

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Normal Butanol

BY GRINNELL JONES AND S. M. CHRISTIAN

The viscosity of methanol was determined recently in this Laboratory by an improved technique.¹ It is planned to extend the work to other alcohols to permit a comparison of the viscosities of the members of this homologous series and to study the effect of variation in temperature on the viscosity of these liquids. The present paper reports measurements on the viscosity of normal butanol at 0 and 25°.

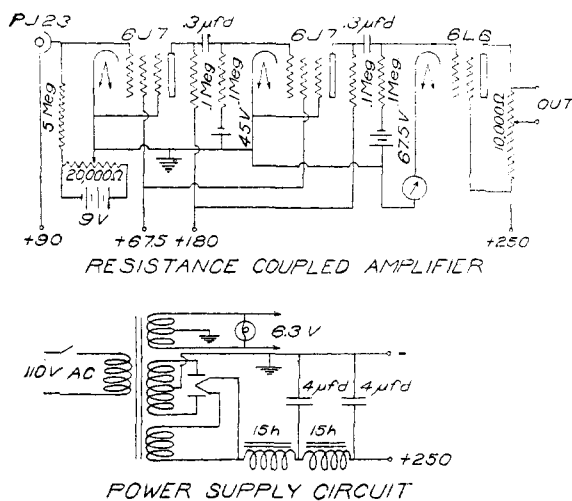


Fig. 1.

Sixteen hundred grams of Eastman best quality normal butanol (b. p. 116–118°) was treated with 50 g. of freshly ignited calcium oxide and boiled for four hours with a reflux condenser with the outlet protected from atmospheric moisture. The butanol was then decanted from the lime and treated with 15 g. of magnesium turnings and again boiled for four hours with the reflux condenser.² It was then distilled through a 75-cm. fractionating column. After rejection of a small low-boiling fraction the bulk of the liquid came over within a range of 0.02° at 117.70° (760 mm.). The density was determined by three 50-cc. pycnometers to be d_{25}^4 0.80572 and d_0^4 0.82460. These figures agree with the best measurements available³ in the literature within the precision of our measurements of the boiling point.

The method of determining the viscosity will not be

(1) Grinnell Jones and H. J. Fornwalt, *THIS JOURNAL*, **60**, 1688 (1938).

(2) H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931).

(3) R. F. Brunel, J. L. Crenshaw and E. Tobin, *THIS JOURNAL*, **43**, 575 (1921), give b. p. 117.71° and d_{25}^4 0.8057; J. A. V. Butler, D. W. Thomson and W. H. MacLennan, *J. Chem. Soc.*, 675 (1933), give b. p. 117.71° and d_{25}^4 0.8055; J. A. V. Butler, C. N. Ramchandani and D. W. Thomson, *ibid.*, 282 (1935), give b. p. 117.71° and d_{25}^4 0.80593; M. Wojciechowski, *J. Research Natl. Bur. Standards*, **17**, 721 (1936), gives b. p. 117.726°.

described in detail because it was essentially the same as that used with methanol and described in previous papers from this Laboratory. The F viscometer was used and the butanol was transferred to the instrument by quantitative distillation in a vacuum. Just as in the case of methanol, this method of filling the viscometer gave more consistent results than the use of transfer pipets. The only change in the apparatus was the use of a new and more sensitive thermionic amplifier between the photoelectric cell and the chronograph. The new amplifier was designed by Dr. W. C. Anderson of the Cruft Laboratory of Harvard University, to whom we express our thanks. Figure 1 gives a conventionalized wiring diagram showing the photoelectric cell and the three-stage resistance-coupled amplifier. Because the passage of the meniscus across the light-beam is slow, occupying over a second in the case of butanol at 0°, the amplifier has to be adapted to very low frequencies. The new amplifier gives a current gain of about 75,000 at a frequency of one cycle per second, which is quite exceptional. In this low-frequency range direct-current amplification is more common, but is not suitable here, as it is a changing current which has to be recorded. The greater sensitivity has the advantage that the adjustment of the optical system is less critical, which is a great convenience; and it is no longer necessary to overload the lamps, which with the old arrangement sometimes caused delay by burning out during an experiment. There is a separate photocell fixed on each of the thermostats, and the one to be used is readily connected to the amplifier by a shielded jack. Thus one amplifier serves both thermostats, unlike the former arrangement. The new arrangement of apparatus is much simpler and more compact than the earlier one.

The surface tension correction was computed by the equation

$$\Delta\eta = 0.00035 \left(1 - \frac{\sigma_c}{\sigma_0} \frac{d_c}{d_0} \right) \eta$$

based on the calculations of Jones and Fornwalt for this instrument. For this purpose the value of the surface tension⁴ was taken as 24.2 dynes per cm. at 25° and 26.2 dynes per cm. at 0°, giving

TABLE I
VISCOSITY OF NORMAL BUTANOL

| | 0° | 25° |
|-----------------------------|---------|---------|
| Density d_4^t | 0.8246 | 0.80572 |
| Relative viscosity, uncorr. | 2.9046 | 2.9006 |
| Kinetic energy correction | +0.0027 | 0.0098 |
| Surface tension correction | +0.0006 | 0.0006 |
| Viscosity relative to water | 2.9079 | 2.9110 |
| Absolute viscosity | 0.05216 | 0.02605 |

(4) T. W. Richards and J. H. Matthews, *THIS JOURNAL*, **30**, 8 (1908); R. C. Ernst, E. E. Litkenhous and J. W. Spanyer, Jr., *J. Phys. Chem.*, **36**, 842 (1932); "International Critical Tables," Vol. IV, p. 451.

the correction $\Delta\eta = 0.000205 \eta$. The results are shown in Table I.

It is remarkable that although the absolute viscosity of butanol is reduced by one half in going from 0 to 25°, the viscosity relative to that of water is almost unchanged.

Previous determinations of the viscosity are shown below.

| | 0° | 25° |
|---|----------|-----------|
| T. Thorpe and J. Rodger, interpolated from other temp., <i>Phil. Trans. London</i> , 185A , 537 (1894) | (0.0520) | (0.02577) |
| W. Herz and P. Schuftan, <i>Z. physik. Chem.</i> , 101 , 284 (1922) | | 0.02463 |
| J. Timmermans and F. Martin, interpolated from other temp., <i>J. chim. phys.</i> , 25 , 428 (1925) | | (0.02640) |
| R. C. Ernst, E. E. Litkenhous and J. W. Spanyer, Jr., <i>J. Phys. Chem.</i> , 36 , 842 (1932) | | 0.02465 |
| V. C. G. Trew and G. M. C. Wat- | | |

| | | |
|--|---------|----------|
| kins, <i>Trans. Faraday Soc.</i> , 29 , 1310 (1933) | | 0.025641 |
| Jones and Christian, this paper | 0.05216 | 0.02605 |

Trew and Watkins give a low boiling point (117.25°) and a high density (d_{25}^{25} 0.80849, d_{25}^{25} 0.80613) which indicates that their material may have contained water. Ernst, Litkenhous and Spanyer actually give 0.002465, which is presumably a misprint for 0.02465. Their boiling point and density indicate that their material was of good quality. The figures ascribed to Thorpe and Rodger and to Timmermans and Martin are obtained by interpolation from measurements at other temperatures.

Summary

The density and viscosity of normal butanol have been determined at 0 and 25°.

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Organic Sulfides: Specific Gravities and Refractive Indices of a Number of Aliphatic Sulfides

By GEORGE W. AYERS, JR., AND M. S. AGRUSS

During the course of an investigation involving the simple aliphatic sulfides, most of the values given in the literature for the specific gravities and refractive indices of these substances were found to be in error. It was therefore necessary to prepare these substances in a pure state for the determination of the constants mentioned above.

The specific gravities¹ and refractive indices of ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl and isoamyl sulfides are shown in Tables I and II. All specific gravity values have been corrected for the buoyancy of air and, wherever necessary, for the cubical expansion of glass. Practically all of the values reported represent averages of three separate determinations in 5-cc. glass pycnometers. The refractive indices were determined by means of an Abbe refractometer. Calibrated thermometers were used throughout the present work.

It is of interest to note that the specific gravities of the normal sulfides at 0° are very nearly identical. The values for the iso-aliphatic sulfides are

(1) Findlay, "Practical Physical Chemistry," Fourth Edition, 1929, p. 38.

TABLE I
SPECIFIC GRAVITIES OF ALIPHATIC SULFIDES

| Sulfide | d_4^4 | d_{20}^{20} | d_{25}^{25} | Expansion | |
|------------------|---------|---------------|---------------|--------------------------------------|----------------------|
| | | | | $V_t = V_0(1 + At + \frac{Bt^2}{2})$ | (for range 0 to 25°) |
| | | | | $(\times 10^{-4})$ | $(\times 10^{-4})$ |
| Ethyl | 0.8524 | 0.8331 | 0.8299 | 1.439 | -14.2 |
| <i>n</i> -Propyl | .8525 | .8358 | .8319 | 1.042 | -2.0 |
| Isopropyl | .8306 | .8135 | .8092 | 1.039 | 0.8 |
| <i>n</i> -Butyl | .8535 | .8386 | .8348 | 0.864 | 1.2 |
| Isobutyl | .8427 | .8262 | .8232 | 1.182 | -9.4 |
| <i>n</i> -Amyl | .8532 | .8390 | .8350 | 0.745 | 5.0 |
| Isoamyl | .8476 | .8323 | .8284 | .899 | 1.0 |

TABLE II
REFRACTIVE INDICES OF ALIPHATIC SULFIDES

| Sulfide | n_D^{20} | n_D^{25} | $M\bar{R}_D$ (Found) | | $M\bar{R}_D$ (Calcd.) | n_D^{25} Sulfur (Found) |
|------------------|------------|------------|----------------------|-------|-----------------------|---------------------------|
| | | | 20° | 25° | | |
| Ethyl | 1.4428 | 1.4395 | 28.69 | 28.61 | 28.64 | 7.98 |
| <i>n</i> -Propyl | 1.4481 | 1.4456 | 37.88 | 37.87 | 37.88 | 7.97 |
| Isopropyl | 1.4381 | 1.4354 | 38.16 | 38.15 | 37.88 | 8.25 |
| <i>n</i> -Butyl | 1.4529 | 1.4504 | 47.14 | 47.13 | 47.11 | 7.99 |
| Isobutyl | 1.4463 | 1.4439 | 47.24 | 47.19 | 47.11 | 8.07 |
| <i>n</i> -Amyl | 1.4556 | 1.4532 | 56.44 | 56.46 | 56.35 | 8.07 |
| Isoamyl | 1.4520 | 1.4499 | 56.51 | 56.55 | 56.35 | 8.15 |
| | | | | | | Average 8.07 |

much smaller than those for the normal aliphatic sulfides. These relations are shown in Fig. 1.