Frank E. Hoecker

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tematic error in the heat capacity of oxygen from velocity of sound measurements.[12, 13]

Comparison of the reported heat capacity[12, 13] of oxygen from velocity of sound measurements with the value obtained by other methods, shows that the former is too low by the heat capacity due to the first vibrational state up to

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[12] Shilling and Partington, Phil. Mag. **6**, 920 (1928).
[13] King and Partington, Phil. Mag. **9**, 1020 (1930).

about 1000°K. At 1400°K, where the second vibrational state should contribute an appreciable amount to the heat capacity, the difference is still greater. This indicates that neither the first or second vibrational levels are activated by the sound wave even at these temperatures.

Measurements of the relative velocity of sound are being continued at higher frequencies where the experimental error will be lower.

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Dielectric Constants of Extremely Dilute Solutions

FRANK E. HOECKER, *Department of Physics, University of Kansas**

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The dielectric behavior of unusually dilute solutions of ethyl alcohol in the nonpolar solvents benzol and carbon tetrachloride have been investigated down to 0.00007 mole-fraction concentration of alcohol. This concentration of molecules corresponds to a gaseous pressure of only 1.5 cm of Hg. The effect of an apparently anomalous behavior often present in the usual method of treating data has been eliminated by a slightly different treatment. Effects of association are entirely absent up to concentrations nearing 0.01. Molecular polarizations of alcohol at 24.5°C, evaluated by least squares from data using the two solvents, agree closely; they also agree well with accepted vapor data. Taking over the molecular refraction of alcohol from optical data, the electric moment of the ethyl alcohol molecule is found to be $(1.700 \pm 0.006) \times 10^{-18}$ from benzol solution and $(1.674 \pm 0.005) \times 10^{-18}$ from carbon tetrachloride solution. These are felt to be unusually reliable for solution values; they compare favorably indeed with the two best vapor values, 1.696×10^{-18} by Miles and 1.686×10^{-18} by Knowles. Accurate density-concentration relationships for very dilute alcoholic solutions are given.

MANY writers have investigated the behavior of polar liquids in nonpolar solvents by way of determining the electric moment of the dissolved molecule. The usual procedure[1] is to assume that the molecular polarization of the solution P_{12} is the sum of the contributions of the solvent and the solute; thus

$$P_{12} = P_1 c_1 + P_2 c_2,$$

where P_1 and c_1, and P_2 and c_2 are the molecular polarizations and the mole-fraction concentrations of the solvent and the solute, respectively. Calculations of P_2 from observed values of P_{12} at various concentrations, using a fixed value of P_1 observed for the pure solvent, show that the molecular polarization P_2 of the polar solute varies in general with concentration. This varia-

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* Now at University of Kansas City, Kansas City, Missouri.
[1] See, for example, Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, 1931).

tion is attributed to association. It is customary to plot values of P_2 *versus* the solute concentration c_2, and extrapolate this curve to zero concentration. It is assumed that the solute polarization so obtained is free from effects of association. That this is essentially true is evidenced by the fact that electric moments calculated in this way for many molecules agree fairly well with moments obtained from vapor studies. Nevertheless one is impressed by the fact that, to the best of the author's knowledge, no worker has obtained data on sufficiently dilute solutions and at the same time of sufficient accuracy to show that the solute polarization P_2 actually does become constant at some low concentration, thus indicating complete lack of association effects. In fact in certain instances where investigators were forced by sparing solubility of the solute to use extremely dilute solutions, apparently anomalous results were
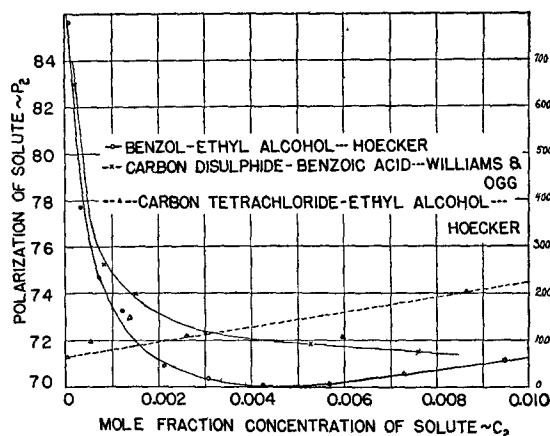
FIG. 1.

obtained. This is indicated by the curve through the cross-points of Fig. 1, plotted by the author from data by Williams and Ogg.[2] The writer obtained similar results in some early measurements on ethyl alcohol in extremely dilute benzol solution; these are shown by circle points in the same figure. Such behavior precludes any possibility of proper extrapolation to zero concentration.

Recently, Müller and Mortier[3] have observed similar effects on several alcohols (not including ethyl alcohol) using various solvents. They state that such an effect will always be observed whenever sufficiently precise measurements are made on extremely dilute solutions of polar solute in nonpolar solvent, and interpret the effect as the result of the varying effect of the solvent upon the association mechanism of the solute.

The present work was undertaken with the hope of obtaining accurate data on extremely dilute solutions to see whether the solute polarization actually does become constant at low concentration and remain at this fixed value for all lower concentrations. If such is possible, one would presumably be able to obtain a much more reliable value of zero concentration intercept than is usually obtained by extrapolation from a region where association effects are still present. The polar liquid studied was ethyl alcohol. This was dried by refluxing over CaO and later distilling over sodium. The nonpolar liquids used were benzol, carbon tetrachloride,

and carbon disulfide. Every precaution was taken to obtain liquids of high purity.

The heterodyne beat apparatus used for dielectric constant measurements was designed to insure precision measurements of extremely small capacity changes. In its ultimate form it was essentially that described by Stranathan,[4] except that it was not a.c. operated. The critical oscillator was stabilized as suggested by Llewellyn,[5] and was inclosed in a constant-temperature water bath which contained also the test condenser. The standard precision condenser described by Stranathan[6] was used to measure the small increases in capacity caused by addition of small quantities of the solute. Capacity changes as small as $0.006\mu\mu f$ could be measured. The test condenser and mixing reservoir were constructed of brass; Pyrex was used for insulation in the condenser. This condenser was mounted permanently in the constant-temperature bath and arranged so that the mixing reservoir could be attached to transfer a solution without exposing the solution to the air. This reduced evaporation effects materially. A method of successive dilutions was used in mixing solutions.

Because of the precision required in these measurements, it was necessary to make accurate determinations of the variation of density of the solution with concentration of alcohol. A special type of pycnometer described by Parker and Parker[7] was used. It is believed these density-concentration relationships are the most precise available on these solutions. Measurements made on solutions of various mole-fraction concentrations ranging from 0.0004 to 0.10, all at 24.5°C, show that the change in density due to addition of alcohol is strictly linear. A least-squares solution involving measurements at fifteen concentrations shows that the density of a benzene-ethyl alcohol solution is given by

$$d = (0.87197 \pm 0.000055) - (0.06717 \pm 0.00048)C_2.$$

From measurements on nine solutions of ethyl alcohol in carbon tetrachloride

$$d = (1.585547 \pm 0.0000013) \\ - (0.51191 \pm 0.00017)C_2.$$

[2] Williams and Ogg, J. Am. Chem. Soc. 50, 94 (1928).
[3] Müller and Mortier, Physik. Zeits. 36, 375 (1935).
[4] Stranathan, Rev. Sci. Inst. 5, 334 (1934).
[5] Llewellyn, Proc. I. R. E. 19, 12 (1931).
[6] Stranathan, Rev. Sci. Inst. 5, 315 (1934).
[7] Parker and Parker, J. Phys. Chem. 29, 132 (1925).

From measurements on nineteen solutions of ethyl alcohol in carbon disulfide

Undried $\quad d = (1.25601 \pm 0.00018)$
$$- (0.49787 \pm 0.00347)C_2,$$

Dried $\quad d = (1.2561096 \pm 0.0000078)$
$$- (0.51548 \pm 0.00107)C_2.$$

In the above statements the probable errors do not include any differences which might arise because of the purity of the solvent itself.

The dielectric polarization has been measured for fifty-seven solutions ranging from 0.00007 to 0.15 mole-fraction concentration of ethyl alcohol in benzene; forty-one of these solutions were under 0.01 concentration. Similar measurements have been made on forty solutions of ethyl alcohol in carbon tetrachloride, ranging from 0.00007 to 0.02 in concentration of alcohol. Thirty-four solutions of ethyl alcohol in carbon disulfide have been studied, all under 0.03 concentration. When the data from benzene solution are plotted in the usual manner, P_2 versus c_2, the anomalous behavior shown by the curve through circles in Fig. 1 is apparent at low concentrations. An extremely small error in the measurement of the molecular polarization P_1 of the pure solvent could cause this behavior; or the presence of small quantities of alcohol may actually increase slightly the polarization of the solvent benzene. At any rate it is hopeless to try to obtain a zero concentration intercept. The author has therefore chosen to treat the data in a manner entirely equivalent to that used in vapor studies. In such studies one obtains the molecular polarization of the vapor dielectric at a particular temperature from the slope of the linear curve of $(K-1)/(K+2)$ versus the ideal gas pressure p'. Since $P_2 c_2$ is proportional to $(K-1)/(K+2)$, and since c_2 is a function of p', the author has plotted $P_2 c_2$ versus c_2 in Fig. 2. The slope of this curve at any concentration gives the molecular polarization of the solvent at that concentration. The resultant curve is actually linear for both benzene and carbon tetrachloride solutions up to concentrations of 0.01 of alcohol. The polarization of alcohol is therefore constant over this extreme range of concentration from 0.00007 to 0.01; no measurable association effects exist within this range. To the best of the author's knowledge, this has never been demonstrated before. Data above 0.01 concentration have not been plotted, for in this vicinity association effects become apparent in each case. In benzene solutions association causes a slow but definite increase in the molecular polarization of alcohol; the curve becomes concave upward. In the case of carbon tetrachloride solutions, observations were not extended sufficiently above one percent to make certain of any association effect; it appears likely however that association starts appreciably between one and two percent concentration.

Observations made on ethyl alcohol, carbon disulfide solutions, which, when plotted in the above manner yield a rather irregular curve starting from zero concentration with essentially the same slope as that of the two curves shown but with slight downward concavity, are not shown here because there was some evidence of a very slight chemical action between the brass of the test condenser and the solution when carbon disulfide was used. The obvious alternative interpretation of this behavior, that association is not completely absent even at these low concentrations in carbon disulfide, seems hardly reasonable, since it is unlikely that alcohol molecules associate at these low concentrations when in carbon disulfide and do not when in carbon tetrachloride or benzol.

Since association effects are entirely absent over the wide range of concentration from 0.00007 to 0.01 shown in Fig. 2, the slope of the resultant line should give a reliable value for the
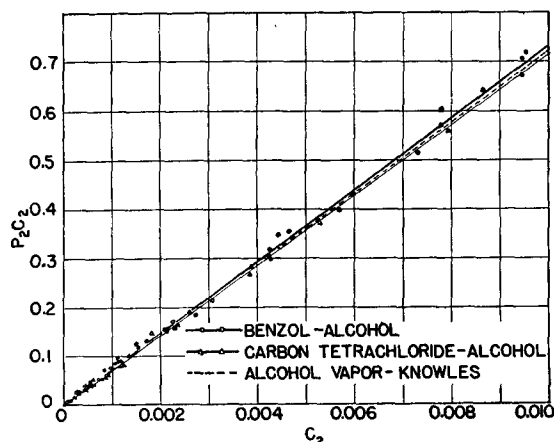

FIG. 2.

molecular polarization of ethyl alcohol at this temperature. A least-squares solution for the slope of this curve for ethyl alcohol-benzene solutions gives

$$\text{Slope} = P_2 = 73.16 \pm 0.42.$$

Intercept on the P_2C_2 axis $= 0.0034 \pm 0.0016$.

A similar solution for ethyl alcohol carbon tetrachloride solution gives

$$\text{Slope} = P_2 = 71.31 \pm 0.33.$$

Intercept on the P_2C_2 axis $= 0.00002 \pm 0.001$.

These two polarizations are seen to agree rather well. Knowles[8] has published data on ethyl alcohol vapor at 24.55°C obtained from measurements on twenty-eight different pressures of alcohol ranging from 0.2 to 6 cm of Hg. For comparison purposes his curve has been extended with the slope he specified and is shown dashed in Fig. 2. At this temperature he obtains a molecular polarization of 72.8. The author's values fall on either side of this. The author's data shown in the same figure covers a range of equivalent pressures from 1.5 to 200 cm of Hg. Thus the author's and Knowles' data overlap considerably, and the agreement between vapor and dilute solution data is rather remarkable.

The small intercept specified above for the ethyl alcohol-benzene curve, whether it be real or accidental, is consistent with the anomalous behavior apparent when data are plotted in the usual manner as in Fig. 1. The curve for ethyl alcohol-carbon tetrachloride solutions yields no intercept; and the data yield a fairly well defined intercept when plotted similar to Fig. 1. The author certainly would not claim that the intercept of the ethyl alcohol benzol curve is real, although Müller and Mortier[3] certainly consider the analogous effect observed by them on other substances to be so, and subgroups taken under quite different conditions seem to show the peculiar behavior rather consistently. One can appreciate how small an error is necessary to cause erratic behavior at extremely low concentrations only after making calculations involving

such measurements. In fact considerable published data on vapors show analogous erratic behaviors at low pressures if the data are treated as one commonly treats solutions. The author wishes to emphasize that he has in no way eliminated this peculiar behavior at low concentrations but he has suggested a method of treating it so that the inaccuracies necessarily introduced do not appreciably effect calculation of the molecular polarization.

The electric moment of the alcohol molecule may be calculated from the polarization found above, along with the molecular refraction taken over from optical data. The electric moment is given by

$$u = 1.272 \times 10^{-20}((P_0 - A)T)^{\frac{1}{2}},$$

where P_0 is the molecular polarization when freed from association and where A is the polarization due to other than molecular doublets. Taking A as 12.9 as calculated from the index of refraction one calculates the moment of the ethyl alcohol molecule to be

$u = (1.700 \pm 0.006) \times 10^{-18}$ from benzene solution

and $\quad u = (1.674 \pm 0.005) \times 10^{-18}$

from carbon tetrachloride solution.

These values compare favorably with each other and agree unusually well with two reliable values obtained from vapor studies, 1.696×10^{-18} by Miles,[9] and 1.686×10^{-18} by Knowles.[8]

Certain writers[10] have maintained that moments evaluated from benzene solution data must be multiplied by a certain factor greater than one in order to agree with moments obtained from vapor studies. The present findings are quite contrary to this. The agreement of moments here found is in all cases consistent with the probable errors; and actually the most probable value found from benzene solution is the highest of the group.

In conclusion the writer wishes to express his gratitude to Professor J. D. Stranathan for his continued interest in the progress of this work.

[8] Knowles, J. Phys. Chem. **36**, 2554 (1932).

[9] Miles, Phys. Rev. **34**, 964 (1929).
[10] See, for example, Müller (quoted). Chem. Soc. J. 1846–49 (1934).