

Recent advances in montmorillonite/alkylammonium

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Abstract. Montmorillonite/alkylammonium compounds have good process performance, which are widely used in the paint, textile, printing ink, high temperature grease, daily cosmetics, environmental protection, polymer modification and other industries. This article reviews the recent advances of organic modification of montmorillonite/alkylammonium compounds process, the adsorption characteristics of different modifier on montmorillonite, the structure characteristics and gel performance of montmorillonite/alkylammonium, the influence mechanism is analyzed, and the research direction in this field is also prospected.

1. Introduction

Montmorillonite is a kind of silicate mineral with a typical TOT layered structure, and the interlaminar domain in layers of TOT nanocells is a huge inner surface space. This interlayer domain is a good chemical reaction site with the characteristics of interlayer exchange, interlayer adsorption, interlayer catalysis, interlayer polymerization, and interlayer pillaring [1].

Isomorphic substitutions in montmorillonite is very common, for example, Al^{3+} for Si^{4+} in the tetrahedral sheets or Mg^{2+} for Al^{3+} in the octahedral sheets, which lead to negative charges in montmorillonite layer. In order to balance these negative charges, the montmorillonite layer can attract some metal ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc, and these ions can be replaced by other cations in the environment. If the metal ions between the montmorillonite layers are replaced by organic cations, the surface of the montmorillonite will change from hydrophilic to lipophilic, and the organo-modified montmorillonite has good swelling property, high dispersibility and thixotropy in the organic medium. The compounds have a very low chemical activity, which are insoluble in organic liquids, do not react with organic systems, are not only resistant to dilute acids and alkali, but also have good water resistance and thermal stability, so the compounds are widely used in the paint, textile, printing ink, high temperature grease, daily cosmetics, environmental protection, polymer modification and other industries [2-8].

2. Recent Advances

2.1. Study of the Organo-Modified Process

Montmorillonite organic modifiers are mainly surfactants, especially alkyl ammonium salt surfactants. The organic modification of montmorillonite is essentially the adsorption and intercalation of organic modifier on montmorillonite. After the organic cations intercalate the interlayer of montmorillonite, due to the space effect, the intercalated organics extrude the water molecules in the original layers. At the same time, the organic functional groups carried by the organic cations form organic phases on the



montmorillonite layers, making the montmorillonite layer become lipophilic [9].

Smith [10] was the first to modify montmorillonite with ammonium ion as a modifier in an aqueous medium, and successfully synthesized organic montmorillonite, which laid a theoretical foundation for the subsequent study of synthesis and application of montmorillonite/alkyl ammonium complexes.

Nowadays, in the synthesis of montmorillonite/alkylammonium compounds, long-chain alkyl quaternary ammonium salts are commonly used as modifiers, and intercalation reactions with montmorillonite dispersed in an aqueous medium. However, not all alkylammonium salts are suitable for the preparation of organic montmorillonites. If the alkyl ammonium salt carbon chain is too short and has high solubility in water, after the intercalation, it is not conducive to the formation of a hydrophobic film on the surface of the montmorillonite. On the other hand, alkylammonium salts with long carbon chains has low solubility, poor dispersion in water, and is difficult to form stable compounds with montmorillonite.

There are many factors affecting the properties of montmorillonite/alkyl ammonium complexes, including the crystal properties of montmorillonite, the types of alkyl ammonium, and the preparation process conditions [11-15]. The key parameters that need to be strictly controlled include the concentration of the montmorillonite suspension, the modification temperature, the modification time, the type and amount of the modifier, the washing method, the drying temperature, and etc.

2.2. *The Adsorption Characteristics of Modifiers on Montmorillonite*

Adsorption mechanisms of organic modifiers on solid surfaces include ion exchange adsorption, ion pair adsorption, hydrogen bond formation adsorption, electron polarization adsorption, dispersion force adsorption, and hydrophobic adsorption [16], etc.

With regard to the adsorption characteristics of alkylammonium on montmorillonite, some researchers have found that there are two stages when the organic cations enter the montmorillonite layer during the modification: the first is the formation of a neutral complex, metal cations in the montmorillonite layer are subjected to equivalent exchange of ions with external organic cations; the second is the formation of charged complexes; that is when all the metal cations are completely replaced, the organic cations can continue to enter the interlaminar domain, thereby charging the montmorillonite. Chiou[17] et al. believed that the total amount of organic cations adsorbed by montmorillonite is greater than its CEC due to the organic cations formed between the montmorillonite layers, which can form a distribution phase between the montmorillonite layers and the organic cations or organic molecules can continue to be adsorbed after the exchange of the organic cations with the metal ions due to non-Coulomb force between organic substances inside and outside the interlayer [18]. Seung Yeop Lee et al. [19] studied the adsorption properties of hexadecyltrimethylammonium (HDTMA) on montmorillonite by means of adsorption isotherms, X-ray diffraction, and transmission electron microscopy. He found that the adsorption of HDTMA on montmorillonite resulted in swelling and irregular wavy layer structure of montmorillonite, adsorption of HDTMA that exceeds the cation exchange capacity of montmorillonite by hydrophobic bonds can affect the structure of montmorillonite.

The alkyl ammonium adsorbed on the smectite has certain stability. Yang Liuyan[20] et al. studied the stability of montmorillonite/alkylammonium and found that the stability of the complexes gradually decreased with the increase of the adsorption amount of cetyltrimethylammonium, and the cetyltrimethylammonium-montmorillonite with adsorption amount of cetyltrimethylammonium below 0.7 CEC has good stability, and the stability of the composite under alkaline conditions is better than that under acidic conditions; the stability of the complex is almost unaffected by temperature between room temperature and 70°C. Boyd [21] et al. studied the stability of montmorillonite/alkylammonium complexes by means of surfactant desorption, he found that the cetyltrimethylammonium cation adsorbed by ion exchange has good stability in the montmorillonite layers when the loading amount of cetyltrimethylammonium is below 0.49 CEC; and the adsorption of cetyltrimethylammonium by hydrophobic bonds is less stable in layers of montmorillonite when the cetyltrimethylammonium loading in montmorillonite is over 1.95 CEC.

In summary, researchers have done a lot of research work on the adsorption characteristics of alkyl ammonium (cation) in montmorillonite, and have also achieved certain research results, but overall it

lacks systematicness and comprehensiveness. The influencing factors on the adsorption characteristics of montmorillonite on alkylammonium have not deeply considered the influence of the crystallization properties of montmorillonite and alkyl ammonium molecular structure on its adsorption characteristics and the corresponding adsorption model for different situations have not been systematically studied. The adsorption mechanism of alkylammonium on montmorillonite involves the main (montmorillonite) and guest (alkylammonium) factors. The conclusions obtained by considering one of the factors alone are not comprehensive and unscientific. Therefore, the adsorption characteristics of alkylammonium under the influence of multiple factors in the interlayer of montmorillonite is still a topic that needs further study in the theory and application of montmorillonite/alkylammonium synthesis.

2.3. The Structure Characteristics of Montmorillonite/Alkylammonium

During the preparation of the montmorillonite/alkylammonium compounds, Alkyl ammonium is exchanged and adsorbed to the interlayer of montmorillonite. Because of the space effect, the layer spacing of montmorillonite/alkylammonium will change, at present; small-angle X-ray diffraction technology is still a common research method for this kind of research.

There have been many reports on the degree of expansion of the layer spacing in montmorillonite/alkylammonium, but the differences between the different researchers are quite large, the results obtained by using the same alkyl ammonium under almost the same experimental conditions are not comparable. KHATIB [22] et al. used dioctadecyl-dimethylammonium to synthesize montmorillonite/alkylammonium, and the interlayer distance was 2.418nm. Moraru[23] used dioctadecyl-dimethylammonium and octadecyl-benzyl ammonium as intercalation agents to synthesize montmorillonite/alkylammonium, the interlayer spacing of which is 2.35-2.52 nm, he used short carbon chain such as tetramethylammonium as intercalation agent, and the interlayer spacing of the synthesized montmorillonite/alkylammonium is only 1.38 nm. Weng Zuhua [24] et al. used octadecyl trimethylammonium chloride (SOAC), dioctadecyl dimethylammonium chloride (DOAC) and trioctadecyl methylammonium chloride (TOAC) as intercalation agent to synthesize montmorillonite/alkyl ammonium, they found that with the number of long carbon chains increases (from one to three), the interplanar spacing of montmorillonite/alkyl ammonium gradually increases (from 1.52 nm to 2.63 nm, 3.80 nm and 3.91nm, respectively). Chen Defang [25] et al. used trimethylammonium, octadecyl trimethylammonium and dioctadecyl dimethylammonium to synthesize the montmorillonite/alkylammonium compounds with interplanar spacing of 2.653nm, 2.964nm, 3.999nm, indicating that with the increase of the carbon chain length, the interplanar spacing of the synthesized montmorillonite/alkylammonium complexes is increased.

Some researchers believe that there is a dynamic change in the structure of the compounds during the synthesis of montmorillonite/alkylammonium. Soares [26] et al. used TG and XRD techniques to study the structure of the synthesized montmorillonite/alkylammonium (octadecyl trimethylammonium chloride) compounds with different organic ammonium concentrations and reaction times and found that the TG curve shows two weight loss peaks at 295°C and 395°C when the concentration of organic ammonium was high. However only one weight loss peak (395°C) occurs when the concentration is low, and the interlayer spacing of montmorillonite/alkylammonium obtained with different reaction times varies from 1.83 to 2.15 nm, i.e. the structure of montmorillonite/alkylammonium shows a dynamic change with modification time. Zhu Jianxi.[27] et al used cetyltrimethylammonium ion (HDTMA⁺) as the pillared liquid and adopted XRD analysis for the interlayer structure of the synthesized pillared montmorillonite at different concentrations, found that with the increase of the concentration of pillaring reagent, the change of arrangement of organic cations can be summarized as the following: Lateral monolayer – Lateral bilayer – Paraffin monolayer – pseudotrilayer – Paraffin bilayer, the results show that montmorillonite/alkylammonium complexes with different structural parameters and arrangement modes can be synthesized by using the same alkylammonium at different concentrations. The authors [28] used octadecyl trimethylammonium as an intercalating agent to explore the effect of modification time on the interlayer spacing, when the amount of octadecyl trimethylammonium is 1.1-1.2 CEC, with the increase of the modification time, the structure of the montmorillonite/alkylammonium complex was reduced from 6.58745nm to

2.163393nm, and the structure gradually transitioned from the mixed layer to the single layer structure. Therefore, the influence mechanism and control method of this structural dynamic change of montmorillonite/alkyl ammonium complexes still need to be further studied.

The difference in crystal plane spacing of montmorillonite/alkylammonium indicates the difference in the arrangement of alkylammonium in the montmorillonite layer. Lagaly [29] believed that the length of alkane chain and layer charge density of smectite have a certain influence on the arrangement of organic ammonium cations: when the organic quaternary ammonium cation has short carbon chain (carbon number is less than 10), the arrangement of the montmorillonite layers is Lateral monolayer, and the interlayer spacing is about 1.36 nm; when the organic quaternary ammonium cation chain is longer (more than 10 carbon atoms), the arrangement of the montmorillonite layers is Lateral bilayer, pseudotrilayer, Paraffin monolayer, Paraffin and Paraffin bilayer. Slade [30] used hexadecyltrimethylammonium bromide (HDTMA) as an intercalation agent to intercalate montmorillonite with different interlayer charges and found that the layer charge number had an effect on the interlayer spacing of intercalated products: when the number of charge per unit cell is low (<0.5), HDTMA shows a lateral monolayer in layers of montmorillonite; when the unit cell charge is 0.5-1.0, HDTMA shows a Lateral bilayer arrangement in the montmorillonite layers; when the number of unit cell charges is higher (>1.0), HDTMA shows a slanting arrangement in the montmorillonite layers.

The analysis of the arrangement characteristics of the organic cations in the montmorillonite layer above is mainly based on the net height of the interlayer of the montmorillonite/alkylammonium prepared and the length of the alkyl ammonium carbon chain. However, the above arrangement cannot be explained when the net height of the montmorillonite/alkylammonium layer is much larger than the alkyl ammonium carbon chain length of the alkyl ammonium cation. Obviously, the structural model of montmorillonite/alkylammonium compounds is difficult to reasonably describe and analyze from the perspective of single alkyl ammonium geometry.

In recent years, researchers have begun to use molecular simulation techniques to study the adsorption mechanism of organic modifier in montmorillonite and the structural characteristics of synthetic compounds. Pospíšil [31] used molecular mechanics simulation (MM) and molecular dynamics simulation (MD) to study the properties of cetylpyridinium (CP) and cetyltrimethylcationic (CTA⁺) montmorillonite. The results show that the interlayer structure of the two smectite composites is significantly different. Among them, the host and guest of the hexadecyltrimethyl cation (CTA⁺) montmorillonite has a stronger electrostatic effect. Wei Jingming [32] simulated the molecular environment and the arrangement of long-chain alkyl groups in the inter-layer of montmorillonite by means of MD simulation method and found that when the dosage of Alkyl ammonium is 1.0 CEC, the arrangement of alkyl chain in the montmorillonite layers is lateral bilayer in the presence of a small amount of water (dry); when the dosage of Alkyl ammonium is 2.0 CEC, the alkyl chain is Paraffin bilayer in the interlaminar domain, and the head of the alkyl chain is near the tetrahedral sheet. Zhou Qing [33] et al. simulated the structural models of organic montmorillonites with different CTMA⁺ loadings by molecular dynamics simulations and found that different arrangements of montmorillonite CTMA⁺ have different arrangements. In the case of 0.25 CEC, it is a horizontal double layer. When 0.5 CEC to 1 CEC, it shows a staggered arrangement, and the d(001) value increases significantly. When above 1CEC, CTMA⁺ adsorbed into the interlayer is stratified in the vertical direction, and the layer number increase with the increase of load capacity.

From the above research we can see, the researches mainly use the spectroscopy research methods to calculate the arrangement of alkylammonium in the montmorillonite layer according to the crystal plane spacing of the compound and the size of the molecular structure of the alkylammonium modifier used. However, there are few studies on the influence mechanism of the charge on the montmorillonite layer and the formation mechanism of the supersize layer spacing. And no systematic and comprehensive scientific theory has been established on the factors and mechanisms influencing the formation and changes of montmorillonite/alkylammonium structures.

2.4. The Gel Performance of Montmorillonite/Alkylammonium

The thixotropic gels formed by montmorillonite/alkyl ammonium compounds in organic solvent

systems is the main application characteristics. The montmorillonite/alkylammonium compounds with excellent gel properties should have the following characteristics: the montmorillonite interlayer organic cation must have sufficient coverage and stability at the layer; the composite layered assembly is easily peeled and dispersed; the face of the compound sheet needs a certain positive charge and after being dispersed, the layer can dissociate an appropriate amount of organic cations to exhibit a corresponding negative charge.

The gelation properties of montmorillonite/alkylammonium compounds are affected by the crystallization properties of the montmorillonite, the type of modifiers, the modification process, post-treatment of the products and others. Jordan [34] first to systematically studied the gelation properties of montmorillonite/alkylammonium compounds in organic solvents and pointed out that the length of aliphatic carbon chain in alkylammonium had a certain influence on the gel properties of the complexes. When the number of carbon atoms in the carbon chain is large (>12), the compounds can show significant lipophilicity. Moraru [23] studied the effect of different chain lengths of alkylammonium on the gelation properties of montmorillonite and found that montmorillonite/alkylammonium synthesized by long chain alkylammoniums such as dioctadecyl dimethyl ammonium and octadecyl benzyl ammonium are more easily dispersed and gelled in organic media. The larger the distance between montmorillonite layers, the easier it is to form gels, and the alkyl ammonium/montmorillonite synthesized by short-chain alkylammonium such as tetramethylammonium cannot form gels in organic media. At the same time, the degree of organic modification of montmorillonite also has significant influence on the gelation properties of the synthesized product: the gelation properties of the composites are best when the amount of alkylammonium modifier is 0.8-1.0CEC, but the gel strength of the composites decreases sharply when the amount of modifier is greater than 1.0CEC. In addition, the gel strength of compounds formed by different polar organic solvents also varies greatly; the gel strength of compounds in benzene and alkyl substituted benzene is lower than that in the more polar chlorobenzene, benzonitrile, and nitrobenzene. Jin-Ho Choy [35] et al. studied the effect of different functional groups on the dispersibility of montmorillonite/alkyl ammonium complexes and found that the alkyl quaternary ammonium salt synthesized complexes have better dispersibility in non-polar solvents and the quaternary ammonium salts containing hydrophilic functional groups have good dispersibility in non-polar solvents and water.

Some researchers [36,37] have studied the synthesis process conditions affecting the gel properties of montmorillonite/alkylammonium and found that the main factors affecting the gel properties of the compound are the carbon chain length, the amount of alkylammonium, and the reaction time; the montmorillonite/alkylammonium complex synthesized by the long-chain alkylammonium has better gelation. When the amount of organic modifier is much smaller than the CEC value or the amount is much larger than CEC value, the reaction time is insufficient or too long, all of which are not conducive to the formation of gel. The authors' studies [38] have shown that the montmorillonite/alkylammonium complexes prepared by the higher-layer charged montmorillonite have worse gelling properties than the compounds synthesized by lower layer-charged montmorillonites. When the interlayer spacing $d_{(001)}$ of montmorillonite is moderately swelled, the product has the best gelling performance, the compounds with large layer spacing has poor gel properties.

In summary, it can be seen that the gel properties of the montmorillonite/alkylammonium compounds are the result of multiple interactions, Therefore, we can study the occurrence of alkylammonium in montmorillonites, the layer charge of montmorillonite and the molecular structure of alkylammonium, explore the mechanism and rules of the above action factors, and then optimize the gel properties and control methods of montmorillonite/alkylammonium compounds is still a very important research prospect.

3. Prospect

From the above research, the researchers have done a lot of work in the field of the synthesis process of the montmorillonite/alkylammonium, the adsorption mechanism of alkylammonium in the montmorillonite, and the structure and gel properties of the montmorillonite/alkylammonium,

However, the study of these scientific problems, especially for the adsorption properties of different alkyl ammonium in the montmorillonite interlayer with different crystal characteristic, the dynamic variation rule of the structure and the gel properties of montmorillonite/alkylammonium complex are still lack of systematic and in-depth study during the modification process.

The author believes that the structural optimization and application performance control of montmorillonite/alkylammonium complexes should be as research goals, the basic research on the adsorption characteristics of different alkylammonium in montmorillonites with different crystal characteristics should be taken as the starting point; in terms of research methods, it should be combined with modern molecular modeling techniques, systematically study The effects of modification process conditions, surface electrical properties of montmorillonite and molecular structure of alkylammonium on the structure and gelation properties of montmorillonite/alkylammonium complex, which provides a theoretical and technical basis for the predesign of montmorillonite/alkylammonium complexes with certain structure and application properties.

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References

- [1] Wu P and Liao Z. 2000 *J. Chinese Journal of Nature*, **01** pp 25-32.
- [2] Wang C, Xie S, Chen D and Li Y. 2000 *J. Liaoning Chemical Industry*, **1** pp 36-39.
- [3] Hu Z, Zhong X and Li Y. 1999 *J. Non-metallic Minerals*, **22(6)** pp 22-24.
- [4] Sun H, Peng T and Liu F. 2002 *J. Journal of Southwest University of Science and Technology (Natural Science Edition)*, **17(3)** pp 74-78.
- [5] Ding R, Yang F and Sui S. 2002 *J. Oilfield Chemistry***19 (4)** pp 297-300.
- [6] Li J, Zhu L and Cai W. 2004 *J. China Environmental Science*, **24(6)** pp 665-9.
- [7] Will P G, Andrew N and Paul P. 2004 *J. Clays Clay Miner*, **52(2)** pp192-203.
- [8] Zhu L and Chen B. 2006 *Organic bentonite and its application in pollution control* Beijing: Science Press,
- [9] Huang J. 1996 *J. Chinese Journal of Structural Chemistry*. **15** pp 438-443.
- [10] Smith C R. 1934 *J. J Am Chem Soc*.**56 (7)** pp 1561-63.
- [11] Rong K, Liu K and Long X. 1997 *J. Paint & Coatings Industry*, **4** pp13-15+2.
- [12] Wang C, Li Y, Chen D. 2000 *J. Journal of Xi'an Jiaotong University*, **34(8)** pp 88-91.
- [13] Vasily N M. 2001 *J. Appl Clay Sci* **19(1)** pp 11-26.
- [14] Chen Y, Guo F and Yan J. 1999 *J. Non-metallic Mines*, **22(6)** pp15-16.
- [15] Sun H, Peng T, Liu F and Li G. 2002 *J. Non-metallic Minerals*, **25(3)** pp 10-13.
- [16] Zhao G. 1991 *J. Physical Chemistry of Surfactants*. Beijing: Peking University Press.
- [17] Chiou C T and Kile D E. 1998 *J. Environ. Sci. Technol*, **32** pp 338-43.
- [18] Feng B, Zhang Y and Gong K. 2002 *J. Chemistry Bulletin***7** pp 440-4.
- [19] Lee S Y and Kim S J. 2002 *J. Clays Clay Miner***50 (4)** pp 435-45.
- [20] Yang L. 2004 *Mechanism and Application of Organic Montmorillonite and Microorganism in the Treatment of Organic Pollutants*. (Beijing: Environmental Science Press).
- [21] Xu S, Sheng G and Boyd S A. 1997 *J. Advances in Agronomy*, **59** pp 25-62.
- [22] Khatib K, Pons C H, Bottero JY, François M and Baudin I. 1995 *J. Journal of Colloid and Interface Science*. **172(2)** pp317-23.
- [23] Moraru V N. 2001 *J. Applied Clay Science*, **19(1-2)** pp 11-26.
- [24] Weng Z, Huang S, Zheng Y and Zhao J. 2001 *J. China Surfactant Detergent & Cosmetics*, **(5)** pp 8-9.
- [25] Chen D, Wang C and Li Y. 2000 *J. Journal of Xi'an Jiaotong University*, **34(8)** pp 92-95.

- [26] Soares V L P, Nascimento R S V, Menezes V J and Batista L. 2004 *J. Journal of Thermal Analysis and Calorimetry*. **75(2)** pp 671-6.
- [27] Zhu J, He H, Guo J, Yang D and Xie X. 2003 *J. Chinese Science Bulletin*. **48(3)** pp 302-6.
- [28] Lu X, Song M and Qiu J. 2006 *J. Mining and Metallurgical Engineering*, **(6)** pp 57-61.
- [29] Lagaly G. 1981 *J. Clay Miner.* **16(1)** pp 1-21.
- [30] Slade P G and Gates W P. 2004 *J. Appl Clay Sci.* **25(1)** pp 93-101.
- [31] Pospíšil M, Capková P, Weiss Z, Malác Z and Simoník J. 2002 *J. J Colloid Interface Sci*, **245(1)** pp126-132.
- [32] Wei J, Yang H, Zhu J, Shen W and Yuan P. 2009 *J. Journal of Mineralogy and Petrology*,**29(1)** pp 33-37.
- [33] Zhou Q, Zhu J, He H, Yuan P and Zhou J. 2011 *J. Bulletin of Mineralogy, Petrology and Geochemistry* (Suppl). **30** p 338.
- [34] Jordon J W, Hook B J and Fimlayson C M. 1950 *J. J Phys Colloid Che.***54(8)** pp 1196-208.
- [35] Choy J H, Kwak S Y, Han Y S and Kim B W. 1997 *J. Mater Lett.*, **33(3-4)** pp 143-7.
- [36] Song M. 2005 *Study on the Optimization of the Preparation of Organic Montmorillonite and Its Structural Alternation* (Qingdao: Shandong University of Science and Technology).
- [37] Zhou Q. 2015 *Molecular Simulations of the Montmorillonite Interlayer microstructure and the Sorption towards Organics* (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences).
- [38] Qiu J, Chen P, Zhang Y and Lu X. 2007 *J. Journal of Mineralogy and Petrology*, **27(1)** pp36-39.