

The Dielectric Constant of Methyl Disulfide

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The temperature dependence of the dielectric constant of methyl disulfide has been determined at 5° intervals in the range 25–50° C. The dielectric constant of methyl disulfide is 9.6 at 25° and decreases to 8.8 at 50° C.

DURING THE COURSE of an investigation concerned with the physical properties of sulfur-containing nonaqueous solvents it was desirable to know the dielectric constant of methyl disulfide and its variation with temperature. A thorough search of the literature revealed that the temperature dependence of the density, viscosity, and refractive index of methyl disulfide was known with great accuracy (2); however there was only one report of the dielectric constant and the temperature of measurement was not specified (1). Further the temperature dependence of the dielectric constant was unknown.

EXPERIMENTAL

Commercial methyl disulfide, a gift from the Crown Zellerbach Corporation, was purified by distillation through a 1.3 × 0.02 meter vacuum jacketed column packed with Berl saddles. The middle fraction was retained for the experimental work and had a density and refractive index measured at the sodium D line of 1.0565 grams/ml. and 1.5226, respectively, at 25°. These values differed slightly from those of Haines and coworkers (2); therefore a final check on purity was made by gas chromatography. A Beckman GC-2 gas chromatograph equipped with a graphical integrator and a 14 ft. column packed with a 20 per cent dispersion of squalane on 40–60 mesh fire brick was used to analyze the sample. The analysis indicated the presence of a foreign component which made up less than 0.03% of the total sample; no other impurities were found.

Cell calibration, capacitance measurements, temperature control, and calculation of the dielectric constants were the same as described previously (6). Water which has a dielectric constant of 78.3 at 25° (4) was used as the calibration liquid and all measurements were made at a frequency of 10 megacycles.

RESULTS AND DISCUSSION

The discrepancies in the density and refractive index between this work and those of Haines and coworkers are probably due to differences in temperature control or to other minor procedural variables which are not readily apparent.

The data which describe the variation of the dielectric constant of methyl disulfide with temperature are in Table I.

The experimental values for methyl disulfide are about 35% greater than those reported for the corresponding monosulfide (7) and about 30% greater than ethanethiol (8) at comparable temperatures.

Table I. Dielectric Constant of Methyl Disulfide as a Function of Temperature

| Temp., °C. | ϵ |
|------------|------------|
| 25.0 | 9.6 |
| 30.0 | 9.4 |
| 35.0 | 9.2 |
| 40.0 | 9.1 |
| 45.0 | 8.9 |
| 50.0 | 8.8 |

These differences in the dielectric constants are related to the change in dipole moments which occur in going from methyl sulfide to methyl disulfide. The reported values of the dipole moments are methyl sulfide, 1.50 Debye from Stark effect measurements (5) and methyl disulfide, 1.96 Debyes at 30° by the heterodyne beat method (3) which are in the proper order for the observed differences in the dielectric constant. The effect of altering the dipole moment appears to be quite important since the change in the number of dipoles/cc. cannot account for this variation in the dielectric constant.

The reported values of the dielectric constant have been rounded to the nearest 0.1 unit and are probably correct to within 2%. Since the results are reported only to one decimal it is not possible to say with certainty that the dielectric constant has a non linear temperature dependence. However, from studies made on other systems this appears to be the rule rather than the exception.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for support of this research.

LITERATURE CITED

- (1) Crown Zellerbach Corporation, Chemical Products Division, Camas, Wash., "Dimethyl Disulfide," 1961.
- (2) Haines, W.E., Helm, R.V., Bailey, C.W., Ball, J.S., *J. Phys. Chem.* **58**, 270 (1954).
- (3) Kushner, L.M., Carin, G., Smyth, C.P., *J. Am. Chem. Soc.* **72**, 477 (1950).
- (4) Malmberg, C.G., Maryott, A.A., *J. Research Natl. Bur. Standards* **56**, 1 (1956).
- (5) Pierce, L., Hayashi, M., *J. Chem. Phys.* **35**, 479 (1961).
- (6) Vaughn, J.W., Sears, P.G., *J. Phys. Chem.* **62**, 183 (1958).
- (7) Walden, P., *Z. Physik Chem.* **46**, 103 (1903).
- (8) Wang, Y.L., *Ibid.* **B45**, 323 (1940).

RECEIVED for review October 21, 1963. Accepted March 2, 1964.