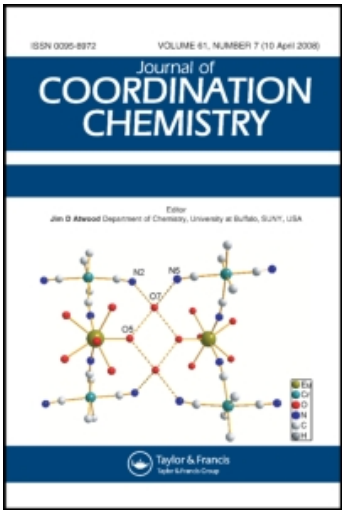

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Interaction mode between Congo red–Sm(III) complex and herring sperm DNA

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Spectroscopic and viscosity methods were applied to investigate the mechanism of interaction between Congo red (CR)–Sm(III) complex and herring sperm DNA by using acridine orange as a spectral probe in Tris-HCl buffer (pH 7.40). The binding ratio of $Sm(III)(CR)_3$: DNA is 5 : 1, the apparent molar absorptivity of $\varepsilon_{Sm(III)(CR)3\text{–}DNA}$ is $4.80 \times 10^5\,L\,(mol\,cm)^{-1}$ and the bonding constant of $Sm(III)(CR)_3$ interacting with DNA is $K^{\theta}_{26^{\circ}C} = 1.11 \times 10^7\,L\,mol^{-1}$. The thermodynamic parameters are $\Delta_r H^{\theta}_m = 5.40 \times 10^4\,J\,mol^{-1}$, $\Delta_r S^{\theta}_m = 3.16 \times 10^2\,J\,(mol\,K)^{-1}$, $\Delta_r G^{\theta}_{m26^{\circ}c} = -4.03 \times 10^4\,J\,mol^{-1}$. The results confirm that the interaction between $Sm(III)(CR)_3$ complex and DNA is a partial intercalation, and the reaction process is entropy favorable.

Keywords: Congo red; Sm(III) complex; Herring sperm DNA; Interaction

1. Introduction

Studies on the interaction of nucleic acids with metal complexes have gained prominence [1–3]. These studies are closely related to the replication of DNA *in vivo*, mutation of genes, and action mechanisms of some DNA-targeted drugs [4–6]. Factors that determine the affinity and selectivity in binding of small molecules to DNA would be valuable in the design of new diagnostic and therapeutic agents. Metal complexes with rational design for the specific sequence of DNA could give efficient binding and cleavage [7]. Various interactions of metal complexes with DNA are known. An electrostatic interaction that extends the negatively charged phosphates outside the DNA double helix, interaction with grooves of DNA, and intercalation in which the base pairs of DNA unwind to accommodate the intercalating agent are some important binding modes [8]. Numerous analytical techniques, including UV-Vis absorption, circular dichroism (CD) spectroscopy, fluorescence spectroscopy, nuclear magnetic resonance, luminescence, etc. [9–11], have been used to study these interactions.

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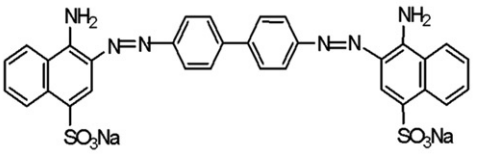

Figure 1. Molecule structure of CR.

Instead of the traditional histological birefringence test [12, 13], Congo red (CR) which is known for its dyeing behavior and optical activity (its molecular structure is shown in figure 1) is a sensitive diagnosis tool for amyloidosis. CR complex may bind with DNA by intercalation as a rigid planar structure. Sm(III) complexes have antibacterial, anticancer, and anti-diabetes activities. Therefore, the interaction between CR–Sm(III) complex and herring sperm DNA (hsDNA) may be useful for the development of potential probes for DNA structure and new therapeutic reagents.

In this article, CR–Sm(III) complex was synthesized and characterized by IR spectrum and elemental analysis. The binding of CR–Sm(III) complex with DNA has been investigated systematically by spectroscopic method and viscosity measurements, because small molecule–DNA interaction may be experimentally monitored by changes in the intensity and position of the spectroscopic peak responses or changes in dynamic viscosity.

2. Experiment and methods

2.1. *Experiment*

2.1.1. Preparation of the complex. The complex was prepared by concentrating stoichiometric amounts of samarium chloride and CR in water, recirculated on a water bath at 40°C for 10 h. After standing for several days, brownish precipitate was formed. The sample was washed by absolute ethanol and dried in an oven for 5 h. Finally, we got brownish precipitate of $Sm(C_{32}H_{24}N_6O_6S_2)_3Cl_3(H_2O)_4$. IR spectral data of CR: $\nu_{NH_2} = 1607$, $\nu_{R-SO_2-OR} = 1363$, $\nu_{R-SO_3-M^+} = 1322$, 1324, $\nu_{S=O} = 1061$, $\nu_{C=C} = 755$, 1119; IR spectra data of Sm–CR: $\nu_{NH2} = 1612$, $\nu_{R-SO_2-OR} = 1375$, $\nu_{S=O} = 1061$, $\nu_{C=C} = 758$, 1114, $\nu_{Sm-O} = 408$. The sulfonic acid group coordinates to Sm(III). Elemental analysis (%): C 50.31, H 3.53, N 10.99, S 8.38 (experimental data); C 50.39, H 3.50, N 11.02, S 8.40 (theoretical value). MS m/z: 2286(M^+, 100).

2.1.2. Reagents and materials. HsDNA was purchased from Sigma Biological Co. and used as received. Purity of DNA was checked by monitoring the ratio of absorbance at 260–280 nm. The ratio was 1.89, indicating that the DNA was free from protein. The DNA was dissolved in doubly distilled deionized water with 50 mmol L^{-1} NaCl and dialyzed for 48 h against a buffer solution at 4°C. The concentration of hsDNA stock solution was determined according to the absorbance at 260 nm by using the extinction coefficients of 6600 L $(mol\,cms)^{-1}$.

All samples were dissolved in Tris-HCl buffer (The concentration of Tris is $0.05\,mol\,L^{-1}$ by addition of HCl solution of concentration $0.05\,mol\,L^{-1}$. An acidometer was used to examine the pH of the buffer). Sm_2O_3 was purchased from Beijing Fangzheng rare metal lab company (99.99%) and dissolved in dense HCl; the HCl was slowly vaporized to give $SmCl_3$ solution in different concentrations. Acridine orange (AO) was purchased from Shanghai-China medicine chemical plant (A.R.). CR was purchased from Shanghai-China medicine chemical plant (A.R.). Other reagents were at least of analytical grade and used without purification.

2.1.3. Instruments. IR spectra ($400–4000\,cm^{-1}$) were recorded as KBr pellets on a Spectrum One FTIR system (PE company, America). The absorption spectra were carried out with a UV-210 spectrophotometer (SHIMADZU company, Japan). Fluorescence spectra were recorded on a FL-4500 spectrofluorophotometer (SHIMADZU company, Japan). CD measurements were recorded on a Jasco-815 spectropolarimeter (Japan Spectroscopic Ltd., Japan). Carbon, hydrogen, and nitrogen were obtained using a Vario EL CUBE (Vario company, General). Gas chromatography mass spectrometry experiments were carried out on a Polaris Ion trap type (USA Thermo Fisher, USA). The pH was recorded on a pHS-2C acidometer (Fangzhou technology company, China).

2.2. *Methods*

2.2.1. Absorption spectral measurements. Three milliliter solution in 1.00 cm quartz cells, containing appropriate concentration of a certain solution, was titrated by successive additions of another stock solution. Titration was done manually by using a micro-injector. Each injection is 10 μL, therefore the volume change is negligible. Appropriate blanks corresponding to buffer were used as the reference. Absorption spectra were measured after 5 min.

2.2.2. Fluorescence spectral measurements. Three milliliter solution in 1.00 cm quartz cells, containing appropriate concentration of a certain solution, was titrated by another stock solution. Titration was done manually by using a micro-injector. Each injection is 10 μL, therefore the volume change is negligible. The widths of both the excitation slit and the emission slit were 5.00 nm, and the excitation wavelength was 411.7 nm. The fluorescence spectra were measured after 5 min.

2.2.3. Viscosity measurements. Viscosity experiments were carried out by using a viscometer, which was immersed in a thermostated water-bath at room temperature. An appropriate amount of Sm(III)$(CR)_3$ was added into the viscometer to give a value of $c_{Sm(III)(CR)3}$, while keeping the DNA concentration constant. The flow times of samples were repeatedly measured with an accuracy of ±0.2 s by using a digital stopwatch. Flow times were measured after thermal equilibration of 30 min. Each sample was measured at least three times and from these values an average flow time was calculated. The data obtained were presented as $(\eta/\eta_0)^{1/3}$ *versus* $c_{Sm(III)(CR)3}$, where

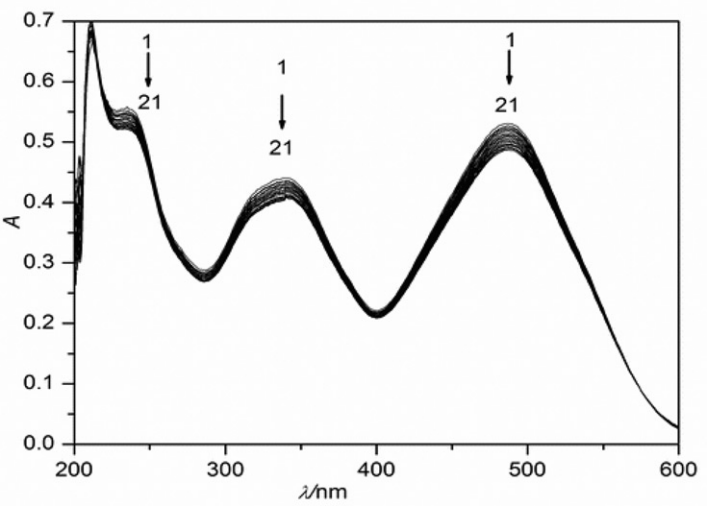

Figure 2. Effects of Sm(III) on the absorption spectra of CR; $c_{CR} = 5.06 \times 10^{-5}\,mol\,L^{-1}$; $c_{Sm(III)} = 5.06 \times 10^{-4}\,mol\,L^{-1}$ (10 μL per scan; $1 \sim 11 : 0 \sim 100\,\mu L$).

η and η_0 are the viscosity of DNA in the presence and absence of $Sm(III)(CR)_3$, respectively.

2.2.4. CD spectroscopy measurements. CD spectra were recorded on a J-815 Jasco spectropolarimeter at room temperature. The CD spectra of DNA with $Sm(III)(CR)_3$–DNA were recorded from 200 to 450 nm with a scan rate of 50 nm min^{-1}.

3. Results and discussion

3.1. *Interaction between CR and Sm(III)*

The UV-Vis absorption changes of CR in the presence of Sm(III) (with increasing concentration) were examined in the Tris-HCl buffer (pH 7.40). From figure 2, the absorptions of the complex show clear hypochromicity. Therefore, it can be deduced that there is an interaction between Sm(III) and CR to eventually form a Sm(III)–CR complex.

In order to determine the stoichiometry of Sm(III) complex, the molar ratio experiment was done at 236 nm. Molar ratio plots of CR with $SmCl_3$ are shown in figure 3. The binding ratio of the complex was: $n_{Sm} : n_{CR} = 1 : 3$. According to the Lambert–Beer law, the molar apparent absorption coefficient of $Sm(III)(CR)_3$ was $\varepsilon = 3.13 \times 10^4\,L\,(mol\,cm)^{-1}$.

3.2. *Absorption spectra: Sm(III)–CR complex interaction with DNA*

Absorption spectra of $Sm(III)(CR)_3$ are given in figure 4. Upon addition of DNA, the characteristic peaks at 344 and 493 nm of $Sm(III)(CR)_3$ show clear hypochromicity,

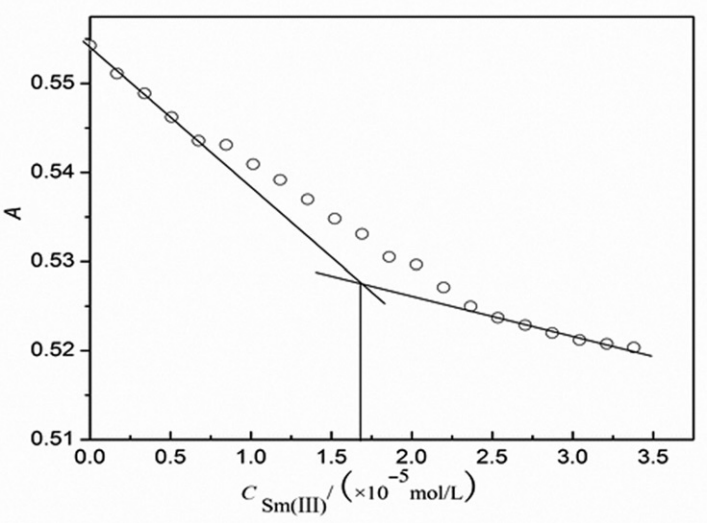

Figure 3. Molar ratio plots of Sm–CR system; $c_{CR} = 5.06 \times 10^{-5}\,mol\,L^{-1}$.

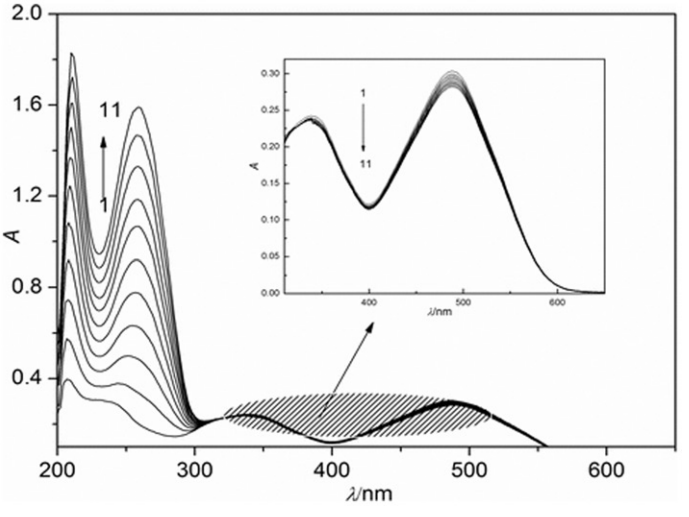

Figure 4. Effects of DNA on the absorption spectra of Sm(III)$(CR)_3$; $c_{Sm(III)(CR)3} = 1.00 \times 10^{-5}\,mol\,L^{-1}$; $c_{DNA} = 1.20 \times 10^{-5}\,mol\,L^{-1}$ (10 μL per scan; $1 \sim 11 : 0 \sim 100$ μL).

and at 207 nm (figure 5) show an increase in molar absorptivity (hyperchromism) as well as a slight red shift (3 nm). Hyperchromism results from the damage of the DNA double helix structure. Hypochromism and red shift are associated with intercalative binding of the complex to the helix because of the strong stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA [14, 15]. Hypochromicity, hyperchromism, and red shift usually take place if Sm(III)$(CR)_3$ intercalates into DNA [16, 17].

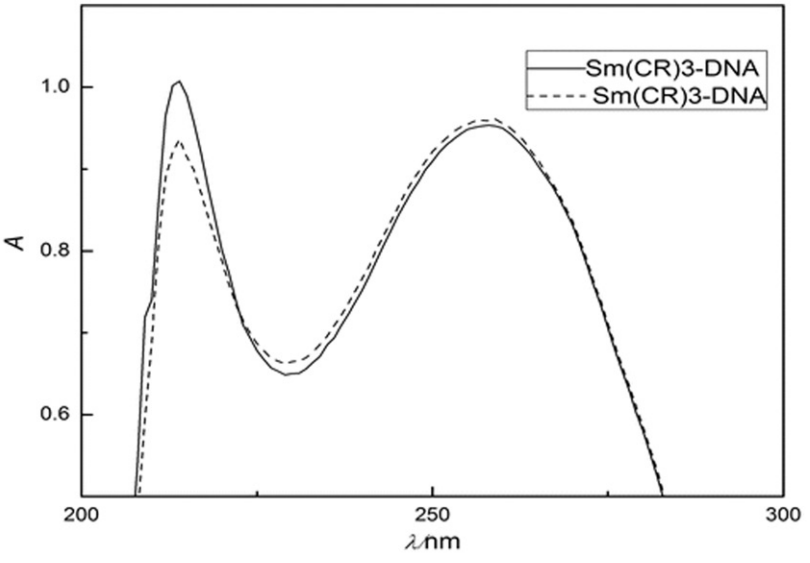

Figure 5. Absorption spectra of Sm(III)(CR)$_3$ + DNA and Sm(III)(CR)$_3$ − DNA (pH 7.40). $c_{Sm(III)(CR)3} = 1.00 \times 10^{-5}$ mol L^{-1}; $c_{DNA} = 2.00 \times 10^{-6}$ mol L^{-1}; $c_{Sm(III)(CR)3-DNA} = 2.00 \times 10^{-6}$ mol L^{-1}.

Molar ratio method was also used to discuss the binding ratio of Sm(III)(CR)$_3$ with DNA at 209 nm. The binding ratio is shown in figure 6: $n_{Sm(III)(CR)_3} : n_{DNA} = 5 : 1$. According to Lambert–Beer law ($A = \varepsilon bc$) the apparent molar absorption coefficient $\epsilon = 4.80 \times 10^5$ L (mol cm)$^{-1}$ was calculated.

3.3. *Thermodynamic parameters*

The absorption relationship between the complex and DNA is expressed by [18, 19] a double reciprocal equation

$$1/(A_0 - A) = 1/A_0 + 1/(K \times A_0 \times c_{DNA}) \quad (1)$$

where A_0 is the absorbance of Sm(III)(CR)$_3$ in the absence of DNA, A is the absorbance of Sm(III)(CR)$_3$ in the presence of DNA, K is the binding constant between Sm(III)(CR)$_3$ and DNA, c_{DNA} is the concentration of DNA. The double reciprocal plots of $1/(A_0 - A)$ *versus* $1/c_{DNA}$ are linear (at 18°C and 26°C) and the binding constants were calculated (figure 7): $K^{\theta}_{18^\circ C} = 6.25 \times 10^6$ L mol^{-1}, $K^{\theta}_{26^\circ C} = 1.11 \times 10^7$ L mol^{-1}. According to the relations of K^{θ}, $\Delta_r H^{\theta}_m$, and T

$$\ln K^{\Theta}_2/K^{\Theta}_1 = -\Delta_r H^{\Theta}_m(1/T_2 - 1/T_1)/R \quad (2)$$

where K^{θ}_1 – standard binding constant of Sm(III)(CR)$_3$ and DNA at 18°C, K^{θ}_2 – standard binding constant of Sm(III)(CR)$_3$ and DNA at 26°C, T_1 is 291.15 K, T_2 is 299.15 K, $\Delta_r H^{\theta}_m$ is standard molar reaction enthalpy. Then $\Delta_r H^{\theta}_m = 5.40 \times 10^4$ J mol^{-1} was deduced, showing an endothermic reaction. According to

$$\Delta_r G^{\theta}_m = -RT \ln K^{\Theta} \quad (3)$$

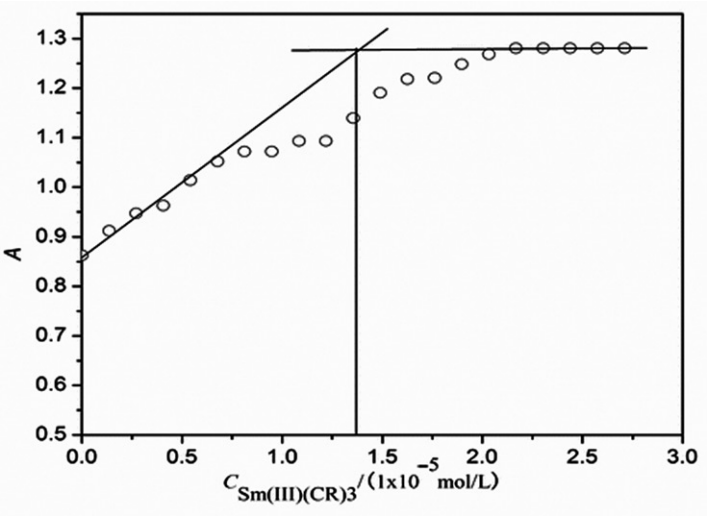

Figure 6. Molar ratio plots of Sm(III)$(CR)_3$–DNA system; $c_{DNA} = 2.70 \times 10^{-6}$ mol L^{-1}.

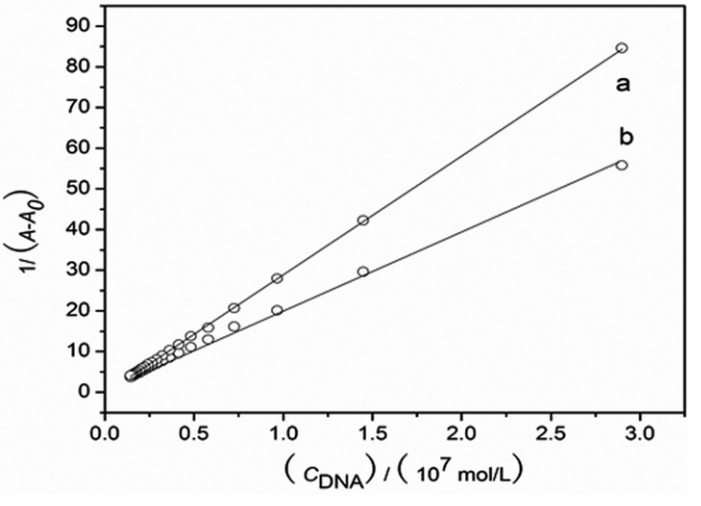

Figure 7. Double reciprocal plots of Sm(III)$(CR)_3$–DNA system (pH = 7.40); $c_{Sm(III)(CR)3} = 1.73 \times 10^{-6}$ mol L^{-1}; $c_{DNA} = 5 \times 10^{-4}$ mol L^{-1} (a: 18°C; b: 26°C).

where $\Delta_r G_m^\theta$ refers to the standard molar reaction Gibbs free energy, T is 299.15 K and K^θ refers to the standard binding constant of Sm(III)$(CR)_3$ and DNA at 26°C, $\Delta_r G_m^\theta = 4.03 \times 10^4$ J mol^{-1} was deduced, showing spontaneous interaction between Sm(III)$(CR)_3$ and DNA. According to the Gibbs–Helmhotz equation

$$\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\Delta_r S_m^\Theta, \tag{4}$$

where $\Delta_r S_m^\theta$ refers to the standard molar reaction entropy, T is 299.15 K. Then $\Delta_r S_m^\theta = 3.16 \times 10^2$ J (mol K)$^{-1}$ was deduced. The result suggests that $\Delta_r S_m^\theta$ is the driving

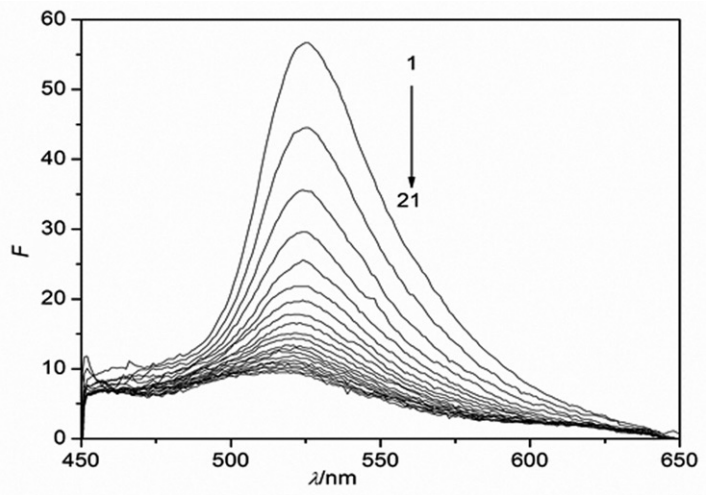

Figure 8. Effects of Sm(III)$(CR)_3$ on fluorescence spectra of DNA–AO; $c_{DNA-AO} = 2.00 \times 10^{-7}\,mol\,L^{-1}$, $c_{Sm(III)(CR)3} = 3.00 \times 10^{-5}\,mol\,L^{-1}$ (10 μL per scan, $1 \sim 21 : 0 \sim 200\,\mu L$).

force in this reaction. Interaction of Sm(III)$(CR)_3$ and DNA is highly energetically favorable at room temperature and the binding reaction is driven mainly by entropy.

3.4. *Fluorescence measurements using AO as probe*

The interaction between metal complex and DNA has been studied by a fluorescence spectral technique using AO as probe. The fluorescence of DNA is weak, so fluorescence probes can obtain information on the structure and quantity of DNA. AO is a selective fluorescent cationic dye, and in general, is structurally similar to other planar dyes, for example, those of the acridine, thiazine, and xanthene kind [20]. Compared with the common fluorescent probe, ethidium bromide (EB), the AO dye offers lower toxicity, higher stability, and convenience of use. Therefore, AO has been widely used in various biological systems, inserting between two adjacent base pairs in DNA helix and increasing fluorescence intensity.

Figure 8 shows the fluorescence of DNA–AO in different concentrations of Sm(III)$(CR)_3$. DNA–AO is efficiently quenched by adding Sm(III)$(CR)_3$, suggesting that AO is replaced by Sm(III)$(CR)_3$, and Sm(III)$(CR)_3$ can bind to DNA by intercalation [21].

3.5. *Viscosity method*

Hydrodynamic measurements that are sensitive to length change (i.e., viscosity and sedimentation) are regarded as the least ambiguous and the most critical tests of binding in solution in the absence of crystallographic structural data [22]. A classical intercalation mode is known to cause a significant increase in the viscosity of a DNA solution because its presence forced these base-pairs away from each other, therefore

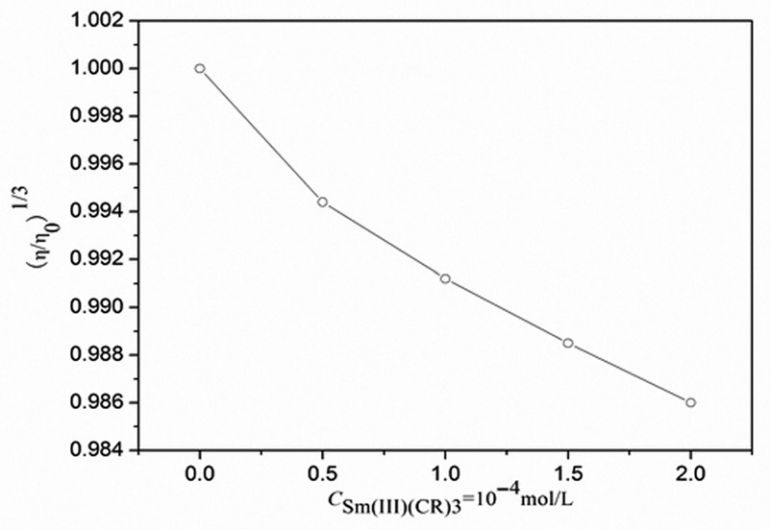

Figure 9. Variation of the relative viscosity of DNA (pH = 7.40); $c_{DNA} = 1.00 \times 10^{-4}\,mol\,L^{-1}$.

unwinding the double helix and lengthening DNA. In contrast, a partial intercalation mode could bend (or kink) the DNA helix and reduce its effective length and, concomitantly, its viscosity; non-intercalative binding causes no obvious increase of DNA viscosity [22, 23].

To further clarify the binding of the metal complex with DNA, viscosity measurements were carried out. The changes in relative viscosity of DNA with increasing concentration of Sm(III)$(CR)_3$ are shown in figure 9. The relative viscosity of DNA decreased with increasing amounts of Sm(III)$(CR)_3$, demonstrating that Sm(III)$(CR)_3$ binds to DNA by partial intercalation, causing a kink in the DNA helix and reducing the length and viscosity [24–26].

3.6. *CD spectroscopy*

The CD spectral analysis is very useful to investigate morphological changes in the DNA double strands due to interaction with small molecules. The band at 275 nm, due to base stacking, and the band at 249 nm, due to right-handed helicity of the strands, are very sensitive to interaction with such small molecules. Any change in the base-stacking pattern or the helicity of the strands is manifested by either a change in the band position, the intensity, or both. A simple electrostatic interaction or groove binding has nearly no insignificant effect on the band at 275 nm, whereas the same band undergoes considerable change in intensity due to intercalation by small molecules [27, 28]. The CD spectra of hsDNA and the Sm(III)$(CR)_3$–DNA complex are shown in figure 10. The CD spectra of hsDNA in the presence of Sm(III)$(CR)_3$ decrease significantly, especially at 249 nm. Intercalated complexes, which weaken base stacking and make double helix unwinding, should decrease intensities of CD bands [29].

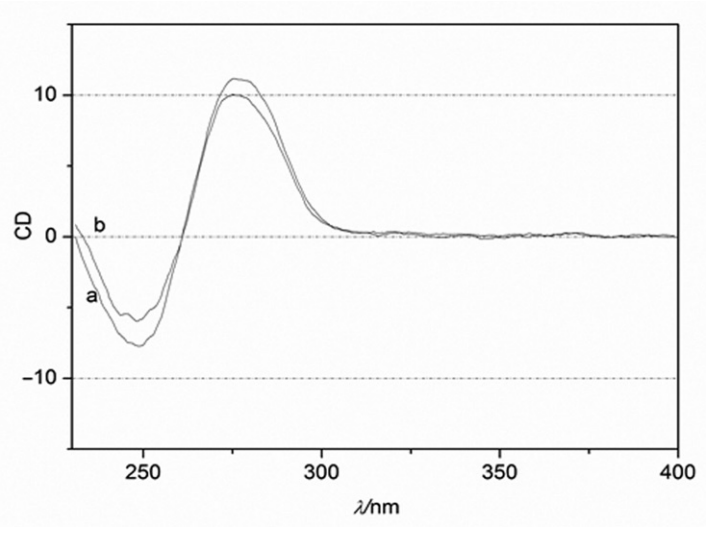

Figure 10. Sm(III)$(CR)_3$ effect on CD spectra of hsDNA; $c_{DNA} = 1.00 \times 10^{-5}\,mol\,L^{-1}$; $c_{Sm(III)(CR)3\text{–}DNA} = 1.00 \times 10^{-5}\,mol\,L^{-1}$ (a: DNA; b: Sm(III)$(CR)_3$–DNA).

4. Conclusions

The interaction of Sm(III)$(CR)_3$ with hsDNA has been studied by spectroscopic and viscosity methods. The binding ratio of Sm(III)$(CR)_3$: DNA is 5 : 1, the apparent molar absorptivity is $4.80 \times 10^5\,L\,(mol\,cm)^{-1}$, and the bonding constant of Sm(III)$(CR)_3$ with DNA is $K^{\theta}_{26^\circ C} = 1.11 \times 10^7\,L\,mol^{-1}$. The obtained thermodynamic parameters demonstrate that the interaction between Sm(III)$(CR)_3$ and DNA is driven mainly by entropy. In fluorescence probe studies, Sm(III)$(CR)_3$ is able to displace AO intercalated into DNA. Combined with CD spectroscopy and viscosity methods, the results indicate that the interaction mode between Sm(III)$(CR)_3$ and hsDNA is partial intercalation.

Acknowledgments

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