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Determination of the Magnetic Susceptibilities of Liquids Dissolving Oxygen by the Viscometer Method and a New-Type Linear Law of Susceptibility

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The magnetic susceptibilities of a number of liquids dissolving oxygen have been determined by an improved viscometer method at 298.15 K and 105.3 kPa; it has been confirmed that they are nicely expressed using the Wiedemann's additivity law, and it is found that they are perfectly linear with the volume fraction of oxygen in the atmosphere in contact with liquids: a new-type law of susceptibility. It is shown that the effects of dissolved air are not canceled out unless the susceptibility of an oxygen-free liquid is used as the reference value, even when the solubilities of oxygen in the sample and the reference liquids are equal, causing a real error to an extent as much as 1.7%.

About 40 years ago, Eggleston, Evans, and Richards[1] pointed out experimentally that most of the diamagnetic susceptibilities of organic liquids reported in the past are in error by an amount as much as 1.7%, corresponding to the effect of dissolved oxygen. Soon thereafter, French and Harrison[2] stressed by demonstration that in real observations the error caused by not being careful of dissolved atmospheric oxygen is not so serious, as pointed out by Eggleston et al., since the oxygen effect on the liquid sample is nearly canceled out by the presence of oxygen in the reference used. Despite these two published comments on this subject, leaving much to be open, almost all of the earlier researchers measured the susceptibilities of liquids or solutions without considering the dissolved air. Recently, the present author and a co-worker reported on an improved viscometer method[3,4] which is very useful for the determination of the magnetic susceptibilities of diamagnetic liquids. The present paper concerns an accurate determination using the method involving the magnetic susceptibilities of a number of organic liquids equilibrating with air of different compositions. Further, it clarifies the difference in the two seemingly conflicting conclusions of Eggleston et al.[1] and of French et al.[2] In addition, a new-type linear-law of susceptibility is proposed.

Principle

First, the principle of the viscometer method is briefly described, since this method is unfamiliar. A capillary viscometer cell of the modified Ubbelohde-type shown in Fig. 1 is placed in a magnetic field so that the lower end of the capillary is in the center of the pole gap of an electromagnet, while the capillary part extends vertically, through the inhomogeneous region, outside of the field. The liquid in the capillary is forced to flow down due the dual action of the gravitational and magnetic forces acting on it into the environmental gas that occupies the dead space below the capillary. Supposing that a liquid of a certain volume requires a time of t_H to flow down through the capillary of the viscometer under action of an external magnetic field of the strength (H), one may write the Poiseuille's equation as follows:

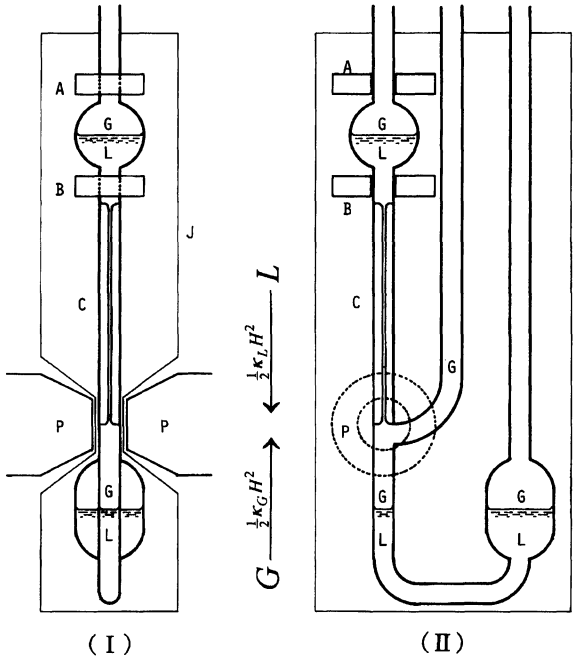

Fig. 1. Schematic representation for the G–L contact in a viscometer cell and the magnetic forces acting on G and L; (I), Front view, and (II), side view. G, gas phase; L, liquid phase; C, capillary; A and B, detectors; P, the position of the pole pieces of electomagnet; J, water jacket cabinet.

$$\frac{1}{t_H} = C[d_{\mathrm{L}} g\tilde{h} + \frac{1}{2}(\kappa_{\mathrm{L}} - \kappa_{\mathrm{G}})H^2], \tag{1}$$

where C is a constant determined by the geometry of the cell and by the viscosity of the flowing liquid; g is the acceleration due to gravity, $\tilde{h}$ the mean effective head of the liquid, d_{L} the density of the liquid, and κ_{L} the volume magnetic susceptibility of the liquid phase (L) in equilibrium with the gas phase (G) whose susceptibility is κ_{G}. Here, the gas is assumed to dissolve in the liquid without any chemical reactions. In the absence of a field, Eq. 1 reduces to a simple form, such as $1/t_0 = Cd_{\mathrm{L}}g\tilde{h}$, where t_0 is the time of flow in the absence of a field. We now introduce a new parameter, τ, defined by

$$\tau(\mathrm{G}) \equiv \frac{t_0 - t_H}{t_H} = \frac{K}{d_{\mathrm{L}}}(\kappa_{\mathrm{L}} - \kappa_{\mathrm{G}}), \quad K = \frac{H^2}{2g\tilde{h}}, \tag{2}$$

where K is a cell-constant, as long as t_H is measured under the same field strength (H). For a two-component gaseous mixture of oxygen (O) and nitrogen (N) equilibrating with a working liquid in the cell, one may write Wiedemann's rule for the apparent susceptibility (κ_{G}), of a gas mixture saturated with the vapor of the working liquid at a given temperature (T) and pressure (P), as follows:

$$\kappa_{\mathrm{G}} = \kappa^{\circ}_{\mathrm{O}} x_{\mathrm{O}} + \kappa^{\circ}_{\mathrm{N}} x_{\mathrm{N}} + \kappa^{\circ}_{\mathrm{V}} x_{\mathrm{V}}, \tag{3}$$

where $\kappa^{\circ}_{\mathrm{O}}$, $\kappa^{\circ}_{\mathrm{N}}$, and $\kappa^{\circ}_{\mathrm{V}}$ denote the volume susceptibilities of pure oxygen, pure nitrogen and pure vapor of the liquid at a given condition, respectively, and x_{O}, x_{N}, and x_{V} are the volume fractions of these gases in the same sequence. Converting the susceptibility of species i (κ°_i) per unit volume into that (χ°_i) per unit mass, by the aid of the definition formula, $\kappa^{\circ}_i \equiv d_i \chi^{\circ}_i$, and using the abbreviation d_i ($\equiv d^{\circ}_i x^{\circ}_i$), one may write an equation for the specific susceptibility ($\chi_{\mathrm{L}}(\mathrm{G})$) of the liquid equilibrating with the gaseous mixture. From Eqs. 2 and 3 we have

$$\chi_{\mathrm{L}}(\mathrm{G}) = \frac{\tau(\mathrm{G})}{K} + \frac{d_{\mathrm{O}}\chi^{\circ}_{\mathrm{O}} + d_{\mathrm{N}}\chi^{\circ}_{\mathrm{N}} + d_{\mathrm{V}}\chi^{\circ}_{\mathrm{V}}}{d_{\mathrm{L}}}. \tag{4}$$

Generally speaking, the difference in the diamagnetic susceptibilities between the liquid and vapor is usually very small and, in addition, the magnitude of the last term, $d_{\mathrm{V}}\chi^{\circ}_{\mathrm{V}}/d_{\mathrm{L}}$ in Eq. 4, is very slight. Thus, identifying $\chi_{\mathrm{L}}(\mathrm{G})$ and $\chi^{\circ}_{\mathrm{V}}$, one obtains the following expression:

$$\chi_{\mathrm{L}}(\mathrm{G}) = \frac{1}{d_{\mathrm{L}} - d_{\mathrm{V}}}\left[\frac{d_{\mathrm{L}}\tau(\mathrm{G})}{K} + d_{\mathrm{O}}\chi^{\circ}_{\mathrm{O}} + d_{\mathrm{N}}\chi^{\circ}_{\mathrm{N}}\right]. \tag{5}$$

Equation 5 is a basic equation for determining the susceptibilities of liquids which dissolve oxygen by the present method.

Experimental

Measuring Cell. The volume of the upper globular part of the cell is about 5×10^{-6} m^3; the capillary is about 0.1 m in length and 0.3×10^{-3} m in diameter. In contrast to the original method,[5)] in which the viscometer cell of the Ostwald type is used, and the upper globular part is in a homogeneous magnetic field that is sufficiently wide to cover this part, the present method has the following convenient points. A much smaller magnet may be used, since the more limited homogeneous region of the magnetic field and a narrower gap of the pole pieces are used. Furthermore, the mean-effective heads of the liquids are automatically maintaind at a same value, irrespective of the volumes of the liquids in the cell. As compared with the horizontal-type cell,[4)] the vertical cell used here has a comparable reproducibility (±0.02%) for different sample liquids and easier handling of the cell, though less sensitivity.

Measurements Bofore the measurements, the liquid in the cell was saturated with the gas by passing it through the liquid for about 10 min at a flow rate of about 1.2×10^{-6} m^3 s^{-1}; the dead space of the cell was fully replaced by the same gas by means of an operation tube connected to the cell. The gas flow rate was then reduced to 0.3×10^{-6} m^3 s^{-1}, and alternate measurements of the flowing times (t_0 and t_H) were followed repeatedly as the tube was connected to the cell. The flowing times were read off at an accuracy of ±0.001 s. The details of the operation-tube system were illustrated in a previous paper.[3)] Both before and after every measurement of τ under a gaseous mixture, the measurement was repeated under nitrogen in order to check the recovery of $\tau(\mathrm{N})$ to its original level. By this procedure we could obtain indirect information that no chemical change occurred in the liquid upon dissolving the gaseous sample. The temperature and pressure were kept constant at 298.15±0.01 K and 105.32±0.13 kPa (790±1 mmHg).

The cell-constant K was evaluated, using Eq. 5 based on the τ-value of water measured under nitrogen, using the χ-value of -0.7205×10^{-6} cm^3 g^{-1}# for water. The result was 1.15×10^6 kg^2 m^{-2} s^{-2} A^{-2} under a magnetic flux density of 1.99 T, the highest available at a maximum magnetizing current of 4 A (±0.01%). (The χ-value of water used here as a standard was obtained from a literature-value[6)] of -0.7200×10^{-6} cm^3 g^{-1} at 291 K using an empirical relation[7)] for its temperature dependence.) In the electromagnet used, pole-pieces were of 2×10^{-2} m diameter and the tips were fixed to have about a 7.5×10^{-3} m gap. The density of the liquid (d_{L}) was measured by using a precision density meter (SS-D-200T of Shibayama Scientific Co.), which gave the oscillation periods of the sample cell and the reference cell paralleled to each other. The densities (kg m^{-3}) of the gases (d_{O}, d_{N}, and d_{V}, respectively) were computed by the following equations (assuming ideal gases):

$$d_{\mathrm{O}} = 3.85 \times (P - p)\phi/T, \tag{6a}$$

$$d_{\mathrm{N}} = 3.37 \times (P - p)(1 - \phi)/T, \tag{6b}$$

and

$$d_{\mathrm{v}} = 0.12 \times pM/T, \tag{6c}$$

where p (kPa) is the vapor pressure of a liquid having a molecular weight of M at a given temperature (T(K)); ϕ is the volume fraction of oxygen in the mixed gas.

Materials. Nitrogen and oxygen were obtained from commercial sources with purities exceeding 99.9%, from which gaseous mixtures (an artificial air) of appropriate compositions were prepared. These artificial and atmospheric airs were dried by successive passage through silica gel and diphosphorus pentaoxide, and, finally, through a membrane filter (FM-22; Fuji Photo Film Co.). The compositions of the airs were analyzed by a gas-chromatographic technique. Water was purified by sub-boiling distillation from a quartz still after deionization. Methanol, ethyl acetate, acetone, dimethyl sulfoxide, toluene, benzene, cyclohexane, heptane, 2,2,4-trimethylpentane, and carbon tetrachloride were Dotite Spectrosol solvents for spectroscopy (Dojindo Co.). Ethylbenzene and cyanobenzene were Tokyo Kasei guaranteed reagents; the remainer was a Wako guaranteed reagent. Aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, and acetic acid were dried and distilled just before

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#Note that cgs units are used hereafter. In SI units the volume susceptibility is dimentionless and numerically equal to 4π times the cgs value.

measuring, while the other solvents were used without further purification.

Results and Discussion

More than 25 measurements were repeated to yield a mean τ-value. The τ-values measured under atmospheric and artificial air samples (oxygen + nitrogen) having different compositions are shown in Table 1. The $\chi_L(G)$-values were obtained from these experimental τ-values in combination with the necessary physicochemical data listed in Table 2, and are shown in Table 3 and Fig. 2; the calculation was carried out using a value of 107.3×10^{-6} cm^3 g^{-1} for the specific susceptibility of oxygen (χ_O°), which had been previously determined by the present author,[8] and -0.43×10^{-6} cm^3 g^{-1} for that of nitrogen (χ_N°), which appeared in the Landolt–Börnstein table.[10] As can be seen in every case (Table 3), the susceptibility of nitrogen-saturated liquid ($\chi_L(N)$) falls in the lowest level compared with that of air-saturated liquid ($\chi_L(\text{Air})$); further, the value of $\chi_L(G)$, as shown in Fig. 2, is strictly linear with the volume fraction of oxygen in air. The relation may be expressed according to the following empirical formula:

$$\chi_L(G) = \chi_L(N) + [\chi_L(O) - \chi_L(N)]\phi, \tag{7}$$

where $\chi_L(O)$ represents the susceptibility of a liquid saturated with pure oxygen at a given temperature and pressure. This is a new linear relation of the susceptibility for liquids in equilibrium with air. As an example verifiable of this law (Eq. 7), the ϕ-values (the oxygen content) of atmospheric air are determined by calculations involving the observed $\chi_L(G)$-values for various liquids; the results are listed in the last column of Table 3: They are found to be thoroughly consistent with each other, and in good agreement with the ϕ-values determined by different methods.[11]

According to Wiedemann's law, on the other hand, the susceptibility of a liquid equilibrating with a gas mixture (G, an air), can be expressed as follows:

$$\chi_L(G) = w_L\chi_L^\circ + w_O\chi_O^\circ + w_N\chi_N^\circ, \tag{8}$$

where w_L, w_O, and w_N denote the weight fractions of the working liquid, dissolved oxygen, and dissolved nitrogen, respectively. Since most liquids scarcely change their density upon the dissolution of gasses, it is allowable to put approximately $w_L=1$, and further to make the conversion $w_O=(d_O/d_L)L(O)$ and $w_N=(d_N/d_L)L(N)$, where $L(O)$ and $L(N)$ denote the solubilities (Ostwald coefficients) of oxygen and nitrogen in liquid, respectively. Thus, instead of Eq. 8, one has

$$\chi_L(G) = \chi_L^\circ + \frac{d_O L(O)}{d_L}\chi_O^\circ + \frac{d_N L(N)}{d_L}\chi_N^\circ. \tag{9}$$

As long as $\chi_L(G)$ and $\chi_L(O)$ are measured under the same experimental conditions (T and P) the volume fraction (ϕ) of oxygen (obtained from Eqs. 6 and 9),

$$\phi = \frac{\chi_L(G) - \chi_L(N)}{\chi_L(O) - \chi_L(N)}, \tag{10}$$

should give a consistent value, irrespective of actually executed temperature and pressure. Equation 10 is identical to Eq. 7. Thus, the empirical formula of Eq. 7 is necessarily obtained from Wiedemann's law if the gas behaves ideally (within experimental errors), and if Henry's law is applicable for the experimental conditions.

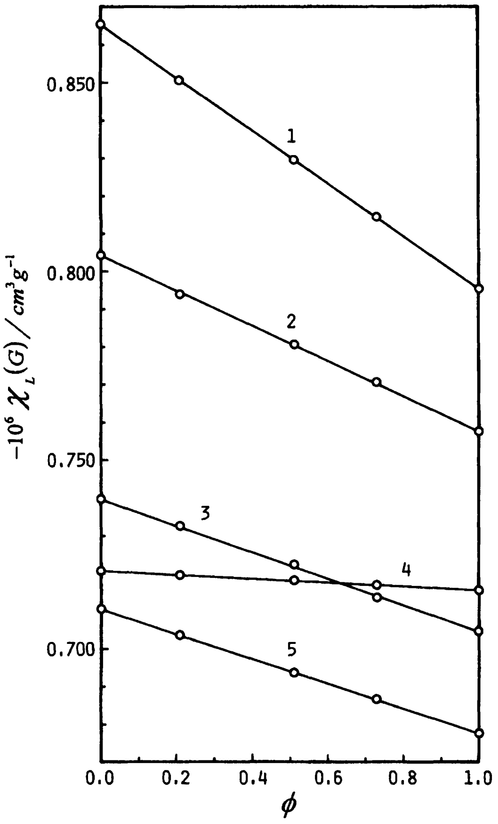


Fig. 2. Relationships between observed susceptibilities of liquids equilibrating with atmospheric and artificial airs and the volume fractions of oxygen. 1, heptane; 2, cyclohexane; 3, ethylbenzene; 4, water; 5, benzene.

The effect of dissolved oxygen on the susceptibility of a diamagnetic liquid was reported for the first time by Eggleston et al.,[1] who pointed out the presence of an error in the literature-values (as mentioned above). A comparison of the susceptibilities of various liquids found in the literature ($\chi_L(\text{Lit})$) with those determined in this work ($\chi_L(N)$) is given in Fig. 3, where the normalized quantity defined by the following equation is taken:

$$\delta \equiv [\chi_L(\text{Lit}) - \chi_L(N)]/[\chi_L(\text{Air}) - \chi_L(N)]. \tag{11}$$

One may seen that nitrogen-saturated values measured by Eggleston et al., i.e., -0.7081×10^{-6} cm^3 g^{-1} for benzene and -0.8665×10^{-6} cm^3 g^{-1} for heptane, are in fairly good agreement with our results. Further-

Table 1. τ(G)-Values ($-10^3\ \tau$) Measured under Air of Different Oxygen Contents (%) at 298.15 K

Materials	O_2/%				
	0	Air	51	73	100
Water	10.437	10.853	11.454	11.893	12.426
Methanol	9.912	10.273	10.796	11.182	11.637
Acetic acid	7.817	8.152	8.629	8.978	9.406
Ethyl acetate	8.980	9.284	9.737	10.052	10.471
Acetone	8.301	8.589	8.997	9.302	9.668
Dimethyl sulfoxide	8.282	8.669	9.207	9.610	10.086
Ethylbenzene	10.715	11.120	11.699	12.106	12.635
Toluene	10.462	10.840	11.395	11.795	12.274
Nitrobenzene	7.385	7.708	8.192	8.522	8.957
Cyanobenzene	9.207	9.585	10.125	10.510	11.004
Benzene	10.287	10.639	11.136	11.506	11.950
Aniline	9.887	10.306	10.909	11.336	11.870
N-Methylaniline	10.108	10.518	11.112	11.550	12.053
N,*N*-Dimethylaniline	10.346	10.755	11.333	11.761	12.277
Cyclohexane	11.642	11.999	12.529	12.909	13.368
Heptane	12.544	12.933	13.498	13.924	14.410
2,2,4-Trimethylpentane	12.779	13.149	13.690	14.099	14.585
Carbon tetrachloride	6.403	6.569	6.816	6.988	7.211
Carbon disulfide	7.639	7.793	8.019	8.182	8.377

Table 2. Physico-Chemical Data of Liquids at 298.15 K

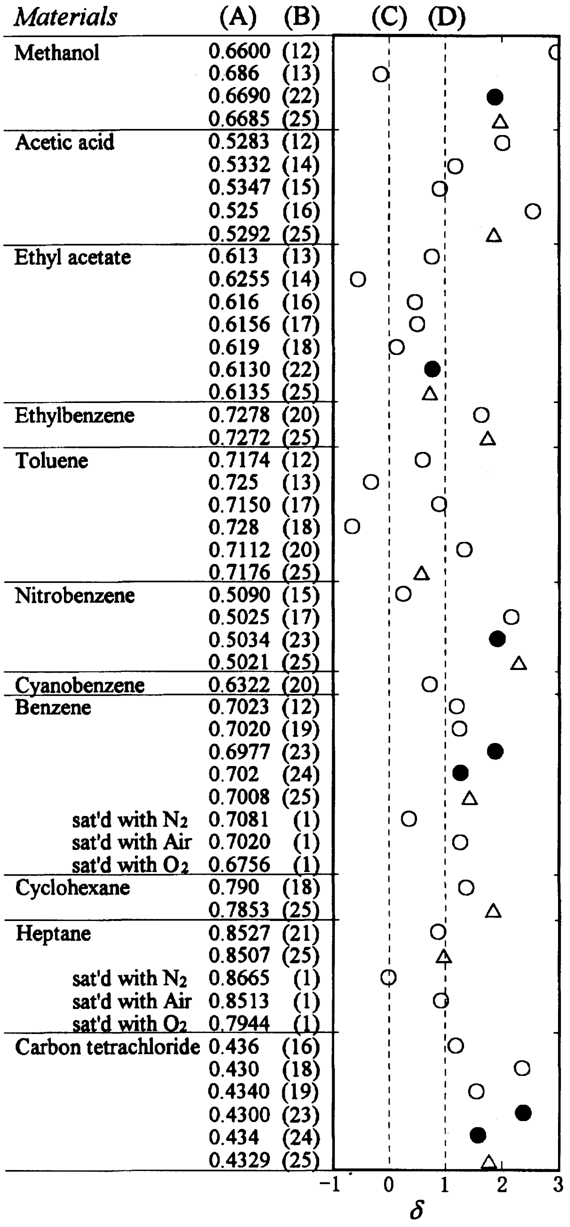
Materials	Molecular weight	Density	Vapor pressure[a)]
	M	$10^{-3}\ d_L/\mathrm{kg\,m^{-3}}$	p/kPa
Water	18.02	0.997044[b)]	3.145
Methanol	32.04	0.786622	16.265
Acetic acid	60.05	1.043473	2.054
Ethyl acetate	88.11	0.894359	12.1
Acetone	58.08	0.784739	29.401
Dimethyl sulfoxide	78.13	1.095697	0.095
Ethylbenzene	106.17	0.862788	1.267
Toluene	92.14	0.862022	3.765
Nitrobenzene	123.11	1.198100	0.036
Cyanobenzene	103.12	1.000332	0.81
Benzene	78.11	0.872531	12.665
Aniline	93.13	1.017457	0.04
N-Methylaniline	107.16	0.981940	0.064
N,*N*-Dimethylaniline	121.18	0.951763	0.099
Cyclohexane	84.16	0.773636	13.031
Heptane	100.21	0.679377	6.098
2,2,4-Trimethylpentane	114.23	0.687558	6.562
Carbon tetrachloride	153.82	1.584509	14.565
Carbon disulfide	76.14	1.255427	47.633

a) Estimated from literature-values at near 298.15 K in CRC Handbook (1981).
b) Taken as the reference.

more, the validity of relation (10) is also shown in their values, giving the volume fractions of oxygen (ϕ) in atmospheric air to be 0.211 for heptane and 0.188 for benzene, in agreement with an authentic value determined by a different method. However, many of the other literature-values are, irrespective of the method used, show slightly less diamagnetism than do the observed values of χ_L(N), and distribute around the values of χ_L(Air), (δ=1), rather than χ_L(N), (δ=0).

For the error ($\Delta\chi$) involved in the susceptibility determined by the Gouy method without taking care of dissolved air, French et al.[2)] gave the following expression and demonstrated that the effect of dissolved air would be canceled out by that in the reference liquid used:##

##The sign of the susceptibilities are taken to be negative for diamagnetism and positive for paramagnetism, just opposite to those taken by French et al.[2)]



Materials	(A)	(B)
Methanol	0.6600	(12)
	0.686	(13)
	0.6690	(22)
	0.6685	(25)
Acetic acid	0.5283	(12)
	0.5332	(14)
	0.5347	(15)
	0.525	(16)
	0.5292	(25)
Ethyl acetate	0.613	(13)
	0.6255	(14)
	0.616	(16)
	0.6156	(17)
	0.619	(18)
	0.6130	(22)
	0.6135	(25)
Ethylbenzene	0.7278	(20)
	0.7272	(25)
Toluene	0.7174	(12)
	0.725	(13)
	0.7150	(17)
	0.728	(18)
	0.7112	(20)
	0.7176	(25)
Nitrobenzene	0.5090	(15)
	0.5025	(17)
	0.5034	(23)
	0.5021	(25)
Cyanobenzene	0.6322	(20)
Benzene	0.7023	(12)
	0.7020	(19)
	0.6977	(23)
	0.702	(24)
	0.7008	(25)
sat'd with N_2	0.7081	(1)
sat'd with Air	0.7020	(1)
sat'd with O_2	0.6756	(1)
Cyclohexane	0.790	(18)
	0.7853	(25)
Heptane	0.8527	(21)
	0.8507	(25)
sat'd with N_2	0.8665	(1)
sat'd with Air	0.8513	(1)
sat'd with O_2	0.7944	(1)
Carbon tetrachloride	0.436	(16)
	0.430	(18)
	0.4340	(19)
	0.4300	(23)
	0.434	(24)
	0.4329	(25)

Fig. 3. Comparison of the susceptibilities measured in this work and found in literatures for various liquids. (A), literature-values, $\chi_L(\text{Lit})$; (B), the reference number. (C) and (D) indicate the levels of $\chi_L(\text{N})$ and $\chi_L(\text{Air})$ measured in this work, respectively. δ, normarized quantity defined by Eq. 11. ○, Gouy method; ●, Quincke method; △, Tortion balance method.

$$\Delta\chi = \chi_L^\circ - \chi_L(\text{Air}) - \frac{F_R F^\circ}{B d_L}\left(\frac{1}{F_R} - \frac{1}{F_R^\circ}\right), \tag{12}$$

where F_R and F_R° denote the Gouy forces on the specimens of the air-saturated and air-free liquids used as a reference, respectively; F° is the Gouy force on a similar specimen of air-free sample, and B is a constant which is characteristic of the equipment used. This equation can be rewritten by using a modified relation, $\chi_L(\text{Air}) = \chi_L^\circ + L(\text{Air})\kappa_A^\circ/d_L$, which is obtainable from Eq. 9 on application to air, as follows:

$$\Delta\chi = \chi_L^\circ - \chi_L(\text{Air}) + \frac{F^\circ \kappa_A^\circ}{F_R^\circ d_L} L_R(\text{Air}) \tag{13}$$

and

$$\Delta\chi = \kappa_A^\circ F^\circ \left[\frac{L_R(\text{Air})}{F_R^\circ d_R} - \frac{L(\text{Air})}{F^\circ d_L}\right], \tag{14}$$

where κ_A° is the volume susceptibility of air, and $L(\text{Air})$ and $L_R(\text{Air})$ are the solubilities of air in the sample and the reference liquids, respectively, under given experimental conditions (T and P). According to Eq. 13, when water is used as a reference, or when deaeration is carried out one-sidedly on the reference, such a quantity, $\chi_L^\circ - \chi_L(\text{Air})$, the first member of $\Delta\chi$, would result in a real error, because the second member of Eq. 13 usually vanishes, due to the slightest solubility of air in water. Nevertheless, water has been used more often than not as a primary reference, since it is the most familiar and purest substance available with ease, and that it has a susceptibility with sufficient accuracy. In contrast to this, accoridng to Eq. 14, as the effects of dissolved oxygen were seemingly to be canceled out when both sample and reference liquids behave equally regarding their physical properties, such as gas solubility, Gouy force (or magnetic susceptibility), and density. In fact, such properties of benzene (that used as a reference in the demonstrative experiments conducted by French et al.[2]) are of comparable magnitude to those of most organic liquids, respectively.

To solve this conflict, let's consider, for example, measurements of the susceptibility of the same material as the reference liquid. Regardless of the procedures, whether the deaerations for the sample and the reference liquids are carried out or not, the same value as the susceptibility of the reference liquid used should be obtained, and the cancellation seemingly becomes perfect, as is shown in Eq. 14. However, if the reference value used includes an error corresponding to the effect of dissolved air in itself, the obtained results should show less diamagnetism than a pure liquid, χ_L°. Thus, a cancellation can never be expected as long as the reference value containing the error caused by dissolved air is used, even when the physical properties of the reference liquid are equal to those of the sample liquids. In practice, however, as a standard reference, many workers in the past used the susceptibility of water, -0.7200×10^{-6} cm^3 g^{-1},[15,19,22—25] or the value of benzene, -0.7020×10^{-6} cm^3 g^{-1},[14,16,18,20] which was the same as the value previously determined without deaeration by the Gouy method,[19,24] using that value of water as the standard reference. Such a serious situation may also occur when using methods other than the Gouy method, as long as the susceptibility is determined relative to the reference. Thus, the greater part of the susceptibility data reported in the past may involve an error that corresponds to the effect of dissolved air, as pointed out by Eggleston et al.[1] as well as to in-

Table 3. Observed Susceptibilities of Liquids Equilibrating with Atmospheric and Artificial Airs of Different Oxygen Contents(%) at 298.15 K and the Volume Fraction of Atmospheric Oxygen Computed from the Data Using Eq. 7

Materials	Susceptibilities $-10^6\chi_L(G)/\mathrm{cm^3\ g^{-1}}$					Volume fraction ϕ(Air)
	0%	Air	51%	73%	100%	
Water	0.7205[a]	0.7193	0.7180	0.7169	0.7153	0.2_3
Methanol	0.6845	0.6763	0.6652	0.6571	0.6462	0.21_4
Acetic acid	0.5397	0.5340	0.5256	0.5194	0.5119	0.20_5
Ethyl acetate	0.6203	0.6108	0.5985	0.5884	0.5783	0.22_6
Acetone	0.5736	0.5652	0.5530	0.5444	0.5334	0.20_9
Dimethyl sulfoxide	0.5718	0.5704	0.5675	0.5659	0.5628	0.1_6
Ethylbenzene	0.7398	0.7325	0.7221	0.7133	0.7047	0.20_8
Toluene	0.7224	0.7141	0.7032	0.6947	0.6837	0.21_4
Nitrobenzene	0.5099	0.5065	0.5032	0.4991	0.4962	0.25
Cyanobenzene	0.6356	0.6310	0.6244	0.6187	0.6135	0.20_8
Benzene	0.7105	0.7037	0.6937	0.6867	0.6776	0.20_7
Aniline	0.6825	0.6812	0.6796	0.6774	0.6756	0.1_9
N-Methylaniline	0.6978	0.6948	0.6910	0.6884	0.6830	0.20_3
N,*N*-Dimethylaniline	0.7142	0.7102	0.7039	0.6996	0.6938	0.19_6
Cyclohexane	0.8041	0.7939	0.7807	0.7704	0.7574	0.21_8
Heptane	0.8663	0.8505	0.8285	0.8132	0.7921	0.21_3
2,2,4-Trimethylpentane	0.8826	0.8662	0.8436	0.8278	0.8076	0.21_9
Carbon tetrachloride	0.4422	0.4370	0.4301	0.4244	0.4184	0.21_8
Carbon disulfide	0.5278	0.5250	0.5214	0.5186	0.5148	0.21_5
	Gas-chromatographic analysis					0.210±0.005
	Literature value[11]					0.2099

a) Taken as the standard.

Table 4. Calculated Susceptibilities of Liquids Saturated with Air and Oxygen at 298.15 K Using Eq. 15[a]

Materials	$-10^6\chi_L(G)/\mathrm{cm^3\ g^{-1}}$ Air	Oxygen	Solubility,[b] $L(\mathrm{O})/\mathrm{m^3\ m^{-3}}$
Water	0.720(−0.097)[c]	0.716(−0.098)	0.03104
Methanol	0.676(0.044)	0.646(−0.031)	0.2476
Acetone	0.566(−0.141)	0.536(−0.485)	0.2794
Ethylbenzene	0.731(0.205)	0.699(0.815)	0.242
Toluene	0.714(0.014)	0.683(0.102)	0.24
Benzene	0.704(−0.043)	0.680(−0.352)	0.2079
Aniline	0.681(0.029)	0.674(0.237)	0.0603
N-Methylaniline	0.696(−0.172)	0.688(−0.727)	0.0658
N,*N*-Dimethylaniline	0.710(0.028)	0.693(0.055)	0.139
Cyclohexane	0.794(−0.013)	0.758(−0.079)	0.278
Heptane	0.851(−0.059)	0.794(−0.239)	0.36
2,2,4-Trimethylpentane	0.867(−0.092)	0.809(−0.173)	0.3725
Carbon tetrachloride	0.438(−0.228)	0.423(−1.087)	0.246

a) Used the values of $\chi_L(\mathrm{N})$ measured in this work. b) IUPAC "Solubility Data Series,"[9] selected from the numerical data. c) Values in parentheses are the difference(%) between observed and calculated susceptibilities.

strumental imprecision. According to our estimations, for example, the errors amount to 1.7% for heptane.

In the diamagnetic study of a solution, the effects of the intermolecular interactions on the susceptibility are often discussed.[26,27] In the case of a solution, a sufficient cancellation cannot take place, even when a just value is taken as the reference, because the solubility of the gases in solution is different from that of pure component solvents, which can be used as a secondary reference; that is, the ideality is lost due to the nonlinearity of the gas solubility with the composition of the mixed-solvent systems.[9,28] On the other hand, the effects of intermolecular interactions are usually very slight in solutions.[26]

It is thus concluded that the complete removal of dissolved oxygen from both the reference and sample is the most important condition for studying the diamagnetic properties of liquids or solutions. In addition, it is preferable to use water as the reference, since its susceptibility (-0.7200×10^{-6} cm^3 g^{-1} at 271 K),$^{6)}$ is impaired to only a slight extent by the oxygen effect, and the empirical relation of its temperature dependence$^{7)}$ is given with high accuracy; further, it is available as the purest sample. The values of $\chi_L(\mathrm{N})$ for the various liquids presented here are accurate within ±0.05% as the real values (χ_L°) if the accuracy of the susceptibility of water taken as a reference is so much. On the other hand, the accuracy of the $\chi_L(\mathrm{G})$-values are limited by the stability of the gas pressure (±0.13%).

As is well known, many of the organic solvents weakly interact with the dissolving oxygen, and give charge-transfer absorption bands. These bands are appreciable, even in such simple molecules as water, methanol or heptane.$^{29)}$ Generally, since the change in the electronic states of a molecule affects its magnetic property, one may compare the $\chi_L(\mathrm{G})$-values observed here and those calculated form Wiedemann's additive law.

Since χ_N° is very small, by a factor of as much as 1/1000 compared with χ_O°, $\chi_L(\mathrm{G})$ is virtually obtainable, with an error of ±0.01%, by instead taking $\chi_L(\mathrm{N})$ the sum of the 1st and 3rd terms on the right-hand side of Eq. 9. Then, substituting the numerical values for the density of oxygen, one may obtain the following equation for the practical use:

$$\chi_L(\mathrm{G}) = \chi_L(\mathrm{N}) + 3.85\times10^{-3}\cdot\frac{(P-p)\phi L(\mathrm{O})\chi_\mathrm{O}^\circ}{Td_L}. \qquad (15)$$

The value of $\chi_L(\mathrm{G})$ estimated using the Eq. 15 and the solubility data used there are listed in Table 4. They are fairly close to the observed values listed in Table 3. Strictly speaking, the difference between the observed and calculated values is very slight in *N,N*-dimethylaniline, while it is a considerable extent for carbon tetrachloride. The difference found in the later case far exceeds the experimental error, and seems to be directly proportional to the volume fractions of oxygen. Contrary to this, although the magnitude of the above interaction is remarkable in *N,N*-dimethylaniline, it is not appreciable in carbon tetrachloride.$^{29)}$ Large differences are also found in ethylbenzene and *N*-methylaniline, and are not explicable by the interaction effect. It is thus probable that such a difference is not due to the molecular interaction between organic liquid and oxygen, but is caused by the poor accuracy of the solubility data used in the calculation. The interaction effects on the magnetic susceptibilities are not so large as to be detectable. This conclusion is quite limited due to the accuracy of the solubility data for oxygen.

References

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

2) C. M. French and D. Harrison, *J. Chem. Soc.*, **1956**, 466.

3) K. Sueoka and T. Ikeda, *Bull. Chem. Soc. Jpn.*, **50**, 2124 (1977)

4) K. Sueoka, *Bull. Chem. Soc. Jpn.*, **64**, 916 (1991).

5) T. Ikeda and H. Yoshioka, *J. Phys. Chem.*, **72**, 4392 (1968).

6) F. G. Baddar, O. M. M. Hilal, and S. Sugden, *J. Chem. Soc.*, **1949**, 132.

7) J. S. Philo and W. M. Fairbank, *J. Chem. Phys.*, **72**, 4429 (1980).

8) K. Sueoka and T. Ikeda, *Bull. Chem. Soc. Jpn.*, **52**, 659 (1979).

9) IUPAC, "Solubility Data Series," Pergamon Press, New York (1981), Vol. 7.

10) Landolt und Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Springer Verlag, Berlin (1967), II Band, 10 Teil.

11) "International Critical Tables," McGraw-Hill, New York (1926), Vol. 1, p. 3939.

12) W. Rogie Augus and W. K. Hill, *Trans. Faraday Soc.*, **39**, 185 (1943).

13) K. Venkateswarlu and S. Sriraman, *Bull. Chem. Soc. Jpn.*, **31**, 211 (1958).

14) C. M. French, *Trans. Faraday Soc.*, **43**, 356 (1947).

15) B. Cabrera and H. Fahlenbrach, *Z. Physik.*, **89**, 682 (1934).

16) K. Venkateswarlu and S. Sriraman, *Trans. Faraday Soc.*, **53**, 433 (1957).

17) F. G. Baddar and S. Sugden, *J. Chem. Soc.*, **1950**, 308.

18) S. Sriraman and V. Shanmugasundaram, *Bull. Chem. Soc. Jpn.*, **37**, 395 (1964).

19) C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

20) C. M. French, *Trans. Faraday Soc.*, **50**, 1320 (1954).

21) W. Rogie Angus, G. I. W. Llewelyn, and G. Stott, *Trans. Faraday Soc.*, **55**, 887 (1959).

22) D. B. Woodbridge, *Phys. Rev.*, **48**, 672 (1935).

23) S. Seeley, *Phys. Rev.*, **49**, 812 (1936).

24) J. R. Lacher, R. E. Scurby, and J. D. Park, *J. Am. Chem. Soc.*, **71**, 1797 (1949).

25) S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949).

26) P. W. Selwood, "Magnetochemistry," Interscince, New York (1956), pp. 107—108.

27) A. Weiss and H. Witte, "Magnetochemie," Verlag Chemie, Weinheim (1973), pp. 96—106.

28) J. P. O'Connell and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.*, **3**, 347 (1964); R. Battino, T. R. Rettich, and T. Tominaga, *J. Phys. Chem. Ref. Data*, **13**, 563 (1984).

29) D. F. Evans, *J. Chem.Soc.*, **1953**, 345; A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956); H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).