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**DIELECTRIC CONSTANTS OF SOME ORGANIC SOLVENT-WATER
MIXTURES AT VARIOUS TEMPERATURES**

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Introduction.—In recent theories of the behavior of electrolytes in solution, the dielectric constant of the medium plays a very important role. Debye and Pauling¹ have discussed the various factors that influence the dielectric constant of the medium in the immediate neighborhood of an ion. They found that in very dilute solutions the dielectric constant of the pure solvent is the proper value to use for the so-called "limiting law." Furthermore, it has been shown that changes of the dielectric constant of the medium are closely connected with corresponding changes of the velocity of homogeneous reactions in solutions. An approach to a theoretical interpretation of the relation of these medium changes to the simultaneous changes in the velocity of certain catalyzed reactions has been given by Harned and Samaras.²

The measurement of the dielectric constant of conducting solutions is still very much a matter of controversy, and definite, reliable results seem as yet not to have been obtained. On the other hand, the measurement of the dielectric constant of a pure non-conducting solvent does not offer any particular difficulties and may be carried out according to a number of different methods. However, even the purest solvent has some conductivity, and the reliability of the measurement decreases rapidly with increasing conductance. Many solvents act as very weak acids or bases, showing large increases of the dissociation constant with increasing temperature and thus also giving less reliable data for their dielectric constant. Mixtures of solvents have sometimes, already at ordinary temperatures, a relatively high conductance, probably due to the medium effect of one solvent upon the dissociation constant of the other. Therefore it is important to select a method of measurement the results of which would be influenced as little as possible by the conductance of the solvent or the solvent mixture used.

¹ Debye and Pauling, *THIS JOURNAL*, **47**, 2129 (1925).

² Harned and Samaras, *ibid.*, **54**, 9 (1932).

Apparatus.—The measurements presented in this paper have been carried out according to the method given by Astin.³ The maximum potential drop of an impressed electromotive force of constant frequency is measured across a conducting condenser in a resonance circuit with this condenser in series with a non-conducting condenser. At maximum the conductance of the first condenser cancels out in the expression for its capacity, which is a function of a number of terms that may be kept constant. Thus, the capacity of the conducting condenser may be measured directly from the change in the capacity of a standard condenser placed in parallel with it. A diagram of the entire system is shown in Fig. 1.

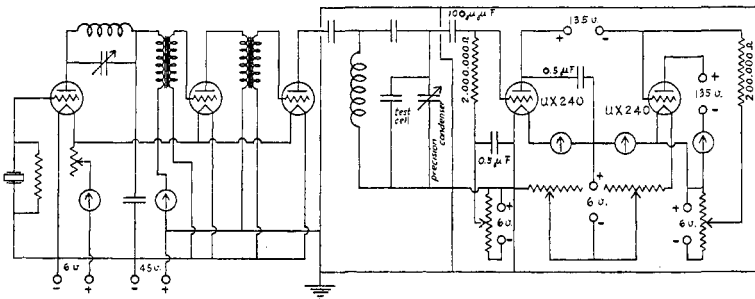


Fig. 1.—Wiring diagram for dielectric constant apparatus.

A General Radio high frequency piezo-electric oscillator, Type 375, was coupled to the measuring circuit through a small variable air condenser with a total capacity of about 100 micro-microfarads. The frequency of the oscillator was very near 2,000,000, corresponding to a wave length of 150 meters. A quartz plate with a frequency of 1,000,000 was also tried out, but it was found that the minimum on the vacuum tube voltmeter was somewhat sharper at the higher frequency. The oscillator was placed on a large shield above the shielded box containing the vacuum tube voltmeter and the measuring circuit, with which it was connected through a short antenna. The very loose coupling used by Astin between antenna and measuring circuit was found to be insufficient, but it was also found that an increase within the limits of the capacity of the small coupling condenser used did not change the value obtained for the capacity of the test condenser to any measurable extent.

The self-inductance in the measuring circuit had nine complete turns at a distance of 2 millimeters from each other and the diameter of the coil was 7 cm. The non-conducting condenser was a General Radio, Type 246-L, variable air condenser, which was set at a value of about 700 micro-microfarads. The standard condenser parallel to the test condenser was a General Radio, Type 222, precision condenser with a total capacity of 1500 micro-microfarads. The zero point of the apparatus with the test condenser out was adjusted in such a way that all readings on the precision condenser were obtained on the part of the scale where the capacity varied linearly with the setting. To remove the influence of body capacity, the precision condenser was turned from the outside of the shielding.

The construction of the vacuum tube voltmeter is clearly shown in Fig. 1 and further elaboration is unnecessary. The maximum potential drop was indicated by a

³ Astin, *Phys. Rev.*, **34**, 300 (1929).

Weston model 322 quadruple range direct current microammeter. At lower temperatures, and using solvent mixtures that did not contain large amounts of water, the minimum observed on the microammeter was very sharp and it would have been possible to set the precision condenser with an accuracy of 1 part in 5000, if the backlash had not made this impossible. The backlash seemed to amount to about one division in the drum. At high temperatures and using solvent mixtures high in water content, the sharpness of the minimum decreased rapidly, and in some cases it was impossible to obtain good readings at temperatures over 80°. The various parts of the electrical circuit system were not temperature controlled, and therefore the zero point of the apparatus showed small irregular variations up and down, which made it necessary to redetermine this point for almost every other measurement. The errors due to the temperature variations of the circuits are very small and relatively unimportant.

The construction of the test condenser is shown in Fig. 2. The circular plates made of tantalum were 1 mm. thick, 5 cm. in diameter, and placed at a distance of about 2 mm. from each other, thus giving the empty condenser a capacity of about 10.2 micro-microfarads. For a measurement, the filled test condenser was suspended in the center of a large oil thermostat placed right beside the shielded box for the measuring circuit and the vacuum tube voltmeter. The holder for the test condenser was made of fiber and it was carried by two long fiber rods clamped to a horizontal metal bar above the thermostat. The lead from the measuring circuit to the test condenser was made as short as the conditions allowed.

At temperatures higher than that of the surroundings, the oil thermostat was regulated by a series of mercury thermoregulators set at different temperatures. At lower temperatures the viscosity of the oil increased so much that the stirring provided became insufficient and a close regulation with a cooling coil was made impossible. To obtain readings at 20° or lower, the oil was cooled by a stream of water through a long coil of 1-cm. copper tubing pressed flat against the sides of the thermostat. The cooling water lowered the temperature of the oil-bath very slowly to a few degrees below 20°. When the temperature had shown a variation of about 0.1° or less during one hour, the capacity of the test condenser immersed in the oil was determined. All readings below 20° were interpolated to be valid at this temperature. The oil-bath could be heated at the rate of about 1° temperature rise per minute by forcing high pressure steam through the cooling coil. When the desired temperature had been reached and properly regulated, about half an hour or more was allowed to elapse before the capacity of the test condenser was determined. It was found repeatedly that almost complete equilibrium was reached within fifteen minutes after the desired temperature had been attained.

The calibration of the apparatus was carried out using water as standard liquid. The dielectric constant of water over a large temperature range has recently been determined with great accuracy by Drake, Pierce and Dow⁴ and Wyman,⁵ according to two quite different methods. The values obtained for pure water according to the two methods agreed so closely that the error at 20° certainly must be considerably

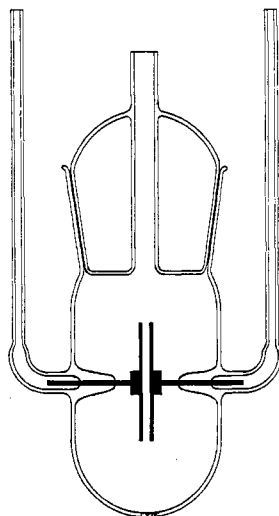


Fig. 2.—Test condenser.

⁴ Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

⁵ Wyman, *ibid.*, **35**, 623 (1930).

less than 0.1%. Standardization of the apparatus described above with benzene, the usual procedure, would have given a very large probable error since both the capacity of the test condenser and the dielectric constant of benzene were relatively small. The close agreement between the values obtained by Wyman and those presented in this paper for the dielectric constant of water at various temperatures was regarded as a sufficient test of the reliability of the apparatus.

Materials.—It was considered undesirable to use any other organic solvents than those which could be obtained easily in a state of high purity, in large quantities, and at a comparatively low price. In order to obtain a sharp minimum on the microammeter, it was necessary to use solvents having a very small conductivity, and all impurities acting as electrolytes had to be removed carefully. Traces of non-conducting impurities did not seem to have any appreciable effect on the measurements, but great efforts were made to obtain the pure organic solvents used as free from water as possible.

(1) Water was obtained from a large Barnstead still. Its conductance at ordinary temperatures was less than 10^{-6} and good readings could be obtained up to 100° .

(2) Methyl alcohol, Baker's Analyzed, absolute and acetone free, was dried with sufficient sodium metal to take care of about 5% of water. The alcohol was slowly fractionated, rejecting the first and last 500 cc. from a batch of 5 liters.

(3) Ethyl alcohol, ordinary absolute alcohol, was dried with sufficient sodium metal to take care of about 5% of water and then slowly fractionated, rejecting the first liter. About ten liters was treated in one operation.

(4) *n*-Propyl alcohol, Eastman Kodak Co., was dried with sodium metal and then fractionated, rejecting the first 500 cc. A batch of about 5 liters was treated and approximately 500 cc. left undistilled.

(5) Isopropyl alcohol was obtained from Dr. A. S. Brown, who, with greatest care, had chemically purified, dried and fractionated a sample of about 2000 g.

(6) *Tert.*-butyl alcohol, Eastman Kodak Co., was dried with anhydrous magnesium sulfate and fractionated. The melting point was 24.0° and it did not rise any further after two fractionated freezings.

(7) Ethylene glycol, Eastman Kodak Co., was dried with burnt, pulverized lime for two days. Then the glycol was poured off and distilled in vacuum. The first 500 cc. was rejected and about 500 cc. left undistilled from a batch of about 3 liters.

(8) Glycerol, Baker's Analyzed, was boiled in vacuum during three to four hours with precipitated and carefully washed calcium carbonate. At first, water containing small amounts of glycerol distilled over. Then the pressure started to drop, and, when it had gone below one millimeter of mercury, the first 250 cc. was rejected. After collecting about 1500 cc., approximately one liter was left in the still. The distillate was absolutely colorless, with a hardly perceptible odor, and it had an exceedingly high viscosity.

(9) Acetone, Baker's Analyzed, was treated in batches of about three liters with a small amount of very concentrated phosphoric acid and immediately distilled, then dried with burnt powdered lime for a day, poured off and redistilled. Acetone, Eastman Kodak Co., from the bisulfite compound, dried with anhydrous sodium sulfate and redistilled, gave almost exactly the same value for the dielectric constant as the sample prepared from Baker's acetone.

The distilled solvents were stored in Pyrex bottles which, after cleaning, had been rinsed out several times with conductivity water and then dried in a small oven at a temperature of about 200° . Each one of the dried and redistilled organic solvents employed gave excellent readings at all temperatures used. Beside the measurements carried out with water mixtures of the solvents given above, a few results were obtained for solutions of mannitol and sucrose in water.

(10) Mannitol, Th. Schuchardt, Görlitz, Germany, was recrystallized four times from conductivity water and then dried in vacuum to constant weight.

(11) Sucrose, Kahlbaum, Germany, for calorimetric measurements, was used without further purification. It was impossible to obtain good readings at sugar concentrations up to 40% and at higher temperatures. The values given below for solutions in this range are interpolated from the measurements of Kockel⁶ and recalculated to the value given in this paper for the dielectric constant of pure water at the particular temperature of the sugar solution.

Measurements and Results.—All organic solvent–water mixtures were made up by weight in amounts of about 300–400 g., with an average error in the concentration of the components less than 0.05%. The test condenser always was filled almost completely with the liquid to be used. At higher temperatures some solvent mixtures showed a more or less pronounced tendency to develop slight concentration gradients in the cell. This was counteracted by taking the cell out of the bath and by shaking it gently for two minutes about five to ten minutes before the measurement. The measurement itself required about ten minutes, approaching the minimum from both sides and taking the average of all readings. After a series of measurements had been completed for a given liquid, the test condenser was thoroughly cleaned and dried at a temperature of about 200°. It was found that the presence of the slightest trace of oil on the plates in the test condenser gave erroneous results. Therefore, the cell was cleaned when considered necessary with hot concentrated sulfuric acid and then the acid was washed away with boiling conductivity water. The temperature at which the measurements were carried out was recorded with a solid stem thermometer for total immersion calibrated against thermometers certified by the Bureau of Standards.

The results of the measurements with pure solvents are summarized in Table I. The data obtained for all solvent mixtures and solutions of

TABLE I
DIELECTRIC CONSTANT AT VARIOUS TEMPERATURES OF (1) METHYL, (2) ETHYL,
(3) *n*-PROPYL, (4) ISOPROPYL, (5) ISOBUTYL, (6) *Tert.*-BUTYL ALCOHOL,
(7) ETHYLENE GLYCOL, (8) GLYCEROL AND (9) ACETONE

Temp., °C.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
20	32.35	25.00	20.81	18.62	16.68	3.76	38.66	41.14	19.56
25	...	24.20	9.90	19.10
30	30.68	23.55	19.54	17.38	15.27	9.37	36.80	39.22	18.67
40	29.03	22.20	18.25	16.23	14.00	8.44	34.94	37.30	17.80
50	27.44	20.87	17.11	15.06	12.83	7.67	33.21	35.53	16.98
60	25.97	19.55	15.88	14.03	11.75	6.96	31.58	33.82	...
70	...	18.31	14.90	13.00	10.80	6.45	29.93	32.14	...
80	13.86	11.91	9.89	5.90	28.45	30.63	...
90	12.93	...	9.08	..	26.95	29.20	...
100	8.19	..	25.61	27.88	...

⁶ Kockel, *Ann. Physik*, **77**, 417 (1925).

mannitol and sucrose are collected in Tables II to XI. The dielectric constant of pure water at 20° is set equal to 80.37 in accordance with the measurements of Wyman. The values given for solutions of sucrose up to 40 weight per cent. were interpolated from the measurements of Kockel as indicated above. Since most investigations of the behavior of solutions have been carried out at 25°, the data in Tables I to XI were carefully

TABLE II
DIELECTRIC CONSTANT OF METHYL ALCOHOL-WATER MIXTURES

Alcohol, wt. %	20°	30°	40°	50°	60°
0	80.37	76.73	73.12	69.85	66.62
10	75.84	72.37	68.90	65.66	62.77
20	71.02	67.48	64.13	61.06	58.24
30	66.01	62.71	59.53	56.59	53.94
40	61.24	58.06	54.82	52.17	49.52
50	56.53	53.47	50.40	47.82	45.28
60	51.53	48.58	45.64	43.22	41.22
70	46.46	43.63	41.04	38.81	36.68
80	41.46	38.98	36.66	34.62	32.74
90	36.80	34.62	32.56	30.67	28.91
100	32.35	30.68	29.03	27.44	25.97

TABLE III
DIELECTRIC CONSTANT OF ETHYL ALCOHOL-WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	74.60	67.86	64.53	61.49	55.70
20	68.66	62.41	59.22	56.40	50.81
30	62.63	56.73	53.79	51.04	45.88
40	56.49	51.08	48.36	45.80	40.93
50	50.38	45.30	42.92	40.66	36.51
60	44.67	40.02	37.72	35.66	31.82
70	39.14	34.88	32.86	30.87	27.30
80	33.89	29.83	28.10	26.31	23.20
90	29.03	25.64	24.08	22.51	19.80
100	25.00	22.20	20.87	19.55	...

TABLE IV
DIELECTRIC CONSTANT OF *n*-PROPYL ALCOHOL-WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	73.52	66.81	63.66	60.65	54.77
20	66.54	60.24	57.23	54.49	49.01
30	59.21	53.46	50.72	48.19	43.00
40	51.68	46.55	44.08	41.76	37.53
50	44.29	39.70	37.38	35.39	31.42
60	37.51	33.54	31.49	29.71	26.22
70	31.56	28.20	26.42	24.92	21.84
80	26.83	23.89	22.39	20.95	18.28
90	23.34	20.67	19.37	18.07	15.81
100	20.81	18.25	17.11	15.88	13.86

TABLE V

DIELECTRIC CONSTANT OF ISOPROPYL ALCOHOL-WATER MIXTURES					
Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	73.11	66.33	63.12	60.24	54.83
20	65.72	59.56	56.61	53.87	49.01
30	58.40	52.71	50.18	47.58	43.13
40	51.07	45.86	43.54	41.35	37.31
50	43.68	39.16	37.03	35.05	31.49
60	36.28	32.45	30.67	28.90	25.67
70	29.57	26.30	24.85	23.34	20.67
80	24.44	21.63	20.26	19.03	16.70
90	20.95	18.48	17.11	16.02	13.83
100	18.62	16.23	15.06	14.03	11.91

TABLE VI

DIELECTRIC CONSTANT OF <i>tert.</i> -BUTYL ALCOHOL-WATER MIXTURES					
Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	71.75	64.91	61.84	58.83	52.87
20	62.93	56.77	53.82	50.87	45.14
30	54.17	48.33	45.44	42.96	38.47
40	45.38	40.01	37.35	34.93	30.59
50	36.59	32.16	29.80	27.80	24.24
60	28.91	25.02	23.01	21.30	18.41
70	22.30	19.00	17.41	16.29	13.94
80	17.23	14.60	13.44	12.51	10.45
90	12.97	10.93	10.00	9.36	7.66
100	...	8.44	7.67	6.96	5.90

TABLE VII

DIELECTRIC CONSTANT OF ETHYLENE GLYCOL-WATER MIXTURES					
Glycol, wt. %	20°	40°	60°	80°	100°
0	80.37	73.12	66.62	60.58	55.10
10	77.49	70.29	63.92	58.02	...
20	74.60	67.52	61.20	55.36	...
30	71.59	64.51	58.37	52.59	...
40	68.40	61.56	55.48	49.81	...
50	64.92	58.25	52.30	46.75	...
60	61.08	54.53	48.75	43.68	39.13
70	56.30	50.17	44.98	40.19	35.94
80	50.64	45.45	40.72	36.36	32.52
90	44.91	40.43	36.35	32.58	29.27
100	38.66	34.94	31.58	28.45	25.61

TABLE VIII

DIELECTRIC CONSTANT OF GLYCEROL-WATER MIXTURES					
Glycerol, wt. %	20°	40°	60°	80°	100°
0	80.37	73.12	66.62	60.58	55.10
10	77.55	70.41	63.98	58.31	...
20	74.72	67.70	61.56	56.01	...
30	71.77	64.87	58.97	53.65	...

TABLE VIII (Concluded)

Glycerol, wt. %	20°	40°	60°	80°	100°
40	68.76	62.03	56.24	51.17	...
50	65.63	59.55	53.36	48.52	...
60	62.03	55.48	50.17	45.39	41.08
70	57.06	51.41	46.33	41.90	38.07
80	52.27	46.92	42.32	38.30	34.70
90	46.98	42.26	38.19	34.47	31.34
100	41.14	37.30	33.82	30.63	27.88

TABLE IX

DIELECTRIC CONSTANT OF ACETONE-WATER MIXTURES

Acetone, wt. %	20°	25°	30°	40°	50°
0	80.37	78.54	76.73	73.12	69.85
10	74.84	73.02	71.37	68.07	65.01
20	68.58	66.98	65.34	62.28	59.45
30	62.48	61.04	59.47	56.77	54.17
40	56.00	54.60	53.23	50.82	48.52
50	49.52	48.22	46.99	44.81	42.81
60	42.93	41.80	40.75	38.86	37.04
70	36.51	35.70	34.63	33.03	31.44
80	30.33	29.62	28.74	27.50	26.20
90	24.61	23.96	23.38	22.32	21.26
100	19.56	19.10	18.67	17.80	16.98

TABLE X

DIELECTRIC CONSTANT OF PURE AQUEOUS SOLUTIONS OF MANNITOL

Temp., °C.	0 Wt. %	5 Wt. %	10 Wt. %	15 Wt. %	20 Wt. %
20	80.37	79.66	78.84	78.07	...
25	78.54	77.83	77.12	76.30	75.47
30	76.73	76.06	75.18	74.47	73.64
40	73.12	72.40	71.57	70.87	70.10
50	69.85	69.16	68.33	67.57	66.74
60	66.62	65.85	65.08	64.38	63.61

TABLE XI

DIELECTRIC CONSTANT OF PURE AQUEOUS SOLUTIONS OF CANE SUGAR BETWEEN 10-40 WT. % ACCORDING TO KOCKEL, 50-70 WT. % ACCORDING TO ÅKERLÖF

Temp., °C.	0 Wt. %	10 Wt. %	20 Wt. %	30 Wt. %	40 Wt. %	50 Wt. %	60 Wt. %	70 Wt. %
10	84.2	81.5	78.8	75.9	72.8
20	80.4	78.0	75.4	72.6	69.8	65.7	61.2	55.0
30	76.7	74.2	71.7	68.9	66.1	62.4	58.2	52.5
40	73.1	70.7	68.3	65.7	63.0	59.4	55.5	50.1
50	69.9	67.5	65.0	62.5	59.8	56.3	52.5	47.6
60	66.6	64.4	62.0	59.4	56.8	53.4	49.8	45.1
70	63.5	61.2	58.8	56.2	53.6	50.5	47.1	42.7
80	60.6	58.2	55.8	53.2	50.5	47.6	44.3	40.3
90	57.8	55.4	52.9	50.4	47.7	38.0
100	55.1	52.7	50.2	47.6	44.8	35.7

interpolated to this standard temperature. The result of this interpolation is summarized in Table XII.

TABLE XII
DIELECTRIC CONSTANT AT 25° OF (1) METHYL, (2) ETHYL, (3) *n*-PROPYL,
(4) ISOPROPYL, (5) *Tert.*-BUTYL ALCOHOL, (6) ETHYLENE GLYCOL,
(7) GLYCEROL, (8) ACETONE-WATER MIXTURES, (9) MANNITOL
AND (10) CANE SUGAR SOLUTIONS

Wt. %	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5
10	74.1	72.8	71.8	71.4	70.0	75.6	75.7	73.0	77.1	76.3
20	69.2	67.0	64.9	64.1	61.3	72.8	72.9	67.0	75.5	73.6
30	64.3	61.1	57.7	56.9	52.6	69.8	70.0	61.0	..	70.9
40	59.6	55.0	50.3	49.7	43.9	66.6	67.1	54.6	..	67.9
50	54.9	49.0	43.0	42.5	35.4	63.2	64.0	48.2	..	64.2
60	50.1	43.4	36.4	35.3	27.9	59.4	60.0	41.8	..	59.9
70	45.0	38.0	30.7	28.7	21.4	54.7	55.6	35.7	..	54.2
80	40.1	32.8	26.1	23.7	16.5	49.3	50.6	29.6
90	35.7	28.1	22.7	20.3	12.4	43.7	45.5	24.0
100	31.5	24.3	20.1	18.0	9.9	37.7	40.1	19.1

Discussion of the Results.⁷—In Fig. 3 has been plotted the logarithm of the dielectric constant of the pure solvents indicated. Every curve has been drawn as a straight line and in all cases this gives, without any doubt, the best representation of the results, or, in mathematical form:

$$D = ae^{-bT} \quad (1)$$

where a and b are empirical constants and T is absolute temperature. A simple relation of this kind has a great value for interpolation purposes and therefore is well worth testing over as large a temperature range as possible. There are, however, various difficulties connected with this problem. The dielectric constant is known for very few liquids with certainty over a large range of either high or low temperatures, and in the latter case it should also be observed that the dispersion range with decreasing temperature may extend to wave lengths of many meters. For methyl and ethyl alcohols the most reliable data obtained at low temperatures seem to be those of Abegg and Seitz⁸ at infinite wave length. Older data for the dielectric constant of higher alcohols show already at ordinary temperatures considerable discrepancies with the results in this paper. Furthermore, as has been shown by the investigations of Mizushima, dispersion occurs at low temperatures for these alcohols at large wave lengths and an extrapolation to a static value is always somewhat uncertain. Therefore, older measurements at low temperatures are not directly comparable with the data in Table I. Instead, equation 1 has been tested using a number of measurements of Smyth and Morgan⁹ for ethyl bromide and chlorobenzene from -92 to $+126^\circ$, of Smyth and Stoops¹⁰

⁷ To save space comparison with data in literature is omitted.

⁸ Abegg and Seitz, *Z. physik. Chem.*, **29**, 242 (1899).

⁹ Smyth and Morgan, *THIS JOURNAL*, **50**, 1547 (1928).

¹⁰ Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

for 2,2-dimethylpentane from -120 to $+80^\circ$. Measurements of the latter with other hydrocarbons give practically the same result. As the numerical values do not interest, only a graphical representation is shown in Fig. 4. The scale used for plotting the logarithm of the dielectric constant has been varied for the different compounds in such a way

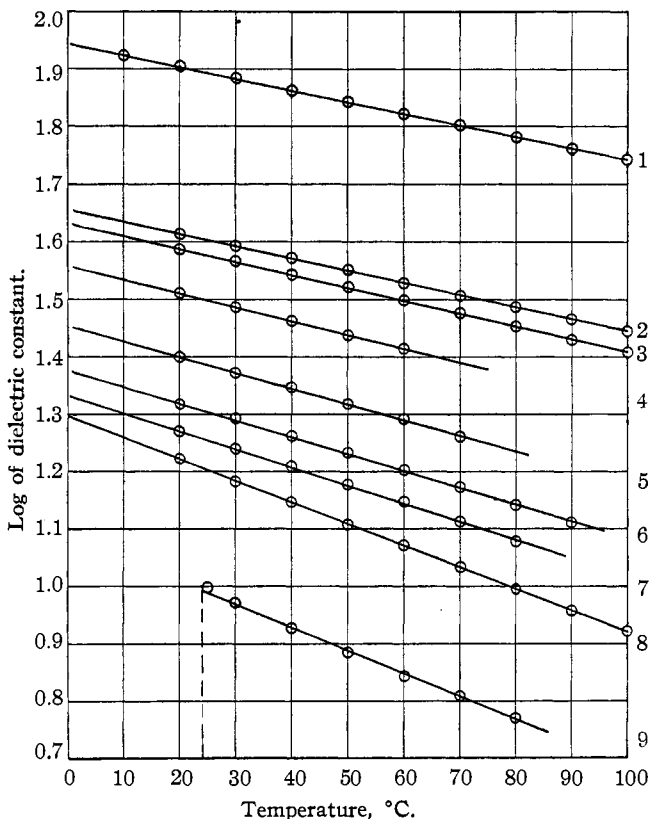


Fig. 3.—Curves for the logarithm of the dielectric constant of the pure solvents plotted against temperature. The curves represent (1) water, (2) glycerol, (3) ethylene glycol, (4) methyl, (5) ethyl, (6) *n*-propyl, (7) isopropyl, (8) isobutyl and (9) tertiary butyl alcohols.

as to give all lines a slope of the same order of magnitude. The variety of liquids represented in Fig. 4 is quite small, but every line seems to indicate that equation (1) is valid within the experimental errors over a temperature range of at least 150° . The constant b in equation (1) is a very important factor in the theory for heats of dilution. The integral heat of dilution is equal to the ionic electrical potential energy at the concentration given less that at infinite dilution multiplied by the factor

$(1 + T/D \cdot dD/dT)$, which is characteristic of the particular solvent used. Differentiation of equation (1) gives immediately

$$\frac{T}{D} \cdot \frac{dD}{dT} = -bT \quad (2)$$

In the following tables, ten-logarithms have been used for the calculation of all values of $\log a$ and b . Before using the b values in equation (2), they should therefore be multiplied with the factor 2.3026.

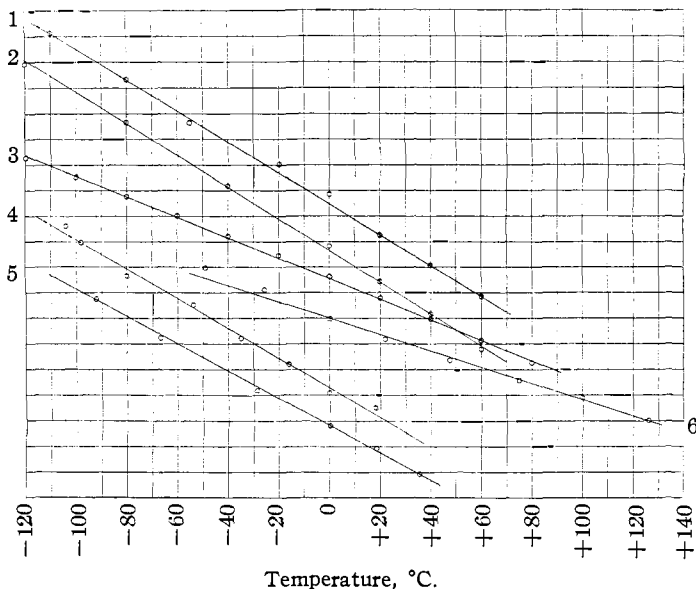


Fig. 4.—Curves for the logarithm of the dielectric constant of various compounds plotted against temperature. The lines represent (1) methyl, (2) ethyl alcohol, (3) 2,2-dimethylpentane, (4) dimethyl ether (according to measurements of Isnardi, *Cont. est. cienc. fis. mat.*, 3, No. 53(1922)), (5) ethyl bromide and (6) chlorobenzene.

Using equation (1), graphical interpolation of the data in Table I gives the following expressions for the calculations of the dielectric constant of the pure solvents with varying temperature

(1) Methyl alcohol	$\log D = 1.5099 - 0.00234 (t - 20)$
(2) Ethyl alcohol	$1.3979 - 0.00264 (t - 20)$
(3) <i>n</i> -Propyl alcohol	$1.3183 - 0.00293 (t - 20)$
(4) Isopropyl alcohol	$1.2700 - 0.00311 (t - 20)$
(5) Isobutyl alcohol	$1.2222 - 0.00386 (t - 20)$
(6) <i>Tert.</i> -butyl alcohol	$0.9870 - 0.00400 (t - 25)$
(7) Ethylene glycol	$1.5872 - 0.00224 (t - 20)$
(8) Glycerol	$1.6142 - 0.00212 (t - 20)$
(9) Acetone	$1.2914 - 0.00201 (t - 20)$

If the variation of the dielectric constant of two pure solvents with temperature may be calculated from the expressions given above, it is reasonable to assume that the dielectric constant of any mixture of the two behaves in the same way. This has been found to be the case, and in Table XIII is given a summary of the constants derived for the equations for methyl, ethyl and *n*-propyl alcohols, in Table XIV for ethylene glycol, isopropyl and tertiary butyl alcohol-water mixtures. All constants are given with 20° as reference temperature, except in the case of pure tertiary butyl alcohol, as noted above.

TABLE XIII
CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANT OF METHYL, ETHYL
AND *n*-PROPYL ALCOHOL-WATER MIXTURES WITH VARYING TEMPERATURES

Alcohol, wt. %	Methyl alcohol- water mixtures		Ethyl alcohol- water mixtures		<i>n</i> -Propyl alcohol- water mixtures	
	log <i>a</i>	<i>b</i>	log <i>a</i>	<i>b</i>	log <i>a</i>	<i>b</i>
0	1.9051	-0.00205	1.9051	-0.00205	1.9051	-0.00205
10	1.8799	- .00208	1.8727	- .00209	1.8664	- .00210
20	1.8505	- .00212	1.8367	- .00214	1.8231	- .00216
30	1.8190	- .00218	1.7968	- .00221	1.7724	- .00225
40	1.7865	- .00225	1.7520	- .00230	1.7133	- .00234
50	1.7513	- .00234	1.7024	- .00240	1.6455	- .00243
60	1.7120	- .00244	1.6500	- .00250	1.5740	- .00252
70	1.6658	- .00252	1.5926	- .00262	1.5000	- .00261
80	1.6160	- .00248	1.5300	- .00272	1.4300	- .00271
90	1.5648	- .00242	1.4625	- .00268	1.3710	- .00282
100	1.5099	- .00234	1.3979	- .00264	1.3183	- .00293

TABLE XIV
CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANTS OF ETHYLENE
GLYCOL, ISOPROPYL AND *Tert.*-BUTYL ALCOHOL-WATER MIXTURES WITH
VARYING TEMPERATURES

Alcohol, wt. %	Ethylene glycol- water mixtures		Isopropyl Alcohol- water mixtures		<i>Tert.</i> -butyl alcohol- water mixtures	
	log <i>a</i>	<i>b</i>	log <i>a</i>	<i>b</i>	log <i>a</i>	<i>b</i>
0	1.9051	-0.00205	1.9051	-0.00205	1.9051	-0.00205
10	1.8893	- .00210	1.8640	- .00208	1.8558	- .00216
20	1.8727	- .00215	1.8177	- .00213	1.7989	- .00230
30	1.8548	- .00222	1.7664	- .00220	1.7338	- .00250
40	1.8351	- .00230	1.7082	- .00228	1.6565	- .00274
50	1.8124	- .00237	1.6403	- .00238	1.5634	- .00298
60	1.7859	- .00240	1.5597	- .00249	1.4610	- .00322
70	1.7505	- .00242	1.4709	- .00262	1.3485	- .00340
80	1.7045	- .00238	1.3894	- .00277	1.2364	- .00360
90	1.6523	- .00231	1.3225	- .00294	1.1120	- .00380
100	1.5872	- .00224	1.2700	- .00311	0.9870 ^a	- .00400

^a Reference temperature for pure *tert.*-butyl alcohol 25°.

The molecular dielectric polarization P_{12} of a mixture of two compounds is given by the equation

$$P_{12} = \frac{D - 1}{D + 2} \frac{f_1 M_1 + f_2 M_2}{d} \quad (3)$$

where f_1 and f_2 denote mole fractions, M_1 and M_2 molecular weights and d density of the mixture. Equation (3) is supposed to be used only for solu-

TABLE XV

DATA FOR THE POLARIZATION CURVE OF GLYCEROL-WATER MIXTURES AT 20° AND
CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANT OF THESE MIXTURES

Glycerol, wt. %	$\log a$	b	D	d	f	P_{12}
0	1.9051	-0.00205	80.37	0.9982	0.0000	17.40
10	1.8896	- .00207	77.55	1.0221	.0213	18.20
20	1.8734	- .00209	74.71	1.0470	.0466	19.68
30	1.8560	- .00211	71.78	1.0727	.0774	21.24
40	1.8373	- .00214	68.75	1.0995	.1154	23.14
50	1.8171	- .00217	65.63	1.1263	.1637	25.57
60	1.7890	- .00220	61.52	1.1533	.2269	28.77
70	1.7563	- .00220	57.05	1.1808	.3135	33.15
80	1.7154	- .00217	51.93	1.2079	.4391	39.68
90	1.6688	- .00214	46.65	1.2347	.6380	49.59
100	1.6142	- .00212	41.14	1.2609	1.0000	67.94

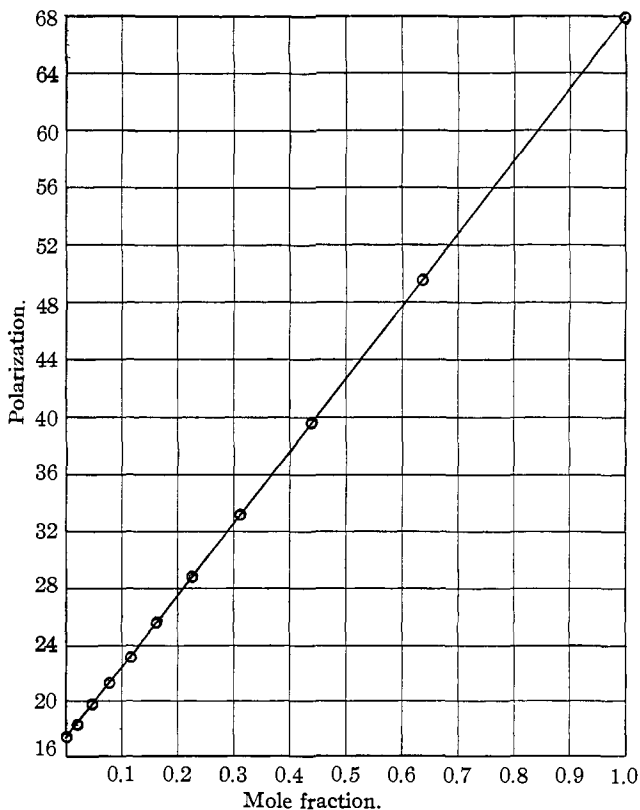


Fig. 5.—Curve for the dielectric polarization of glycerol-water mixtures at 20° according to equation (3).

tions of non-associated compounds in non-polar solvents. It has, however, been applied by Wyman to ethyl alcohol-water and by Graffunder and Heymann to ethyl alcohol and acetone-water or nitrobenzene mixtures. Both investigators found a linear variation of the polarization with the mole fraction of one of the compounds present. Glycerol is far more highly polar and has an enormously greater viscosity than either ethyl alcohol or acetone and a comparison of the polarization curve for glycerol-water mixtures with the straight lines found for the mixtures mentioned above has therefore some interest. In Table XV is given a summary of all the data necessary for the plotting of the polarization curve for glycerol-water mixtures. In the table are also included the constants to be employed for the calculation of the temperature variation of the dielectric constant of these mixtures.

The polarization data for glycerol-water mixtures are plotted in Fig. 5. The points all lie in a straight line, and thus we have obtained the same general result as previously found by Wyman and Graffunder and Heymann for other organic solvent-water mixtures. However, this result was partly to be expected since the mole fraction term in equation (3) varies approximately linearly and the dielectric constants of all the mixtures are high. The same holds true in the case of the mixtures measured by the investigators mentioned above. The calculation of the dielectric constant of alcohol-water mixtures from the known polarizations of the pure compounds would, assuming linear variation with the mole fraction, accordingly, give values of low accuracy.

Summary

Using a resonance method at a wave length of 150 meters, the dielectric constant at various temperatures has been measured for a series of water mixtures of the following organic solvents: (1) methyl, (2) ethyl, (3) *n*-propyl, (4) isopropyl, (5) tertiary butyl alcohol, (6) ethylene glycol, (7) glycerol and (8) acetone. The dielectric constants of a few pure aqueous solutions of mannitol and cane sugar have also been measured at various temperatures.

The results have been compared with corresponding data in the literature, and, in general, fairly good agreement has been found. In some instances a short discussion has been given of the results in order to indicate why the present data probably are nearer the true values than the older ones.

It has been found that the change with temperature of the dielectric constant of all the compounds employed for the measurements presented in this paper may be expressed with considerable accuracy by the equation

$$D = ae^{-bT}$$

where D is the dielectric constant, a and b are empirical constants, and T is temperature. The equation has also been tested using a number of series

of data in the literature. Straight line variation of the logarithm of the dielectric constant with temperature was generally found in every case over the entire range the measurements had been carried out.

Equations for the change with temperature of the dielectric constant of the pure solvents and the solvent-water mixtures have been obtained through large scale graphical interpolation. As a rule, the calculated values agree very well with the observed ones. A short discussion has been given of the polarization of glycerol-water mixtures.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,
No. 96]

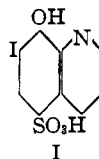
7-IODO-8-HYDROXYQUINOLINE-5-SULFONIC ACID AS A REAGENT FOR THE COLORIMETRIC DETERMINATION OF FERRIC IRON

BY JOHN H. YOE

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7-Iodo-8-hydroxyquinoline-5-sulfonic acid (I) dissolves in water to give a bright yellow solution which reacts with ferric ions, yielding blue to green colored solutions, the color and intensity varying with the iron concentration. The reaction is very sensitive and is best carried out in a solution acid to methyl orange paper. Ferrous ions give no color reaction and hence the reagent may be used to distinguish between ferrous and ferric iron. The color does not fade on standing, an advantage over the thiocyanate method.



Solutions

Standard Solutions of Various Ions.—Each standard solution was prepared from a good grade of salt, usually nitrate, chloride or sulfate, in the case of metallic ions, and from the potassium or sodium salt in the case of the non-metallic ions. Redistilled water was used (unless otherwise stated) and all solutions were kept in 30-ml. bottles that had been thoroughly cleaned and steamed out. Each bottle was fitted with a Pyrex glass dropper capped with a rubber stopper and nipple. Each dropper was calibrated, the capacities ranging from 18 to 28 drops per ml. The solutions were arranged according to the Periodic Chart and held in place on a wooden board, 45.5 cm. × 68.5 cm., in which were bored holes to carry the bottles. The concentration of the solutions was 400 mg. of the respective ion per liter, that is, 400 parts per million. Most of the solutions were aqueous, a few were in dilute acid (HCl, HNO₃ or H₂SO₄), and several were in concentrated acid.

In addition to the above solutions, more concentrated ones were prepared in the case of sodium, potassium, calcium and magnesium for use in preparing salt solutions for the determination of iron. These solutions contained 10 mg. of metallic ion per ml.

Standard Ferric Iron Solution.—A weighed quantity of pure ferrous ammonium sulfate, FeSO₄·(NH₄)₂SO₄·6H₂O, was dissolved in water, a few drops of concentrated sulfuric acid added and the iron oxidized by boiling with a little bromine. The excess bromine was expelled by boiling, the solution cooled to room temperature, transferred to