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A Study of Dyestuff Aggregation. Part III—The Effect of Levelling Agents on the Aggregation of Some Anionic Dyes

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SUMMARY

The disaggregating properties of four commonly used dyestuff levelling agents and of urea, in combination with a range of five anionic dyestuffs, were determined at 55°C and 95°C. Urea is the only compound investigated which very effectively disaggregated all of the dyestuffs studied. The disaggregating properties of the four levelling agents appear to depend on specific dyestuff–levelling agent interactions. No general explanation can be given in the absence of detailed published information about the chemical composition of two of the levelling agents.

1 INTRODUCTION

Earlier studies[1] on the aggregation of some anionic wool dyestuffs have shown that all but one of these dyestuffs **I–VI**, which were selected because they caused levelling difficulties in their application to wool, are highly aggregated in aqueous solution even at temperatures approaching 100°C.

Practical dyeing recipes usually contain levelling agents which control the rate of sorption of dyestuff by the fibre and also probably have an effect on the extent of aggregation of the dyestuffs. The purpose of this investigation was to examine the action of some commonly used proprietary levelling agents, namely AM20, Albegal A and B (Ciba–Geigy), Antarox CO-880 (American Cyanamid) and of urea. AM20 is our code name for a product

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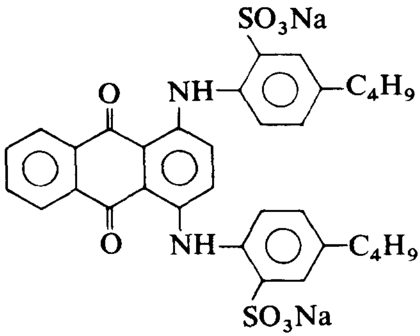

I
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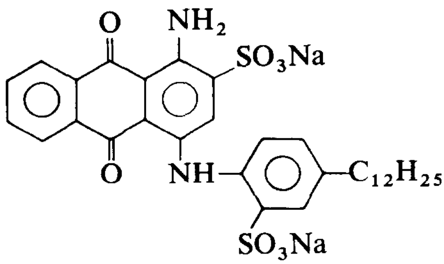

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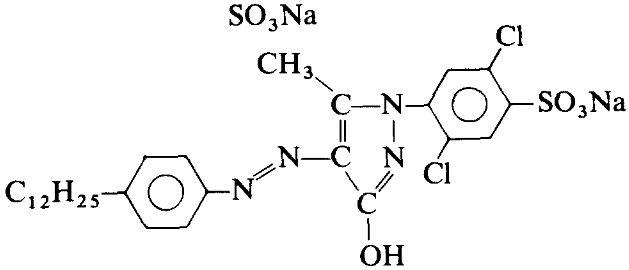

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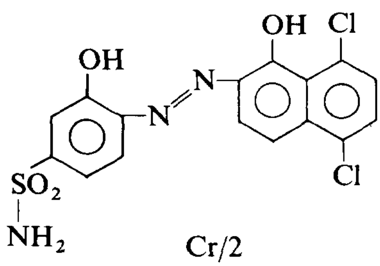

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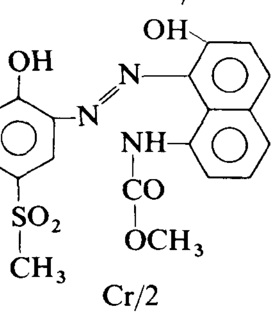
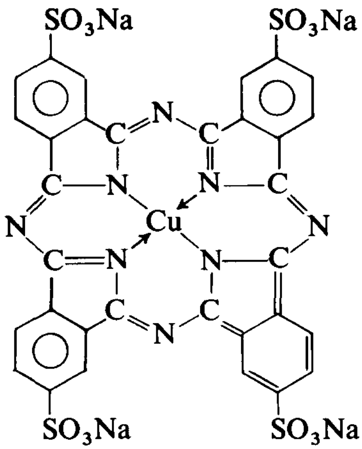


V



VI

whose structure is revealed; an ethylene-oxide adduct of a fatty acid amide, it is weakly cationic and is recommended as a levelling agent in the application of the more easily levelling anionic wool dyestuffs and in the application of anionic dyestuffs to polyamide fibres. Albegal A and B are substituted alkylamine polyglycol ethers with amphoteric properties. Algebal A is recommended for dyeing with 1:2 metal complex, acid and mordant dyestuffs, whereas Albegal B is recommended for dyeing with reactive dyestuffs (Lanasol, Ciba–Geigy). Antarox CO-880 is an adduct of a branched nonylphenol and ethylene oxide, containing an average of 30 ethylene oxide moles for each mole of nonylphenol (NP30) and has been shown to slow down the rate of sorption of 1:2 metal complex dyestuffs.[2]

The highly aggregated dyestuffs **I**–**V** used in our previous studies[1] were selected for further investigation and the effect of the above agents on their aggregation determined at 55°C (the beginning) and at 95°C (the end of the dyeing cycle).

2 EXPERIMENTAL

The light-scattering technique and the methods of calculation of particle sizes have been described by Datyner *et al.*[3] and Hüglin.[4] Since the effects of any interactions (e.g. charge effects) on the measured values of the weight-average molecular weight, M_W, have not been accounted for in this work, these and the weight-average aggregation numbers, N_W, stated are apparent quantities only.

The weight-average molecular weights of the dyestuffs, in the presence of the levelling agents or urea, were calculated from the light-scattering data by considering that the solution of the levelling agent or urea was the solvent for the dyestuff. Thus the value for $G_{(solvent)}$ in eqn (4) of ref. 3 is the scattering value for the solution of levelling agent or urea and $G_{(solution)}$ is the scattering value for the solution of dyestuff in the solvent.

The commercial dyestuffs were purified by the methods described by Datyner and Pailthorpe.[1] Sodium dodecyl sulphate (SDS) (Henkel and Cie GmbH, Dusseldorf, 99·99% pure), analytical-grade sodium chloride and urea were used without further purification. NP30 was purified by the method described by Craven and Datyner.[5] AM20 (33% solids), Albegal A (56% solids) and Albegal B (57% solids) were used without further purification.

The surface tension of aqueous solutions of the levelling agents was measured on a du Noüy surface tension balance.

3 RESULTS AND DISCUSSION

3.1 Critical micelle concentration by surface tension

Critical micelle concentrations (CMCs) were determined from surface tension data in the usual way. The plot for NP30 at 25°C, shown in Fig. 1, is typical of all the plots obtained and the results for all levelling agents and for SDS are given in Table 1. The CMC of SDS was determined as a check and found to be in excellent agreement with published data.[6] Our value for the CMC of NP30 is smaller than previously published values by Schick[7] and by Craven and Datyner,[5] but it must be borne in mind that the samples stemmed from different sources and, as the chemical is not simple, purification does not give simple identical products.

The CMC of NP30 is only marginally affected by the presence of salt, whereas the CMCs of AM20, Albegal A and B, which are ionic, are significantly reduced in the presence of salt.

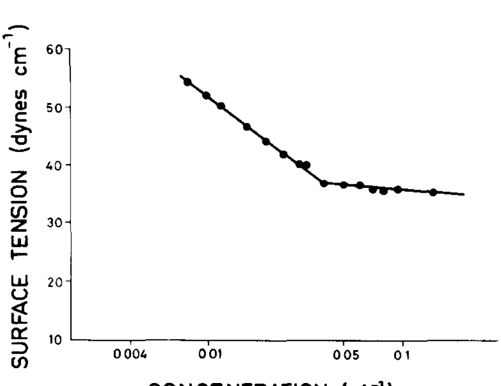


Fig. 1. Surface tension values versus log (concentration) for NP30 at 25°C.

TABLE 1
Critical Micelle Concentrations by Surface Tension

Compound	*Formula*	*Molecular weight*	*CMC (g litre⁻¹)*	
			Water, 25°C	*0·03M-NaCl 55°C*
Sodium dodecyl sulphate	$C_{12}H_{25}OSO_3Na$	288·4	2·33	—
NP30	$C_9H_{19}C_6H_4O(C_2H_4O)_{30}H$	1 540	0·045	0·035
AM20	$C_{18}H_{37}CONH(C_2H_4O)_{20}H$	1 177	0·400	0·010
Albegal A	Not disclosed		0·040	0·015
Albegal B	Not disclosed		0·045	0·015

Hine and McPhee[2] used a 0·3 g litre^{-1} solution of NP30, which is well above the CMC found for all levelling agents in 0·03M-NaCl used in this work and hence this concentration was also used for all levelling agents except Albegal B, where 0·5 g litre^{-1} was required to obtain stable solutions.

3.2 Micellar behaviour of levelling agents

The formation of surfactant micelles can be described mathematically by the Closed Association Model,[4] in which:

$$nM_1 \underset{}{\overset{K_a}{\rightleftharpoons}} M_n \tag{1}$$

$$K_a = \frac{[M_n]}{[M_1]^n} \tag{2}$$

where M_1 is the monomer molecular weight, K_a is the molar association constant, and n is the micellar association number.

Light scattering determines the weight-average molecular weight

$$M_W = \frac{C_1 M_1^2 + C_n M_n^2}{C_1 M_1 + C_n M_n} \tag{3}$$

and

$$C = C_1 + nC_n \tag{4}$$

where C is the total concentration (mol), C_1 is the concentration of monomers, C_n is the concentration of n-mers, and M_W is the weight-average molecular weight.

The above four equations can be readily solved to give:

$$K_a C^{n-1} = \frac{(n-1)^{n-1}(N_W - 1)}{n(n - N_W)^n} \tag{5}$$

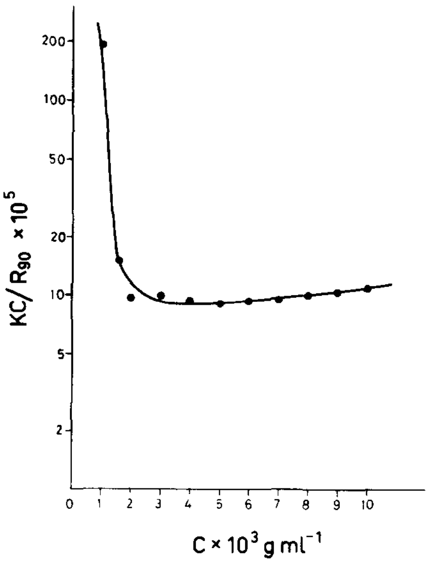


Fig. 2. Light-scattering results for sodium dodecyl sulphate in 0·03M-NaCl at 25°C.

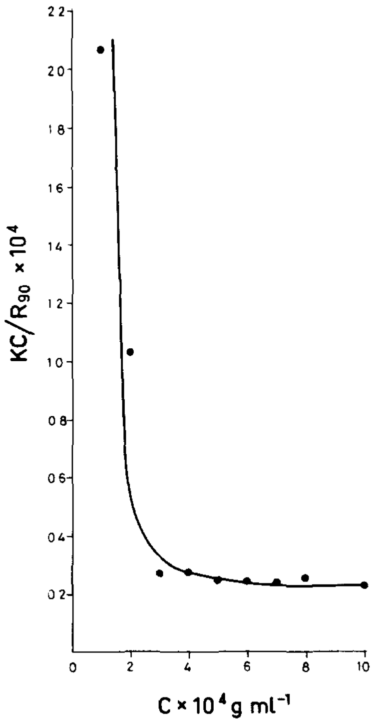


Fig. 3. Light-scattering results for NP30 in 0·03M-NaCl at 55°C.

where $N_W = M_W/M_1$ is the weight-average micelle association number, and

$$M_W = M_1 N_W = [KC/R_{90} - 2A_2 C]^{-1} \qquad (6)$$

where K is the optical constant, R_{90} is the Rayleigh ratio at 90°, and A_2 is the second virial coefficient.

The combination of eqns (5) and (6) allows one to calculate K_a, n and A_2 from light-scattering data because KC/R_{90} and C are known. The mathematical solution was obtained by an iterative process as suggested by Hüglin.[4]

SDS was used in our earlier work[3] to check the calibration of our instrument. The Debye[8] method of presentation was used and a value of $60 + 5$ was determined for the weight-average micellar number (N_W). The same data were analysed by the above method, as shown in Fig. 2. The best fit was obtained for a micellar number (n) of 67 and a virial coefficient (A_2) of $2{\cdot}5 \times 10^{-3}$ ml g^{-1} with a CV% (coefficient of variation %) in log K_a of 2%.

The light-scattering data for NP30, AM20, Albegal A and Algebal B were analysed in the same manner and the results are summarised in Table 2; a typical result for NP30 is given in Fig. 3.

TABLE 2
Micellar Size of Levelling Agents

	Water, 25°C	*0·03M-NaCl 55°C*	*0·03M-NaCl 75°C*	*0·03M-NaCl 95°C*
NP30				
n	51	42	42	37
A_2 (ml g^{-1})	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$
$\log K$	196·33	163·02	158·03	139·68
AM20				
n	17	36	20	20
A_2 (ml g^{-1})	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$
$\log K_a$	69·54	145·30	79·96	79·52
Albegal A				
n	133	224	112	70
A_2 (ml g^{-1})	$2{\cdot}5 \times 10^{-3}$	$2{\cdot}0 \times 10^{-3}$	$2{\cdot}0 \times 10^{-3}$	$2{\cdot}0 \times 10^{-3}$
$\log K_a$	589·00	970·55	487·72	304·68
Albegal B				
n	104	42	32	24
A_2 (ml g^{-1})	$4{\cdot}0 \times 10^{-3}$	$4{\cdot}0 \times 10^{-3}$	$4{\cdot}0 \times 10^{-3}$	$4{\cdot}0 \times 10^{-3}$
$\log K_a$	415·04	158·02	116·42	88·85

The value of 51 for NP30 in water at 25°C is in good agreement with the value of 55 obtained under the same conditions (despite the different CMC) by Schick *et al.*[9] Values for NP30 in 0·03M-NaCl at 55°C, 75°C and 95°C, as shown in Table 2, indicate that the micellar size does not appear to vary significantly with temperature. Although normally one would expect the micellar size of a non-ionic surfactant to increase with increasing temperature, significant increases in size only begin to occur when the cloud-point is reached.[10] In the case of NP30, the highest temperature used, 95°C, is significantly lower than its cloud point, 110°C.[5]

The micellar size of AM20 at 25°C in water is 17. Under the experimental conditions used (0·03M-NaCl at 55°C) the micellar size increases to 36, largely due to action of salt, and as the temperature is increased, the micellar size decreases. Both Albegal A and Albegal B decrease in micellar size as the temperature increases from 55°C to 95°C.

3.3 Action of levelling agents on dyestuff aggregation

The results for the four levelling agents and urea, at 55°C and 95°C, are given in Tables 3 and 4 respectively.

NP30 has only a small disaggregating effect on dyestuffs **I** and **II**.

TABLE 3

Aggregation Numbers (N_W) for Dyes in the Presence and Absence of Levelling Agents at 55°C

Dye	*0·03M-NaCl*[a]	*0·03M-NaCl + 0·3 g litre⁻¹ NP30*	*0·03M-NaCl + 0·3 g litre⁻¹ AM20*	*0·03M-NaCl + 0·3 g litre⁻¹ Albegal A*	*0·03M-NaCl + 0·5 g litre⁻¹ Albegal B*	*0·03M-NaCl + 300 g litre⁻¹ urea*
I	210	160	160	810	20[b] $K = 2{\cdot}3 \times 10^6$	35
II	920	550	370[b] $K = 7{\cdot}6 \times 10^8$	2 434	20[b] $K = 2{\cdot}3 \times 10^6$	20
III	6 990	270	330[b] $K = 5{\cdot}5 \times 10^8$	242 000	65[b] $K = 2{\cdot}0 \times 10^7$	80
IV	5 560	290[b] $K = 6{\cdot}1 \times 10^8$	1 870	1 220	1 480	95
V	7 440	330[b] $K = 8{\cdot}3 \times 10^8$	350	280	910	75

[a] From earlier work.[3]

[b] The aggregation behaviour is concentration-dependent and the value quoted has been calculated at 3×10^{-5} g litre^{-1}. K is the molar association constant (litre mol^{-1}).

TABLE 4

Aggregation Numbers (N_W) for Dyes in the Presence and Absence of Levelling Agents at 95°C

Dye	*0·03M-NaCl*[a]	*0·03M-NaCl*[a] *+0·3 g litre*$^{-1}$ *NP30*	*0·03M-NaCl* *+0·3 g litre*$^{-1}$ *AM20*	*0·03M-NaCl*[a] *+0·3 g litre*$^{-1}$ *Albegal A*	*0·03M-NaCl* *+0·5 g litre*$^{-1}$ *Albegal B*	*0·03M-NaCl* *+300 g litre*$^{-1}$ *urea*
I	130[b] $K = 8 \times 10^8$	90	130	420	15[b] $K = 1{\cdot}1 \times 10^6$	20
II	200	240	110[b] $K = 6{\cdot}4 \times 10^7$	1 115	16[b] $K = 1{\cdot}4 \times 10^6$	15
III	3 080	230	320[b] $K = 5{\cdot}2 \times 10^8$	8 575	37[b] $K = 7{\cdot}1 \times 10^6$	13
IV	1 790	200[b] $K = 3{\cdot}0 \times 10^8$	2 060	650	820[b] $K = 5{\cdot}0 \times 10^9$	75
V	910	180[b] $K = 2{\cdot}5 \times 10^8$	220[b] $K = 3{\cdot}7 \times 10^8$	244	137	28

[a] From earlier work.[3]

[b] The aggregation behaviour is concentration-dependent and the value quoted has been calculated at 3×10^{-5} g litre^{-1}. K is the molar association constant (litre mol^{-1}).

However, diffusion measurements on these dyestuffs in the presence of NP30 carried out by Craven and Datyner[5] at a higher surfactant/dyestuff ratio at 45°C, indicate a slight increase in the aggregation of dyestuff **I** and slight decrease in the aggregation of dyestuff **II**. One must be careful in making such a comparison because in light scattering the weight-average molecular weight is measured, whereas diffusion gives the number-average molecular weight. Increases in the cloud-point of NP30 and a reduction in its CMC indicate that NP30 interacted with the two dyestuffs.[5]

In the case of dyestuff **III** the weight-average aggregation number is reduced from 6990 to 270 at 55°C and from 3080 to 230 at 95°C. A similar effect was observed for the two premetallised dyestuffs, **IV** and **V**, where aggregation is reduced by at least one order of magnitude, an effect observed both at 55°C and 95°C.

AM20 has only a small disaggregating effect on dyestuffs **I** and **II** and is less effective on dyestuff **IV** than is NP30. However, AM20 is very effective in disaggregating dyestuffs **III** and **V** at both 55°C and 95°C.

Whilst Algebal A is effective on dyestuffs **IV** and **V**, it appears to increase the aggregation of dyestuffs **I**, **II** and **III**. On the other hand, Albegal B disaggregates dyestuffs **I**, **II** and **III** very effectively and dyestuffs **IV** and **V** much less so.

Urea disaggregates all five dyestuffs considerably and it is interesting to note that the disaggregation of dyestuffs **I**, **II** and **III** is similar in extent to that produced by Albegal B.

4 CONCLUSION

Urea is the only compound investigated which greatly disaggregates all the dyestuffs studied. The disaggregating properties of the four levelling agents appear to depend on specific dyestuff–levelling agent interactions and no general explanation can be given in the absence of detailed published information about the chemical composition of two of the levelling agents.

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