The Aggregation Tendencies of Acid Wool Dyes in Saline Solutions.

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[Reprint Order No. 4744.]

The salting-out from aqueous solution of acid dyes by ammonium nitrate is discussed. The salting-out tendency is not related essentially to the proportion of solubilizing groups in the dye molecule, and various classes of dyes behave differently.

The generalisations as to the nature of the crystal-habit modification processes of inorganic salts with dyes contained in a preliminary notice by one of us (Whetstone, *Nature*, 1951, **168**, 663) were derived with the tacit assumption on the basis of results by Speakman and Clegg (*J. Soc. Dyers Col.*, 1934, **50**, 348) that, in view of the relatively high degree of sulphonation of most crystal-habit modifying dyes, single dye molecules rather than dye micelles were the active agents in the modifications. Evidence consistent with this assumption can now be presented from a direct study of the aggregation tendencies of a number of crystal-habit modifying dyes in ammonium nitrate solutions of various concentrations.

Experimental

The very convenient technique due to Fürth (*Kolloid Z.*, 1927, **41**, 300) using a " micro-diffusion cell " was ideally suited to the investigation since it is essential that the dye solutions under examination should contain electrolyte, to avoid errors due to the setting up of a diffusion potential. Dye concentrations of from 0·021 to 0·125% in ammonium nitrate solutions were studied. A brief account of the conclusions from the study of aggregation tendencies is given, since the dyes concerned were of the " acid wool " type rather than the " substantive cotton " type mostly studied, and the results may be of assistance to other workers in this field.

The radius r was obtained from the Stokes–Einstein equation $D = \boldsymbol{R}T/6\pi\eta\boldsymbol{N}r$, whereupon, with some assumptions, it was possible to calculate the approximate degrees of aggregation in ammonium nitrate solution of the dyes considered from the equation $A = 4\pi r^3 d\boldsymbol{N}/3M$, M being the molecular weight of the dye.

Owing to the uncertainty about the density, d, of the micelles it was difficult to calculate absolute aggregation tendencies from the average radii of dye aggregates deduced from the diffusion coefficients; the value of 1·5 was taken as an approximation to the densities in general. The degree of aggregation, A, was found always to increase on raising either the salt or the dye concentrations. However, stability to coagulation was found not to depend directly on degree of aggregation. For instance, the bisazo-dye EJ (2-naphthylamine-5 : 7-disulphonate→1-naphthylamine-7-sulphonate→2-naphthol-3 : 6-disulphonate), although aggregated to about five times as large a micelle as the monoazo-dye BD (1-naphthylamine-5-sulphonate→2-naphthol-3 : 6 disulphonate), was the more stable in 60% ammonium nitrate solutions.

The following Table shows the typical behaviour of the various dyes considered in ammonium nitrate solutions.

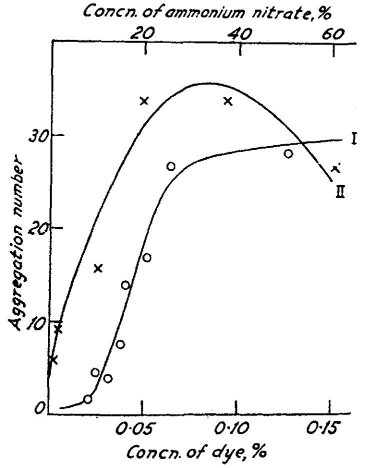
Aggregation behaviours of acid wool dyes of various types in ammonium nitrate solutions.

Dye	Concn., %		A	Stability of solution
	of NH_4NO_3 solution	of dye		
Acid Magenta	60	0·06	1·4	Perfectly stable
Amaranth	60	0·06	6·4	Rather unstable
,,	16·7	0·025	10	Stable
BD	16·7	0·025	3·2	Unstable
B2J	16·7	0·025	5·4	Very unstable
EJ	60	0·125	30	Unstable
,,	60	0·06	27	Rather unstable
,,	60	0·036	7·8	Stable
,,	60	0·021	1·7	Stable
,,	37	0·06	34	Stable
,,	10	0·06	16	Stable
,,	0	0·06	—	Perfectly stable

DISCUSSION

The orientation of the solubilizing groups was considered by Speakman and Clegg to be important in deciding aggregation tendencies. Their observation that the higher the degree of sulphonation in proportion to the molecular weight, the lower appeared to be the aggregation tendency, does not accord with the aggregation behaviour of the azo-dye B2J (*p*-sulphanilic acid→2-naphthol-3 : 6-disulphonate) as compared with Amaranth (1-naphthylamine-4-sulphonate→2-naphthol-3 : 6-disulphonate) as judged by their solubilities in 60% ammonium nitrate solution or most other salt solutions; whereas Amaranth usually dissolves readily, the former dye is almost completely salted out. However, as measured in 16·7% solution, the aggregation of B2J is the lesser, which again shows that degree of aggregation and solubility are not directly related.

Acid Magenta, possibly the most notable habit modifier for ammonium nitrate, is strongly soluble and has a negligible aggregation tendency, the average molecular aggregation deduced at 0·06% dye concentration being only 1·4. It is noteworthy that of all the dyes studied Acid Magenta alone cannot form O–H–N hydrogen bonds, the only possibility being N–H–N bonds which are known to be weak (Rice, " Electronic Structure and Chemical Binding," McGraw-Hill, New York, 1940).



Plots of aggregation against concentration of dye in 60% ammonium nitrate and against concentration of ammonium nitrate solution containing 0·06% of dye EJ are shown in curves I and II respectively. Curve II shows a value of 0·66 for the aggregation in the purely aqueous solution of the dye. This is due to the error caused by the presence of a diffusion potential. It is seen that in both curves the aggregation approaches unity at low concentrations. This implies that the system considered is reversible, and that at each concentration there may be an equilibrium aggregate ⇌ monomer. Since in the micro-diffusion cell there will be a concentration gradient, any aggregation number obtained in this investigation can only be an approximation especially in view of the other assumptions made. The postulate that monomeric dye molecules are responsible for crystal-habit modification is thus concordant with the observations.

The above findings have all been with dyes of a relatively high degree of sulphonation. A relatively small number of crystal-habit modifying dyes of low sulphonation are known which are strongly soluble in saline solutions (*e.g.*, sodium 1 : 4 : 5 : 8-tetra-aminoanthraquinone-2-sulphonate); their solubility is ascribable to other polar-solubilising groups than sulphonate. It is quite probable that weakly soluble dyes active as habit modifiers are adsorbed as micelles.

In view of the unpredictable effects of increasing dye concentration on its molecular aggregation, it is evident that the measurements of crystal-habit modifying powers of dyes based on a relatively small degree of habit change at low dye concentrations are incapable of extrapolation to yield reliable indications of habit-modifying power at high dye concentrations.

The authors express their gratitude to Dr. E. K. Pierpoint, who prepared many of the azo-dyes used in pure and salt-free condition by the method of Robinson and Mills (*Proc. Roy. Soc.*, 1931, *A*, **131**, 576).

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[*Received, October* 21*st*, **1953**.]