A block polyether designed quantitatively by HLD concept for recovering oil from wastewater

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HIGHLIGHTS

- For the first time HLD theory is used to design new polyethers for oily wastewater.
- The designed block polyethers have a great ability to decrease oil in water.
- The block polyethers could separate the oil and suspended solid selectively.
- The block polyethers could not re-produce adhesive sludge in applications.

ARTICLE INFO

ABSTRACT

So far, the functional polymer molecular design is both a hot research topic, but also a difficult problem. In this paper, a new principle of designing polyether for recovering oil from wastewater has been proposed according to the hydrophilic–lipophilic deviation (HLD) concept. The key parameter of polyether (ethylene oxide/propylene oxide) has been calculated. The designed polymer has been synthesized, and the oil removal experiment has been performed to confirm the effectiveness. The droplet-to-planar coalescence experiment was used to study the deoiling mechanism. The results showed that the designed and synthesized block polyether was effective in deoiling of oily wastewater. The deoiling mechanism indicated that the addition of synthesized polymer can promote the coalescence of oil droplets to realize phase separation.

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1. Introduction

Our environment is continuously suffered from pollutants. As one of the mostly existed pollutants, industrial waste water commonly contains hydrocarbon or oil-like pollutants. Such wastes widely exist in many industrial applications in the form of oil-in-water (O/W) emulsions, such as petroleum exploitation and processing, tramp oils from machine tool coolants, utility operations, sanitary sewage, bilge and ballast water, and so on. The discharge of O/W emulsions would result in safety hazards and ecosystem problem to aquatic life. Therefore, the treatment of oil-in-water emulsions is an essential and important process in environmental protection.

Current methods for treating O/W emulsions include traditional physical and chemical methods. Usually, both of the methods are utilized together. Physical methods, such as skimming systems, dispersants and sorbents, seldom generate secondary pollution [1]. However, it is not available to assure the high separation efficiency within limited time and space by physical methods. It is almost impossible to recover oil from the O/W emulsions to accord the standard only by physical method in a short time. As for many of the industrial applications have strict restriction on processing time, a more complex approach should be involved. Adequate dosage of chemicals can accelerate the treating process and promote the efficiency. At present, the most commonly used chemicals for treating oil-in-water emulsions are flocculants, such as cationic polyacrylamide, polyaluminium chloride, etc [2,3]. These flocculants make the action by way of electrostatic attraction. Since the oil droplets in the water are anionic, the cationic polymers can easily reduce the stability of oil-in-water emulsions by

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electrostatic charge neutralization. However, the interaction usually gives rise to a great number of adhesive sludges, caused by the precipitation of oil droplets and suspended solids combined, which adhere to the pipes and influence the equipment operation. In addition, the resultant sludges are difficult to be separated from water in the following pollutant treatment. In this circumstance, it is important to separate the oil and suspended solid selectively, which means not only recovering oil but also avoiding the adhesive sludges at the same time.

The block polyether is an ideal choice for separating emulsions. Though using block polyether as demulsifiers has been 90 years of history, the emulsions are usually W/O emulsions [4,5]. Whether block polyether can be used to separating O/W emulsions needs some theoretical and experimental supports. For the stability of emulsions, there are two main mechanisms that are responsible for providing colloidal stability: steric and electrostatic stabilization, which are created through adsorption of surfactants, polymers, or fine solids onto the droplet interface [6]. Several approaches have been proposed to explain the surfactant's role in the past 50 years, such as Griffins' Hydrophile Lipophilic Balance (HLB) [7], Winsor's R ratio, Shinoda's phase inversion temperature (PIT) [8,9] and the more recent expression proposed by Salager [10,11], which resorts to the surfactant affinity difference (SAD) or its dimensional equivalent hydrophilic–lipophilic deviation (HLD). Indeed, the emulsion stability is affected by many terms and conditions including temperature, electrolyte concentration, oil composition, surfactant type and concentration. It is the only the HLD concept that takes these physiochemical parameters into account, and generalized formulation index linked to the phase behavior of surfactant–oil–water systems [12]. The optimum formulation (HLD = 0) corresponds to the formulation where the unstable emulsion is observed because at this point, the affinity of emulsifier for oil and for water is the same. Conversely, this special point can be used to design an emulsion breaker. When the HLD is close to 0, the so-called surfactant becomes a real demulsifier.

In this paper, a specific block copolymer of ethylene oxide (EO) and propylene oxide (PO), named DMEA-mnpq, had been designed by HLD concept for separating oil-in-water emulsions. It was shown that DMEA-mnpq designed by HLD can recover oil selectively without suspended solid in wastewater. To the best of our knowledge, this is the first quantitative design of chemical agent for treating O/W emulsions.

2. Materials and methods

2.1. Materials

All the chemicals used in the experiments were analytical grade and supplied by KeLong Reagent Company, Chendu, China. N, N-dimethylethanolamine (DMEA) was the acceptor of block copolymers of EO and PO. The oily wastewater and O/W emulsions were obtained from one offshore oilfield in China. The oil content in water (OiW) was 4724 mg/L.

2.2. Synthesis of block polyether

The four blocks polyether DMEA-mnpq was prepared and characterized according to Ref. [4] and listed in S2 of Supporting information. The structure was shown in Fig. 1. n:m:p:q represented the weight ratio of different blocks. As for DMEA1231, e.g., the weight ratio of the four blocks was 1:2:3:1. The details of synthesis were described as below.

A high pressure stainless steel autoclave (China) of 2 L capacity, 5000 psi maximum pressure and 500 °C maximum temperature was utilized to achieve both the propoxylation and ethoxylation
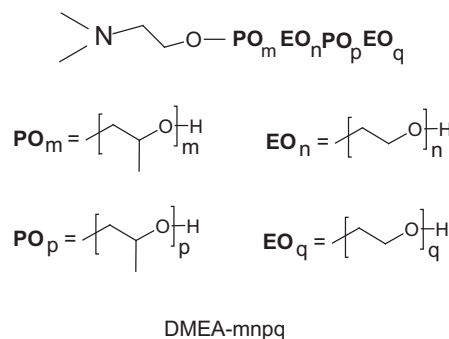

Fig. 1. Structure of DMEA-mnpq.

reactions. The propoxylation of DMEA was carried out according to the following process: DMEA (10 g) and KOH (3.0 g, acting as catalyst) were added into the autoclave. The autoclave was vacuumized. Then, the temperature was gradually raised to 135 °C. Finally, 990 g of PO was introduced gradually (keep the pressure in autoclave lower than 0.4 MPa) through a pressure pipette mounted over the inlet valve, which was connected to a nitrogen cylinder. Nitrogen was utilized to force the PO inside the reactor. And the stirrer was set at a speed of 300 rpm.

As PO was consumed in the reaction, the pressure dropped to a minimum and the entire PO was consumed. Heating was stopped, and the contents were cooled gradually to ambient temperature by means of a cooling coil inside the reactor with cold water. Then intermediate compound propoxylated DMEA was obtained to conduct the next ethoxylation.

200 g of propoxylated DMEA and 1.8 g of KOH were put in the autoclave at first. 400 g EO was introduced to do the ethoxylation. The reaction conditions for ethoxylation are similar to that of the propoxylation with the exception of the temperature set to be 120 °C instead of 135 °C. After this ethoxylation, according to the similar method, 600 g PO and 200 g EO were put in the autoclave successively and consumed. At last, DMEA1231 was obtained.

2.3. The theory for design of block polyether based on HLD

For a surfactant–oil–water system, the phase behavior and emulsion properties are commonly affected by many factors. The effects of these factors can be expressed as an empirical correlation known as the hydrophilic–lipophilic deviation (HLD), which is derived from surfactant affinity difference equation to describe emulsion systems [13]. The HLD equation for non-ionic surfactant is:

$$HLD = b(S) - K \times N_{c,o} - \varphi(A) + c_T(T - T_{ref}) + C_{ni} \qquad (1)$$

where S is the salinity of the aqueous phase in wt% NaCl (in g/100 mL), b is 0.13 for sodium chloride. $b(S)$ in Eq. (1) accounts for the "salting out" of the non-ionic surfactant. K ranges from 0.1 to 0.2, for numerous surfactants-oil combinations, but a value of 0.17 is typically used for most surfactants. $N_{C,O}$ is the number of carbons in the alkane oil phase (also known as alkane carbon number or ACN). As described by the HLD concept, for a given surfactant–oil–water emulsion, its stability has been determined by the HLD value of surfactant. Negative, zero or positive HLD values suggest the formation of O/W type, the change in emulsion type form W/O to O/W, W/O type, respectively.

For non-alkane oils, the term equivalent alkane carbon number (EACN) is employed. For example, the EACN of toluene is approximately one, which reflects the polar nature of this oil [14]. The $N_{C,O}$ of oil in wastewater was measured by interface tension method [15,16] and its value is 9.2. The function $\varphi(A)$ depends on the type