

[CONTRIBUTION FROM THE ZOÖLOGICAL LABORATORY, HARVARD UNIVERSITY]

THE DIELECTRIC CONSTANT OF MIXTURES OF ETHYL ALCOHOL AND WATER FROM -5 TO 40°

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The following study of the dielectric constant of mixtures of alcohol and water was undertaken in connection with certain problems relating to amino acids in solution. In view, however, of the lack of any complete set of data on the subject, it appeared worth while to extend the measurements over the entire range of concentrations and over as wide a range of temperatures as practicable and to present the results independently. This seems to be justified by the frequent use of alcohol-water mixtures as solvents and by the importance of a knowledge of the dielectric constant in such cases in order to understand the behavior of the resulting systems. For instance, as has been so often pointed out, the dielectric constant controls largely the dissociation of dissolved electrolytes. Again, it is fundamental in the modern theory of activity coefficients and occurs prominently in Debye's expression for solubility. Moreover, it may be of importance to know not only the dielectric constant itself but also its variation with the temperature, as in connection with heats of dilution.

The value of the dielectric constant of pure ethyl alcohol at 20° given by the "International Critical Tables," Vol. VI, is 25.7 ± 0.2 . This figure is based on measurements made at different temperatures and at audio frequencies by various observers (see below, Fig. 4). Nernst,¹ Walden,² Turner,³ and Grimm and Patrick⁴ all made use of the method of the capacity bridge, which involved in all cases a calibration of the bridge with standard liquids of known dielectric constants, assumed correct. A certain amount of trouble was encountered in regard to conductivity. Thus Grimm and Patrick report that great care had to be taken to avoid traces of water, which introduced sufficient conductivity to make it impossible to obtain bridge settings. Landoldt and Jahn,⁵ on the other hand, used the electrometer method originally developed by Cohn and Arons. Their results are based on a comparison of alcohol with *m*-xy'ene, the dielectric constant of which was obtained by averaging their own and Tereschin's values.

Other observations at very low temperatures (Dewar and Flemming, Abegg and Seitz) are irrelevant to the present case. It is, however, of

¹ W. Nernst, *Z. physik. Chem.*, 14, 622 (1894).

² P. Walden, *ibid.*, 70, 569 (1910).

³ B. B. Turner, *ibid.*, 35, 385 (1900).

⁴ F. V. Grimm and W. A. Patrick, *THIS JOURNAL*, 45, 2794 (1923).

⁵ H. Landoldt and H. Jahn, *Z. physik. Chem.*, 10, 289 (1892).

interest in relation to the question of dispersion to consider the following results at high frequencies:

	Meters	°C.	
Thwing ⁶	12	20	24.2
Falkenburg ⁷	5	20	23.9
Cole ⁸	6	18	27.0
Cole ⁸	3	18	27.0
Cole ⁸	2.59	18	27.4
Drude ⁹	2.29	18	24.1
Drude ⁹	0.75	20	22.0
Lampa ¹⁰	0.04-0.08	Temperature unspecified	4.8-6.2

Of these observers Thwing made use of a resonance method taken from Hertz and Falkenburg of the second method of Drude, while Cole and Drude employed the method of standing waves on wires, and Lampa measured directly the refraction of a beam of waves. Both Colley¹¹ and Potapenko¹² also studied the dielectric constant of alcohol over a range of wave lengths from about 55 to 90 cm. and, although the agreement of the two observers is so poor as to render the results uncertain, there appears to be an undoubted variation of the dielectric constant with frequency in this range. In fact, on the basis of these and Lampa's results, there seems to be no question that as the wave length is decreased below about one meter, we begin to encounter dispersion.

A careful study of dispersion was made by Mizushima¹³ in the case of several of the alcohols by a resonance method. He showed quite clearly that an anomalous dispersion, and associated with it an absorption giving rise to the same apparent effects as conductivity, may appear as the wave length is diminished below a few meters, the lower the temperature the longer the wave length at which the process begins. This is in accordance with Debye's concept of relaxation time, the effect of temperature being due primarily to its influence on viscosity. Specifically, in the case of ethyl alcohol, at a wave length of 9.5 meters, the dielectric constant was found to rise at first as the temperature was lowered and then (by -60°) actually to decrease. At the same time traces of absorption were apparent at this frequency even at room temperature. This last fact would indicate that even at 20° the values of the dielectric constant

⁶ C. B. Thwing, *Z. physik. Chem.*, 14, 286 (1894).

⁷ G. Falkenburg, *Ann. Physik.*, 61, 145 (1920).

⁸ A. D. Cole, *ibid.*, 57, 290 (1896).

⁹ P. Drude, *ibid.*, 58, 1 (1896); 61, 466 (1897).

¹⁰ A. Lampa, *ibid.*, 61, 79 (1897).

¹¹ A. R. Colley, *Physik. Z.*, 10, 329, 471, 657 (1910).

¹² G. Potapenko, *Z. Physik.*, 20, 21 (1923).

¹³ S. Mizushima, *Bull. Chem. Soc. Japan*, 1, 47, 83, 115, 143, 163 (1926); *Physik. Z.*, 28, 418 (1927).

determined at 9.5 meters or thereabouts may be slightly below the static values. Evidence in regard to this point is considered below.

As regards the dielectric constant of mixtures of alcohol and water, the only data are those of Nernst,¹ made with the capacity bridge at audio frequency. Nernst's values were obtained at about 18° and unfortunately cover only a restricted range of concentrations. Their agreement with the results of the writer is discussed later (see Table III).

The method employed in the present investigation was one recently developed by the writer and described in detail elsewhere.¹⁴ It is a form of resonance method but differs from most other methods based on the same principle in that determinations are made by changes of frequency instead of by changes of capacity or inductance. It has the advantage that it yields absolute results and when used at high frequencies requires only small amounts of material. It is based on the relation between the natural period of a small, rigid, all metal circuit, which we will call the resonator, consisting of an inductance and capacity, and the dielectric constant of the surrounding medium. If the period of the circuit is determined first in air (ideally in a vacuum) and then in the medium, the dielectric constant of the latter is given at once by the square of the ratio of the two (*i. e.*, the period in the medium divided by the period in air, squared). In practice it is often more convenient to make use not of air but of some standard liquid whose dielectric constant is well known, *e. g.*, water, as a reference point. This in fact was done in the present investigation.

In order to determine the natural period of the resonator, the latter is suspended by a fine thread in the medium and brought into the field of an oscillator whose frequency is controlled by a rotating condenser equipped with a dial and vernier accurately graduated in arbitrary units. The frequency of the oscillator is then varied until it is made to correspond with the natural period of the resonator. The criterion of this point is the sudden change in the plate current of the oscillator caused by the absorption of power by the resonator, just as when the frequency of an oscillator is determined with an ordinary wave meter. The dial reading corresponding to this resonance point is noted and the frequency of the oscillator is then varied in both directions and the settings are recorded at which the latter is found to beat with a piezo electric oscillator with which it is coupled and which serves as a very accurate standard of frequency. From the various nearby beat settings arising from known harmonic combinations (these may be identified with a wave meter) it is an easy matter to interpolate graphically to an accuracy of a few hundredths of a per cent. the frequency corresponding to the resonance point.

The resonator employed for the measurements on the alcohol-water mixtures consisted of two concentric cylinders of brass tubing joined with a semicircular loop of brass rod (see Fig. 1). In order to prevent corrosion and provide a clean surface the structure was gold plated. The over-all diameter of the resonator was about 2.5 cm. and the height 4 cm. Its natural period in air, which was checked from time to time, was found to correspond to a wave length of 1.517 meters or a frequency of 1.977×10^8 . As a matter of fact this frequency was above the upper limit of the oscillator (about

¹⁴ J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

1.35×10^8 or $\lambda = 2.2$ meters) and, as already remarked, was determined indirectly from the period of the resonator in distilled water, by using the values of the dielectric constant given by Wyman. Owing to this procedure any errors in these values are, of course, carried over directly into the present results, but the uncertainty in regard to water in the neighborhood of 20° is considerably less than 0.1% and can introduce no practical difficulty in the present case where the experimental error is of at least this magnitude. This may be seen from a comparison of the value for the dielectric constant of water at 25° given by Drake, Pierce and Dow, namely, 78.57, with Wyman's figure 78.54 for the same temperature.

In order to make measurements the resonator just described was suspended in a glass bottle containing about 700 cc. of solution by a very fine cotton thread passing round the rubber stopper (see Fig. 1). This is far more than enough liquid to include sensibly all the field of the resonator and any errors due to stray lines of force extending outside the bottle must be far less than the errors involved in the resonance settings and frequency determinations.¹⁵ A 0.1° thermometer was supported by the stopper, the bulb extending into the liquid but lying well above the resonator so as not to affect the measurements. In this way the temperature could be observed directly at any time. In order to give a thorough stirring and insure uniformity of temperature a fine stream of air was bubbled through the bottle just before each reading was taken. The temperature itself was varied from about -10° to approximately 40° for all solutions measured. This was accomplished by placing the bottle in a larger glass vessel containing water or a freezing mixture of alcohol and water of desired temperature. In order to obtain the lower temperatures it was essential not to use freezing mixtures containing salt or any electrolyte since the consequent conductivity results in power absorption which affects the oscillator when the system is brought into its field.

Measurements were made over this range of temperature for alcohol-water mixtures of fixed composition at nearly 10% (by volume) intervals from pure alcohol to pure water. The solutions were made up at room temperature by diluting measured volumes of alcohol to 1000 cc. with water in 1-liter volumetric flasks, and the composition was checked by density determinations in all but a few cases. The stock solution of alcohol used throughout the work was a high-grade commercial alcohol of purity guaranteed greater than 99.5%. The density of this alcohol at 22.8° was found to be 0.7868, a figure in exact agreement with the value given for pure alcohol at this temperature by the "International Critical Tables." In the

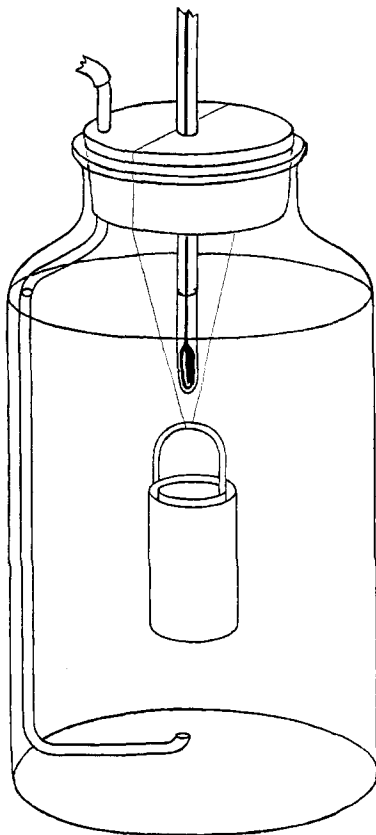


Fig. 1.

¹⁵ The question of the amount of liquid required adequately to surround the resonator is discussed by Wyman.

results tabulated below concentrations are also expressed in terms of grams of alcohol per gram of solution, a quantity independent of temperature.

In accordance with the nature of the method all different values of the dielectric constant of the alcohol-water mixtures were measured at different frequencies (or wave lengths). These need not be tabulated, however, since, in accordance with what has already been said, the frequency corresponding to any particular value may be obtained directly by dividing the square root of that value into the frequency of the resonator in air (1.977×10^8). Nevertheless it is worth pointing out that the shortest wave length used in the investigation was 7.302 meters (in the case of pure ethyl alcohol at 39.3°), and that the longest was 13.971 meters (in the case of 10% alcohol at -3.5°).

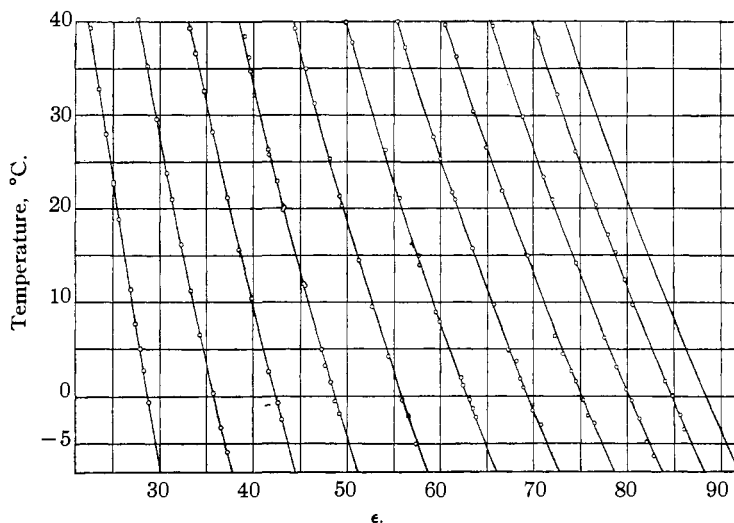


Fig. 2.—Variation of the dielectric constant, ϵ , of alcohol-water mixtures with temperature. Taken from left to right the curves correspond to the following concentrations of alcohol (grams per 100 grams of solution): 100; 85.3; 73.2; 62.5; 52.3; 42.4; 33.2; 24.4; 16.2; 8.0; and 0.0.

The results for any given alcohol-water mixture over the range of temperature studied (-10 to $+40^\circ$) can be fitted to an accuracy within the experimental error of the determinations by an equation of the second degree in regard to temperature

$$\epsilon = a - b(t - 20) + c(t - 20)^2 \quad (1)$$

This is illustrated by Fig. 2, in which experimental values are shown by circles and the curves correspond to equation (1) with properly chosen values of the constants. For this reason it is unnecessary to tabulate all the experimental points and it is sufficient to list values of the three constants in equation (1) for each of the alcohol-water mixtures studied.

This is done in Table I. It is to be noted that a is the value of the dielectric constant at 20°.

TABLE I
VALUES OF THE CONSTANTS a , b , AND c FROM EQUATION 1 FOR ALCOHOL-WATER MIXTURES OF THE FOLLOWING COMPOSITIONS. THE VALUES FOR WATER ARE CALCULATED FROM WYMAN'S RESULTS¹⁴

<u>Cc. alcohol</u> 100 cc. soln. at 20°	100	89.6	79.7	70.6	60.2	50.0	39.9	29.7	20.0	10.0	0
<u>Alcohol, g.</u> 100 g. soln.	100	85.3	73.2	62.5	52.3	42.4	33.2	24.4	16.2	8.0	0
a	25.07	31.13	36.98	42.65	48.93	54.97	60.96	66.34	71.23	75.67	80.37
b	0.159	0.192	0.225	0.256	0.286	0.320	0.342	0.359	0.365	0.366	0.369
$c \times 10^4$	2	5	8	10	13	14	15	15	14	12	7

From the results embodied in Table I it is a simple matter to construct curves showing the variation of the dielectric constant with composition of the solution at fixed temperatures, and these are given in Fig. 3.

For the convenience of those who may work with alcohol-water mixtures of fixed composition made up at 20° on a volume percentage basis (*i. e.*, cc. of alcohol per cc. of solution), it seems worth while to tabulate directly values of the dielectric constant at a variety of standard temperatures for solutions of regular composition expressed in this way. This is done in Table II.

TABLE II
VALUES OF THE DIELECTRIC CONSTANT OF ALCOHOL-WATER MIXTURES AT VARIOUS TEMPERATURES. VALUES FOR PURE WATER ARE TAKEN FROM WYMAN'S RESULTS¹⁴

<u>Cc. alcohol</u> 100 cc. soln. at 20°	100	90	80	70	60	50	40	30	20	10	0
<u>Alcohol, g.</u> 100 g. of soln.	100	85.7	73.5	62.0	52.1	42.4	33.3	24.6	16.2	8.0	0
40°	21.97	27.24	32.62	38.27	43.87	49.13	54.64	59.57	64.42	68.82	73.27
30°	23.50	29.01	34.64	40.53	46.33	51.91	57.62	62.73	67.72	72.15	76.75
25°	24.28	29.95	35.72	41.76	47.70	53.44	59.16	64.45	69.47	73.89	78.54
20°	25.07	30.89	36.81	42.99	49.06	54.97	60.90	66.17	71.23	75.67	80.37
10°	26.68	32.86	39.13	45.64	52.03	58.30	64.47	69.91	75.02	79.45	84.13
0°	28.32	34.93	41.62	48.49	55.30	61.92	68.33	73.93	79.08	83.46	88.03
-5°	29.17	36.26	42.92	50.00	57.01	63.83	70.38	76.05	81.22	85.56	(90.04)

It now remains to compare the present results with those of other investigators already referred to. In this connection we will consider first the figures for pure alcohol. These all correspond to wave lengths from about 7.3 to 8.0 meters. For purposes of comparison they are shown graphically in Fig. 4 together with the other values. It is evident from Fig. 4 that there is a pretty wide scatter among the latter and that the present results are not far from the average. The point of most importance to consider, however, is the question of any systematic differences associated with frequency. The reason for this is the possibility of the present results being slightly lower than the static values owing to the

effects of anomalous dispersion, a possibility raised by the work of Lampa, Colley, Potapenko and Mizushima, as already mentioned. If we turn first to studies at audio frequencies, where there is no question of dispersion, it appears that the writer's results are in very close agreement with the values of Landoldt and Jahn. At the same time they are con-

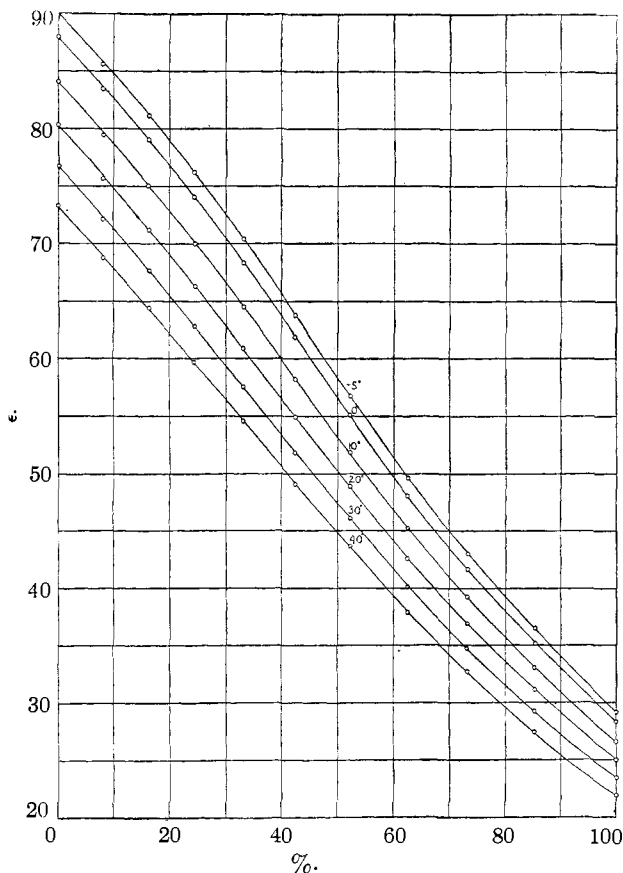


Fig. 3.—Variation of the dielectric constant, ϵ , of alcohol-water mixtures with composition (grams alcohol per 100 grams of solution) at different temperatures.

siderably below the single point given by Turner, a discrepancy which might, however, arise from the fact that Turner states that he failed to take precautions as to the purity of his alcohol. They appear also to be slightly below the other values obtained by the bridge method, though whether or not the discrepancy is significant is hard to say. On the other hand, when we pass on to the figures of Cole, Drude and Falkenburg obtained at wave lengths from 2-6 meters, it appears that the values, diver-

gent as they are, lie about equally above and below the audio frequency values and include the present results in their scatter.¹⁶ In view of some uncertainty, however, in regard to a fundamental point it was decided to make measurements by the present method at other frequencies.

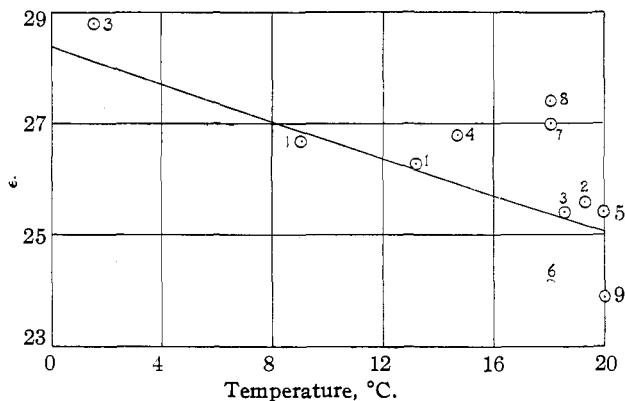


Fig. 4.—Values of the dielectric constant, ϵ , of ethyl alcohol obtained by different observers, indicated by number as follows: 1, Landoldt and Jahn (audio); 2, Nernst (audio); 3, Walden (audio); 4, Turner (audio); 5, Grimm and Patrick (audio); 6, Drude (2.29 meters); 7, Cole (6 meters and 3 meters); 8, Cole (2.59 meters); 9, Falkenburg (5 meters). The smooth curve represents the author's values.

For this purpose two other resonators were employed, one having a natural period in air corresponding to $\lambda_0 = 3.429$ meters (determined directly) and the other a period given by $\lambda_0 = 0.4107$ meter (determined indirectly in water). With these and the original resonator the following results were obtained on a sample of alcohol of 99.8% purity (determined from the density)

- (a) ($\lambda_0 = 3.429$) at 23.6° , $\lambda = 17.005$, $\epsilon = 24.59$
- (b) ($\lambda_0 = 1.517$) at 24.6° , $\lambda = 7.493$, $\epsilon = 24.39$
- (c) ($\lambda_0 = 0.4107$) at 24.7° , $\lambda = 3.972$, $\epsilon = 24.37$

Reduced to 25° by means of the data given in Table I, these three values of the dielectric constant become, respectively, 24.37, 24.34 and 24.33. From this agreement it is clear that down to a wave length of at least four meters any variation in the dielectric constant arising from dispersion lies

¹⁶ Since this paper was written the attention of the author has been called to a set of values of the dielectric constant of pure ethyl alcohol recently reported by Smyth and Stoops.¹⁷ The results were obtained with the bridge method at a frequency of 600 meters over a wide range of temperature and yield a value of the dielectric constant of 23.8 at 20° . This figure is 7.4% below the value given by the "International Critical Tables" and 5.2% below the author's value. The probable error attributed to their results by Smyth and Stoops is somewhat less than 2%.

¹⁷ C. P. Smyth and W. N. Stoops, *THIS JOURNAL*, 51, 3312 (1929).

within the experimental error of the determinations. The present results may therefore be accepted as representing static values of the dielectric constant.

In regard to the results for mixtures of alcohol and water, the extent of their agreement with the values of Nernst is sufficiently clear from Table III.

TABLE III
COMPARISON OF VALUES

Grams alcohol per 100 grams of soln.	Nernst's values at 20° ^a	Author's values at 20°
50	49.4	50.34
60	43.9	44.20
70	38.7	38.55
80	34.1	33.56
90	29.8	29.12
100	26.5	25.07

^a These are the smoothed and recalculated values given by "International Critical Tables," Vol. VI.

One other point appears worthy of remark. It is unfortunately quite impossible to give any interpretation of the polarization¹⁸ of solutions of

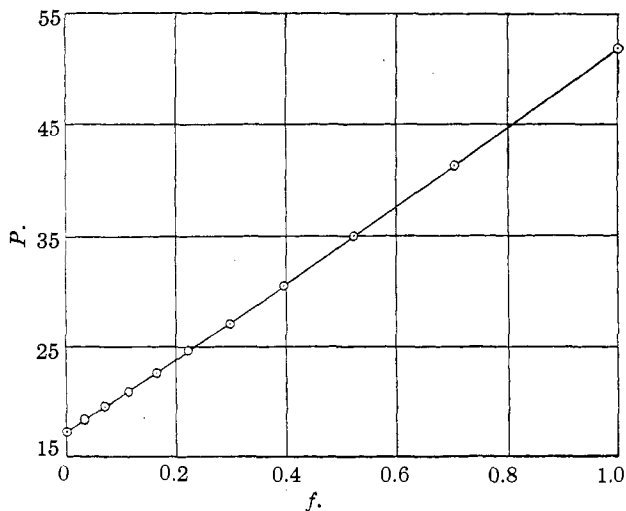


Fig. 5.—Variation of polarization, P , of alcohol-water mixtures at 20° with mole fraction, f , of alcohol.

¹⁸ The polarization P_{12} of a solution of two components is defined by the equation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{(f_1 M_1 + f_2 M_2)}{\rho}$$

in which the f 's and M 's refer to mole fractions and molecular weights, respectively, ρ denotes density, and ϵ is the dielectric constant (see Debye¹⁹).

¹⁹ P. Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929.

polar liquids such as alcohol and water in terms of molecular properties and dipole moments. Indeed the Mosotti hypothesis on which the expression for the polarization is based is generally supposed to break down entirely in such cases. In view of this it is therefore not without interest to observe that the polarization of the alcohol mixtures, calculated for 20° from the data given above, is so nearly a linear function of the mole fraction of alcohol (water) as shown in Fig. 5. In general, this would, of course, only be expected for non polar liquids.

The writer wishes to express his thanks to Professor E. J. Cohn for the facilities of his laboratory during the course of this investigation.

Summary

Values of the dielectric constant of alcohol-water mixtures from -5 to 40° have been determined for the entire range of composition. The method employed was one recently developed by the author, based on the determination of the natural period of a small all metal circuit completely immersed in the medium. The frequency varied from 2.15×10^8 to 4.10×10^8 ($\lambda = 3.971$ meters and 7.302 meters, respectively). In the case of pure alcohol the dielectric constant was shown to be independent of frequency between $\lambda = 3.972$ meters and $\lambda = 17.005$ meters. A comparison has been given of the author's results with such data in the literature as already existed.

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DISCONTINUITIES IN ADSORPTION ISOTHERMS

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Introduction

In a previous paper² it was shown that the adsorption of hydrogen by nickel at low temperatures increased with pressure in a markedly discontinuous manner. Subsequently the same phenomenon was reported in greater detail³ for another sample of nickel, and also for copper.

Recently Allmand and Burrage⁴ have reported a large number of adsorption isotherms which show discontinuities, observed for the most part with charcoal, and to some extent with silica. They point out that several

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² Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

³ Benton and White, paper read at the Atlanta meeting of the American Chemical Society, April, 1930.

⁴ Allmand and Burrage, (a) *Proc. Roy. Soc. (London)*, **A130**, 610 (1931); (b) *J. Phys. Chem.*, **35**, 1692 (1931).