THE SCATTERING OF LIGHT BY COLLOIDAL DYE SOLUTIONS

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Summary

An experimental study of the intensity and state of polarisation of the transversely scattered light in the case of some direct dye solutions of different dye and salt concentrations and at different temperatures, has been made. Therefrom certain general conclusions regarding the shape, size and anisotropy of the dye micelles have been arrived at.

1. Introduction

The state of aggregation and the particle size of colloidal substantive dyestuffs have been studied extensively in view of the close relation that exists between these properties and the kinetics of the dyeing process. Methods used were mainly those of diffusion, conductivity, osmotic pressure, etc. The fact that these dyes are also colloidal electrolytes introduces, however, complications in such measurements. For instance, the existence of a potential gradient in the solution causes accelerated diffusion. Further, it is also probable that the dye solutions are polydisperse and disturbances arise due to the more rapid diffusion of the smaller particles. It would therefore be of advantage to employ light scattering methods for a determination of particle size, etc., using a static system where results can be represented with less ambiguity. As such, the author has carried out an investigation of the depolarisation factors of some colloidal dye solutions, aqueous as well as alcoholic, and their variation with temperature and the concentration of a foreign inorganic electrolyte.

2. Experimental Details and Results

All the dyes used (except Congo Red which was a Kahlbaum indicator sample and was used as such) were direct dyes kindly presented by the Imperial Chemical Industries (India) Ltd., and were purified by the method of Robinson and Mills (1931). The final products were free from electrolyte impurities and were air dried at 100° C. and stored in a desiccator over P_2O_5. All the stock solutions were made in pure dust-free double distilled solvent and stored in resistance glass flasks.

The depolarisation measurements were carried out using a 25-ampere carbon arc and the Cornu method. Precautions were taken to eliminate errors due to stray light and to reduce the convergence correction to a minimum. The cell used was a pyrex glass cylinder with flat ends. A side tube was attached at the centre to enable cleaning and filling the cell. The cell was immersed in an electrically heated water-bath having three plane glass windows, the two corresponding to the flat ends of the cell being used for the incident and the transmitted light, the one at right angles to these being used for viewing the scattered beam.

The intensity of scattering in the transverse direction was measured using an Osram photocell and a valve bridge amplifier similar to that used by R. Ananthakrishnan (1934). The linearity of response of the photocell for the range of intensities studied was checked before use and in all the later measurements the intensity was taken to be proportional to the final amplified photo current. The intensity of the incident beam was adjusted to be of the same value before each measurement with the help of a Weston photronic cell meter. The intensity measurements were made in the case of the three dyestuffs, Benzopurpurine 4 B, Chrysophenine G, and Durazol Fast Rubine BS and the results have been shown graphically in Fig. 1 (the values for Chrysophenine G have been reduced by a factor of 10 to bring them to the same scale), while the depolarisation factors are given in Tables I and II. In the last column of Tables I, II and III are given values of $\Delta\rho_{u}$, *i.e.*, the difference between the observed and calculated values of ρ_{u} (S. R. Sivarajan, 1951) and to a first approximation it is a measure of the

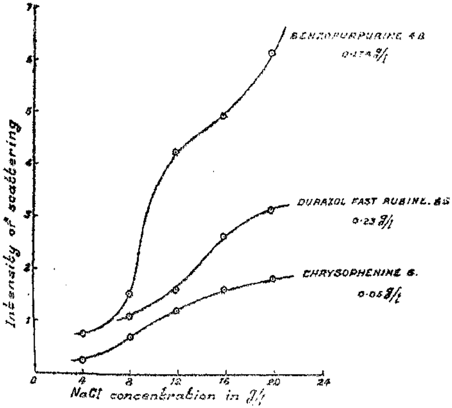

FIG. 1. Variation of Intensity of Scattering with NaCl Concentration

TABLE I

	Concentration of NaCl in g./litre	ρ_u	ρ_v	ρ_h	$\triangle \rho_u$
Chrysophenine G. 0·05 g./litre	20–8	26	15	100	0
Benzopurpurine 4B 0·134 g./litre	20	12	4·5	58	2·4
	16	8	3·4	73	1·4
	12	14	6·7	86	0·4
Durazol Fast Rubine BS 0·23 g./litre	20	23	10·5	68	4·5
	16	22	10·2	75	3·5
	12	20	10·6	90	1·0

TABLE II

	Temp. in °C.	ρ_u	ρ_v	ρ_h	$\triangle \rho_u$
Benzopurpurine 4B 0·082 g./litre NaCl = 12 g./litre	25	8·5	3·6	70	1·5
	50	16	5·8	50	5·0
	65	20	8·8	56	3·8
Durazol Fast Rubine BS 0·23 g./litre NaCl = 12 g./litre	25	20	10·5	90	1
	50	20·6	11·2	95	0·6
	85	22	12·5	100	0
Chlorazol Fast Scarlet 4 BS 0·1086 g./litre NaCl = 12 g./litre	25	27	12	70	6
	60	37	13	53	14
	85	30	11	66	10
Congo Red 0·1 g./litre NaCl = 10 g./litre	25	12	4·5	55	3·5
	65	12	4·5	35	3·5
	85	8	2·5	..	2·1
Durazol Fast Orange 2 GS 0·15 g./litre NaCl = 30 g./litre	25	53	13·2	27	30
	55	60	8·8	17	44
	70	15	4·0	60	7·3
Durazol Red 2 BS 0·073 g./litre NaCl = 4 g./litre	25	2	..	..	..
	50	4	0·93	..	2·5
	60	7	3·0	..	1·2

size of the particle. For purposes of comparison the depolarisation values of electrolyte free aqueous and alcoholic solutions of the dyes have been given separately in Table III.

3. DISCUSSION

Chrysophenine G.—In this case, the dye micelles are small ($< 1/20\,\lambda$), and highly anisotropic as $\rho_h = 100\%$, $\triangle\rho_u = 0$ and ρ_v is large. This conclusion also explains qualitatively the intense scattering and flow birefringence observed in these solutions in the presence of sodium chloride and is in agreement with its other known physical properties (Holmes and Standing, 1945; Martin and Standing, 1949).

TABLE III

Dyestuff	Solvent	ρ_u	ρ_v	ρ_h	$\Delta\rho_u$
Chrysophenine G ..	Water	26	7·4	36	12·3
	Alcohol	14·7	3·8	35	7·4
Benzopurpurine 4 B ..	Water	32	4·5	15·5	23·4
	Alcohol	15·6	4·5	35·0	7·0
Durazol Fast Orange 2 GS	Water	20	4·9	30·7	10·7
	Alcohol	12	1·7	..	8·7
Congo Red ..	Water	28	14·9	82	2
	Alcohol	44	28·3	100	0
Durazol Red 2 BS ..	Water	12·5	3·8	40	5·2
	Alcohol	2·5	0·5	..	1·5

From Table III it can be seen that in an alcoholic solution the dye is more dispersed and the micelles are smaller and more spherical in shape than in an aqueous solution. Also it has been observed by the author that even the addition of very large amounts of salt did not bring about coagulation and flow birefringence.

Finally, it is interesting to note that while the intensity of scattering increases with increasing salt concentration, the depolarisation values remain unaltered. The average micellar size appears therefore to remain the same and the intensity changes are probably due to an increase in the number of anisotropic scattering centres when the salt concentration is varied.

Benzopurpurine 4 B.—The observed depolarisation values indicate that the dye micelles are anisotropic and are not small compared to the wavelength of light and with increase of the salt concentration the size of the micelle also increases. On the other hand, the effect of temperature as it is varied from 25° to 65° is to increase the size of the micelle up to an intermediate temperature of about 50° C. after which there is a decrease. This temperature of maximum micellar size is found to be a function of the salt and the dye concentration.

This dye, like the others, is less aggregated in an alcoholic solution than in an aqueous solution.

Durazol Fast Rubine BS.—From Fig. 1 it is seen that the intensity of scattering increases with increasing salt concentration. The $\Delta\rho_u$ values also increase similarly but ρ_v remains unaltered. Thus the particle size seems to increase with increasing salt concentration the anisotropy being nearly the same. With increase of temperature there is a uniform decrease in size and at 85° C. the dye is dispersed to a large extent with a slight increase in the anisotropy also.

Chlorazol Fast Scarlet 4 BS.—In this case the dye micelles are larger and more anisotropic than those of Benzopurpurine 4 B. But the effect of temperature is the same as for the latter, the micelle having a maximum size at an intermediate temperature of 60° C., though the anisotropy does not vary appreciably.

Congo Red.—The measured depolarisation values using incident white light may be expected to correspond roughly to λ 6000. But it is found that the depolarisation values observed by the author do not agree with those reported earlier by R. S. Krishnan (1937). This small difference is probably due to the difference in the quality of the sample used. The effect of temperature on the Congo Red solution is to decrease uniformly the size of the micelle and make it more spherical in shape.

Durazol Fast Orange 2 GS and Durazol Red 2 BS.—The effect of temperature on aggregation is the same in both these dyestuffs and is similar to that observed in the case of Benzopurpurine 4 B. Durazol Red 2 BS appears to possess the most spherical micelles of all the dyes studied so far.

Finally we may summarise the observations as follows: these dye solutions invariably possess ultramicroscopic micellæ which, however, vary as regards both size and anisotropy from dye to dye. The effect of electrolytes in general is to increase the degree of aggregation. Also in the case of markedly colloidal dyes like Benzopurpurine 4 B, there exists a particular temperature of maximum micellar size, which is a function of the salt and dye concentrations. Since these dyes contain a relatively small proportion of hydrophilic to hydrophobic groups, one can understand the larger degree of dispersion in an organic solvent like alcohol where the bulk of the molecules are solvated and thus protected from others in solution. For the same reason, the influence of electrolytes on aggregation will be less than in an aqueous solution where only a small percentage of hydrophilic groups such as $-\mathrm{COOH}$ $-\mathrm{SO_3H}$; $-\mathrm{NH_2}$; $-\mathrm{OH}$, etc., will be solvated.

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