

Citation:

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Chemistry. — “*Contributions to the theory of dyeing*” (First communication) by Prof. H. R. KRUYT and Miss J. E. M. VAN DER MADE. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of June 30, 1917).

1. Three different explanations have been suggested for the way in which dyes are taken up by fibres and other solids. First a merely chemical combination of dye and fibre was suggested; but a chemical theory gave rise to so many contradictions, that, as soon as the theory of solid solutions was developed, it was tried to explain dyeing in agreement with the new theory. But in this way it was just as impossible to bring experiments and theory into harmony, and the new knowledge in the chemistry of colloids, especially that of the phenomena of adsorption and of the electricity of contact, gave a better starting-point for the explanation of the way in which wool, silk, cotton etc. take dyes from their solutions in water, both when electrolytes are added and when this is not the case. FREUNDLICH, in collaboration with several pupils (LOSEV¹⁾, NEUMANN²⁾), stated the fact, that amorph. carbon takes the dye from its solution in quite the same way as textile-fibres do; PELET³⁾ has made numerous investigations with his pupils on this subject⁴⁾. It may be stated that nowadays the interpretation of the process of dyeing as a phenomenon of electro-adsorption is generally accepted.

This point of view may be summarized as follows: the faculty of the fibre to take up the dye depends on the electric potential at the confines of fibre and solution, in connection with the sign of the electric charge of the dye-ions. The fibres and charcoal are charged negatively with regard to water, therefore they generally adsorb the basic dyes better than acid dyes. Every influence increasing the negative charge of the adsorbentia, will increase the adsorption

¹⁾ Zeitschr. f. physik. Chem. 59, 284 (1907).

²⁾ Zeitschr. f. physik. Chem. 67, 538 (1909).

³⁾ The results of these investigations are brought together in the interesting monograph PELET-JOLIVET, Die Theorie des Färbeprozesses (Dresden 1910).

⁴⁾ BANCROFT and his pupils too have paid much attention to the process of dyeing of late years. A summary of the theory of dyeing can be found: W. D. BANCROFT, Journ. of physical chemistry 18, 1, 118 and 385 (1914).

of basic dyes. All inorganic compounds and their ions are adsorbed in nearly equal amounts from solutions of equal molecular concentration, excepted the ions of H, OH and of the heavy metals, which show an abnormally high adsorption. So the hydroxides of the alkali-metals will add to the negative charge, for the OH ion is adsorbed more fully than the metal-ion. The same will be caused by alkali salts of polybasic acids, as the negative ion has a greater electric charge than the kation; and again the same will be the case by adding salts of organic acids, because organic ions are more fully adsorbed than anorganic ones. When dyeing with acid dyes, we shall meet with an exactly opposite effect of electrolytes, dyeing being increased by acids, by salts of bi- and trivalent kations and of organic ones. Influences, diminishing the process of dyeing, may easily be inferred to the same line of thought.

PELET's investigations are in perfect accord with the above theory, both for the adsorption of the dyes itself and for the influence of dyes and electrolytes on capillary electric phenomena.

2. W. REINDERS¹⁾ lately published a paper in which he drew the conclusion that there remained much doubt about the connection between dyeing and the phenomena of adsorption. He had made investigations on the ratio in which a solution in water gave the dye to another phase, which was not a solid with great development of surface, but which was a liquid; the dyesolution was shaken with isobutylic alcohol. First the distribution of the dye in the two layers showed to be not in harmony with the distribution-law. In the second place he remarked in those cases, that whether acid or alkali increased the process of dyeing, the transition of the dye into the alcohol layer was also favoured. He came to the conclusion that these facts pointed clearly to a solution theory, and that it was of no use to refer to the theory of adsorption.

The interesting question, that was brought forward again by that paper, induced us to make the following investigation. First of all we are of opinion that for a good solution of this intricate problem it is of the greatest importance to avoid all unnecessary complication; therefore we shrink from drawing conclusions from experiments, when alkali or acid is present together with the dye. For these bodies often cause a chemical change in the molecule of the dye, in which case we have to deal with a chemical phenomenon and the process of dyeing simultaneously. So we have studied the

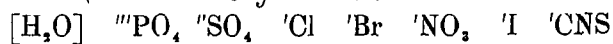
¹⁾ Koll. Zeitschr. 13, 96 (1913).

distribution of the dyes between water and isobutylic alcohol when only the sodium salts¹⁾ of different acids were present.

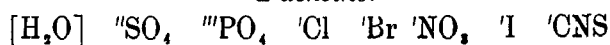
1 ccm. of the solution of the electrolyte (12 millimol p. L.) was added to 2 ccm. of a 0.5% solution of the dye (the first experiment was made, of course, with 1 ccm. of pure water). Then 2 ccm. of isobutylic alcohol were added and the whole was shaken in a tube with a glass stopper.

As the result we give the series in which the salts favour the transition from the waterlayer to the alcohol. From the left to the right the ions are written in the same series as they cause the alcohol to take a darker colour, resp. the waterlayer to take a brighter tinge. When two ions are united with a brace, we wish to express that the difference of colour was too small to decide about their sequence.

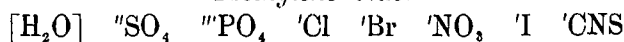
Crystal violet.



Fuchsine.

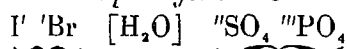


Methylene blue.

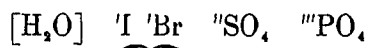


The first thing that strikes us is the fact that the ions are placed in the sequence of the so called *lyotropic series of anions*. The sequence of the ions is the same as regards their influence on the solubility of other bodies; the salting out of proteids; the influence on surface tension; enlargement of swelling; the kinetics of many reactions etc. These three dyes were basic, but when acid ones are taken we can expect the anions to have either no influence at all or an opposite one. Indeed we found such an influence though very weak.

Naphtolyellow S.



Alcaliblu.



3. PELET's theory of dyeing suggests an increasing adsorption of basic dyes when NaCl, still more when Na₂SO₄ and even much more when Na₂HPO₄ is added to the dyeing tub; we found however that the adsorption by the alcohol was not increased according to the

¹⁾ We only used NH₄CNS in staed of NaCNS.

basicity of the anions but according to their lyotropic strength. Lyotropically SO_4 and PO_4 are nearly equal, but Cl has a sharply different position, contrary to the sequence of basicity. Operating with neutral salts we therefore seem to have missed the parallelism REINDERS found with acids and alkalies.

One is inclined to consider the transition of the dye from the water to the alcohol layer as the process of salting out, so common to the emulsoids. Indeed the CNS ion, the extreme term of the series, caused precipitation after 24 hours,¹⁾ when brought to the dye solution in water to an amount of 4 millimol p. L., (the same concentration as the electrolytes had in the water-layer before the alcohol was added). It is evident that dyes, showing in many respects the properties of lyophobic colloids, are salted out by electrolytes in the sequence of the lyotropic series; and it is therefore easy to understand that lyotropic influences (it would be preferable to say *hydrotropic* here) cause a distribution of the dye in such a way, that the most active ion causes the greatest transition of the dye to the alcoholic layer.

4. Our knowledge about the influence of neutral salts on dyeing is however small. The dissertation of BACCIO BECCARI²⁾, a pupil of PELET, is the only systematical investigation we know, and even in this methylene blue is the only basic dye, and Na_2SO_4 and Na_2HPO_4 are the only neutral salts considered. The sequence in which that dye is taken up is this: solution in water — solution containing Na_2SO_4 — solution with Na_2HPO_4 , all according to PELET's theory³⁾.

As we thought it interesting to know whether lyotropic phenomena had any influence on the process of dyeing, we have made investigations about the quantity of dye adsorbed in the presence of the sodium salts of PO_4 , SO_4 , Cl , Br or NO_3 .

For dyes we took methylene blue, crystal violet and auramine; bloodcoal was the adsorbens. In each series the initial concentration and the amount of coal were exactly equal. The concentration at the end of the process was estimated by PELET and GARUTI's volume-

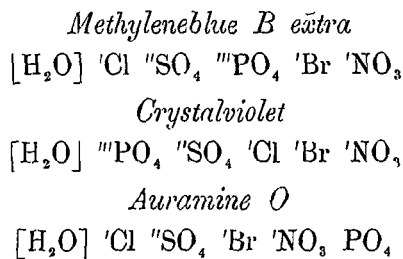
¹⁾ When in contact with isobutylic²⁾ alcohol, a precipitate could only be seen after some weeks at the boundary of the layers.

²⁾ Diss. Lausanne: Etude des relations des phénomènes de teinture et d'adsorption. (Florence 1908).

³⁾ Investigations of A. WILD, mentioned in PELET JOLIVET's book p. 98, show the following sequence in the case of methyleneblue: $\text{H}_2\text{O}—\text{Cl}—\text{SO}_4—\text{PO}_4$.

metric method¹⁾; methylene blue was measured by naphtholyellow S, crystalviolet by picrate of sodium and auramine by alcaliblu.

The adsorption showed to have been increased by the salts in this sequence:



In these series the ion which effects the adsorption is mostly placed at the right.

5. These results of our first series of measurements indicate that the interpretation must be more complicated than one should think from PELET's theory. When only the ions of 'Cl, "SO₄ and "'PO₄ are taken into consideration our results are in harmony with this theory with regard to methyleneblue and auramine, the increasing influence is added to with the basicity of the anions.

But the 'Br and 'NO₃ ion already show the importance of lyotropic influence. So we may draw the conclusion that dyeing is affected by the two sorts of phenomena; — when two ions are of nearly equal lyotropic strength, it will be possible for their electro-adsorptive character to preponderate and therefore to fix the sequence; when, however, there is great lyotropic difference between two ions, this fact will be decisive. With crystal violet the lyotropy of the salts is so predominant that no other influence can be noticed in the sequence.

An exact interpretation of lyotropic phenomena is always difficult because lyotropy can have so many different effects. Even the supposition that the cause of lyotropy is to be found in the power to combine with watermolecules, the so called "solvation", — though acceptable in many respects — leads to so many consequences, that the explanation remains totally arbitrary, as long as we cannot verify our theoretical conclusions with many series of experiments. We intend therefore to extend our researches to several dyes, electrolytes and adsorbentia. But we may call attention now already to the fact that the importance of lyotropy is not in contradiction with a theory regarding the process of dyeing as a phenomenon of adsorption, though this complication has remained un-

¹⁾ Bull. de la Soc. Vaudoise des Sc. nat. 43, 1 (1907).

considered till now¹⁾. For without sufficient reason it is only *electro-adsorbative-phenomena* that have been compared with the process of dyeing; the investigation of FREUNDLICH and POSER²⁾ showed however that such a way of interpretation is quite insufficient. Adsorption is not determined by electrical causes only, besides there is certainly a non electrical adsorption, determined by the surface tension according to GIBBS' law. As the lyotropic series shows the sequence in which the ions influence surface tension, it will be clear that the principle of adsorption explains both the importance of valency and lyotropic strength.

Attention must all the same be directed to the possibility, that the electrolytes do not leave the dyesolutions itself³⁾ unaltered. The peculiar condition of dyesolutions, often polydispers with the character of a pseudo-binary system⁴⁾, make the problem all the more complicated; only a wide investigation of each sort of influence by itself can make it clear. Hence we already made a beginning with such experiments.

Utrecht, June 1917.

VAN 'T HOFF-laboratory.

¹⁾ The only investigation showing the lyotropic influence on dyeing is to be found Biochemical Journal 1 175 (1906). BAYLISS made some researches on the dyeing of filtering paper by congo-red in presence of salt; the influence of these salts proved to be as according to the lyotropic series. BANCROFT (loc. cit.) does not mention this paper, PELET-JOLIVET does, but only in connection with other questions. So BAYLISS' paper came to our knowledge only when this investigation was closed.

²⁾ Koll. Beih. 6, 297 (1914).

³⁾ See I. TRAUBE, Koll. Beih. 3, 237 (1912).

⁴⁾ The remarkable observation DROOGLEEVER FORTUYN published [These Proceedings 23 1380 (1915)] have convinced us again on this point. It is obvious that in a solution of new fuchsine in water there are two kinds of molecules, a coloured and a non coloured one, which are in equilibrium with one another. And in water this equilibrium is reached only after a long time and as by absorption only the coloured modification is taken away, some days are wanted to colour the water again after it has been decoloured by coal (acetic acid seems to catalyse). It is a wellknown phenomenon that a solution of fuchsine is decoloured by alcali as the dye is changed into the pseudo base; still such a solution will dye silk [JACQUEMIN, C.R. 82, 261, (1876)] and wool. But the red colour returns too when the solution is shaken with isoamylic- or isobutylic alcohol [WITT, Farber Zeitung 1, 1 (1891)]. The same thing occurs when we shake a solution decoloured in the same way as followed by DROOGLEEVER FORTUYN, with isobutylic alcohol; this suggests that water is a solution of a pseudo base, which was present already in the primary solution. Perhaps this is also the reason, why the adsorption of dyes seems to take much more time than that of other bodies. The regeneration of dye, the only component which has really been adsorbed, from the carbinol base, which is even not in real solution (as an ultramicroscopic investigation shows), makes it appear as if the process of adsorption should be slow in this case.