Preparation of Permanent Red 24 Nanoparticle by Oil in Water Microemulsion

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ABSTRACT: *Permanent red 24 (1-(2,4-Dinitro-phenylazo)-naphthalen-2-ol) is a family member of azo dyes. Azo dyes have so many industrial applications. In this study, permanent red 24 nano pigments were prepared by microemulsion as a novel method. The effects of different experimental parameters for nano pigment preparation were studied. The investigated parameter include surfactant nature, solvent, surfactant, cosurfactant, and pigment percentage in microemulsion formulation. Optimal formulation determined for nano pigment preparation. Performing the process under the optimal formulation leads to the production of nano pigment with an average size of about 85 nm. The nano pigment was characterized by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS). The DLS measurements confirm TEM analysis.*

KEYWORDS: *Permanent red 24; Microemulsion, Nanoparticle; Organic; Surfactant.*

INTRODUCTION

In chemistry research, azo dyes considered as an important dye groups due to their versetile applications such as color filters [1] dye sensitized solar cells [2], biosensors [3], textile, paper. Also they have desirable properties such as wide colour range, good fastness properties, and tinctorial strength (colour density). Investigations on the functionalized azo dyes, based on heterocycles and aromatics, have made significant progresses on dye chemistry in recent years[4,5]. One of the intersting fields of chemistry is the study of color nanoparticles and nanopigments. They have different properties than micronized color and pigments. Homogeneity, light fastness, high-temperature stability, migration fastness are some desirable characteristic of color and pigment nanomaterials. [6]. Nanopigment and nanocolour have versetile applications in the field of bioanalysis, photocatalysis, photonic, and organic light-emitting diode, medicine, ink and textile industries [7-9]. Academic studies investigate organic nanoparticles synthesis with different methods such as grinding,

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crystallization, wet and jet milling, supercritical fluids, spray freezing into liquid nitrogen, and spray drying[10-13]. These methods have so many shortcomings such as difficulty in controlling the particle size, broad size distribution of particles, requirement of high temperature for solvent evaporation, and limitations for scale up and safe processing [14-16]. microemulsion is one of the known method for nanoparticle synthesis[17-21]. These systems are optically transparent, thermodynamically stable and easily manufactured, consisting of nano-sized miclles for the preparation of nano-particles[22-23]. Although the preparation of inorganic nanoparticles in microemulsions is already widespread[24-25], but academic research in organic nanoparticles by microemulsion method is not well developed.

In this study, in continues our investigation about organic nanoparticle preparation by microemulsion method[26,27], permanent red 24 nanopigment has been synthesized. All factors contribute microemulsion preparation, investigated and discussed. The moleqular structure of permanent red 24 are presented in Fig. 1.

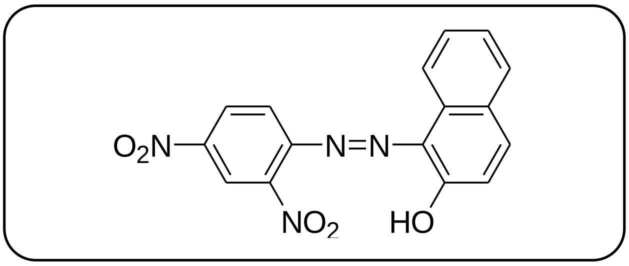

Fig. 1: Molecular structure of permanent red 24.

EXPERIMENTAL SECTION

Materials and Instruments

Permanent red 24 purchased from Aagile Labs Division of Tyger Scientific. All chemicals were purchased from Merck and Sigma-Aldrich. All solvents and other chemicals were reagent grade and used without further purification. Freezing have been done by refrigerator -80 °C. Drying process was carried out using a Christ lyophilizer (model4-2α). Size and shape of nanoparticles were observed by transmission electron microscope (TEM, Philips-CM 120) operated at 100 keV.

Preparation of permanent red 24 nanopigments

Typical procedure of microemulsion preparation: in the first step in order to solvent preparation, red 24 pigment (0.07 g) was dissolved in n-butyl acetate (2.5 g), then surfactant (1.5 g), co-surfactant (1g) and water (5g) were added and stirred manually. In the second step, the microemulsion suspension was freeze for 24 hr. The frozen suspension was lyophilized. In the lyophilizing step all of the solvent was evaporated from the frozen microemulsion. The resultant solid is a mixture of the surfactant and nanopigment. The surfactant was separated from the nanopigment by washing the mixture four times with water as follows: deionized water (100 mL) was added to the powder (1 g) obtained from the lyophilization step. The mixture was stirred manually until all of the surfactant had dissolved in the water**.** Ultimately by centrifuging the suspension, all of the nanopigment was precipitated**.** The water was decanted, and the nanopigment was dried at room temperature.

RESULT AND DUSUSSION

Influence of the components in microemulsion preparation

In order to preparation limpid and thermodynamically stable microemulsion, different experimental conditions applied. In microemulsions formulation, combination of two immiscible phases (water and oil), surfactant molecules cause the formation a monolayer at the interface between the oil and water, with the hydrophilic head groups in the aqueous phase and the hydrophobic tails of the surfactant molecules dissolved in the oil phase. Therefore proper choose of surfactant is essential; therefore three different Surfactant Include Anionic (SDS), cationic (CTAB) and nonionic (Tween 80) used. Also it is notable in ternary systems such as microemulsions, where two immiscible phases (water and oil) are present with a surfactant, one of the most important key is proper choose of organic phase. Application of suitable organic phase cause proper microemulsion formation. In order to study this factor properly, effect of four different red 24 pigment solvents of as organic phase applied. THF, dichloromethane, ethyl acetate and n- butyl acetate have been used. Formulations contain n-butyl acetate as organic solvent remained transparent. The observing of these phenomena may be rooted mainly due to low miscibility of n-butyl acetate in water rather than other solvents (THF, hexane and ethyl acetate). Also n-butyl acetate has higher boiling point (126 ˚C). All formulation of microemulsion contains different ingredient percentage presented in Table 1.

Table 1: Effect of surfactant nature and component percentage in microemulsion formulation.

Entry	Surfactant	Water (%)	Solvent (%)	(Surfactant+ cosurfactant) (%)	result
1	SDS	50	15	35	+
2	SDS	50	25	25	+
3	SDS	50	35	15	-
4	Tween80	50	15	35	+
5	Tween80	50	25	25	+
6	Tween80	50	35	15	-
7	CTAB	50	15	35	+
8	CTAB	50	25	25	+
9	CTAB	50	35	15	-

Table 2: Effect of surfactant and cosurfactant percentage in microemulsion formulation.

Entry	Organicphase (%)	surfactant	Alcohol (%)	Surfactant (%)	result
1	25	CTAB	5	20	+
2	25	CTAB	10	15	+
3	25	CTAB	15	10	-
4	25	CTAB	20	5	-
5	25	Tween 80	5	20	+
6	25	Tween 80	10	15	+
7	25	Tween 80	15	10	-
8	25	Tween 80	20	5	-
9	25	SDS	5	20	+
10	25	SDS	10	15	+
11	25	SDS	15	10	-
12	25	SDS	20	5	-

As shown in Table 1, three experimental parameters, including the surfactant nature, solvent and (surfactant + cosurfactant) percent studied at three different levels. Results indicated limpid microemulsion obtained by formulation contained 15-25 % solvent and 35-25 % (surfactant+ cosurfactant) (Entry 1,2,7,8 and 9).

To find formulation contain most amount of solvent; formulation contained solvent 25% and (surfactant+ cosurfactant) 25% selected. For more elucidation, effect of alcohol and surfactant percentage studied separately and result presented in Table 2. It indicates formulations contain 15-20% of surfactant and 5-10% alcohol were limpid and stable (entry1, 2, 5, 6, 10 and 11).

In the final step, pigment percentage effect in solvent investigated. Therefore different microemulsion includes water 50 %, surfactant 15%, alcohol 10%, solvent 25 % and by different pigment percentage prepared. All formulations presented in Table 3. Also three surfactants for all formulation applied. As result just microemulsion by application CTAB as surfactant was limpid and stable. Observation these phenomena may be due to pigment nature and the presence of NO_2 groups in pigment structure.

Table 3: Effect of pigment percentage in microemulsion formulation.

Entry	Surfactant	N-butylacetate (%)	Pigment (%)	result
1	CTAB	80	20	-
2	CTAB	85	15	-
3	CTAB	90	10	-
4	CTAB	95	5	-
5	CTAB	97	3	+
6	CTAB	98	2	+
7	Tween80	80	20	-
8	Tween80	85	15	-
9	Tween80	90	10	-
10	Tween80	95	5	-
11	Tween80	97	3	-
12	Tween80	98	2	-
13	SDS	80	20	-
14	SDS	85	15	-
15	SDS	90	10	-
16	SDS	95	5	-
17	SDS	97	3	-
18	SDS	98	2	-

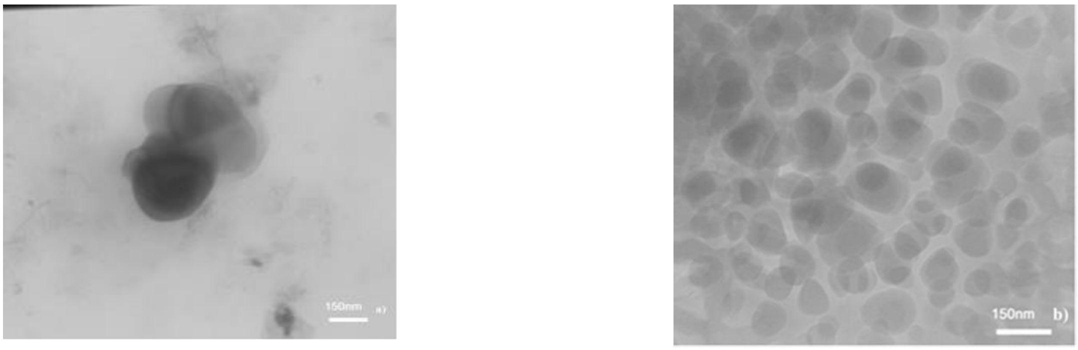

Fig.2 TEM image of permanent red 24 nano particle after separation from CTAB a) formulation contain 3% pigment b) formulation contain 2% pigment

Preparation of permanent red 24 nanoparticles under the optimum conditions of the microemulsion method

In order to decrease surfactant percentage and made a formulation contain most amount of pigment, tow microemulsion formulation in optimum condition chose and include: water 50%, solvent 25% has been loaded by 2 and 3% pigment, CTAB 15% and 2-propanol 10%.

Characterization of permanent red 24 nanopigments by TEM

In optimum conditions, permanent red 24 nano particle observed by TEM and images are presented in Fig. 1. This image indicate pigment particles in formulation contain 3% pigment, size of particle is 200 nm and in the formulation contain 2% pigment average size of particle is 85 nm.

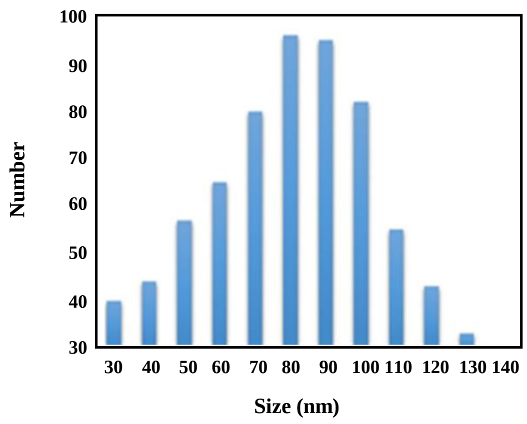

Fig. 3: Number distribution of nanopigment.

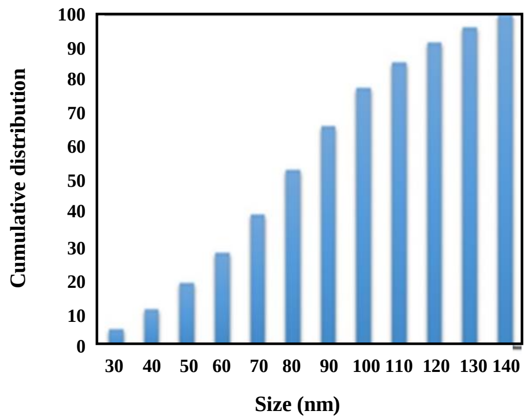

Fig. 4: Cumulative distribution of nanopigment.

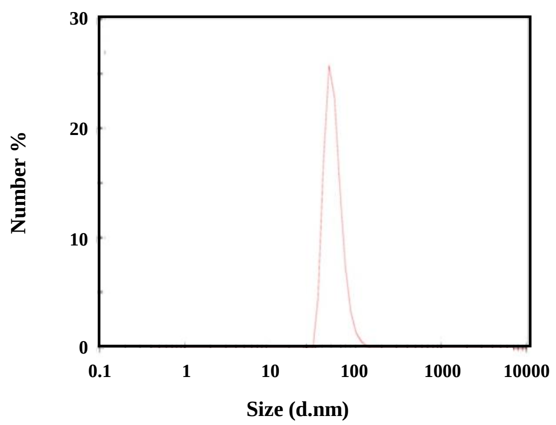

Fig. 5: DLS curve of nanopigment after separation from CTAB.

Almost all particles have spherical morphology. In order to visualize particle size distribution, Particle size distribution diagram of optimum sample is present in Fig. 3 and cumulative distribution diagram of particle size is present in Fig. 4.

Characterization of nanopigment by DLS

One analysis to investigation nanopigment in solution after surfactant separation is dynamic light scattering (DLS) apparatus. Fig. 5 represents DLS curves of Permanent red 24 nanoparticles in optimum condition. As Fig. 5 shows, curve is mono-modal fairly sharp. It indicates nanopigments obtain from microemulsion are mono-disperse and almost uniform. This analysis confirms that the synthesis of Permanent red 24 by oil in water microemulsion had been completely successful. Also curve indicate the average size of particle is around 85 nm. By the way, the DLS measurements confirm TEM analysis.

CONCLUSIONS

This study describes an interesting scientific idea of preparing permanent red 24 nano particle by oil in water microemulsion. Different parameters such as surfactant nature, solvent, surfactant, alcohol and pigment percentage in microemulsion formulation investigated. Result indicated optimum microemulsion formulation contain: (n-butylacetate 25%, permanent red 24 2%, 2-propanol 10%, CTAB 15% and water 50%). After separating pigment particles from surfactant, spherical permanent red 24 nanopigments with an average diameter of 85 nm obtained as shown in Fig. 2. Nano particles have homogenous (small) size distribution based on the TEM images and DLS analysis.

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