BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (8), 2124—2127 (1977)

# Determination of Magnetic Susceptibilities of Diamagnetic Liquids by an Improved Viscometer Method

Kazuo Sueoka and Toshio Ikeda*
*Department of Chemistry, Johsai University, Sakado, Saitama 350-02*
**Department of Chemistry, Shizuoka University, Shizuoka 420*

(Received December 25, 1976)

An improved viscometer method is presented for the determination of the magnetic susceptibility of a liquid with a complete exclusion of the oxygen effect. The method was found to be excellent even in determining the magnetic susceptibilities of diamagnetic liquids, giving results accurate to within ±0.05%. The influence of air (or oxygen) was also discussed.

Previously, one of the present authors reported a viscometer method[1] for the determination of the magnetic susceptibilities of paramagnetic liquids by measuring the rate of flow of liquid through the capillary of a viscometer of the Ostwald type under the action of an external magnetic field. In the present study, the measuring device was improved using a modified Ubbelohde viscometer so that one may determine accurately the diamagnetic susceptibilities of liquids as well even by using an electromagnet of a comparatively small size. The diamagnetic susceptibilities of some organic liquids measured with the use of the improved cell under nitrogen were found to be in good agreement with those values reported in the literature within a range of deviation such as was pointed out by Eggleston *et al.*[2]

## Theoretical

A modified capillary viscometer of the Ubbelohde type (Fig. 1) is placed in a magnetic field so that the lower end of the capillary is in the center of a gap between the pole pieces of an electromagnet, while its capillary part extends vertically, through the inhomogeneous region, outside of the field. Then, a liquid in the capillary of the cell is forced to flow down by the action of gravity downwards and by that of the magnetic force upwards (or downwards, as the case may be), both acting simultaneously on the liquid when it passes through the inhomogeneous region of the field.

The Hagen-Poiseuille expression for the flow of a liquid may be written as

$$\frac{1}{t_{\mathrm{H}}} = \frac{\pi r^4}{8lv\eta}\left(\rho g\tilde{h}+\frac{1}{2}\kappa H^2\right), \tag{1}$$

where $t_{\mathrm{H}}$ is the time required by the liquid of a certain volume, $v$, to flow down in the presence of the field through a capillary with a certain radius, $r$, and a certain length, $l$; $g$ is the acceleration of gravity; $h$ is the mean effective head of the liquid; the $\rho$, $\eta$, and $\kappa$ symbols represent the density, the viscosity coefficient, and the volume magnetic susceptibility of the liquid respectively; $H$ denotes the local magnetic field strength near the center of the pole-pieces gap of the magnet. Denoting by $t_0$ the time of flow of the liquid in the absence of an external magnetic field, one may write $1/t_0=\pi r^4\rho g\tilde{h}/8lv\eta$. Since $\eta$ is practically independent of the field of such an order of strength as is used here, we obtain from Eq. 1 the following relation:

$$\frac{t_0-t_{\mathrm{H}}}{t_{\mathrm{H}}} = \frac{\kappa H^2}{2\rho g\tilde{h}} = \frac{\chi H^2}{2g\tilde{h}}, \tag{2}$$

where $\chi$ represents the mass magnetic susceptibility of the liquid. Equation 2 is the basic equation for determining the magnetic susceptibility in the present method. As is clear in Eq. 2, the time, $t_{\mathrm{H}}$, should be longer than $t_0$ for diamagnetic liquids, while it is shorter for paramagnetic liquids. Upon taking into consideration the fact that the present type of viscometer is so made that the mean effective head, $h$, is controlled automatically to an exactly fixed value in every measurement, one may always be allowed to write

$$\frac{t_0-t_{\mathrm{H}}}{t_{\mathrm{H}}\chi} = K, \tag{3}$$

so long as $t_{\mathrm{H}}$ is measured under the same field strength, $H$, where $K$ is a constant characteristic of the cell used and is dependent on $H$, but entirely independent of the nature of the liquid. If once the constant, $K$, is determined for a certain standard liquid substance, such as water, whose magnetic susceptibility is known accurately, the susceptibilities of all the other liquid substances can be determined by merely measuring the two corresponding quantities, $t_0$ and $t_{\mathrm{H}}$, of the sample to be studied.

## Experimental

*Materials.* Commercial nitrogen with a purity of more than 99.9% was dried by passing silica gel and phosphorus pentaoxide through. The water was purified by sub-boiling distillation from a pure quartz still after deionization. The benzene, carbon tetrachloride, methanol, 2,2,4-trimethylpentane, and cyclohexane were Dotite Primasol solvents, while the toluene, dioxane, ethyl acetate, heptane, hexane, 2-propanol, and acetone were Dotite Spectrosol solvents obtained from the Dojindo Co. The other solvents, such as, acetic acid, ethanol, and nitrobenzene, were of the Wakō Guaranteed Reagent grade. These organic solvents were used without further purification.

*Capillary Cell.* A capillary viscometer cell of a modified Ubbelohde type, equipped with a thermostat jacket, was fixed in the pole gap of a magnet so that the lower end of its capillary part was located at the center of the pole gap of the magnet, while its upper part extended vertically out of the magnetic field through the inhomogeneous region of the field. Figure 1 shows the experimental equipment, where a capillary cell made of Pyrex glass is fixed upright in duplicated water jacket cabinets made of poly(vinyl chloride). The cabinets are covered with foam polystylene to which a glass window, W,

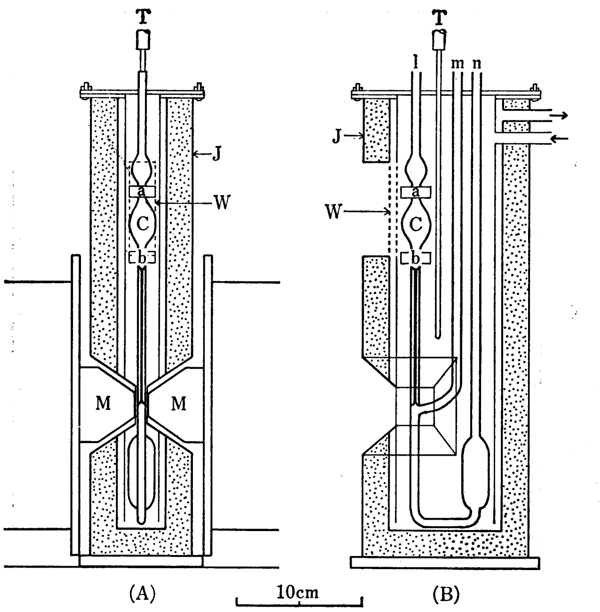

Fig. 1. Experimental setup, A, Front view, and B, side view. C, Capillary cell; a and b, detectors of viscometer; W, glass window; M, magnet; J, cabinet made of poly(vinyl chloride) covered with foam polystylene; T, thermistor. The openings, l, m, and n, connected to the operation tube (Fig. 2).

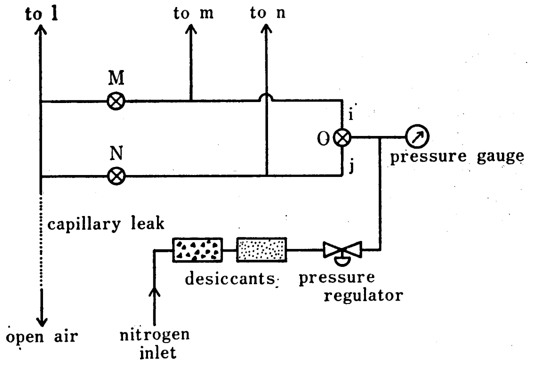

Fig. 2. Connection diagram of the operation tube.

is attached at the level of the upper globular part, C, of the cell.

*Magnet.* A Weiss-type 100-kg electromagnet manufactured by Nihon Kohmitsu Kenkyusho was used. The magnet pole pieces, about 20 mm in tip diameter, were set at a separation of 8 mm. The magnetic field was controlled using a stabilized dc source (±0.01%) up to 4 A, corresponding to a maximum field of 18800 Oe. The magnetic-field strength was calibrated with a Yokogawa gauss meter, type 3251, at the center of the pole gap.

*Measuring.* Prior to measuring, the liquid sample which was to be put in the cell was saturated with nitrogen by passing nitrogen through the liquid for about 10 min, and the residual inside space of the cell was fully filled with nitrogen by the aid of an operation tube (Fig. 2) connected to the cell. After this, until the measurement came to an end, nitrogen was continually allowed to flow through the operation tube so that the liquid in the cell was never exposed to air again. When it was necessary to shift the liquid sample up to the globular part, C, of the cell, a moderate pressure slightly higher than the exterior was applied by introducing nitrogen through the operation tube during the measurements, while the inside pressure was kept constant. The direction of the flow of nitrogen was controlled, as occasion called for, by operating three magnetic valves made of Teflon in the way indicated in Table 1. The time of flow of the liquid was measured to an accuracy of ±0.01 s using a viscometer of the Shibayama Scientific Co. provided with an electric detector connected to an electronic clock for monitoring the passage of the meniscus of the liquid. The temperature around the cell was controlled at 20±0.01 °C by circulating thermostated water. The measurement of the flow time was repeated alternately in the presence or in the absence of the magnetic field, and the value of $(t_0-t_H)/t_H$ was calculated for each step. The observed values were found to become closely reproducible after several repetitions of measurements in the beginning. Twenty or fifty measurements were averaged to calculate the magnetic susceptibility.

Table 1. Operation of M, N, and O valves

| | M | N | O |
|---|---|---|---|
| Removing air | close | open | i |
| Shifting up liquid | close | close | j |
| Measuring | open | open | j |

## Results and Discussion

The results are shown in Fig. 3. In all cases a perfect linear relation may be seen passing through the point of origin. These results can be expressed by the following experimental formula:

$$\frac{t_0-t_H}{t_H} = \alpha H^2, \tag{4}$$

where α should, in comparison with Eq. 2, be proportional to the mass susceptibility, χ, of the liquid in such a way that $\alpha=\chi/2gh$; this has proved to be true experimentally as well, as may be seen in Table 2. Thus, Eq. 3 was well confirmed.

The susceptibilities were calculated by the aid of Eq. 3 for some liquids, taking water as a standard reference. The results are shown in Fig. 4 and Table 3. The observed values of χ are found to be reproducible within ±0.05% and are in good agreement with the

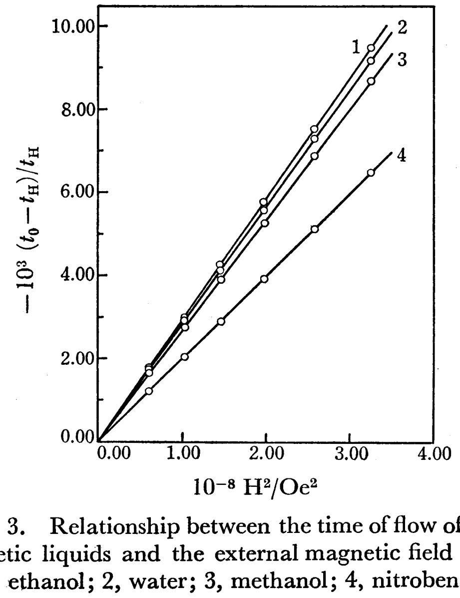

Fig. 3. Relationship between the time of flow of diamagnetic liquids and the external magnetic field strength: 1, ethanol; 2, water; 3, methanol; 4, nitrobenzene.

TABLE 2. COMPARISON OF $\alpha$ VALUES WITH MAGNETIC SUSCEPTIBILITIES OF LIQUIDS AT 20 °C

| Materials | $-10^{11}\alpha^{a)}$ dyn$^{-1}$ cm$^2$ | $-10^6\chi_{\text{lit}}{}^{b)}$ e.m.u. | $-10^5\alpha/\chi_{\text{lit}}$ dyn$^{-1}$ cm$^2$ e.m.u.$^{-1}$ |
|---|---|---|---|
| Water | 2.82 | 0.719 | 3.92 |
| Methanol | 2.67 | 0.660—0.669 | 4.05—3.99 |
| Ethanol | 2.91 | 0.717—0.736 | 4.06—3.95 |
| Benzene | 2.76 | 0.675—0.707 | 4.09—3.90 |
| Nitrobenzene | 2.00 | 0.500—0.505 | 4.00—3.96 |
| Toluene | 2.82 | 0.711—0.722 | 3.97—3.91 |

a) Mean of 10 measurements.
b) Obtained by the conversion of the molar magnetic susceptibilities, $\chi_M$, Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," II Band, 10 Teil, Springer Verlag, Berlin (1967).

literature values. However, strictly speaking, most of them are slightly larger than the literature values, except for acetone and cyclohexane.

As is shown in Fig. 5 for benzene, the observed value of $(t_0-t_H)/t_H$ was practically attained within about 2 min after nitrogen was passed through; this is its final steady state value, observed after the complete removal of air from the cell. Since, in the present work, the passage of nitrogen was carried out for a sufficiently long time (more than 10 min), the influence of air that was found in the cell in the beginning, including the liquid sample, could be assumed to be reduced to the limits of accuracy of this method, *i.e.*, within ±0.05%.

Eggleston *et al.*[2] pointed out experimentally that most of the diamagnetic susceptibilities reported in the past are in error by an amount corresponding to the effect due to dissolved air. The magnetic susceptibility of a liquid dissolving air may be expressed in the following relationship:

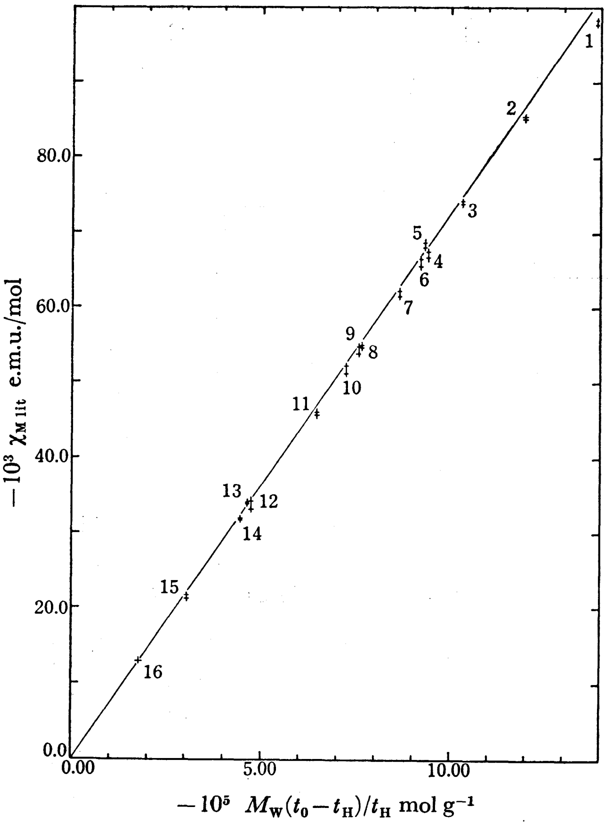

Fig. 4. Relationship between the $(t_0-t_H)/t_H$ value found at a fixed magnetic-field strength of 18800 Oe and the literature values of the magnetic susceptibility of the liquids. $M_w$, molecular weight. 1,2,2,4-trimethylpentane; 2, heptane; 3, hexane; 4, carbon tetrachloride; 5, cyclohexane; 6, toluene; 7, nitrobenzene; 8, benzene; 9, ethyl acetate; 10, dioxane; 11, 2-propanol; 12, ethanol; 13, acetone; 14, acetic acid; 15, methanol; 16, water.

TABLE 3. DIAMAGNETIC SUSCEPTIBILITIES OF LIQUIDS IN $10^{-6}$ e.m.u. AT 20 °C

| Liquids | $t_0{}^{a)}$ s | $t_H{}^{a,b)}$ s | $-10^3\cdot$ $(t_0-t_H)/t_H$ | This work $-\chi$ | $-\chi_M$ | Literature$^{c)}$ $-\chi_M$ |
|---|---|---|---|---|---|---|
| Water | $397.54_0$ | $401.51_8$ | $9.90_7$ | 0.7192*$^{c)}$ | 12.96$^{c)}$ | 12.96 |
| Methanol | $297.57_8$ | $300.41_1$ | $9.43_0$ | $0.684_6$ | $21.9_3$ | 21.15—21.60 |
| Ethanol | $616.89_2$ | $623.27_4$ | $10.23_9$ | $0.743_3$ | $34.2_4$ | 33.05—34.18 |
| 2-Propanol | $1259.46_0$ | $1273.10_9$ | $10.72_1$ | $0.778_3$ | $46.7_8$ | 45.68—46.02 |
| Acetic acid | $478.49_1$ | $482.06_8$ | $7.42_0$ | $0.538_7$ | $32.3_5$ | 31.6 —31.9 |
| Acetone | $163.65_0$ | $164.96_2$ | $7.95_3$ | $0.577_3$ | $33.5_3$ | 33.64—33.99 |
| Carbon tetrachloride | $248.04_6$ | $249.57_1$ | $6.11_0$ | $0.443_6$ | $68.2_3$ | 66.6 —67.45 |
| Hexane | $200.06_9$ | $202.49_0$ | $11.95_6$ | $0.867_9$ | $74.8_0$ | 73.80—74.42 |
| Heptane | $243.12_2$ | $246.06_3$ | $11.95_2$ | $0.867_7$ | $86.9_5$ | 85.20—85.5 |
| 2,2,4-Trimethylpentane | $295.12_8$ | $298.76_3$ | $12.16_7$ | $0.883_3$ | $100.9_0$ | 97.58—98.34 |
| Ethyl acetate | $203.85_0$ | $205.61_4$ | $8.57_9$ | $0.622_8$ | $54.8_7$ | 53.9 —54.28 |
| Dioxane | $507.16_0$ | $511.34_8$ | $8.19_0$ | $0.594_6$ | $52.3_9$ | 51.1 —52.16 |
| Cyclohexane | $509.00_5$ | $514.69_6$ | $11.05_7$ | $0.802_7$ | $67.5_6$ | 68.04—68.7 |
| Benzene | $297.19_8$ | $300.13_5$ | $9.78_6$ | $0.710_4$ | $55.4_9$ | 54.7 —55.00 |
| Nitrobenzene | $676.28_1$ | $681.05_3$ | $7.00_7$ | $0.508_7$ | $62.6_3$ | 61.53—62.15 |
| Toluene | $272.55_2$ | $275.30_1$ | $9.98_5$ | $0.724_9$ | $66.7_9$ | 65.54—66.52 |

$\chi_M$: molar susceptibility. *: Taken as the standard. a) Mean of 20—50 measurements. b) Measured in 18800 Oe. c) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," II Band, 10 Teil, Springer Verlag, Berlin (1967).

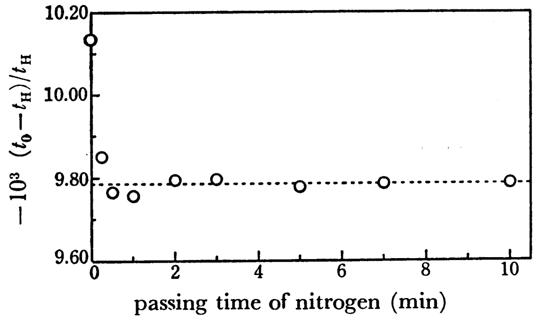

Fig. 5. Effect of atmospheric air in the cell on the flow time of benzene. (The broken line shows the level to be observed under ideal conditions when the air in the cell is completely removed. Such ideal conditions might be nearly attained, for example, by means of the freeze-pump technique and finally by saturation with nitrogen using the operation tube.)

$$\chi = \chi^\circ + \frac{\rho_{\text{air}}}{\rho}\beta\chi_{\text{air}}, \tag{5}$$

where $\chi^\circ$ and $\chi_{\text{air}}$ are the mass magnetic susceptibilities of a deaerated pure liquid and of air respectively, $\beta$ is the solubility of air in the liquid, and $\rho$ and $\rho_{\text{air}}$ are the densities of the liquids and of air respectively. Since $\chi$ and $\chi^\circ$ for diamagnetic liquids are opposite in sign to $\chi_{\text{air}}$, and since the last term of Eq. 5 is of an order of magnitude of about $10^{-8}$ e.m.u., $\chi$ should be observed to be less than $\chi^\circ$ by a fraction as small as 1.0—1.4% in most of the organic liquids studied here. This estimate is in nice agreement with the deviation found from the data reported in the past with regard to the susceptibilities of liquids of the same kinds as studied here. On the other hand, the influence of the dissolved air upon the $\chi$ value of water, which was adopted as the standard reference here, is only 0.14%. Thus, it seems certain that most literature values for organic liquids are spoiled by the dissolved air, except those given by Eggleston *et al.*,[2] who were unique in making measurements of the susceptibility with sufficient care to deaerate the sample. The values of the present work (Table 3) are found to be very close to those $\chi$ values, $-0.7081$ and $-0.8665 \times 10^{-6}$ e.m.u., given by Eggleston *et al.*[2] for benzene and heptane respectively, though there still remaining deviations of about 0.2—0.3%.

In order to get reliable results, it is preferable to make measurements in as strong a magnetic field as possible, not to speak of the necessity of a severe regulation of the temperature, because even a slight change in the temperature may cause a considerable change in the viscosity and, consequently, in the flow time. The advantages of the present method are: (1) The extensively homogeneous region of the magnetic field is not needed, because the meniscus of the liquid at the lower end of capillary does never shift throughout the measurement of the flow time; (2) the outside diameter of the cell near the lower end of the capillary part in the pole gap is so small that there is no need to use an electromagnet of a large scale; a small size magnet such as used here is sufficient; (3) the influence of air (or oxygen) that spoils the measurement of the diamagnetic susceptibility can be eliminated almost completely; and (4) it has been confirmed experimentally that an occasional slight shock or vibration in the table on which the magnet is mounted has practically no appreciable effect on the observed values.

## References

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2) B. C. Eggleston, D. F. Evans, and R. E. Richards, *J. Chem. Soc.*, **1954**, 941.