The effect of ethylene oxide groups in dodecylamine polyoxyethylene ether on rutile flotation

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Abstract: To study the number of ethylene oxide (EO) groups effect on the flotation of rutile, three collectors with different EO number were evaluated: AC1203 (with three EO number), AC1210 (with ten EO number), AC1215 (with fifteen EO number). In addition to the flotation experiments, zeta potential measurements, collector adsorption experiments and XPS analysis were conducted to elucidate the adsorption mechanism. The results of flotation demonstrated that dodecylamine polyoxyethylene ether exhibited a profound collecting ability towards rutile mineral, it was worth mentioned that the recovery of rutile decreased with the increase of EO number. On the basis of zeta potential tests and XPS analysis, both protonated and neutral tertiary amine groups could act with rutile surface through electrostatic effect and hydrogen bond interaction. Furthermore, the results of collector adsorption experiments showed that with the increase of EO number, a lower adsorption density of collectors on rutile surface could be caused due to the steric hinder effects.

Keywords: rutile flotation, dodecylamine polyoxyethylene ether, ethylene oxide groups, steric hinder effect, adsorption mechanism

1. Introduction

Rutile, as one kind of oxidized minerals, was widely applied for the production of titanium white pigment (Li et al., 2016; Chen et al., 2018). Froth flotation was one of the primary mineral processing approaches for separation of rutile (Xu et al., 2017). In froth flotation, the collector (a kind of surfactant) selectively attached to the target mineral by using its polar group (Somasundaran and Wang, 2006), and then its hydrophobic group attached to air/nitrogen bubbles which delivered the mineral particles to the slurry surface (Ackerman et al., 1987).

Commonly, surfactants for flotation of rutile minerals were categorized into anionic and cationic collectors. For example, sodium oleate, water-soluble petroleum sulfonate, styryl phosphoric acid, benzyl arsenic acid, alkyl-imino-bismethylene phosphoric acid, and hydroximic acid were considered to be the effective collector for rutile (Li et al., 2016.; Zhao et al., 2007), but there were many deficiencies in them. For example, some of them were of high viscosity but poor foam mobility, while others consumed a lot of energies to maintain its solubility and activity. Furthermore, some of them were harmful to the environment.

Besides of these kinds of collectors, fatty amine polyoxyethylene ether, a cationic surfactant contained ethylene oxide [-(CH$_2$CH$_2$O)-, abbreviated as EO] and nitrogen group, was considered to be an alternative collector due to its profound collecting ability and environmental friendliness. It was well established that the application of a flotation collector with tailored structure could significantly improve selective flotation (Nagaraj and Farinato, 2016). As surfactants with the same hydrophobic

group, the properties of surfactants were mainly depended on the compositions and structure of hydrophilic headgroups. And small changes in molecular structures of flotation collectors could potentially lead to drastic changes in the strength and selectivity of collector adsorption (Liu et al., 2017). For example, Prime and Whitesides described the influence of the length and number of EO chains on the adsorption of proteins (Prime and Whitesides, 1991). In the flotation of low rank coal, increasing the number of EO in the $C_{12}EOn$ reduced the necessary amount of reagentand the greater selectivity could be achieved at the same time (Li et al., 2018).For the inhibition performance of alkyl ethoxy carboxylates against $CaCO_3$, it actually depended on the EO number, and the inhibition performance decreased with increasing the EO number (Wang et al., 2016). However, the effect of EO number on the adsorption and surface modification of rutile had not yet been studied.

The purpose of this work was to investigate the effect of the EO number on the flotation of rutile and to find whether a longer polar hydrophilic group or a shorter one was advantageous for increasing the recovery of rutile. The structure of the collectors selected in this paper was presented in Fig. 1. And three collectors with increasing EO number were chosen for the experiments. The adsorption mechanism of collectors on rutile surface was evaluated by zeta potential measurements, collector adsorption experiments and XPS analysis.
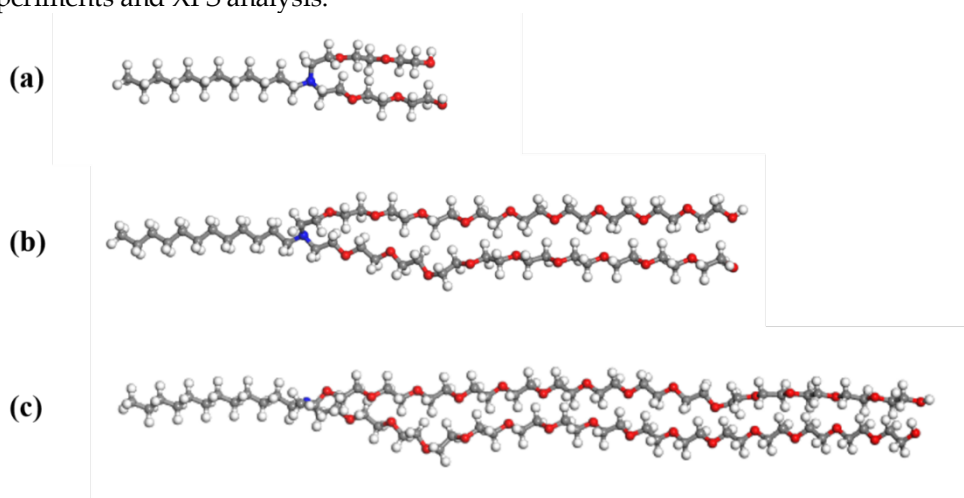

Fig. 1. Molecular structures of (a) AC1203, (b) AC1210, (c) AC1215. The color representation was as follows: red, oxygen atoms; white, hydrogen atoms; gray, carbon atoms; blue, nitrogen atom

2. Materials and methods

2.1. Materials and reagents

Single mineral of rutile used in this study was obtained from the Honghai mine located in Hainan province, China. The mineral was crushed and ground by using agate mortar. The products were then dry sieved to obtain the particle size of 38~74μm for pure mineral flotation experiments. A portion of the sample was further ground to-2μm for X-ray diffraction (XRD) and chemical analysis. The XRD analysis results and chemical compositions for rutile sample were presented in Fig. 2 and Table 1, respectively. And the results demonstrated that the purity of rutile sample was very high (more than 98%).

Industrial grade fatty amine polyoxyethylene ether (AC1203, AC1210, AC1215) used as collectors for the micro-flotation experiments were purchased from Haian petrochemical plant in Jiangsu province, China. HCl and NaOH (Chemical pure) were diluted to 0.1mol/L and 0.01mol/L and used as the pH regulators in the experiments. Deionized water (resistivity 18.25MΩ·cm, 298.15K) obtained from the Milli-Q Direct 16 (Millipore Q, USA) was used throughout the experiments.

Table 1. Chemical compositions of rutile sample (wt. %)

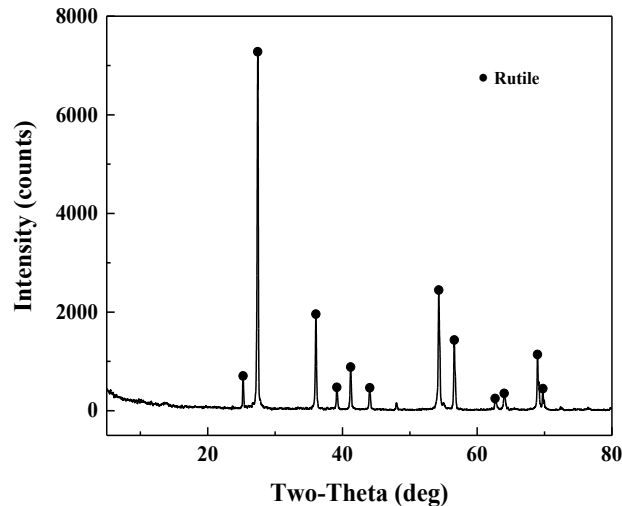| Sample	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	MnO	Fe_2O_3
Rutile	-	-	-	0.42	0.02	98.03	-	0.41

Fig. 2. XRD patterns of the rutile

2.2. Methods

2.2.1. Micro-flotation tests

The micro-flotation tests of single rutile sample were performed by using XFG-Ⅱ flotation machine (Fig. 3) with 40 cm^3 micro-flotation cell (Gao et al., 2016a; Gao et al., 2016b), and the stir speed fixed at 1750 rpm. The mineral suspension was prepared by adding 3.0 g of rutile (38~74μm) into 40 ml deionized water in the micro-flotation cell. The pH value of mineral suspension was adjusted to the target value with the addition of 0.1 mol/L HCl or 0.01 mol/L NaOH solutions before adding collectors. After the required amount of collectors were added, the pulp was agitated for 180s, and then froth was collected as flotation concentrates for 240s. All flotation tests were carried out at room temperature around 298.15 K. Finally, the froth and sink products were filtered and dried, and weighed to calculate the flotation recovery of rutile under various flotation conditions.

Fig. 3. XFG flotation machine for micro flotation tests

2.2.2. Zeta potential measurements

In order to investigate the adsorption phenomenon between collectors and rutile surface, zeta potential measurements were conducted and the changes of zeta potential were recorded (Liu et al., 2019a; Liu, et al., 2019b). The zeta potentials of the rutile sample were measured using the Malvern Zetasizer (Malvernstruments). 50 mg mineral sample (-2μm) was mixed in 1×10^{-3}mol/L KNO$_3$ background electrolyte solution. The suspension was conditioned by corresponding reagents at pH=6. After

magnetic stirring for 300s and setting for 600s, the supernatant of the dilute fine-particle suspension was obtained for the zeta potential measurement.

2.2.3. Adsorption experiments

In each test, 0.1 g of sample and a certain amount of deionized water and collector solution were placed into the beaker. After the slurry pH value was adjusted to 6, the solution was stirred for 1800s to ensure adsorption equilibrium. Then the supernatant liquid was sufficiently centrifuged separation from solution, and the concentration of residual collector was measured by SPECORD 200 (Jena, Germany) ultraviolet spectrophotometer. The measurement wavelengths of the three collectors were 192nm (AC1203), 195nm (AC1210) and 197nm (AC1215), respectively. The collector adsorption capacity on the surface of minerals could be calculated through formula 1:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \qquad (1)$$

where Q_e is the collector adsorption capacity on the surface of minerals (mol/g), C_0 is the initial concentration of collector in slurry (mol/L), C_e is the residual concentration of collector in slurry (mol/L), V is slurry volume (L), m is the mass of sample (g).

2.2.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out by using the Thermo Fisher ESCALAB 250 XPS system. AC1203 was chosen as the representative collector to investigate the adsorption mechanism, and the rutile samples were prepared as described in Section 2.2.1. The slurry was filtrated and rinsed thoroughly with deionized water to remove any weakly absorbed reagent. The filtered products were dried in a vacuum oven at 338.15K and then used for XPS analysis.

3.   Results and discussion

3.1. Micro-flotation of rutile

The micro-flotation tests were conducted to reveal flotation behaviors of rutile with the three collectors at different pH value and different collector concentration.
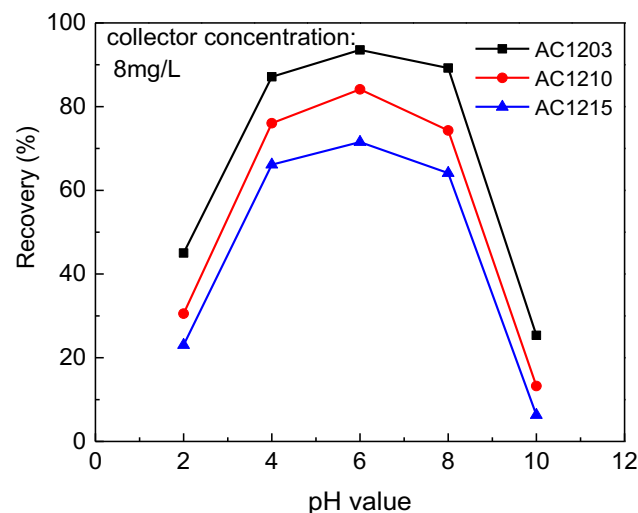

Fig. 4. Flotation recovery of rutile as a function of pH value

As shown in Fig. 4, in the pH range from 2 to 10, the collection performance of the three collectors for rutile all increased first and then decreased with the increase of pH value. The recovery rate of rutile reached the maximum at pH=6, which were 93.55% (AC1203), 84.12% (AC1210) and 71.52% (AC1215). The result of zeta potential measurement showed that the point of zero charge of rutile in deionized water was about pH=3.54, which was consistent with the result of other researchers (Chen et al., 2020). When pH<3.54, the rutile surface potential was positive and the cationic collectors could not adsorb on

the rutile surface. Therefore, the flotation of rutile could be interpreted as the collector interacting with hydroxylated titanium sites through hydrogen bonding that was demonstrated in the result of XPS analysis, simultaneously, a portion of the rutile particles were floated up by entrainment. In the pH range from 3.54 to 6, the collection performance of the three collectors for rutile increased greatly with the increase of pH value, the reasonable explanation was that the rutile surface potential changed from positive to negative, resulting in a large amount of cationic collectors adsorbed on the rutile surface. In the pH range from 6 to 10, the collection performance of the three collectors for rutile decreased rapidly, the reasonable explanation was that the decrease of H^+ concentration in the slurry leaded to the decrease in the protonation ability of the collectors, thereby reducing the adsorption capacity of collector on the rutile surface. Furthermore, in the pH range from 2 to 10, the order of the collection performance of three collectors for rutile was always AC1203 > AC1210 > AC1215.
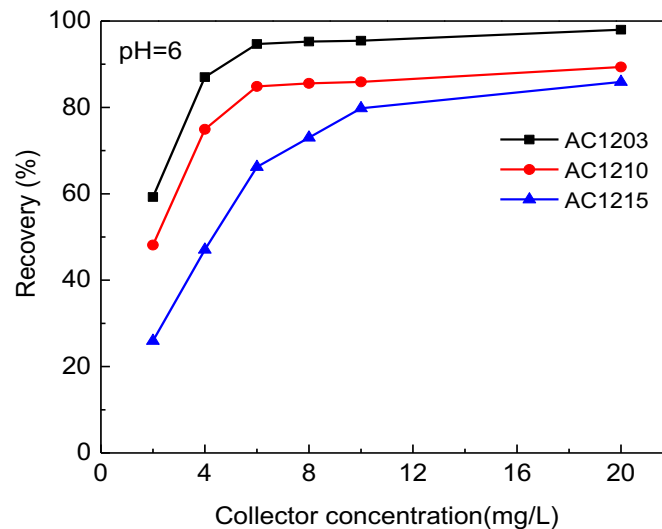

Fig. 5. Flotation recovery of rutile as a function of collector concentration (pH=6)

Fig. 5 showed the flotation recovery of rutile as a function of concentration in the presence of different collectors at pH=6. It could be seen clearly that all of three collectors displayed the similar rising trend, but the collecting power reduced with increasing EO number, it was consistent with the result of adsorption experiments at pH=6 that the collector adsorption capacity reduced with increasing EO number. These three tertiary amines differ from each other because of the substituent groups on nitrogen. These different substituents probably caused the difference in flotation behavior of three collectors for rutile. Moreover, the different length of EO leaded to the different inductive effect, which caused the ammonium groups to follow specific rules when collecting rutile (Papini et al., 2001; Liu et al., 2011b).

3.2. Zeta potential measurement results

In order to understand the interaction mechanism between collectors and mineral surface, the zeta potentials were examined at pH=6 and collector concentration was conditioned at 8mg/L.

From Fig. 6 it could be found that the original rutile potential appeared at -27.6 mV, after interaction with collectors, this value shifted to -17.7 mV (AC1203), -24.4 mV (AC1210), and -26.7 mV (AC1215), respectively. On the basis of previous research results, tertiary amines have an N atom with sp3 hybridization and a lone pair of electrons in a 2s orbital, which can bind strongly with protons because of the unoccupied orbital. After interacting with H^+ the tertiary amines became cationic collectors (Liu, et al., 2011a):

$$H_3C-(CH_2)_{10}-CH_2-NR_2+H^+ \Leftrightarrow H_3C-(CH_2)_{10}-CH_2-NR_2H^+ \qquad (2)$$
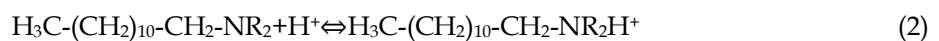
From the formula it could be concluded that these collectors in the form of cationic mainly acted with negatively charged rutile surface through electrostatic force effect. In addition, the shorter length of EO structure would result in weaker space steric effect and easier to be protonated. Meanwhile, the

result of the adsorption experiment showed that the less amount of EO, the more adsorption of protonated collector on the rutile surface, thereby shifted the potential of rutile surface towards more positive direction. Some researchers reported that after tertiary amine cations steadily adsorbed on Kaolinite (001) plane, the shapes of substituent groups bonding to N atom in final state were deflected and twisted compared with that in initial state (Liu et al., 2011b), the underlying reason may be the steric effect aroused from substituent groups. The bigger space size of substituent groups caused the stronger space steric effect and leaded to the higher deflected and twisted extent. The larger steric effect caused the stronger solvent effect, which decreased the ability of the amine to become protonated. The larger steric effect also decreased the possibility of a cationic tertiary ammonium ion adsorbed onto the rutile surface.
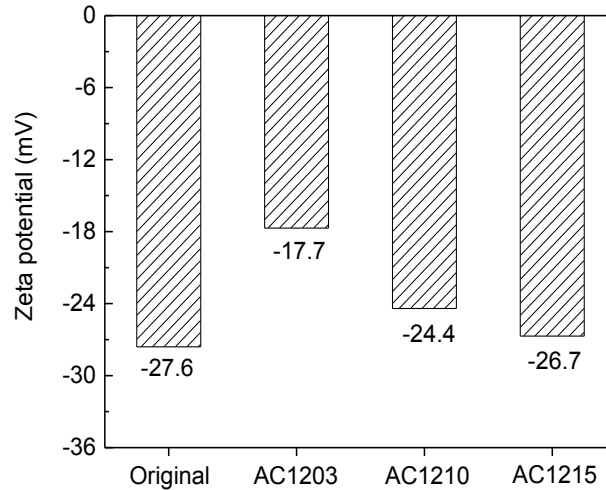

Fig. 6. Zeta potential of rutile in the presence and absence of different collectors (pH=6, collector concentration: 8mg/L)

3.3. Adsorption experiment

In order to study the influence of the number of EO in three collectors (AC1203, AC1210, AC1215) on its adsorption capacity on rutile surface, the adsorption quantity of collectors was measured at pH=6 and room temperature (293.15 K), the initial concentrations of collectors were 5×10^{-5}, 25×10^{-5}, 45×10^{-5}, 65×10^{-5}, 85×10^{-5}, 105×10^{-5} and 125×10^{-5} mol/L, respectively. And the isotherms of three collectors adsorption to rutile were presented in Fig. 7.
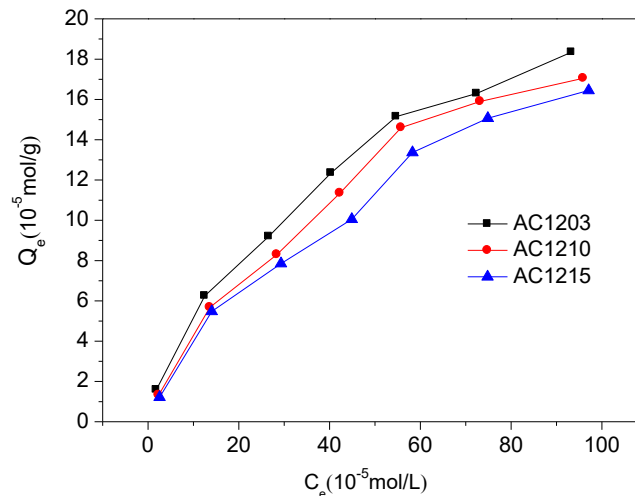

Fig. 7. Adsorption isotherms of the different collectors on the rutile surface

As seen from Fig. 7, the adsorption quantity of three collectors on rutile surface all increased with the increase of collector equilibrium concentration and the order of the adsorption quantity of three

collectors was always AC1203 > AC1210 > AC1215, the result was in good agreement with the flotation test and zeta potential measurement.

Langmuir and Freundlich equations were usually used to describe the adsorption model of reagents acting on mineral surface (Sun et al., 2019; Wang et al., 2019), so that were used in this article. The linear expression of Langmuir equation is as follows:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$ (2)

The linear expression of Freundlich equation is as below:

$$log Q_e = log K_F + \frac{1}{n} log C_e$$ (3)

where C_e is the concentration of residual collector in the solution during adsorption equilibrium (mol/L); Q_e is the adsorption capacity of collector on rutile during adsorption equilibrium (mol/g); Q_m is the maximum monolayer adsorption capacity (mol/g); K_L and K_F are adsorption constants related to the maximum adsorption capacity; and $1/n$ is the unevenness of adsorption (Sun et al., 2019).

The fitting results are presened in Fig. 8 and corresponding parameters were listed in Table 2. The fitting results showed that the R^2 values of Freundlich isotherm model were all larger than that of Langmuir isotherm model for three collectors, so it could be concluded that the Freundlich isotherm model can better describe the adsorption process of dodecylamine polyoxyethylene ether on the rutile surface, and it indicated the collectors adsorbed on the rutile surface through multilayer adsorption. It was in good agreement with the conclusion that the dodecylamine polyoxyethylene acted with the rutile surface through electrostatic interaction and hydrogen bonding. By the way, from table 2 it could be noticed that with the increase of EO number, corresponding $1/n$ value followed as 1/1.43, 1/1.18 and 1/1.11, respectively, which deeply demonstrated that collectors with shorter substitute group tended to adsorb on rutile surface more easily.
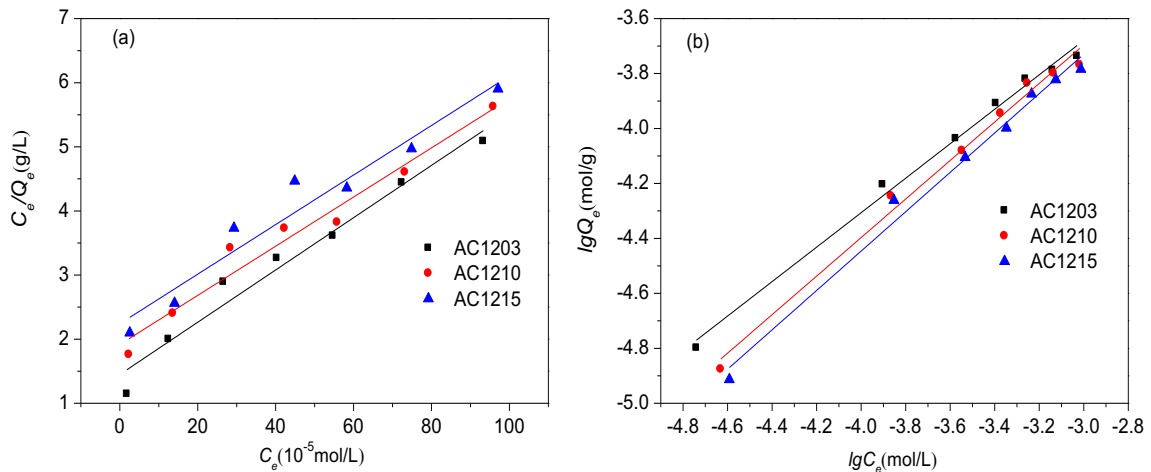

Fig. 8. Fitting results of Langmuir(a) and Freundlich(b) models

Table 2. The parameters for Langmuir and Freundlich models

Collector	Langmuir			Freundlich		
	K_L (10^5L/mol)	Q_m (10^{-5}mol/g)	R^2	K_F (10^{-2}mol/g)	n	R^2
AC1203	0.028	24.53	0.96339	1.59	1.59	0.99222
AC1210	0.020	26.08	0.95916	2.56	1.43	0.98714
AC1215	0.017	25.87	0.94024	2.63	1.40	0.98551

3.4. XPS analysis

On the basis of our previous study, fatty amine polyoxyethylene ether collector tended to interact with rutile mineral through hydrogen bond interaction and elactrostatic force effect, in which protonated

nitrogen atoms and neutral tertiary amine groups played essential role. In this regard, XPS analysis was employed to further demonstrate the detailed valence state information about nitrogen element, and AC1203 was chosen as the representative sample for analysis.

Fig. 9 showed the high resolution of N 1s on rutile surface. It could be found that the N 1s were mainly composed of two components. The peak at 401.42 eV was assigned to protonated NH^+, while the peak at 399.33 eV may be corresponded to neutral tertiary amine in AC1203. The results were somewhat in consistent with the phenomenon we observed before, which further demonstrated that such kind collector was expected to float rutile mineral mainly via hydrogen bond and electrastatic interaction (Li et al., 2020).
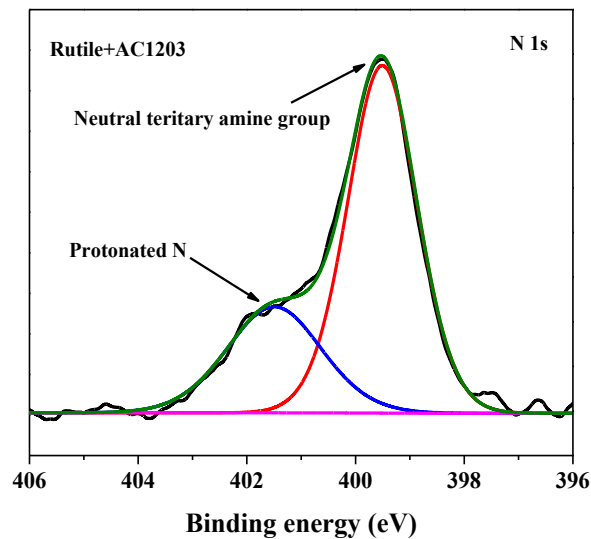

Fig. 9. N 1s spectra of rutile surface after AC1203 treatment (pH=6, collector concentration: 8mg/L)

4. Conclusions

The result of flotation experiments showed that the optimal pH value of flotation rutile with three collectors with different length of EO all was 6, and the collecting ability decreased with the increase of EO number.

In addition, based on the measurements of zeta potential, rutile surface was found to be negatively charged at pH 6, protonated tertiary amine groups were expected to act with the surface through electrostatic interaction. Meanwhile, smaller deviation of potential indicated less collector could adsorb on rutile surface, which was mainly ascribed to the stronger steric effect caused by the increase of EO number.

The result of collectors adsorption experiment showed that the order of the adsorption quantity of three collectors on rutile surface was AC1203>AC1210>AC1215, which was in good agreement with the flotation test and zeta potential mesurement. The fitting results of adsorption model showed that the Freundlich isotherm model can better describe the adsorption process of dodecylamine polyoxyethylene ether on the rutile surface.Furthermore, the results of XPS analysis demonstrated that there was a hydrogen bonding between neutral tertiary amine groups and hydroxylated titanium sites as well.

Acknowledgments

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