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# Diamagnetic Susceptibilities of Ionic Functional Groups

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The diamagnetic susceptibilities of various series of organic compounds containing one or two ionic functional groups were measured by Guoy's method. The diamagnetic susceptibilities of ionic functional groups in organic compounds were determined by calculations according to an additive property of the magnetic susceptibility in a combination of Pascal's method with the diamagnetic susceptibilities of $Na^+$, $K^+$, $Cl^-$, and $Br^-$, which are given by Pascal. The results showed that the diamagnetic susceptibilities of $\cdot COO^-$, $\cdot SO_3{}^-$, $\cdot NH_3{}^+$, and $\cdot N(CH_3)_3{}^+$ are $-12.3\times10^{-6}$, $-29.2\times10^{-6}$, $-13.0\times10^{-6}$, and $-39.8\times10^{-6}$ $cm^3\,mol^{-1}$, respectively. It became possible to estimate the diamagnetic susceptibilities of organic compounds containing ionic bonds consisting of the above-mentioned ionic functional groups.

It was reported in a previous paper that the diamagnetic susceptibilities of inorganic phosphates and organic phosphate esters were measured.[1] It is known that the diamagnetic susceptibility of an organic compound can be calculated by summing the diamagnetic susceptibility of each part of the molecule. Weiss and Witte have discussed[2] the various methods for calculating the diamagnetic susceptibility according to an additive property. These methods can be applied to inorganic compounds. The diamagnetic susceptibilities of inorganic salts can be calculated if the diamagnetic susceptibilities of the anion and the cation are known. For wide applications of calculating the diamagnetic susceptibility of organic compounds, it is fundamentally worth collecting the diamagnetic susceptibility of all parts of a molecule.

Although there have been many papers concerning the diamagnetic susceptibilities of organic compounds,[2—6] only a few papers have been found concerning the diamagnetic susceptibilities of the ionic functional groups, themselves, such as $\cdot COO^-$ and $\cdot NH_3{}^+$.[7] The ultimate purpose of this study was to calculate the diamagnetic susceptibility of organic compounds containing ionic bonds without requiring measurements. We thus tried to measure the diamagnetic susceptibilities of organic compounds containing ionic functional groups. Accordingly, the diamagnetic susceptibilities of $\cdot COO^-$, $\cdot SO_3{}^-$, $\cdot NH_3{}^+$, and $\cdot N(CH_3)_3{}^+$ were determined. The diamagnetic susceptibilities of the salts of carboxylate, sulfonate and alkylammonium calculated by using Pascal's method[2] were compared with those obtained experimentally.

## Diamagnetic Susceptibility of an Ionic Functional Group

The molar diamagnetic susceptibilities of alkyl compound salts containing an ionic functional group ($\chi_M$) can be expressed by

$$\chi_M = n\chi(\cdot CH_2\cdot) + \chi(X) + \chi(\cdot H) + \chi(Y), \qquad (1)$$

where "$\cdot$" is expressed as one of the electrons in an covalent bond, and $n$ is the number of $CH_2$ groups; the $\chi$'s denoted the following:

$$\underbrace{H}_{\chi(\cdot H)} : CH_2CH_2 : \text{- - - -} : \underbrace{CH_2}_{\chi(\cdot CH_2\cdot)} : \underbrace{X^+(\text{or } X^-)}_{\chi(X)}\ \underbrace{Y^-(\text{or } Y^+)}_{\chi(Y)}$$

When plots of $\chi_M$ measured against $n$ fall on a straight line with respect to the homolog of alkyl compounds, we obtain $\chi(\cdot CH_2\cdot)$ from the slope of the line. $\chi(X)$ can be calculated from the intercept of this line by using known values of $\chi(\cdot H)$ and $\chi(Y^-)$, or the $\chi(Y^+)$ proposed by Pascal. The necessary diamagnetic susceptibilities of the atoms and ions were cited from Landolt–Bornstein Neue Serie.[8]

## Experimental

**Measuring Apparatus.** The diamagnetic susceptibilities were measured in the same manner as described in a previous paper.[1]

**Materials.** All of the chemicals used were of guaranteed grade or the best commercially grade available. Alkylammonium bromides were prepared by neutralizing alkylamine with a hydrobromide solution. The disodium salts of adip-

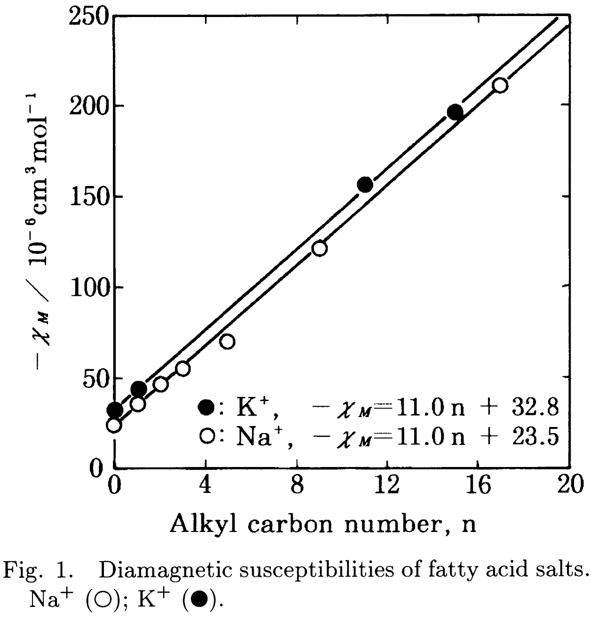

Fig. 1. Diamagnetic susceptibilities of fatty acid salts. $Na^+$ (○); $K^+$ (●).

inic and sebacic acids were prepared by mixing each free acid with the requisite amount of sodium hydroxide. The nitrogen contents in alkylammonium bromides were determined by the Kjeldahl method. The sodium ion contents in disodium salts were determined with a sodium-ion electrode. The obtained results deviated within 1% from the calculated values. All of the chemicals were measured after pulverization and being dried.

The experimental error in our measurement of the diamagnetic susceptibility was estimated to be within 3%.

## Results and Discussion

**Diamagnetic Susceptibilities of Organic Compounds Containing an Ionic Functional Group.** The diamagnetic susceptibilities of the sodium and potassium salts of fatty acids (sodium alkanesulfonates, alkylammonium chlorides and bromides, and alkyltrimethylammonium bromides) were measured. Each plot of the diamagnetic susceptibilities against the alkyl carbon number ($n$) was found to fall on a straight line (Figs. 1, 2, 3, and 4). The slopes obtained from six straight lines were in the region between $-10.7\times10^{-6}$ and $-11.1\times10^{-6}$. The slopes were independent of the species of the counter ion, that is, the sodium or potassium ion in Fig. 1, and the chloride or bromide in Fig. 2. The intercepts corresponded to the diamagnetic susceptibilities of HCOONa and HCOOK in Fig. 1, and those of $NH_4Cl$ and $NH_4Br$ in Fig. 2. The molar magnetic susceptibility of the methylene group was concluded to be $-(11.0\pm0.3)\times10^{-6}$ cm$^3$ mol$^{-1}$. According to Pascal's method, two values of $\chi(\cdot CH_2\cdot)$ were calculated to be $-11.86\times10^{-6}$ and $-11.36\times10^{-6}$, respectively. The former was obtained by using 2.93 and 6.00 (given in Table 1) for the $-\chi\times10^{-6}$ of hydrogen and carbon, respectively. The latter was obtained by using 2.0 and 7.36, which were proposed by Weiss and Witte.[2] The observed results presented in this paper are almost in accord with the latter within the experimental error. Therefore, $-\chi\times10^{6}=2.0$ and 7.36 for hydrogen and carbon was used for calculating the diamagnetic susceptibilities.

Table 1. The Diamagnetic Susceptibilities of Atoms and Ions Cited from Landolt–Bornstein Neue Serie II/11

| | $-\chi\times10^6$ cm$^3$ mol$^{-1}$ | |
|---|---|---|
| | The Pascal constants for ions ($A$) | Diamagetic susceptibilities of closed-shell ions ($B$) |
| $Na^+$ | 9.2 | 5 |
| $K^+$ | 18.5 | 13 |
| $Cl^-$ | 21.0[a] | 26 |
| $Br^-$ | 30.6[a] | 36 |
| H | 2.93 (2.0[b]) | |
| C | 6.00 (7.36[b]) | |
| N (aliphatic) | 5.57 | |
| O (carboxyl) | 3.36 | |

a) Obtained by subtracting $-\chi(Na^+)$, $-\chi(K^+)$ from $-\chi(NaCl)=30.2\times10^{-6}$, $-\chi(KBr)=49.1\times10^{-6}$.
b) Weiss and Witte proposed.[2]

Table 2. The Diamagnetic Susceptibilities of Ionic Functional Groups

| Ionic functional group | $-\chi\times10^6$ cm$^3$ mol$^{-1}$ | |
|---|---|---|
| | Calculated with data ($A$, $B$) in Table 1<br>($A$) | ($B$) |
| $\cdot COO^-$ | 12.3 | 17 |
| $\cdot NH_3{}^+$ | 13.0 | 8 |
| $\cdot SO_3{}^-$ | 29.2 | 33 |
| $\cdot N(CH_3)_3{}^+$ | 39.8 | 34 |

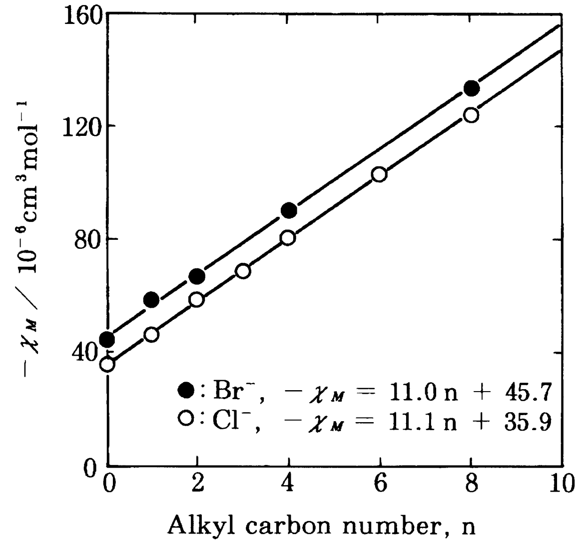

Fig. 2. Diamagnetic susceptibilities of alkylammonium halides. $Cl^-$ (○); $Br^-$ (●).

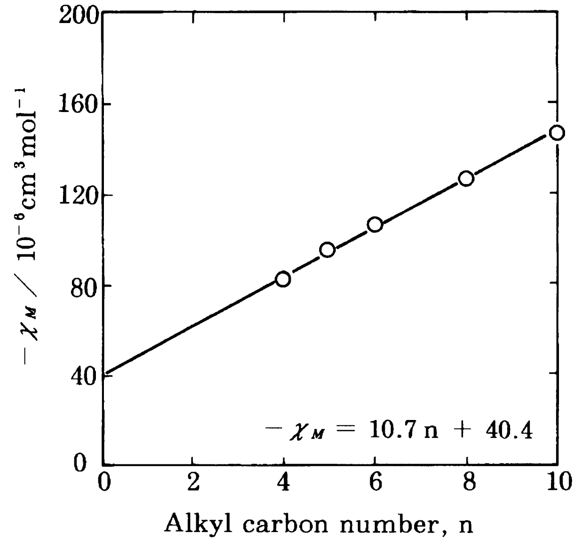

Fig. 3. Diamagnetic susceptibilities of sodium sulfonates.

**Diamagnetic Susceptibilities of Ionic Functional Group.** The diamagnetic susceptibilities of the ionic functional groups were calculated using Eq. 1

Table 3. The Diamagnetic Susceptibilities of Compounds Containing Two Ionic Functional Groups

| | $-\chi\times10^6$ cm$^3$ mol$^{-1}$ | | |
|---|---|---|---|
| | Measured ($M$) | Calculated ($C$) with data ($A$, $B$) in Table 1 ($A$) | ($B$) |
| Glycine | 42.8 | 36.8(−14.0)[a] | 36(−15.9)[a] |
| L-Alanine | 52.3 | 49.0(−6.3) | 49(−6.3) |
| L-Valine | 74.6 | 72.5(−2.8) | 72(−3.5) |
| L-Leucine | 84.8 | 83.9(−1.1) | 84(−0.9) |
| DL-2-Aminooctanoic acid | 106 | 106 (0) | 105(−0.9) |
| $\beta$-Alanine | 48.2 | 48.1(−0.2) | 48(−0.4) |
| $\gamma$-Aminobutyric acid | 58.3 | 59.5(+2.1) | 59(+1.2) |
| 6-Aminohexanoic acid | 84.4 | 82.2(−2.6) | 82(−2.8) |
| 11-Aminoundecanoic acid | 136 | 139 (+2.2) | 139(+2.2) |
| Disodium oxalate | 46.0 | 43.2(−6.1) | 44(−4.3) |
| Disodium malonate | 53.9 | 54.6(+1.3) | 55(+2.0) |
| Disodium succinate | 63.2 | 65.9(+4.3) | 67(+6.0) |
| Disodium adipate | 84.8 | 88.6(+4.5) | 89(+5.0) |
| Disodium sebacinate | 128 | 134 (+4.7) | 135(+5.5) |
| Taurine | 48.6 | 64.9(+33.5) | 64(+31.7) |
| Sodium 2-hydroxyethanesulfonate | 61.1 | 68.4(+11.9) | 68(+11.3) |

[a] The values in parenthesis show $(C-M)/M\times100$.

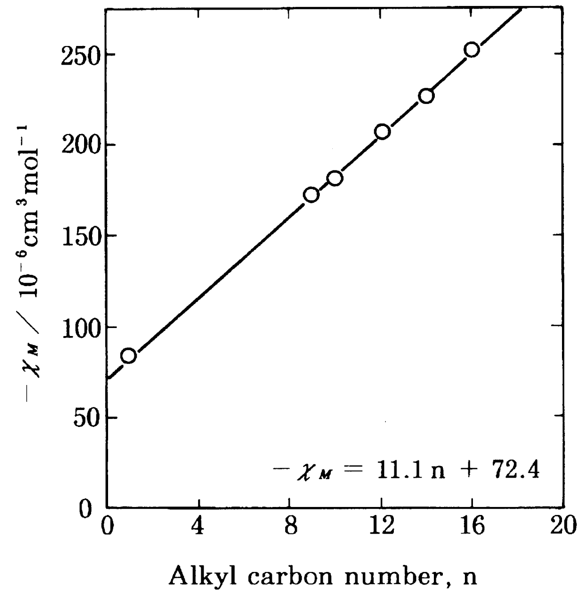

Fig. 4. Diamagnetic susceptibilities of alkyltrimethylammonium bromides.

along with the known values (Table 1). The results are summarized in Table 2. Different values for each ionic functional group were obtained. These results were found to depend on the diamagnetic susceptibilities of the inorganic ion used.

The diamagnetic susceptibilities of COOH and $NH_2$ obtained by Pascal's method were 16.08 and 9.57 cm$^3$ mol$^{-1}$, respectively. The groups of COOH and $COO^-$, as well as those respectively. The groups of COOH and $COO^-$, as well as those of $NH_2$ and $NH_3{}^+$, have the same number of electrons (23 and 9, respectively). The diamagnetic susceptibility of $H^+$ is defined to be zero. Comparing the diamagnetic susceptibilities of $\cdot COO^-$ and $\cdot NH_3{}^+$ in Table 2 with those of COOH and $NH_3$, the ionization of the functional group resulted in a big change in the diamagnetic susceptibility.

**Diamagnetic Susceptibilities of Organic Compounds Containing Two Ionic Functional Groups.** The diamagnetic susceptibilities of the organic compounds containing two ionic functional groups were measured and compared with the diamagnetic susceptibilities calculated by using different values in Table 2. The results are shown in Table 3. $\omega$-amino acids were considered to have carboxylate and ammonium groups.

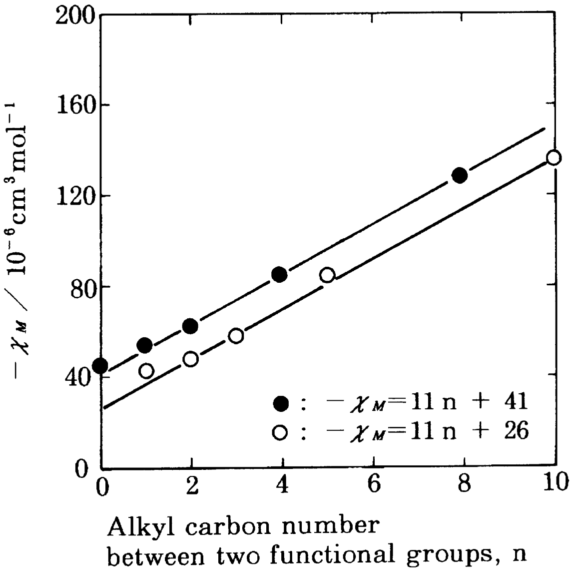

Fig. 5. Diamagnetic susceptibilities of $\omega$-amino acids (○) and disodium carboxylates (●).

A smaller deviation of the values in parenthesis in Table 3 was generally found in the case of calculating with the values given by (*A*), rather than (*B*). We therefore concluded that the diamagnetic susceptibilities of the ionic functional groups should be determined from a calculation with the values given by Pascal, proposed by Weiss and Witte.

In this connection, plots of the diamagnetic susceptibilities of the $\omega$-amino acids and dicarboxylates against the number of methylene groups were found to fall on straight lines, having a slope of 11.0, as shown in Fig. 5. This result confirms that the diamagnetic susceptibility of $CH_2$ group is equal to $-11.0\times10^{-6}$ $cm^3\,mol^{-1}$.

**Glycine, Taurine and Sodium 2-Hydroxyethanesulfonate.** Table 3 shows that the observed diamagnetic susceptibilities of glycine, taurine, and sodium 2-hydroxyethanesulfonate were quite different from the calculated values, as compared with the other compounds.

In the case of glycine, the carboxylate and ammonium groups were attached to one $CH_2$ group. The electric field produced by both ionic functional groups might spread into a microspace, in which the $CH_2$ group of glycine is located. Consequently, this intramolecular electric field might exert some influence on an external magnetic field, which is applied to glycine for measuring the diamagnetic susceptibility. Since the other $\alpha$-amino acid received a smaller effect, the electric field might cover within the limits of the CH group.

A bulky functional group, $\cdot SO_3^-$, might occupy a dominant space in the small molecules, taurine and sodium 2-hydroxyethanesulfonate. In the case of taurine, the electric field produced by the sulfonate and ammonium groups might cover the entire molecule. Therefore, the observed diamagnetic susceptibility of taurine was explained to strongly deviate from the calculated value. A similar speculation can be applied to the sodium 2-hydroxyethanesulfonate case.

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