A MEMS Vibrating Edge Supported Plate for the Simultaneous Measurement of Density and Viscosity: Results for Nitrogen, Methylbenzene, Water, 1-Propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd, and Polydimethylsiloxane and Four Certified Reference Materials with Viscosities in the Range (0.038 to 275) mPa·s and Densities between (408 and 1834) kg·m^{-3} at Temperatures from (313 to 373) K and Pressures up to 60 MPa

Anthony R. H. Goodwin,* Claire V. Jakeways, and Maria Manrique de Lara

Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, CB3 0EL, United Kingdom

The complex resonance frequency of a vibrating edge supported plate fabricated by the methods of MicroElectroMechanical Systems (MEMS) has been described by Goodwin et al. (*J. Chem. Eng. Data* **2006**, *51*, 190−208) and can be used to determine the density and viscosity of fluids. Working equations are required to relate the measured and desired quantities. In this article, two decoupled equations are used: one for density, the other for viscosity. For density, two expressions were evaluated. The first has been reported by Harrison et al. (*Proc. SPIE* **2006***, 6111*, 61110D) and contains three adjustable parameters, while the second is a purely empirical expression with two coefficients. For viscosity, the expression reported by Goodwin et al. (*J. Chem. Eng. Data* **2006**, *51*, 190−208) was used. The complex resonance frequency was measured for nitrogen, methylbenzene, water, 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd, polydimethylsiloxane, and four certified reference materials at temperatures between (313 and 373) K and pressures up to 60 MPa where the fluid viscosity is known to vary from (0.038 to 275) mPa·s and the densities cover the range (408 to 1834) kg·m^{-3}. The unknown parameters in the semiempirical working equations were determined by calibration. The empirical expression for density with adjustable parameters determined solely with measurements on methylbenzene provided estimates of density within ± 2 % at viscosities between (0.1 and 100) mPa·s. The viscosities were found to differ by less ± 30 % from the accepted values when the coefficient was determined with methylbenzene.

Introduction

Petroleum reservoir fluids have densities in the range (300 to 1300) kg·m^{-3} and viscosities from 0.05 mPa·s, for natural gas, to 10^4 mPa·s for heavy oil.[1] For recoverable conventional and Newtonian hydrocarbon liquids, the density is often within the range (700 to 1000) kg·m^{-3}, while the viscosity is between (0.5 and 100) mPa·s.[2–5] To perform value and exploitation calculations with sufficient rigor, the petroleum industry requires measurements of density and viscosity with overall uncertainty of 1 % and 10 %, respectively.[6]

In a previous article,[6] an edge supported vibrating plate was described for the measurement of density and viscosity. The transducer was fabricated by the methods of MicroElectroMechanical Systems (MEMS). The measured complex resonance frequency was combined with a semiempirical model to determine density and viscosity. The model was validated in ref 6 by exposing the MEMS to methylbenzene and octane with densities between (619 and 890) kg·m^{-3} and viscosities in the range of (0.205 to 0.711) mPa·s and in ref 7 by immersion in argon at densities between (79 and 767) kg·m^{-3} and viscosities in the range (26 to 57) μPa·s. In refs 6 and 7, the coefficients of the working equations were determined with methylbenzene and argon, respectively. Harrison et al.[8] reported measurements with the MEMS immersed in fluids with viscosities between (0.4 and 100) mPa·s at densities in the range (600 to 1500) kg·m^{-3} and introduced alternative working equations. The measurements reported here for fluids with viscosity between (0.038 and 275) mPa·s and densities in the range (408 to 1834) kg·m^{-3} at temperatures between (313 and 373) K and pressures up to 60 MPa were used to evaluate the published models and propose a further working equation for the determination of density from the measured resonance frequency.

Working Equations

The response of an edge supported plate immersed in a fluid has been discussed in the literature[6,9–24] with the majority of the semiempirical models arising from consideration of an added mass and a damping coefficient.[11,12,14–21,25–27] The model reported in ref 6 was based on the response of an elastic solid plate in an inviscid fluid and is similar to the approach reported by Cumberbatch[28] and Cumberbatch and Fitt.[29] Working equations based on the Navier−Stokes equations have been reported[30–32] but will not be used in this work.

Cantilever beams, exposed to air, have been used to actuate and detect the motion of a sphere immersed in a fluid[33–35] and the response of the coupled cantilever and sphere interpreted with adaptations of an expression presented by Landau and Lifshitz.[36] The working equations proposed by Harrison et al.[8] were obtained from these concepts so that the density can be approximated by the relationship

---

* To whom correspondence should be addressed. Present address: Schlumberger, 125 Industrial Blvd, Sugar Land, TX 77478. Tel.: +1 281 285 4962. Fax: +1 281 285 8071. E-mail: agoodwin@slb.com.

10.1021/je700675h CCC: $40.75

$$\rho \approx \frac{C_1}{f^2} - \frac{C_2}{f^2}\left(\frac{\eta}{\rho 2\pi f}\right)^{1/2} - \frac{C_3}{f^2}\left(\frac{\eta}{\rho 2\pi f}\right) \qquad (1)$$

In eq 1, ρ and η are the fluid density and viscosity, respectively, f the measured frequency, and C_1, C_2, and C_3 coefficients determined by calibration. Equation 1, which includes the ratio of viscosity to density, was derived assuming the sphere radius was much greater than the viscous skin-depth.

In both refs 6 and 8, the viscosity was determined from

$$\eta = \frac{C_4}{\rho f^3}\left\{\frac{2g}{f} - \frac{2g(p=0)}{f(p=0)}\right\}^2 \qquad (2)$$

providing a second equation relating the product of density and viscosity. In eq 2, $f(p = 0)$ is the resonance frequency in a vacuum, g the resonance half-line width when the MEMS is immersed in a fluid, $g(p = 0)$ the value obtained in a vacuum, ρ the fluid density, and C_4 a constant determined by calibration. The constant of proportionality in eq 2 includes the effective area of the plate. Equations 1 and 2 and eq 26 of ref 6 have been used in this work.

The C_i of eqs 1 and 2 include the elastic properties, density, and dimensions of the plate that are all assumed to be constant. For the purpose of distinguishing between the functional forms of the working equations, these assumptions are insignificant.[6,7]

Other workers[37–41] have considered the vibration of a plate immersed in fluid as a function of separation from a stationary solid object. The results reported in refs 40 and 42 suggest the resonance frequency is affected when the oscillator of dimensions about 1 mm is separated from the solid object by less than 1 mm; these results are consistent with both our preliminary measurements[42] and the calculations of Green and Sader.[43] The plate used in this work was separated from the nearest object by more than 1 mm.

Apparatus and Experimental Procedures

The design, fabrication, and packaging of the MEMS vibrating edge supported plate and apparatus used to perform the measurements have been discussed in detail elsewhere,[6] and only the essential features are provided here. The MEMS (with serial number W2C16) used for the measurements reported here was not the same device used in refs 6, 7, and 8, although it was taken from the same wafer fabrication process.

The uncertainty in the determination of resonance frequency depends on the Q $\{= f/(2g)\}$ of the resonance. In this work, Q varied between 1.6 and 40 which is sufficient to obtain the density and viscosity with uncertainties less than 1 % and 10 %, respectively.

The MEMS and the pressure gauge used to measure pressures greater than 0.1 MPa were thermostatted in a stirred fluid bath. The temperature of the bath fluid was stable to within ± 3 mK as determined with a long-stem platinum resistance thermometer calibrated on ITS-90. The temperature fluctuations lead to an uncertainty of less than 0.01 % in both density and viscosity because $|(\partial\rho/\partial T)_p| < 2\ \mathrm{kg \cdot m^{-3} \cdot K^{-1}}$ and $|(\partial\eta/\partial T)_p| < 12\ \mathrm{mPa \cdot s \cdot K^{-1}}$.

Pressures of about 0.1 MPa were measured using a resonating quartz barometer (Paroscientific 740-16B with a maximum operating pressure of 0.11 MPa) with an uncertainty cited by the supplier of 0.008 % of full-scale (about 8.8 Pa). Pressures greater than 0.1 MPa were generated with an ISCO model 100 DX positive displacement pump with an upper operating pressure of about 68 MPa and measured with a resonant quartz transducer with an uncertainty of $\delta p/\mathrm{MPa} = \{1 \cdot 10^{-4} \cdot (p/\mathrm{MPa}) + 0.022\}$.[6] In the worst case, the $\delta p \approx 0.029$ MPa corresponds to an uncertainty in density of about 0.02 % when for nitrogen, at $T = 323$ K and $p = 7$ MPa, $(\partial\rho/\partial p)_T \approx 3.4\ \mathrm{kg \cdot m^{-3} \cdot MPa^{-1}}$; $(\partial\rho/\partial p)_T$ increases with decreasing pressure, and at $p \leq 20$ MPa, the pressure measurement gives rise to $\delta\rho/\rho > 0.2$ %.[7]

Table 1. Viscosity η and Density ρ at Temperature T of the Certified Reference Materials for Viscosity (CRMV) Used in This Work

CRMV	T/K	η/mPa·s	ρ/kg·m^{-3}
750	293.15	1096	874.4
	298.15	751.7	871.5
	310.93	318.1	863.7
	313.15	277.9	862.3
	323.15	158.2	856.4
	372.04	22.51	827.4
	373.15	21.77	826.9
60	293.15	133.1	860.5
	298.15	98.92	857.2
	310.93	50.47	849.3
	313.15	45.44	848.0
	323.15	29.35	841.8
	372.04	6.522	811.7
	373.15	6.352	810.9
20	293.15	36.16	849.6
	298.15	28.39	846.4
	310.93	16.50	838.2
	313.15	15.17	836.7
	323.15	10.68	830.1
	372.04	3.168	798.8
	373.15	3.103	798.4
10	293.15	11.990	839.8
	298.15	9.930	836.6
	313.15	6.076	826.5
	323.15	4.616	820.0
	373.15	1.705	787.0

The following measurement procedure was adopted for each fluid: (1) the apparatus was thermostatted at about 373 K; (2) the apparatus was evacuated, with a turbo-molecular pump, to a pressure (as indicated by an ionization gauge located near the pump) of less than $< 10^{-2}$ Pa for at least 24 h; (3) the system was then flushed with at least 50 cm^3 of either methylbenzene or petroleum ether supplied from an ISCO positive displacement pump; (4) the apparatus cooled to and thermostatted at either $T = 313$ K or $T = 323$ K; (5) step 2 was repeated; (6) the apparatus was filled with the fluid to be investigated; (7) the complex resonance frequency was measured at constant temperature and pressure; (8) an aliquot of the sample was flushed through the apparatus; (9) steps 7 and 8 were repeated at least thrice until the relative difference in resonance frequency between flushes was $< 10^{-4}$; and (10) the complex frequency was measured at temperatures between (313 and 373) K.

Materials. The certified reference materials for viscosity (CRMV) used for these measurements were obtained from Paragon Scientific Ltd., UK, and are listed in Table 1. The supplier measured the kinematic viscosity with a long capillary Master Viscometer according to ASTM D 2164 and cited an expanded uncertainty in the kinematic viscosity of 0.25 % relative to water, for which the uncertainty in viscosity at $T = 298$ K and $p = 0.1$ MPa is 0.25 %.[44] The supplier provided densities that were measured in accordance with ASTM D 1480 with an uncertainty of 0.02 %. The expanded uncertainty of the dynamic viscosity is 0.35 % assuming no additional uncertainty arises from the step-up procedure.[45] Density and viscosity of the CRMVs are listed in Table 1 for which the average density is (858 ± 16) kg·m^{-3} and the viscosity varies from (0.5 to 275) mPa·s.

Methylbenzene was supplied by Riedel-de Haën with a mass fraction purity greater than 0.998 and a mass fraction of water less than $3 \cdot 10^{-4}$. The methylbenzene was degassed by vacuum sublimation and dried over a 0.4 nm molecular sieve for about 24 h. The nitrogen was Research grade supplied by BOC with a minimum stated mole fraction purity of 0.999995.

The polydimethylsiloxane polymer of molecular formula $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$ was supplied by Dow Corning, USA, with $10 \le n \le 12$, while the 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd type Y04 with molecular formula $CF_3O[CF_2C(CF_3)FO]_n(CF_2O)_mCF_3$ was supplied by Solvay Solexis S.A., Bollate, Italy, with $4 \le n \le 6$ and $10 \le m \le 15$ and an average molar mass of about 1.8 $kg \cdot mol^{-1}$. Both fluids were used without further purification or analysis.

The water was deionized and degassed under vacuum prior to use. The electrical conductivity was about $(1.2 \pm 0.5) \cdot 10^{-4}$ $S \cdot m^{-1}$ reported by Pashley et al.[46] for degassed water which is greater than the standard value of $5.5 \cdot 10^{-6}$ $S \cdot m^{-1}$ of Kohlrausch and Heydweiller.[47]

No analyses of the chemical composition have been performed, and we have assumed for the sample used there were no variations in chemical composition from those provided by the supplier.

Calibration. The complex resonance frequency of the MEMS was determined when the plate was immersed in methylbenzene at a temperature of 313 K and pressures below 68 MPa and all CRMVs listed in Table 1 at $T = 313$ K and ambient pressure. These measurements were combined with the density and viscosity of methylbenzene[48] and the values in Table 1 to obtain the values for C_1, C_2, and C_3 of eq 1 listed in Table 3, which accommodated the data with a standard deviation $s(\rho)$ of 6 $kg \cdot m^{-3}$ $\{100 \cdot s(\rho)/\langle\rho\rangle = \pm 0.7\ \%\}$. The densities determined at a temperature of 313 K using eq 1 with the C_1, C_2 and C_3 listed in Table 3 deviate from the values obtained for the CRMV of Table 1 or ref 48 within about ± 1 %; the differences as a function of viscosity are random. Based on the measurements performed, we have been unable to identify the source of these differences; a plausible source is a chemical impurity. Nevertheless, we take the average of the absolute differences of s ± 1 % over this range of viscosities as a measure of the anticipated precision in the measurements of density with this instrument.

Other subsets of the measurements were considered as calibrants to determine the $C_{i,s}$, and these alternative combinations included the following: (1) methylbenzene at $T = 348$ K and all CRMV 750 at temperatures of (313, 323, and 373) K; and (2) solely methylbenzene at $T = 323$ K. Item 1 returned deviations that differed insignificantly from those obtained with the C_1, C_2, and C_3 listed in Table 3. For item 2, the viscosity range was between (0.44 and 0.65) $mPa \cdot s$, and when the resulting expression was extrapolated to fluid of higher density and viscosity, the error in density increased systematically with increasing viscosity; for example, for CRMV 750 with $\eta(313\ K) \approx 275\ mPa \cdot s$, the estimated density was in error by about 50 %.

The $Q\ \{= f/(2g)\}$ obtained from Table 2 and density and viscosity obtained from the correlation of Assael et al.[48] were used to determine parameter C_4 of eq 2 listed in Table 3 that accommodated the viscosity of ref 48 with an average deviation of $100 \cdot s(\rho)/\rho = \pm 1.1\ \%$. This is taken as a measure of the anticipated precision in the measurements of viscosity.

Literature Density and Viscosity. Values of the density and viscosity of the CRMV were taken from Table 1. The densities of Table 1 for each CRMV were fit to a linear interpolation equation, whereas the viscosities were represented by the rule of Vogel[49] and interpolated to temperatures < 0.1 K from those of the cited values for the CRMV. This procedure introduced a negligible additional error in the viscosity of the CRMV. For polydimethylsiloxane and 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd, the density and viscosity reported by Jakeways and Goodwin[50] were used because their measurements were performed on aliquots of the same samples.

The density and viscosity of nitrogen were determined from the Helmholtz function reported by Span et al.[51] and the transport property correlation of Lemmon and Jacobsen;[52] both literature sources were coded within the National Institute of Standards and Technology, Standard Reference Database 23, Version 7.1, commonly known by the acronym REFPROP.[53] For water, the density and viscosity were obtained from the correlations of Wagner and Pruβ[54] and Kestin et al.[55] as revised by ref 56, respectively. The density and viscosity of methylbenzene were determined from the correlation of Assael et al.[48] For all fluids, the density was estimated with an uncertainty < 0.1 %, while the viscosity was < 1 % except for polydimethylsiloxane and 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd where the error in viscosity was < 4 %. For the purpose of this work, we assume the thermophysical properties listed in Table 1 and obtained from refs 48 and 50 to 56 are exact.

Results and Discussion

The resonance frequency, f, and resonance line half-width, g, of the first eigenmode of the MEMS edge supported plate obtained at temperatures between (323 and 423) K and pressures below 68 MPa are listed in Table 2 when immersed in the following fluids: nitrogen, water, methylbenzene, polydimethylsiloxane, and 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd, and the CRMV listed in Table 1. The density and viscosity obtained from eqs 1 and 2, with the calibration coefficients $C_{i,s}$, with $i = 1$, 2, 3, and 4 of Table 3, are listed in Table 4. The uncertainties listed in Table 2 were obtained from 2 times the standard deviation of N measurements at each temperature and pressure. The uncertainties cited in Table 4 are dominated by the major source of uncertainty arising from the calibration to determine the $C_{i,s}$, with $i = 1$, 2, 3, and 4 of 0.7 % for density and 1.1 % for viscosity. The density and viscosity of Table 4 were obtained using the accepted values of density and viscosity from Table 1 and ref 48 in the left-hand side of the equality of eqs 1 and 2. A second calculation was performed with the density and viscosity required on the left of eqs 1 and 2 taken from Table 4. The densities obtained from the second calculation differ insignificantly from those of Table 4 at $\eta \le 100\ mPa \cdot s$. For CRMV 750 at $T = 313$ K, the density estimates differed by 14 %. This result is not surprising because at $T = 313$ K the cited viscosity for CRMV 750 is 275 $mPa \cdot s$ which is 0.48 times less than that listed in Table 4. The viscosities obtained when the density was taken from Table 4 differ from those of Table 4 by < 2 %.

The deviations of the densities of Table 4 from the accepted values of Table 1 and the refs 48, 50, 51, 53 and 54, shown in Figure 1 as a function of viscosity, reveal the values obtained for 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd differ by about −4 % at all temperature studied. However, the deviations are systematic when plotted as a function of density with differences that vary almost linearly from 6 % at a density of about 380 $kg \cdot m^{-3}$ to −4 % at a density of about 1800 $kg \cdot m^{-3}$.

The viscosities of Table 4 are shown in Figure 2 as deviations from either the values in Table 1 or refs 48, 50, 52, 53, 55, and 56 as a function of viscosity. The results obtained for CRMV 750 at temperatures of (313 and 323) K differ from the cited

Table 2. Resonance Frequency f and Half Line Width g for the (0,1) Eigenmode of the Edge-Clamped Plate Obtained from N Measurements When Immersed in Fluid i at Temperature T and Pressure p^a

i	N	T/K	p/MPa	f/Hz	g/Hz
water	2	313.184 ± 0.006	0.10084 ± 0.00002	3591.9 ± 4.9	68.1 ± 5.0
	3	323.155 ± 0.006	0.10088 ± 0.00002	3609.4 ± 1.2	67.4 ± 2.2
	3	373.065 ± 0.006	0.10266 ± 0.00002	3622.42 ± 0.54	61.42 ± 0.55
750	2^b	313.184 ± 0.006	0.10176 ± 0.00002	2732.25 ± 0.26	832 ± 53
	2^b	323.155 ± 0.006	0.10169 ± 0.00002	2969.8 ± 2.1	680 ± 47
	2^b	373.065 ± 0.006	0.10207 ± 0.00002	3564.94 ± 0.27	317 ± 10
60	2	313.184 ± 0.006	0.10222 ± 0.00002	3412.1 ± 2.6	415.8 ± 6.3
	3	323.155 ± 0.006	0.10090 ± 0.00002	3553.5 ± 4.1	310.3 ± 3.5
	2	373.065 ± 0.006	0.10245 ± 0.00002	3805.2 ± 1.3	163.66 ± 0.70
20	2	313.184 ± 0.006	0.09975 ± 0.00002	3614.5 ± 1.8	272.9 ± 5.8
	3	323.155 ± 0.006	0.10141 ± 0.00002	3682.8 ± 1.9	233.36 ± 0.87
	2	373.065 ± 0.006	0.10324 ± 0.00002	3867.6 ± 1.2	131.8 ± 1.1
10	3	313.184 ± 0.006	0.09975 ± 0.00002	3760.6 ± 4.2	179.7 ± 2.7
	2	323.155 ± 0.006	0.10101 ± 0.00002	3793.6 ± 1.1	163.2 ± 1.3
	2	373.065 ± 0.006	0.10309 ± 0.00002	3923.2 ± 1.7	106.5 ± 1.4
polydimethylsiloxane	2	313.184 ± 0.006	0.10269 ± 0.00002	3442.35 ± 0.74	250.9 ± 2.6
	2	323.155 ± 0.006	0.10268 ± 0.00002	3481.2 ± 3.4	241.0 ± 1.0
	2	348.122 ± 0.006	0.10263 ± 0.00002	3563.1 ± 2.3	196.4 ± 3.3
	2	373.065 ± 0.006	0.10241 ± 0.00002	3634.79 ± 0.40	171.2 ± 1.3
1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd	2	313.184 ± 0.006	0.10220 ± 0.00002	2474.2 ± 1.9	225 ± 15
	2	323.155 ± 0.006	0.10227 ± 0.00002	2520.4 ± 1.2	188.2 ± 1.2
	2	348.122 ± 0.006	0.10234 ± 0.00002	2618.86 ± 0.38	138.1 ± 4.1
	2	373.065 ± 0.006	0.10166 ± 0.00002	2690.424 ± 0.038	108.27 ± 0.63
nitrogen	1	323.155 ± 0.006	50.401 ± 0.054	5596.1119 ± 0.038	28.30 ± 0.28
	1	323.155 ± 0.006	60.477 ± 0.056	5596.1119 ± 0.038	28.30 ± 0.28
methylbenzene	4^b	313.180 ± 0.006	0.10394 ± 0.00002	3857.69 ± 0.91	56.02 ± 0.34
	3^b	313.181 ± 0.006	11.218 ± 0.046	3833.23 ± 0.50	58.07 ± 0.18
	2^b	313.182 ± 0.006	19.594 ± 0.048	3817.83646 ± 0.00060	59.59 ± 0.51
	2^b	313.18 ± 0.006	29.339 ± 0.050	3802.176 ± 0.089	61.47 ± 0.85
	2^b	313.181 ± 0.006	39.938 ± 0.052	3785.56 ± 0.85	63.6 ± 1.0
	2^b	313.181 ± 0.006	49.859 ± 0.054	3771.38 ± 0.92	65.26 ± 0.48
	2	323.151 ± 0.006	0.10361 ± 0.00002	3878.4 ± 1.1	54.03 ± 0.03
	2	323.152 ± 0.006	8.941 ± 0.046	3855.89 ± 0.57	55.29 ± 0.50
	2	323.151 ± 0.006	19.999 ± 0.048	3835.48 ± 0.63	57.23 ± 0.27
	2	323.151 ± 0.006	29.507 ± 0.050	3819.05 ± 0.16	58.60 ± 0.27
	2	323.151 ± 0.006	39.806 ± 0.052	3802.177 ± 0.065	60.75 ± 0.52
	2	323.151 ± 0.006	50.254 ± 0.054	3786.93 ± 0.30	62.55 ± 0.33
	2	323.151 ± 0.006	59.628 ± 0.056	3774.12 ± 0.64	64.33 ± 0.14
	3	348.115 ± 0.006	0.10379 ± 0.00002	3930.94 ± 0.26	49.18 ± 0.41
	2	348.115 ± 0.006	9.081 ± 0.046	3904.19 ± 0.26	50.38 ± 0.12
	2	348.115 ± 0.006	19.989 ± 0.048	3880.27 ± 0.20	52.32 ± 0.30
methylbenzene	3	348.115 ± 0.006	30.001 ± 0.05	3860.94 ± 0.52	53.96 ± 0.13
	2	348.115 ± 0.006	40.000 ± 0.052	3842.82 ± 0.11	55.25 ± 0.67
	3	348.115 ± 0.006	50.470 ± 0.054	3825.78 ± 0.23	56.93 ± 0.94
	3	348.115 ± 0.006	60.457 ± 0.056	3810.3 ± 1.0	58.68 ± 0.39
	3	348.115 ± 0.006	68.296 ± 0.058	3800.01 ± 0.33	59.51 ± 0.75
	2	348.115 ± 0.006	67.827 ± 0.058	3800.48 ± 0.35	59.76 ± 0.56

[a] The uncertainties were determined from the standard deviation of the mean of N observations and are at a confidence interval of 0.95. [b] Used for calibration.

Table 3. Values of C_i, with $i = 1, 2, 3$, and 4 of Equations 1 and 2

C_1	C_2	C_3	C_4
$\mathrm{kg \cdot m^{-3} \cdot s^{-2}}$	$\mathrm{kg \cdot m^{-4} \cdot s^{-2}}$	$\mathrm{kg \cdot m^{-5} \cdot s^{-2}}$	$\mathrm{m^2 s^2}$
$1.293521 \cdot 10^{10}$	$-4.86552 \cdot 10^{13}$	$7.783278 \cdot 10^{16}$	$5.50 \cdot 10^{15}$

values by about (110 and 60) %, respectively, and have been excluded from Figure 2 to permit expansion of the ordinate by a factor of 3 and permit clarification of the differences at $\eta \leq$ 100 mPa·s. The viscosities shown in Figure 2 differ by up to ± 35 % which is 3.5 times the desired uncertainty of the transducer.[6] The viscosity obtained for CRMV 60 at a temperature of 313 K of 45 mPa·s differs by about 5 % from eq 2, while those determined at higher temperatures of (323 and 373) K with viscosities of (30 to 6) mPa·s differ by between (26 and 32) % from the cited values. These differences for CRMV 60 might arise from the presence of an impurity. The viscosities of Table 4 when plotted as deviations from either the values in Table 1 or the literature[48,50,52,53,55,56] as a function of density reveal no other significant systematic differences over those shown in Figure 2.

The relative deviations shown in Figure 1 and Figure 2 might arise from one or more of the following plausible sources: (1) the naivety of the assumption used to derive eq 1; (2) variations in the chemical composition; and (3) uncertainty in the literature values. In view of the refs 48, 50, 51, 52, 53, 54, 55, and 56 and the statements concerning CRMVs in ref 45, item 3 is unreasonable and will not be considered further. No measurements were performed to negate item 2 as a source of error. However, the effect of variations in chemical composition on the measured density and viscosity can be estimated. For viscosity, worst case contamination would occur for methylbenzene contaminated with CRMV 750 for which $(1/\eta)(\partial\eta/\partial x)_{T,p} \approx 560$ and implies a mole fraction $x = 0.0002$ of the CRMV 750 would introduce an uncertainty in viscosity of 10 %. For density, the worst case contamination would be 1-propene,1,1,2,3,3,3-

hexafluoro-oxidized-polymd because $(1/\rho)(\partial\rho/\partial x)_{T,p} \approx 100$ for which a mole fraction of less than 10^{-4} would be required to introduce an error of 1 %.

The assumptions used to obtain eq 1 are the subject of the remainder of this discussion, and these are as follows:[8] (1) the edge-supported plate can be approximated by a sphere-on-a-string; and (2) the radius of the sphere is much greater than about 5 times the viscous skin-depth. The plate has dimensions on the order of 1 mm, and when immersed in a fluid of viscosity 100 mPa·s, the viscous skin-depth is on the order of 0.1 m and criterion 2 is not obeyed. Unfortunately, the resonance frequency predicted by numerical solution of the model based on the Navier–Stokes[31] is about twice the measured value and does not eliminate the requirement for the inclusion of adjustable parameters and calibration measurements.

However, a plot of the product $f(\rho)^{1/2}$ as a function of $\{\eta/(\rho f)\}^{1/2}$ reveals a quadratic trend in accord with an empirical equation of the form

$$\rho \approx \frac{k_1}{f^2} - \frac{k_2}{f^2}\left(\frac{\eta}{\rho}\right)^{1/2} - \frac{k_3}{f^2}\left(\frac{\eta}{\rho}\right) \tag{3}$$

Equation 3 is consistent with eq 1 and can be recast as

$$\rho \approx \left[\frac{m_1}{f} - \frac{m_2}{f}\left(\frac{\eta}{\rho}\right)^{1/2}\right]^2 \tag{4}$$

The parameters m_1 and m_2 of eq 4 were determined from a combination of the measurements with methylbenzene at $T = 313$ K from Table 2 and the density and viscosity estimated from ref 48 with the result $m_1 = 1.825185 \cdot 10^6\ \mathrm{kg^{1/2} \cdot m^{-5/2} \cdot s^{-1/2}}$ and $m_2 = 1.137072 \cdot 10^5 \cdot \mathrm{kg^{1/2} \cdot m^{-3/2} \cdot s^{-1}}$. The densities determined from eq 4 are shown as deviations from the literature values in Figure 3 as a function of viscosity. The deviations when plotted as a function of density lie within the assigned expanded uncertainty of the measurement, and the systematic variation of the deviations with increasing density observed with eq 1 and coefficients of Table 4 are not present with eq 4. For 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd, the density

Table 4. Density and Viscosity Obtained from Equations 1 and 2 for *N* Measurements When Immersed in Fluid *i* at Temperature *T* and Pressure *p*[a]

i	N	T/K	p/MPa	ρ/kg·m^{-3}	η/mPa·s
water	2	313.184 ± 0.006	0.10084 ± 0.00002	974 ± 14	0.84 ± 0.14
	3	323.155 ± 0.006	0.10088 ± 0.00002	967 ± 14	0.804 ± 0.067
	3	373.065 ± 0.006	0.10266 ± 0.00002	967 ± 14	0.666 ± 0.025
750	2	313.184 ± 0.006	0.10176 ± 0.00002	864 ± 12	574 ± 75
	2	323.155 ± 0.006	0.10169 ± 0.00002	865 ± 12	254 ± 35
	2	373.065 ± 0.006	0.10207 ± 0.00002	846 ± 12	22.9 ± 1.7
60	2	313.184 ± 0.006	0.10222 ± 0.00002	852 ± 12	47.1 ± 1.9
	3	323.155 ± 0.006	0.10090 ± 0.00002	830 ± 12	21.52 ± 0.86
	2	373.065 ± 0.006	0.10245 ± 0.00002	812 ± 12	4.37 ± 0.14
20	2	313.184 ± 0.006	0.09975 ± 0.00002	851 ± 12	15.64 ± 0.85
	3	323.155 ± 0.006	0.10141 ± 0.00002	841 ± 12	10.48 ± 0.32
	2	373.065 ± 0.006	0.10324 ± 0.00002	808 ± 11	2.695 ± 0.095
10	3	313.184 ± 0.006	0.09975 ± 0.00002	833 ± 12	5.62 ± 0.22
	2	323.155 ± 0.006	0.10101 ± 0.00002	828 ± 12	4.47 ± 0.15
	2	373.065 ± 0.006	0.10309 ± 0.00002	799 ± 11	1.655 ± 0.066
polydimethylsiloxane	2	313.184 ± 0.006	0.10269 ± 0.00002	932 ± 13	15.09 ± 0.56
	2	323.155 ± 0.006	0.10268 ± 0.00002	921 ± 13	13.28 ± 0.44
	2	348.122 ± 0.006	0.10263 ± 0.00002	904 ± 13	8.02 ± 0.34
	2	373.065 ± 0.006	0.10241 ± 0.00002	888 ± 12	5.64 ± 0.19
1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd	2	313.184 ± 0.006	0.1022 ± 0.00002	1759 ± 25	32.3 ± 4.4
	2	323.155 ± 0.006	0.10227 ± 0.00002	1747 ± 24	20.78 ± 0.66
	2	348.122 ± 0.006	0.10234 ± 0.00002	1704 ± 24	9.47 ± 0.62
	2	373.065 ± 0.006	0.10166 ± 0.00002	1656 ± 23	5.20 ± 0.17
nitrogen	1	323.155 ± 0.006	50.401 ± 0.054	409.6 ± 5.7	0.038 ± 0.010
	1	323.155 ± 0.006	60.477 ± 0.056	443.8 ± 6.2	0.040 ± 0.010
methylbenzene	4	313.180 ± 0.006	0.10394 ± 0.00002	847 ± 12	0.461 ± 0.016
	3	313.181 ± 0.006	11.218 ± 0.046	857 ± 12	0.507 ± 0.016
	2	313.182 ± 0.006	19.594 ± 0.048	864 ± 12	0.541 ± 0.020
	2	313.180 ± 0.006	29.339 ± 0.050	870 ± 12	0.583 ± 0.028
	2	313.181 ± 0.006	39.938 ± 0.052	877 ± 12	0.634 ± 0.031
	2	313.181 ± 0.006	49.859 ± 0.054	882 ± 12	0.675 ± 0.024
	2	323.151 ± 0.006	0.10361 ± 0.00002	839 ± 12	0.421 ± 0.013
	2	323.152 ± 0.006	8.941 ± 0.046	848 ± 12	0.451 ± 0.018
	2	323.151 ± 0.006	19.999 ± 0.048	857 ± 12	0.491 ± 0.016
	2	323.151 ± 0.006	29.507 ± 0.050	863 ± 12	0.522 ± 0.017
	2	323.151 ± 0.006	39.806 ± 0.052	870 ± 12	0.569 ± 0.022
	2	323.151 ± 0.006	50.254 ± 0.054	876 ± 12	0.611 ± 0.020
	2	323.151 ± 0.006	59.628 ± 0.056	882 ± 12	0.654 ± 0.020
	3	348.115 ± 0.006	0.10379 ± 0.00002	820 ± 11	0.333 ± 0.014
	2	348.115 ± 0.006	9.081 ± 0.046	830 ± 12	0.358 ± 0.011
	2	348.115 ± 0.006	19.989 ± 0.048	840 ± 12	0.394 ± 0.014
methylbenzene	3	348.115 ± 0.006	30.001 ± 0.050	847 ± 12	0.426 ± 0.013
	2	348.115 ± 0.006	40.000 ± 0.052	855 ± 12	0.453 ± 0.021
	3	348.115 ± 0.006	50.470 ± 0.054	862 ± 12	0.488 ± 0.027
	3	348.115 ± 0.006	60.457 ± 0.056	868 ± 12	0.526 ± 0.019
	3	348.115 ± 0.006	68.296 ± 0.058	872 ± 12	0.545 ± 0.025
	2	348.115 ± 0.006	67.827 ± 0.058	872 ± 12	0.550 ± 0.022

[a] The uncertainties were determined from the standard deviation of the mean of *N* observations and are at a confidence interval of 0.95.

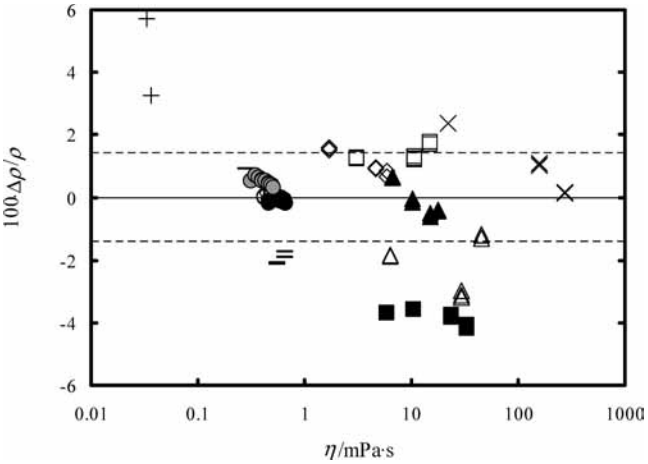

Figure 1. Fractional deviations $\Delta\rho/\rho = \{\rho(\text{eq }1) - \rho(\text{lit.})\}/\rho(\text{lit.})$ of the experimental densities, ρ(eq 1), of Table 4 (obtained from eq 1 with the calibration coefficients C_1, C_2, and C_3 listed in Table 3) from the accepted values of either Table 1 or refs 48, 50, 51, 53, and 54, ρ(lit.), as a function of viscosity η. ●, methylbenzene at $T = 313$ K; ○, methylbenzene at $T = 323$ K; gray filled circle with black outline, methylbenzene at $T = 348$ K; +, nitrogen at $T = 323$ K; −, water at $T = (313, 323, \text{and } 373)$ K; ◇, CRMV 10 at $T = (313, 323, \text{and } 373)$ K; □, CRMV 20 at $T = (313, 323, 348, \text{and } 373)$ K; △, CRMV 60 at $T = (313, 323, \text{and } 373)$ K; ×, CRMV 750 at $T = (313, 323, \text{and } 373)$ K; ▲, polydimethylsiloxane at $T = (313, 323, 348, \text{and } 373)$ K; ■, 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd at $T = (313, 323, 348, \text{and } 373)$ K. The dashed line is the estimated expanded uncertainty of the measurements.

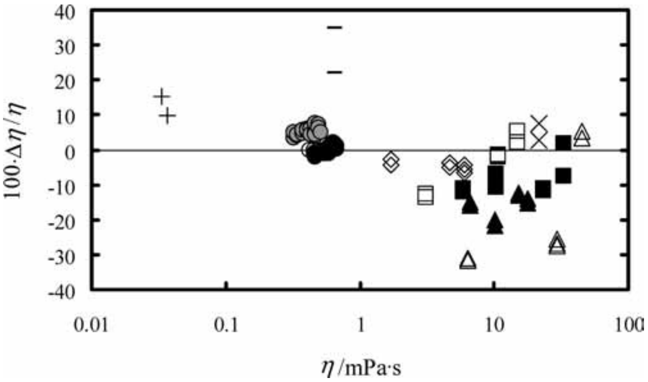

Figure 2. Fractional deviations $\Delta\eta/\eta = \{\eta(\text{eq }2) - \eta(\text{lit.})\}/\eta(\text{lit.})$ of the experimental viscosities η(eq 2) of Table 4 (obtained from eq 2 with the calibration coefficient C_4 listed in Table 4) from the accepted values of either Table 1 or refs 48, 50, 52, 53, 55, and 56, η(lit.), as a function of viscosity η. ●, methylbenzene at $T = 313$ K; ○, methylbenzene at $T = 323$ K; gray filled circle with black outline, methylbenzene at $T = 348$ K; +, nitrogen at $T = 323$ K; −, water at $T = (313, 323, \text{and } 373)$ K; ◇, CRMV 10 at $T = (313, 323, \text{and } 373)$ K; □, CRMV 20 at $T = (313, 323, 348, \text{and } 373)$ K; △, CRMV 60 at $T = (313, 323, \text{and } 373)$ K; ×, CRMV 750 at $T = (313, 323, \text{and } 373)$ K; ▲, polydimethylsiloxane at $T = (313, 323, 348, \text{and } 373)$ K; ■, 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd at $T = (313, 323, 348, \text{and } 373)$ K.

obtained from eq 4 is within the expanded uncertainty of 0.7 % at densities up to 1800 kg·m^{-3} and viscosities of the order of 10 mPa·s; the densities obtained from eq 1 differed by more than 4 %. For CRMV 750, with a viscosity of up to 275 mPa·s, the densities differed by about ± 5 %. We conclude eq 4 is, albeit empirical, better able to provide density from the measured frequency than eq 1 with a calibration fluid of density about 860 kg·m^{-3} and viscosity about 0.6 mPa·s.

Equation 26 of ref 6 was also considered as an alternative method of obtaining density assuming the physical properties of silicon and the plate dimensions are constants that permit eq 26 of ref 6 to be recast in the simplified form

$$\rho = k_1/f^2 + k_2 \tag{5}$$

In eq 5, f is the frequency and k_1 and k_2 are empirical coefficients adjusted to best fit the data for methylbenzene at $T = 323$ K (for which the viscosity is about 0.5 mPa·s) listed in Table 2 combined with the density from ref 48 to be $k_1 = 1.174549 \cdot 10^{10}$ kg·m^{-3}·s^{-2} and $k_2 = 57.73035$ kg·m^{-3}. The density obtained from eq 5 differs, as Figure 4 shows, systematically from the reference values at both viscosities lower and higher than about 0.5 mPa·s; the reference value is illustrated with a vertical dashed line. This confirms the conjecture of ref 6 that eq 26 of

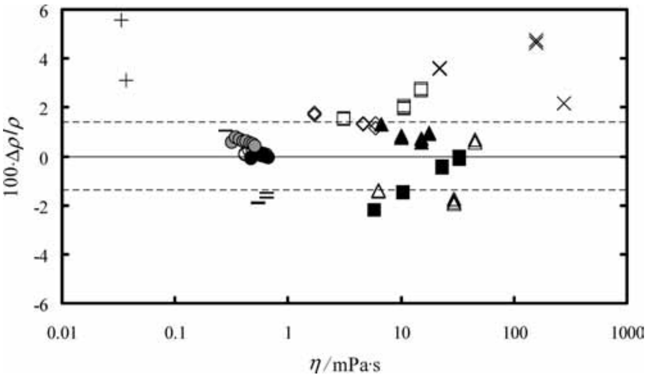

Figure 3. Fractional deviations $\Delta\rho/\rho = \{\rho(\text{eq }4) - \rho(\text{lit.})\}/\rho(\text{lit.})$ of the experimental densities ρ(eq 4) obtained from eq 4 (with the m_1 and m_2 determined with the data for methylbenzene at $T = 313$ K listed in Table 2) from the accepted values of either Table 1 or refs 48, 50, 51, 53, and 54, ρ(lit.), as a function of viscosity η. ●, methylbenzene at $T = 313$ K; ○, methylbenzene at $T = 323$ K; gray filled circle with black outline, methylbenzene at $T = 348$ K; +, nitrogen at $T = 323$ K; −, water at $T = (313, 323, \text{and } 373)$ K; ◇, CRMV 10 at $T = (313, 323, \text{and } 373)$ K; □, CRMV 20 at $T = (313, 323, 348, \text{and } 373)$ K; △, CRMV 60 at $T = (313, 323, \text{and } 373)$ K; ×, CRMV 750 at $T = (313, 323, \text{and } 373)$ K; ▲, polydimethylsiloxane at $T = (313, 323, 348, \text{and } 373)$ K; ■, 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd at $T = (313, 323, 348, \text{and } 373)$ K. Dashed lines are the estimated expanded uncertainty of the measurements.

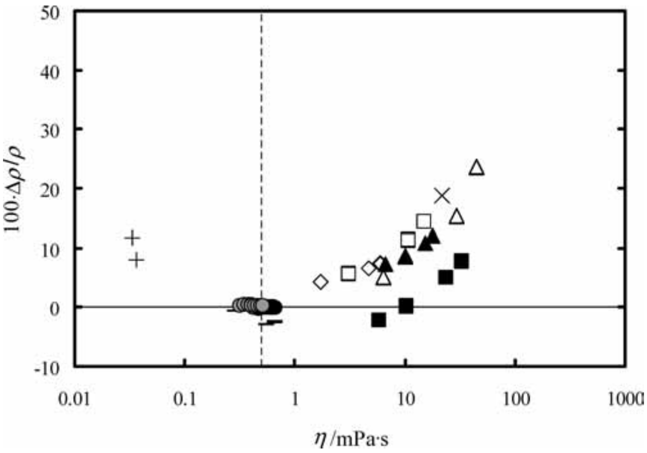

Figure 4. Fractional deviations $\Delta\rho/\rho = \{\rho(\text{eq }5) - \rho(\text{lit.})\}/\rho(\text{lit.})$ of the densities ρ(eq 5) obtained from eq 5 (with the k_1 and k_2 determined with the data for methylbenzene at $T = 323$ K listed in Table 2) from the accepted values of either Table 1 or refs 48, 50, 51, 53, and 54, ρ(lit.), as a function of viscosity η. ●, methylbenzene at $T = 313$ K; ○, methylbenzene at $T = 323$ K; gray filled circle with black outline, methylbenzene at $T = 348$ K; +, nitrogen at $T = 323$ K; −, water at $T = (313, 323, \text{and } 373)$ K; ◇, CRMV 10 at $T = (313, 323 \text{ and } 373)$ K; □, CRMV 20 at $T = (313, 323, 348, \text{and } 373)$ K; △, CRMV 60 at $T = (313, 323, \text{and } 373)$ K; ×, CRMV 750 at $T = (313, 323, \text{and } 373)$ K; ▲, polydimethylsiloxane at $T = (313, 323, 348, \text{and } 373)$ K; ■, 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd at $T = (313, 323, 348, \text{and } 373)$ K. The vertical dashed line denotes the viscosity of the calibrant.

ref 6 was only suitable for fluids of the same viscosity as the calibrant.

Finally, in ref 8, the exponent 2 on the right-hand side of eq 2 was replaced with an adjustable parameter, and as expected, a regression with an additional empirical parameter decreased the differences between the viscosities obtained from the MEMS and the literature values by a factor of about 0.75.

Conclusion

The intent of these measurements was to evaluate working equations that link the measured complex frequency of the vibrating object immersed in a fluid to the density and viscosity. The models presented are in many respects naïve[6,8] compared with those described elsewhere;[30,31] however, the empirical expression for density of eq 4 provided estimates of density within a factor of 2 of the desired uncertainty at viscosities between (0.1 and 100) mPa·s over the desired range even when the calibration coefficients were adjusted solely using measurements with methylbenzene. Equations 4 and 2 suffice when the results are considered acceptable with uncertainties of ± 5 % in density and ± 30 % for viscosity.

Acknowledgment

The authors acknowledge Eric Donzier and Olivier Vancauwenberghe, both of Schlumberger-Doll Research, for their efforts with the design of the MEMS, Fredrick Marty and Bruno Mercier, both of ESIEE, for fabricating the MEMS, and Christopher Harrison, of Schlumberger-Doll Research, and Gerry Meeten, of Schlumberger Cambridge Research, both for stimulating conversation.

Literature Cited

(1) Meyer R. F.; Attanasi, E. Natural Bitumen and Extra Heavy Oil, 2004 Survey of Energy Resources, Trinnaman, J., Clarke, A., Eds. for the World Energy Council; Elsevier: Amsterdam, 2004; Chapter 4, pp 93−117.

(2) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Vibrating Wire Viscometer with Wire Diameters of (0.05 and 0.15) mm: Results for Methylbenzene and Two Fluids, with Nominal Viscosities at $T = 298$ K and $p = 0.1$ MPa of (14 and 232) mPa·s, at Temperatures between (298 and 373) K and Pressures below 40 MPa. *J. Chem. Eng. Data* **2005**, *50*, 647–655.

(3) Lundstrum, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D. R.; Trusler, J. P. M.; Marsh, K. N. Measurement of the Viscosity and Density of Two Reference Fluids, with Nominal Viscosities at $T = 298$ K and $p = 0.01$ MPa of (16 and 29) mPa·s, at Temperatures between (298 and 393) K and Pressures below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1377–1388.

(4) Sopkow, T.; Goodwin, A. R. H.; Hsu, K. Vibrating Wire Viscometer with Nominal Wire Diameter of 0.15 mm: Measurement of The Viscosity of Two Certified Reference Fluids, with Nominal Viscosities at $T = 298$ K and $p = 0.1$ MPa of (16 and 29) mPa·s, at Temperatures Between (298 and 353) K and Pressures Below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1732–1735.

(5) Kandil, M. E.; Harris, K. R.; Goodwin, A. R. H.; Hsu, K.; Marsh, K. N. Measurement of the Viscosity and Density of a Reference Fluid, with Nominal Viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at Temperatures Between (273 and 423) K and Pressures below 275 MPa. *J. Chem. Eng. Data* **2006**, *51*, 2185–2196.

(6) Goodwin, A. R. H.; Donzier, E. P.; Vancauwenberghe, O.; Fitt, A. D.; Ronaldson, K. A.; Wakeham, W. A.; Manrique de Lara, M.; Marty, F.; Mercier, B. A Vibrating Edge Supported Plate, Fabricated by the Methods of Micro Electro Mechanical Systems for the Simultaneous Measurement of Density and Viscosity: Results for Methylbenzene and Octane at Temperature between (323 and 423) K and Pressures in the Range (0.1 to 68) MPa. *J. Chem. Eng. Data* **2006**, *51*, 190–208.

(7) Goodwin, A. R. H.; Fitt, A.; Ronaldson, K.; Wakeham, W. A. A Vibrating Plate Fabricated with the Methods of Micro Electro Mechanical Systems (MEMS): Measurement of the Density and Viscosity of Argon at Temperatures Between 323 and 423 K at Pressures up to 68 MPa. *Int. J. Thermophys.* **2006**, *27*, 1650–1676.

(8) Harrison, C.; Ryu, S.; Goodwin, A.; Hsu, K.; Donzier, E.; Marty, F.; Mercier, B. A MEMS Sensor for the Measurement of Density-Viscosity for Oilfield Applications SPIE Photonics West 2006, in Reliability, Packaging, Testing, and Characterization of MEMS/MOEMS V. Tanner, D. M.; Ramesham, R., Eds; *Proc. SPIE* **2006**, *6111*, 61110D.

(9) Kanwal, R. P. K. Vibrations of an elliptic cylinder and a flat plate in a viscous fluid. *Z. Angew. Math. Mech.* **1955**, *35*, 17–22.

(10) Raiteri, R.; Grattarola, M.; Butt, H.-J.; Skládal, P. Micromechanical cantilever-based biosensors. *Sens. Actuators, B* **2001**, *79*, 115–126.

(11) Weigert, S.; Dreier, M.; Hegner, M. Frequency shifts of cantilevers vibrating in various media. *Appl. Phys. Lett.* **1996**, *69*, 2834–2836.

(12) Oden, P. I.; Chen, G. Y.; Steele, R. A.; Warmack, R. J.; Thundat, T. Viscous drag measurements utilizing microfabricated cantilevers. *Appl. Phys. Lett.* **1996**, *68* (26), 3814–3816.

(13) Kirstein, S.; Mertesdorf, M.; Schönhoff, M. The influence of a viscous fluid on the vibration dynamics of scanning near-field optical microscopy fiber probes and atomic force microscopy cantilevers. *J. Appl. Phys.* **1998**, *84*, 1782–1790.

(14) Bergaud, C.; Nicu, L. Viscosity measurements based on experimental investigations of composite cantilever beam eigenfrequencies in viscous media. *Rev. Sci. Instrum.* **2000**, *71*, 2487–2491.

(15) Ahmed, N.; Nino, D. F.; Moy, V. T. Measurement of solution viscosity by atomic force microscopy. *Rev. Sci. Instrum.* **2001**, *72*, 2731–2734.

(16) Vidic, A.; Then, D.; Ziegler, Ch. A new cantilever system for gas and liquid sensing. *Ultramicroscopy* **2003**, *97*, 407–416.

(17) Maali, A.; Hurth, C.; Boisgard, R.; Jai, C.; Cohen-Bouhacina, T.; Aimé, J.-P. Hydrodynamics of oscillating atomic force microscopy cantilevers in viscous fluids. *J. Appl. Phys.* **2005**, *97*, 074907-1–074907-6.

(18) Elmer, F.-J.; Dreier, M. Eigenfrequencies of a rectangular atomic force microscope cantilever in a medium. *J. Appl. Phys.* **1997**, *81*, 7709–7714.

(19) Sader, J. E. Frequency response of cantilever beams immersed in viscous fluids with applications to the atomic force microscope. *J. Appl. Phys.* **1998**, *84*, 64–76.

(20) Chang, T.-P.; Liu, M.-F. On the natural frequency of a rectangular isotropic plate in contact with fluid. *J. Sound Vib.* **2000**, *236*, 547–553.

(21) Dareinga, D. W.; Thundat, T.; Jeon, S.; Nicholson, M. Modal analysis of microcantilever sensors with environmental damping. *J. Appl. Phys.* **2005**, *97*, 084902.

(22) Chon, J. W. M.; Mulvaney, P.; Sader, J. E. Experimental validation of theoretical models for the frequency response of atomic force microscope cantilever beams immersed in fluids. *J. Appl. Phys.* **2000**, *87*, 3978–3988.

(23) Lindholm, U. S.; Kana, D. D.; Chu, W.-H.; Abramson, H. N. Elastic vibrations characteristics of cantilever plates in water. *J. Ship Res.* **1965**, *9*, 11–36.

(24) Leissa, A. W. Vibration of plates, NASA Special publication 160, 1969.

(25) Woodward, J. G. A vibrating plates viscometer. *J. Acoust. Soc. Am.* **1953**, *25*, 147–151.

(26) Thundat, T.; Wachter, E. A.; Sharp, S. L.; Warmack, R. J. Detection of mercury vapor using resonating microcantilevers. *Appl. Phys. Lett.* **1995**, *66*, 1695–1697.

(27) Wilson, T. A.; Campbell, G. A.; Mutharasan, R. Viscosity and density values from excitation level response of piezoelectric-excited cantilever sensors. *Sens. Actuators, A* **2007**, *138*, 44–51.

(28) Cumberbatch, E.; Wilks, G. An analysis of a vibrating element densitometer. *Math. Eng. Ind.* **1987**, *1*, 47–66.

(29) Cumberbatch, E.; Fitt, A. *Mathematical Modelling: case studies from industry*; Cambridge University Press: Cambridge, U.K., 2001; pp 66−79.

(30) Manrique de Lara, M.; Atkinson, C. Sensors, 2004. *Proc. IEEE* **2004**, *2*, 828–831.

(31) Manrique de Lara, M. Development of an Integrated Model of Vibrating Element Fluid Property Sensor, Ph.D. Thesis, University of London, 2005.

(32) Ronaldson, K. Mathematical modeling of MEMS densimeters and viscometers, Ph.D. Thesis, University of Southampton, U.K., 2006.

(33) Patois, R.; Vairac, P.; Cretin, B. Measurement of fluid properties with a near-field acoustic sensor. *Appl. Phys. Lett.* **1999**, *75*, 295–297.

(34) Patois, R.; Vairac, P.; Cretin, B. Near-field acoustic densimeter and viscosimeter. *Rev. Sci. Instrum.* **2000**, *71*, 3860–3863.

(35) Chen, G. Y.; Warmack, R. J.; Thundat, T.; Allison, D. P.; Huang, A. Resonance response of scanning force microscopy cantilevers. *Rev. Sci. Instrum.* **1984**, *65*, 2532–2537.

(36) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics*; Pergamon: New York, 1959.

(37) Clarke, R. J.; Cox, S. M.; Williams, P. M.; Jensen, O. E. The drag on a microcantilever oscillating near a wall. *J. Fluid Mech.* **2005**, *545*, 397–426.

(38) Clarke, R. J.; Jensen, O. E.; Billingham, J.; Williams, P. M. Three-dimensional flow due to a microcantilever oscillating near a wall: an unsteady slender-body analysis. *Proc. R. Soc. A* **2006**, *462*, 913–933.

(39) Clarke, R. J.; Jensen, O. E.; Billingham, J.; Pearson, A. P.; Williams, P. M. Stochastic Elastohydrodynamics of a Microcantilever Oscillating Near a Wall. *Phys. Rev. Lett.* **2006**, *96*, 050801.

(40) Chen, G. Y.; Warmack, R. J.; Huang, A.; Thundat, T. Harmonic response of near-contact scanning force microscopy. *J. Appl. Phys.* **1995**, *78*, 1465–1469.

(41) Naik, T.; Longnire, E. K.; Mantell, S. C. Dynamic Response of a cantilever in liquid near a solid wall. *Sens. Actuators, A* **2003**, *102*, 240–254.

(42) Harrison, C.; Tavernier, E.; Vancauwenberghe, O.; Donzier, E.; Hsu, K.; Goodwin, A. R. H.; Marty, F.; Mercier, B. On the response of a resonating plate in a liquid near a solid wall. *Sens. Actuators, A* **2007**, *134*, 414–426.

(43) Green, C. P.; Sader, J. E. Small amplitude oscillations of a thin beam immersed in a viscous fluid near a solid surface. *Phys. Fluids* **2005**, *17*, 073102-1–073102-12.

(44) ISO. International Standard 3105, 1976.

(45) Künzel, W.; van Wijk, H. F.; Marsh, K. N. *Viscosity in Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed. For International Union of Pure and Applied Chemistry; Blackwell Scientific: Oxford, 1987; pp 45−72.

(46) Pashley, R. M.; Rzechowicz, M.; Pashley, L. R.; Franics, M. J. De-Gassed Water Is a Better Cleaning Agent. *J. Phys. Chem. B* **2005**, *9*, 1231–1238.

(47) Kohlrausch, F.; Heydweiller, A. *Z. Phys. Chem.* **1894**, *14*, 317.

(48) Assael, M. J.; Avelino, H. M. T.; Dalaouti, N. K.; Fareleira, J.M.N.A.; Harris, K. R. Reference correlation for the viscosity of liquid toluene from 213 to 373 K at pressures to 250 MPa. *Int. J. Thermophys.* **2001**, *22*, 789–799.

(49) Vogel, H. The law of the relation between the viscosity of liquids and the temperature. *Phys. Z.* **1921**, *22*, 645–646.

(50) Jakeways, C. V.; Goodwin, A. R. H. The viscosity and density of 1-propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd and polydimethylsiloxane at temperatures from 313 to 373 K and a pressure of 0.1 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 1093–1097.

(51) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A Reference Quality Thermodynamic Property Formulation for Nitrogen. *J. Phys. Chem. Ref. Data* **2000**, *29*, 1361–1433.

(52) Lemmon, E. W.; Jacobsen, R. T. Viscosity and Thermal Conductivity Equations for Nitrogen, Oxygen, Argon, and Air. *Int. J. Thermophys.* **2004**, *25*, 21–69.

(53) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. *REFerence fluid PROPerties program 23 version 7.1* Physical and Chemical Properties Division National Institute of Standards and Technology: Boulder, Colorado.

(54) Wagner, W.; Pruβ, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.

(55) Kestin, J.; Sengers, J. V.; Kamgar-Parsi, B.; Levelt Sengers, J. M. H. Thermophysical Properties of Fluid H2O. *J. Phys. Chem. Ref. Data* **1984**, *13*, 175–183.

(56) Revised Release on the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance, IAPWS, 1997.

Received for review November 15, 2007. Accepted April 9, 2008.

JE700675H