ON THE REACTION BETWEEN ALIZARIN AND SODIUM ALUMINATE IN AQUEOUS SOLUTION.

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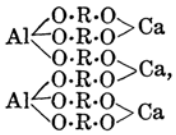
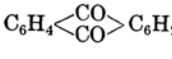
Hitherto many chemists studied the composition of the turkey-red, the formula $2Al_2O_3 : 3CaO : C_{14}H_8O_4$ was proposed by Rosenstiehl[1]; the formula $Al_2O_3(CaO)_2(C_{14}H_6O_3)_5$ by Saget[2]; Al_2O_3, CaO, $(C_{14}H_6O_3)_3$, H_2O by Liechti and Suida[3]. Recently R. Mohlau[4] gave the formula

(1) *Bull. Soc. Ind. Mulhouse*, 1875, 56.
(2) *Moniteur scientifique* 1883, 1086.
(3) *Mitt. d. Rechnol. Gew. -Museum, Wien,* **2** (1885), 26; **3** (1886), 5.
(4) *Ber.*, **46** (1913), 443.



where R means  and

moreover there are many other researches on the reaction-products of alizarin and alumina.

A few years ago, Bull and Adams studied the reaction of hydrochromic oxide or hydrous ferric oxide on sodium alizarate and concluded that in that case no true chemical compound was formed but adsorption compound. Williamson[1] researched the reaction between sodium alizarate and aluminium hydroxide. For this purpose he tried to determine the amount of sodium hydroxide, the by-product of the reaction, but could not get a reasonable datum, so he concluded that in this reaction no true aluminium alizarate is formed but an adsorption complex.

Now it is not too much to say that alizarin is almost insoluble in water at any condition, cold or hot, while it is easily soluble in the aqueous solution of sodium aluminate, giving a deep red colouration immediately, either cold or hot, and the author observed that if the former is added over a certain limit, its excess remains in state of yellow crystalline suspension in the coloured liquid and is easily visible under microscope. So the author thinks that some reaction might have occurred between these two compounds and it will be very interesting to research the reaction, since the reaction-product might be considered to have connection to Turkey-red from the point of view of the chemical constitution.

Experimental.

The Purification of Alizarin. The methods of the purification are proposed by many researchers. According to Graebe and Lieberman[2] the sublimation process which Schutzenberger proposed is best applicable for alizarin. Lieberman[3] dissolved alizarin in excess of a dilute sodium hydroxide solution and into the solution is passed carbon dioxide; then 2/3 part of the dyestuff is precipitated as acid sodium salt, while the co-existing isopurpurin remains in the solution. The precipitate of the acid salt is filtered and decomposed with hydrochloric acid. Schunk[4] reported that

(1) *J. phy. Chem.* **28** (1924), 891.
(2) *Ann. Spl.*, **7** (1870), 301.
(3) *Ann.*, **183** (1876), 206.
(4) *Ann.*, **66** (1846), 187.

alizarin recrystallized from alcohol loses its crystalline water at 100°C. and sublimes by heating in a test-tube at 215°C. But afterwards he and Roemer[1] reported that alizarin begins to sublime at 110°C. and by continuous heating at ca. 140°C., and in this way it is able to purify from its homologues. Perkin[2] gave some notice about the sublimation process. As to other methods of purification, alcohol and ether are generally used as solvents. Toluene is proposed by Liebermann[3] to remove purpurin. Then the author, with the intention to know the best condition for purifying the raw alizarin, find that toluene is the best solvent and that even with toluene it is very difficult to get pure alizarin, although recrystallizations are repeated; so he modified the Liebermann's method as follows:—

Two grams of E. Merck's dry alizarin is dissolved in 2 litres of sodium hydroxide (ca. 1/20 N.) and filtered without suction, lest the glutinous solution causes to choke the filter paper. If the concentration of sodium hydroxide solution is too strong, the solution will become very slushy and take long time to filter, though the volume is small. Into the filtrate a current of carbon dioxide is slowly passed so long as almost of bubbles disappear. The dark red solution thus obtained is filtered off and the precipitate, acidic sodium alizarate, is neutralized with ca. 1 N. hydrochloric acid very slowly. This precipitate, normal alizarin, is filtered with Buchner's funnel and once more repeated the above treatment. Then the precipitate is washed with water until no trace of chlorine-ion is present and recrystallized twice with 250 c.c. of pure toluene. Thus purified alizarin melts at 286–288.5°C. and now it is boiled with 500 c.c. of saturated alum solution for about one hour in order to remove the residual homologues, filtered off while hot. This treatment is repeated twice more and once more recrystallized with 250 c.c. of toluene and at last with 300 c.c. of pure alcohol to remove a trace of toluene. After dried at 100°C., it melts at 288.5–289.5°C. (uncor.).

Analytical Study of the Product. On the quantitative estimation of alizarin, Knecht and Hibbert[4] reported that the alcoholic solution of alizarin is reduced by the titanous trichloride. This is only one with regard to the method of estimation of alizarin; but this method is not applicable in this case. The author dissolved 0.0600 gr. of pure alizarin in 250 c.c. of toluene, i.e. 1/1000 mol solution.

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(1) *Ber.*, **13** (1880), 41.
(2) *J. Soc. Chem. Ind.*, **14** (1895), 1026.
(3) *Ber.*, **35** (1902), 1781.
(4) *J. Soc. Dyers Col.*, **31** (1905), 241.

And an aqueous solution of sodium aluminate is stocked for about one month in order to settle the insoluble matter as much as possible, then the mol concentration, 0.0372 Al, is determined by Lunge's method.[1]

These two solutions are poured into a well-stoppered bottle of a suitable capacity in a certain proportion and shaken for several hours at room temperature and then left to stand for a few hours. Now the supernatant toluene solution is pipetted out of the bottle and after adding certain volume of alkali, 1.16 N., compared with the standard alkali solution of alizarin colorimetrically, using Duboscq colorimeter.

The volumes of both reagents are recorded in Table 1. In this table, from A to G, each of them has too much amount of aluminate

Table 1.

No.	0.001-mol aliz. solution taken, in c.c.	Aluminate sol. taken		Colour of the upper layer after shakings.
		concentration in mol.	Volume in c.c.	
A	10	0.0372	10	colourless
B	5	0.0372	10	colourless
C	11	0.0372	10	colourless
D	10	0.0372	5	colourless
E	10	0.0372	1	colourless
F	10	0.0037	10	colourless
G	10	0.0037	5	colourless
H	10	0.0037	1	light yellow
I	10	0.00037	10	light yellow
J	10	0.00037	5	yellow
K	10	0.00037	1	yellow

for alizarin, because there is no alizarin remains in the upper layers. But in the last four (H~K), certain amount of alizarin remains in toluene even after shaking and the amount is determined by colorimetry, adding sodium hydroxide solution to obtain a bluish violet solution of sodium alizarate. These results are recorded in Table 2. Here, α-series, for example H_α, means the upper layer, i. e. the toluene solution of alizarin after the reaction is completed. And β-series means the 1/1000 mol toluene solution of alizarin, viz. standard solution.

(1) *Z. angew. Chem.* **3** (1890), 227, 293.

Table 2.

No.	Toluene sol. of alizarin, taken in c.c.	1.16 N. NaOH solution, added in c.c.	Colorimeter reading in mm.			
			No. of measurement			Average value, magnified.
			1	2	3	
H_α	5	10	28.2	20.7	16.6	10000
H_β	2	10	3.0	1.9	1.4	942
I_α	5	10	24.3	15.6	20.1	10000
I_β	1	10	6.7	4.3	5.8	2800
J_α	5	10	12.4	8.1	17.2	10000
J_β	1	10	19.0	12.0	26.5	15182
K_α	2	10	9.8	7.9	6.6	10000
K_β	1	10	17.0	13.8	11.6	17464

Now, if the equal volumes of both α- and β-series are used, the numerical values of β-series, referred to $\alpha = 10000$ as the standard, are calculated as follows:

$2 : 5 = X : 942$,

$X = 377$ for H_β, if the equal volume as H_α taken. In this way above values are collected as shown in Table 3.

Table 3.

No.	Relative value	Comparing with the original solution, the conc. of alizarin diminished to
H_α	10000	377/10000
H_β	377	
I_α	10000	560/10000
I_β	560	
J_α	10000	3037/10000
J_β	3036	
K_α	10000	8732/10000
K_β	8732	

Hence, the fractions in Table 3 mean the values showing the free alizarin uncombined with aluminate. Table 4 represents those combined with aluminate.

Table 4.

No.	The fractional values that reacted with the sodium aluminate
H_α	1—(377/10000) = 9623/10000
I_α	1—(560/10000) = 9440/10000
J_α	1—(3036/10000) = 6964/10000
K_α	1—(8732/10000) = 1268/10000

Table 5 shows actual volumes of the 1/1000 mol solutions.

Table 5.

No.	Alizarin solution in c.c.	Aluminate solution in c.c.
H_α	9.62	3.72
I_α	9.44	3.72
J_α	6.96	1.86
K_α	1.27	0.37

From this table one can get easily the ratio in mol, the alizarin to the aluminate, as follows, Table 6.

Table 6

No.	Ratio in mol (Alizarin/Aluminate)	Average value
H_α	962/372 = 2.6	
I_α	944/372 = 2.5	3.1
J_α	696/186 = 3.7	
K_α	127/ 37 = 3.4	

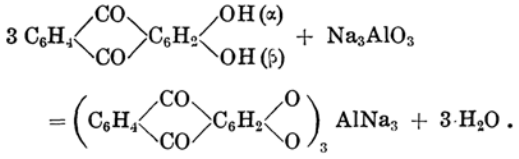
From these experiments, it is clear that the reaction, which takes place between the alizarin and the sodium aluminate, is not a kind of adsorption but true chemical reaction. Of course, there are some colloidal particles coexist and therefore between these colloidal substances and the reaction-product, sodium aluminium alizarate, certain adsorption may occur. On the whole, the reactions between alizarin and sodium aluminate are two kinds, the one is true chemical and the other of an adsorption.

The author expresses his hearty thanks to Prof. Dr. J. Inouye for the kind help in carrying out this research.

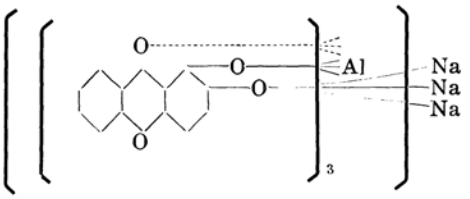
Summary.

1. The method of purification of alizarin is proposed.

2. A deep orange, hydrophile colloidal substance is produced when alizarin is added into an aqueous solution of sodium aluminate. The mechanism of the reaction may be as follows;



And the constitutional formula will be



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