AN ARRANGEMENT OF THE ELECTROMETER METHOD FOR MEASURING THE DIELECTRIC CONSTANTS OF ELECTROLYTES

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Abstract

The electrometer method described by A. P. Carman (Phys. Rev. **24**, 396, 1924), has been modified to meet difficulties of heating effects, of buoyance, of electrolytic polarization, and of exact measurement of potential differences between the fixed plates and the needle plates. The method is particularly adapted to the measurement of relative dielectric constants of water and aqueous electrolytes, even where the concentrations and resulting conductivity of the electrolytes are considerable.

THE electrometer method, described by A. P. Carman in 1924,[1] has been changed in order to overcome some difficulties that appeared in practice, particularly in its application to measuring the dielectric constants of electrolytes. The new arrangement is shown in Fig. 1. The vertical plates A and B, and the corresponding needle plates C_1 and C_2, are charged as in the original arrangement by sliding contacts with the potentiometer wire,
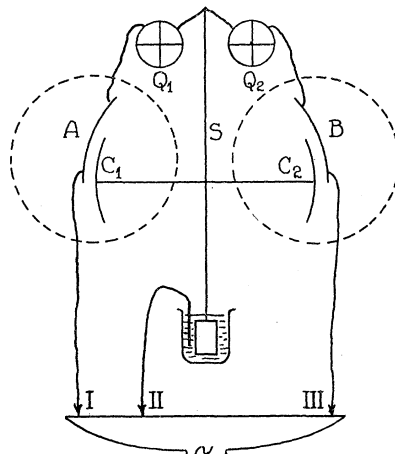

Fig. 1. Schematic diagram of apparatus.

but the connection with the needle is now made through a wire dropped from the center of the needle into a beaker of sulphuric acid. This wire ends in a fairly heavy metal bob which serves to lower the center of gravity of the needle and also acts as a damper. The potential differences between the two pairs of condenser plates are measured by two electrostatic voltmeters Q_1 and Q_2, connection for these voltmeters with the needle being made through

[1] A. P. Carman, Phys. Rev. **24**, 396 (1924).

the phosphor bronze suspension ribbon S. When the plates A and C_1 are immersed in a fluid of dielectric constant k_1, and the plates C_2 and B in a fluid of dielectric constant k_2, and the opposing torques on the needle are balanced by adjusting the potential differences $V_1 - V_2 (=E_1)$, and $V_2 - V_3$ $(=E_2)$, we get $A_1 k E^2 = A_2 k_2 E^2$, where A_1 and A_2 are factors depending upon the sizes and the positions of the attracted pairs of plates. If the dielectric on the right side is changed to one of dielectric constant k_3, and the new balance is for potential differences E_3 and E_4, we get $A_1 k_1 E_3^2 = A_2 k_3 E_4^2$. It follows directly that

$$k_3/k_2 = E_2^2 E_3^2 / E_1^2 E_4^2$$

This assumes that A_1 and A_2 remain constant. For non-conducting liquids, the potential differences may be taken as directly proportional to the resistances of the segments of the potentiometer wire (assuming no inductance), but for conducting liquids, the calculations are not simple, and particularly where the conductivities are different, as in the comparison of "pure" water and a fairly concentrated electrolyte. In such cases, the currents on the two sides of the potentiometer wire may be very unequal. In one case we had practically zero current on one side, and nearly an ampere on the other side. It became necessary then to measure the differences of potentials directly across the plates. With these larger currents, the fine ribbon suspension changed its elastic properties because of heating, and so it was necessary to have the connection with the needle through an independent wire dropped into a conducting liquid.

For the electrostatic voltmeters, we used at first two Kelvin multicellular voltmeters, each of range 30–150 volts, and got only fair results, since the instruments are sluggish and, being pointer instruments, do not indicate very small changes of potential. We then improvised electrostatic voltmeters from Dolezalek electrometers, using them idiostatically and attaching large paper dampers to the stems of the needles. These voltmeters were used ballistically for rapidity of reading. A calibration curve was made before each run of readings, and then check readings were taken at frequent intervals. The potential source for the calibration was a set of small storage cells, the e.m.f.'s of which were known by means of a potentiometer and a standard cell. Potential readings could be repeated with these voltmeters to within a half of one percent.

Another factor that was troublesome with the original instrument was the difference of buoyancy on the two immersed plates of the needle. This difference tilted the plates very slightly, but apparently enough to alter relative positions and distances, so that the factors A_1 and A_2 in the equation of equilibrium could no longer be considered as constant. In the original arrangement, this buoyancy change was compensated by shifting small weights along the horizontal arms of the needle, but this required an auxiliary observation to verify the compensation. When a heavy bob was attached to the wire dropping into the sulphuric acid, it was found that there were no buoyancy shifts for any liquids that were tried. This would of course be

expected, where the density differences were very small, as in the case of water, and an aqueous solution.

Our experience has been that with an electromotive force of the ordinary frequency of 60 cycles per second, there are electrolytic polarization effects. We have recently used a motor generator set giving 500 cycles per second, and have had no disturbing polarization effects for the voltages used and with the electrolytes that we have tested. A difficulty in the force method for electrolytes lies in the rapidly changing temperatures due to heating by the considerable currents through the dielectric. This requires very rapid and simultaneous observations of force and potentials, but this difficulty is not peculiar to the force method. It has been overcome by interpolating from a curve of dielectric constants and temperatures.

The method was tested with a series of non-conducting liquids and the values obtained for the dielectric constants show good agreement with each other and with the generally accepted values for these liquids. These values are shown in Table I at 24°C with a 60 cycle alternating electromotive force with 110 volts total. The balance was against water except for the dielectric constant of water, and that was against air. This last is, of course, an extreme test, owing to the great difference between the dielectric constants of air and water.

TABLE I

Dielectric constants k of various non-conducting liquids.

Liquid	k	Liquid	k
Water (conductivity about 10^{-6})	81.5	Methyl Alcohol	35.0
	79.8		35.7
	81.0		35.8
	79.5		
Mean	80.4	Acetone	24.0
			24.7
Turpentine	2.46		
	2.45	Chloroform	5.6
	2.47		
		Xylol	2.46
			2.47

While the electrometer method is capable of good results for non-conducting liquids, and may have advantages in some cases, its most valuable application at present is likely to be found in the comparison of the dielectric constant of an aqueous electrolyte with that of water. It will be shown later, that with the arrangement described above, it has been possible to obtain the relative dielectric constants of water and aqueous electrolytes of equivalent concentrations of 0.02 and beyond—a result apparently only possible at present with a force method.

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