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Preparation of pentaerythritol-β-cyclodextrin ether and application in the extraction process of oil-containing drill cuttings

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ABSTRACT

Cyclodextrins are widely used in medicine, daily chemicals and other fields, because of its special physical and chemical properties and excellent biological characteristics, but due to the limitation of poor solubility, various modification methods have become a research hotspot for scientific researchers. In this paper, pentaerythritol was selected as raw material, pentaerythritol was combined with cyclodextrin 6-position hydroxyl group to prepare pentaerythritol-β-cyclodextrin ether, and two effective characterization methods were used to characterize the product. Since pentaerythritol as an extractant for oil-bearing drill cuttings or oil-containing sludge has been used in oil drilling and other fields, this paper is applied by oil-containing drill cuttings treatment in East China Sea oil and gas fields, and the field application results show that pentaerythritol-β-cyclodextrin ether as a solvent for oil-containing drill cuttings extraction treatment has high efficiency, can greatly reduce the footprint of the device, and is especially suitable for offshore platforms with limited space, and the solid phase oil content rate of oil-containing drill cuttings generated after extraction treatment is 1.04%, which meets the environmental protection emission standards for offshore oil-bearing drill cuttings. In addition, part of the mineral oil can be recovered.

KEYWORDS: cyclodextrin; pentaerythritol; pentaerythritol-β-cyclodextrin ether; oil-containing drill cuttings; extraction

β-Cyclodextrin (β-CD) is widely recognized as the fundamental progenitor in the realm of supramolecular compounds, owing to its distinctive structural attributes of a "hydrophobic inner cavity and hydrophilic outer cavity". The solubility of all three prevalent cyclodextrin crystals, be it α-, β-, or γ-type, in aqueous solutions is exceedingly limited [1]. This intrinsic characteristic inadvertently hampers the practical application of cyclodextrin. Among these crystals, β-cyclodextrin, which boasts the highest yield, exhibits a solubility of 1.58 g β-CD/100 mL water at room temperature [2]. Consequently, numerous techniques have been developed to heighten the solubility of cyclodextrins, including the employment of eutectic solvents and coordination complexes. However, the most basic and fundamental approach remains chemical modification. To date, the primary focus of β-CD modification revolves around the three active hydroxyl groups present on the external surface, namely the -OH group at the C-6 position, as well as the -OH groups at the C-2 and C-3 positions. Due to disparate locations and diverse chemical environments, their respective reactivities vary significantly. Both theoretical speculation and experimental validation have unequivocally substantiated that the -OH group at the C-6 position exhibits the highest reactivity due to its potent nucleophilicity. In stark contrast, the nucleophilicity of the -OH groups at the C-2 and C-3 positions pales in comparison [3-5]. Conversely, pentaerythritol, an archetypal representative of polyols, encompasses four hydroxyl groups within its molecular structure, all of which possess comparable reactivity. As a consequence of the heightened electronegativity of oxygen atoms within the molecular architecture of pentaerythritol when juxtaposed with that of hydrogen, these oxygen atoms acquire a negative propensity, rendering them amenable to nucleophilic attack by the hydroxyl groups of cyclodextrin [6, 7].

1 Preparation of pentaerythritol-β-cyclodextrin ether

1.1 Experimental reagents and instruments

The main reagents and instruments used to prepare pentaerythritol-β-cyclodextrin ether are shown in Table 1.

Table 1 Reagents and main instruments used for the preparation of pentaerythritol-β-cyclodextrin ether

Reagent or instrument name	Reagent or instrument manufacturer	Reagent purity or instrument model
β-CD	Chengdu Cologne Reagent Co., Ltd	Biochemical reagents
Pentaerythritol	Chengdu Cologne Reagent Co., Ltd	Analyze pure
Epichlorohydrin	Chengdu Cologne Reagent Co., Ltd	Analyze pure
NaOH	Chengdu Cologne Reagent Co., Ltd	Analyze pure
KOH	Chengdu Cologne Reagent Co., Ltd	Analyze pure
Ethanol	Chengdu Cologne Reagent Co., Ltd	Analyze pure
Concentrated hydrochloric acid	Chengdu Cologne Reagent Co., Ltd	37%（quality score）
Fourier transform infrared spectrometer	Beijing Ruili Analytical Instrument Co., Ltd	WQF-520
Nuclear magnetic resonance spectrometer	Bronk spectrometer company（BRUKER）	ASCEND-400

1.2 Synthesis method

In the implementation of nucleophilic reactions, it is common practice to use intermediate reagents with high electronegativity to speed up the reaction process. The strong electronegativity of the chlorine atom connected to the carbon atom in the epichlorohydrin structure causes the carbon atom connected to it to be electropositive, making the electrophilic reaction with pentaerythritol stronger.

When β-CD undergoes a nucleophilic reaction, first the epoxy group of epichlorohydrin reacts with the -OH on β-CD and is etherified to form pentaerythritol-β-cyclodextrin ether. The synthetic route of pentaerythritol-β-cyclodextrin ether is shown in Figure 1.

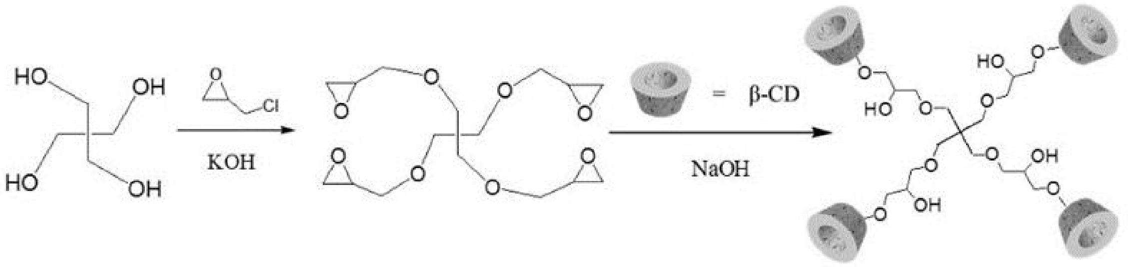

Figure 1 Synthetic route of pentaerythritol-β-cyclodextrin ether

The specific preparation process is as follows:

First, dissolve 2.5 g of KOH evenly in 25 mL of distilled water, add 1.36 g of pentaerythritol, and stir to raise the temperature to 90°C. Continue stirring at a constant temperature for 2 hours and then cool to 5°C; slowly add 3.2 mL of epichlorohydrin to the above solution. , mix evenly at 5°C for 2 hours; after the above solution is left at room temperature for 10 hours, a total of 48 g of β-cyclodextrin is added in 4 times, the temperature is raised to 35°C, stirring is continued for 24 hours, and finally concentrated to 45-50 by evaporation under reduced pressure. mL, and then precipitated in 300 mL of absolute ethanol, filtered, washed repeatedly with distilled water, and dried at high temperatures to obtain pentaerythritol-β-cyclodextrin ether.

2 Product structural characterization

Infrared and nuclear magnetic resonance are considered to be the most basic methods for characterization of compound structures. This study used a Fourier transform infrared spectrometer produced by Beijing Rayleigh Analytical Instrument Co., Ltd. and a nuclear magnetic resonance spectrometer produced by Bronk Spectrometer Company for structure confirmation.

2.1 Infrared spectrum characterization

β-CD and the prepared product pentaerythritol-β-cyclodextrin ether were mixed and ground with potassium bromide at a mass ratio of 1:100, then pressed into tablets, and IR analysis was performed on an infrared spectrometer. The IR of β-CD and pentaerythritol-β-cyclodextrin ether are shown in Figure 2.

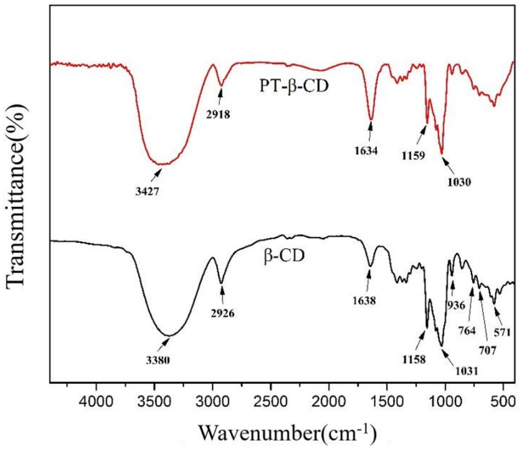

Figure 2 IR spectra of β-CD and pentaerythritol-β-cyclodextrin ether (PT-β-CD)

It can be seen from the IR spectrum 2 that β-cyclodextrin and pentaerythritol-β-cyclodextrin ether absorb at the positions of 3380 cm^{-1}, 1638 cm^{-1}, 2926 cm^{-1} and 936 cm^{-1} peak. The author of the paper believes that the first two places belong to strong absorption and should be caused by the stretching vibration of -OH, and the last two places should belong to -CH_2 and are caused by the stretching vibration. The peaks located at 1158 cm^{-1} and 1031 cm^{-1} should be the absorption peaks of C-O-C group and C-O group. 764 cm^{-1}, 707 cm^{-1} and 571 cm^{-1} are the absorption peaks of the pyranose ring, which are caused by the vibration of the pyranose ring skeleton. Compared with the absorption peak of β-cyclodextrin, the absorption peaks at 1634 cm^{-1} and 2918 cm^{-1} are unique to pentaerythritol-β-cyclodextrin ether, and the 1634 cm^{-1} peak is stronger and should It is O-H bending vibration, and the 2918 cm^{-1} peak is weak and is classified as -CH_2 stretching vibration.

2.2 NMR characterization

The 1H NMR spectra of β-cyclodextrin and pentaerythritol-β-cyclodextrin ether were measured on an ASCEND 400 NMR spectrometer using deuterated water (D_2O) solvent. The chemical shift reference values of deuterated solvent peaks are: deuterated water 4.70 ppm, deuterated chloroform 7.26 ppm and deuterated dimethyl sulfoxide 2.48 ppm. The obtained 1H NMR is shown in Figure 3.

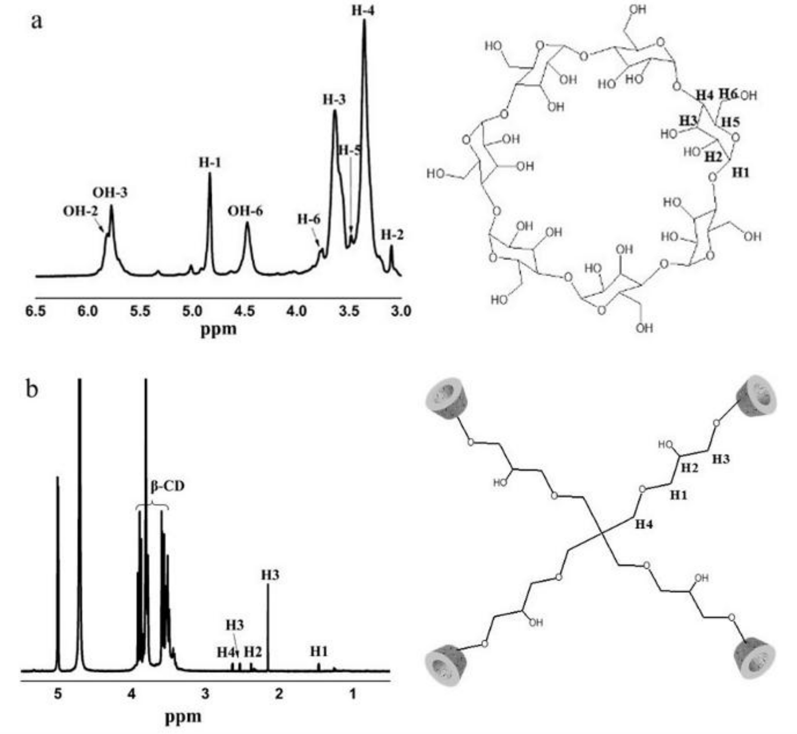

Figure 3 ^{1}H NMR spectra of β-cyclodextrin and pentaerythritol-β-cyclodextrin ether. (a) β-cyclodextrin; (b) Pentaerythritol-β-cyclodextrin ether

It can be seen from the 1H NMR spectrum of β-cyclodextrin in Figure 3a that at 4.84 ppm, it is the proton chemical shift of O-CH-O in the glucose unit structure. The chemical shifts of C-2, C-3, C-4, C-5, and C-6 protons in the glycosidic bond skeleton correspond to 3.09 ppm, 3.63 ppm, 3.36 ppm, 3.48 ppm, and 3.76 ppm respectively. The chemical shifts of the -OH protons at the C-6 position, C-2 and C-3 positions are 4.48 ppm, 5.82 ppm and 5.78 ppm respectively.

It can be seen from the 1H NMR spectrum of pentaerythritol-β-cyclodextrin ether in Figure 3b that the proton peak of β-CD appears at 3.42-4.98 ppm, while the proton peak of pentaerythritol glycidyl ether appears at 1.2-3.42 ppm. At the proton peak of pentaerythritol glycidyl ether-OH is $\delta=4.98$ ppm. The above chemical shift analysis and the aforementioned IR analysis showed that pentaerythritol-β-cyclodextrin ether was successfully prepared.

3. Application in solvent extraction of oily drill cuttings

The production process of oil-containing drilling cuttings is usually that the optimized oil-based drilling fluid returns to the surface along with the broken formation cuttings during the drilling process. First, solid-liquid separation is performed through devices such as vibrating screens, and the leakage part of the 200-mesh vibrating screen returns. The mud pool continues to be used after simple formula adjustment, and the muddy solid phase mixture containing cuttings is called oil-containing drilling cuttings. The production process is shown in Figure 4.

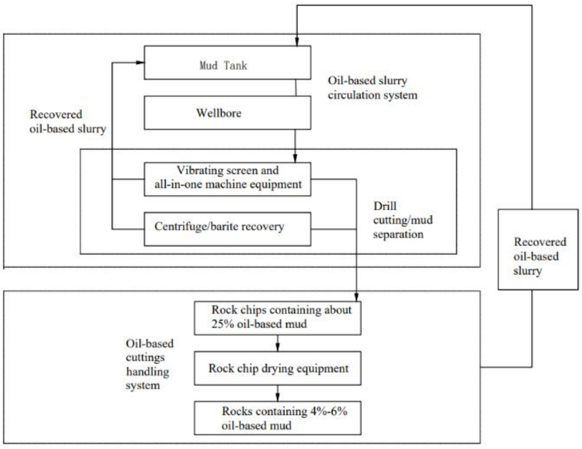

Figure 4 The process of generating oil-containing drill cuttings

Commonly used processing methods for oil-bearing drill cuttings include solvent extraction, froth flotation, ultrasonic and microwave irradiation, pyrolysis, electrokinetic methods, centrifugation and freeze-thaw [8]. In comparison, solvent extraction is a simple and practical technique in which oily drill cuttings are vigorously mixed in a solvent to remove solid particles, water and other impurities. The mineral oil components and solvents in the oil-containing drill cuttings are separated through distillation, and the solvent and mineral oil are recycled [9]. During this process, oily drill cuttings are mixed with certain solvents in varying proportions to help extract the mineral oil components in the oily drill cuttings

(Figure 5)

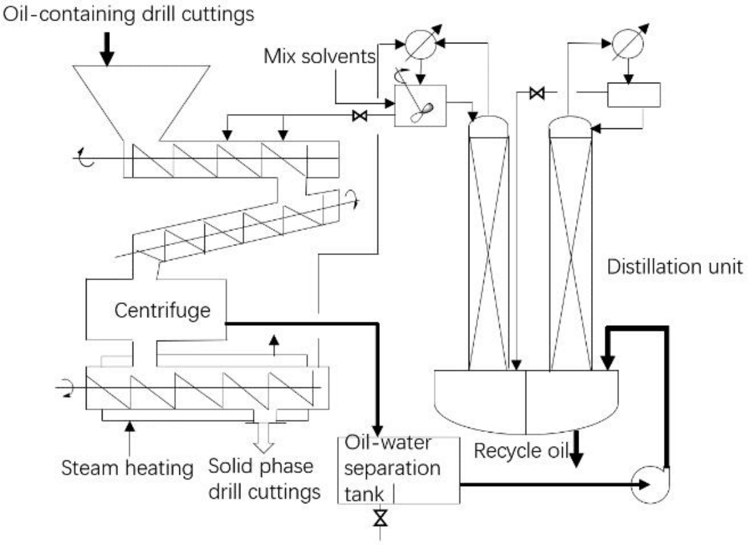

Figure 5 Solvent extraction process for oily drill cuttings

The most commonly used extraction solvents include propane trimethylamine, chloroform, methyl ethyl ketone, pentaerythritol, etc. [10-13]. Petroleum ether, hexane, toluene and benzene are also often used as extraction solvents for oily drill cuttings [14, 15]. Experiments were conducted on these solvents to analyze the physical and chemical characteristics during the treatment of oily drill cuttings. The evaluation results show that the solvent extraction method can effectively dispose of oil-containing drill cuttings and reduce the oil content of the solid part to 1%. In another study, three solvents, cyclohexane, ethyl acetate, and methyl ethyl ketone, were used, supplemented by two forms of ultrasonic extraction [16]. Ultrasonic assistance greatly improved the extraction efficiency of oil-containing drill cuttings, and a mineral oil extraction efficiency of 68.8% was obtained within 20 s.

Generally speaking, solvent extraction is one of the best methods for recovering oil from oily sludge, mainly because of its low environmental impact and short incubation period. To transplant this method to the treatment of oily drill cuttings, you only need to adjust the process parameters to reduce the oil content of the solid phase to meet the emission standards of the local environmental protection department. The other processes and parameters are no different from the treatment of oily sludge [17 -20]. The use of organic solvents to treat oily drill cuttings may increase operating costs, and safer, more effective, and cheaper alternatives are urgently needed for industrial installations [21-23]. On the other hand, in order to reduce the possibility of secondary pollution of harmful gases, steam evaporation devices can be used to increase the safety of the process [24, 25]. Table 2 shows the processing results of oil-containing drill cuttings on a CNOOC drilling platform (a mixture of 0.4% pentaerythritol glycidyl ether and 99.6% cyclohexane).

The processing results of oil-containing drill cuttings on a CNOOC drilling platform are shown in Table 2.

Table 2 Treatment results of oil-bearing drill cuttings on a drilling platform of CNOOC

Serial number	Processing cuttings volume/t/d	Emissions/t	Oil content in solid phase/%	Amount of mineral oil recovered/t
1	14.5	12.11	1.05	2.37
2	13.8	12.64	1.01	2.12
3	13.6	11.92	0.98	2.11
4	14.6	12.42	1.11	2.38
5	13.9	12.82	1.02	2.31
6	14.4	12.01	1.03	2.36
7	14.7	12.64	1.02	2.19
8	13.1	11.91	0.97	2.12
9	14.8	12.82	1.12	2.48
10	15.9	13.82	1.12	2.91
average	14.33	12.51	1.04*	2.34

The aforementioned well site evaluation shows that the oil content in the solid phase under the same process conditions of the same device using only cyclohexane as the extraction solvent is 1.22%.

4 Conclusion

(1) Pentaerythritol-β-cyclodextrin ether is prepared by the method in this article, which has the characteristics of easy availability of raw materials, simple preparation process, and environmental friendliness.

(2) Both infrared spectra and nuclear magnetic resonance spectra show that the prepared substance is structurally confirmed to be a pentaerythritol-β-cyclodextrin ether compound.

(3) Pentaerythritol-β-cyclodextrin ether is used as a solvent for the extraction and treatment of oil-bearing drill cuttings. It is highly efficient and can greatly reduce the footprint of the device. It is especially suitable for offshore platforms with limited space.

(4) The solid phase oil content of the oil-containing drill cuttings produced after extraction treatment is 1.04%, which meets the processing requirements of offshore platforms and can be directly discharged into the sea. In addition, some mineral oil can also be recovered.

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