The Electrical Conduction of Organic Dye Complex Salt between Cationic and Anionic Dyes*

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Many investigations have been made into the semiconducting properties of organic dyes. All classes of the dyes—cationic, anionic or non-ionic—exhibit a small conductivity in the dark. In all these ionic dyes but oxalate, the anion of the cationic dye and the cation of the anionic dye consist of inorganic ions. Concerning the cationic dyes with the triphenylmethane structure, Nelson reports that the dark conductivity is greatly changed by a change of anion.[1]

It is supposed that cationic and anionic dyes together make a salt which is composed of organic cations and organic anions, many combinations of the two dye ions being possible. The present paper will deal with the dark conductivity of some organic dye complex salts.

Experimental

Material.—Malachite green, crystal violet and methylene blue were selected as the cationic dyes, and eosine Y, erythrosine, rose bengal and acid rhodamine were selected as the anionic dyes. All the dyes except erythrosine were recrystallized three times; erythrosine was purified by repeated precipitations.

Organic dye complex salts were prepared by dissolving both component dyes in water at room temperature. To take the dye complex salt between malachite green and eosine as an example, it was prepared as follows. A 2/100 molar aqueous solution of malachite green and a 1/100 molar aqueous solution of eosine are stirred together, and then stirring is continued for another hour. The crystalline product thus obtained is washed with water until the washed water is almost colorless, and recrystallized twice from alcohol. Organic dye complex salts obtained in the same way are tabulated in Table I.

Measurement. — The electrical resistivity was measured on a compressed disk made under 5 t/cm^2 in a vacuum, with silver electrodes by the DC method.

Results and Discussion

The mole ratio between the components of the dye complex salts, as calculated from the carbon percentage, does not always agree with the theoretical composition anticipated from the chemical structures of the component dyes. However, the composition of the dye complex salts is supposed to be as shown in the first column of Table I. Seyewetz[2] and Pelet-Jolivet[3] have reported that a 2 mol. portion of fuchsine combines with 1 mol. of eosine or erythrosine, and also that methylene blue makes a product of a definite composition with eosine.

The absorption sepctra of complex salts were measured in an alcohol solution. Generally, the wavelengths of the absorption peaks were nearly identical with those of the components.

Some absorption spectra of the solid film were also measured. Of these, the absorption spectrum of $(MB)_2(RB)$ is shown in Fig. 1; it is quite different from that of a solution. Its longest-wavelength absorption band is split into two bands in spite of the fact that no splitting is found in the solid absorptions of the two component dyes.

Electrical Property.—The relation between the current and the applied voltage obeyed Ohm's

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[1] R. C. Nelson, *J. Chem. Phys.*, **20**, 1327 (1952).

[2] M. A. Seyewetz, *Bull. Soc. Chim. France* [3], **23**, 618 (1900); *Compt. rend.*, **130**, 1770 (1900).

[3] M. L. Pelet-Jolivet, ibid., **145**, 1182 (1907).

TABLE I. PROPERTIES OF ORGANIC DYE COMPLEX SALTS

Composition*	Color of powder	Decomp. p. (approx.) °C	C %		Elec. properties	
			Found	Calcd.	ρ_{20}, Ω cm.	ε, eV.
$(MG)_2(EO)$	dark purple	160	62.24	60.75	5.8×10^{13}	2.35
$(MG)_2(ER)$	dark brown	240	53.78	53.10	2.4×10^{12}	1.73
$(MG)_2(RB)$	purple	155	50.48	48.62	3.1×10^{14}	1.42
$(MG)(AR)$	dark green	220	64.00	67.70	1.1×10^{10}	1.24
$(CV)_2(EO)$	dark green	190	58.68	60.44	2.3×10^{13}	1.41
$(CV)_2(ER)$	dark purple	195	52.95	53.25	1.7×10^{13}	1.31
$(CV)_2(RB)$	greenish brown	175	51.50	48.98	1.7×10^{11}	2.33
$(CV)(AR)$	dark green	120	62.85	67.14	3.5×10^{11}	1.98
$(MB)_2(EO)$	dark green	190	49.04	51.42	2.5×10^{9}	1.32
$(MB)_2(ER)$	dark green	185	42.75	44.53	3.0×10^{9}	1.10
$(MB)_2(RB)$	brown	200	42.05	40.54	1.3×10^{10}	1.32
$(MB)(AR)$	green	210	57.85	61.33	2.5×10^{12}	1.17

* Cationic part of malachite green, crystal violet and methylene blue are abbreviated as MG, CV and MB, respectively. Anionic part of eosine, erythrosine, rose bengal and acid rhodamine are abbreviated as EO, ER, RB and AR, respectively.

law. In $(CV)_2(RB)$, for example, the relation obeyed Ohm's law up to 3460 V./cm. at least. In (MG)(AR), however, the current is proportional to the voltage to the power of 1.5. The resistivity at 20°C (ρ_{20}) and the band gap energy (ε), as calculated from the temperature dependence of the resistivity by the equation $\rho=\rho_0\exp(\varepsilon/2kT)$, are tabulated in Table I. The values of the resistivity and the band gap energy for dye complex salts fall in the 10^9—10^{15} Ωcm. and 1.1—2.3 eV. ranges respectively. The values of ρ_{20} and ε change with the change in the partner ion in dye complex salt. Generally the complex salts of methylene blue have low values in ρ_{20} and ε.

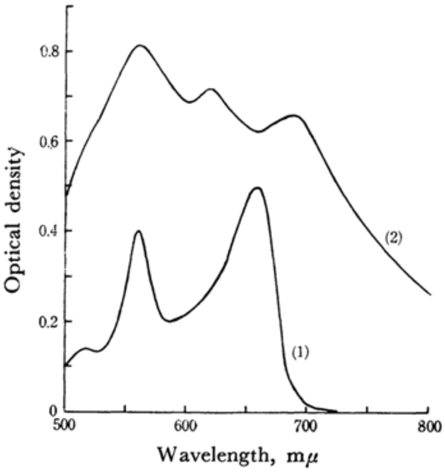

Fig. 1. Absorption spectra of dye complex salt between methylene blue and rose bengal.
(1) alcohol solution (2) solid film

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