



An insight into the solvent effect on photo-, solvato-chromism of spiropyran through the perspective of intermolecular interactions



Weiguo Tian, Jintao Tian*

Institute of Materials Science and Engineering, Ocean University of China, Songling Road 238, Qingdao 266100, People's Republic of China

ARTICLE INFO

Article history:

Received 4 December 2013

Received in revised form

16 January 2014

Accepted 24 January 2014

Available online 6 February 2014

Keywords:

Spiropyran

Photochromism

Solvatochromism

Hansen solubility parameter

Intermolecular interactions

Kinetics

ABSTRACT

The solvent effect on photochromism and solvatochromism of the SP (1'-ethyl-3', 3'-dimethyl-6-nitrospiro [chromene-2, 2'-indoline]) is investigated in details. The photochromic phenomena indicate that the change of solvents can reverse the thermodynamic equilibrium between the ring-close Spiropyran and ring-open Merocyanine. Therefore, a more appropriate definition is suggested to emphasize the thermodynamic nature of the positive and negative photochromism; furthermore, a generalized definition of chromism is raised as a reference. Hansen solubility parameter is originally employed to analyze the roles of different intermolecular interactions in the solvatochromism of SP in diverse solvents. The kinetics of spiropyran in nonpolar solvents exhibits stepwise first order of reaction that does not follow the regular situation.

© 2014 Published by Elsevier Ltd.

1. Introduction

As a typical bi-stable molecular system, spiropyrans can reversibly convert between two the colorless ring-close form SP and the colored ring-open form MC (Merocyanine). Such conversion can be triggered by several external stimulants, for instance electromagnetic irradiation, solvents, temperature and pH, etc. Correspondingly, the material exhibits photochromism [1], solvatochromism [2], thermochromism [3], and acidochromism [4]. Inspired by the switchable characteristic between the two forms with different remarkable properties, e.g. absorption spectra, dipole moment, dielectric constant, geometrical structure, and coordination property etc., abundant valuable materials have been fabricated for specific applications, such as optical data storage [5], molecule switches [6], logic gates [7], sensors [8], bio-imaging [9], controlled release [10], controllable wettability [11] and so on.

The term “photochromism” was first propounded by Hirshberg in 1950s [12]. It is simply defined as a reversible conversion of a chemical species induced in one or both direction by absorption of electromagnetic irradiation between two forms (A and B) with different absorption spectra and other physical properties. The

reversibility is the main criterion for photochromism, i.e., the photogenerated species must be capable of being reversed to its original state either thermally or by subsequent irradiation with specific wavelength. In general, the isomerization process of A to B if A is colorless or pale and B is colored ($\lambda_{\max, B} > \lambda_{\max, A}$) is referred to the positive photochromism, per contra, the negative photochromism [13]. Although the photochromism of spiropyrans has been intensively investigated since the pioneering work by Fisher and Hirshberg et al. [14], some issues are still debatable and worthy of further discussion. Typically, the factors leading to a better stabilization of the MC forms, such as high polar environment [15], hydrogen bonding [16], polymer matrix [17], conjunction with macromolecules [18] and complexation with metal ions [19], can force spiropyrans to behave in negative photochromism. Experimentally, some spiropyrans with groups like free hydroxyl, carboxyl, or nitro groups, also exhibit negative photochromism because of a better stability of the zwitterionic MC form in most solvents. Based on these facts, such term “negative photochromic compound” [20] comes out as if such spiropyran can only perform negative photochromism. However, a few observations against this concept have been reported. The proportion of hydrophilic/hydrophobic constituents in environment [21], or the polarity of media [22] can switch the process between positive and negative photochromism for same species. In other words, the concept “positive or negative photochromic compound” from an isolated standpoint of molecular

* Corresponding author. Tel.: +86 532 66781690; fax: +86 532 66781320.
E-mail address: jttian@ouc.edu.cn (J. Tian).

structures without a further concern about environmental effects might be inappropriate. In this article, the photochromism of the SP (1'-ethyl-3', 3'-dimethyl-6-nitrospiro [chromene-2, 2'-indoline]) in different solvents with distinct polarity were re-evaluated, and our observations confirmed our statements.

Solvatochromism is another meaningful property of spiroopyrans and can produce plenty of useful applications [23]. The term “solvatochromism” is defined to describe the reversible alteration of the ultraviolet–visible (UV–Vis) absorption spectroscopic properties (position, intensity and band shape) of a chemical species induced by solvents, specifically, the polarity of solvents²⁴. It has been verified experimentally that only those molecules with π -electron conjugated system, such as MC, can exhibit solvatochromism [24]. Hence, solvatochromism is a property of the ring-open MC form. Usually, a bathochromic (or red) shift with increasing solvents polarity is called “positive solvatochromism” or the “negative solvatochromism” in contrast. It is clear that various intermolecular interactions are involved in solvatochromism, such as dispersion force, hydrogen bonding, and polarity, etc. and many parameters or scales have been suggested to estimate the solvents effects on solvatochromism. However, what explicit roles these interactions play in solvatochromism is still uncertain. In this article, in order to figure out the effect of solvents on solvatochromism of spiroopyran, more than twenty kinds of solvents have been investigated in details. Furthermore, Hansen solubility parameter is originally exploited to estimate the solvatochromism of the SP and it works well. Besides the photochromism and solvatochromism, the special kinetic characteristics of the SP dissolved in solvents at the ends of the polarity scale also interest us greatly for a further discussion.

2. Experimental

2.1. The synthesis of the SP (1'-ethyl-3', 3'-dimethyl-6-nitrospiro [chromene-2, 2'-indoline])

The SP was synthesized according to the literature [25]. All the reagents and solvents were purchased commercially (Aldrich) and used without further purification. The ¹HNMR spectra were recorded with an NMR spectrometer (Bruker Avance III 600). The FTIR spectra were taken with the Bruker Tensor 27 spectrometer.

2.00 g, 0.00635 mol indolium iodide (**1**) and 0.60 g, 0.0070 mol piperidine were dissolved in 15 mL distilled ethanol and stirred for 1 h. Then 1.1 g, 0.0066 mol 5-nitrobenzaldehyde (**2**) was added into the solution and the mixture was refluxed for 3 h. About half of the solvent was removed by vacuum evaporation. After cooling to room temperature, the precipitate was obtained by filtration. The solid product was further purified via recrystallization in ethanol for twice. Finally, the pale cyan powder (0.10 g, 4.7%) of the product was obtained. It was characterized by FTIR (Fig. S1) and ¹HNMR (Fig. S2) spectra. FTIR (Sample/KBr = 1%, the assignments of the peaks, cm⁻¹; Ar-H, 3060; -CH₃, 2960, 2866, 1454, 1378; -CH₂-, 2934, 1334; -C=C-, 1650; Ar-C, 1605, 1570, 1485; -C-O-, 1025). ¹HNMR (CDCl₃, 5 mg/7 ml, δ , ppm; 1.17, m, 6H, -CH₃ × 2; 1.29, s, 3H, -CH₃; 3.17–3.24, 3.30–3.35, m, 2H, N-CH₂; 5.84, s, 1H, 5.86, s, 1H, -CH=C-; 6.58–7.2, m, 4H, Ar-H in indoline moiety; 7.99–8.02, m, 3H, Ar-H in chromine moiety).

2.2. The absorption spectra analysis of the MC

All the measurements were carried out at ambient temperature (25 °C) and the concentration of the spiroopyran solution was set at 10⁻³ mol/L. The UV–Vis absorption spectra were recorded with U-3010 spectrophotometer (Hitachi). The intensity of UV irradiation source was 200 mV/cm² and the luminous flux of the white light

source was 200 Lumens. The irradiation sources were fixed right above the samples and the distance was set at 15 cm.

3. Results and discussion

3.1. The thermodynamic nature of positive and negative photochromism

The photochromic properties of the SP in different solvents are shown in Fig. 1. The spiroopyran solutions exhibit positive photochromism in non-polar solvents like hexane (SP₃) and petroleum ether (SP₄). The obtained stable solutions in darkness are colorless and it can convert into a colored state after ultraviolet irradiation (SP → MC). On the contrary, the solutions display negative photochromism in polar solvents such as methanol (MC₁) and ethanol (MC₂), and the original states in darkness are colored and can transform into colorless forms under visible light irradiation (MC → SP). It indicates that same spiroopyran compound may exist in either SP form or MC form that depends on the solvent polarity, consequently, behaves with opposite photochromism. Therefore, the concepts like positive or negative photochromic compound are quite inaccurate. Several basic standpoints should be clearly declared. Firstly, the “same spiroopyran compound” in context before is inherited from a conventional concept. The SP and the MC definitely are not the same chemical species because there is a cleavage of C–O bond during the isomerization process. Obviously, it also cannot be treated as solvatochromism since only the physical interactions are involved in solvatochromism [26]. Another should be noted is that both the colored and colorless solutions are the mixtures of SP and MC forms [27] with giant differences in proportion, i.e., the amount of the MC in the colorless solution is by no means zero. Herein, it is believed that the positive or negative photochromism of spiroopyrans should be the consequence of the competition between the two forms in isomerization. The validity of such supposition must be built on the foundation of conversion loops of spiroopyran in Fig. 1.

- (I). When the SP powder was dissolved in diverse solvents and then directly stored in darkness without any irradiation for a

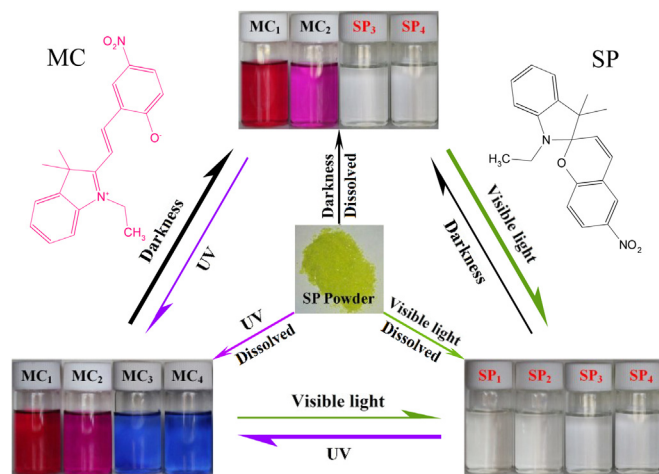


Fig. 1. The photochromic conversion loops of the SP dissolved in different solvents induced by different irradiation conditions: UV irradiation (365 nm, purple arrows), visible light irradiation (green arrows), and storage in darkness (black arrows). The solvents exploited in solutions from 1 to 4 in subscript are methanol, ethanol, *n*-hexane and petroleum ether with a decrement in polarity, respectively. The concentration of all solutions is set at 10⁻³ M. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/176240>

Download Persian Version:

<https://daneshyari.com/article/176240>

[Daneshyari.com](https://daneshyari.com)