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# Determination of Magnetic Susceptibility of Liquids by a Sensitive Viscometer Method

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A sensitive viscometer method is presented for precise measurements of the magnetic susceptibility of liquids. This method can be applied to a determination of the diamagnetic susceptibilities of various materials and the temperature dependence of the susceptibility for water. Measurements show that this method has a sensitivity of ±0.005% and a reproducibility of ±0.02%.

Various methods have been proposed for the precise measurement of the magnetic susceptibility.[1–5] Recently, a highly sensitive susceptometer based on a superconducting quantum interference device (SQUID) appeared.[6] This method can be used to detect susceptibility changes of ±0.0001% of a sample; in susceptibility measurements, the reproducibility (± 0.02%) is limited by the sample preparation technique, and the precision is limited by the availability of a standard reference value and density data regarding the conversion to mass susceptibility. Previously, the present author and a co-worker reported an improved viscometer method,[9,10] which is adaptable for both pure liquids and solutions, in addition to gas in the dead space of a measuring cell. This method gives the mass susceptibility without a density conversion that is accurate to within ±0.05%. Additional advantages of the method are: 1) the influence of dissolved air in a liquid sample can be easily almost completely eliminated; 2) a small size magnet can be used; 3) a definite sample volume is unnecessary; and 4) automatic measuring is possible. Since the susceptibility can be easily obtained precisely, it is possible to improve the method's sensitivity for a more precise measurement of the susceptibility.

In this paper, a new type cell is discussed which was designed to improve the sensitivity; its performance is also demonstrated.

## Theoretical

A capillary cell is placed in a magnetic field so that the lower end is in the center of a gap between the pole pieces of an electromagnet, while its upper grobular part is outside the field. The susceptibility of a liquid, $\chi_L$, may be written as

$$\chi_L = \frac{2g\tilde{h}}{H^2}\tau_L + (1-\beta_G)\frac{\rho_G}{\rho_L}\chi_G + \frac{\rho_V}{\rho_L}\chi_V, \tag{1}$$

where

$$\tau_L = (t_0 - t_H)/t_H. \tag{2}$$

Here, $t_0$ and $t_H$ are the flowing times in the absence and the presence of the field, $H$, respectively; $g$ the acceleration of gravity; $\tilde{h}$ the mean-effective-head of the liquid; $\rho$ the density; and $\beta$ the gas solubility in the liquid. Subscripts, L, V, and G indicate the values for the sample liquid, the liquid vapor, and the operating gas, respectively.

Regarding a relative measurement of sample 1 and sample 2, considering $\chi_V \simeq \chi_L$ for each sample,

$$\frac{\chi_L(1)}{\chi_L(2)} = \frac{\tau_L(1)}{\tau_L(2)}[1 + P(1) - P(2)], \tag{3}$$

where

$$P(1) = \frac{\rho_G(1)\chi_G}{\rho_L(1)\chi_L(1)}[1-\beta_G(1)] + \frac{\rho_V(1)}{\rho_L(1)}, \tag{4-a}$$

and

$$P(2) = \frac{\rho_G(2)\chi_G}{\rho_L(2)\chi_L(2)}[1-\beta_G(2)] + \frac{\rho_V(2)}{\rho_L(2)}. \tag{4-b}$$

When sample 2 is taken as a standard reference, the following equation may be practically used instead of Eq. 4-a:

$$P(1) = \frac{\rho_G(1)\tau(2)\chi_G}{\rho_L(1)\tau(1)\chi_L(2)}[1-\beta_G(1)] + \frac{\rho_V(1)}{\rho_L(1)}. \tag{4-c}$$

Allowing for a deviation of ±0.01% (approximately $\pm 0.0001 \times 10^{-6}$ emu/g[†]), the P(1)−P(2) term of Eq. 3 is negligible, and one can use

$$\frac{\chi_L(1)}{\chi_L(2)} = \frac{\tau_L(1)}{\tau_L(2)}. \tag{5}$$

The sensitivity, $K$, of this method is

$$K = \frac{\Delta\tau_L}{\Delta\chi_L} = \frac{H^2}{2g\tilde{h}}, \tag{6}$$

where the second and third terms of Eq. 1 are considered to be negligible. Then, a more sensitive

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[†] Note that cgs units are used hereafter. In SI units the volume susceptibility is dimensionless and numerically equal to $4\pi$ times the cgs value.

method must be obtained by designing the measuring cell that gives a more reduced mean-effective-head.

## Experimental

**Materials.** The water was purified by sub-boiling distillation from a quartz still after deionization. Acetic acid was purified by distillation from the Wako Guaranteed reagent. Methanol, carbon tetrachloride, and benzene were Dotite Primasol solvents (Dojindo Co.) and were used without purification. Nitrogen was obtained from commercial sources with purities exceeding 99.9%.

**Capillary Cell.** A horizontal-type capillary cell equipped with a thermostat jaket was fixed to a magnet so that the exit end of its capillary part was located at the center of the pole gap, while its inlet part protruded out of the magnetic field through the inhomogeneous region of the field. Figure 1 shows the experimental equipment. A capillary cell made of Pyrex glass is fixed upright in duplicated water jacket cabinets made of poly(vinyl chloride). These cabinets are covered with foam polystyrene. Detectors for meniscus-passage are attached at positions a and b of the cell. The detectors comprise two pairs of light-emission diodes and photo transistors molded in poly(vinyl chloride). A vertical-type capillary cell used for a comparison was the same as that used in previous studies.[9,10]

**Magnet.** The electromagnet is the same type as that used in previous studied.[9,10] The pole gap was set to approximately 7 mm. The magnetic field-strength available at a maximum current of 4 A was 19.7 kOe ($1\,\mathrm{kOe}=(1/4\pi)\times 10^3\,\mathrm{A\,m^{-1}}$), calibrated with a Yokogawa gauss meter (Type 3251). The magnetizing current was controlled using a regulated Kikusui (Model PAD-110-5L) power supply (±0.01%), throughout the measurements.

**Measurements.** Prior to the measurements, any air dissolved in the liquid sample and the cell dead space was fully replaced by nitrogen by means of an operation tube connected to the cell. A detailed description of this procedure was given in a previous paper.[9] The time of liquid flow was measured to an accuracy of ±0.001 s. The electronic apparatus to measure the flow time was made by the present author. The temperature around the cell was monitored by a Takara Kogyo (Model D111) thermistor thermometer. The thermometer was calibrated against a mercury standard thermometer with 0.1 °C divisions. The stability of the temperature was controlled to be ±0.01 °C. Measurements of the flow time were repeated alternately in both the presence and absence of the magnetic field, and the $\tau$-value was calculated for each step. The polarity of the magnetic field was alternately changed for each step by turnning the direction of the magnetizing current. Fifty measurements were averaged in order to calculate the magnetic susceptibility.

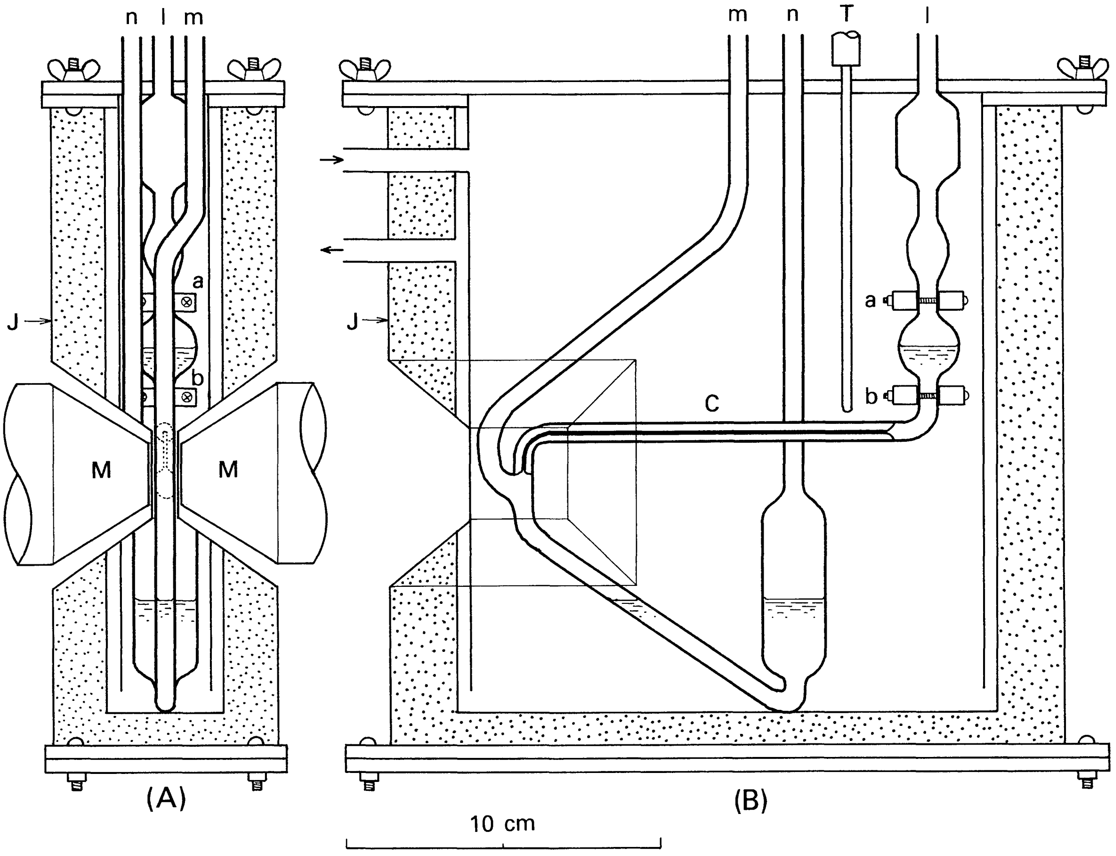

Fig. 1. Experimental setup, A, Front view, and B, side view. C, Capillary of about 0.5 mm (i.d.); a and b, detectors for meniscus passage; M, magnet; J, cabinet made of poly(vinyl chloride) covered with foam polystyrene; T, thermistor. The openings, l, m, and n, connected to the operation tube.[9]

## Results and Discussion

The experimental results for water obtained by means of this cell for different magnetic field strengths are shown in Fig. 2, in comparison with the previous cell. A straight line passing through the origin and having a large slope can be seen, the slope of which is expressed from Eq. 1 as

$$\alpha = \frac{1}{2g\tilde{h}}\left[\chi_L - (1-\beta_G)\frac{\rho_G}{\rho_L}\chi_G - \frac{\rho_V}{\rho_L}\chi_V\right]. \tag{7}$$

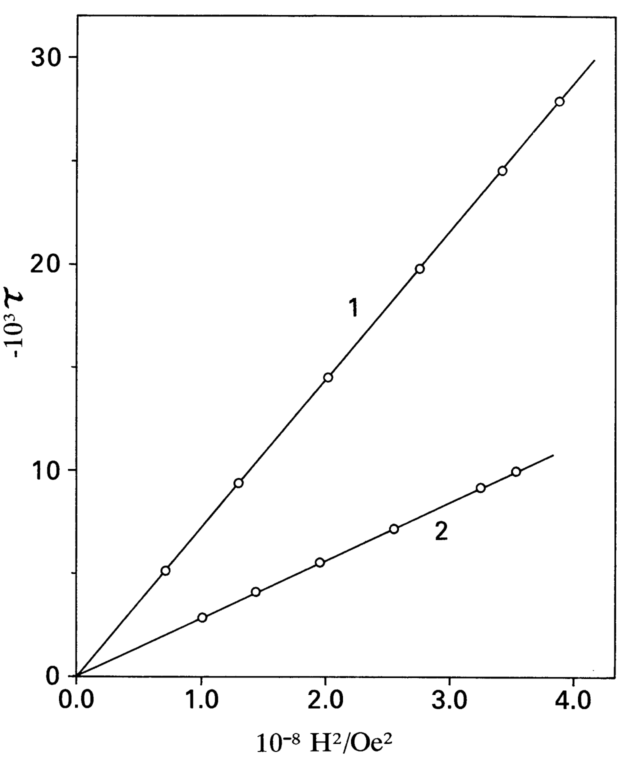

Fig. 2. Relationship between $\tau$-value and the external magnetic field-strength measured for water: 1, this cell; 2, previous cell.

The sensitivity ratio at the same magnetic field strength between the different types of cells can be written using the respective $\alpha$-values for the same material, as $K_H/K_V = \alpha_H/\alpha_V$. Here, H and V indicate the respective types of cells in the present and previous studies. The $\alpha$-values for various materials obtained by this cell are listed in Table 1, and are compared with those of the previous cell. It may be seen that the sensitivity is higher than that of the previous cell by about 2.56 times, and that the ratio reproducible in different materials is within ±0.05%. The accuracy of these values is limited by the reproducibility of magnetic field-strength measurements.

The $\tau$-values for various liquids measured at maximum magnetic field strength are listed in Table 2; the field strength was kept constant during all measurements. In the case of water under this condition, the difference in the flow times, $t_0 - t_H$, was about −10 s, for a flow time of about 400 s. From Eq. 2, the deviation of the $\tau$-value for water may be evaluated to be ±0.01% when the error of the flow time is ±0.001 s. The reproducibility of the values for different samples of the same material was at least ±0.02% for water and benzene, while it was ±0.05% for the other organic liquids. Since the allowance of Eq. 5

Table 1. Comparison of the $\alpha$-Values for Various Liquids Measured by Different Cells at 20 °C

| Materials | $-10^{11}\alpha$/dyn$^{-1}$ cm$^2$ | | $\alpha_H/\alpha_V$ |
|---|---|---|---|
| | This cell | Previous cell | |
| Water | 7.182 | 2.803 | 2.562 |
| Methanol | 6.833 | 2.668 | 2.561 |
| Acetic acid | 5.380 | 2.099 | 2.563 |
| Carbon tetrachloride | 4.427 | 1.729 | 2.560 |
| Benzene | 7.094 | 2.769 | 2.562 |
| Mean | | | $2.561_6(1_0)$[a] |

a) The uncertainty in parenthesis is one standard deviation in units of the last quoted mean value.

Table 2. Diamagnetic Susceptibilities of Liquids Measured by Different Cells in emu at 20 °C

| Materials | This cell | | Previous cell | | Literature[a] |
|---|---|---|---|---|---|
| | $-10^3\tau$ | $-10^6\chi$ | $-10^3\tau$[b] | $-10^6\chi$ | $-10^6\chi$ |
| Water | 27.860 | 0.7192[c] | $9.90_7$ | 0.7192[c] | 0.7192[c] |
| Methanol | 26.505 | 0.6842 | $9.43_0$ | $0.684_6$ | 0.661—0.675 |
| Acetic acid | 20.868 | 0.5387 | $7.42_0$ | $0.538_7$ | 0.527—0.532 |
| Carbon tetrachloride | 17.174 | 0.4433 | $6.11_0$ | $0.443_6$ | 0.432—0.438 |
| Benzene | 27.520 | 0.7104 | $9.78_6$ | $0.710_4$ | 0.700—0.704 |

a) Landolt–Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," II Band, 10 Teil, Springer Verlag, Berlin (1967). b) Measured in 18.8 kOe. c) Taken as the standard.

(±0.01%) exceeds the best reproducibility, one can use this equation to calculate the magnetic susceptibilities of each material. The results are listed in Table 2. A good agreement between the values measured using the previous cell can be seen, while the literature values are slightly smaller than the results by an amount corresponding to the effect due to dissolved air.[9,11] In the present method, dried nitrogen was used as the operating gas and no continuous change of the $\tau$-value was observed. Therefore, the error due to the effect of dissolved air can be almost completely excluded. However, the organic liquids used here absorbed a slight amount of moisture when exposed to air. Thus, the smaller reproducibility for the organic liquids may be mainly caused by the irregular contamination due to atmospheric moisture during sampling. In fact, good reproducibility was obtained for benzene, owing to the small difference in its susceptibility compared to that of water. The method's reproducibility when using this cell is considered to be within ±0.02% ($\pm 1.5 \times 10^{-10}$ emu g$^{-1}$); such a value was obtained for water. It is difficult to estimate the absolute accuracy of the susceptibility since the absolute value of the susceptibility of water is poorly known.[12]

The diamagnetic susceptibility of a liquid slightly changes with the temperature.[13,14] In particular, accurate coefficients using the susceptibility change of water have been determined using the SQUID method.[7] If the $H^2/2g\bar{h}$ term in Eq. 1 is kept constant for different temperatures, the present cell may be applicable to measure the temperature dependence of the susceptibilities of diamagnetic liquids. The change in $g$ is negligibly small ($\leqq 1 \times 10^{-6}$ m s$^{-2}$) and the value of $H$ can be held practically constant throughout a measurement. Moreover, the change in the mean-effective-head is small, since it is of the order of the linear expansion coefficient of a cell made of Pyrex glass, about $3.3 \times 10^{-6}$ K$^{-1}$. Thus, one may test the sensitivity by measuring the temperature coefficients for water. In this case, Eq. 3 may be written as

$$\frac{\chi(T)}{\chi(20)} = \frac{\tau(T)}{\tau(20)}[0.999317 + 0.60 \times \frac{\rho_G(T)}{\rho_L(T)}], \qquad (8)$$

where the ratio of the susceptibility at $T$ in °C to that at 20 °C is taken. The experimental results are listed in Table 3, and are in good agreement with those obtained by the SQUID method.[7] The observed $\chi(T)/\chi(20)$ ratios are fitted to a palabolic equation,

$$\chi(T)/\chi(20) = 1 + a(T - 20) + b(T - 20)^2, \qquad (9)$$

by a least-squares method and the analyzed result is shown in Fig. 3. The temperature coefficients are listed in Table 4, and are compared with the reported values obtained by various observers. Earlier studies have been contradicted due to oxygen contamination of samples as well as to instrumental imprecision.[11]

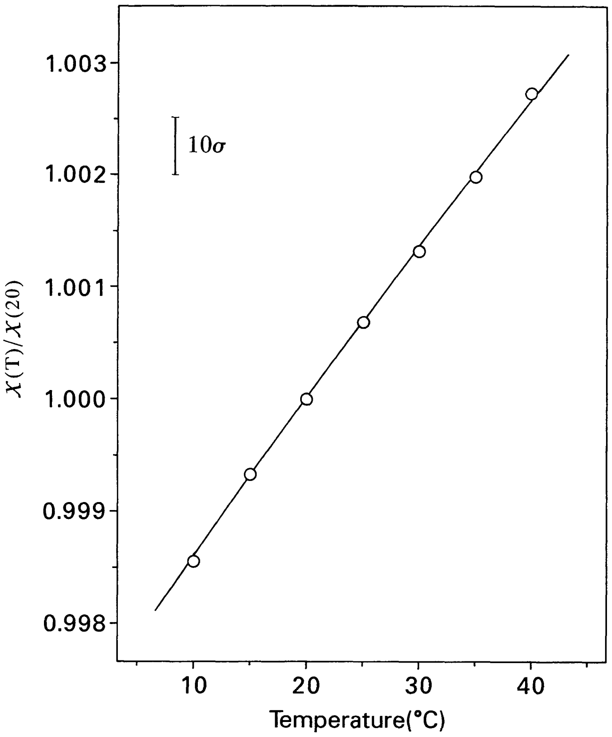

Fig. 3. Change in the mass susceptibility of water with temperature, relative to the value at 20°C. The solid line is a best fit second-order polynomial, Eq. 9. The half diameter of the circle is approximately one standard deviation of the data points.

Table 3. Susceptibilities for Water Observed at Various Temperatures

| Temperature | $-10^3\tau(T)$ | $\tau(T)/\tau(20)$ | $\chi(T)/\chi(20)$ | |
|---|---|---|---|---|
| °C | | | This work | SQUID[a)] |
| 10.0 | 27.819 | $0.99852_8$ | 0.99855 | 0.99860 |
| 15.0 | 27.841 | $0.99931_8$ | 0.99932 | 0.99930 |
| 20.0 | 27.860 | $1.00000_0$ | 1.00000 | 1.00000 |
| 25.0 | 27.879 | $1.00068_2$ | 1.00067 | 1.00069 |
| 30.0 | 27.897 | $1.00132_8$ | 1.00131 | 1.00138 |
| 35.0 | 27.916 | $1.00201_0$ | 1.00198 | 1.00206 |
| 40.0 | 27.937 | $1.00276_4$ | 1.00273 | 1.00273 |

a) Values calculated using a third-order polynomial, reported in Ref. 7.

Table 4. Comparison of the Temperature-Coefficients for Water Measured by Different Observers Using Different Methods[a]

| Observers | $10^4a/\mathrm{K}^{-1}$ | $10^6b/\mathrm{K}^{-2}$ | $100\sigma[n]$[b] | Method | References |
|---|---|---|---|---|---|
| Cabrera and Fahlenbrach (1933) | 1.15 | | | Faraday | Ref. 1 |
| Auer (1933) | 1.26 | | | Quinke | Ref. 2 |
| Wills and Boeker (1934) | 1.30 | −0.7 | | Quinke | Ref. 3 |
| Seely (1937) | 1.423(58)[c] | −1.05(33) | $0.009_0$[4] | Quinke | Ref. 4 |
| Cini and Torrini (1968) | 1.363(22) | 0.11(14) | $0.008_4$[49] | Gouy | Ref. 5 |
| Philo and Fairbank (1980) | 1.38954(78) | −0.1251(47) | $0.0001_0$[16] | SQUID | Ref. 7 |
| Day (1980) | 1.3687(39) | −0.073(23) | $0.0002_8$[6] | SQUID | Ref. 8 |
| This author | 1.383(29) | −0.22(18) | $0.005_1$[7] | | |

a) The values for Refs. 4, 5, 7, and 8 were recalculated using data in the range 10—40 °C, presented in respective papers. b) $\sigma$ is the standard deviation of the fit and $n$ is the number of data included in the calculation. c) The uncertainty in parentheses is one standard deviation in units of the last quoted coefficient.

The present results are in good agreement with the most pricise data[7] within each uncertainty. As estimated from the standard deviation, the sensitivity, or limit, of detection of the method is considered to be ±0.005% ($\pm 0.4\times 10^{-10}$ emu $\mathrm{g}^{-1}$); this represents the best performance among various methods based on classical principles. The higher sensitivity than the stability of the magnetizing current used here may be interpreted in terms of the performance: that the method gives a susceptibility that is measured in a time-averaged magnetic field. The accuracy of the susceptibility determined by this method is seriously limited by the availability of a standard value. It is reasonable to use water as a standard in order to maximize the precision, since its nature is never influenced by atmospheric moisture and the best reproducibility available.

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