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Adsorption Isotherms on Cotton of Direct Sky Blue FF from Aqueous Ethanolic Solutions

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SUMMARY

Adsorption isotherms at 80°C for Direct Sky Blue FF (C.I. Direct Blue 1) on cotton in the presence of variable amounts of NaCl (2, 10, 15 and 50 g litre^{-1}) and ethanol (v/v) (0, 5, 10, 20, 30, 40, 50, 60%) were measured.

The Langmuir equation has been used to describe the equilibrium except for the measurements obtained at 15 g litre^{-1} of NaCl and 50% and 60% of ethanol, and at 50 g litre^{-1} of NaCl and 20% of ethanol for which the distribution law was followed. The saturation values increased markedly with the salt concentration. The concentration of ethanol influenced the adsorption in two ways; one was a depressing action and the other an accelerating action. The increasing concentration of ethanol decreased the degree of association of the dye and the adsorption was Langmuir type; at 15 g litre^{-1} of NaCl and 50% and 60% of ethanol, and 50 g litre^{-1} of NaCl and 20% of ethanol the degree of association of the dye increased and the adsorption was distribution type.

1. INTRODUCTION

Attempts have been made to dye cellulosic fibres with acid, direct and reactive dyes from a nonaqueous medium. Limited information is available on the dyeing of cellulosic fibres with direct dyes from organic solvents. This is mainly due to the fact that direct dyes are insoluble in the

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chlorinated solvents used on a commercial scale, and cellulosic fibres swell very little in such solvents. Therefore the use of water or a suitable polar solvent at the same stage is almost inevitable for dye solubilization and to promote fibre swelling.

Peters and Stevens[1,2] attempted to dye cotton and viscose with direct, acid and reactive dyes from solvents such as *n*-butanol, *n*-amyl alcohol, *n*-hexanol, etc., containing a small amount of water. The Delaware Valley Section of AATCC[3] reported the dyeing of cotton with direct dyes from dimethylformamide and dimethylformamide–perchloroethylene–ethylene glycol–ethylether solvent mixtures. Silver[4] reported the dyeing of cellulosic fibres with direct dyes from an emulsion system containing dye, emulsifying agent, water, glycerol, and perchloroethylene. Blanchard[5] attempted to dye cotton with direct and sulphur dyes from glycol and glycol ether solvents. Chavan, Bose and Datta[6,7] suggested the use of solvents such as acetone and mixtures of acetone–trichloroethylene containing small proportions of water or dimethylformamide for applying reactive dyes on water or aqueous alkali swollen cotton. Chavan and Miles[8] reported the use of dimethylformamide-trichloroethylene solvent mixtures for dyeing of cotton with direct and acid dyes. Chavan and Subramanian[9] attempted to dye cotton from a mixture of dimethylformamide and various nonpolar solvents and Chavan and Venkata Rao[10] studied the adsorption equilibrium of acid dyes from different ratios of dimethylformamide–trichloroethylene solvent mixtures. Goldthwait[11] has described the dyeing of cotton in absolute ethanol and methanol, and the adsorption of direct dyes on cellulose fibres from aqueous alcoholic solutions has been reported by Suda and Nakajima.[12,13]

The study of dyeing equilibria is the basis for understanding the dyeing mechanism.

The results of dyeing equilibrium measurements are usually expressed in the form of adsorption isotherms in which the variation in the concentration of dye on the fibre with the concentration of dye in solution at constant temperature is studied. The results of dyeing equilibrium measurements for cellulose were usually expressed in the form of the Freundlich isotherm.[14–17] Evidence has been accumulated for the formation of a monolayer of dye and therefore the data of the isotherms have been correlated with the Langmuir isotherm.[18–23]

Recently we reported studies on the adsorption equilibrium of Congo Red on cotton in aqueous ethanolic solutions and in the presence of variable amounts of NaCl.[24] The Langmuir equation has been used to describe the adsorption equilibrium. Adsorption isotherms with 5% ethanol in the presence of 3, 4 and 5 g litre^{-1} of NaCl were different from those measured in the absence of ethanol. The saturation value calculated from the isotherm with 5 g litre^{-1} NaCl and 5% ethanol was greater than that obtained in the absence of ethanol.

We report here studies on the adsorption equilibrium of Direct Sky Blue FF (C.I. Direct Blue 1) on cotton in aqueous ethanolic solutions (v/v) and in the presence of NaCl with the aim of studying the effect of NaCl and ethanol on the adsorption isotherms.

2. EXPERIMENTAL

Materials

Cotton fibre was purified by scouring for 30 min at 60 °C in a bath containing 0·5% neutral soap solution. The fibre was then washed throroughly, allowed to stand in several changes of distilled water over a period of two days and then dried at room temperature. NaCl was of analytical reagent quality. Direct Sky Blue FF (C.I. Direct Blue, sodium salt) was a purified sample from a commercial sample (Aldrich compound) using the method of Robinson and Mills.[30]

Measurements

The adsorption isotherms for the adsorption of Direct Sky Blue FF on purified cotton fibre were carried out in 100 ml Pyrex conical flasks. 0·5 g sample of cotton fibre and 50 ml of solution containing a known amount of dye, NaCl and ethanol (v/v) were used. The flasks containing the fibre and the dye solution were maintained at 80 °C (±0·1 °C) for periods ranging from 48 to 144 hours. This period was found to be sufficient for reaching equilibrium. The initial bath concentrations varied from 0·05 g litre^{-1} to 3·5 g litre^{-1}. The concentration of dye on the fibre was measured after extraction of the dye from the fibre with 25% aqueous pyridine at about 80 °C. All dye concentrations were determined spectrophotometrically.

3. RESULTS AND DISCUSSION

From a knowledge of the equilibrium at 80 °C between dye on cotton and the amount of dye left in solution the adsorption isotherms were constructed. The isotherms are characterized by an initial rising portion followed by a flat plateau where the adsorption remains practically constant over a wide range of dyebath concentrations. They then show a fairly rapid increase in adsorption with increasing dye concentration. The plateau indicates that a limiting value exists for dye adsorption and that the dye is present as a monomolecular layer on the cellulose surface.[18] The height of the plateau increases but its length decreases with increasing salt concentration. At the end of the plateau the dye uptake increases apparently without limit and this has been associated with the multilayer formation of dye on cellulose. The shortening of the plateau with increasing salt concentration is due to aggregation of the dye that rapidly increases with the salt concentration.[14-17] In Fig. 1 are shown the adsorption isotherms in aqueous solutions at different salt concentrations.

In the presence of ethanol the height of the plateau decreases but its length increases with increase in the percentage of ethanol, and this can be explained by means of the disaggregating effect of ethanol on the dye.[14,24] Figure 2 shows, as an example, the adsorption isotherms at 2 g litre^{-1} of NaCl and at different ethanol percentages.

The adsorption isotherms measured at 15 g litre^{-1} of NaCl and 50% and 60% of ethanol, and those at 50 g litre^{-1} of NaCl and 20% of ethanol, are different from those measured at the other concentrations of NaCl and ethanol (Fig. 3).

In order to understand the dyeing mechanism in the different dyeing conditions we undertook a systematic study of the adsorption isotherms of Direct Sky Blue FF. The basic assumption of Langmuir adsorption is that a dye is adsorbed by specific sites of the fibre, and when the sites are occupied, they are no longer available for adsorption of further dye. The Langmuir isotherms are then characterized by an initial rising portion followed by a plateau where the adsorption remains practically constant. If we consider only the first part of the isotherm, namely up to values of the uptake not greater than that of the plateau, the Langmuir equation should be used to describe the equilibrium up to this point[17]

$$[\mathrm{D}]_{\mathrm{f}} = K_{\mathrm{L}}(S - [\mathrm{D}]_{\mathrm{f}})[\mathrm{D}]_{\mathrm{s}} \qquad (1)$$

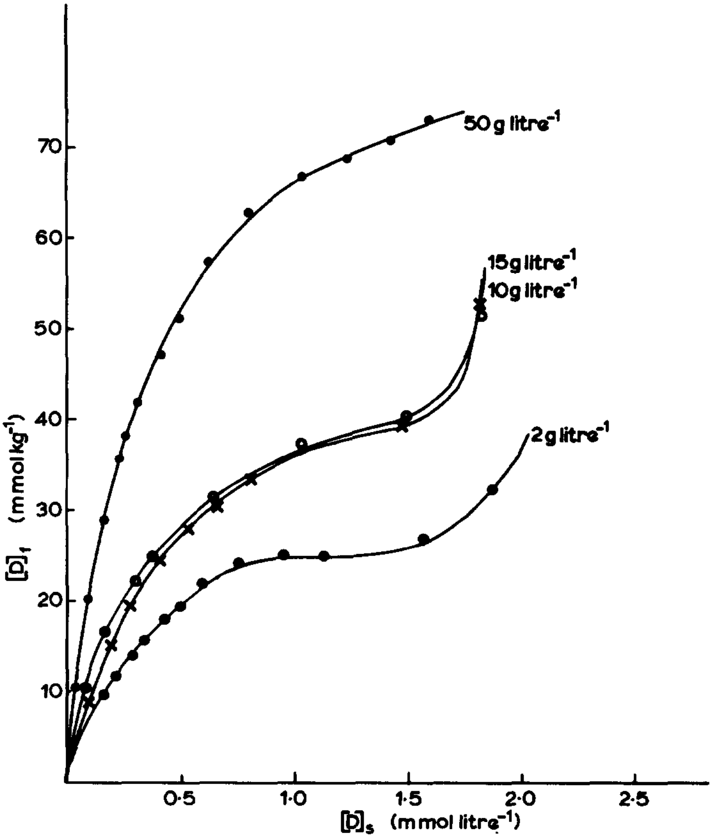

Fig. 1. Equilibrium adsorption isotherms in aqueous solution in the presence of NaCl.

where $[D]_f$ is the dye concentration on the fibre (mmol kg^{-1}), $[D]_s$ is the dye concentration in the dyebath (mol litre^{-1}), K_L is the equilibrium constant, and S the saturation value (mmol kg^{-1}), related to the number of sites available to the dye. Equation (1) can be also written

$$\frac{[D]_f}{[D]_s} = K_L(S - [D]_f) \qquad (2)$$

and then the plot of $[D]_f/[D]_s$ against $[D]_f$ is linear with K_LS as intercept and K_L as slope.

The Langmuir adsorption type for the dyeing of cellulose with direct dyes is supported by our previous results on Congo Red[24] and by those of Daruwalla and D'Silva[25,26] and of Porter *et al.*[21,27] The results here

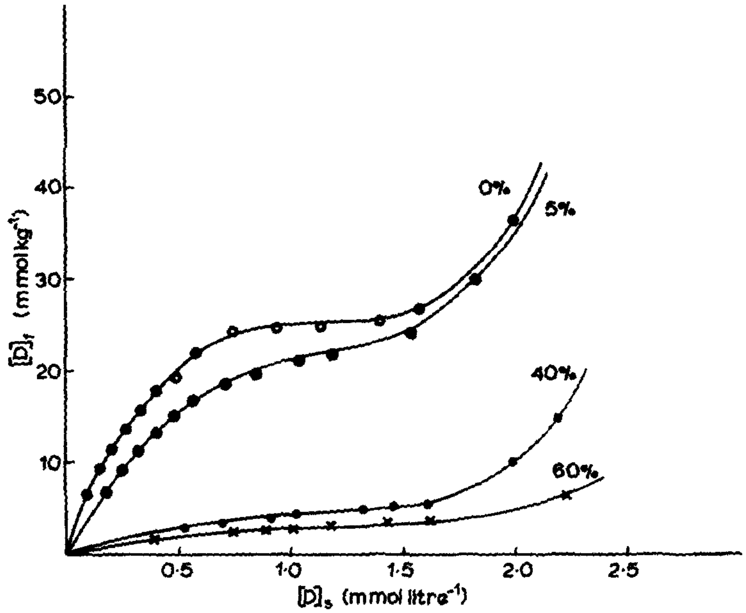

Fig. 2. Equilibrium adsorption isotherms at 2 g litre^{-1} of NaCl and in the presence of different percentages of ethanol.

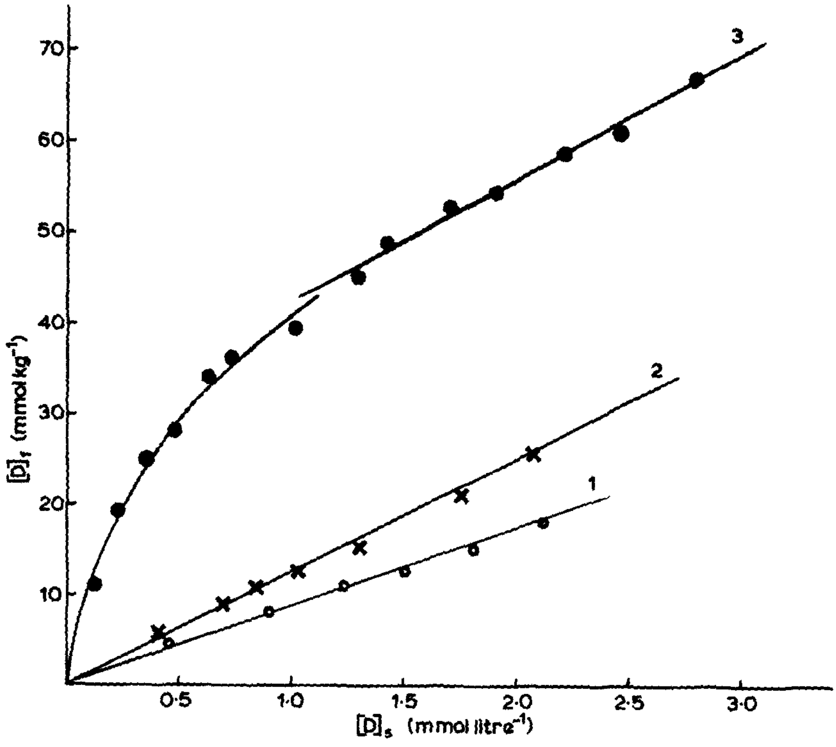

Fig. 3. Equilibrium adsorption isotherms in the presence of different amounts of NaCl and EtOH (1: 15 g litre^{-1} of NaCl and 50 % of ethanol; 2: 15 g litre^{-1} of NaCl and 60 % of ethanol; *3: 50* g litre^{-1} of NaCl and 20 % of ethanol).

reported show that the Langmuir isotherm, equation (2), fits the data very well. In Figs 4 and 5 are reported, as an example, the plots of $[D]_f/[D]_s$ against $[D]_f$ for the measurements at 15 g litre^{-1} and 50 g litre^{-1} of NaCl and different % EtOH.

The saturation values (mmol kg^{-1}) are reported in Table 1. Saturation values increase markedly with salt concentration. This has been attributed to the variation of the dielectric constant of the medium, making it possible for the dye anions to come into closer proximity to one another as the salt concentration increases. Moreover, the dielectric repulsion of dye anions by cellulose also decreases as salt concentration is increased and this will raise the saturation value.[21] Saturation values decrease with ethanol concentration and this can be due to the disaggregating effect of the ethanol, so that the critical concentration for aggregation of the dye increases.[14,28] Figures 6 and 7 show the effect of

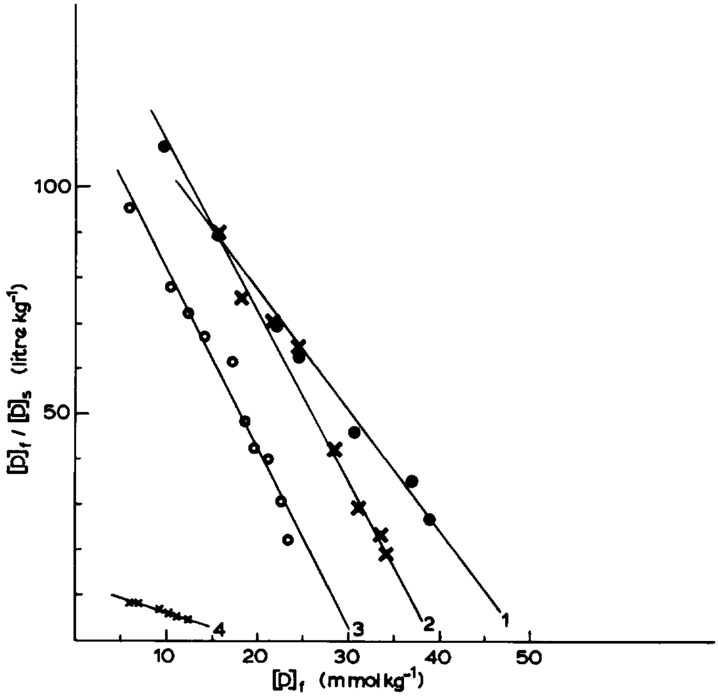

Fig. 4. Langmuir plot of $[D]_f/[D]_s$ against $[D]_f$ for the adsorption at 15 g litre^{-1} of NaCl and different percentages of ethanol (1: 0% ethanol; 2: 5% ethanol; 3: 10% ethanol; 4: 40% ethanol).

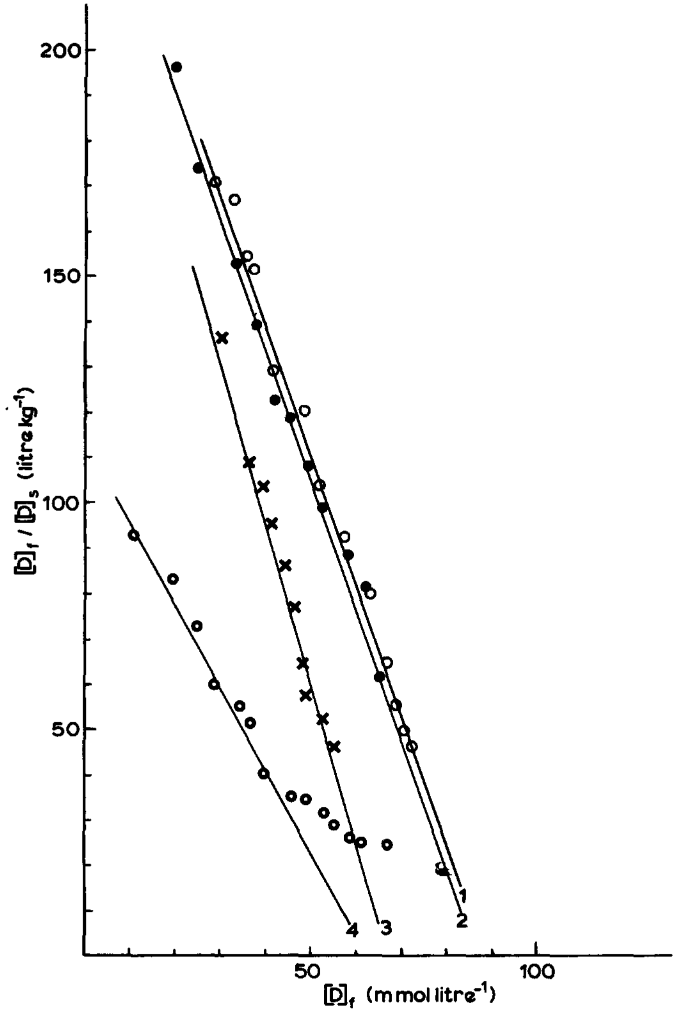

Fig. 5. Langmuir plot of $[D]_f/[D]_s$ against $[D]_f$ for the adsorption at 50 g litre^{-1} of NaCl and different percentages of ethanol (1: 0% ethanol; 2: 5% ethanol; 3: 10% ethanol; 4: 20% ethanol).

the concentration of NaCl and ethanol on the saturation values respectively.

The adsorption isotherms at 15 g litre^{-1} of NaCl and 50% and 60% of ethanol, and at 50 g litre^{-1} of NaCl and 20% of ethanol are different from those obtained in the other dyeing conditions. From Fig. 3 it is evident that there is a linear relationship between $[D]_f$ and $[D]_s$ at all the dye

TABLE 1

Saturation Values at Different Concentrations of NaCl and Ethanol

NaCl (g litre^{-1})	*% Ethanol (v/v)*						
	0	*5*	*10*	*20*	*30*	*40*	*60*
2	35·2	33·3	18·2	14·7	13·5	11·3	7·07
10	46·3	41·1	26·3	19·4	—	14·5	—
15	49·5	46·1	31·3	—	—	18·5	—
50	89·4	86·1	67·0	63·4	—	—	—

concentrations for the measurements at 15 g litre^{-1} of NaCl and 60 % of ethanol, and at about dyebath concentration greater than $1{\cdot}4 \times 10^{-3}$ mol litre^{-1} for the measurements at 50 g litre^{-1} of NaCl and 20 % of ethanol. The results indicate that, starting from this dye bath concentration, the distribution law is followed.

The basic assumption in the distribution model is that the dye is distributed between fibre and solution phase according to eqn (3)

$$\frac{[\mathrm{D}]_\mathrm{f}}{[\mathrm{D}]_\mathrm{s}} = K_\mathrm{D} \tag{3}$$

where $[\mathrm{D}]_\mathrm{f}$ is the quantity of dye on the fibre (mol kg^{-1}) and $[\mathrm{D}]_\mathrm{s}$ is the concentration of dye in solution (mol litre^{-1}).[29]

Thus a linear isotherm is expected to terminate at a point where one of the phases is saturated. The adsorption has been regarded as a solution

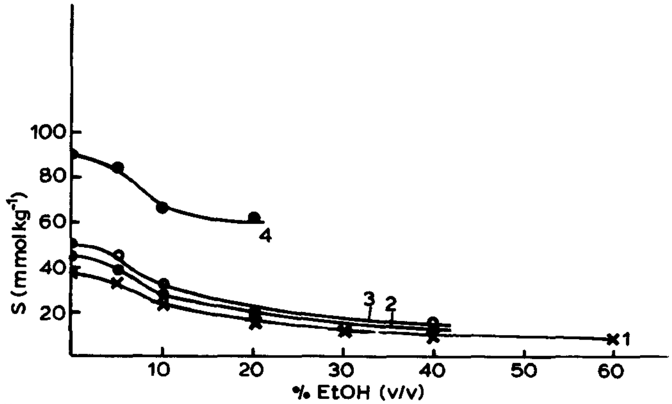

Fig. 6. Effect of the concentration of ethanol at different concentrations of NaCl on the saturation values (1: 2 g litre^{-1} NaCl; 2: 10 g litre^{-1} NaCl; 3: 15 g litre^{-1} NaCl; 4: 50 g litre^{-1} NaCl).

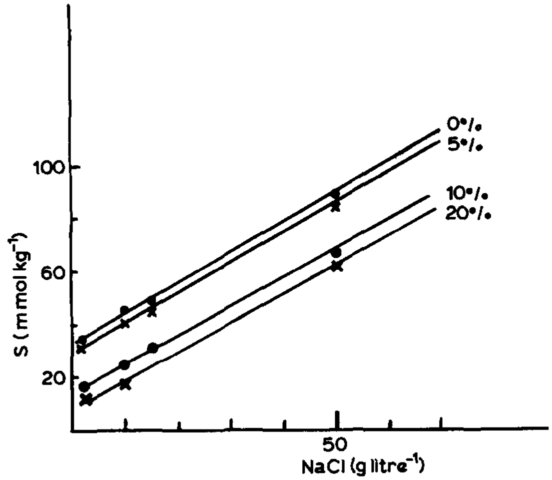

Fig. 7. Effect of the concentration of NaCl at different percentages of ethanol on the saturation values.

process and the extent of dye adsorption from a solution of given concentration, at equilibrium, may be defined by a partition coefficient.

This kind of adsorption isotherm was obtained by several authors for anionic dyes on cotton from solvent mixtures.[1,2,8,10] Suda and Nakajima[12,13] reported adsorption isotherms of direct dyes on cotton from aqueous alcoholic solutions. The isotherms were interpreted in terms of a combination of Langmuir and distributions isotherms. The distribution type was more dominant when dyeing was carried out from aqueous alcoholic solutions as compared to aqueous dyeing.

The measurements obtained up to 15 g litre^{-1} of NaCl and 40 % of ethanol, and those at 50 g litre^{-1} of NaCl, 10 % and 20 % of ethanol, at dyebath concentration lower than $1{\cdot}4 \times 10^{-3}$ mol litre^{-1}, show that the increasing concentration of ethanol decreases the degree of association of the dye and the adsorption is Langmuir type.[12,13,21,24–27] The adsorption isotherms obtained at 15 g litre^{-1} of NaCl and 50 % and 60 % of ethanol, and 50 g litre^{-1} of NaCl and 20 % of ethanol, at dyebath concentration greater than $1{\cdot}4 \times 10^{-3}$ mol litre^{-1}, show that the degree of association of the dye is increased[28] and the adsorption is distribution type[12,13] with K_D values 8·13, 11·7 and 13·35 respectively.

The results here reported thus show that the adsorption of Direct Sky Blue FF on cotton is influenced by the proportions of NaCl and ethanol. From the results obtained at 15 g litre^{-1} and 50 g litre^{-1} of NaCl it is evident that the proportion of ethanol influences the adsorption in two ways. At low percentages, the ethanol shows a disaggregating effect on the dye, and then the critical concentration for aggregation of the dye increases with subsequent decrease in the saturation values. At high percentages, the ethanol increases the degree of association of the dye, and the adsorption of aggregated dye (K_D) then increases with increasing ethanol concentration.

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