

# On the Physics and Chemistry of Dyeing Phenomena

By Professor Dr. *K. H. Meyer*

## IV. On Phenomena observed in the Dyeing of Silk and Wool

By *H. Fikentscher* and *K. H. Meyer*

*The behaviour of silk towards acids and acid dyestuffs:*

The behaviour of silk towards acids and acid dyestuffs has been the subject of constant investigation from many different starting points.

*Gelmo* and *Suida*<sup>1)</sup> studied the influence of acids, alkalies and salts on the dyeing capacity of animal textile fibres. *Walker* and *Appleyard*<sup>2)</sup> investigated the adsorption of

1) *Gelmo* and *Suida*, *Monatsh. Chem.* 1905, 855; 1906, 225.

2) *Walker* and *Appleyard*, *J. of the Chem. Soc.* 69 (1896) 1347.

acids by silk according to the strength of the acids. As they used mainly weak organic acids they failed to observe the law of equivalent absorption of all acids. Georgievicz<sup>3)</sup> explained the capacity of silk to absorb picric acid and Indigo disulphonic acid by means of the adsorption isotherm. E. Elöd observed occurrences in the weighting and mordanting of animal fibres<sup>4)</sup> and the action on the fibre of the liberated acid, further the influence on the dyeing process of the concentration of hydrogen ions<sup>5)</sup>. C. C. Schmidt<sup>6)</sup>, Walter M. Scott<sup>7)</sup> and others studied the conditions of equilibrium between acids, acid dyestuffs and silk. Salvaterra<sup>8)</sup> investigated the equivalent absorption of acids by animal fibres by means of numerous acid dyestuffs applied to silk. He did not however obtain a constant equivalent value, apparently because he made his dyeings in a neutral bath, he used too low a concentration and after dyeing rinsed before determining the quantity of dyestuff taken up. When calculated in equivalents his values vary considerably and are generally too low to correspond to the true basic equivalents of silk.

#### The preparation of the silk:

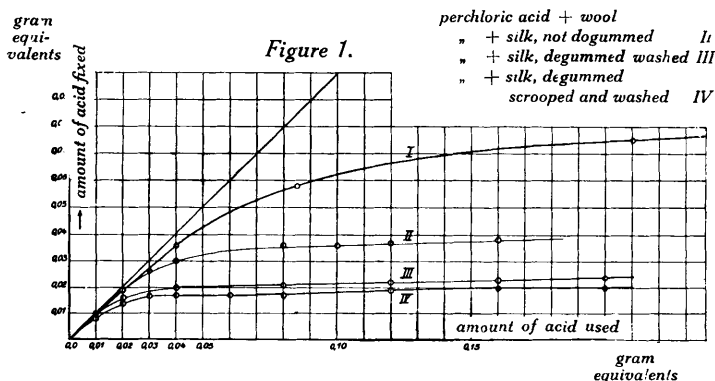
The nature of the silk is of great importance in the following tests. For the experiments described pure natural silk was generally

acid of 0.024 equivalents for 100 gr. silk. If the silk after de-gumming is first "scooped" with dilute acetic acid and then rinsed, the limit value falls to 0.019 probably because certain basic components are dissolved out by scooping. The limit value of the silk before de-gumming, i. e. whilst still containing 20% silk gum or sericin, shows 0.038 equivalents; of this figure 0.018 are due to the 75% fibroin and 0.020 equivalents to the 25% sericin so that 100 gr. sericin are capable of combining with 0.08 equivalents perchloric acid, thus equalling the value determined for the wool fibre. The experiments were mainly performed with de-gummed silk because it is in this state that silk is generally dyed and processed.

The water content was repeatedly determined in various samples of silk because silk can absorb a large quantity of water without appearing moist. Under the conditions chosen the water content was found to vary only slightly between 6,3 and 7,3%. It was maintained at a constant figure for the whole lot by storing in large glass flasks with rubber stoppers. The values given refer in all cases to this de-gummed silk, weighed air-dry.

#### The capacity of silk for taking up acids and acid dyestuffs:

The basic equivalent of silk was determined by its absorption of simple and complex coloured and uncoloured acids from solutions of different concentrations. If a graph is constructed from the figures obtained, the quantities of acid used being plotted on the abscissa



used; it was first de-gummed (freed from sericin) in a warm solution of Marseilles soap free from caustic alkali and then thoroughly rinsed in distilled water. The silk fibroin obtained had a capacity for taking up perchloric

and the quantities taken up by the silk on the ordinate in gramme equivalents, curves are obtained which — as with wool<sup>9)</sup> — at first rise steeply but soon approach a parallel to the abscissa (see figure 1). If a rather high concentration of acid is used the silk is distinctly attacked chemically. New basic groups are set free and at the same time a slight but progressive rise of the limit value takes place.

3) Georgievicz, Monatsh. Chem. 1894, 709; 32 (1911) 1075.  
 4) E. Elöd, Kolloidchem. Beih. 19 (1925) 320; Ztschr. angew. Chem. 38 (1925) 199.  
 5) E. Elöd, Ztschr. f. ang. Chem. 38 (1925) 837 and 1112.  
 6) C. C. Schmidt, Ztschr. phys. Chem. 15 (1894) 60.  
 7) W. M. Scott, Ztschr. Chem. 1926 I 2406.  
 8) Salvaterra, Monatsh. Chem. 34 (1913) 255; J. prakt. Chem. (2) 88, 502.

9) K. H. Meyer and H. Fikentscher, Melliand Textilberichte VIII (1926) 605.

The conditions were so arranged that equilibrium could be established. 5gr. de-gummed silk were treated in the thermostat for 5 hours at 54—60° in 200 ccm liquor (and in 400 ccm liquor with the diluted dyestuff solutions) and then allowed to stand overnight at the temperature of the room. Whenever the acids could be titrated with caustic soda the quantity of acid taken up by the silk was determined indirectly by titration of the liquor before and after the test. In the case of dyestuff acids reducible with titanium trichloride the indirect method was frequently checked by the direct titration of the dyestuff on the fibre. The quantities of acid used and fixed were always calculated for 100 gr. silk and then given in equivalents.

The reaction time allowed of 5 hours at 50—60° suffices for the attainment of equilibrium as shown by the tests made with perchloric acid and Orange I acid. (Table I.)

**Table 1**  
*Influence of the duration of the reaction on the acid absorption*

gramme equivalents of acid (for 100 gr. silk)			
used	fixed		
	5 hours		20 hours
	perchloric acid		
0,020	0,016		0,016
0,040	0,020		0,020
0,080	0,021		0,021
0,120	0,022		0,022
0,161	0,022		0,024
0,216	0,024		0,024
	Orange I acid		
0,095	0,018		0,018

All dyestuff acids can not be obtained in a well crystallised form. The following experiment shows that it is by no means necessary for the determination of the limit value to have the pure dyestuff acid. For the absorption it is immaterial whether the free acid by itself or the dyestuff salt with the addition of an equivalent quantity of a mineral acid is used.

**Table 2**

Orange I + hydrochloric acid		Orange I free acid	
gramme equivalents		gramme equivalents	
used	fixed	used	fixed
0,022	0,0124	0,022	0,0121
0,045	0,0140	0,044	0,0146
0,064	0,0162	0,066	0,0170
0,086	0,018	0,088	0,0180

In the competition of the two acids for the basic groups of the silk the formation of the salt is brought about first by the acid which yields the more difficultly soluble salt, in this case the dyestuff acid.

A test made of the absorption by silk of the most diverse acids and acid dyestuffs gives a similar picture to that obtained with wool (9), Table 3.

*A constant quantity of silk will always fix maximum equivalent quantities of acids, quite independently of the nature of the acid. The values vary more than with wool and lie round a mean of 0.0124.*

The values obtained with titanium trichloride are lower than those obtained with caustic soda. Then reason is that the silk gives up to the acid liquor basic constituents which neutralise a portion of the acid in the

liquor and are at the same time titrated by the acidimetric method but not by the reduction method.

**Table 3**

Name of the acid or dyestuff acid	Molecular or equivalent weight	Concentration	The maximum fixed by 100 gr. silk	
			grammes	gramme equivalents
(titrated with caustic soda)				
perchloric acid . .	100,5	$\frac{n}{20}$	2,4	0,024
hydrochloric acid	36,5	$\frac{n}{20}$	0,8	0,022
sulphuric acid . .	98,08	$\frac{n}{20}$	1,18	0,024
formic acid . . . .	46	$\frac{n}{5}$	0,88	0,019
acetic acid . . . . .	60	$\frac{n}{2,5}$	1,44	0,024
benzoic acid . . . .	122,5	$\frac{n}{50}$	3,05	(±0,003) 0,025
B-naphthalene sulphonic acid	208,1	$\frac{n}{20}$	6,05	0,029
2,6 naphthol sulphonic acid . .	224,1	$\frac{n}{20}$	6,05	0,027
Naphthol Yellow S . . . . .	314,1	$\frac{n}{10}$	9,10	0,029
aniline 3,5-disulphonic acid > acetoacetic anilide . . . . .	441	$\frac{n}{20}$	6,6	0,030
(titrated with titanium trichloride)				
sulphanilic acid > a-naphthol . . . .	328	$\frac{n}{80}$	5,9	0,018
aniline > G Salt	408	$\frac{n}{20}$	4,28	0,021
O-anisidine > dichlorobenzoyl K acid . . . . .	626	$\frac{n}{100}$	6,58	0,021

In the experiments with the free acid of Orange I it was possible owing to the low solubility of its salts to isolate these soluble basic constituents of the silk. If on completion of the test with Orange I the silk is removed from the liquor there appears in the latter gradually, often only after a few days, a precipitate of peculiarly fibrous crystals which show a distinct double refraction and give a Roentgen diagram differing from that obtained with Orange I acid crystals or silk dyed with Orange I. By titrating the Orange I acid contained in the precipitate the molecular weight of the base was determined at about 90. From 100gr. silk about 0,46—0,66grammes corresponding to 0,0048—0,0073 gramme equivalents of basic silk constituents go into the liquor which easily explains the difference mentioned.

Accordingly as these soluble silk constituents are considered or neglected the mean limit value is 0.020 or 0.024 gramme equivalents for 100 gr. silk. To fix 1 gramme equi-

valent of acid therefore about 5000 gr. or 4200 gr. of silk are required. The equivalent is thus 3—4 times as great as that of wool, i. e. silk is capable of fixing only  $\frac{1}{3}$ — $\frac{1}{4}$  the quantity of acid which can be taken up by wool. This corresponds to the lower affinity in dyeing of the acid dyestuff for silk.

The basic groups of silk are of different strengths corresponding to their varying constitution and are to some extent very weak as is shown by the partial hydrolysis of their salts with mineral acids.

There is of course a still stronger hydrolysis if the weaker organic acids are used (formic, acetic) and this can only be restrained by a large excess of acid. These acids therefore only reach the limit value in a high concentration (see formic and acetic acid, table 3).

#### Dissolving capacity of silk and wool:

With most monobasic, aromatic acids the limit value is over 0.024 and with some dyestuffs which are mentioned later it is considerably higher. If the possibility of the formation of molecular compounds according to *P. Pfeiffers*<sup>10)</sup> is disregarded this higher figure can only be explained by adsorption or solution. That silk, like acetate silk, is capable of "dissolving" substances will be shown later.

The acid dyestuffs named in Table 4 are all monobasic. They are taken up by the silk much above the equivalent of 0.024 whereas the corresponding dibasic acids appear to behave normally. (Table 3.) Also with wool the results obtained are indicative of solution. (Picric acid Table 4.) But the amount of acid taken up by the wool through the formation of salts is in itself so considerable that it can scarcely be claimed that a further quantity is taken up by solution.

Table 4

Fibre	Dyestuff	Limit value for 100 gr fibre
silk (normal 0,024)	picric acid	0,040
	sulphanilic acid aceto acetic anilide	0,046
	aniline benzoyl S acid	0,037
wool (normal 0.08)	picric acid	0,104

The phenomenon of solution manifests itself even more plainly with the *basic dyestuffs* than with the acid dyestuffs. The acid equivalent of the animal fibres is admittedly not so exactly determinable because of their sensitivity to alkalies, but when  $\frac{n}{100}$  caustic soda solution is used there is obtained as the *maxi-*

10) P. Pfeiffer, Ztschr. f. ang. Chem. 39 (1926) 253.

*imum value* for the acid equivalent of the uninjured fibres a figure of 0.019 gramme equivalents for 100 gr. silk and 0.018 gramme equivalents for 100 gr. wool representing the quantity of alkali taken up. Methylene Blue however is, for example, taken up by the fibres far beyond these values, if care is observed to neutralise with ammonia the hydrochloric acid which is set free. The acid groups present in the silk and wool are not therefore sufficient to neutralise the quantity of dye base taken up. Solution must also have taken place for the salt formation.

#### Structure of silk:

Silk fibroin shows a crystalline Roentgen diagram<sup>11)</sup> whereas wool does not. The proportion of the crystalline part to the amorphous is not yet known with accuracy. The question is now whether the crystallites which are not discernible with the microscope enter into the reaction in the same way as the amorphous substance by which they are surrounded or whether for the fixation of the acid it is only the amorphous portion that is mainly active. In favour of the latter assumption is the fact that silk which is saturated with Orange I does not differ in any respect in the Roentgen screen from silk<sup>12)</sup> which is undyed. The crystallites of the dyed silk are thus not measurably affected by the dyestuff which has penetrated to them. It is remarkable that filaments (silkworm)<sup>13)</sup> which are drawn artificially from the gland contents of the silkworm show a much lower capacity for taking up acids and acid dyestuffs than is shown by the natural silk fibres although the origin of both is the same (Table 5).

Table 5

Name of the acid	Limit value	
	for silkworm	for silk (see Table 3)
perchloric acid.....	0,011	0,024
sulphuric acid.....	0,010	0,024
p-toluol sulphonic acid ..	0,0105	— —
B-Naphthalene sulphonic acid .....	0,016	0,029
2-6-Naphthol sulphonic acid .....	0,014	0,027
sulphanilic acid-a-Naphthol (Orange 1 acid)..	0,011	0,018

The limit values for silkworm are about half as high. It is probable that in the natural

11) Herzog, Ber. of the Deutsche Chem. Ges. 53 (1925) 2164.

12) after the researches of Dr. Brill, Oppau.

13) used for angling-line.

spinning process a small portion of the amorphous basic silk gum (see above) with which the silk worm covers his double thread, enters into the fibroin and remains there even when the silk is degummed. From the above results it appears very probable that the crystalline portion does not play a part in the fixation of the acid.

*The absorption of o-Nitraniline by silk, wool and other proteins:*

The capacity of silk for dissolving dyestuff beyond its equivalent has instigated experiments with inert bodies which do not form salts. They are in fact taken up not only by the silk but also by the wool according to the law of Henry and so present an example of a dissolving process. O-nitraniline which was found to be useful in investigating the dyeing phenomena in the case of cellulose esters<sup>14)</sup> has also proved to be the most suitable substance for the present experiment. The dyeings have no fastness whatever but it is just because of this that equilibrium is easily obtained from both sides which is desirable for a solubility test.

The fibres were placed in o-nitraniline solutions of different concentrations and left usually for 14 days at the temperature of the room for complete equilibrium to be obtained. The concentration was determined analytically before and after the experiment by titration with nitrous acid. The colorimetric estimation was rendered difficult because of the liquors becoming more or less cloudy, particularly in the case of the wool. The ratio of concentration in the liquor, i. e. the coefficient of dispersion is shown in the following tables.

**Table 6**  
*Dispersion of o-nitraniline between wool and water*

grammes nitraniline in 400ccm water used for 5 gr wool	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_W}{C_{Fl}}$
	in 100 ccm liquor $C_{Fl}$	in 100 gr wool $C_W$	
0,02	0,0045	0,040	8,9
0,04	0,0089	0,082	9,2
0,08	0,0172	0,220	12,8
0,10	0,0214	0,288	13,4
0,16	0,0345	0,44	12,8
0,24	0,0512	0,70	13,7
0,32	0,0677	0,98	14,4
0,40	0,0840	1,26	15,0

The equilibria in the case of wool nearly obey the law of Henry and do so very closely in the case of silk and silkworm. The coefficient of dispersion for wool comes out at about 14; for silk and silkworm it is the same within the margin of error and shows 24 to 25.

<sup>14)</sup> K. H. Meyer and C. Schuster, *Melliand Textilberichte VI* (1925) 737.  
K. H. Meyer, C. Schuster and W. Bülow, *Melliand Textilberichte VII* (1926) 29.

**Table 7**

grammes nitraniline in 400ccm water used for 5 gr silk	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_S}{C_{Fl}}$
	in 100 ccm liquor $C_{Fl}$	in 100 gr wool $C_S$	
0,02	0,0038	0,096	25,2
0,04	0,0076	0,192	25,2
0,06	0,0117	0,260	22,6
0,08	0,0152	0,386	25,4
0,12	0,0187	0,508	27,4
0,16	0,0302	0,780	25,8
0,24	0,0455	0,16	25,5
0,32	0,0622	1,42	22,8
0,40	0,0720	1,92	25,2

**Table 8**  
*Dispersion of o-nitraniline between silkworm and water*

grammes o-Nitraniline in 100ccm water used for 3 gr silkworm	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_{Sw}}{C_{Fl}}$
	in 100 ccm liquor $C_{Fl}$	in 100 gr silk $C_{Sw}$	
0,0194	0,0119	0,25	21
0,029	0,0166	0,41	25
0,0388	0,0221	0,56	25
0,0595	0,0346	0,83	24
0,0774	0,0450	1,08	24
0,097	0,0540	1,43	26
			mean 24

If the character of the wool is altered by chemical action the coefficient of dispersion is also altered. For an acetylated wool (about 2—3% acetyl) the following equilibrium was obtained:

**Table 9**  
*Dispersion of o-nitraniline between acetylated wool and water*

grammes nitraniline in 400 ccm water used for 5 gr acetylated wool	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_{W ac.}}{C_{Fl}}$
	in 100 ccm liquor $C_{Fl}$	in 100 gr acetylated wool $C_{W ac.}$	
0,02	0,0038	0,096	25,3
0,04	0,0080	0,158	19,8
0,06	0,0118	0,26	22,1
0,08	0,0152	0,386	25,3
0,12	0,0193	0,454	23,5
0,16	0,0325	0,60	18,5
0,24	0,0470	1,04	22,1
0,32	0,0622	1,42	22,8

The fibres formed from protein thus possess very considerable capacity for dissolving. This hitherto unobserved phenomenon is apparently common to all albuminous substances, as the equilibrium determinations with another amorphous albuminous body, a water-insoluble casein, gave the same results:

*Table 10*  
*Dispersion of o-nitraniline between casein and water*

grammes nitraniline in 100ccm water used for 1,5 gr casein	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_K}{C_{FI}}$
	in 100 ccm liquor $C_{FI}$	in 100 gr casein $C_K$	
0,01105	0,00828	0,185	22
0,0221	0,0152	0,460	30
0,0414	0,0304	0,733	24
0,0627	0,0447	1,20	27
0,0842	0,0574	1,79	31
0,102	0,0718	2,01	28
			mean 27

The dissolving power of different albuminous substances does not vary essentially; this is evident from a consideration of the very high dissolving power of low acid amides of similar percentage composition. A comparison may be made between the composition of acetyl ethylamine and that of wool and silk:

	wool %	silk fibroin %	acetyl ethylamine %
Carbon	50	48,5	55
hydrogen	7	6,4	10,3
oxygen	25	26,7	18,4
nitrogen	15—17	18,4	16
sulphur	2—4	—	—

In the case of acetyl butylamine for example it has been found that 100 ccm will dissolve 28.14 gr. o-nitraniline at C°. The solubility of o-nitraniline being 0.1 gr. in 100 ccm water the coefficient of dispersion between acetyl butylamine and water is about:

$$\frac{C_{amide}}{C_{H_2O}} = \frac{28}{0.1} = 280.$$

Between the animal fibres and the cellulose esters there are accordingly only differences in degree in their capacity for dissolving o-nitraniline (see figure 2). With both kinds of fibre the quantity taken up follows the law of Henry and is only very much higher (about ten times) in the case of the cellulose esters than with the animal fibres. (Table 11.)

*Table 11*

fibre	coefficient of dispersion of o-nitraniline
acetate silk . . . . .	180
nitro silk . . . . .	234
silk . . . . .	25
silkworm . . . . .	24
wool . . . . .	14
acetylated wool . . . . .	25

### Conclusion

Silk being an animal fibre and approaching so nearly to wool in its composition, exhibits in the presence of acids and acid dyestuffs a very similar behaviour. It fixes all acids in the form of salts in proportion to their equivalents.

The capacity for fixing acid is with wool 3—4 times as great as with silk. The latter however has a very much higher capacity for dissolving monosulphonic acids and inert substances. The process of dyeing animal fibres with acid dyestuffs depends upon both of these operations of solution and salt formation which to some extent overlap one another.

In their dissolving power there is between the cellulose esters and the animal fibres only a difference in degree; the cellulose esters dissolve for example about ten times as much o-nitraniline as is dissolved by the animal fibres.

### General observations

In former treatises we have described as solution and not as adsorption the property of taking up substances possessed by acetate silk, nitro-cellulose, natural silk and wool in so far as it follows the law of Henry<sup>15)</sup>. The forces behind these two phenomena are exactly the same and depend upon the molecular attraction between the molecules of the solvent or substrates and the dissolved or adsorbed substance.

The difference is that in a liquid all its molecules exert a molecular attraction whilst with solid "adsorbing" substances only that portion of the molecules or ions lying on the surface can do so for reasons of space. If the quantity of these surface molecules is very large in comparison with the quantity of "adsorbed" molecules we have a similar relationship to that of a dilute solution in a liquid in which the number of the "taking up" mole-

<sup>15)</sup> Compare too Georgievicz and Springer, Mon. 21 (1900), 845; Mon. 34 (1913) 744, 751.

cules is very large in comparison with the number of the dissolved molecules.

Correspondingly the quantitative line of the equilibrium curves is with low concentrations also the same in both cases; absorption is a linear function of concentration (Henry's law). In these cases consequently no decision can be arrived at between "solution" and "adsorption" based upon the curves obtained.

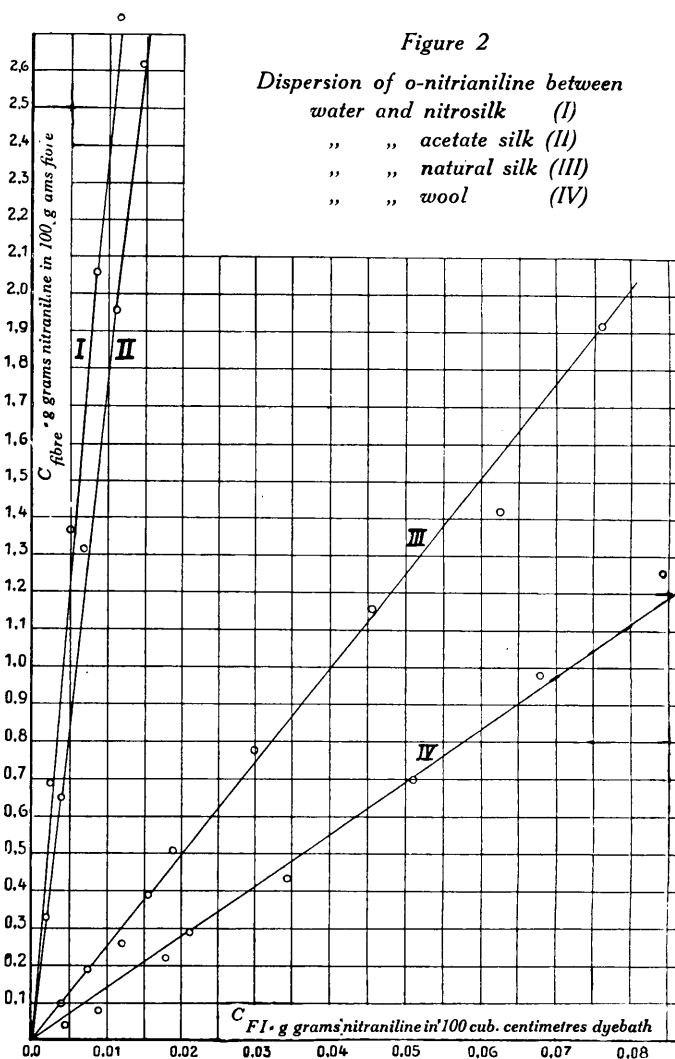
If we will now, as is possible in principle, describe as superficial adsorption the equilibrium curves obtained which up to high concentrations obey Henry's law, we shall be obliged as above explained to assume that the available surface is much larger than the total surface of the adsorbed molecules. This assumption permits of an approximate calculation as we know now that adsorption almost always occurs in a single molecule layer and the area which would be covered by a given quantity of nitraniline in a single molecule layer can be calculated. If the inner surface of the fibre is considered equal to this area and from this is calculated the approximate size of the particles which form the fibre, values are obtained which correspond about to the size of the particle shown by nitrocellulose in a state of solution.

From this it follows that the single particles which form the inner surface of the fibre are identical with the molecules determined in solution, i. e. we can in this case rightly speak of a solution throughout the whole volume.

A similar condition obtains in the case of selective adsorption and the chemical reaction of colloids. The words "selective adsorption" are used to describe the preferential (selective) taking up of certain substances from surface mixtures e. g. in the formation of salts. The formation of salts of the animal fibres appears to us not to be a surface reaction in this sense but a reaction throughout the fibre.

The basic equivalent of wool with a mean of about 1200 is so low that the corresponding reacting particles even if they had to be considered as polyvalent and their equivalent

Figure 2  
Dispersion of *o*-nitraniline between  
water and nitrosilk (I)  
" " acetate silk (II)  
" " natural silk (III)  
" " wool (IV)



weight of 1200 to be multiplied correspondingly, can be regarded entirely as molecules. Whereas with the cellulose esters and with wool the processes of solution and salt formation bring about equilibria throughout the entire volume without any noticeable effect on the structure or an appearance of surface saturation, with silk the partially crystalline structure appears essentially to influence the dyeing process. As we have seen above the molecules lying within the crystallites of the silk do not take part in the reaction of dyeing. Correspondingly the silk takes up acid dyes far less than wool. In this case where the extraordinary size of the inner surface of the viscous liquid is replaced by the smaller surface of a mixture of crystallites and their intermediary substances, the phenomena of adsorption, surface reaction, are more clearly

apparent. Probably in this way can be explained the tinctorial relationship of natural silk to the chemically dissimilar cotton (with

which adsorption is a decisive factor), this being particularly shown in the behaviour towards substantive dyestuffs.