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Spectrofluorometric study of complexation of some amino derivatives of 9,10-anthraquinone with β-cyclodextrin

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Abstract

Complexation reactions between 1-amino-9,10-anthraquinone (AA1), 1-amino-2-methyl-9,10-anthraquinone (AA2), 1-amino-2,4-dimethyl-9,10-anthraquinone (AA3) and 1-amino-2-ethyl-9,10-anthraquinone (AA4) and β-cyclodextrin were studied spectrofluorometrically, under optimized experimental conditions. The formation constants of the resulting 1:1 β-cyclodextrin complexes were evaluated and found to decrease in the order AA4 > AA1 > AA3 > AA2. Possible reasons for the observed stability sequence are discussed based on the structures proposed for the resulting inclusion complexes.

Keywords: β-cyclodextrin; Aminoanthraquinones; Inclusion complex; Stability; Spectrofluorometry

1. Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides which contain a relatively non-polar internal cavity. These interesting compounds are well known to form inclusion complexes with a wide variety of hydrophobic guest molecules of different sizes [1]. The formation of such inclusion complexes with CDs improves the physical, chemical and biological properties of guest molecules and, consequently, it has lead to the extensive application of CDs to a wide variety of industrial, pharmaceutical and chemical areas [1–6]. 9,10-Anthraqinone derivatives, as the largest group of naturally occurring quinines, are of fundamental importance both in industry [7,8] and medicine [9–14]. They are well known to play an outstanding role in drug structure and in the treatment of various human cancers [9,10,12–14]. Bioreduction and redox cycling are supposed to play a key role in the activation of many anthraquinone-based drugs under aerobic conditions [9]. Information about the interaction of anthraquinone derivatives with CDs could obviously be of critical importance from both industrial and pharmaceutical points of view.

In recent years, we have been involved in the synthesis [15,16], acid–base [17–19], electrochemical [20–22] and supercritical fluid CO_2 solubility studies [23–26] and some analytical applications [27–30] of different derivatives of 9,10-anthraquinone and 9-anthrone. In this work, we have studied the interaction of four recently synthesized amino derivatives of 9,10-anthraquinone [31] with β-cyclodextrin in aqueous solution spectrofluorometrically. The structures of aminoanthraquinones used are shown in Fig. 1.

2. Experimental

2.1. Reagents

Reagent grade β-cyclodextrin, ammonium chloride, ammonia and methanol were purchased from Merck chemical company and used as received. Aminoanthraquinones AA1–AA4 were synthesized and purified as described elsewhere [31]. Doubly distilled deionized water was used throughout. All fluorescence spectra were recorded at

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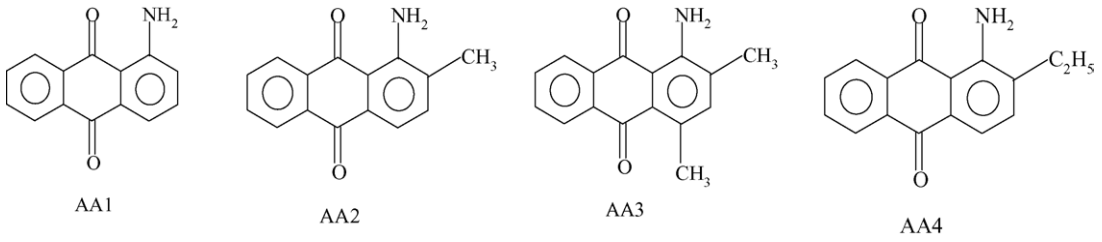

Fig. 1. Structures of aminoanthraquinone derivatives.

15.0 ± 0.1 °C on a Perkin-Elmer luminescence spectrometer LS-30, equipped with a xenon lamp; a 7 μl fused silica flow cell and a prestaltic pump. Excitation and emission bandwidths were both set at 10 nm. pH measurements were made with a Metrohm 692 pH/ion meter using a combined glass electrode.

3. Results and discussion

The fluorescence excitation and emission spectra of aminoanthraquinone derivatives AA1–AA4 were obtained in aqueous solution in the absence and presence of increasing amount of β-cyclodextrin. The resulting spectra are shown in Fig. 2. In all cases, in the absence of β-cyclodextrin, the excitation and emission spectra showed two low intensity unresolved maxima centered at about 480, 520 and 560, 600 nm, respectively. However, addition of excess β-cyclodextrin produced significantly enhanced intensity excitation and emission spectra with a single maximum centered at about 500 and 590 nm, respectively. The observed behavior is due to the inclusion complexation of anthraquinone molecules with β-cyclodextrin [32]. In fact, the structural conformation of the β-cyclodextrin molecule can safely protect the fluorescing singlet state of the guest molecules, included inside its cavity, from external quenchers [1–6]. Moreover, a consequence of inclusion complex formation with β-cyclodextrin would be the hindered rotation of the guest molecules as well as a considerable decrease in the relaxation of the solvent molecules. Both of these effects can result in a decreased vibrational deactivation of the excited guest molecules and, consequently, in increased fluorescence intensity of the system.

Different chemical variables were investigated in order to obtain the best measurement conditions and the maximum fluorescence signal.

In order to overcome the low solubility of the aminoanthraquinones in aqueous solution, their 1.0×10^{-3} M solutions were first prepared in methanol. Then, 25.0–50.0 μl of the methanolic stock solutions were diluted to 10.0 ml with an aqueous 0.1 M ammonium chloride–ammonia buffer solution of pH 8.5 and, after transferring into the thermostated titration vessel, the fluorescence intensity measurements of increasing concentration of β-cyclodextrin in stirring solution (~300 rpm) were carried out.

The influence of β-cyclodextrin on the fluorescence intensity of the aminoanthraquinone derivatives used was studied by keeping their concentration constant at 5.0×10^{-6} M and varying the cyclodextrin concentration from 0.0 to 5.0×10^{-4} M (Fig. 3). As it is seen from Fig. 3, at cyclodex-

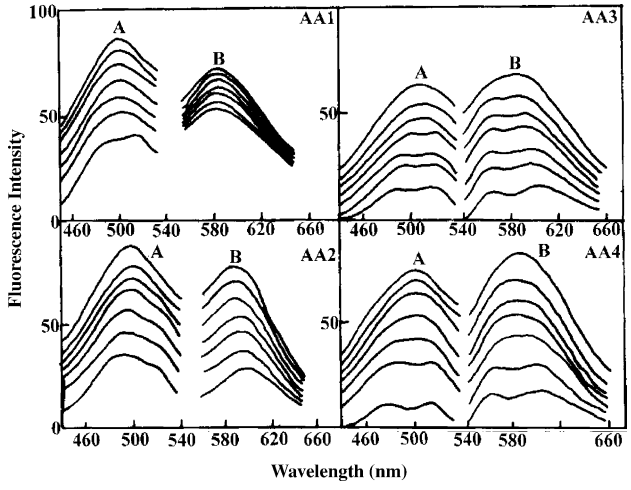

Fig. 2. Excitation (A) and emission (B) spectra of different aminoanthraquinones in the presence of increasing concentration of β-cyclodextrin. The β-cyclodextrin concentrations from the bottom to the top are: 0.0, 1.0×10^{-4}, 2.0×10^{-4}, 3.0×10^{-4}, 4.0×10^{-4}, 5.0×10^{-4}, 6.0×10^{-4} M.

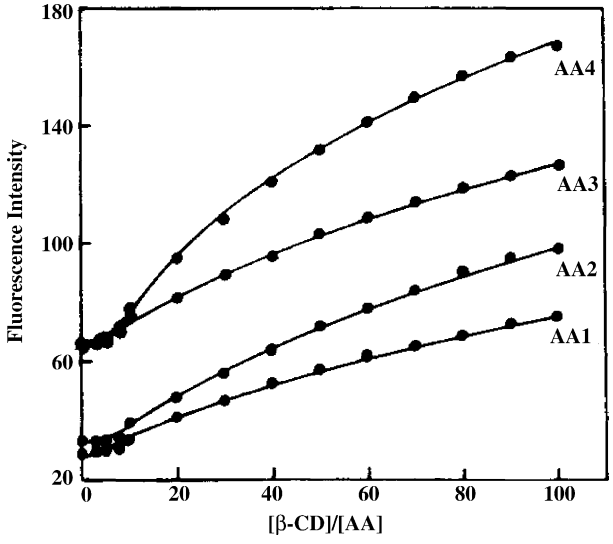

Fig. 3. Fluorescence intensity vs. [β-cyclodextrin]/[AA] mole ratio plots for different aminoanthraquinones.