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Determination of aliphatic amines using fluorescence intensity of 4-methyl umbelliferone

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Abstract

Effect of aliphatic amines and their concentration on fluorescence intensity of 4-methyl umbelliferone (4-MU) one of coumarin derivative were investigated. This compound has blue light emission under UV lamp in methanolic solution. Spectral investigation of 4-MU solution containing amine compounds showed lower intensity at 350–410 nm (quenching region) and higher intensity at 430–500 nm (enhancing region) as compared to pure methanolic solution of 4-MU. Fluorescence intensity at isoemitting point was independent from concentration of amines. The variation of fluorescence intensity could be used for determination of aliphatic amines in both quenching and enhancing region. Linear ranges for determination of amines in the quenching region were obtained from Stern-Volmer diagram of 4-MU. Determination of amines at fluorescence enhancing region using inverse fluorescence intensity against inverse amine concentration (bireciprocal plot) were investigated and related equations was also proposed.

Keywords: Aliphatic amines; 4-Methyl umbelliferone; Fluorescence quenching; Fluorescence enhancing; Stern-Volmer plot

1. Introduction

Coumarines are compounds originating from the nature that can be used in industry, they are broadly used in cosmetics, in food and drinks as a flavouring. They occur in ethereal oils of many plants, e.g. cinnamon (*Cinnamonum zeylanicum*). Coumarins owe their class name to coumarou, the vernacular name of thetonka bean (*Dipteryx odorata*), from which coumarin itself, was isolated in 1820 [1]. Coumarin derivatives are hetrocyclic compounds containing oxygen atom and carbonyl group. Most of them have a very efficient fluorescing ability. The photophysical properties of these compounds depend on their nature and position of a substituent group in the parent molecule and also change due to a change in the surrounding media. Coumarin compounds are widely investigated due to their importance as laser dyes, as non-linear optical chromophores and as excellent probe to study of solvation dynamics in the homogeneous solutions as well as organized media [2–8].The numerous coumarin heterodimers were synthesized and explored the possibility of their applications as laser dyes [9] as organic scintillators [10] and as triplet sensitizers [11,12].

In a series of works effect of solvents, substituents and temperature on the various photophysical properties of coumarin compounds were reported [13–16]. The biological activity of coumarin and more complex related derivatives appears to be based on the coumarin nucleus [17–19]. Biological effects observed include anti-bacterial [20], anti-thrombotic, vasodilatory [21] and anti-HIV agent [22].

Umbelliferone or 7-hydroxy coumarin is one of the most important members of coumarin families. Umbelliferone and its methyl derivatives can be found in some of the *Umbellifera* plant family but the main source of these compounds is a plant named *Ferula galbaoferula* and is found in a vast area in Damavand and Alborz in Iran. The chemical structure of 4-methyl umbelliferone is shown in Fig. 1.

2. Experimental

2.1. Reagents

All chemical reagents were purchased from Fluka (Buches, switzerland). These reagents were 4-methyl umbelliferone (β),

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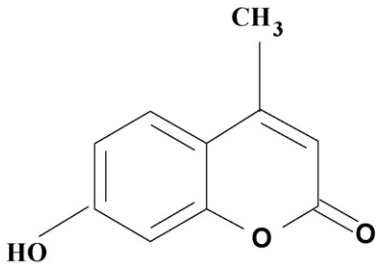

Fig. 1. The chemical structure of 4-methyl umbelliferone.

butyl amine, dibutyl amine, ethylamine (70% in water), diethyl amine, triethyl amine, methylamine (40% in water), isopropyl amine, α-methyl benzyl amine, ammonia (25% in water), tetramethyl ammonium hydroxide (25% in water) and HPLC grade methanol for preparing of 4-methyl umbelliferone solution.

2.2. Apparatus

The fluorescence spectrums were recorded using a spectrofluorimeter LS-50B Perkin-Elmer (Beaconsfield, UK). The software used to record fluorescence spectrum was FL-winlab. Experiments were carried out at ambient temperature 28 °C with magnetic stirring in the fluorimeter cell.

2.3. Procedure

Ten solutions containing different aliphatic amines with concentration of 1, 10^{-1}, 10^{-2}, 5×10^{-2}, 10^{-3} mol/l were prepared. Fluorimeter cell (1 cm) was filled with 2 ml 10^{-5} mol/l 4-MU in methanol. To investigate, effect of amines on the fluorescence intensity of 4-MU, 100–250 μl of amine solutions were added to 2 ml of 10^{-5} mol/l of 4-MU to get final concentration of amines in range of (4.97×10^{-5} to 5.27×10^{-2} mol/l in 4-MU solution).

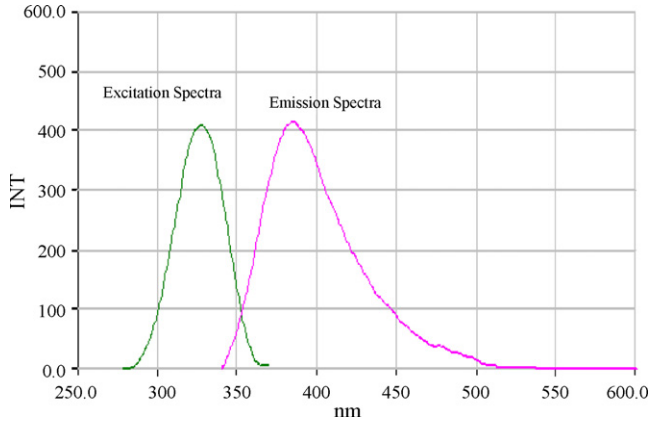

Fig. 2. Excitation and emission spectra of 4-methyl umbelliferone in methanol.

The excitation monochromator was set at 329 nm. The emission monochromator were set at 385 and 450 nm in the absence and presence of amines, respectively. The excitation and emission spectra are shown in Fig. 2.

3. Results and discussions

In preliminary experiments, it was found that the addition of amine to 4-MU solution results in an intense blue fluorescent under UV lamp. The fluorescence intensity of 4-MU varies with variation of concentration of amine. The typical fluorescence spectrum of 4-MU containing variable amounts of isopropyl amine in methanol, is shown in Fig. 3. This figure shows a wavelength (isoemission point) which is independent of amine concentration. In protic solvent such as methanol, especially under UV radiation, 4-MU dissociate into hydrogen ion and its anion. The concentration of anion is related to the concentration of amine. The fluorescence intensity in the region of 350–410 nm and 430–500 nm are due to the neutral and anion forms of 4-MU,

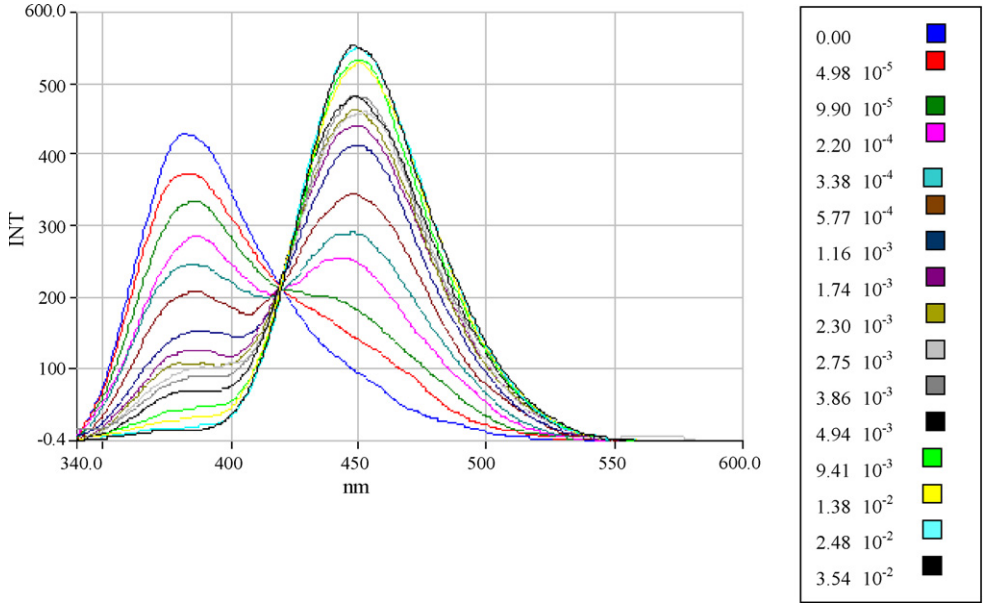

Fig. 3. A typical fluorescence spectrum of the 4-methyl umbelliferone with different concentration of dibutyl amine.