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CONDUCTIVITY OF ANILINE-NITROBENZENE MIXTURES

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INTRODUCTION

Nitrobenzene might conceivably accept protons from aniline because unshared electron pairs on oxygen could hold the protons. The resulting ionized system should be more conductive to electricity than the components. The increase should be demonstrable by a sufficiently sensitive measuring device.

Such a device exists in the arrangement often used for measuring the high resistance of the insulating sheath put around electrical cable. The circuit and manipulation are fully described in many laboratory manuals of electrical measurement (Smith, 1948). The essential apparatus is shown in Figure 1. The H-cell containing the organic liquid under study replaces the cable in the original circuit.

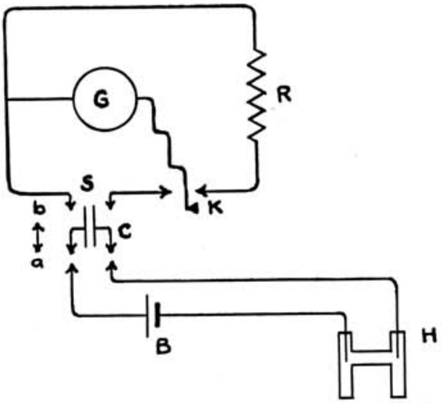

FIG. 1.—The equipment: *G*, ballistic galvanometer; *R*, damping resistance; *K*, double-contact, high-insulation key; *S*, double-pole, double-throw, short-throw switch; *C*, precision condenser; *B*, working battery; *H*, conductivity cell; *a*, *b*, charge and discharge positions, respectively, of *S*.

A charge from the battery of fixed voltage is allowed to leak through the unknown resistance for a measured time and into a standard condenser. The condenser is then discharged through a ballistic galvanometer, and the deflection is noted. A similar observation is also made with the unknown resistance bypassed, so that the condenser becomes charged to the full potential difference of the battery. The unknown resistance can be calculated from the time, capacity, and deflections. For the present purpose the equation is solved for the reciprocal of the resistance, which is the conductivity. Thus arranged, it is

$$\frac{1}{r} = l = \frac{c}{t} \log_e \frac{\Theta_0}{\Theta_0 - \Theta}$$

where r is the high resistance being measured, l is the conductivity corresponding, c the capacitance of the condenser, t the time of charge, Θ the deflection after the slow charge, and Θ_0 the deflection after the rapid charge. The respective units are ohms, farads, seconds, and arbitrary scale divisions. The prime standards are the calibrated condenser and the timer.

The specific conductivity L is calculated from the observed conductivity l, and the cross-sectional area and length of the conducting path in the H-cell containing the organic liquid. If A be the cross-sectional area in square centimeters and d the length in centimeters,

$$l = L \frac{A}{d} \quad \text{or} \quad l \frac{d}{A} = L$$

This equation expresses the fact that conductivity increases with increasing area of path, and that it decreases with increasing length. L, which is the specific conductivity, would equal l if the factor $\frac{d}{A}$ were equal to unity. The factor $\frac{d}{A}$ is the cell constant. By combining the above two equations and passing to common logarithms, the final full working equation of the experiment is assembled, thus:

$$L = 2.30 \frac{dc}{At} \log_{10} \frac{\Theta_0}{\Theta_0 - \Theta}$$

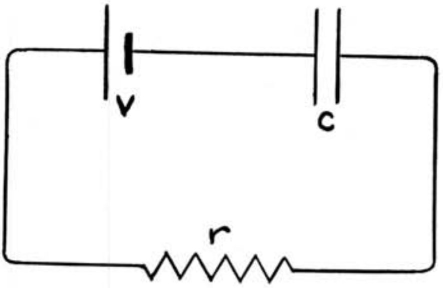

Fig. 2.—Circuit elements for derivation: V, voltage; C, capacitance; r, resistance.

The first equation is derived by reference to Figure 2. The circuit there shown contains a steady voltage v in series with a resistance of r ohms and a capacitance of c farads. At any instant, t seconds after closing the circuit, a current of i amperes is flowing, and a charge of q coulombs has accumulated upon the condenser. By Kirchoff's second law of circuits,

$$v = ri + \frac{q}{c}; \quad \text{or} \quad v = r \frac{dq}{dt} + \frac{q}{c}$$

since the current is the rate of change of charge. The charge is increasing and the current decreasing, both at diminishing rates; the process continues for an infinite time. Separating variables and integrating yields an equation containing a constant of integration. The constant of integration can be evaluated by substitution of initial conditions (q is zero when t is zero). Full details can be found in the manual already cited.

EXPERIMENTAL

The working equipment consisted of a Leeds and Northrup standard condenser, of 0.500-mfd. capacity, stated by the maker to be accurate to 0.25%; a Leeds and Northrup ballistic galvanometer of 2000-ohms resistance and 26-second period, and a rated sensitivity of 2×10^{-9} coulombs per scale division; a high-insulation contact key; a high-insulation short-throw double pole, double throw switch; a dry cell; a 10,000-ohm damping resistance; the H-cells, with platinum electrodes and samples of cross-tubing; rods to slip-fit inside the cross-tubing samples; micrometer calipers; and electrical laboratory timer capable of being read to 0.1 second; an improvised air thermostat; and the necessary chemicals, together with the means of purifying and preserving them.

The manipulation was as already outlined. The time of charge was 2.00 minutes. The cross-sectional area of each H-cell's horizontal limb was determined from the diameter of the slip-fit rod accompanying the cross-tube sample. The length between the electrodes was determined by simple sighting on a centimeter ruler. One cell had a constant of 294, the other 90.9. The arbitrarily-chosen temperature of measurement was 31.7 ± 0.3° C. The discharge was made to occur as soon as possible after termination of the period of charge, to minimize leakage of electricity from the condenser. The key was held down until the maximum deflection had passed and was then released. The release short-circuited the galvanometer through its prescribed critical damping resistance, thus bringing the galvanometer movement to rest in the minimum time.

The nitrobenzene and the aniline were repeatedly vacuum - distilled from ''technical grade'' stock. Only the material boiling within a restricted range was kept. The components were stored in open beakers kept in separate desiccators. These desiccators were charged with calcium chloride and were filled with natural gas. When material had to be stored more than a few days before use, it was redistilled. Both components had pale yellow colors, nearly alike. The mixtures had orange-brown colors.

Specific conductivities were determined by the above-outlined process for a series of mixtures of nitrobenzene and aniline. The two available H-cells were used in irregular alternation. The production of a

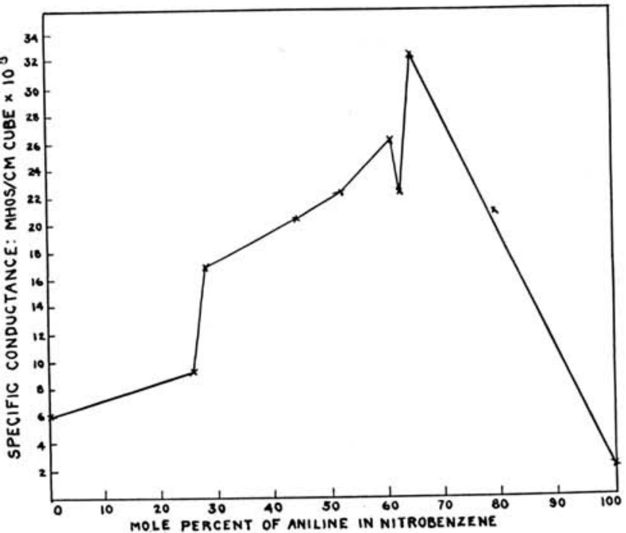

FIG. 3.—Conductivity of aniline-nitrobenzene system.

TABLE 1.—Conductivities of the Aniline-Nitrobenzene System.

Mole % aniline	$\Theta_0 = 20.8$ Θ deflection	$\frac{d}{A}$ cell constant	K x 10^8 specific conductivity x 10^8
0.0	3.05	294	6.24
24.8	8.35	294	9.08
27.4	16.43	90.9	18.53
43.0	8.84	294	20.4
53.3	17.92	90.9	23.6
61.8	18.52	90.9	26.4
62.8	17.48	90.9	21.8
66.7	11.75	294	32.8
81.9	16.87	90.9	19.40
100.0	4.22	90.9	2.66

fairly smooth curve in spite of this is considered to be a check on the correctness of the theory. The results are summarized in Table 1, and are represented graphically in Figure 3.

SUMMARY

Because the maximum conductivity is achieved at about 0.67 mole percent of aniline in nitrobenzene, each of two molecules of aniline are considered to give one proton to a molecule of nitrobenzene. Unshared electron pairs on the oxygen atoms of the latter compound are assumed to be the means of proton acceptance. The color change observed on mixing the components is taken to support the idea of ionic compound formation.

ACKNOWLEDGMENT

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LITERATURE CITED

SMITH, A. 1948. Electrical measurements in theory and application. Macmillan Co., New York, pp. 57-61.