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Theoretical evaluation of flotation performance of carboxyl hydroxamic acids with different number of polar groups on the surfaces of diaspore (010) and kaolinite (001)

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Abstract The adsorption behaviors of three carboxyl hydroxamic acids on diaspore (010) and kaolinite (001) have been studied by density functional theory (DFT) and molecular dynamics (MD) method. The results indicated that carboxyl hydroxamic acids could adsorb on diaspore surface by ionic bonds and hydrogen bonds, and adsorb on kaolinite surface by hydrogen bonds. The models of carboxyl hydroxamic acids adsorbed on diaspore and kaolinite surfaces are proposed.

Keywords Adsorption · DFT · Diaspore · Dynamic · Flotation reagent

Introduction

Aluminum oxide mineral resources in China are diasporic bauxite with high silica, high alumina content and low Al_2O_3/SiO_2 (A/S) mass ratio, and the gangue minerals in this type of resource are mainly kaolinite, pyrophyllite and illite [1]. Flotation separation is a better approach to increase A/S mass ratio for bauxite so as to use the advanced Bayer process [2, 3]. Theoretically, two approaches can be applied in the flotation desilication of diasporic bauxite: one is direct flotation characterized by the flotation of diaspore and the depression of aluminosilicates, the other is reverse flotation characterized by the flotation of aluminosilicates and the depression of diaspore. No matter which approach is employed, the flotation reagent, especially the collector, is critical to the flotation separation process.

Carboxyl hydroxamic acid [4] is a kind of direct flotation reagent with carboxyl group and hydroxamic group in a molecular structure. Our laboratory has been developing three types: mono-carboxyl and mono-hydroxycarbamoyl type, mono-carboxyl and double-hydroxycarbamoyl type, and double-carboxyl and double-hydroxycarbamoyl type according to the number of the polar groups [5]. Traditionally, test of flotation performance is mainly conducted by experimental methods, such as flotation experiment, FTIR spectroscopy, zeta potential measurements, x-ray photoelectron spectroscopy and adsorption amounts, but these experimental methods are high-cost, time-consuming, and deficient in elucidating flotation mechanism. In order to overcome these shortages, computer simulation methods have been introduced for either flotation performance or detailed flotation mechanism exploration.

Among all computer simulation methods, quantum chemistry calculation has been used to evaluate the flotation performance of flotation reagents, which is a quantitative means in studying the flotation efficiency of a reagent. As an accurate method in quantum chemistry calculation, total electron calculation is suitable for dealing with small systems, but time-consuming for large systems. With this method, the capability of flotation molecules can be predicted with analysis of global and partial reactivity, such as energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the Fukui indices, etc. [6–9]. Compared with quantum chemistry method, dynamics method would be a better choice for large

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systems to reduce the computation time. With molecular dynamic methods, the adsorption state of flotation monolayer formed on diaspore (010) and kaolinite (001) can be investigated by analysis of radial distribution functions (RDF), interaction and cohesive energy of monolayer. However, molecular dynamic method fails in providing detailed information about molecular active area. Obviously, it would be more feasible and comprehensive to assess the flotation performance by combination of the above two methods, which can provide complementary information about mechanism from different aspects. So the flotation performance of three carboxyl hydroxamic acids is evaluated via combination of quantum chemistry and dynamic method in this paper.

The work has studied the flotation behaviors of three molecules: 2-carboxyl-6-methylcyclohexane carboxamic acid (CMCA) [10], 3-bis(hydroxycarbamoyl) undecanoic acid (BHUA) [11], and 2-bis(hydroxycarbamoyl) octyl maleate (BHOM), as shown in Fig. 1. CMCA is mono-carboxyl and mono-hydroxycarbamoyl type, BHUA is mono-carboxyl and double-hydroxycarbamoyl type, and BHOM is double-carboxyl and double-hydroxycarbamoyl type, while the nonpolar of CMCA is six-ring carbon atoms, and the nonpolar of BHUA and BHOM is both chain carbon atoms. The influence of polar and nonpolar groups on the flotation performance of these compounds was investigated by quantum chemical calculations and molecular dynamic methods.

Computational details

Quantum chemical method

The research had been carried by density functional theory (DFT), together with the functional of B3LYP and the standard double-zeta plus polarization 6-31G+(d) basis set [12].

The calculations were carried out for the selective molecules. The geometry of all compounds under investigation was determined by optimizing all geometrical variables without any symmetry constraints. The harmonic frequencies were computed from analytical derivatives for all species in order to define the minimum-energy structures. According to DFT theory [13–15], the HOMO energy, the LUMO energy, and the Fukui functions were also obtained at the basis set level to analyze the active area of flotation reagents [16, 17].

Separate calculations on anionic system (N_{k+1}) and cationic system (N_{k-1}) have been used to imply relaxation of orbitals from the neutral system (N_k) with the following equations [18, 19]:

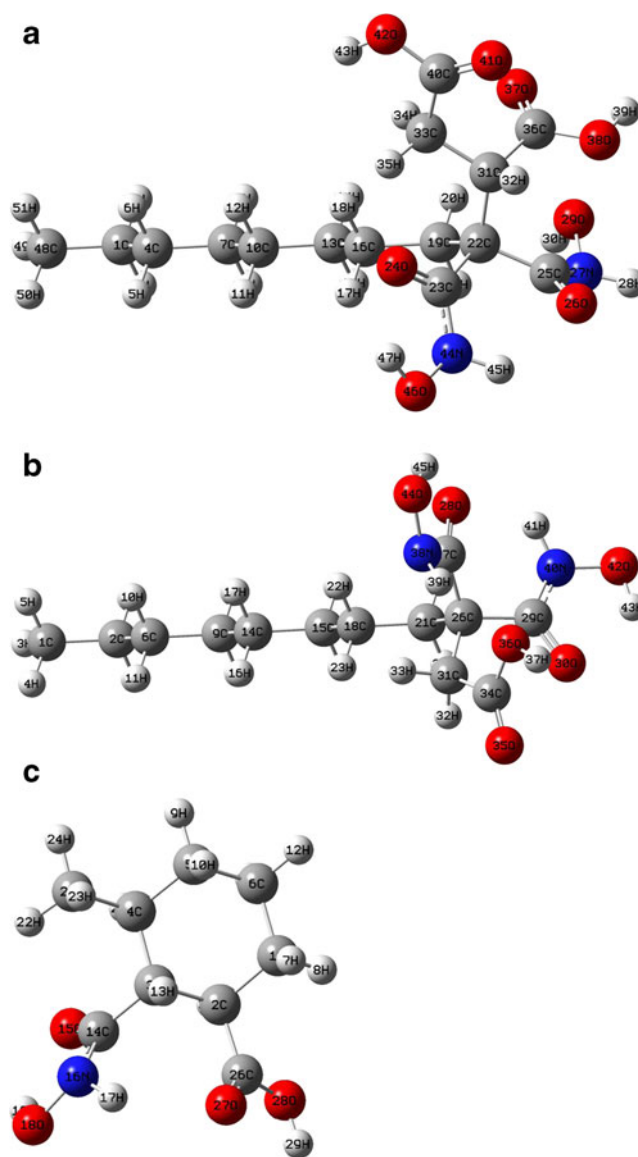$$f^+ = q(N_{k+1}) - q(N_k)$$

Fig. 1 Optimized geometries for the three molecules calculated by DFT, **a**, **b**, and **c** is BHOM, BHUA, and CMCA, respectively

$$f^- = q(N_k) - q(N_{k-1}),$$

where q is the gross charge of atom k in the molecule and N_k is the number of electrons. The calculations were performed using Gaussian 03 [20]. In all models simulation results were calculated in vacuum [21, 22].

LogP value was completed by ACD-Labs. The starting structure of flotation reagent was obtained by gaussian simulation. The result of logP value was then gained by introducing the starting structure into the software [23].

Dynamics simulations

Also, the molecular dynamics simulations were performed using materials studio software. Diaspore (010) and kaolinite

(001) surfaces were chosen for the simulation study [24]. The optimized carboxyl hydroxamic acids were added onto the as-built mineral surfaces, and the 'vacuum slab' with the height of 20 Å was put upon the carboxyl hydroxamic acids-mineral system with 3D periodic boundary condition. The box of diaspore (010) sets is 20.18 Å×26.55 Å×38.48 Å and that of kaolinite (001) ones is 20.89 Å×27.22 Å×35.32 Å, both in 1 slab layer. The minerals surfaces were fixed before simulations. The MD simulation for each case study was performed long enough to observe several cycles of thermal vibration. MD calculation was then carried out for 1,000,000 ps and the interval of each MD simulation step was typically 1 fs (femtosecond). All calculations in this section were carried out at the initial temperature of 298 K, using constant number of particles, constant volume and constant temperature (NVT) ensembles. The further 100 ps MD simulation was performed under the same conditions to record the trajectory of all the atoms in the system for analysis [25, 26].

The dynamic behavior of the carboxyl hydroxamic acids can also be illustrated by tracking the interaction energy of the carboxyl hydroxamic acid molecules. Generally, the interaction energy is estimated from the difference between the potential energy of the composites system and the potential energy for the large molecules and the corresponding surface as follows:

$$E_{surface-molecular} = E_{total} - (E_{carboxyl\ hydroxamic\ acids} + E_{surface})$$

$$E_{binding} = -E_{surface-molecular},$$

where E_{total} is the total potential energy of the composite, $E_{surface}$ is the energy of the diaspore or kaolinite surface without the molecules and $E_{carboxyl\ hydroxamic\ acids}$ is the energy of the compounds without the surface using Materials studio [27].

Results and discussion

Molecular orbital energy calculation

In the flotation progress, the function of nonpolar groups is hydrophobic to make minerals grain away from aqueous solution. So it might be measured by the hydrophobic index logP referring to a substance in *n*-octane and water partition coefficient values. The greater the logP value, the more lipophilic the substance, whereas smaller, more hydrophilic. The order of logP values calculated about the molecules is BHOM>BHUA>CMCA in Table 1, and the collecting capacity of CMCA is weakest because of the negative logP value of CMCA. As a result, CMCA should be very weak in collecting minerals, which agrees with the result of the flotation test. On account of the same nonploar group

between BHOM and BHUA, the collective ability would be determined by polar groups.

Table 1 presents the calculated energy levels of the HOMO and LUMO for the selected compounds. Frontier orbital theory is useful in predicting adsorption with surface mineral atoms. Terms involving the frontier MO could provide dominative contribution, because the inverse dependence of stabilization energy on orbital energy difference. Moreover, the gap between the LUMO and HOMO energy levels of the molecules listed in Table 1 was another important factor that should be considered. Reportedly, excellent flotation reagents are usually those organic compounds which not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. According to this, it means that the collecting efficiency of the molecule between diaspore (010) and kaolinite (001) is affected by the LUMO energy and HOMO energy. The higher the HOMO energy of the flotation reagent, the greater trend of donating electrons to the metal atoms, and the higher the flotation collective efficiency on minerals.

As the LUMO-HOMO energy gap decreased, the efficiency of flotation improved. The quantum chemistry calculations revealed that the collecting capacity of the carboxyl hydroxamic acids is following the order BHOM>BHUA= CMCA. Considering the effect of the logP value together, the carboxyl hydroxamic acids are in the order of BHOM> BHUA>CMCA in the collecting capacity. In a word, BHOM is expected to be the most active in the reaction.

Subsequently, Table 2 shows the highest occupied molecular orbital, the lowest unoccupied molecular orbital of the molecules under study. From this figure, it is known that for the molecules HOMO energy is mainly concentrated in the range of -CONHOH group of the selective molecules, and the group of -COOH is hardly contributed to the HOMO energy; meanwhile, the group of -CONHOH is contributed to the LUMO energy. It shows that the number of the -CONHOH group affects the character of the reagents in collecting diaspore and agrees with the result of flotation test that the collecting capability of the reagents with double -CONHOH groups is much better than the single one.

Local reactivity of the selected flotation candidates

A presentation of the HOMO orbital and LUMO orbital was calculated and listed in Table 2, which indicates that the active sites for electrophilic and nucleophilic attack are located mainly on -CONHOH and little on -COOH.

Fukui functions make it possible to rationalize the reactivity of individual molecular orbital contributions thus accounting for the response of the whole molecular spectrum and not only of the frontier orbital [28]. The reactivity indices are not directly attained experimentally and only the relative trends between theoretical data and experimental

Table 1 Quantum chemical derived for carboxyl hydroxamic acids calculated with DFT method and dynamic parameters

^a△E is the gap of LUMO and HOMO

Collector	$E_{dsurface-molecular}$ kcalmol^{-1}	$E_{ksurface-molecular}$ kcalmol^{-1}	$\square E^a$, eV	HOMO, eV	LUMO, eV	logP
BHOM	−585.56	−560.28	0.21	−0.26	−0.05	2.92
BHUA	−481.05	−464.76	0.22	−0.26	−0.04	1.28
CMCA	−316.73	−316.65	0.22	−0.25	−0.03	−0.18

information can be compared and analyzed. The Fukui indices for each one of the atoms in the molecules have been calculated. An analysis of the Fukui indices along with the distribution of charges provides a more complete scheme of the reactivity of the studied molecules. The calculated Fukui indices for all the charged species (k^{+1} and k^{-1}) as well as the neutrals (k) of each of the carboxyl hydroxamic acids are presented in Table 3. Simply, only the charges and Fukui functions over the nitrogen, oxygen, and carbon atoms are presented.

Table 2 Frontier molecular orbital and functions for flotation agents calculated by DFT

Table 3 Calculated Mulliken atomic charges and functions for the three carboxyl hydroxamic acids

Molecules	Atom	qk	qk+1	qk−1	Fk+	Fk−
BHOM	19C	−1.83	−0.66	−1.79	1.17	0.04
	22C	1.60	0.82	1.66	0.78	0.06
	23C	0.08	0.02	0.06	0.07	0.02
	24O	−0.49	−0.55	−0.38	0.06	0.11
	25C	0.54	0.67	0.51	0.13	0.03
	26O	−0.41	−0.52	−0.33	0.11	0.08
	27N	−0.39	−0.54	−0.35	0.15	0.03
	29O	−0.46	−0.22	−0.42	0.24	0.04
	31C	−0.23	−1.02	−0.29	0.78	0.06
	33C	−0.72	−0.27	−0.64	0.45	0.08
	36C	0.56	0.65	0.54	0.09	0.02
	37O	−0.34	−0.34	−0.29	0.00	0.05
	38O	−0.53	−0.51	−0.52	0.02	0.01
	40C	0.60	0.40	0.58	0.20	0.02
	41O	−0.37	−0.40	−0.27	0.03	0.10
	42O	−0.55	−0.50	−0.52	0.05	0.03
	44N	−0.47	−0.50	−0.42	0.02	0.05
	46O	−0.28	−0.32	−0.11	0.03	0.17
BHUA	21C	−0.03	−0.09	0.09	0.06	0.12
	26C	−0.26	−0.28	−0.41	0.02	0.15
	27C	0.41	0.45	0.37	0.03	0.04
	28O	−0.55	−0.66	−0.49	0.10	0.06
	29C	0.59	0.56	0.57	0.03	0.02
	30O	−0.49	−0.56	−0.37	0.07	0.12
	31C	−0.59	−0.67	−0.50	0.09	0.09
	34C	0.59	0.60	0.55	0.01	0.04
	35O	−0.41	−0.48	−0.37	0.06	0.05
	36O	−0.67	−0.65	−0.69	0.02	0.01
	38N	−0.47	−0.50	−0.43	0.04	0.04
	40N	−0.46	−0.49	−0.40	0.03	0.06
	42O	−0.26	−0.30	−0.09	0.05	0.16
	44O	−0.32	−0.36	−0.21	0.04	0.11
CMCA	1C	−0.35	0.08	−0.33	0.43	0.02
	2C	−0.41	−2.65	−0.38	2.24	0.03
	3C	−0.03	1.11	−0.24	1.14	0.22
	4C	0.06	−1.00	0.09	1.06	0.04
	5C	−0.34	0.91	−0.34	1.25	0.01
	6C	−0.59	0.70	−0.57	1.29	0.02
	14C	−0.03	−2.21	0.01	2.18	0.04
	15O	−0.49	−0.46	−0.32	0.03	0.17
	16N	−0.38	−0.26	−0.28	0.13	0.10
	18O	−0.33	−0.34	−0.10	0.01	0.24
	21C	−0.85	−0.89	−0.78	0.04	0.07
	26C	0.72	0.95	0.71	0.23	0.01
	27O	−0.47	−0.46	−0.40	0.01	0.07
	28O	−0.56	−0.33	−0.52	0.23	0.04

The local reactivity is analyzed by means of the condensed Fukui function, which allows us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. Thus, the site for nucleophilic attack will be the place where the value of f_k^+ is a maximum. In turn, the site for electrophilic attack is controlled by the value of f_k^-. It reveals that the most reactive sites of the molecules integrating with the Mulliken charge are O and N atoms on the polar groups for electrophilic attack. The mulliken charge of the atoms by gaussian 03 simulation is negative to afford the electrons, and the polar atoms of BHUA in Fig. 1 with negative charge. At the same time, the order of f_k^- is 42O>30O >44O>28O>40N >35O>38N>36O, and the O atoms in -CONHOH like 42O, 30O, 44O, 28O are largest, so they have stronger electrical ability than N atoms or others. In one word, the O atom of -CONHOH group makes the main contributions in electrophilic process.

Radial distribution functions of the supermolecular structure and the interaction mode by dynamic simulations

The binding energy in Table 1 has a positive value by dynamic simulation. As the value of the binding energy $E_{surface-molecular}$ increases, the more easily the molecular adsorbs on the diaspore (010) or kaolinite (001). BHOM possesses the maximum binding energy to the diaspore (010) or kaolinite (001), and BHUA second. High values of binding energy indicate that BHOM molecules are expected to give the highest adsorptive efficiency in the theoretical views. Besides, the theoretical results agree with the conclusion of floating diaspore and kaolinite, that is, the order of collecting capacity is BHOM > BHUA > CMCA.

From further research, we found that it was important whether the reaction took place or not between the flotation reagent and mineral surface (diaspore (010) or kaolinite (001)), affecting the results of flotation tests for diaspore and kaolinite.

The molecular dynamic simulations are performed to study the adsorption behavior of BHUA on diaspore (010) and kaolinite (001) surfaces. The geometry optimization of the studied system is carried out using an iterative process, in which the atomic coordinates are adjusted until the total energy of a structure is minimized, i.e., it corresponds to a local minimum in the potential energy surface.

The distance between the active atoms of BHUA and the Al, H atoms on diaspore (010) and kaolinite (001) was measured through the radial distribution function (RDF) analysis (in Fig. 2). Generally, the values of aiguille in the range of 3.5 Å in the g(r)~r figure are considered to be mainly composed of chemical bonds and hydrogen bonds, as well as the values beyond the range of 3.5 Å are mainly
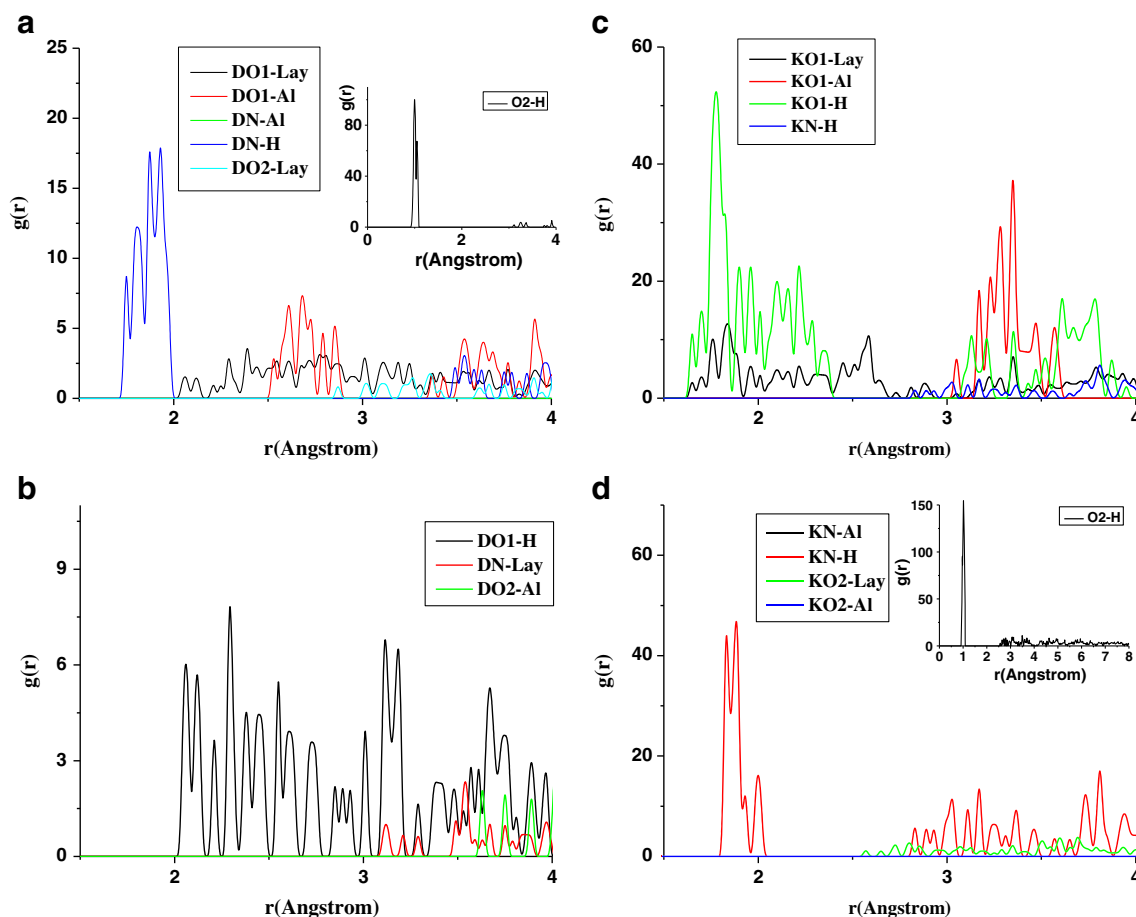
Fig. 2 a, b The interaction between polar atoms in BHUA and Al, H atom of diaspore (010), or all surfaces by RDF analysis c, d The interaction between polar atoms in BHUA and Al, H atom of kaolinite (001), or all surfaces by RDF analysis

representing the bonds including van der Waals (vdw) and Coulomb force. The RDF analysis indicates that the distance between oxygen atoms of C=O groups and Al of the diaspore (010) is respectively around 2.61 Å near to the sum of the radius values of the two atoms when the highest peak of $g(r)_{Al-O} \sim r$ curve appears, and the interaction of C=O···Al affects the high peaks of interaction of C=O and diaspore (010), indicating oxygen atoms of C=O groups and Al of the

diaspore (010) in the ionic bonds. And the oxygen atoms also tend to form strong hydrogen bonds in Figs. 3a and 2a and b. Otherwise, O atom of C=O groups and Al of the kaolinite (001) in vdw or Coulomb force, O atom of C=O groups and the kaolinite (001) in hydrogen bonds in Figs. 2c and d and 3b, especially O2. It is shown that O and N atoms have strong hydrogen bond with H of diaspore (010) and kaolinite (001).

Fig. 3 Equilibrium adsorption configurations of collectors BHUA on a diaspore (010) and b kaolinite (001) surfaces obtained by molecular dynamic simulations
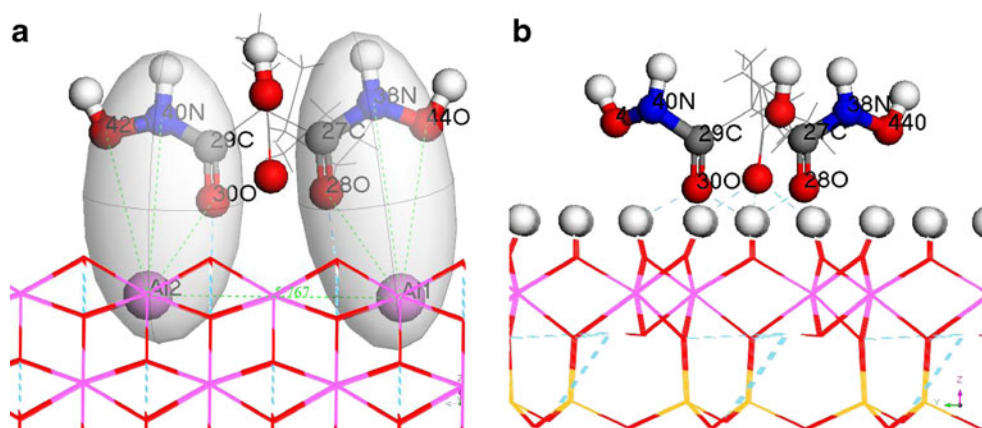
From the previous discussion we can see that the active reaction of the carboxyl hydroxamic acid is the -CONHOH group, and the active atoms are O atoms of >C=O and O atoms of -NHOH. At the same time, it is easy to form ring structure because they are just 5 or 6 apart between these atoms and the Mulliken charge of O atoms of >C=O and -NHOH is high, so a new mode of interaction between molecules and mineral surfaces is put forward with dynamic simulation as an example of BHUA in Fig. 3. The studied system reaches equilibrium only if both the temperature and energy of the system reach balance, and every molecule positioned anywhere on the mineral surfaces would select one or several adsorption sites by their active atoms. On the base of these, we can build interaction mode of carboxyl hydroxamic acids and diaspore (010) surface which is obviously ionic bonds and hydrogen bonds to the ring chelation. In Fig. 3a, the gray oval transparent ellipses show the 5 atom rings, and the members of each ring are respectively 42O, 40 N, 29C, 30O and 28O, 27C, 38 N, 44O, and two O atoms of C=O containing O of C=O in -COOH group also form 7 atom rings. For the dynamic simulation of BHUA-kaolinite system, the O atoms of C=O tend to forming hydrogen bonds (blue dotted line in Fig. 3a and b).

In short, it is implied that the interaction capacity of BHUA with the diaspore (010) is more than that with the kaolinite(001), and it is found that 5- or 7-member chelate system in the simulation progress for BHUA and the diaspore(010) was formed. While the interaction force is hydrogen bonds between BHUA and kaolinite (001).

Conclusions

(1) The collector properties of carboxyl hydroxamic acid were studies by means of density function theory. The calculated electronic parameters involved in the activity of the collectors confirmed that the -CONHOH group affects the pattern of activity. BHOM shows better collective ability to both diaspore and kaolinite, but BHUA has better selectivity in separation of diaspore against kaolinite.

(2) According to DFT calculation and dynamics simulations, the chelating adsorption model is built, and the research further confirms the activity of atoms to diaspore (010) by both ionic bonds and hydrogen bonds, while hydrogen bonds on kaolinite (001) by RDF analysis.

(3) Molecular modeling was used to evaluate the structural, electronic and reactivity parameters of the carboxyl hydroxamic acids in relation to their effectiveness as collectors.

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