

Reversed Phase Transfer Catalysis Used in the Synthesis of Red Pigments

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Reversed phase transfer catalysis (RPTC) method was applied in the synthesis of red pigments. The method consists in the transfer of the aryldiazonium cation, 4-nitrobenzenediazonium ($O_2N-C_6H_4-Na \equiv N^+$), from aqueous medium into organic phase (dichloroethane) in the form of a lipophilic ion pair $[O_2N-C_6H_4-Na \equiv N^+DS^-]$ by the catalyst used (sodium dodecylsulfate, Na^+DS^-). Azocoupling reaction, between 4-nitrobenzenediazonium chloride and arylamides of 3-hydroxy-2-naphthoic acid (Naphthols-AS, coupling components) takes place in organic phase. Through this unconventional method of synthesis the speed of reaction is increased and also a good purity of the synthesized compounds is obtained. The compounds were characterized by UV-VIS, FT-IR, and Mass Spectrometry.

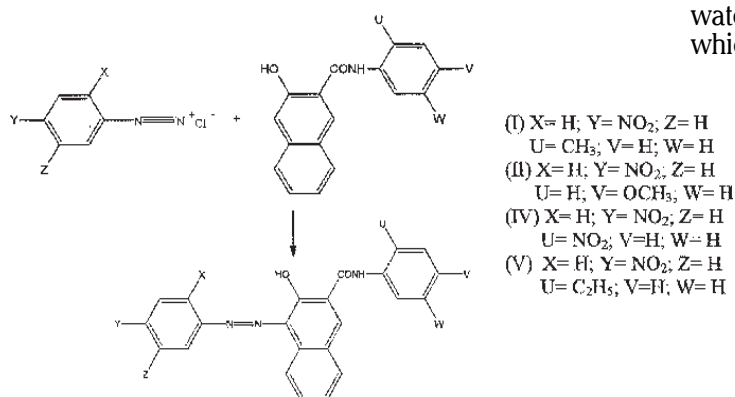
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Colour is an important and ubiquitous part of our everyday life and even since pre-historic times, colours, being inorganic or organic, they have had profound anthropological, psychological, aesthetic, functional and economic impact on society. The dyes are well known for their ability to absorb in UVIS (400-700nm) and due to this capacity they appear coloured, being widely used both in the textile and food industry [1-4]. Colourants are either dyes or pigments. Organic dyes are soluble substances mostly applied to various substrates from solution. A general characteristic of dyestuffs is their ability to provide colour in monomolecular disperse form solely by selective absorption of visible light. Organic pigments, on the other hand, are finely divided, coloured particulate solids which are practically insoluble in most solvents and in the media in which they are incorporated by adequate dispersion techniques. Organic pigments impart colour by selective absorption and/or scattering of visible light.

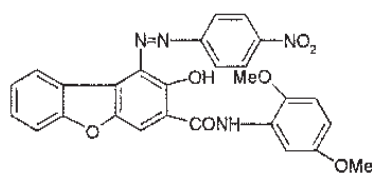
In the last few decades, organic pigments have experienced rapid growth becoming an industry of significant commercial potential. The use of organic pigments for different fields will highly increase in the next decades [5-7].

Developed and patented in 1911, the naphthol chemicals represent a large group of azo dyes and pigments (about 20% of all synthetic organic pigments available, over 50 pigments in the red category alone). Originally used as cotton dyes, they were soon launched as pigments and first used in artists' paints in the 1920's. The most important group for artists is the Naphthol-AS pigments.

The colour range is concentrated in the long wavelength end of the spectrum, including warm orange, scarlet, different reds, carmines, maroon, violet and brown [8-10]. Naphthols are non-toxic, often extremely saturated, and in watercolors are semitransparent and strongly staining pigments. The middle reds are especially brilliant: they are traditionally used to make lipstick. Lightfastness in watercolors varies from poor to very good, so it matters which specific pigments you choose [11,12].



Pigments I, II, IV and V



Pigment III

Scheme 1

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Technically significant Naphtol-AS pigments are therefore divided into two groups, according to the type of substituent grafted on the diazo-component structure:

- simple substituent, such as Cl, NO₂, CH₃ or OCH₃;
- sulfonamide groups and/or carbonamide groups.

In the latter case, more than one carbonamide group may be introduced through the coupling component [13,14].

The arylamides of o-hydroxy-arylcarboxylic acids (so called Naphthols-AS) are coupling components for the synthesis of water insoluble azoic dyes which are formed on the fiber, exhibiting also the character of pigments after dyeing. Obviously they can also be synthesized as pigments [15].

Pigments based on arylamides of AS-Naphthols type were obtained by azocoupling reactions in alcoholic alkaline solutions. The increased pH favors hydrolysis of amidic group. To avoid this side reaction pH must be near to neutral. Also in order to increase the solubility of arylamide the reaction temperature usually is high, around 60°C, which can lead to the degradation of the diazonium salt [16].

In this work we report the results obtained in synthesis of pigments by coupling 4-nitrobenzenediazonium chloride with arylamides of 3-hydroxy-2-naphthoic acids in reversed phase transfer catalysis method (scheme 1), using sodium dodecylsulfate (SDS) as a transfer catalyst for the diazonium ion.

Experimental part

Materials and methods

Solvents: dichloroethane, toluene, nitrobenzene (Chemopar Bucharest) were used without purification. Precursors: p-Nitroaniline, NaNO₂, HCl 37% were purchased from Aldrich and used as received. AS-Naphthols were synthesized in our laboratory. Catalyst: sodium dodecyl sulfate 95% was supplied by Sigma-Aldrich.

General procedure:

A mixture of 0.133 g (7.22x10⁻⁴ M) 4-nitrobenzenediazonium chloride compound (synthesised freshly) in 3 mL water, 0.1g (3.6x 10⁻⁴ M) 3-hydroxi-2-carboxylic acid 2-methyl-anilide in 15 mL dichloroethane and 0.01 g sodium dodecylsulfate (Na⁺DS⁻) as catalyst was vigorously stirred at room temperature. The color development was rapid and the reaction was finished when the coupling component was consumed. The reaction was monitored using an aryl-diazonium salt solution on filter paper. During the reaction the compounds precipitate and were isolated by filtration.

The molar ratio aryl-diazonium salt:coupling component is 2:1 and the catalyst quantity is maintained constant.

Spectra recording:

UV-VIS spectra were recorded on a CECIL CE 7200 Spectrophotometer using dimethylformamide solutions of the precursors and products.

FT-IR spectra were recorded on a Jasco FT-IR 4200 Spectrometer using KBr pellets.

The melting points were determined with Boetius apparatus.

Mass spectra were obtained using a mass spectrometer Esquire 6000 ESI (electrospray ionization) from Bruker-Daltonik. All the compounds were diluted before measurements; at 5 pmol/μl (each ml of solution contained 50 μL ammonia sol 25%). The introduction of the sample into the electrospray was directly made with a micro syringe. The solution was injected into the spray chamber by a Hamilton syringe, with a constant flow of 240 μL/h.

The API-ESI (Atmospheric Pressure Interface-Electrospray Ionization) generates ions, focuses and transports them into the ion trap mass analyzer. All the mass spectra were obtained in the positive and negative mode. For these compounds the negative mode offers better results than the positive mode. Moreover, at these concentrations it was possible to obtain MS² spectra.

Results and discussion

The term phase transfer catalysis (PTC) is first used in literature in 1947, and it becomes official in 1971 at Starks' proposal [17]. The fundamental works of Starks regarding the explanation of reaction mechanism and the possibilities of using this method, have led to increasing interest of the scientists, thus, in a relatively short period of time, hundreds of works treating this subject have been published [18].

The principle of phase transfer catalysis (PTC) is based on the ability of certain agent, the "phase transfer agent", to facilitate the transport of one reagent from one phase into another (immiscible) wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases. However, it is also necessary that the transferred species to be in an active state for effective phase transfer catalytic action, and the phase transfer agent to be regenerated during the organic reaction. PTC finds applications in a variety of reactions. Primary applications are in nucleophilic substitution reactions and in reactions in the presence of bases involving the deprotonation of moderately and weakly acidic organic compounds. Reactions carried out using PTC include oxidations, reductions, polymerizations, transition metal co-catalyzed reactions, synthesis of carbenes and further reactions of carbenes, addition reactions, condensations, and so on, which are often part of a multistep synthesis process for fine chemicals manufacture [19]. Besides the typical (normal) PTC reactions involving nucleophile reactants and cationic catalyst, this technique can be applied to reactions involving electrophile reagents and anionic catalyst. In "Reversed phase transfer catalysis" (RPTC) a cationic reactant from aqueous phase is continuously transferred into organic phase in the form of a lipophile ion pair with a non-nucleophile anion catalyst, and react with the second reactant in the organic phase [20]. This method is less used and the first time it was applied for the synthesis of Naphtol-AS pigments by us. The aryl-diazonium cations are relatively stable electrophile reagents in aqueous medium. Being weak electrophile agents they do not attack the usual anionic phase transfer catalyst. So the azocoupling reaction is an electrophile substitution suitable to "reversed phase transfer catalysis".

When a mixture of diazonium chloride in water, arylamide in organic solvent and sodium dodecylbenzenesulfonate as catalyst was vigorously stirred at 20°C the colour development was rapid and the reaction was finished when coupling component was consumed.

The influence of the water : dichloroethane and aryl-diazonium salt:coupling component ratio and upon the coupling reaction was tested. The one presented above, 3:15 ratio (water : dichloroethane, v/v), is the optimum one. Other organic phases were tried also: toluene and nitrobenzene.

In toluene the reaction proceeds with a lower rate. The formed dye is soluble in nitrobenzene, fact that makes the separation of the product difficult. The coupling reaction was also performed in a biphasic system, in the absence of sodium dodecylsulfate. The reaction mixture becomes

Table 1
THE CHARACTERISTICS OF OBTAINED PIGMENTS

Dye	X	Y	Z	U	V	W	Melting point, °C	λ , nm
I	H	NO ₂	H	CH ₃	H	H	196	505
II	H	NO ₂	H	H	OCH ₃	H	202	510
III	-	-	-	-	-	-	282	476
IV	H	NO ₂	H	NO ₂	H	H	208	524
V	H	NO ₂	H	C ₂ H ₅	H	H	198	521

gradually orange. At a molar ratio aryl-diazonium salt:coupling component 2:1 a dye of high purity and a yield of 98% is obtained, compared to the amount of AS-Naphthol (coupling component). The pigment **III** is out of series because this molecule has a ring of 5 atoms in comparison with the base structure, the compound is insoluble, yield is lower and the melting point higher. The purity of dyes was verified by HPLC and TLC on precoated Kieselgel plates using as eluent benzene: acetone 24:1, (I) $R_f = 0.68$; (II) $R_f = 0.72$; (III) $R_f = 0.78$; (IV) $R_f = 0.80$; (V) $R_f = 0.78$.

The synthesized dyes were characterized by m.p., UV-VIS, IR and Mass Spectroscopy. The melting points and the absorption maxima for respective dyes are presented in table 1.

All compounds were characterized by infrared spectroscopy. In figure 1 is presented a IR spectrum for red pigment (I) obtained by this unconventional method.

In the IR spectrum of the obtained pigments there are intense absorption bands at $\nu_{(N=N)} = 1454 \text{ cm}^{-1}$, $\nu_{(N=N)} = 1502 \text{ cm}^{-1}$ characteristic for the azo group, at $\nu_{(C=O)} = 1680 \text{ cm}^{-1}$ characteristic for the carbonamidic group, at $\nu_{(O-H)} = 3629 \text{ cm}^{-1}$, at $\nu_{(C-N)} = 1342 \text{ cm}^{-1}$, $\nu_{(aromatic-CH_3)} = 3049 \text{ cm}^{-1}$, at $\nu_{(aromatic-NO_2)} = 1550 \text{ cm}^{-1}$ [21, 22].

Mass spectra were obtained in the positive and negative mode. Negative ion mass spectra showed more intense peaks than the positive ion mass spectra. In figure 2 it is shown the negative ion mass spectrum of pigment **II**, in

which the fragmentation of the dye, by eliminating the negative ions is presented as follows: $m/z=234.0$ [M,-B-NO]; $m/z=264.0$ [M,-B]; $m/z=292.1$ [M-B]; $m/z=398.1$ [M-NO₂]; $m/z=413.1$ [M-NO]; $m/z=426.0$ [M-O]. The value $m/z=442.0$ [M] corresponds to the molecular peak of pigment **II**. In figure 3 is observed the fragmentation of pigment **III** in a different way from that of pigment **II**, so: $m/z=274.9$ [M-B-OH]; $m/z=286.0$ [M-A-NO₂]; $m/z=301.2$ [M-B-O]; $m/z=421.3$ [M-NO₂-OH]; $m/z=456.3$ [M-N₂]; $m/z=484.0$ [M]. This distinction between the two spectra (fig. 2 and fig.3) is due to the different structures, which involve different polar character of the two compounds. In figure 4 it can be seen a clear resemblance between mass spectra of pigments **II** and **IV**: $m/z=306.2$ [M-C]; $m/z=337.2$ [M-2NO₂]; $m/z=381.1$ [M-NO₂-NO]; $m/z=410.0$ [M-NO₂]; $m/z=440.0$ [M-OH]; $m/z=456.0$ [M]. A different aspect in the mass spectrum of pigment **IV** compared with pigment **II** is next: $m/z=306.2$ [M-C], which justify the presence of two groups NO₂ in the molecule, groups with a strong electronegative character which favours this scission. Mass spectrum of the pigment **III** has following result: $m/z=218$ [M,-A-NO₂]; $m/z=234$ [M,-A-OH]; $m/z=265$ [M,-A]; $m/z=382$ [M,-NO]; $m/z=394.1$ [M-NO₂]; $m/z=412.1$ [M]; $m/z=440$ [M]. These results confirm obtaining the desired compounds [23,24].

Rufer [25] shown that the azocoupling reaction can be accelerated in water by micelle catalysis, using an anionic surfactant. The mechanism is clearly different to that

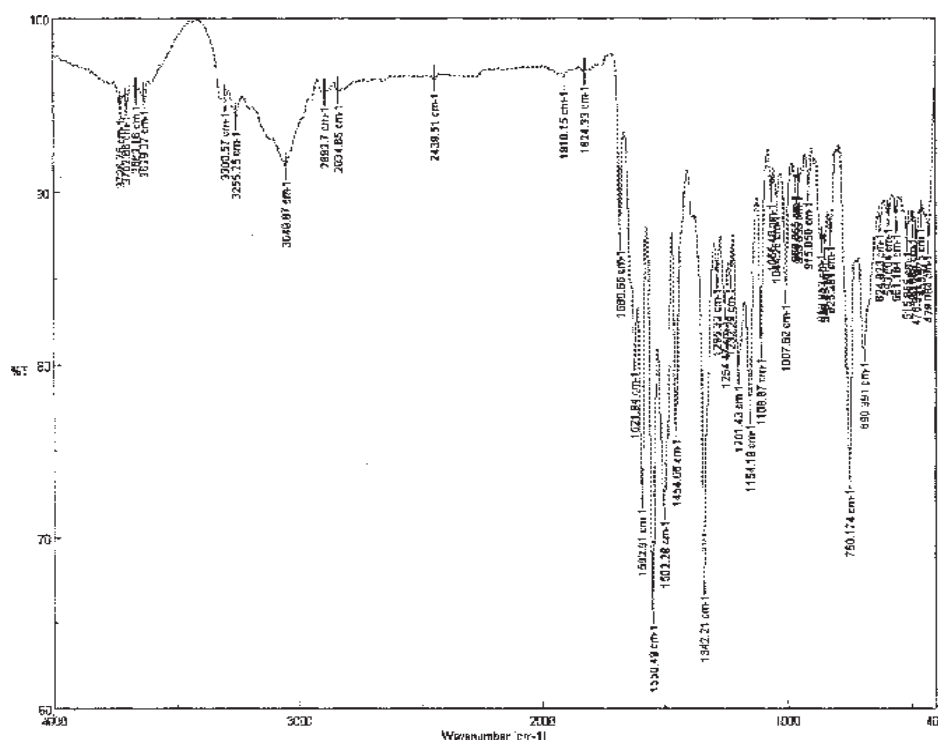


Fig. 1. The IR spectrum for red pigment (I)

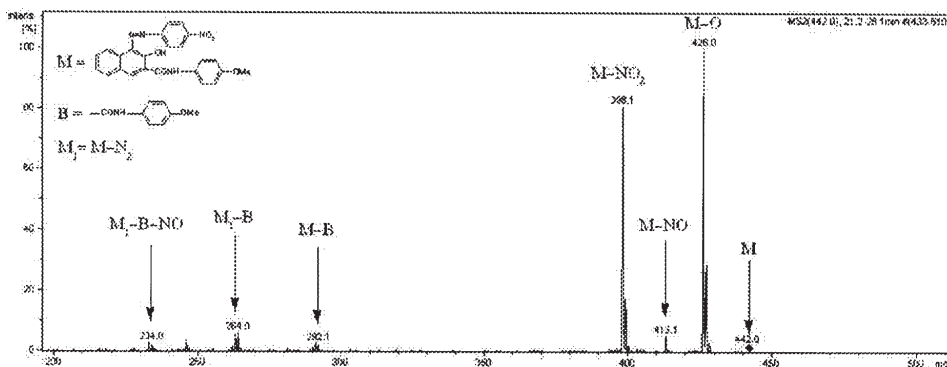


Fig. 2. The negative ion mass spectra of pigment II

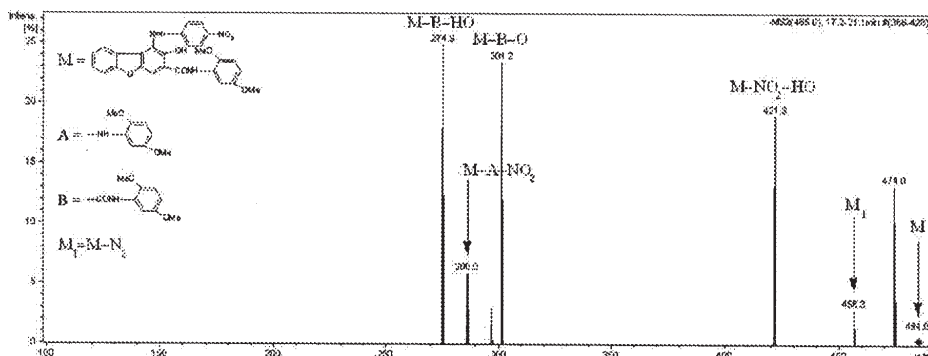


Fig. 3. The negative ion mass spectra of pigment III

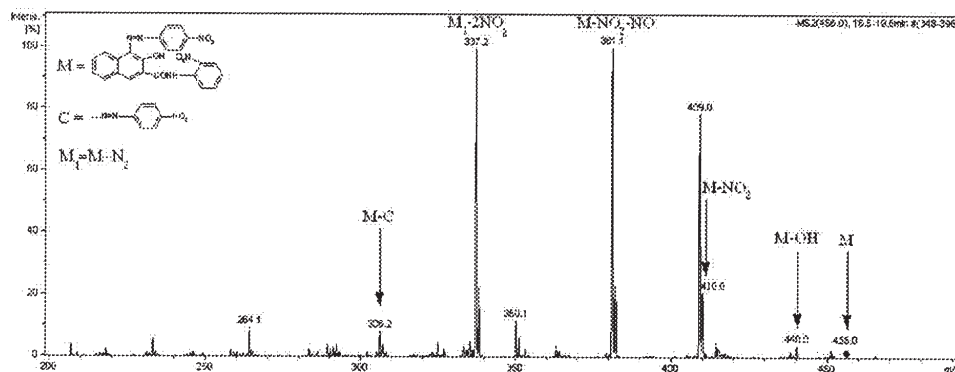


Fig. 4. The negative ion mass spectra of pigment IV

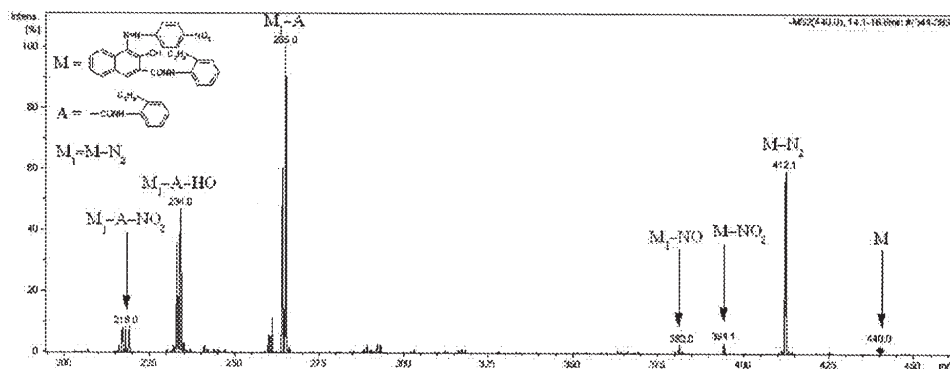


Fig. 5. The negative ion mass spectra of pigment V

operating in the present case, and acceleration is due to an enhanced local concentration effect within micelles. The micellar role of anionic surfactants used as catalysts, over the critical micellar concentration (CMC) was not studied. The interphase transport of cations, probably, takes place by forming lipophile ions pairs with surfactant anions.

Sodium dodecylsulfate ($\text{Na}^+ \text{DS}^-$) was used as phase transfer catalysts and it may be assumed that the dodecyl sulfate anion associates with the aryl-diazonium ion and transports it into organic phase.

This mechanism can be influenced by:

- partition of the transport agent, the interphasic catalyst, between aqueous phase and organic phase;

- catalyst structure (and eventually its aggregate state), as well as the reactivity of the ionic pair in the weakly polarized medium of the organic solvent;

- different behaviour of the present species in phase transfer catalysis conditions compared to other reaction conditions;

- implicated kinetics;

- the hydration state of anions in organic phase.

The reactivity of the aryl-diazonium cation is thereby increased by minimization of solvent interactions, and coupling reaction takes place [26].

The azocoupling reaction in a position to the OH group, practically nonionised, took place with a surprisingly high speed and this may be explained by the fact that the reaction partners are low solvated in organic medium. In

presented reaction conditions (pH - acid in aqueous medium) the diazonium salt is in the most reactive form for electrophile substitution reaction. This fact contributes to high rate of coupling. Diazonium salt, being stable in acidic medium, the side reactions are negligible and the obtained dyes had high purity. The purity of dyes was verified by TLC. The reaction temperature was room temperature for RPTC reactions, comparative with that for classical procedures at 60°C. This also reduces the side reactions and the reaction time, which was of two hours, while by the classical method was 5-6 h.

Conclusions

Reversed phase transfer catalysis (RPTC) was applied in synthesis of Pigments Red. Using this method the reaction rate is increased, the reaction time is decreased and high purity compounds are obtained. With increasing of nucleophilic character of coupling components increase their reactivity and yield.

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