THE MAGNETIC ANISOTROPY OF CARBON DISULPHIDE*

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The anisotropies in the molar magnetic susceptibilities of OCS and CO₂ have recently been recorded as \(-8.4 \times 10^{-6}\) e.m.u.\(^1\) and \(-6 \times 10^{-6}\) e.m.u.\(^1,2\) respectively. From these data Taft and Dailey\(^1\) predicted that the magnetic anisotropy of CS₂ would be larger than that of OCS. In the present work we have used the Cotton-Mouton effect to obtain an experimental estimate of the magnetic anisotropy of CS₂.

Solutions of carbon disulphide (b.p. 46°) in carbon tetrachloride were prepared and were found to exhibit the following magnetic birefringences at 20° and with sodium light.

\[
\begin{array}{cccccccc}
10^5 \omega_2 & 1177 & 2408 & 2569 & 3168 & 3927 & 4528 \\
-10^{15} \Delta C & 5.9 & 12.2 & 13.2 & 15.7 & 20.0 & 23.8 \\
\end{array}
\]

whence \(10^{15} \Delta C / \omega_2 = -0.51\)

The weight fraction of the solute is here denoted by \(\omega_2\); \(\Delta C\) is the difference between the magnetic birefringences of the solution and the solvent.

The magnetic birefringence of carbon tetrachloride cannot be detected with the present apparatus.\(^3\) Techniques used have been described previously.\(^4\)

The molar Cotton-Mouton constant of carbon disulphide as a solute in carbon tetrachloride emerges as \(-0.73 \times 10^{-15}\). Burge and Snellman\(^5\) have earlier reported a value of \(-0.8082 \times 10^{-15}\) in the same solvent but at a wavelength of 5461 Å.

If the anisotropy\(^*\) \((\beta_1 - \beta_3)\) in the electro-optical polarizability of CS₂ is known and the magnetic-field dependence of its polarizability\(^6\) is neglected, the magnetic anisotropy\(^*\) \((k_1 - k_3)\) of CS₂ can be calculated using the relationship

\[
\omega(mC_2) = (4\pi N/45kT)(\beta_1 - \beta_3)(k_1 - k_3)
\]

where \(\omega(mC_2)\) is the molar Cotton-Mouton constant of CS₂ at infinite dilution in carbon tetrachloride.

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‡ The 1-direction is taken to be that of the molecular axis.
5 Burge, E. J., and Snellman, O., Phil. Mag., 1949, 40, 1233.

The anisotropy in the optical polarizability of CS$_2$ as a solute in carbon tetrachloride has been deduced from Kerr effect measurements$^7$ as $7.5 \text{ Å}^3$. When our experimental Cotton–Mouton constant is considered in equation (1) together with this polarizability anisotropy, the molecular magnetic susceptibility anisotropy of CS$_2$ emerges as $-2.3 \times 10^{-29}$ e.m.u.

We conclude that the anisotropy, $K_1 - K_3$, in the molar magnetic susceptibility of CS$_2$ is $-14 \times 10^{-6}$ e.m.u. From this value of the magnetic anisotropy and a mean molar susceptibility$^8$ of $-42.2 \times 10^{-6}$, $K_1$ and $K_3$ appear as $-51.5 \times 10^{-6}$ and $-37.5 \times 10^{-6}$. As predicted,$^1$ the magnetic anisotropy of CS$_2$ exceeds those of CO$_2$ and OCS.

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$^8$ Foex, G., "Constantes sélectionnées, diamagnétisme et paramagnétisme", in "Tables de Constantes et Données Numériques." (Masson: Paris 1937.)