# Physical Properties of Tetrahydrothiophene-1,1-Dioxide and 3-Methyltetrahydrothiophene-1,1-Dioxide

J. W. VAUGHN and CONRAD F. HAWKINS
Northern Illinois University, DeKalb, Ill.

**The dielectric constants of tetrahydrothiophene-1,1-dioxide, "sulfolane," and 3-methyltetrahydrothiophene-1,1-dioxide, "3-methyl-sulfolane," were measured at 5°-intervals in the range 25° to 50° C. except where the material exists as a solid. All measurements were made at a frequency of 10 Mc. Viscosities and densities were measured in the same range and used to calculate activation energies of viscous flow and the rates of change of density with temperature. Refractive indices as a function of temperature are included for future identification purposes and for the calculation of dipole moments.**

RECENTLY THE COMPOUNDS tetrahydrothiophene-1,1-dioxide, "sulfolane," and 3-methyltetrahydrothiophene-1,1-dioxide, "3-methylsulfolane," which are potentially useful as nonaqueous solvents became available in quantity. A thorough search of the literature revealed that, although these compounds have been known for many years and utilized as nonaqueous solvents to some extent (*1, 2, 4, 10*), the values of the physical properties such as dielectric constants, densities, viscosities, and refractive indices were either unknown or had not been studied as a function of temperature. In order to evaluate these materials as nonaquous solvents the temperature dependence of the physical constants and the correlation of the differences in these properties with variations in structure were determined.

## EXPERIMENTAL

**Purification of Materials.** Approximately 300 ml. of sulfolane was distilled at reduced pressure through a 1.3 meter Podbielniack column packed with glass helices. A middle fraction of approximately 50 ml. was retained for the experimental measurements. The 3-methylsulfolane was purified similarly.

**Apparatus and Procedure.** The Twin-T bridge assembly, capacitance cells, cell calibration, and the experimental determinations of the dielectric constants were described previously (*13*). Calibration of the capacitance cells was accomplished with air and water as the reference media. The dielectric constant of air was taken as unity and water was taken as 78.3 at 25° C. (*7*). Temperature control within ±0.05° was provided by a 10-gallon water-filled thermostat. The working temperatures were established with a 0.1° thermometer which had been compared with a similar thermometer calibrated by the Bureau of Standards. Stem corrections were applied in all cases and suitable corrections were made to compensate for the temperature drop between the thermostat and the capacitance cells.

Density determinations were made in Reischauer pycnometers which had been previously calibrated with freshly boiled distilled water. All weights were corrected to weights in vacuo.

Viscosity determinations were made using Cannon-Fenske viscometers which were calibrated by the manufacturer. In all cases a viscometer of suitable size was used to ensure negligible kinetic energy corrections. Viscometers were filled under a positive pressure of nitrogen and protected from atmospheric contamination by drying tubes filled with calcium chloride and ascarite. Flow times were determined to 0.01 sec. with a Standard Electric Time Interval timer. All viscosities were run in duplicate and the results agreed within 0.3%.

Refractive index measurements were made by standard methods.

**Calculations.** All data utilized in the calculation of density gradients and activation energies of viscous flow were treated by the method of least squares.

## RESULTS AND DISCUSSION

Data which describe the temperature dependence of the dielectric constants of the two cyclic sulfones are in Table I.

As may be seen from Table I, the replacement of one of the hydrogen atoms on the ring by a methyl group affects the dielectric constant and reduces its value by approximately 14 units. This effect has been reported previously for the introduction of a methylene group into the side chains of certain *N*-substituted amides and replacement of amido hydrogens by methyl groups in benzenesulfonamides (*13*). However, in the case of *N*-ethylacetamide and *n*-propylacetamide the decrease in dielectric constant is only 12 units for this substitution. Conversion of *N*-methylbenzenesulfonamide to *N*,*N*-dimethylbenzenesulfonamide likewise produces a decrease of approximately 12 dielectric units.

For the cyclic sulfones, the per cent decrease of the dielectric constant produced by the methyl group is fairly uniform over the entire temperature range studied, with the greatest decrease, 32.6%, occurring at 30°. For the other temperatures investigated, the introduction of a methyl group depressed the dielectric constant by 31.8 ± 0.3%.

The decrease in dielectric constant upon the addition of a methyl group is greater than that due to a simple reduction in the number of dipoles per cubic centimeter. Thus another effect must be operating simultaneously with the reduction in the number of dipoles to depress the dielectric constant.

One possible explanation for the lowering of the dielectric constant upon the substitution of a methyl group for hydrogen is that the inductive effect of the alkyl group alters the polarity of the S—O bond and changes the dipole moment of the molecule. Unfortunately, the dipole mement of 3-methylsulfolane is unknown and is currently under investigation in this laboratory. A very approximate value

Table I. Dielectric Constants of Sulfolane and 3-Methylsulfolane at 10 Megacycles as a Function of Temperature

| | Temperature, ° C. | | | | | |
|---|---|---|---|---|---|---|
| Compound | 25 | 30 | 35 | 40 | 45 | 50 |
| Sulfolane | . . .[a] | 43.3<br>(44.0), (*1*) | 42.4 | 41.8 | 41.4 | 40.7<br>(42.0), (*2*) |
| 3-Methylsulfolane | 29.4 | 29.2 | 28.9 | 28.6 | 28.1 | 27.8 |

[a] Sulfolane exists as a solid at this temperature.

of the dipole moment of the sulfones can be obtained by direct calculation from the Syrkin equation (*8*, *12*) which is given below:

$$\frac{4\pi}{9kT} N\mu^2 = \frac{\frac{M}{\mathrm{d}}\left[\frac{(\epsilon - 1)}{(\epsilon + 2)} - \frac{n^2 - 1}{n^2 + 2}\right]}{1 - \left[\frac{(\epsilon - 1)}{(\epsilon + 2)}\right]^2} \tag{1}$$

where

$N$ = Avogadro's number
$\mu$ = dipole moment of the sulfone
$k$ = Boltzman constant
$T$ = absolute temperature
$\epsilon$ = dielectric constant of the pure sulfone
$M$ = molecular weight of the sulfone
d = density
$n$ = refractive index of the pure sulfone

The calculated values of the dipole moments for sulfolane and 3-methylsulfolane are 4.90 *D* and 4.38 *D*, respectively, at 30° C. Cumper and Vogel (*3*) have reported a value of 4.82 *D* for the dipole mement of sulfolane in benzene solution at 20°. Although the Syrkin equation does not yield exact values of the dipole moments, the relative order of the moments should be correct. Thus the presence of a methyl group lowers the permanent dipole moment and is accompanied by a decrease in the dielectric constant of the material.

Since the dielectric constants were measured only at a frequency of 10 megacycles, it is uncertain whether the reported dielectric constants are static values. It is possible that the materials are exhibiting anomalous dispersion (*5*, *11*) or the measured values could be affected by conductivity. There is evidence to support the belief that these values of the dielectric constants are not static values. First, the dielectric constant of sulfolane at 50° C. is 1.3 units less than the previously reported value (*2*) which was determined at 200 kc. Second, the difference at 30° is 0.7 unit and the value reported in the current investigation is the lower of the two. This is the expected order of the dielectric constants if either of the previously mentioned effects is present. However, it must be pointed out that with respect to the difference in values at 30°, the difference at 50° appears to be a little too large since dispersion effects usually decrease with increasing temperature and decreasing viscosity.

In all cases, the density data could be described by an equation of the type

$$\mathrm{d}_4^t = \mathrm{d}_4^{t_0} - k\,(t - t_0) \tag{2}$$

where *d*, *t*, *t*°, and *k* are the density in grams per ml., any temperature in the experimental range, the reference temperature which was 30° C. for sulfones and 25° for 3-methylsulfolane, and the least square value for the temperature gradient of density in grams per ml. deg.

The data pertinent to the variation of viscosity with temperature are in Table III. All viscosities are in centipoises.

The viscosity data could be described by the equation

$$\log \eta = A + B\,(1/T) \tag{3}$$

where $\nu$ is the viscosity in poise, $A$ and $B$ are constants obtained from a plot of log $\eta$ *vs.* $1/T$, and $T$ is the absolute temperature. Least square treatment of the viscosity data yields for sulfolane $A = -2.3892$ and $B = 1031.3$. The corresponding values for 3-methylsulfolane are $A = -2.784$ and $B = 1144.1$. Of these two constants, $B$ is the most important since it can be shown that $B = E_{\mathrm{vis}}/2.303R$ (*6*) where $E_{\mathrm{vis}}$ is the activation energy of viscous flow and $R$ is the molar gas constant. The activation energies of viscous flow for sulfolane and 3-methylsulfolane are 4.7 and 5.2 kcal. per mole, respectively. Sulfolane and 3-methylsulfolane would appear to be iso-viscous very near the melting point of sulfolane. This would suggest a possible application of these solvents as a very nearly iso-viscous pair in which the dielectric constant could be varied over a range of some 8 to 12 dielectric units. The decrease in viscosity from sulfolane to 3-methylsulfolane would support the postulate that the methyl group decreases the dipole moment and there by reduces dipole-dipole association. The long liquid range of sulfolane and its moderate dielectric constant would indicate this material to be a relatively good nonaqueous solvent in applications such that a high viscosity can be tolerated.

Table II. Summary of Density and Refractive Index Data for the Cyclic Sulfones

| Compound | Temp., ° C. | Density, Grams/Ml. | $k \times 10^4$ | Refractive Index |
|---|---|---|---|---|
| Sulfolane | 30 | 1.2614<br>(1.2615), (*2*) | 8.16 | 1.4820<br>(1.481), (*10*) |
| | 35 | 1.2568 | | 1.4798 |
| | 40 | 1.2525 | | 1.4783 |
| | 45 | 1.2494 | | 1.4765 |
| | 50 | 1.2447 | | 1.4747 |
| 3-Methylsulfolane | 25 | 1.1873 | 8.32 | 1.4758 |
| | 30 | 1.1833 | | 1.4742 |
| | 35 | 1.1792 | | 1.4725 |
| | 40 | 1.1751 | | 1.4708 |
| | 45 | 1.1711 | | 1.4687 |
| | 50 | 1.1666 | | 1.4668 |

Table III. Summary of the Viscosity Data for the Two Cyclic Sulfones

| | Temperature, ° C. | | | | | |
|---|---|---|---|---|---|---|
| Compound | 25 | 30 | 35 | 40 | 45 | 50 |
| Sulfolane | . . . | 10.286<br>(10.34) (*9*) | 9.033 | 7.974 | 7.116 | 6.312 |
| 3-Methylsulfolane | 11.671 | 10.137 | 8.784 | 7.647 | 6.726 | 5.886 |

ACKNOWLEDGMENT

The assistance of P.G. Sears in the determinations of the dielectric constants is greatly appreciated. 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) Burwell, R.L., Langford, C.H., *J. Am. Chem. Soc.* **81**, 3799 (1959).
(2) Coleman, B.D., Fuoss, R.M., *Ibid.* **77**, 5472 (1955).
(3) Cumper, C.W.N., Vogel, A.I., *J. Chem. Soc.* **1959**, p. 3521.
(4) Deal, C.H., Jr., Evans, H.D.E., Oliver, E.D., Papadopoulas, M.N., *Petrol. Refiner* **38**, 185 (1952).
(5) Debye, P., "Polar Molecules," pp. 77, 95, The Chemical Catalog Co., Inc., New York, 1929.
(6) Glasstone, S., Laidler, K.J., Eyring, H., "The Theory of Rate Processed," pp. 484, 505, McGraw-Hill, New York, 1941.
(7) Malmberg, C.G., Maryott, A.A., *J. Res. Natl. Bur. Std.* **56**, 1 (1956).
(8) Ospov. O.A., Shelomov, I.K., *Zuhr. Fiz. Khim.* **30**, 608 (1956).
(9) Phillips Petroleum Co., Bartlesville, Okla., Cyclic Sulfones Data Sheet, HF-400-61M.
(10) Schury, J., Stubcher, H., *Z. Elektrochim.* **61**, 754 (1957).
(11) Smyth, C.P., "Dielectric Behavior and Structure," pp. 53, 74, McGraw-Hill, New York, 1955.
(12) Syrkin, V.K., *Compt. rend. acad. sci., U.R.S.S.* **35**, 43 (1942).
(13) Vaughn, J.W., Sears, P.G., *J. Phys. Chem.* **62**, 183 (1958).

RECEIVED for review July 26, 1963. Accepted September 5, 1963.

---

# Viscosity of Ternary Liquid Mixtures

R. KALIDAS and G. S. LADDHA
Alagappa Chettiar College of Technology, University of Madras, Guindy, Madras 25, India

**The three-body ternary model proposed by Chandramouli and Laddha to predict viscosities of ternary liquid solutions has been used to analyze the experimental data for acetone–methanol–ethylene glycol system. The experimental data are well correlated.**

THE IMPORTANCE of accurate viscosity data to the chemical engineer cannot be overemphasized. Viscosities of liquid mixtures and the variation of viscosity with temperature are required for solution of many problems concerning heat transfer, mass transfer, and fluid flow. Few investigations have been reported for prediction of viscosities of liquid mixtures from the properties of the pure components (*2, 7, 9*). In most of the liquid mixtures there is no linear relationship between viscosity and composition of the liquid mixture. The equation given by McAllister (*5*) on the basis of Eyring's theory of absolute reaction rates (*3*) correlates the viscosities of binary liquid mixtures with the viscosities of pure components satisfactorily. Chandramouli and Laddha (*1*) have proposed a theoretical equation which is an extension of McAllister's three-body model for binary liquid mixtures to ternary liquid mixtures. The equation fits the published data of Ramanujam and Laddha (*8*) for the system ethanol-water-ethylene glycol.

The prediction of viscosities of these binary and ternary liquid mixtures-acetone-methanol, methanol-ethylene glycol, acetone-ethylene glycol, and acetone-methanol-ethylene glycol—was undertaken at 30° C. McAllister's equation was used to correlate the data of binary mixtures. The equation proposed by Chandramouli and Laddha for ternary liquid systems correlate the data satisfactorily for the acetone-methanol-ethylene glycol ternary system.

## McALLISTER'S BINARY MODEL

McAllister's theory of viscosity of liquid mixtures is based on Eyring's theory of absolute reaction rates. Assuming that for liquid mixtures the free energies of activation for viscosity are additive on a mole fraction basis, McAllister proposed the following equation for three-bodied interactions.

$$\begin{aligned}\log \nu = {} & X_1^3 \log \nu_1 + 3X_1^2X_2 \log \nu_{12} + 3X_1X_2^2 \log \nu_{21} + X_2^3 \log \nu_2 \\ & - \log\left[X_1 + X_2 \frac{M_2}{M_1}\right] + 3X_1^2X_2 \log\left[\frac{2 + M_2/M_1}{3}\right] \\ & + 3X_1X_2^2 \log\left[\frac{1 + 2M_2/M_1}{3}\right] + X_2^3 \log\left(\frac{M_2}{M_1}\right) \qquad (1)\end{aligned}$$

Equation 1 contains only two undetermined constants, $\nu_{12}$ and $\nu_{21}$ at each temperature level and considers the possibility of having a maximum, a minimum, neither, or both for $\nu$, the viscosity of the binary liquid mixture.

## TERNARY MODEL

In a study of the viscosity of a ternary mixture, molecules of types 1, 2, and 3 and their different interactions are considered. These are represented in Figure 1. Only three-bodied interactions in a single plane were considered

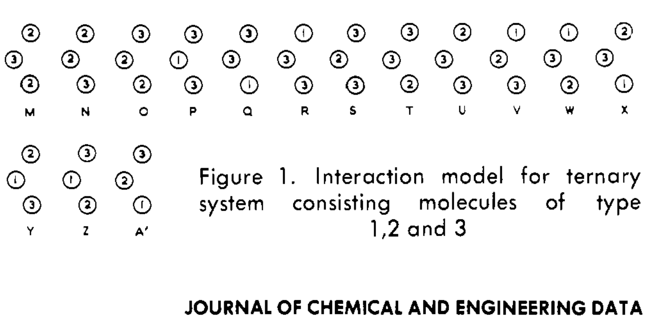

Figure 1. Interaction model for ternary system consisting molecules of type 1,2 and 3