

Article

α -Amino Phosphonic Acid as the Oxidized Ore Collector: Flexible Intra-Molecular Proton Transfer Providing an Improved Flotation Efficiency

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Abstract: The efficient separation of ilmenite is a difficult problem in minerals flotation. For this issue, α -aminooctyl phosphonic acid (APA) was developed as a selective collector to separate ilmenite. The flotation test result showed that APA was more efficient for improving ilmenite recovery compared with octylphosphonic acid (OPA). Adsorption, ZETA and FTIR measurements proved that the chemical interaction between collector APA and the surface of ilmenite was stronger than OPA, while the result is completely opposite in the case of titanite. Moreover, XPS test and DFT calculations indicated that the collector APA was coordinated with the surface of ilmenite through P-O-Fe and P-O-Ti bonding. The amine group in the α -site of the phosphonyl group facilitated APA to be a stable zwitterion in the solution, which greatly enhanced the nucleophilicity of the phosphonic acid group. On the other hand, more appropriate coordination energy was another reason for the superior collecting selectivity of APA than OPA.

Keywords: α -aminooctyl phosphonic acid; flotation; ilmenite; adsorption



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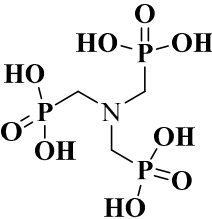
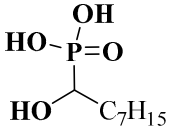
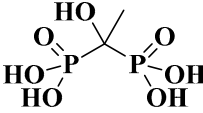
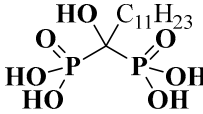
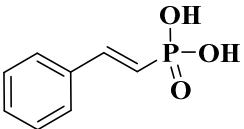
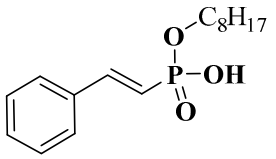
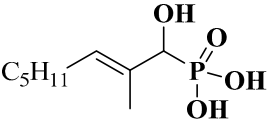
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1. Introduction

Among the organic derivatives of phosphorus, organic phosphonic acids occupy a prominent position. From a synthetic chemistry point of view, the phosphonic acid group has been incorporated into a variety of functional molecules, which are involved in numerous applications in agriculture, bio-pharmaceutical, environmental sciences and other fields [1]. In elusive interface reaction processes, phosphonic acid derivatives are excellent interfacial modifiers. The phosphonic acid group provides phosphonic acid derivatives with unique binding interactions with target surfaces owing to its stereospecificity (trigonal pyramidal geometry), coordination performance (di- or trivalent chelating property) and dual function as a hydrogen acceptor or donor [2].

As early as the 1980s, the phosphonic acid group has been regarded as an active group for the construction of flotation collector molecules and is widely used in flotation fields such as cassiterite and rutile [3]. For example, Zhu et al. used a new synthetic agent DPTUHP (diphenyl α -(3-phenylthioureido) hexylphosphonate) to perform flotation experiments on cerussite mineral and found that DPTUHP is an efficient collector [4]. Over the past 30 years, a number of new collectors (phosphonic acid derivatives) for various minerals have been discovered. Recent examples are listed in Table 1.

Table 1. Recent examples of phosphonic acid derivatives used as flotation collectors.

Molecular Formula and Name	Target Minerals	Finder
 (nitrilotris(methylene))tris(phosphonic acid)	Pentlandite	Liu et al. [5].
 (1-hydroxyoctyl)phosphonic acid	Malachite and Ilmenite	Li et al., Liu et al. [6,7].
 (1-hydroxyethane-1,1-diyl)bis(phosphonic acid)	Chalcopyrite	Huang et al. [8].
 (1-hydroxydodecane-1,1-diyl)bis(phosphonic acid)	Bastnasite	Fan et al. [9].
 (E)-styrylphosphonic acid	Cassiterite and Rutile	Gong et al., Kasomo et al. [10,11].
 octyl hydrogen (E)-styrylphosphonate	Cassiterite	Huang et al. [12].
 (E)-(1-hydroxy-2-methyloct-2-en-1-yl)phosphonic acid	Cassiterite	Tan et al. [13].

Exploiting the synergistic effect of the polyfunctional group is a general strategy to obtain desired interactions in the design and synthesis of ligand [14]. For the polyfunctional phosphonic acid collectors, Li et al. reported that α -hydroxyoctyl phosphonic acid (HPA) is an excellent candidate for the flotation of ilmenite [7]. The neighboring collector molecules coated on ilmenite surfaces formed intermolecular hydrogen bonds by extra hydroxyl, producing a closer alignment of HPA on ilmenite surfaces to render an improved flotation

recovery of ilmenite. Despite the development of the polyfunctional phosphonic acid molecule as collector, there is little precedent on the utilization of nitrogenous phosphonic acid molecules in the flotation of oxidized minerals. In the present study, α -aminooctyl phosphinic acid (APA) was first used as the collector for ilmenite flotation.

2. Materials and Methods

2.1. Materials and Reagents

The ilmenite and titanaugite samples used in this study were from Panzhihua (Sichuan Province, China). After grinding, shaking and sieving, the powdered ilmenite samples of 38–75 μm were used for the flotation test. The mineral samples used for zeta potential measurement, FTIR analysis and X-ray photoelectron spectroscopy (XPS) analysis need to be further ground to about 20 μm . XRF (Epsilon1, Malvern Panalytical, Malvern, UK) (Table 2) shows that the purity of the prepared minerals meets the test requirements. The collector APA is chemically synthesized and purified (as shown in Figure 1) [15]. The NMR data are as follows: ^1H NMR (300 MHz, DMSO): δ = 8.52 (d, 2H), 4.8 (d, 2H), 2.5 (m, 1H), 1.75 (m, 2H), 1.22–1.28 (m, 10H), 0.88 (m, 3H); ^{13}C NMR (125 MHz, DMSO), δ 63.1, 31.9, 29.3, 29.3, 25.8, 23.2, 22.7, 14.1. The synthetic raw material acetamide (CH_3CONH_2), acetyl chloride (CH_3COCl), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), caprylic aldehyde ($\text{CH}_3(\text{CH}_2)_6\text{CHO}$), phosphorus trichloride (PCl_3) and experiment reagents octylphosphonic acid ($\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{P}(\text{OH})_2$), nitrate of potash (KNO_3) were all analytical–reagent grade. The solution pH was adjusted with NaOH and HCl stock solutions (0.1 mol/L). All of the analytical tests were carried out with deionized water (resistivity: 18.3 $\text{M}\Omega\text{ cm}$).

Table 2. Chemical composition of ilmenite sample.

Ilmenite	Element Content (mass %)	TiO ₂ 47.77	Fe ₂ O ₃ 47.75	MgO 1.48	SiO ₂ 1.26	Al ₂ O ₃ 0.56	MnO 0.53	CaO 0.48
Titanaugite	Element Content (mass %)	SiO ₂ 40.3	Al ₂ O ₃ 17.36	TiO ₂ 1.07	Fe ₂ O ₃ 11.17	MgO 7.08	Na ₂ O 2.19	CaO 13.0

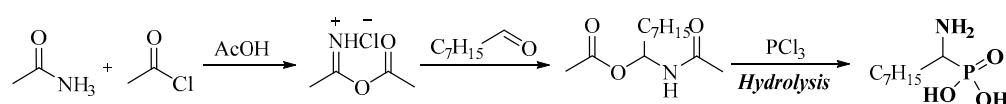


Figure 1. Synthetic methods of APA.

2.2. Flotation Test

A 40 mL XFG-1600 flotation machine (mechanical agitation) was used for a micro-flotation test with a rotating speed of 1700 rpm. The flotation process for each process included the following: (1) pouring 2.0 g of ilmenite (or a mixed mineral of ilmenite and titanaugite (1:1)) and 40 mL of deionized water into a plexiglass cell and stirring for 1 min to prepare a slurry; (2) using pH regulators (HCl or NaOH stock solution) to adjust the pH value of the slurry; (3) adding a flotation collector (APA or OPA solution) and agitating for 3 min; (4) collecting floated particles as flotation concentrate for 3 min and unfloated particles as the flotation's tailing; (5) filtering, drying, and weighing the flotation concentrate and tailing. Figure 2 was the detailed process of a single mineral flotation test. The recovery (percentage by weight) of ilmenite was calculated based on the dry weight of the flotation concentrates and tailings. To assess the accuracy of the flotation test, each test was repeated three times, and the mean value was reported. Error bars in the micro-flotation test results represent one standard deviation of uncertainty obtained from three independent runs.

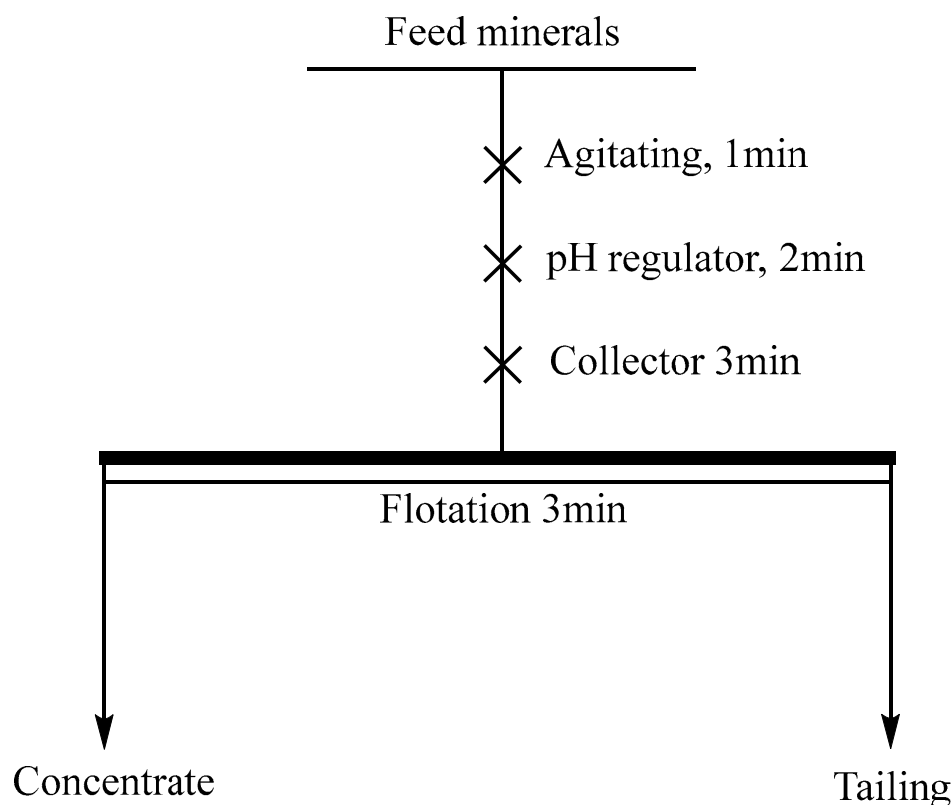


Figure 2. Flowsheet of pure mineral flotation test.

2.3. Adsorption Test

The adsorption test was carried out on the XFG-1600 flotation machine (mechanical agitation) at a rotating speed of 1700 rpm. The condition was the same as that of the micro-flotation test. After the completion of flotation, the remaining suspension in the plexiglass cell was left to stand, and then, the supernatant was taken for determination. The concentration of APA or OPA in aqueous solution was determined by a Shimadzu TOC-V CPH analyzer. The carrier gas (O_2 , purity and GT; the flow rate of 99.9) was 0.45 L/min and the temperature of the catalyst chamber (Pt/Al_2O_3) was 973 K. The CO_2 concentration generated was measured using a non-dispersed infrared (NDIR) detector. Each experiment was repeated 3 times, and the average was taken. The error bars in the adsorption tests results represent one standard deviation of uncertainty obtained from three independent runs. Total carbon, organic carbon and inorganic carbon were measured. The adsorption capacity was calculated by Equation (1)

$$Q_e = \frac{V(C_0 - C_e)}{WS} \quad (1)$$

where Q_e is the adsorption amount of APA or OPA on ilmenite (mol/m^2), C_0 is the initial concentration of the collector (mol/L), C_e is the equilibrium concentration of APA or OPA (mol/L), V is the volume (L), W is the mass (g) of ilmenite, and S is the specific surface area of ilmenite (m^2/g).

2.4. Zeta Potential Measurement

A Delsa-440Sx Zeta measuring instrument (Malvern Instruments, UK) equipped with a rectangular electric swimming pool was used to measure the zeta potential of ilmenite samples. The electrolyte solution used was KNO_3 solution (0.01 M). Freshly ground samples (0.002 g of ilmenite, less than 2 μm) were dispersed in 40 mL of electrolyte solution and stirred. The addition of flotation reagents (including collector and activator) was

determined according to the experimental requirements and flotation process, and the pH value of the suspension was continuously monitored to reach the expected value. The superfluid containing fine particles was then transferred to a folded capillary cell (making sure there are no bubbles in the cell) for zeta potential measurement. The final result was measured three times and averaged.

2.5. FTIR Spectroscopic Measurement

Spectrum One (Version BM, Perkin Elmer, Waltham, MA, USA) was used to record the infrared spectra which described the interactions between the collector and mineral surface. For the sample preparation, 2.0 g of purified ilmenite was ground to less than 2 μm and added to the flotation tank of an XFG-1600 flotation machine. The corresponding flotation collector was then added and stirred for 5 min. Whereafter, the pulp was filtered; afterwards, the obtained mineral particles were washed 3 times with deionized water and then vacuum dried.

Finally, the prepared samples were ground, mixed with spectrographic grade KBr, and compressed into tablets for measurement.

2.6. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed using the Ka-Alpha 1063 (Thermo Scientific Co., Waltham, MA, USA) spectrometer. Three groups of samples were prepared with APA or OPA or without collector (blank control group) under the same conditions (as the flotation test). Then, the samples were filtered and thoroughly rinsed with deionized water with the same pH value. All binding energies are referenced to the neutral C1s peak at 284.8 eV to compensate for the surface charge effect.

2.7. DFT Calculation

DFT calculation is a suitable method to analyze the interaction between the collector and the metal ion sites on the mineral surface [16,17]. In this work, Gaussian 16 software (Gaussian 16) was used to perform high-precision DFT calculations under B3LYP-D3BJ(SMD)/def2-SVP theory to explore the characteristics of the coordination model (between molecules and metal ions). In the calculation process, the metal ions on the mineral surface are considered as isolated metal ions in the water, because this simplification can reduce the calculation cost and ensure almost identical experimental simulations.

3. Result and Discussion

3.1. Micro-Flotation Test of Single Minerals

To examine the flotation performance of APA on the flotation of ilmenite, this work began with the single mineral flotation test to compare the collecting efficiency of APA and OPA toward ilmenite at the same pH value (Figure 3a) and collector dosage (Figure 3b). The result showed that a pulp pH value = 6 and collector concentration = 4×10^{-5} M were the optimized flotation conditions for these two collectors, and the recovery of ilmenite could reach 87% via APA, while that of OPA was 76%. In addition, the flotation recovery of ilmenite by using APA as a collector was much higher than that of OPA within the test pH value range and collector dosage (more than 20%). It is worth noting that the performance of the two collectors was suppressed under strong acidic or alkaline condition (more than 20 percentage points off the peak); the recovery of ilmenite flotation increases first and then decreases with the increase in pH value. In strong acidic conditions, the deprotonation of the phosphonic acid group in APA and OPA was repressed, resulting in the weakened coordination effect, while in alkaline condition, hydroxylation of the ilmenite surface was the main reason responsible for the reduced flotation recovery [18]. However, one point could be affirmed: intramolecular proton migration could promote an easier deprotonation of the phosphonic acid group in APA compared with that of OPA (Figure 3c) [19]. The flotation results from Figure 3a,b fully illustrated the superior collecting efficiency of APA for the flotation of ilmenite.

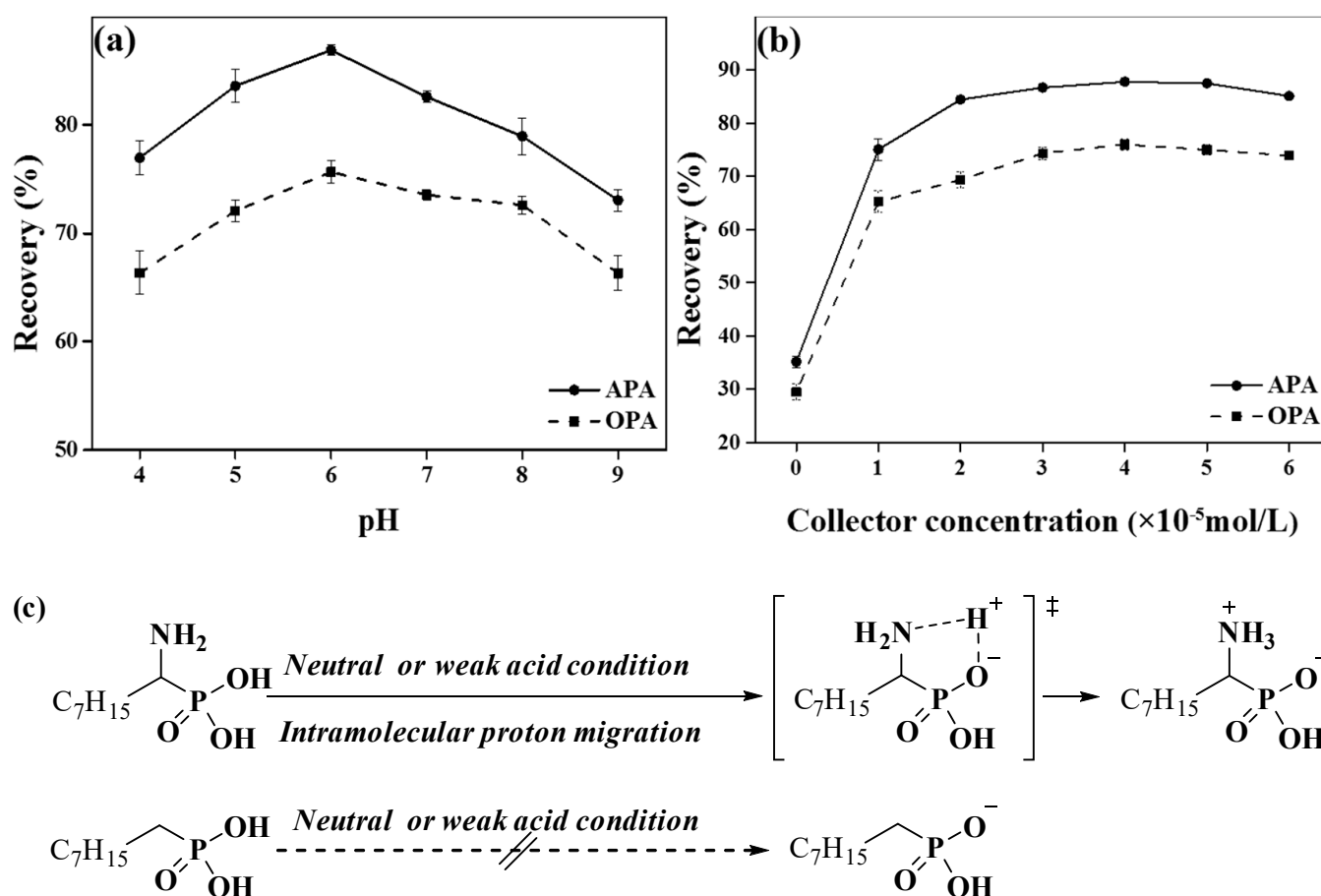


Figure 3. (a) Recovery of ilmenite as a function of pH at collector dosage of 4×10^{-5} M (APA and OPA were used as collector); (b) recovery of ilmenite as a function of collector dosage at pH 6 (APA and OPA were used as collector); (c) the proposed proton transfer process of APA at natural or weak acid condition.

3.2. Micro-Flotation Test of Artificial Mixed Mineral

Titanaugite is the main gangue mineral associated with ilmenite. After confirming the collecting efficiency of APA toward ilmenite, the collecting selectivity of APA toward ilmenite was further investigated. Firstly, Figure 4 shows that the optimized flotation condition for using APA and OPA is pH = 6 and the collector dosage = 4×10^{-5} M. Figure 4a,b shows the effect of pH and the collector concentration on the collecting selectivity of APA. Figure 4a indicated that the recovery of ilmenite and titanium pyroxene increased first and then decreased with the increase in pH; the maximum recovery of ilmenite was 89%, which was much higher than that of titanaugite (44%) at the optimum pH value (pH = 6). Even in a high collector concentration (4×10^{-5} M, Figure 4b), the flotation recovery of titanaugite was only about 20%. In contrast, using OPA as the collector, the recovery of ilmenite and titanium pyroxene increased first and then decreased with the increase in pH. The largest recovery difference between ilmenite and titanaugite is less than 32% under optimized condition (pH = 6 and collector concentration = 4×10^{-5} M, Figure 4c,d), which makes it difficult to achieve the effective separation of ilmenite and titanaugite. The above results adequately illustrated the superior collecting selectivity of APA in the mixed flotation system compared with OPA.

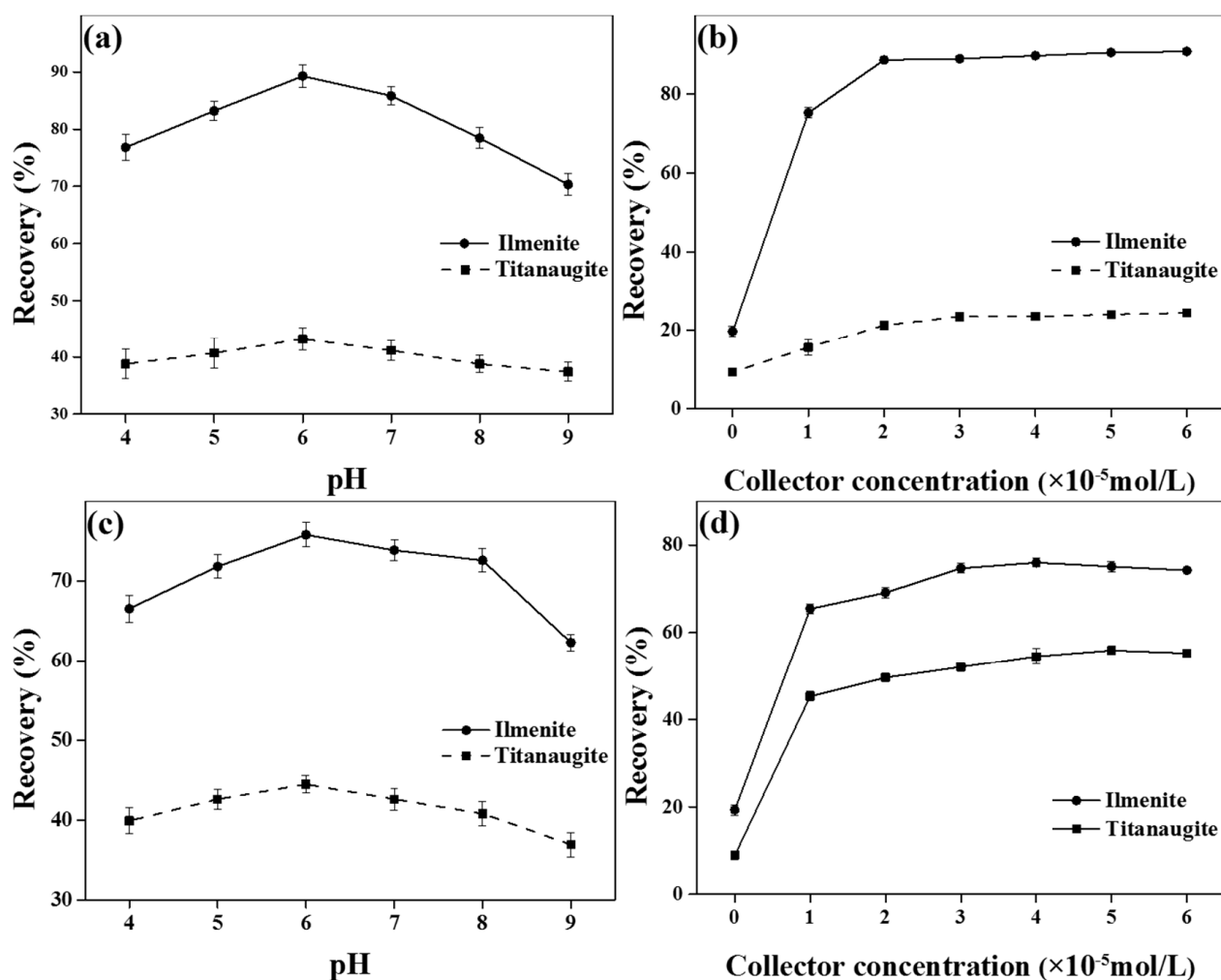


Figure 4. Recovery of ilmenite and titanaugite as a function of pH and collector dosage using APA as collector (a,b); recovery of ilmenite and titanaugite as a function of pH and collector dosage using OPA as collector (c,d).

3.3. Adsorption of APA and OPA on the Surface of Ilmenite

The adsorption behavior of a collector onto a mineral surface plays a vital role in the flotation efficiency and selectivity [20,21]. After a single minerals test, the adsorption behaviors of different collectors were studied. Figure 5a,b show the adsorption capacity of collectors (APA and OPA) on the surface of ilmenite with various pH values and concentrations, respectively. In general, the adsorption amounts of APA and OPA on the ore surface first increased and then decreased with the increase in pH, and they continued to increase with the increase in the concentration of the agent. The adsorption amount of APA was greater than that of OPA in all the pH ranges and dosages tested, which provides a reliable support for the obtained results (APA has a superior collecting efficiency compared with OPA) of single minerals test (Figure 3a,b). With the concentration of APA and OPA increasing, the amount of agent adsorption on the surface of ilmenite increased significantly, and there was no trend of adsorption saturation, which is attributed to the multilayer adsorption of APA and OPA on the surface (the proposed adsorption model is shown in Figure 5d). The amido group and carbonyl group of APA and the carbonyl group of OPA act as hydrogen bond receptors (basic group) to form intermolecular hydrogen bonding. More hydrogen bond acceptors made the intermolecular force of APA stronger, and the amount of adsorption on the surface of ilmenite was more, which was confirmed in Figure 5c and was consistent with the result of Figure 4a,b.

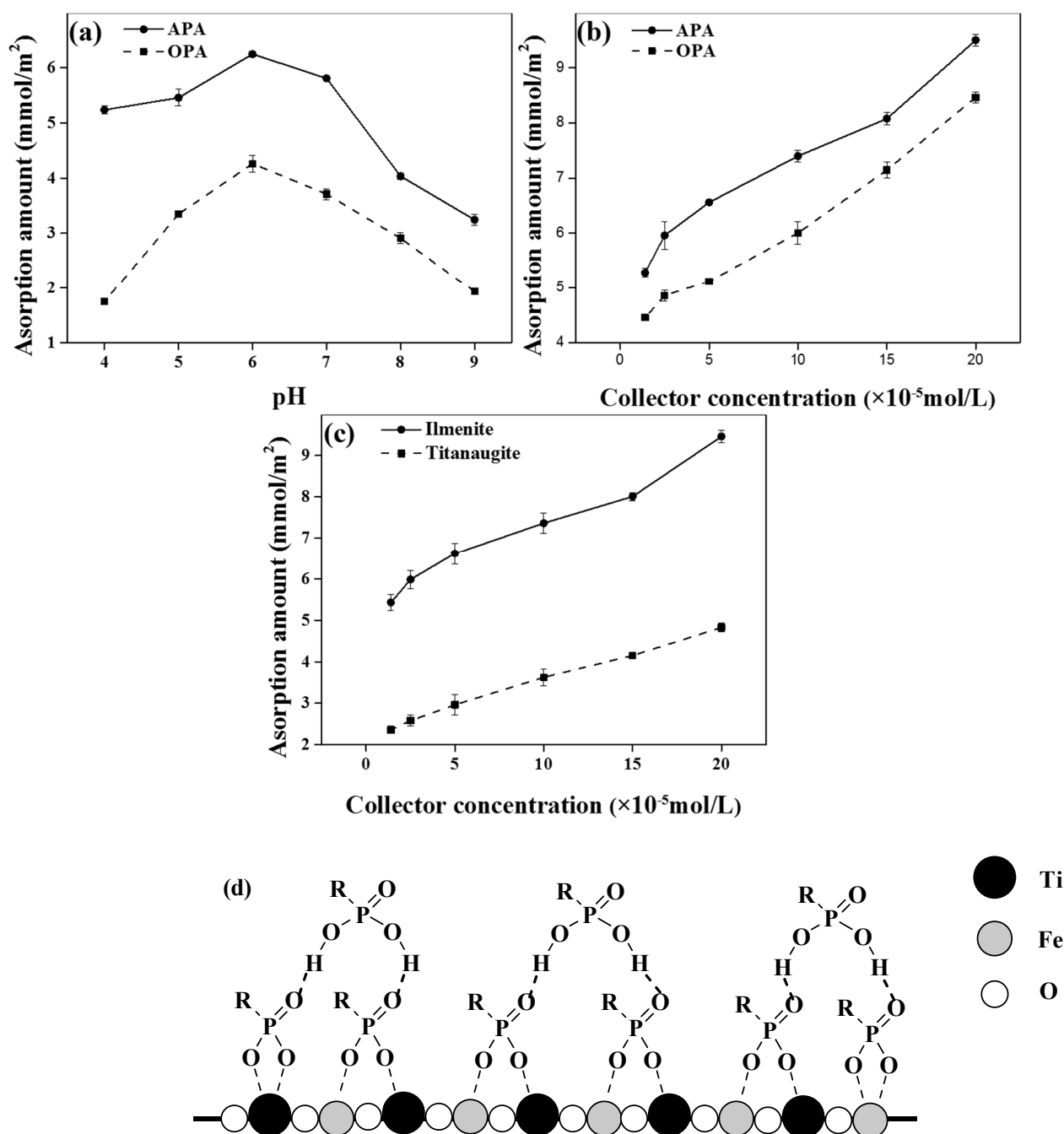


Figure 5. The adsorption amount of APA and OPA onto the surface of ilmenite as a function of pH ((a), collector concentration = 4×10^{-5} M) and collector concentration ((b), pH value = 6); (c) the adsorption amount of APA onto the surface of ilmenite and titanite as a function of APA concentration (pH value = 6); (d) a proposed adsorption model of APA or OPA onto ilmenite surface.

3.4. Zeta Potential Measurements

The change of zeta potential reflects the potential interaction between the collector and mineral surface [22]. Therefore, zeta potential measurement is an effective method to determine electro-kinetic changes on mineral surfaces conditioned in an aqueous system with flotation reagents [23–25]. Figure 6a shows the change of zeta potential of ilmenite with pH value in the absence of a collector or in the presence of collectors (APA/OPA). The isoelectric point (IEP) of original ilmenite was located at pH 6.3, which was consistent with previous reports [26,27]. After the addition of the collectors APA or OPA, the zeta potential of ilmenite shifts to negative. Since the surfaces of ilmenite and APA/OPA

ions have the same charge in flotation pH ranges, it was obvious that the adsorption of APA and OPA on the surface of ilmenite was caused by chemical adsorption rather than electrostatic adsorption [28]. Chemical adsorption was a necessary factor in determining mineral recovery. In solution, APA molecules underwent intramolecular proton transfer, while OPA, a molecule, was thoroughly ionized (Figure 3c). As a result, in the same pulp environment, ionized OPA carries more negative charges than ionized APA. However, after the addition of APA and OPA to ilmenite suspension, respectively, the zeta potential values of the resulting “ilmenite product” were almost the same, indicating that the amount of APA molecules adsorbed on the surface of ilmenite was larger, which was consistent with the results of adsorption capacity test and flotation. Figure 6b shows the changes of the zeta potential of ilmenite and titanaugite in the absence or presence of APA. Without the addition of APA, the isoelectric point (IEP) of titanaugite is 4.2, which is consistent with previous reports [29]. The addition of APA caused the zeta potential of ilmenite and titanaugite to move toward the negative direction, indicating that APA molecules were chemically adsorbed on ilmenite and titanaugite. Moreover, the zeta potential of ilmenite moves much more than that of titanaugite, which indicated that APA was preferentially adsorbed on the surface of ilmenite. The result was consistent with the adsorption capacity test and flotation result [30].

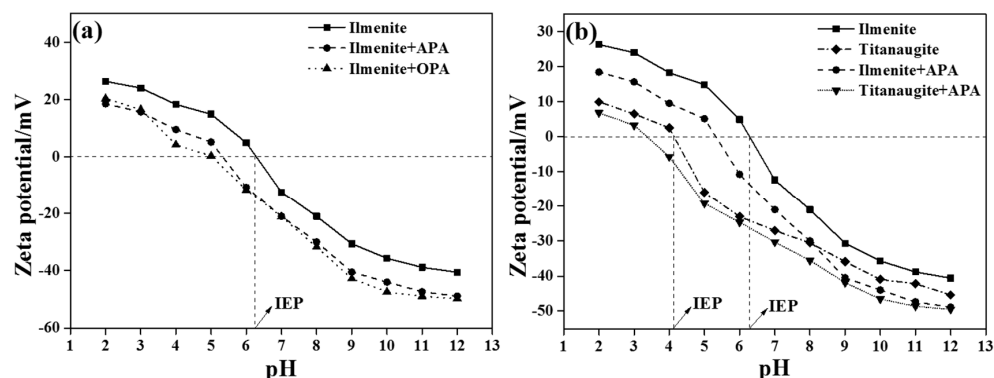


Figure 6. Zeta potentials of ilmenite (a) and titanaugite (b) as a function of pH.

3.5. FTIR Analysis

The adsorption states of the collectors onto the mineral surfaces (ilmenite and titanaugite) were further studied by FTIR. As shown in Figure 7a,b, the characteristic FTIR peaks of ilmenite were concentrated at 1531 cm^{-1} , 973 cm^{-1} and 694 cm^{-1} , and those of titanaugite were concentrated at 1535 cm^{-1} , 1066 cm^{-1} and 980 cm^{-1} . For the FTIR of APA, the peak at 3368 cm^{-1} was the stretching vibration of -OH [31]; the spectral bands at 2956 cm^{-1} , 2920 cm^{-1} and 2852 cm^{-1} were attributed to the stretching vibrations and flexural vibration of C-H [32,33]. The strong peaks at 1601 cm^{-1} and 1653 cm^{-1} were generated by the N-H bending vibration in the primary amine [34], and the C-N stretching vibration in the primary amine produced strong peaks at 1468 cm^{-1} [35]. In addition, the stretching vibration peaks of P-O were at 1026 cm^{-1} , 946 cm^{-1} and 920 cm^{-1} ; the stretching vibration peak of P=O was at 1238 cm^{-1} [36]; and the stretching vibration peak of P-C was at 753 cm^{-1} . After APA reacting with ilmenite, new peaks appeared at 3368 cm^{-1} , 2924 cm^{-1} , 2855 cm^{-1} , 1603 cm^{-1} and 1456 cm^{-1} in the surface of ilmenite, corresponding to peaks of APA at 3368 cm^{-1} , 2920 cm^{-1} , 2852 cm^{-1} , 1601 cm^{-1} and 1468 cm^{-1} , respectively. Almost all of these new peaks moved to different degrees, indicating that APA adhered to the ilmenite surface via chemical adsorption [28]. However, after treating titanaugite particles with APA, neither adsorption bands of APA nor signs of a change of the typical adsorption bands of ilmenite were detected, indicating the negligible interaction between the surface of titanaugite with APA molecules.

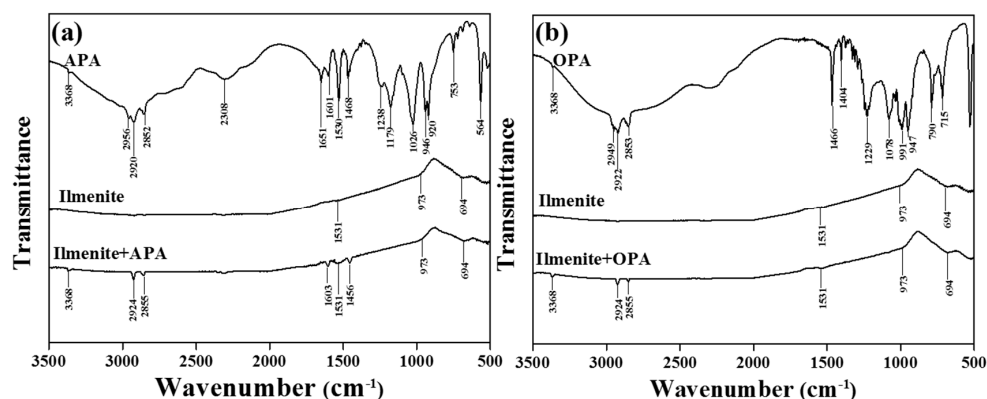


Figure 7. (a) FTIR spectra of ilmenite before and after treating with APA. (b) FTIR spectra of titanaugite before and after treating with APA.

3.6. XPS Analysis

To further verify the interaction and separation mechanisms of APA with ilmenite, high-resolution XPS spectra were analyzed via peak fitting in the absence and presence of APA. Figure 8a shows the survey scan of ilmenite without or with APA treatment. After APA treatment, N1s and P2p XPS peaks appeared on the surface of ilmenite. The atomic surface concentration of elements C1s, O1s, N1s, P2p, Ti2p, and Fe2p determined by XPS was summarized in Table 3; the content of C, O, N elements had increased to varying degrees. These results indicate that APA reacted with the surface of ilmenite.

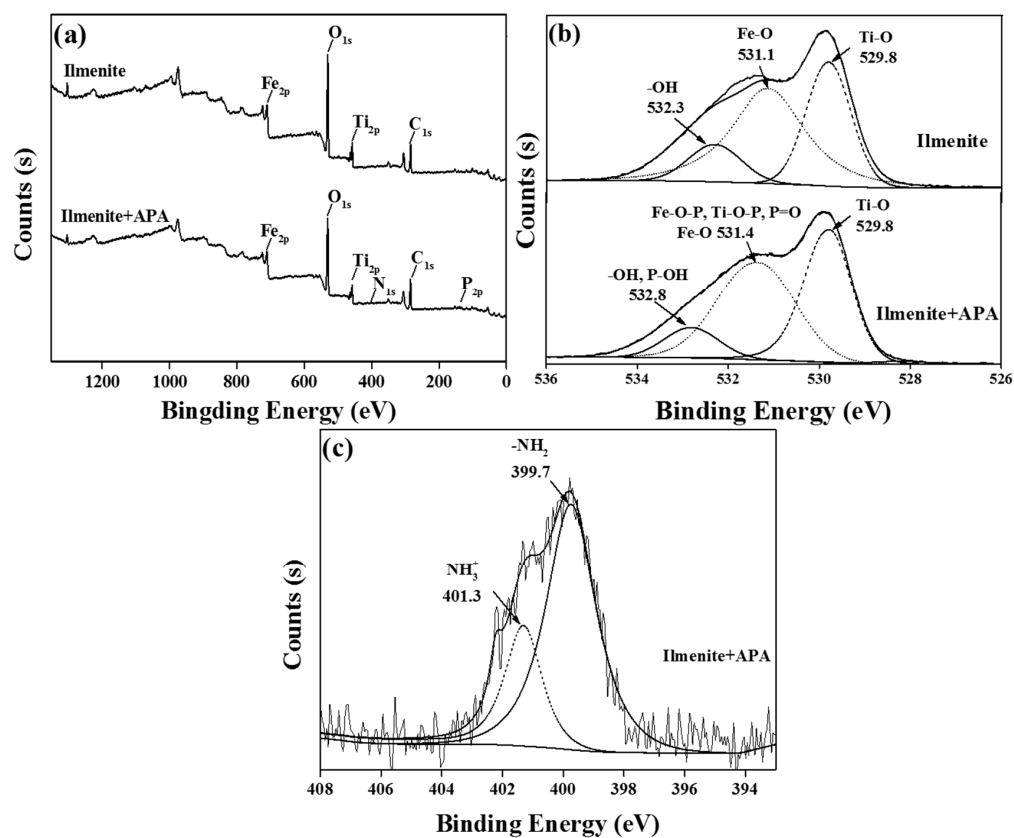


Figure 8. High-resolution XPS spectra of oxygen on ilmenite surface under various conditions ((a): survey scan; (b): O1s XPS spectra of ilmenite before and after conditioning with APA; (c) N1s XPS spectra of ilmenite after conditioning with APA).

Table 3. Relative amounts of elements on the ilmenite surface.

Sample	Element (Mass %)					
	C(1s)	O(1s)	Ti(2p)	Fe(2p)	N(1s)	P(2p)
Ilmenite	34.6	52.46	5.19	7.75	-	-
Ilmenite + APA	40.08	46.6	4.45	6.5	1.08	1.28

In the O1s XPS spectra of the sample (Figure 8b), XPS peaks of untreated ilmenite were composed of three components. Peaks at 529.8 eV, 531.1 eV and 532.3 eV were assigned to the Ti-O, Fe-O and -OH [37,38]. After APA treatment, the peak at around 531.4 eV was assigned to the Fe-O-P, Ti-O-P, P = O and Fe-O [39,40], the peak at 532.8 eV was attributed to the -OH, P-OH, which fully proves that APA had a coordination reaction with ilmenite in the form of P-O-Fe and P-O-Ti.

Next, the role of the amine group in the coordination reaction was explored by N1s XPS spectra. In Figure 8c, peaks at 399.7 eV and 401.3 eV were assigned to -NH₂ and -NH₃⁺ [16,41], while no bond was found between N and metal atoms. The discovery of -NH₃⁺ indicated that the amine group functions as a Lewis base, which could take away the H⁺ on the phosphonic acid hydroxyl group, while the APA molecule becomes a zwitterion, and -O⁻ is easier to coordinate with metal atoms, which was consistent with our previous analysis.

3.7. Computation

Through experiments, we have fully confirmed that the flotation ability of APA is better than OPA, and the responsible reason might be the amine group in APA. To probe into the potential role of the amine in the collector, we performed theoretical investigations on the simplified collector + metal ion model. The zwitterionic property of the α -amino phosphoric acid is revealed by the fact that the zwitterion form is 4.5 kcal/mol lower in energy than the molecule form (as shown in Figure 9a). This implies that under standard condition, the zwitterion is the dominant form, and the nucleophilicity of the phosphate oxygen is greatly enhanced by this intramolecular proton transfer. Such a conclusion is further supported by the computation result where the thermochemistry of the coordination of α -amino phosphoric acid with Ti⁴⁺ ion is -239.2 kcal/mol, which is much more endothermic than the -189.8 kcal/mol of the phosphoric acid (as shown in Figure 9b). Moreover, it also provides an explanation for the pH dependence of the collector performance. When the solution is overwhelmingly acidic due to the fact that the amino group is protonated, the formation of the zwitterion is inhibited. In conclusion, the amino group in the molecule serves as a base to deprotonate the phosphoric acid, making it a better ligand for coordination.

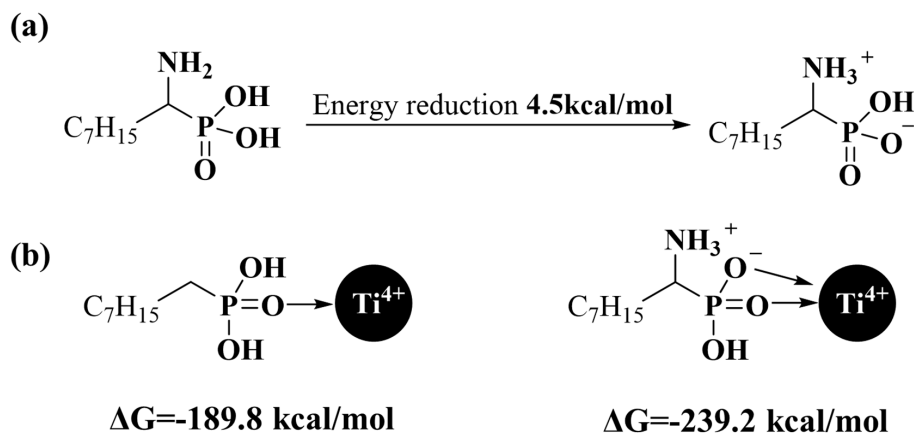


Figure 9. (a) Proton transfer form and energy spectrum of APA molecule; (b) molecular geometry and energy profile of metal ion-OPA complexes and metal ion-APA complexes in solvent.

4. Conclusions

In this work, α -aminooctyl phosphinic acid (APA) was synthesized and applied as a novel collector for the flotation of ilmenite, and traditional collector octylphosphonic acid (OPA) acted as a comparison. The flotation test results showed that the selective separation of ilmenite from titanite could be better achieved by using collector APA. The adsorption measurement showed that under the same conditions, more APA could be adsorbed on the surface of ilmenite than OPA, and the zeta potential measurement indicated that the adsorption of APA toward the surface of ilmenite was chemical adsorption. FTIR, XPS tests and DFT calculations proved that the collector APA was coordinated with the surface of ilmenite through P-O-Fe and P-O-Ti bonding. The amine group provided APA with more stable zwitterions in the solution, which could greatly enhance the nucleophilicity of the phosphonic acid oxygen. This was the main reason that the collector APA had a stronger selectivity than OPA. This study showed that APA had a great potential for industrial applications in ilmenite flotation.

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