly corrosive ZrF<sub>4</sub>-based melts a graphite crucible was used. This crucible could be used in spite of a meniscus effect and in spite of that some of the melt penetrated into the graphite. The basis for the latter correction was simultaneous use of both the imaginary and the real viscosity solutions.

Several new procedures, by the use of the correction terms given below for the meniscus effect and the penetration of melt into the pores of the graphite cup, were applied most conveniently by using Grouvel's program [12], although the approximate solution given by Kestin and Newell [5] could have been used for the measurements of the molten fluoride mixtures.

The use of graphite sets no restriction to temperature up to 2000°C as long as the atmosphere is not oxidizing. However, the vapor pressure above the liquid specimen should not exceed 0.8 atm.

##### 4.1. The Meniscus Effect

Equation (9) is based on the assumption that the liquid surface makes an exact 90° angle with the wall of the oscillating cup. Brockner et al. [3] reported that measurements carried out with different liquid heights showed an increase in the calculated viscosity with decreasing liquid height. This effect was due to a curvature of the surface caused by the surface tension and wetting conditions. This "meniscus" effect can be bypassed by completely filling the cup, but it appears to be impossible to devise a method to fill the cup completely with molten salts.

Experiments with varying amounts of liquid were performed in the system NaZrF<sub>5</sub> to check the meniscus effect in a graphite cup with a fluoride melt. The calculations were performed with a correction term in Eq. (14) given by

$$z'_t = \frac{m}{\rho_t \pi r_t^2} + h \quad (17)$$

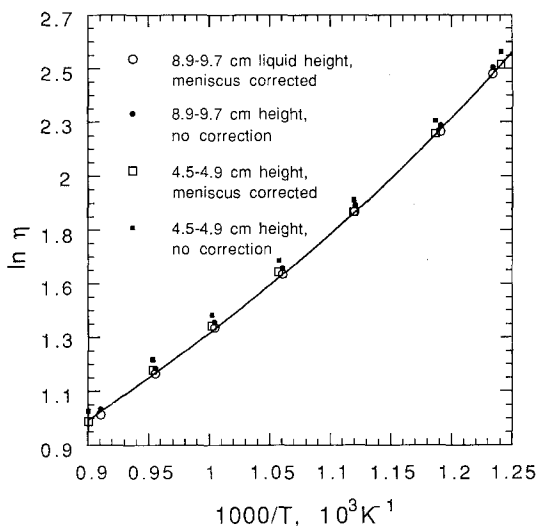


Fig. 4. Viscosity (in mPa · s) of molten NaZrF<sub>5</sub> measured at two different liquid levels for verification of the meniscus effect.

where  $h$  is the additional height due to the meniscus effect. The results are shown in Fig. 4. The calculated viscosities from two experiments with different liquid levels did not deviate more than 0.5% with  $h = 1.0$  mm. This meniscus correction is similar in magnitude to the value given by Brockner et al. [3]. This value for  $h$  was used for the meniscus correction to the calculated viscosity of all fluoride mixtures. The corrections due to the meniscus effect were in the range from  $-2.0$  to  $-6.5\%$  for these measurements, depending on the liquid height.

#### 4.2. Penetration of Melt in the Graphite Cup

The graphite material used in this study has a density of  $1.89 \text{ g} \cdot \text{cm}^{-3}$ . The theoretical density is  $2.28 \text{ g} \cdot \text{cm}^{-3}$ , and the porosity resulted in a variation of the calculated viscosity. The viscosity calculated from the real and imaginary part of Eq. (9) showed discrepancies (in the range 0–10%) increasing with experimental time. The real part of Eq. (9), sensitive to changes in the period of the cup, gave a higher viscosity than the imaginary part, sensitive to perturbations of the damping. A reasonable explanation for this disturbance is penetration of the melt into the pores of the graphite cup, which was in fact observed during measurements of the viscosity of water using the graphite cup.

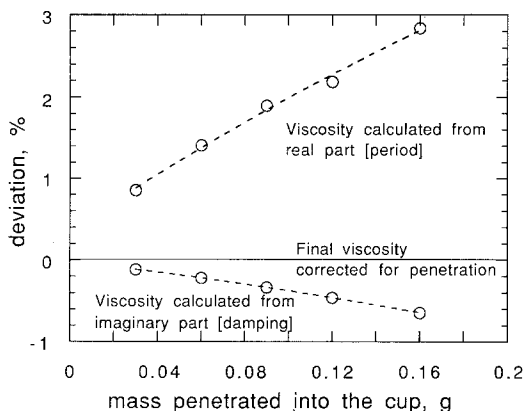
Such a phenomenon causes changes in the period and the moment of inertia of the "empty" cup together with a decrease in the liquid level and further decrease in the measured damping. A satisfactory agreement between the two calculated viscosities was achieved by the following equations:

$$I_t(p) = I_t + \Delta m(r + \Delta r)^2 \quad (18)$$

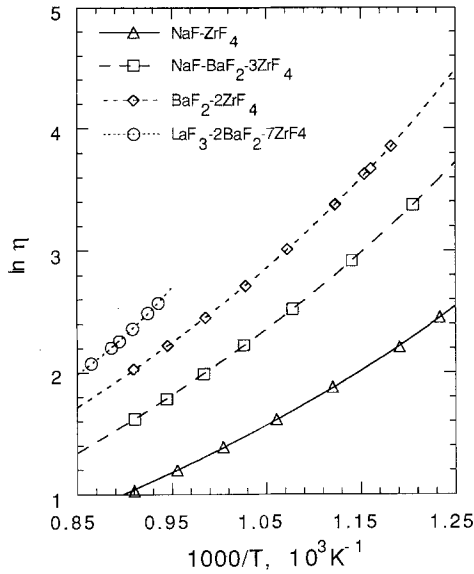
$$T(p) = T \sqrt{\frac{I_t}{I_t(p)}} \quad (19)$$

$$z_t(p) = \frac{m - \Delta m}{\rho_t} \frac{1}{\pi r_t^2} + h \quad (20)$$

where  $p$  denotes penetration of melt with weight  $\Delta m$  at a distance  $\Delta r$  into the cup wall. The melt was arbitrarily assumed to be at an average distance of 0.02 cm from the inside wall of the cup. The  $\Delta m$  values was then allowed to vary freely until the solutions of the imaginary and real parts of Eq. (9) were within 0.5% agreement. Figure 5 illustrates the correction procedure for the penetration phenomenon. The correction is shown to be proportional to the calculated amount of melt penetrated into the wall of the graphite cup. The corrections due to the penetration were in the range from



**Fig. 5.** Illustration of the correction terms for the penetration of the fluoride melts into the graphite oscillating cup. The deviation of the real and imaginary solution from the corrected value is shown as a function of the amount of melt penetrated into the cup. The amount of melt penetrated increased with increased total experimental time at temperatures above the melting point of the salt mixture.



**Fig. 6.** Viscosity (in mPa·s) of some zirconium fluoride-based melts measured using a graphite oscillating cup.

**Table III.** Error Table Giving Computer Calculated Effects on the Viscosity of  $\text{BaZr}_2\text{F}_{10}$  at  $577.8^\circ\text{C}$ : All Increments of the Parameters are Positive

Parameter	Estimated absolute error	Relative error (%)	Change in viscosity, $\Delta\eta$ (%)
Period in $\text{N}_2$	$2 \mu\text{s}$	0.0001	0
Damping in $\text{N}_2$	$1 \times 10^{-5}$	0.85	-0.038
Period	$50 \mu\text{s}$	0.003	-0.004
Damping	$1 \times 10^{-5}$	0.01	0.038
Cup radius	0.005 cm	0.4	-2.142
Liquid density	$0.01 \text{ g} \cdot \text{cm}^{-3}$	0.25	0.216
Moment of inertia	$0.5 \text{ g} \cdot \text{cm}^2$	0.08	0.288
Temperature	$0.5^\circ\text{C}$		-0.015
Meniscus cor.	0.02 cm	0.5	-1.512
Melt penetration	0.1 g		0.481
Sample weight	0.1 g	0.11	-0.386
Total standard deviation $[\sum (\Delta\eta)^2]^{1/2}$			2.72

0 to +6% depending on the temperature, composition, and time of the measurements.

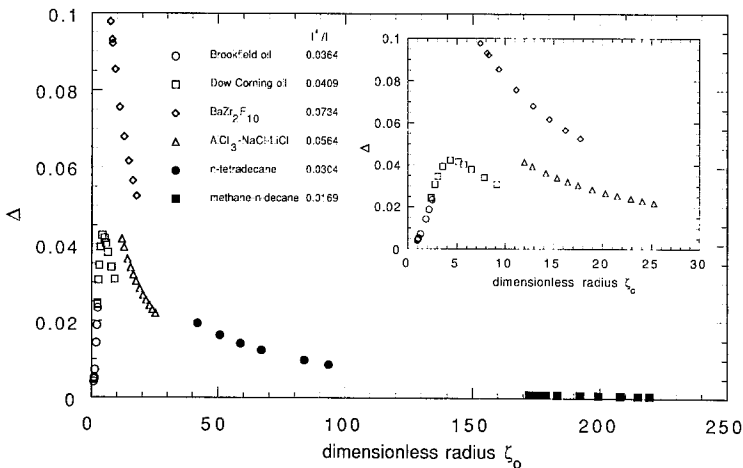
Some viscosity values for some molten ZrF<sub>4</sub>-based mixtures [13] are shown in Fig. 6. Estimated standard deviations in the employed parameters and the corresponding effects on the viscosity using Eq. (9) are given in Table III. The error table is calculated for viscosities in the higher range of the systems studied.

### 5. DAMPING AND TIME OF SWING AS A FUNCTION OF $\zeta_0$

It was expected that the viscosity of the ZrF<sub>4</sub>-based melt was so high that the dimensionless radius reduced by the boundary layer thickness becomes

$$\zeta_0 = R \sqrt{\frac{\rho 2\pi}{\eta T_0}} \approx 4.5$$

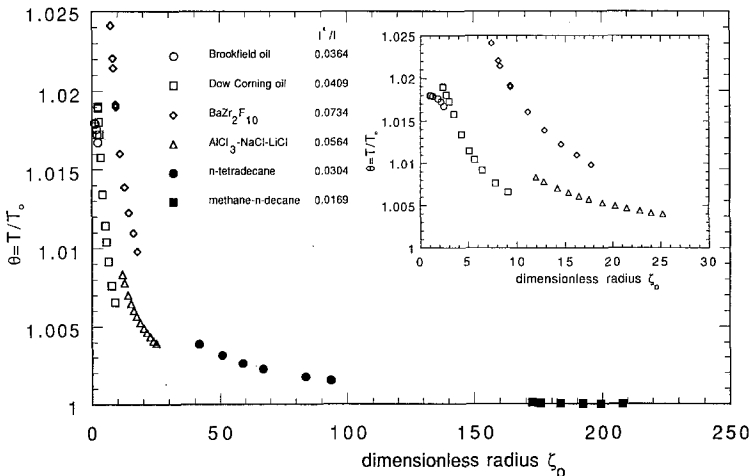
At this value the damping becomes insensitive to the viscosity [7]. For the fluoride melts, however,  $\zeta_0 > 7$ . But in order to test experimentally the calculation of Grouvel and Kestin [7] and also demonstrate the potentials of the present viscometer, a study of two synthetic oils was carried out. The results are given in Table II together with some earlier studies of



**Fig. 7.** Measured values for the damping as a function of the dimensionless radius  $\zeta_0$  for several different liquids. The ratio  $I'/I$  for each liquid is given in the figure. The ratio  $z/R$  is not constant in the plot and is  $\sim 4$  for the two liquids with low viscosities and BaZr<sub>2</sub>F<sub>10</sub> and  $\sim 7-8$  for the other.

low-viscous melts: methane-*n*-decane [12], *n*-tetradecane [4], and  $\text{AlCl}_3\text{-NaCl-LiCl}$  [14]. The viscosity of  $\text{BaZr}_2\text{F}_{10}$  is also presented. The oil studies were carried out only to illustrate the relationship between  $\Delta$ ,  $T/T_0$  versus  $\zeta_0$ , and no error analysis has been performed. The results are shown in Figs. 7 and 8 as functions of the dimensionless radius  $\zeta_0$ . The ratios  $I'/I$  and  $R/z$  are not constant in the figures. It is seen that the theoretical curves calculated by Grouvel and Kestin [7] are well reproduced by the experimental results. For  $\zeta_0$  around 4.5 the damping is independent of viscosity, while the ratio  $T/T_0$  becomes insensitive to the viscosity for  $\zeta_0 < 2$ . This is evident both in the theoretical curves reported by Grouvel and Kestin [7] and in the experimental observations.

Figures 7 and 8 illustrate the capabilities of the oscillational viscometer. With careful measurements the errors in  $\Delta$  and  $T/T_0$  can be as low as  $2 \times 10^{-6}$  and  $7 \times 10^{-6}$ , respectively [10]. It has then been possible to measure viscosities as low as 0.05 mPa·s with satisfactory accuracy [12]. Generally the damping will be most sensitive to the viscosity except when  $\zeta_0$  is around 4.5. In the low-viscosity range  $T/T_0$  varies too little with the viscosity to be useful for viscosity determination. However, in the more intermediate viscosity range 5–50 mPa·s, the viscosity can be reliably determined from both  $\Delta$  and  $T/T_0$  and reliable viscosities have been obtained up to 500 mPa·s.



**Fig. 8.** Measured values for the reduced period as a function of the dimensionless radius for several different liquids. The ratio  $I'/I$  for each liquid is given in the figure. The ratio  $z/R$  is not constant in the plot and is  $\sim 4$  for the two liquids with low viscosities and  $\text{BaZr}_2\text{F}_{10}$  and  $\sim 7\text{--}8$  for the other.



The measurable viscosity range can be expanded by changing the design of the viscometer. The relations between the design of the oscillating assembly and the density and viscosity are factors that should be considered in optimizing the measurements for each type of liquid under investigation. The parameters which can be varied are listed below:

- spring constant of the torsion wire,
- radius of the oscillating cup,
- height-to-radius ratio, and
- ratio  $I'/I$ .

The spring constant of the torsion wire can be increased by increasing the diameter of the wire. The wire can also be made from other metals or alloys with higher stiffness. Different types of wires and different diameters have been successfully applied in the authors' laboratory. Decreasing period of the oscillations and increase in  $A_0$  with increasing spring constant are the important consequences.

By increasing the radius of the cup, the period of the oscillation is decreased and the magnitude of the damping is increased. Higher viscosities can be measured with increased radius combined with a larger spring constant of the torsion wire. The viscosity span might be 5 decades, from 0.05 mPa·s to 5 Pa·s by minor changes in the design of the viscometry. By reducing the period to one-half and increasing the cup radius to the double compared to the present setup, a viscosity of 5 Pa·s would give a dimensionless radius of 1, comparable to the viscosity of 500 mPa·s in Table II. It may be possible to measure viscosities as high as 50 Pa·s with a complete redesign.

The ratio  $I'/I$  between the moment of inertia of the empty oscillating assembly ( $I$ ) and the moment of inertia of the liquid ( $I'$ ) is increased by reducing the total weight of the cup material. The sensitivity of both the period and the damping is increased with increasing  $I'/I$  as shown in Figs. 7 and 8.  $I'/I$  is increased by decreasing the density of the cup material or by decreasing the thickness of the walls of the cup.

With a proper design, the oscillating-cup viscometer has the features of large viscosity and temperature ranges, combined with the possibility to measure noncorrosive liquids at high vapor pressures.

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