DFT study on the polyol sacrificial agents for improved clay tolerance of polycarboxylate superplasticizers

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Abstract: With the gradual scarcity of high-quality sand and gravel resources, the increasing mud content in concrete aggregates could strongly adsorb on polycarboxylate superplasticizers (PCE), greatly reducing their working performance. Modifying the molecular structure of PCE or compounding sacrificial agents can effectively improve the tolerance to clay minerals. In this article, using different small molecule polyols and polypropylene glycol (PPG) as examples, density functional theory (DFT) was employed to simulate the adsorption between clay minerals and hydration products. This exploration aims to further understand the anti-clay performance of various sacrificial agents from the perspective of adsorption energy. Ca-montmorillonite (CaMMT) exhibits the lowest adsorption energy among different clay minerals, making it the preferred site for sacrificial agent adsorption. With an increase in hydroxyl number, the adsorption energy between polyol sacrificial agents and montmorillonite decreases. Among polymeric polyols, the adsorption energy between PPG 600 and montmorillonite is the lowest (-10.86 eV), indicating superior anti-clay performance by preferentially occupying active sites on montmorillonite. As the interlayer spacing of montmorillonite increases, the adsorption energy between PPG 600 and montmorillonite initially decreases and then increases, reaching the lowest value at c=15.5 Å. There are more electron transfers (0.858) compared to the electron gain and loss, confirming more interaction between the sacrificial agents and montmorillonite at 15.5Å. This article also provides a crucial theoretical basis for the structural design of anti-clay sacrificial agents, offering insights into addressing compatibility issues between PCEs and clay minerals.

Keywords: PCE, clay, polyols, sacrificial agent, molecular simulation

1. Introduction

Polycarboxylate superplasticizers (PCE), with a typical comb-like structure formed by the side chain and main chain of polyoxyethylene (polyethylene glycol), have become the most widely used concrete admixture. With the increase of mud content in the sand and gravel aggregates, the main minerals in mud, such as montmorillonite, kaolin, illite, etc., could strongly adsorb on PCEs, adversely affecting the performance of water reducer (Ghanizadeh et al., 2019; Lei et al., 2021; Tan et al., 2016; Wang, 2015). Modifying the molecular structure of PCE or compounding sacrificial agents can effectively improve the tolerance to clay minerals (Rana et al., 2019; Du, 2019; Liu, et al. 2017; Qiu, 2021). Among these methods, structural modification of the PCE molecules can enhance the dispersion performance by changing the shape of

PEO (polyethylene oxide) side chains and introducing functional groups, further improving the adaptability between the superplasticizers and clay (Quainoonet al., 2021; Qi et al., 2020; Li et al., 2021; Borralleras et al., 2019). Fang (2022) synthesized a side chain hyperbranched polycarboxylate

superplasticizer, breaking the traditional comb structure of the PCEs. The steric hindrance of the side chain increased, providing the benefits of high solubility and low viscosity, effectively improving the dispersion effect of the superplasticizer. However, the modification process is typically complicated, and some methods may also damage the spatial hindrance of PCEs. By compounding anti-clay sacrificial agents, the active sites of clay can be preferentially occupied, reducing the consumption of PCE on montmorillonite, thus, the anti-clay performances could be more effective (Bessaies-Bey et al., 2016; Xie et al., 2017). The common sacrificial agents mainly include electrolytes, alkyl quaternary ammonium salt, polyetheramine (PEA) and polymerized polyols (Du, 2019; Govin et al., 2019; Qiu, 2021; Khandelwal et al.2021). Qiu (2021) suggested that polyether amine and alkyl quaternary ammonium sacrificial agents can preferentially diffuse to the surface of montmorillonite, exchange ions with the montmorillonite layer, and seize the adsorption sites of PEO side chains. Due to the steric hindrance effect of the side chains, the intercalation adsorption of PCE side chains could also be hindered. In addition, polyol non-ionic sacrificial agents with PEO structural units would preferentially adsorb on montmorillonite layers via hydrogen bonding, van der Waals forces, and hydrophobic interactions. Werani et al. (2021) reported that when PEG is combined with PCE, the adsorption mechanism on montmorillonite is similar to that of the long side chain as PEO, which mainly manifests as interlayer adsorption, and the saturated adsorption capacity on PEG is 5 times than that of PCEs (Du, 2019).

Although there are different evaluation methods for the measures to suppress the negative effects of clay, for XRD can intuitively reflect the changes in interlayer spacing of clay, and Zeta potential could also characterize the influence of organic compounds on clay potential. However, based on the differences in molecular weight and side chain functional groups of PCEs, the anti-clay performance and mechanism of different sacrificial agents may also vary (Alves et al., 2016; Li et al., 2018; Tian et al., 2022, Xu et al., 2016). There is still relatively insufficient research on how to further optimize the molecular structure of the sacrificial agents, matching the types and amounts of sacrificial agents corresponding to their performance.

Molecular simulation technology can effectively compensate for the shortcomings of macroscopic experiments, and has been widely applied in exploring the complex chemical reaction process and interaction mechanism. Based on our previous findings on the effect of the side-chain length in PCEs (He et al., 2023; Huang et al., 2022), this article will select PEO-like side chain structures, such as small molecule polyols (ethylene glycol, pentaerythritol, etc.), and different molecular weights of polypropylene glycol (PPG) as the non-ionic sacrificial agents. By establishing the adsorption models for non-ionic sacrificial agents with clay minerals and hydration products, the anti-clay performance and mechanism of different sacrificial agents will be explored from the perspective of adsorption energy, further investigating the influence of the interlayer spacing of montmorillonite on the competitive adsorption performance. This research would also help in the structural design of sacrificial agents, achieving the controllable regulation of the anti-clay performance based on the molecular structure differences for the sacrificial agent (Du, 2019; Qiu, 2021; Li et al., 2022; Tan et al., 2017).

2.   Models and calculation method

2.1. Method

The theoretical model and algorithms of molecular simulation technology are constantly improving, while density functional theory (DFT) may find broad application in material synthesis and surface adsorption. In view of our previous research (He et al., 2023; Huang et al., 2022), all DFT calculations were performed using the DMol3 package incorporated in Material Studio (MS) Software. The equilibrium configuration at the lowest energy was determined through geometry optimization using the Becke-Perdew (BP) correction approximation under the generalized gradient approximation (GGA), with a smearing value set at 0.005 unless otherwise specified (He et al., 2023; Huang et al., 2022; Xing et al., 2020).

Building on prior studies, we identified the optimum crystal planes for the clay minerals (Huang Teng, et al., 2022). Additionally, we obtained the hydration product $Ca(OH)_2$ (CH) (101) surface for the following discussions (He et al., 2023).

The adsorption energy in this article was calculated using the equation :

$$E_{ads} = E_{total \text{ (sacrificial agents on CaMMT)}} - (E_{\text{ sacrificial agents}} + E_{CaMMT}) \tag{1}$$

$$E_{ads} = E_{total \text{ (sacrificial agents on Ca(OH)2)}} - (E_{\text{ sacrificial agents}} + E_{Ca(OH)2}) \qquad (2)$$

where E_{ads} is the adsorption energy, and E_{total} (sacrificial agents on CaMMT) is the total energy of different non-ionic sacrificial agents on the montmorillonite. For cases with less adsorption energy, the adsorbability is more likely to occur (He et al., 2023; Huang et al., 2022; Orazi et al., 2020; Xing et al., 2020).

2.2. Calculation models

In this study, diethylene glycol, 1,2,4-butantriol, pentaerythritol, xylitol, etc. were selected as the structural models for polyols, and PPG with molecular weights from 100 to 600 were selected as the structural models for polymeric polyols.

The structures of PPG with different molecular weights after geometric optimization are presented in Fig. 1.
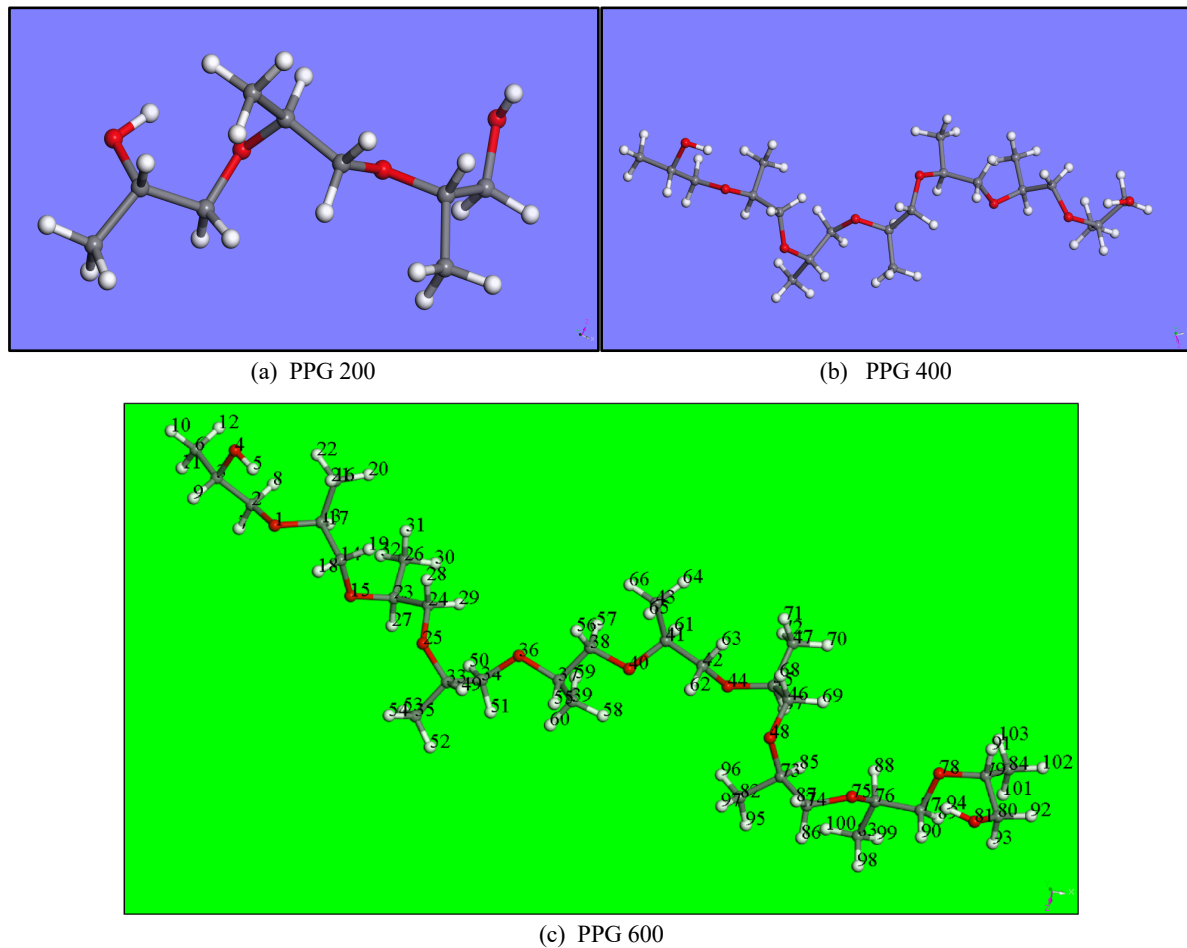

(a) PPG 200   (b) PPG 400

(c) PPG 600

Fig. 1. PPG with different molecular weights after geometric optimization

3. Results and discussion

3.1 Adsorption energy between clay minerals and hydration product

Taking pentaerythritol as an example, the adsorption models between different clay minerals are presented in Fig. 2, while the adsorption energy was compared as shown in Fig. 3 (He et al., 2023; Huang et al., 2022).

The adsorption energy of pentaerythritol in the hydration product $Ca(OH)_2$ is a positive value, indicating that adsorption with hydration products is difficult to occur. While the adsorption energy of pentaerythritol with different clay minerals is negative, with the calculated adsorption energy increasing as follows: montmorillonite < kaolinite < illite. The adsorption energy between pentaerythritol and montmorillonite is the lowest, so the sacrificial agent pentaerythritol can more easily combine with montmorillonite when compounded with PCE, effectively reducing the

consumption of water-reducing admixture. Hence, montmorillonite will be adopted as the representative of clay minerals to further investigate the adsorption performance of different polyol sacrificial agents (Huang et al., 2022; Tan et al., 2016; Qiu, 2021).
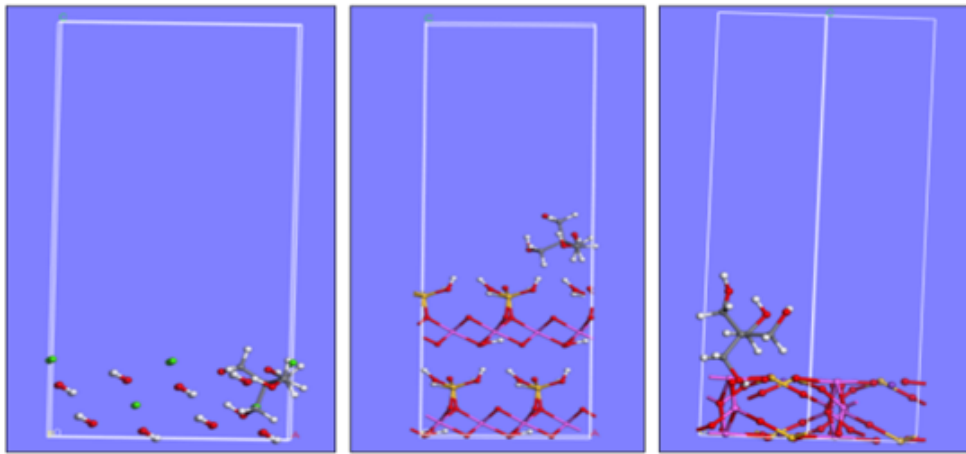
(a) pentaerythritol-Ca(OH)$_2$ (b) pentaerythritol-kaolin (001)   (c) pentaerythritol-illite (020)

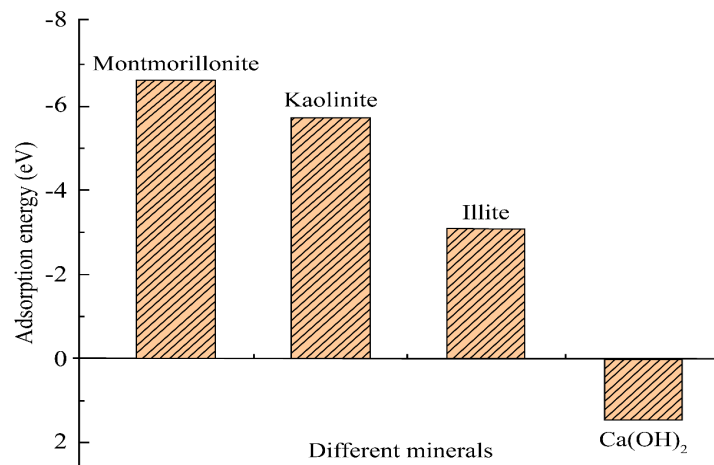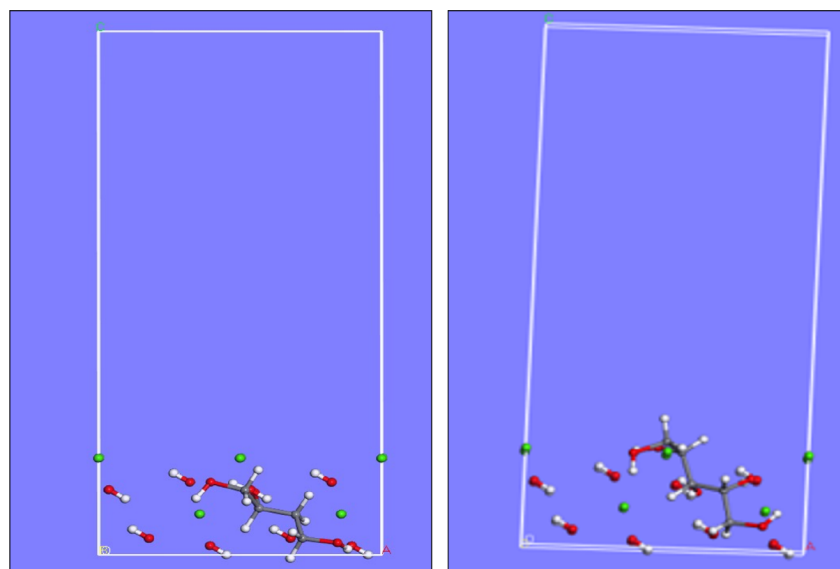Fig. 2. Adsorption models of pentaerythritol and clay minerals

Fig. 3. Comparison of the adsorption energy in the clay minerals and Ca(OH)$_2$

(a) 1,2,4-butantriol-Ca(OH)$_2$ (b) xylitol-Ca(OH)$_2$

Fig. 4. Adsorption models of the non-ionic sacrificial agents and Ca(OH)$_2$

3.2. Anti-clay performance on different non-ionic sacrificial agents

3.2.1. Adsorption energy of different polyols between Ca(OH)₂ and MMT

Taking 1,2,4-butantriol and xylitol as examples, the adsorption models in $Ca(OH)_2$ were established as shown in Fig. 4. The adsorption energy of different polyols in hydration products and montmorillonite was compared as presented in Table 1.

Table.1   Adsorption energy of polyols between the hydration product and montmorillonite

	Functional group	Adsorption (eV)	
		$Ca(OH)_2$	CaMMT
(a)	1,2,4- butantriol ($C_4H_{10}O_3$)	2.9419	-3.2927
(b)	pentaerythritol ($C_5H_{12}O_4$)	1.4297	-6.5935
(c)	xylitol ($C_5H_{12}O_5$)	0.2808	-6.7486
(d)	D-glucose ($C_6H_{12}O_6$)	-0.4012	-5.0723
(e)	diethylene glycol ($C_4H_{10}O_3$)	-0.0150	-2.6994

As the hydroxyl number increases, the adsorption energy between polyols and montmorillonite decreases. The adsorption energy value is -6.75 eV in xylitol, while in diethylene glycol (the diol), the adsorption energy is the highest (-2.70 eV). The priority adsorption order between different polyols and montmorillonite is xylitol > pentaerythritol > D-glucose > 1,2,4-butantriol > diethylene glycol.

Similarly, the adsorption energy between polyol sacrificial agents and hydration products is mostly positive. This ensures that when polyol sacrificial agents are combined with PCE, the sacrificial agent could preferentially adsorb with montmorillonite, thereby reducing the consumption of PCE in the clay. The difference in adsorption energy between montmorillonite and hydration products is the largest in pentaerythritol, indicating better adaptability to PCE (Du, 2019; Huang et al., 2022; Wang et al., 2022).

3.2.2. Adsorption energy of PPG for different molecular weights

The comparison of adsorption energy for PPG in hydration products $Ca(OH)_2$ and montmorillonite is presented in Fig. 5. As the molecular weight of PPG increases, the adsorption energy in $Ca(OH)_2$ shows a trend of decreasing first and then increasing. The adsorption energy is the lowest (-2.52 eV) at PPG 400, while at a molecular weight of 600, the adsorption energy has increased to -0.653 eV.
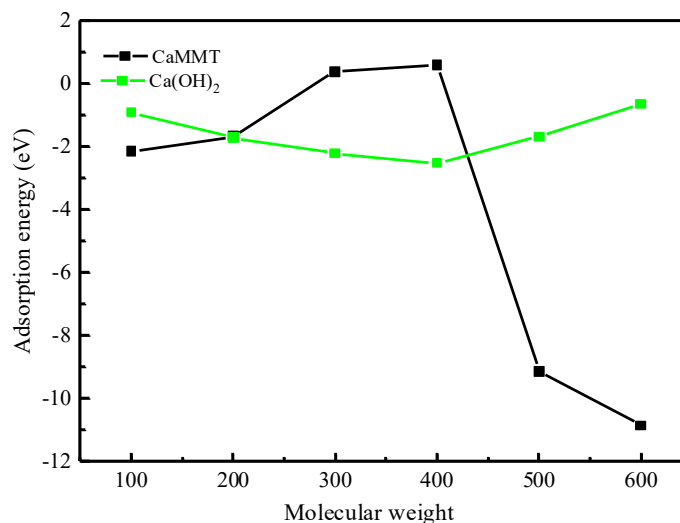

Fig. 5. Adsorption energy of the molecular weight for PPG in $Ca(OH)_2$ and montmorillonite

While the adsorption energy may exhibit a trend of increasing first and then decreasing in montmorillonite. The adsorption energy reaches the maximum value (0.581 eV) at PPG 400. The adsorption energy with montmorillonite is the lowest (-10.86 eV) at PPG 600, while the difference with hydration product $Ca(OH)_2$ is also the largest. The adaptability of non-ionic sacrificial agents and PCEs is mainly related to their competitive adsorption capacity on the cement particles (Du, 2019; Qiu, 2021; Wang et al., 2022). When compounded with different types of PCEs, the adsorption energy of PPG 600 is the lowest, making it easier to bind with montmorillonite, thereby presenting superior anti-clay performance.

3.3. Adsorption energy for the different interlayer spacing of MMT

The interlayer bonding strength of montmorillonite is relatively weak, making it prone to hydration. The layer distance of montmorillonite without adsorbed water is 9.6 Å, and after water absorption, it can reach a maximum of 20.5 Å. Consequently, montmorillonite exhibits characteristics such as easy hydration, dispersion and expansion. For simplification in the calculation, net MMT structural models with no adsorbates in different interlayer were constructed as presented in Fig. 6, so as to explore the effect of different interlayer spacing on the adsorption performance of PPG sacrificial agents. Hence, c =12.5, 15.5, 18.5, and 20.5 Å may correspond to the 1~4 layers of water molecules (Borralleras et al., 2019; Katti et al., 2015; Yu et al., 2019; Zheng et al., 2018).

The adsorption energy between PPG 600 and montmorillonite with different interlayer spacing is calculated as presented in Fig. 7. As the interlayer spacing of montmorillonite increases, the adsorption

(a) c =12.5 Å   (b) c =15.5 Å

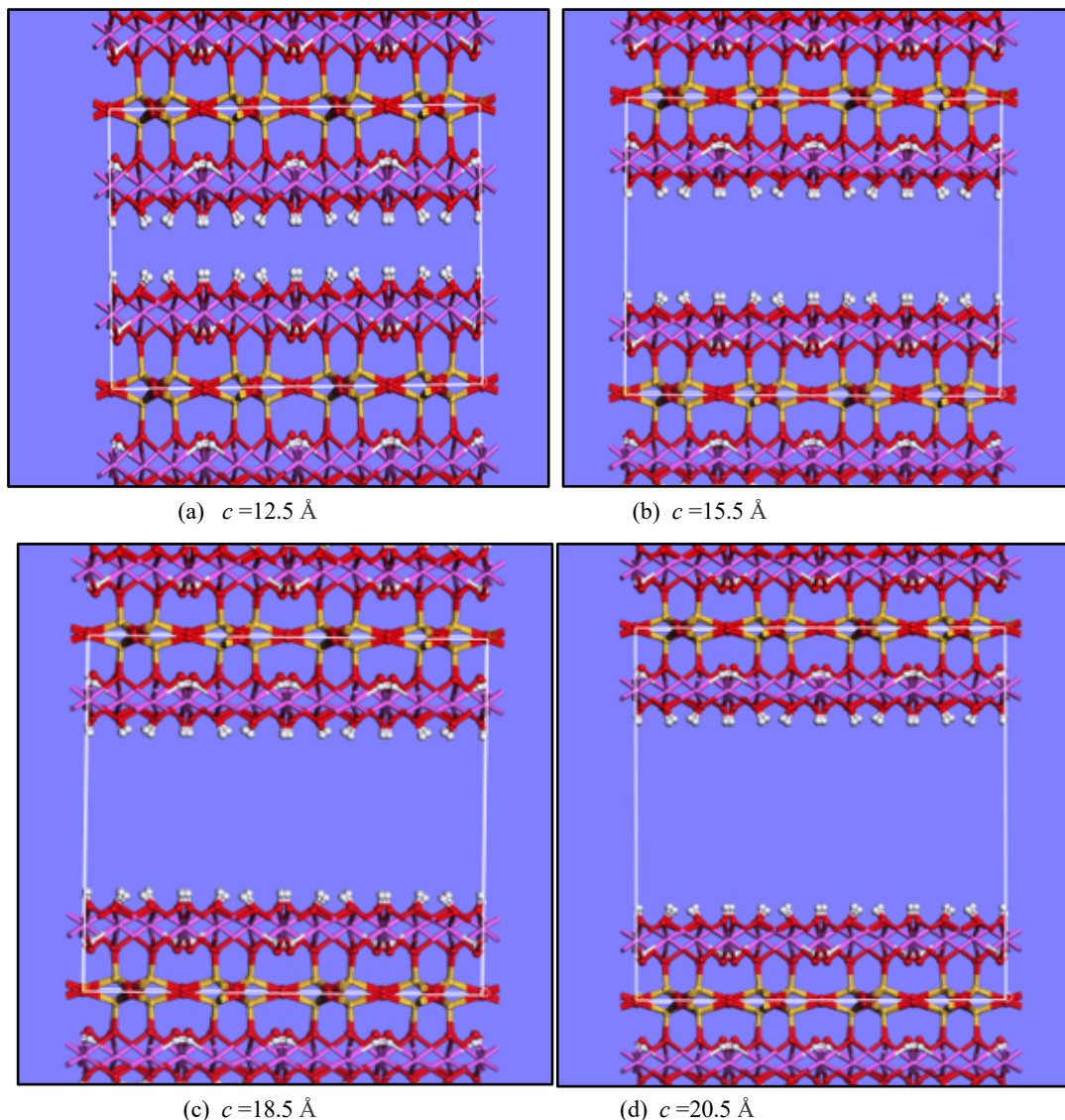(c) c =18.5 Å   (d) c =20.5 Å

Fig. 6. Structural models of different interlayers for montmorillonite

energy shows a trend of first decreasing and then increasing. The adsorption energy is the lowest (-10.86 eV) when the interlayer spacing c =15.5 Å (Fig. 6b), suggesting that the sacrificial agent would be more likely to bind with montmorillonite.
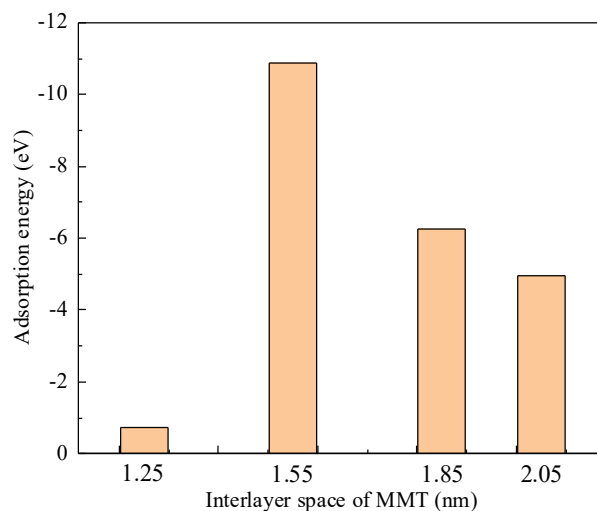

Fig. 7. Adsorption energy between PPG 600 and montmorillonite with different interlayer spacing

3.4. Mulliken charge populations

Furthermore, we can demonstrate the specific charge distribution of different atoms to illustrate the adsorption characteristics between the sacrificial agent and montmorillonite (Fan et al., 2017; He et al., 2023; Huang et al., 2022). Combining the adsorption models between PPG and different interlayer spacing of montmorillonite, for the structural model of PPG 600 as an example (Fig. 1c), Mulliken population analysis for the O atoms before and after adsorption was present in Table. 2.

Table. 2. Comparison of Mulliken charge populations before and after adsorption

	PPG	Interlayer spacing of montmorillonite (Å)		
	(before adsorption)	c = 12.5	c = 15.5	c = 18.5
O (1)	-0.483	-0.455	-0.45	-0.438
O (4)	-0.571	-0.614	-0.59	-0.692
O (15)	-0.461	-0.551	-0.555	-0.394
O (25)	-0.488	-0.664	-0.607	-0.44
O (36)	-0.494	-0.614	-0.593	-0.602
O (40)	-0.484	-0.405	-0.278	-0.363
O (44)	-0.474	-0.5	-0.53	-0.442
O (48)	-0.461	-0.421	-0.449	-0.37
O (75)	-0.468	-0.445	-0.605	-0.61
O (78)	-0.468	-0.482	-0.435	-0.459
O (81)	-0.58	-0.613	-0.63	-0.578

The charge of the O atom in PPG 600 varied to different degrees with diverse interlayer spacing of montmorillonite. For O (40) and O (75) atoms at c =15.5Å, the Mulliken charge population changed from -0.484 to -0.278 and -0.468 to -0.605, respectively. While at c =18.5 Å, the changes were from -0.484 to -0.363 and -0.468 to -0.610. The amount of transferred electrons in c =15.5 Å (0.858) is the largest among the other interlayer spacings, aligning with the adsorption energy presented in Fig. 7, further verifying the higher adsorption characteristics between sacrificial agents and montmorillonite from the perspective of electronic gain and loss.

4. Conclusions

This paper delved into small molecule polyols and diverse PPG molecular weights. By establishing adsorption models for non-ionic sacrificial agents with clay minerals and hydration products, the anti-clay performances and impact of various sacrificial agents were explored from the perspective of

adsorption energy. The influence of montmorillonite interlayer spacing on the competitive adsorption and charge transfer characteristics would also be disclosed, providing important basis for the further research on the molecular structure design of sacrificial agents. The main conclusions are:

(1) The adsorption priority order of polyol sacrificial agents in hydration product $Ca(OH)_2$ and different clays is as follows: montmorillonite > kaolinite > illite > $Ca(OH)_2$. The adsorption energy in montmorillonite was the lowest, thus, the sacrificial agents could preferentially adsorb with montmorillonite. As the number of hydroxyl group increased, the adsorption energy between the polyols and montmorillonite would be decreased. Among them, the adsorption energy in pentaerythritol was lower, and the difference in adsorption energy between the montmorillonite and $Ca(OH)_2$ was the highest. Therefore, when compounded with PCEs, the tolerance to clay minerals could be effectively improved.

(2) As the molecular weight of PPG increased, the adsorption energy in the hydration product first decreased and then increased, while in montmorillonite, the adsorption energy would reach its lowest value (-10.86 eV) at PPG 600. When compounded with different PCEs, the adsorption energy of PPG 600 was lower, which could preferentially occupy the active sites of montmorillonite, thus reducing the consumption of water-reducing agents and presenting more excellent anti-clay performance.

(3) As the interlayer spacing of montmorillonite increased, the adsorption energy between PPG 600 and montmorillonite showed a trend of first decreasing and then increasing. The adsorption energy was the lowest at c =15.5 Å, while the number of electron transfers was also the largest, suggesting that the interaction with montmorillonite was more significant. The interaction mechanism between the non-ionic sacrificial agents and montmorillonite was further revealed from the perspective of electronic gain and loss.

Acknowledgements

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