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Chemistry. — *"The distribution of dyestuffs between two solvents. Contribution to the theory of dyeing."* By Prof. W. REINDERS and D. IRLY Jr. (Communicated by Prof. F. A. H. SCHREINER-MAKERS.)

(Communicated in the meeting of September 28, 1912).

For the explanation of the absorption and retention of dyestuffs by fibres there exist three theories; the chemical theory, the theory of solid solution, and the mechanical or adsorption theory.

According to the first theory ¹⁾ the colouring matter enters into a chemical reaction with a constituent of the fibre with formation of an insoluble product, which is retained in the fibre. This constituent — according to KNECHT, lanolinic acid in wool and sericinic acid in silk — is supposed to have the character of an amphoteric electrolyte and, therefore, to be capable of forming a salt with the base of the basic dyestuffs as well as with the acid of the acid dyestuffs.

An important argument in favour of this theory is the observation that when dyeing with basic dyestuffs there first occurs a dissociation into base and acid, the former then being absorbed by the fibre and the latter retained in the bath.

But it appears, however, that this dissociation also takes place in the absorption of dyestuffs by cotton, by pure cellulose ²⁾ and by inorganic matters such as glass, asbestos, silicates ³⁾, and carbon ⁴⁾ in which substances we surely cannot assume the presence of an acid capable of forming a salt with the dissociated base.

Moreover, the occurrence of such a dissociation in the case of acid dyestuffs is still doubtful ⁵⁾, and it also does not take place with the substantive colouring matters which are absorbed in their entirety. The chemical method of explanation is here a complete failure.

We also might be led to expect that the amount of colouring matter that can be absorbed by a certain fibre would be determined by the quantity of acid or base in that fibre. Only so much colouring matter ought to be taken up as is equivalent to this content in acid or base and a further addition of colouring matter to the bath should not cause any further absorption of the dyestuff by the fibre. More-

¹⁾ KNECHT, Berl. Ber. **21**, 1556, 2804; **22**, 1120 (1889). SUDA, Sitzungsber. der K. Akad. d. Wiss. Wien. **113** II B, 725 (1904); Z. f. angew. Chem. **1909**, 2131.

²⁾ KNECHT, Färberzeitung **18**, 22 (1893/94).

³⁾ GEORGIEVICS, Färberzeitung **19**, 9, 129, 188, 286 (1894/95).

⁴⁾ FREUNDLICH und LOSEV. Z. f. physik. Chem. **59**, 284 (1907); LOSEV, Inaug. Dissert. Leipzig 1907, p. 45.

⁵⁾ LOSEV, l. c. p. 67.

over, the formation of the insoluble precipitate in the fibre could only start when a certain concentration had been attained in the bath.

Neither of these phenomena have, however, been observed. The absorption of the dyestuff increases regularly with its concentration in the bath and there is no question of a discontinuity in this absorption.

The chemical theory is, therefore, an improbable one and is, in fact, rejected by the majority of the investigators of dye absorptions.

The theory of the solid solution has been proposed first by O. N. WITT¹⁾ and was at first universally accepted. WITT, by a number of examples has rendered it indeed plausible that the condition in which the colouring matter is present in the fibre is perfectly comparable with that of a substance in solution, that there is an equilibrium between the dyestuff in the fibre and in the aqueous solution and that the changes in that equilibrium, caused by the addition of another solvent such as alcohol, or of acids or salts, agree qualitatively, exactly with those in the equilibrium between two non-miscible liquids in which a third substance is dissolved.

In the quantitative investigation as to the distribution of the dyestuff between the fibre and the bath, it has been found, however, that this distribution does not take place according to

HENRY'S law, but that the adsorption-formula $\frac{x}{m} = ac^{1/n}$ must be applied.

Mainly on account of this, WALKER and APPLEYARD²⁾ as well as SCHMIDT³⁾, FREUNDLICH and LOSEV⁴⁾, GEORGIEVICS⁵⁾, PELET-JOLIVET⁶⁾ and others conclude that WITT's theory cannot be correct and that the colouration is, in the first instance, an adsorption phenomenon⁷⁾.

Hence, a very high value is attached to this utterly empirical and very elastic formula, which in FREUNDLICH and LOSEV's determinations

¹⁾ Färberzeitung 1890/91, 1.

²⁾ Journ. Chem. Soc. **69**, 1334 (1896).

³⁾ Zeitschr. f. physik. Chem. **15**, 56 (1894).

⁴⁾ l.c. and FREUNDLICH, Koll. Zeitschr. **3**, 212 (1908).

⁵⁾ l.c.

⁶⁾ L. PELET-JOLIVET, Die Theorie des Färbeprozesses, 1910.

⁷⁾ According to FREUNDLICH and LOSEV the fixation of the dye after its absorption, takes place because the colouring matter was either dissolved in a colloidal state and then rendered insoluble by coagulation by the fibre (in the case of substantive dyes), or was dissolved molecularly but converted in the fibre into an insoluble or colloidal non-diffusing substance. As regards this last change the action of another adsorbed substance (the mordant) or of the fibrous matter would, however, have to be considered eventually.

PELET-JOLIVET also regards the fixation of the dye chiefly as a coagulation of colloids.

had actually to be modified so as to agree with the figures obtained.

The question now arises whether this is really justified.

Is the compliance with this formula really such a certain criterion for the presence of a surface condensation, or can we meet with a similar relation in the distribution of a dyestuff over two non-miscible liquids?

Again, are the other properties of the dyed fibre in harmony with the adsorption theory? Is the colouring matter really present at the surface only or must we assume that it has penetrated also in the interior of the same?

We will consider these questions successively.

How is the dyestuff distributed in the fibre?

Some years ago this question was fully discussed by Hugo FISCHER¹⁾, who has most strongly protested against the implicit belief in internal surfaces in colloids. He calls attention to the fact that with starch granules, for instance, the colouration is perfectly homogeneous and argues in detail and on several grounds that the assumption that we are dealing with an adsorption is very improbable. He points out that the appearance of the coloured granule as well as the progressive change of the colouring process with a slowly acting dye stuff such as congo-red makes altogether the impression that this colouration is a phenomenon of solution and not a surface condensation. SUDA²⁾ in his investigations on the dye absorption of starch granules, also states that they are coloured quite homogeneously. The fact that when a dyestuff in the solid condition has a colour different to that of its solution, the fibre always presents the colour of the latter and not that of the former³⁾ also shows that the dyestuff is present in a condition which corresponds with solution.

In the case of several other phenomena which have been described as adsorptions, a doubt now begins to arise whether this view is really quite correct. VAN BEMMELLEN⁴⁾ has already pointed out that with the gels the line between *ad-* and *absorption* is difficult to draw. DAVIS⁵⁾ found that the amount of iodine taken up by carbon increases with the time of action. The iodine diffuses slowly towards the interior of the carbon. MC BAIN⁶⁾ noticed the same in the absorption

¹⁾ Z. f. physik. Chem. **63**, 480 (1908).

²⁾ Sitzungsber. der K. Akad. d. Wiss. Wien **113** IIb, 725 (1904).

³⁾ O. N. WIRT, l.c.

⁴⁾ Z. f. Anorg. Chem. **23**, 321 (1900).

⁵⁾ Journ. Chem. Soc. **91**, 1666 (1907).

⁶⁾ Z. f. physik. Chem. **68**, 471 (1909).

of hydrogen by carbon and concludes that a portion is really adsorbed and that another portion forms a solid solution.

GEORGIEVICS¹⁾, in his later investigations as to the absorption of dilute acids by wool, has also come to the conclusion that in many cases adsorption and solid solution occur together. From very dilute solutions, acids as well as different colouring matters with a constant division factor are absorbed so that this absorption may be considered as a true solid solution.

Adsorption and solution, therefore, go hand in hand and in most cases it is difficult to make out what part appertains to each of these phenomena.

When the nature of the absorbing material causes the diffusion towards the interior to take place with extreme difficulty, as in the case of carbon and silicates, the formation of a solution will take place in the external layers of the substance only and one will get the impression of dealing with a mere surface action or adsorption. In some cases, however, it appears that the colouring matter has penetrated further into the substance. Silicates coloured by fuchsine and methylene blue exhibit a distinct pleochroism²⁾, which shows that the dyestuff has distributed itself homogeneously *into* the silicate and has not deposited merely on the surface.

Cases of true adsorption will occur when the substance is dissolved in the colloidal state and does not dissolve molecularly in the absorption medium. We may then expect either no absorption at all or a complete absorption as colloidal solid solution, or else a complete separation of the colloid at the border layer; this then constitutes adsorption. Instances of this are found in the adsorption of colloidal gold by carbon or by BaSO_4 ³⁾, of As_2S_3 -solution by carbon or by BaSO_4 , of a very fine carbon suspension by paper⁴⁾ and also in the dyeing of wool or cotton with some undoubtedly colloidal dye solutions such as that of the blue acid of congo-red. This colouration however, is not permanent and can be completely removed by washing⁵⁾.

How does a dyestuff distribute itself over two solvents?

In this direction but few determinations have been made. Only in the case of picric acid the distribution between water and

¹⁾ Koll. Zeitschr. 10, 31 (1912),

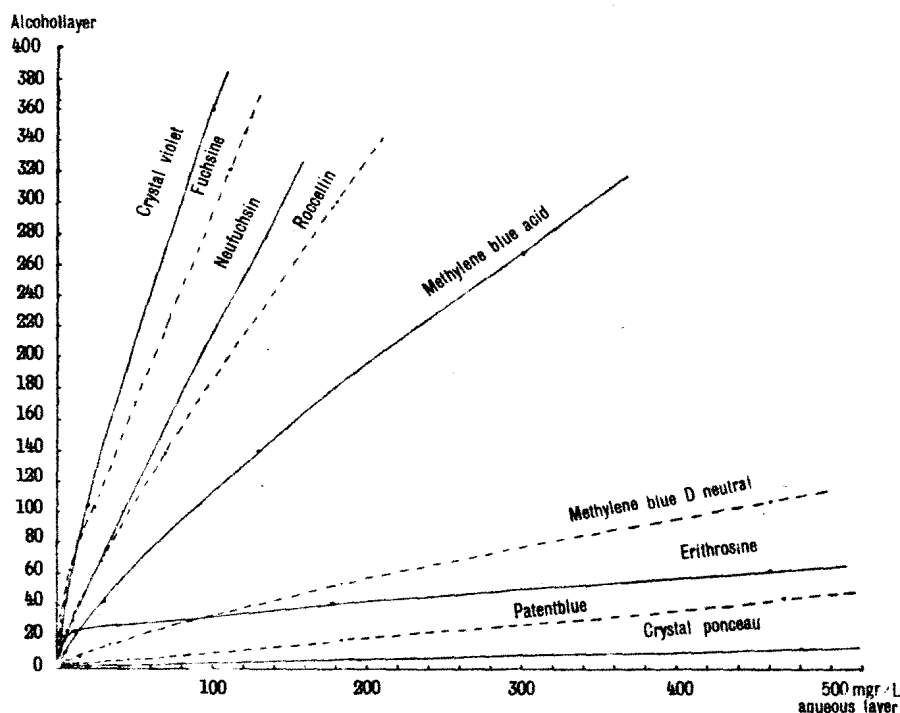
²⁾ T. CORNU, Tschermak's Mineralogische und Petrographische Mitteilungen 1906, 453.

³⁾ L. VANINO, Berl. Ber. 35, 662 (1902).

⁴⁾ SPRING, Beobachtungen über die Waschwirkung der Seifen. Koll. Zeitschr. 4, 161 (1909).

⁵⁾ PELET-JOLIVET, Die Theorie des Färbeprozesses, p. 141

various organic solvents such as amyl alcohol, benzene, chloroform, bromoform and toluene has been investigated and it has been found



that on increasing the concentration an proportionally smaller part remains in the aqueous layer¹⁾. With methylene blue, between aniline and water, the division coefficient is constant²⁾.

We have now measured for a number of dyestuffs the distribution between water and isobutyl alcohol (b.p. 106°). The determination of the colouring matter was effected colorimetrically. The temperature was 25°. The results are united in tables 1—19. The concentrations are indicated therein in mgs. per litre.

From these tables and better still from the curves in fig. 1 it appears that with all these colouring matters, the division coefficient $\frac{c_a}{c_w}$ decreases with the increase in the concentration. If the adsorption relation $c_a = a_w^{1/n}$ is applied we find that $\frac{1}{n}$ varies from 0.3 (with erythrosine A) to 1 (alkali blue and crystal ponceau). In most cases, however, this exponent increases with the rise of the concentration.

This result is surprising. As the investigations of recent years have

¹⁾ W. HERZ, Der Verteilungssatz, Sammlung chem. und chem.-techn. Vorträge 15 (1909).

²⁾ PELET-JOLIVET, Revue gén. mat. col. 1909, 249.

1. *Methyleneblue* G. conc. (Basel).
(Basic dyestuff).

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
1.6	4.3	2.70	0.20	0.633	0.56
5.8	8.7	1.50	0.76	0.939	
15.4	15	0.97	1.19	1.176	
37	24	0.65	1.57	1.38	
78	50	0.64	1.89	1.70	
140	72	0.51	2.14	1.85	0.72
464	156	0.34	2.66	2.19	

2. *Methyleneblue* G. conc.
Aqueous layer 0.33 n. HCl.

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
0.32	2.27	7.09	0.505-1	0.356	0.75
3.2	9.0	2.75	0.505	0.954	
11.6	22.5	1.95	1.064	1.352	"
29.6	43.0	1.45	1.471	1.642	"
130	140	1.08	2.114	2.146	"
304	268	0.88	2.483	2.428	"

3. *Methyleneblue* G. conc.
Aqueous layer 0.003 n. KOH.

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
4.0	18.0	4.50	0.602	1.255	0.75
9.0	32.5	3.61	0.954	1.512	
25	70	2.80	1.398	1.875	"
120	200	1.67	2.079	2.301	"
300	500	1.67	2.477	2.699	"

4. *Methyleneblue* D (Basel).
Neutral.

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
6.8	5.2	0.76	0.832	0.716	0.72
15.0	6.9	0.46	1.176	0.839	
34	15.5	0.45	1.531	1.190	"
184	54	0.30	2.265	1.732	"
460	108	0.24	2.663	2.033	"

5. *Methyleneblue* D.
With 2 equivalents of HCl.

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
7	7.5	1.07	0.845	0.875	0.65
15	10.5	0.70	1.176	1.021	
38	22.4	0.60	1.580	1.350	
165	79	0.48	2.217	1.898	0.84
440	192	0.44	2.643	2.283	

6. *Fuchsine*.
(Basic dyestuff).

C_w	C_a	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
0.75	18	24.0	0.87-1	1.25	0.4
2.5	35	14.0	0.40	1.54	
8.0	62	7.75	0.90	1.79	
24	103	4.30	1.38	2.01	
110	320	2.91	2.04	2.50	0.7
320	620	1.94	2.50	2.79	

7. *Fuchsine*.
With 7 equivalents of HCl.

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
5.3	42	8.0	0.724	1.623	1.0
14	118	8.4	1.146	2.072	
25	232	9.3	1.398	2.365	
52	450	8.65	1.716	2.653	
140	1108	7.91	2.246	3.045	

10. *Crystal ponceau*.
(Acid dyestuff).

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
20	1	0.05	1.301	0.00	1.0
49	1.7	0.035	1.690	0.230	
195	6.0	0.031	2.290	0.778	
480	15.0	0.031	2.681	1.176	

8. *Crystal violet* (Basel).
(Basic dyestuff).

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
0.9	17	18.9	0.95-1	1.23	0.5
2.0	25	12.5	0.30	1.40	
5.3	43.5	8.2	0.72	1.64	
19.5	104	5.3	1.29	2.02	
100	360	3.6	2.00	2.56	0.9
245	820	3.35	2.40	2.91	

11. *Patent blue* (Höchst).
(Acid dyestuff).

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
4.2	1.0	0.24	0.62	0.00	0.6
8.5	2.1	0.25	0.93	0.32	
46	5.4	0.12	1.66	0.73	
184	18.0	0.098	2.26	1.25	
470	45.4	0.095	2.67	1.66	
1140	150	0.13	3.06	2.18	1.0
2250	375	0.17	3.35	2.57	1.25
					1.33

9. *Neufuchsin* (Höchst).
(Basic dyestuff).

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
2.0	12.5	6.5	0.30	1.10	0.5
4.0	17.5	4.4	0.60	1.24	
9.4	30	3.2	0.97	1.48	
28	68	2.4	1.45	1.83	
120	250	2.1	2.08	2.40	
290	600	2.1	2.46	2.78	1.0
780	1560	2.0	2.89	3.19	
1600	3000	1.9	3.20	3.48	
3200	5700	1.8	3.50	3.76	

12. *Erithrosine A*. (Höchst).
(Acid dyestuff).

C_w	Ca	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
1.4	11.0	7.9	0.146	1.041	0.30
4.0	16.8	4.2	0.602	1.225	
10.7	23.4	2.2	1.029	1.369	
38.5	27.7	0.72	1.587	1.442	
178	42	0.24	2.250	1.623	
460	63	0.14	2.663	1.799	"

13. *Roccellin* (Basel).
(Acid dye stuff).

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
1.62	11.77	7.27	0.210	1.061	0.52
4.38	19.5	4.45	0.641	1.290	
14.2	42.6	3.0	1.152	1.629	
30.4	73.6	2.4	1.483	1.867	0.80
65	138	2.1	1.813	2.140	
179	300	1.7	2.253	2.477	

14. *Quinoline yellow* (Fr. Bayer).
(Acid dyestuff).

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
11.5	18	1.60	1.06	1.25	1.0
23	38	1.64	1.36	1.58	"
60	100	1.67	1.77	2.00	"
120	200	1.67	2.08	2.30	"
240	425	1.77	2.38	2.63	"
630	964	1.53	2.79	2.98	"

15. *Quinoline yellow*.
With 10 equivalents of HCl.

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
6.5	36	5.5	0.81	1.56	1.0
12.5	74	6.0	1.10	1.87	"
31	200	6.45	1.49	2.30	"
61	390	6.40	1.78	2.59	"
125	800	6.40	2.10	2.90	"
320	2030	6.39	2.51	3.31	"

16. *Quinoline yellow*.
With 10 aequivalents of KOH.

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cu$	$\log Ca$	$\frac{1}{n}$
12	17	1.40	1.08	1.23	1.0
25	33	1.32	1.40	1.52	"
70	80	1.14	1.84	1.90	"
140	160	1.14	2.15	2.20	"
280	320	1.14	2.45	2.51	"
720	800	1.11	2.86	2.90	"

17. *Alkali blue 6 B.* (Bayer).
(Acid dyestuff).

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
7.9	105	13.3	0.897	2.021	1.0
15.1	212	14.0	1.179	2.326	"
30.2	425	14.1	1.480	2.628	"

18. *Congo-red* (Bayer).
(Substantive dyestuff).

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
9.0	2.2	0.24	0.954	0.342	0.77
19	3.3	0.17	1.279	0.518	"
48	6.5	0.13	1.681	0.813	"
94	12	0.13	1.973	1.079	"
180	21	0.12	2.255	1.322	"
480	42	0.09	2.681	1.623	"

19. *Congo-red*.
With 4 equivalents of KOH.

Cw	Ca	$\frac{Ca}{Cw}$	$\log Cw$	$\log Ca$	$\frac{1}{n}$
6.6	2.4	0.36	0.819	0.380	0.73
17.4	5.4	0.31	1.240	0.732	"
44	10	0.23	1.643	1.000	"
180	27	0.15	2.255	1.431	"
456	60	0.13	2.654	1.778	"

shown that different dyestuffs, particularly the basic and the acid ones, are dissolved molecularly in aqueous solution and, as shown by the conductivity of those solutions, are fairly strongly dissociated electrolytically, whereas the dissociation in alcoholic solution is but trifling, we might expect that the transition into the alcohol layer would increase with a rise of the concentration.

In order to explain this small exponent we can make different suggestions:

1. The molecular size of the colouring matter is greater in the aqueous solution than in the alcoholic one.

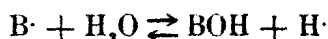
This view finds support in the determinations of KRAFFT¹⁾ on the lowering of the freezing point in aqueous and alcoholic solution. From these the following molecular weights are deduced:

	in water	in alcohol	theoretical
Fuchsine	520—617	320—344	337
Methyl violet	804—870	403—421	408
Benzopurpurin	3000	—	724
Diamine blue	3430	—	999

Hence, the two first basic dyestuffs would possess in water twice as great a molecular weight as in alcohol. These determinations, however, are not in harmony with the measurements of the conductivity power of most of the dyestuffs, dissolved as salts, which is about equal to that of a strongly dissociated binary electrolyte.

2. The dyestuff (BS) in aqueous solution is partly dissociated hydrolytically. By the alcohol the neutral molecules are strongly absorbed, the ions are not. In the case of a basic dyestuff the mols. BOH and BS therefore pass into the alcohol layer.

The hydrolysis equilibrium can be written as



hence

$$c_{BOH} \times c_H = k_1 c_B.$$

or also, because

$$c_{BOH} = c_H$$

$$c_{BOH} = \sqrt{k_1 c_B^{1/2}}$$

To the ordinary electrolytic dissociation of the dye salt applies the formula:

$$c_{BZ} = k_2 c_B \times c_{Z'} = k_2 c_B^2$$

¹⁾ Berl. Ber. 32. 1608 (1899).

If for the dye salt in the aqueous solution, we take it for granted that there is practically a complete dissociation, the concentration of the dye in the aqueous layer C_w may be considered as equal to c_B . If now we call the division coefficients for the molecules BOH and BS k_3 and k_4 we obtain:

$$C_a = k_3 c_{BOH} + k_4 c_{BZ} = \underline{K_1 C_w^{1/2} + K_2 C_w^2}.$$

The first term will be of influence particularly with small concentrations; the second will apply more in the case of increased concentrations.

On applying the adsorption formula, $\frac{1}{n}$ will, therefore, increase with the rise of the concentration. It will start with a value < 1 then become $= 1$ and may subsequently rise to above 1. The line indicating the dependence of the concentration in the alcohol layer on that in the aqueous layer will at first turn its concave side downwards, then exhibit a point of inflexion and finally turn its concave side in an upward direction.

A similar variation of $\frac{1}{n}$ has indeed been observed with a great many dyestuffs even though with most of them no higher values than 1 were obtained. Only with "patent blue" this value was exceeded and $\frac{1}{n}$ rose to 1.3.

In agreement therewith it also appears that in the case of basic dyestuffs, the transition into the alcohol layer is promoted by addition of a base and in the case of acid dyestuffs by addition of an acid and in such a manner that finally everything passes into the alcohol layer (see Table 20).

Reversely, however, by adding acid to a basic dyestuff, or a base to an acid dyestuff, the transition thereof into the alcohol layer is not diminished. Frequently, this even causes an increase in the concentration of the alcohol layer.

This may be partly explained by the diminution in the hydrolysis, and the increase in the concentration of the non-dissociated salts caused thereby. From the changes in colour on increasing the concentration of the acid added, it seems, however, that the reactions are often much more complicated.

Let us take as an example crystal violet. This is a basic dyestuff. Formula $\{(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4\}_2 \cdot \text{C} = \text{C}_6\text{H}_4 = \text{N}(\text{CH}_3)_2 \cdot \text{Cl}$. In a neutral or faintly alkaline solution the colour is violet. On addition of acid the colour turns blue, then green and with still

TABLE 20.

Name of dye.	Distribution in neutral solution	Distribution in acid solution	Distribution in alkaline solution
<i>Methylene blue</i> (basic dyestuff).	Both layers about equally blue.	Same as in neutral solution.	All in the upper layer. The colour slowly changes to mauve.
<i>Crystal-violet</i> (basic dyestuff).	Much more in the alcohol layer. Both layers violet.	More in the alcohol layer. This is violet, the aqueous layer green.	All in the alcohol layer. Colour violet.
<i>Chrysoidine</i> (basic dyestuff).	Alcohol layer dark yellow to brown. Bottom layer pale yellow.	Same as in neutral solution but the colour is more brownish.	All in the alcohol layer. Colour dark yellow.
<i>Fuchsin</i> (basic dyestuff).	More in the alcohol layer. Both layers red.	Most in the alcohol layer. Colour is much darker.	The colour vanishes.
<i>"Neufuchsin"</i> (basic dyestuff).	More in the alcohol layer. Both layers red.	Most in the alcohol layer. Colour red.	All dark brown in the upper layer.
<i>Erythrosine</i> (acid dyestuff).	About equal distribution. Alcohol layer more orange like, the aqueous layer more red.	All in the alcohol layer. Colour orange.	As in neutral solution.
<i>"Wasserblau bläulich" I</i> (acid dyestuff).	About equal distribution; both layers blue.	Much more in the alcohol layer, blue.	All in the alc. layer. Colour orange, afterwards colourless.
<i>Rose Bengale</i> (acid dyestuff).	Equal distribution. Alcohol layer yellowish brown, aqueous layer orange.	All in the alcohol layer; light brown.	Much more in the alcohol layer; red.
<i>Quinoline-yellow</i> (acid dyestuff).	Equal distribution; both layers yellow.	Much more in the alc. layer; yellow.	Much more in the alc. layer; yellow.
<i>Eosine</i> (acid dyestuff).	About equal distribution.	All in the alcohol layer; yellow.	As in neutral solution.
<i>Roccelline</i> (acid dyestuff).	Both layers red.	All in the alcohol layer; red.	Both layers red but much darker than in neutral solution.
<i>Patent blue</i> (acid dyestuff).	Most in the alcohol; both layers blue.	Upper layer darker, aqueous layer more greenish.	All in the aqueous layer. Dark blue.
<i>Crystal-ponceau</i> (acid dyestuff).	Little in the alcohol layer; aqueous layers red.	Much more in the alcohol layer.	Little in the alcohol layer; aqueous layer more brownish.
<i>Congo-red</i> (substantive dyestuff).	Both layers red.	Blue deposit on the plane of demarcation.	All in the alcohol layer; red.
<i>Alkali blue 6 R.</i> Forms a colloidal solution in water, but little coloured, reddish blue and opalescent.	Alcohol layer dark blue; aqueous solution colourless.	As in neutral solution. Aqueous layer somewhat tinged.	All in the alcohol layer with slight reddish colour.
<i>"Indulin spritlöslich"</i> In water an almost colourless colloidal solution.	All with blue colour in the alcohol layer; aqueous layer colourless.	Nearly all in the alcohol layer, blue; aqueous layer somewhat tinged.	All with violet colour in the alcohol layer; aqueous layer colourless.

more acid yellow. From these solutions, however, it always passes into the alcohol layer with a violet colour. The only explanation we can give is this, that the dye adds an H-ion to its 3-valent N-atoms. These additive products might then be blue, green, or yellow, the non-dissociated salt, however, violet. In the alcohol layer the H-ion concentration is much less than in the aqueous layer and so these additive products are formed with more difficulty. By a large excess of HCl the upper layer turns green also. The green solutions also regain their violet colour by strong dilution: the added hydrogen ions are again split off by dilution.

"Patent blue" exhibits a similar behaviour; a very little acid causes the concentration in the alcohol layer to increase, on addition of more acid it again decreases, while the aqueous layer turns first green and afterwards yellow. When the aqueous layer is already yellow, the alcohol layer is still green.

The influence of acid and base was investigated quantitatively with methylene blue, quinoline-yellow and fuchsine.

From table 1, 2 and 3; 6—7; 14, 15 and 16 we notice that with a large excess of acid or base the course of the division curve is quite analogous to that in the neutral solution.

The influence of increasing quantities of acid or base is shown in the following table where in the first column is indicated the number of equivalents of acid or base in solution with one equivalent of colouring matter. The total quantity of dyestuff taken was always the same.

TABLE 21.

Methylene blue <i>D</i> with	c_w	$c_{alc.}$	$c_a : c_w$
very much acid	130	140	1.08
8 eq. acid	140	120	0.86
4 " "	160	80	0.50
2 " "	170	70	0.41
1 " "	170	70	0.41
neutral	170	70	0.41
0.8 eq. KOH	170	70	0.41
2.6 " "	150	86	0.57
6.2 " "	128	160	1.25
10 " "	90	300	3.33

If now we compare the distribution of dyestuffs between water and alcohol with that between water and fibres or other absorbents it appears that :

1. As in the case of the colour absorption by fibrous matters, the so-called adsorption-equation in which $\frac{1}{n} < 1$, also applies to the distribution between water and alcohol.

2. Addition of a base to the solution of basic dyestuffs and of an acid to acid dyestuffs strongly promotes the absorption by fibrous matter ¹⁾ as well as the entry into the alcohol layer.

3. Wool and silk dyed with basic dyestuffs in which the base only has been retained are very readily decolourised by extraction with alcohol. The solubility of the free base, which in water is slight, is large in the fibre and also in the alcohol ²⁾.

4. According to Losev ³⁾ no dyestuff is absorbed by paper fibre from a solution of crystal-violet when this substance is dissolved in butyl alcohol, amyl alcohol, aniline, chloroform or anisaldehyde; the absorption is perceptible from a solution in nitrobenzene, anisol, ethyl malonate or amyl nitrite and strong from the aqueous solution.

If now, we observe the distribution of this dyestuff between water and those solvents it appears that with the first group of solvents it practically disappears from the aqueous layer and that with the second group it distributes itself somewhat evenly over the two layers.

Nitrobenzene makes the only exception as it removes nearly all the dye from water although, according to Losev, no colouring matter is absorbed from it by paper.

This behaviour is now quite comprehensible if we look upon dyeing as being tantamount to *dissolving* the colouring matter in the fibre. For crystal-violet the fibre is a good solvent and water a bad one; the organic solvents of the first group are good, those of the second group are bad solvents. In the distribution of the dyestuff over the fibre and the organic solvent, less dyestuff will be absorbed in the fibre and more will be retained in the solvent, according to the greater solubility of the dyestuff in the latter. The division coefficient $\frac{\text{fibre}}{\text{org. solvent}}$ will be the quotient of that between $\frac{\text{fibre}}{\text{water}}$ and $\frac{\text{org. solvent}}{\text{water}}$.

5. FREUNDLICH and LOSEV have found that the order of adsorption is independent of the nature of the adsorption medium. With carbon

¹⁾ See i.a. PELET-JOLIVET, Koll. Zeitschr. 2, 225 (1908).

²⁾ FREUNDLICH and LOSEV, loc. cit. p. 303.

³⁾ LOSEV, Inaug. Dissert. p. 64.

as well as with silk, wool, cotton and cellulose the order of the three following dyestuffs was: crystal-violet, "neufuchsin", patent blue.

The same order, however, is noticed in the distribution of these dyestuffs between water and alcohol. Here again is shown the great analogy between the absorption of the dyestuff in fibres and the transition of the colouring matter into another solvent, which leads to the assumption that the absorbed dyestuff is present as a solid solution in the fibre.

We, therefore, conclude that the dye absorption in fibres is mainly a phenomenon of solid solution and that the assumption of a surface adsorption is in many cases unnecessary and should, therefore, be discarded.

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Mathematics. — "*On loci, congruences and focal systems deduced from a twisted cubic and a twisted biquadratic curve*". I.
By Prof. HENDRIK DE VRIES.

(Communicated in the meeting of September 28, 1912).

1. In the Proceedings of the Meeting of this Academy on Saturday Sept. 30, 1911, p. 259, Mr. JAN DE VRIES has investigated the locus of the points sending to three pairs of straight lines crossing each other three complanar transversals, and in the Proceedings of the Meeting of Nov. 25, 1911, p. 495, Mr. P. H. SCHOUTE has made the same investigation for the points sending to $(n+2)$ pairs of straight lines crossing each other $(n+2)$ transversals lying on a cone of order n . In the following pages one of the three pairs of lines will be replaced by a twisted cubic, the two others by a quartic curve of the first kind. Through a point P one chord a of k^3 passes and two chords b of k^4 pass; we ask after the locus of the points P for which the line a and the two lines b lie in *one* plane.

We imagine a chord a of k^3 . Through an arbitrary point P of this chord pass two chords b_1, b_1^* of k^4 and in the plane ab_1 lies one chord b_2 which does not meet b_1 on k^4 itself, in ab_1^* one such-like chord b_2^* ; if for convenience sake we call the points of intersection of b_1 and b_2^* with a both Q , then in this way to each point P two points Q correspond. However, it is clear that to each point Q also two points P correspond, so that on a a (2,2) correspondence arises with four coincidences, and for these it is evident that the triplet $a + 2b$ is complanar. However, it is easy to see