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Rapidly probing the interaction between sulfamethazine antibiotics and fulvic acids☆

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ABSTRACT

Antibiotics residuals in the environments receive wide concerns due to the high risk of generating antibiotic resistance. Natural organic matters (NOM) existed in the environments are considered to have the capacity of binding with organic contaminants, consequently influencing their speciation and transformation in the natural environments. To assess the migration of antibiotics in the environments, it is crucial to understand the binding mechanisms between NOM and antibiotics, which is still unclear due to the limit of available research methods. In this study, the interaction between fulvic acids (FA), one of the main components of NOM, and sulfamethazine (SMZ) was characterized by nuclear magnetic resonance (NMR) combined with surface plasmon resonance (SPR) and isothermal titration calorimetry (ITC) technology. The parameters related to kinetics and thermodynamics of the interaction were determined, and the possible mechanisms driving the interaction were also proposed. In addition, density functional theory (DFT) was used to predict the binding mode between FA and SMZ to reveal the interaction mechanism. Results indicate that FA can effectively bound with SMZ to form a stable complex with a binding constant at the level of 10^3 L/mol. The kinetic parameters including association and dissociation constants were 29.4 L/mol/s and 6.64×10^{-3} 1/s, respectively. Hydrophobic interaction might play significant roles in the binding interaction with ancillary contribution of π-π conjunction arising from the aromatic rings stacking of FA and SMZ.

1. Introduction

Sulfonamides are one of the most widely used antibiotics in the world, which have been widely detected in the environments. High risk of antibiotic resistance may generate from the accumulation of these sulfonamides residues in the environments (Makowska et al., 2016; Yang et al., 2011). The speciation of the sulfonamides residues are influenced by the fulvic acids (FA), a typical component of natural organic matters (NOM) existed in the environments (Lian et al., 2015). They are heterogeneous organics with abundant functional groups, which have a strong capacity of binding with the contaminants, and thus affect the speciation and migration of contaminants in the environments (Chen et al., 2017; Lu et al., 2013). Consequently, to assess the potential risk of sulfonamides residues in the natural environments and develop efficient strategies for their remediation, it is crucial to understand the mechanisms of interaction between sulfonamides and FA.

Previous studies on the binding capability of FA are mainly focused on the coordination of various heavy metals by abundant acidic groups (Shi et al., 2016). Recently, the binding ability of FA with aromatic organics such as polycyclic aromatic hydrocarbons (PAHs) have been recognized due to the strong interaction of π-π conjunction (Lu et al., 2013). However, interaction mechanisms between organics and FA are still unclear due to the limit of available research methods. Traditional methods for investigating interactions between FA and organic contaminants i.e. reverse phase separation (Wu et al., 2010) and dialysis (Yamamoto et al., 2003) are quite crude and time-consuming with complex

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pretreatment process. Rapid and sensitive methodologies are required to investigate the interactions between FA and organic contaminants effectively.

Nuclear magnetic resonance (NMR) spectroscopy is capable of exploring both the qualitative and quantitative interactions between organic molecules (Nanny and Maza, 2001; Simpson et al., 2004). However, there exists a major application bottleneck in analyzing complex environmental samples as these molecules should be labeled to avoid the overlapping of signals. This limitation may be overcome, in case of investigating interactions between FA and aromatic-containing contaminants such as sulfonamides. In fact, FA solutions at low concentrations generate very low resonances in the aromatic region of ^{1}H NMR spectra, thereby hardly interfering with the strong proton resonances of aromatic rings (Smejkalova and Piccolo, 2008a). Thus, NMR is very suitable for characterizing the interactions between FA and sulfonamides, and can be used as a rapid and effective method to probe the interaction process quantitatively.

To further understand the binding mechanism, the kinetics and thermodynamics of the interaction also should be characterized (Xu et al., 2016). Surface plasmon resonance (SPR) is a sensitive sensor technology that can study kinetics and binding affinity of the interaction simultaneously (Hoa et al., 2007; Murthy et al., 2008). Isothermal titration calorimetry (ITC), as a principal calorimetric technique, can be used to acquire thermodynamic information of the binding processes (Perry et al., 2005; Tan et al., 2009). Density functional theory (DFT) calculation can provide structural and geometrical information of the molecules involved in the interaction (Luo et al., 2017). The interaction mechanism can be explored in depth by the integration of these methods.

In this work, NMR spectroscopy was applied to probe the interaction between FA and sulfamethazine (SMZ), a typical sulfonamide existed in the environments, as a rapidly quantitative method. SPR combined with ITC was utilized to obtain the kinetic and thermodynamic parameters of the binding process. Moreover, DFT calculation was used to predict possible binding mode of FA and SMZ. The information obtained from different methods could complement each other and illustrate the microscopic mechanism of the binding process, facilitating a better comprehension of speciation and migration of sulfonamides in the environments.

2. Materials and methods

2.1. Reagents

SMZ and deuterated solvents for NMR measurements were from Sigma-Aldrich Co. Ltd. FA was obtained from RCNC Corp., China. The other chemicals were from Sinopharm Chemical Reagent Co., Ltd.

2.2. NMR analysis

NMR measurement was conducted at a proton frequency of 400.13 MHz (Bruker Avance 400, USA) with a 5 mm Bruker inverse broadband probe. The temperature was set as 25.0 ± 0.1 °C. SMZ (0.5 mg) was firstly added with 20 μL DMSO-D_6 to ensure completely SMZ dissolution, and then further diluted in solution D_2O with the final concentration of 1.0 mg/mL. Gradient amounts of FA (0–4.4 mg) were dissolved in 0.5 mL SMZ solution respectively, and transferred to NMR tubes. High concentrations of FA and SMZ were used to enhance the intensity of NMR and thus improve the signal-to-noise ratio of the analysis. The SMZ-FA samples were analyzed for ^{1}H NMR measurement after 4-h equilibrium due to the NMR spectra did not change thereafter. ^{1}H NMR spectra were referenced to the chemical shift of the solvent being 4.709 ppm. All spectra were processed by MestReNova software.

When the exchange between free and bound SMZ is fast on the NMR time scale, the observed chemical shift of SMZ in the NMR experiment is a fraction weighted average of the chemical shift for bound and unbound SMZ (Fielding, 2000):

$$\delta_{obs} = (1 - X_B)\delta_F + X_B\delta_B \tag{1}$$

X_B, the fraction of bound SMZ can be determined by:

$$X_B = \frac{\delta_{obs} - \delta_F}{\delta_B - \delta_F} \tag{2}$$

where, δ_{obs} is experimentally measured chemical shift; δ_F is chemical shift of a nucleus in the free SMZ; δ_B is chemical shift of a nucleus in the FA-SMZ complex.

Langmuir adsorption isotherm is employed to describe the interaction between FA and SMZ (Sheng et al., 2008)

$$\theta = \frac{KG_F}{1 + KG_F} \tag{3}$$

$$G_0 = G_F + G_B = G_F + H_0N\theta \tag{4}$$

where θ, fraction of binding sites in FA occupied by SMZ; K, binding constant (L/mol); G_F, concentration of free SMZ (mmol/L); G_0, known total concentration of SMZ (mmol/L); G_B, concentration of bound SMZ (mmol/L); H_0, known total concentration of FA (mg/L); N, binding capacity of FA (mmol/mg).

Combined with eqs. (3) and (4), we can solve θ as following:

$$\theta = \frac{1}{2}\left[1 + \frac{G_0}{H_0N} + \frac{1}{H_0NK} - \sqrt{\left(1 + \frac{G_0}{H_0N} + \frac{1}{H_0NK}\right)^2 - 4\frac{G_0}{H_0N}}\right] \tag{5}$$

Related to eq. (4), X_B can be also expressed as

$$X_B = \frac{G_B}{G_0} = \frac{H_0N\theta}{G_0} \tag{6}$$

Substituting eq. (5) into eq. (6) and combining with eq. (2) gives

$$2(\delta_{obs} - \delta_F) = \left(1 + \frac{H_0N}{G_0} + \frac{1}{G_0K} - \sqrt{\left(1 + \frac{H_0N}{G_0} + \frac{1}{G_0K}\right)^2 - 4\frac{H_0N}{G_0}}\right)(\delta_B - \delta_F) \tag{7}$$

Accordingly, $2(\delta_{obs} - \delta_F)$ vs H_0/G_0 (i.e. FA/SMZ) was plotted. Parameters N, K and δ_B can be obtained by non-linear fitting of eq. (7) using 1stOpt (7D-Soft High Technology Inc., China).

2.3. SPR analysis

The kinetics of the interaction between FA and SMZ was explored by SPR (Biacore 3000, GE, USA). The detailed measurement procedure could be found in our previous work (Xu et al., 2016). Firstly, SMZ solution (0.5 g/L) prepared with phosphate buffer (PBS, 100 mM, pH 7.0) was immobilized onto a CM5 chip (GE,

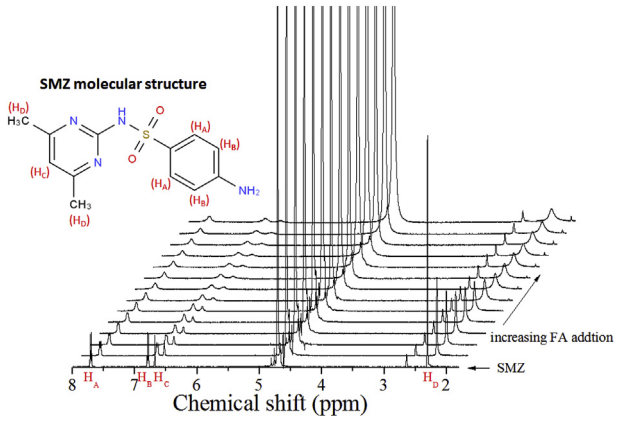

Fig. 1. ^{1}H chemical shifts of SMZ with addtion of FA.

USA) for 20 min with 5 μL/min flow rate. Then, FA of gradient concentration (4.56–36.48 mg/L) in buffer flowed over SMZ-immobilized surface (10 μL/min, 3 min) for association, FA bound to SMZ on the chip and induced increasing signals. Finally, the PBS buffer flowed over the surface (10 μL/min, 7 min) for dissociation, part of the FA bounded to SMZ were released into the buffer and the signals decreased. The surface was regenerated before the next analyte injections. The kinetic parameters including association rate constant (k_a), dissociation rate constant (k_d) and binding constant (K) were determined as described previously (Xu et al., 2016).

2.4. ITC analysis

The thermodynamics of the interaction between FA and SMZ was investigated by ITC (ITC-200, MicroCal, Northampton). The procedure of titration and data analysis was described previously (Xu et al., 2013). Solutions of FA (10 g/L) and SMZ (1 g/L) were prepared with PBS (100 mM, pH 7.0). SMZ was titrated into PBS and FA solution respectively. The titration were completed in 2 μL aliquots injected over 4 s with 120 s equilibrium between injections. Experiments were conducted at 25 °C under stirring rate of 1000 rpm in the working cell of 199.3 μL. Data analysis was performed by Origin 7.0.

2.5. DFT calculation

All the calculations were completed using the DMol3 code (Segall et al., 2002). The structure of FA was obtained from PubChem open chemistry database (https://pubchem.ncbi.nlm.nih.gov/compound/fulvic_acid#section). The geometry structures of the FA-SMZ complex were energy-minimized by an all-electron method within generalized gradient approximation (Perdew et al., 1992) with Perdew-Wang91 (PW91) form (Perdew and Wang, 1992) until the convergence criteria for energy, force and displacement were less than 2×10^{-5} Hartree, 4×10^{-3} Hartree/Å and 5×10^{-3} Å, respectively. The double precision numerical basis sets including polarization were employed. The interaction energy (ΔE_{int}) of FA and SMZ can be defined as follows:

$$\Delta E_{int} = E_{FA\text{-}SMZ} - E_{FA} - E_{SMZ} \quad (8)$$

where $E_{FA\text{-}SMZ}$, E_{FA} and E_{SMZ} were the total energy of FA-SMZ complex, FA and SMZ molecules, respectively.

3. Results and discussion

3.1. Binding strength between FA and SMZ quantified by NMR

The binding strength of FA and SMZ was quantified by NMR method. As the proton resonances of aromatic region were intensive, chemical shifts of four protons (H_A, H_B, H_C, H_D) in SMZ indicated in Fig. 1 were considered. The overlapping of FA and SMZ signals was avoided and the evolution of chemical shifts of SMZ upon addition of FA were displayed in Fig. 2. There existed a doublet at 7.705 ppm (H_A) and a doublet of 6.789 ppm (H_B) in the ^{1}H NMR spectrum of SMZ. H_C and H_D located at 6.68 ppm and 2.306 ppm was owed to free SMZ. The peak intensity of H_D was higher than those of other protons due to six identical protons. Upon addition of FA, all the SMZ proton signals shifted upfield and became progressively broader, as shown in Fig. 1. The broaden of SMZ resonances peaks could be considered as an increased proportion of the bound form, or decreased fraction of the free form, with the increasing mass ratio of FA to SMZ. The peak broadening observed with increasing FA dosage suggested the improved proton relaxation rate due to dipolar interaction arising from restricted mobility of SMZ molecules (Smejkalova and Piccolo, 2008b). The extent of broadening was different for H_A, H_B, H_C and H_D. The ^{1}H NMR peak widths of H_C and H_D were broader than those of H_A and H_B at the same dosage of FA to SMZ (Fig. 1). Simultaneously, the same amount of FA addition induced more significant peak upfield shift for H_C and H_D compared to those for H_A and H_B (Fig. 2). The upfield shift of aromatic proton signals resulted from the increased electron shielding around proton nuclei. Two main reasons might be responsible for the increased electron shielding. One was the formation of π-π conjunction, where the center of magnetic anisotropy shifted out of the SMZ aromatic plane toward the center of newly formed π-π complexes, thereby increasing the electron shielding of all resonating proton nuclei (Viel et al., 2002). The π-π stacks might be formed between SMZ and the aromatic parts of FA, which was validated by DFT calculation below. The other reason might be that the nuclei of SMZ surrounded by the hydrophobic cavities of FA induced enhanced magnetic shielding, leading to an upfield chemical shift. These SMZ molecules could be entrapped in the void of FA so as to increase their solubility. The possible explanation could be further verified by following thermodynamic analysis and DFT calculation.

The binding constants for the different proton signals were quantified based on the regression results of eq. (7) as listed in Table 1. The high R^2 values indicated the reliability of the fitting

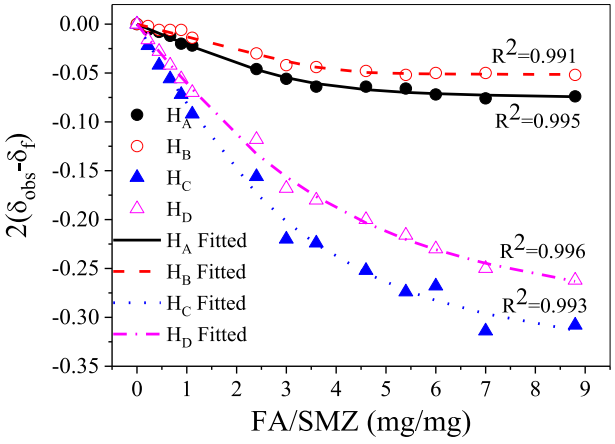

Fig. 2. Changes of ^{1}H chemical shifts for SMZ as function of FA/SMZ ratio in solution.

results. The binding constants for H_A and H_B were similar, and a little higher than those of H_c and H_d, attributing to the different aromatic rings in which the protons were located. Based on the average value of the four protons, the binding constants of SMZ with FA was calculated to be 2.10×10^3 L/mol, which was relatively higher than the binding constants of other contaminants with FA, such as 2,4-dichlorophenol and glyphosate (Mazzei and Piccolo, 2012; Smejkalova and Piccolo, 2008a). The results suggested that sulfonamides had good affinities to FA, and their migration in the environments would be significantly influenced by binding with FA. Therefore, based on the chemical shifts analysis, the binding constant could be acquired with a much easier experimental manipulation and data proceeding.

3.2. Kinetics of the interaction between FA and SMZ

The binding kinetics between FA and SMZ was characterized by SPR. The association and dissociation SPR curves for FA binding with SMZ were displayed in Fig. 3. During the first 130 s, the signal kept constant with the PBS flowing over the chip immobilized with SMZ. When the FA solution flowed over the chip, the FA bound with the SMZ molecules on the chip. The amount of FA molecules combined on the chip increased, leading to a climb trend during the association phase ranged from 130 s to 310 s. Then continuous flow of the PBS dissociated part of the FA molecules from the chip, resulting in a decreasing signal during the dissociation phase from 310 to 550 s. There were four SPR curves corresponding to the gradient concentration of FA flowed over the chip. These SPR curves were generally similar in shapes, exhibiting a rapid signal increase during the association phase reflecting a fast association rate (k_a), and a gradual signal reduction during the dissociation phase reflecting a slow disassociation rate (k_d). The kinetic parameters k_a, k_d, and binding constant K could be fitted from each curve as listed in Table 2. Based on the four curves, the average association constant, dissociation constant and binding constant was calculated to be 29.4 L/mol/s, 6.64×10^{-3} 1/s and 4.52×10^3 L/mol, respectively. This binding constant of 4.52×10^3 L/mol obtained by SPR was comparable to that determined by NMR.

3.3. Thermodynamics of the interaction between FA and SMZ

Based on ITC measurement as shown in Fig. 4, the binding constant (K) and binding enthalpy (ΔH) were regressed to be 11.2×10^3 L/mol and −0.55 kJ/mol, respectively. The binding constant of 10^3 L/mol obtained by ITC was comparable to that determined by NMR and SPR. Compared with previous study (Xu et al., 2016), the affinity of SMZ to FA was much lower than that to humic acids. This could be explained in terms of lower hydrophobicity of FA, which was also found in other works (Moura et al., 2007). The results implied the significance of hydrophobic interaction in the binding process of SMZ with humic substances. The change of Gibbs' energy (ΔG) was calculated to be −23.10 kJ/mol following the equation $\Delta G = -RTlnK$. Similar values of ΔG could be obtained from NMR (−18.95 kJ/mol) and SPR (−20.85 kJ/mol) respectively.

Table 1
Binding constant (K), binding capacity of FA (N) and chemical shift of SMZ in the FA-SMZ complex (δ_B) from NMR analysis.

Protons	K (10^3 L/mol)	N (mmol/g)	δ_B (ppm)	R^2
H_A	3.14	1.09	7.666	0.995
H_B	3.75	1.11	6.762	0.991
H_C	0.91	1.13	6.499	0.993
H_D	0.58	1.08	2.140	0.996

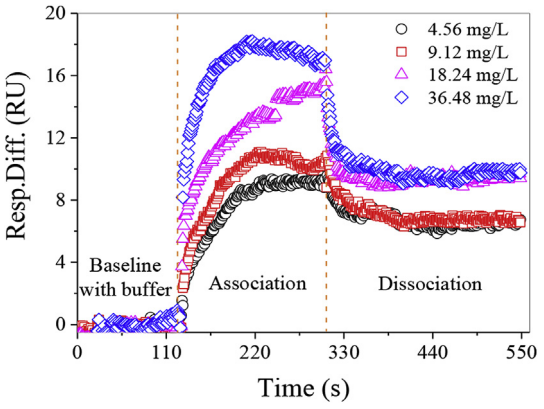

Fig. 3. SPR kinetic analysis of binding of SMZ to FA.

Table 2
Dissociation rate (k_d), association rate (k_a) and binding constant (K) of the interaction between FA and SMZ from SPR analysis.

FA (mg/L)	ka (L/mol/s)	kd (10^{-3} 1/s)	K (10^3 L/mol)
4.56	50	6.15	8.13
9.12	33.1	7.39	4.48
18.24	9.76	6.89	1.42
36.48	24.8	6.13	4.04

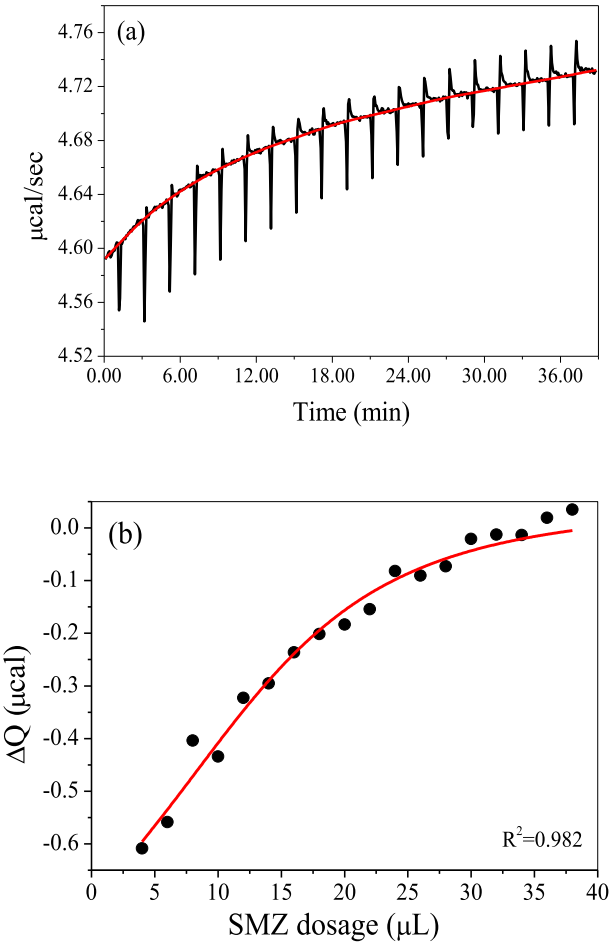

Fig. 4. (a) Thermogram of SMZ binding to FA; and (b) nonlinear regression of the heat vs SMZ dosage.

The negative ΔG value indicated that the binding reaction between FA and SMZ was favorable thermodynamically, consequently forming a stable FA-SMZ complex. The entropy change (ΔS) was calculated to be 75.6 J/mol/K according to $\Delta H = \Delta G - T\Delta S$. The positive ΔS value suggested that the disorder of the reaction system increased with SMZ bound with FA. That was frequently considered as the evidence for a hydrophobic interaction (Lertpaitoonpan et al., 2009; Richter et al., 2009). For the interaction between FA and SMZ, the positive ΔH value was considered as the result of π-π conjunction. However, the absolute value of ΔH for FA bound with SMZ was relatively low. As $|\Delta H| \angle |T\Delta S|$, the binding reaction was mainly driven by the entropy change, attributing to the hydrophobic interaction.

3.4. Geometry structure of FA-SMZ complex predicted by DFT

According to the results obtained from ^{1}H NMR results, six possible geometry structures of SMZ-FA complexes were proposed and the interaction energy for each structure was calculated by DFT calculation based on eq. (8) (Fig. S1). The results indicated that the SMZ-FA structure shown in Fig. 5 with the lowest interaction energy of −78.3 kJ/mol (Table S1) is the most stable configuration. The aromatic ring of SMZ stacked with the aromatic ring of FA, indicating the π-π conjugation made contributions to the interaction between FA and SMZ. Apparently, the distance between FA and the aromatic ring of SMZ where H_A and H_B located was very close, inducing a relatively stronger interaction. The results agreed with the NMR experimental results that the fitted binding constants for H_A and H_B were higher than those of H_c and H_d.

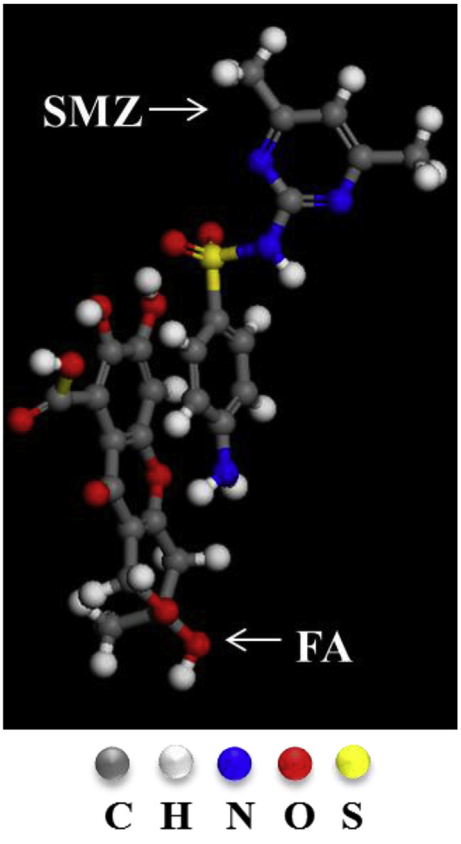

Fig. 5. The most stable structure of FA-SMZ complex based on DFT optimization.

4. Conclusions

In this study, simple and rapid methodologies were developed to characterize the interaction between FA and SMZ by NMR, ITC, SPR and DFT calculation. Results indicated that the binding reaction was favorable thermodynamically, forming a stable FA-SMZ complex with the binding constant at the level of 10^3 L/mol. The association and dissociation constants were calculated to be 29.4 L/mol/s and 6.64×10^{-3} 1/s. Hydrophobic interaction might play significant roles in the binding interaction with ancillary contribution of π-π conjunction arising from the aromatic rings stacking of FA and SMZ, which could be confirmed by DFT simulation. The results implied that NOM existed in the environments governed the speciation of sulfonamides by binding process, consequently influencing the migration and distribution of the sulfonamides in the environments.

The transport and migration of contaminants governed by NOM in the environments is of great importance for human health. Critical information related to the interaction mechanisms between contaminants and NOM is very limited due to the methodology scarcity. In this work, we developed simple and rapid methods to probe the interactions between SMZ and FA from the aspects of affinity, kinetics, thermodynamics and geometry structure. The integration of these methods illustrated the microscopic mechanism of the interaction and could complement each other. These methods could be also applied in investigating the mechanisms of interaction between NOM and other organic contaminants such as polycyclic aromatic hydrocarbons. Our work extends the methodology for exploring the binding processes of contaminants by NOM, facilitating a better comprehension of speciation and migration of contaminants in the environments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.09.002.

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