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The Dielectric Constant of Isopropyl Alcohol Vapor

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The dielectric constant of isopropyl alcohol vapor has been measured at 12 different temperatures between 26.8°C and 190.4°C. At each temperature, measurements were made at many different vapor pressures. It is emphasized that this procedure is highly desirable. The slope, obtained by least squares, of the resulting $(K-1)/(K+2)$ versus pressure curve gives one point on the Debye line. Twelve such points were obtained. Unusually pure isopropyl alcohol was used. The data fall on a Debye line whose equation as obtained by least squares is: $[(K-1)/(K+2)]RT/p' = (17.40 \pm 0.41) + (17,490 \pm 155)/T$. This yields a value $(1.682 \pm 0.007) \times 10^{-18}$ e.s.u. for the electric moment of the isopropyl alcohol molecule. These results agree closely with some previously unreported measurements made by the author three years ago.

IT is becoming more and more important to have available reliable values for the permanent electric moments of various molecules. A survey of the literature covering dielectric studies of dilute solutions shows that a large number of electric moments obtained therefrom appear inconsistent. Numerous of these inconsistencies may disappear when the effect of the solvent¹⁻³ is entirely understood and taken into account; others, where different observers obtain different moments using the same solvent, must be due to experimental error or impure materials. Too many studies are marked by the extreme scarcity of measurements at really low concentrations. Measurements of the character reported by Hoecker⁴ appear much more reliable. A similar survey of dielectric studies of vapors again shows that all too often various workers fail to agree on molecular moments. The author feels that many of these inconsistencies have been introduced likewise through lack of sufficiently extensive data. The present requirement as regards electric moment studies appears definitely one of accuracy and reliability rather than of quantity. With the hope of better fixing some of our moment values, the author, three years ago, obtained data on several alcohol vapors, including the two propyl isomers, and water. The data on water vapor were published.⁵ Those on the alcohols have never been reported. At

the time the measurements were made, it was believed the alcohols used were of high purity. Shortly thereafter, it was found by Cady and Rarick⁶ that the more usual tests of purity often failed to show the presence of appreciable impurities in many of the alcohols. For this reason the author's data were not reported. Recently Cady and Rarick made available to the author some isopropyl alcohol of unquestioned purity, some which they had purified and tested. Dielectric data obtained on this alcohol are presented here.

Dielectric constants were measured by the heterodyne beat method, using previously described apparatus⁷ operating entirely on alternating current, along with a carefully calibrated variable capacity standard.⁸ The vapor condenser with quartz insulators, and the vapor system, were the same as those used in securing previously reported⁵ data on water vapor. Dielectric constants were measured at 12 different temperatures between 26.8°C and 190.4°C. At each temperature, measurements were made at an average of 16 different pressures, ranging from the lowest measurable up to near saturation when such saturated vapor pressure did not exceed one atmosphere. These data are shown in Fig. 1. For the sake of clarity, data are shown for only half of the temperatures used. p'

¹ Müller, *Physik. Zeits.* **38**, 283 (1937).

² Higasi, *Inst. Phys. and Chem. Res., Tokyo, Sci. Papers* **28**, 284 (1936).

³ Frank, *Proc. Roy. Soc.* **152A**, 171 (1935).

⁴ Hoecker, *J. Chem. Phys.* **4**, 431 (1936).

⁵ Stranathan, *Phys. Rev.* **48**, 538 (1935).

⁶ Drs. H. P. Cady and Morgan Rarick of the department of chemistry, University of Kansas. Tests of purity were made through accurate and frequent molecular weight determinations during the fractionation. A description of the apparatus will no doubt be published in the near future.

⁷ Stranathan, *Rev. Sci. Inst.* **5**, 334 (1934).

⁸ Stranathan, *Rev. Sci. Inst.* **5**, 315 (1934).

represents the pressure the vapor would exert were it an ideal gas; it is obtained from the observed pressure p and the van der Waals constants a and b , thus:

$$p' = p[1 + (p/RT)(a/RT - b)].$$

While obtaining data at so many different pressures at each temperature adds enormously to the experimental data and the associated calculations, the author feels that this is a most desirable procedure. Possibly numerous inconsistent dielectric data in the literature can be attributed to its all too infrequent use. The advantages are threefold: (1) The greater number of points alone should yield a more reliable value for the slope of the curve; (2) Having a well-defined curve allows one to judge much more certainly the extent over which the curve is truly linear. Lack of linearity may result from imperfect correction for deviation from the ideal gas law, and certainly results from adsorption of the vapor on the insulator surfaces⁵ in the vapor condenser. The start of such curvature is so gradual that its presence is easily overlooked unless caution is used; (3) The well-defined curve extending to low pressures allows one to evaluate the slope, either graphically or by least squares, without assuming that the curve passes through the origin. The experimental curve may fail to pass through the origin due to any one of the following three causes: Any small error in the zero of the mercury manometer used; failure to correct perfectly for the pressure of the column of liquid, which is not all at the same temperature, present as one builds up the vapor pressure in the test condenser; the possible presence of an effect suggested by Zahn and Miles,⁹ due to lack of thermal equilibrium in an evacuated condenser. To the extent that these errors are constant at any one temperature, they will not affect the slope of the curve; hence, it seems unwise to assume that the curve passes through the origin.

The molecular polarization is given by

$$(K-1)M/(K+2)d$$

$$= (K-1)RT/(K+2)p' = A + B/T,$$

the last equality being a result of the Debye theory. The constant A should be equal to the molecular refraction extrapolated to infinite

⁹ Zahn and Miles, *Phys. Rev.* **32**, 497 (1928).

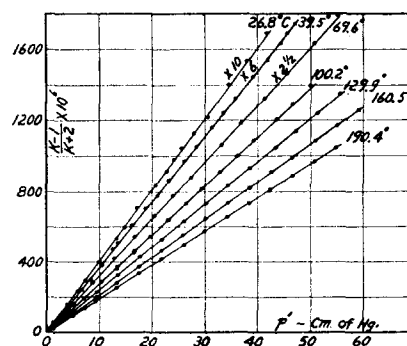


FIG. 1. For the lower temperature curves both ordinate and abscissa have been multiplied by the factor indicated.

wave-length; the permanent electric moment of the molecule can be obtained from the constant B . The molecular polarization at any temperature is obtained from the slope of the corresponding curve in Fig. 1. By plotting the data for any temperature to a large scale, one can judge over what pressure range the curve is linear. At higher temperatures, for which the highest pressures used were far below saturation, the entire curve is linear. At the lower temperatures, slight curvature is apparent at the higher pressures. For each temperature the slope of the best least squares line through all points on the linear section was found. The average number of points on these linear sections was 14; in no case were there less than 8. While some personal error of judgment may still enter in determining the extent of the linear section, the least square solution for the slope of this line is no doubt less subject to personal error than is a purely graphical solution.

Figure 2 shows the products of molecular polarization and absolute temperature plotted against T . The data fall accurately on a straight line, no point being off the line by as much as one percent. Previous data by Kubo,¹⁰ and previous unreported data by the author, are indicated. A least squares solution for the best line through the author's present data gives:

$$(K-1)RT/(K+2)p' = (17.40 \pm 0.41) + (17,490 \pm 155)/T.$$

This yields an electric moment¹¹ of (1.682 ± 0.007)

¹⁰ Kubo, *Inst. Phys. & Chem. Res., Tokyo, Sci. Papers* **26**, 242 (1935); **27**, 65 (1935).

¹¹ This moment is calculated using the Millikan value of e ; if the now indicated higher value of e proves correct, then this and all similarly calculated moments will have to be raised by approximately $\frac{1}{4}$ percent.

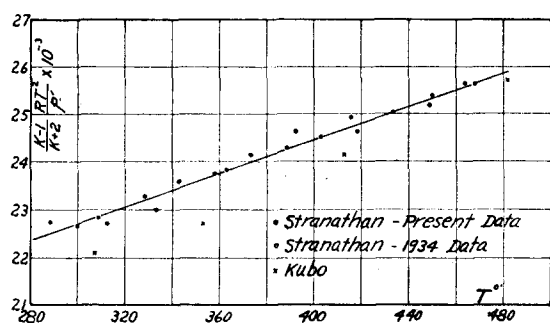


FIG. 2.

$\times 10^{-18}$ e.s.u. for the isopropyl alcohol molecule. The polarization 17.4 contributed by other than the permanent moment is but slightly larger than the electronic molecular refraction, 16.8^{10} , extrapolated to infinite wave-length; it indicates a smaller atomic polarization than found by Kubo. The electric moment here found does not agree well with previous vapor data. Using data at 4 different temperatures, Kubo found:

$$(K-1)RT/(K+2)p' = 21.1 + 15,470/T,$$

yielding a moment 1.58×10^{-18} . On the other hand, the author's present data on undoubtedly pure isopropyl alcohol agree with those obtained but not reported by the author three years ago. At that time the author found, from data at 8 different temperatures ranging from 15.5°C to 194.5°C :

$$(K-1)RT/(K+2)p' = (17.72 \pm 0.77) + (17,432 \pm 295)/T,$$

yielding a moment $(1.679 \pm 0.014) \times 10^{-18}$. While the purity of this earlier sample was not the equal of the present, the sample was of the highest grade obtainable, carefully dried and fractionated; it was no doubt the equal of that used by other workers. Several values for the moment of the isopropyl alcohol molecule have been obtained from dilute solution studies. Mahanti¹² reported a value 1.78×10^{-18} ; Donle¹³ found 1.70; Hennings¹⁴ found 1.63; Mahanti¹⁵ more recently found practically no difference in the moments of various alcohols, giving 1.64 for isopropyl; Higasi¹⁶ reported 1.70, and quotes a value 1.67 obtained from Donle's work. In all

¹² Mahanti, J. Indian Chem. Soc. **6**, 743 (1929).

¹³ Donle, Zeits. f. physik. Chemie Abt. **B14**, 326 (1931).

¹⁴ Hennings, Zeits. f. physik. Chemie Abt. **B28**, 267, 480 (1935).

¹⁵ Mahanti, Zeits. f. Physik **94**, 220 (1935).

¹⁶ Higasi, Inst. Phys. and Chem. Res., Tokyo, Sci. Papers **28**, 284 (1936).

of these studies, a common solvent benzene was used; nevertheless, the values are far from consistent. Some are above and some below the present value reported. Ghosh,¹⁷ judging from dilute solution data, concluded that the primary alcohols have practically identical moments, while the iso-alcohols have noticeably higher moments. Groves and Sugden,¹⁸ considering the data of Miles,¹⁹ Knowles,²⁰ and Kubo,¹⁰ on various alcohol vapors, concluded that there is a small decrease in moment on ascending a homologous series, and a small decrease on passing from a normal to an iso-alcohol; but the authors point out that the effects are not much larger than the experimental error and require further study. Higasi¹⁶ concluded that the moment of an alcohol obtained in solution is always larger than that obtained from vapor measurements. The author feels that most such conclusions regarding the alcohols are far from conclusive until such time as data on both dilute solutions and vapor can be repeated with more consistency than is now apparent.

The author can offer no certain explanation for the discrepancy between Kubo's¹⁰ data and the present data. The difference cannot be attributed to error in calibration. The close agreement of the work of Knowles²⁰ on ethyl alcohol, the author's on water, and unreported work of the author on several alcohols and benzene, with numerous other workers, make it appear impossible that the calibration of apparatus in this laboratory can be appreciably in error. A similar statement can be made regarding many of Kubo's results. Likewise the discrepancy appears rather large to attribute entirely to logical impurities. It is very difficult to separate tert-butyl from isopropyl alcohol by fractional distillation. The boiling point is a very poor test of purity.⁶ If a large amount of tert-butyl were present as impurity, it would lead to a higher molecular refraction and probably to a lower moment.¹⁴ The isopropyl used here was definitely pure. The author is convinced that the general procedure followed in the present measurements is a very desirable one; in previous cases, it seems to have led to entirely reliable results.

¹⁷ Ghosh, Nature **123**, 413 (1929).

¹⁸ Groves and Sugden, J. Chem. Soc. London, 158, Jan. (1937).

¹⁹ Miles, Phys. Rev. **34**, 964 (1929).

²⁰ Knowles, J. Phys. Chem. **36**, 2554 (1932).