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Demulsification of Crude Oil Emulsion Using Polyamidoamine Dendrimers

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Abstract: Six dendrimers with the same polyamidoamine (PAMAM) basic structure but different terminals/generations were synthesized by divergent method. The dendrimers were studied by surface tension measurement at the air-water interface. The demulsification performance for oil/water (O/W) simulated crude oil emulsion and crude oil extract directly from field was investigated. The experimental results indicate that the three dendrimers terminated with ester groups were insufficient demulsifiers for crude oil emulsion. However, the three dendrimers terminated with amine groups exhibited excellent demulsification performance for O/W emulsions. As demulisifers, amine based dendrimers were superior to the commercial polyether ones (SP-169 and BP-169). The possible mechanisms for the nanocontainer effects of the dendrimers, through either surface adsorption or internal encapsulation, were discussed.

Keywords: Dendrimers, oil-in-water emulsions, demulsifications, produced fluid

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INTRODUCTION

Dendrimers are well-defined macromolecules that have a specific size, shape, and chemical functionality. Structurally they are regularly branched from a central core, and a large number of terminal groups surround this core to form a relatively empty interior. This new type of functional macromolecules was simultaneously developed by Tomalia and Newkome in the middle of the 1980s (1, 2). Upto the present, dendrimers have been broadly studied for drug delivery (3, 4), catalysis (5, 6), etc. For all these applications, dendrimers are considered as nanometer sized containers, with the relatively empty interior as the cage and the crowded terminal groups as the steric wall. Sometimes, molecules can be adsorbed onto the surface of dendrimers due to the large number of terminal groups on a dendrimer. The latter effect has also been considered one type of nano-container effect (7). These structural features are also called "dendrimer box" (8) in some special cases, referring to small guest molecules being encapsulated/adsorbed into/onto the dendrimer. This report intends to explore the possibilities of using these nanocontainers with special structures for demulsification.

Oil field emulsions can be formed during either waterflood or steamflood techniques when oil and water mix in the reservoir, at the wellbore, or in surface facilities. Demulsification is an essential industrial process, mainly used for removing water from crude oil. Because of the inevitable complex composition of crude oil and the existence of water, crude oil most likely exists in the form of emulsion with oil emulsified in the water phase. Whether they are created unintentionally or deliberately, emulsions eventually must be destroyed to separate the oil and water phases. Among different methods of demulsification, chemical demulsification is one of the most effective and simplest of methods. The efficiency of demulsification process is largely dependent on the performance of the demulsifier (9).

The solubilization mechanism is one common demulsificaiton mechanisms. It typically means that natural surfactants are dissolved into the bulk phases of demulsifier (10). Encouraged by the excellent performance of dendrimers as nanocontainers for drug delivery, catalysis, etc., we reasoned that dendrimers with properly designed structures might also be used as efficient demulsifiers. They can dissolve/adsorb the natural surfactants into/onto the nanocontainers rapidly, and lead to the destruction of emulsion.

Polyamidoamine (PAMAM), the simplest dendrimers, were chosen to study the demulsification for simulated emulsion. The interior of the dendrimers was designed to be polar but hydrophobic, which should match the properties of a typical surfactant. The outer surface provided by the terminal groups of the dendrimers was varied between charged and uncharged (but still polar). The size of the dendrimers was altered from generation 1 (G1), generation 2 (G2), to generation 3 (G3). Experimental results reveal that the structure of the terminal groups plays a determining role for the targeted demulsification. Efficient demulsification only occurs for amine-terminated dendrimers. In addition, demulsificaiton becomes more efficient as the generation number of dendrimers increases. The results seem to be consistent with the solubilization mechanism of the surfactants onto the surface of the amine-terminated dendrimers through ionic interactions with the negatively charged surfactants although encapsulation of surfactants into dendrimers cannot be completed ruled out.

EXPERIMENTAL

Synthesis of Dendrimers

Ethylenediamine, methyl acrylate, and methanol are analytical reagents from the Shenyang Dongxing Reagent Factory (China).

Synthesis of G1 ester: Ethylenediamine(9.0 g, 0.15 mol) was dissolved in 30 g of methanol, then methyl acrylate (103.2 g, 1.20 mol) was added into the flask. The mixture was stirred 24 hours at 25°C. The solvent and the unreacted methyl acrylate were removed under reduced pressures. A light-yellow liquid G1 ester was obtained.

Synthesis of G1 amine: G1 ester (20.2 g, 0.05 mol) was dissolved in 60 g of methanol, then ethylenediamine (72 g, 1.20 mol) was added into the flask. The mixture was stirred for 24 hours at 25°C. The solvent and unreacted ethylenediamine were removed under reduced pressures. A light-yellow thick liquid G1 amine was obtained.

According to a chemical reaction equation, the above unit reaction was repeated the G2 ester, G2 amine, G3 ester, and G3 amine were obtained respectively (11).

The above dendrimers were studied in literature. To conform to the structures, ^{1}H NMR spectra were recorded for the six dendrimers discussed above using a Varian NOVA 400 MHz NMR spectrophotometer. $CDCl_3$ was used as the solvent. Experimental results (Table 1) indicate that the NMR spectra of the purified dendrimers completely matched those reported by reference (10).

Preparation of Simulated Emulsion

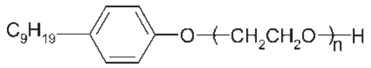
The surfactant polyoxyethylenenonyl phenol ether (OP-7) and sodium dodecyl benzene sulfonate (ABS) are of industrial purity, purchased from the Tianjin Auxiliary Manufactory and Shanghai Auxiliary Manufactory

Table 1. Hydrogen-1 chemical shift of six dendrimers synthesized

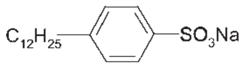
Generation	Chemical shift assignments δ/ppm
G1 ester	(a) 2.50 (b) 2.77 (c) 2.44 (d) 3.67
G1 amine	(a) 2.47 (b) 2.70 (c) 2.36 (d) 3.26 (e) 2.78 (f) 1.96
G2 ester	(a) 2.50 (b) 2.77 (c) 2.36 (d) 3.27 (e) 2.55 (f) 2.77 (g) 2.44 (h) 3.67
G2 amine	(a) 2.43 (b) 2.68 (c) 2.52 (d) 3.21 (e) 2.74 (f) 2.80 (g) 2.36 (h) 3.27 (i) 2.74 (j) 1.55
G3 ester	(a) 2.51 (b) 2.82 (c) 2.37 (d) 3.28 (e) 2.56 (f) 2.78 (g) 2.34 (h) 3.28 (i) 2.56 (j) 2.78 (k) 2.45 (l) 3.68
G3 amine	(a) 2.44 (b) 2.68 (c) 2.34 (d) 3.25 (e) 2.78 (f) 2.68 (g) 2.34 (h) 3.25 (i) 2.78 (j) 2.68 (k) 2.34 (l) 3.25 (m) 2.79 (n) 1.65

[a] Hydrogen is in order from core to outside.

(China), respectively. The crude oil was provided by Daqing Oil Field (China). The molecular structures of surfactants are shown below:



OP-7



ABS

The mixture of 5.0 g of crude oil, 0.1 g of polyoxyethylenenonyl phenol ether (OP-7), 0.1 g of sodium dodecyl benzene sulfonate (ABS), and 94.8 g of water were separately added into the conical flask, the mixture was stirred by a mulser at 5000 rpm. Subsequently, the oil phase was separated, and the simulated crude 1.70% O/W emulsion in the lower layer was collected. This emulsion was found to be stable within the experimental timeframe.

Demulsification for Simulated Crude Oil Emulsion

The demulsification experiments were performed by using the standard bottle-test. The simulated crude oil emulsion and dendrimers were added into the test bottle, the mixture were well mixed by a hand shaking motion for 200 times at a frequency of 2 times/sec. The demulsification ratio was evaluated by demulsifiction ratio (X), which was calculated using the equation,

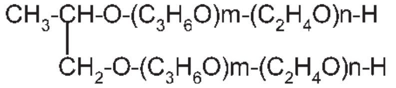
$$X(\%) = (C_0 - C)/C_0 \cdot 100\% \qquad (1)$$

Here, C and C_0 are respectively the oil concentration in the water phase before and after demulsificaiton, which were measured using absorption methods.

Demulsification for the Produced Fluid

The O/W produced fluid (extracted from oil well) used in this study was provided by Daqing Oil Field (China), and the demulsifier SP-169 and BP-169 were purchased from Xian petroleum chemical industry Auxiliary Manufactory (China). The molecular structure of SP-169 and BP-169 are shown below:

$C_{18}H_{37}\text{-}O\text{-}(C_3H_6O)m\text{-}(C_2H_4O)n\text{-}(C_3H_6O)m\text{-}H$ SP-169



$$\begin{array}{l} CH_3\text{-}CH\text{-}O\text{-}(C_3H_6O)m\text{-}(C_2H_4O)n\text{-}H \\ \qquad | \\ \qquad CH_2\text{-}O\text{-}(C_3H_6O)m\text{-}(C_2H_4O)n\text{-}H \end{array}$$

BP-169

RESULTS AND DISCUSSION

The structures of the dendrimers used are shown in Fig. 1. As pointed above, a dendrimer is an organic molecule which regularly branches out from the core (1). The number of branching points from the core to a terminal group determines the generation number of the dendrimer. For instance, a G3 dendrimer means it has three branching points from the core to a terminal group.

For the dendrimer shown in Fig. 1, each generation has two related dendrimers, one terminated with amine groups and the other terminated with ester groups. The interior of the two dendrimers for each generation is the same. Therefore, the solubility of the targeted surfactants in the interior pore of the dendrimers should be similar. Although the terminal groups were varied between amines and esters, all dendrimers in Fig 1 were found to be soluble in water, indicating the hydrophilic nature of these dendrimers.

However, the properties of the dendrimers in Fig. 1 as potential surfactants were found to be substantially different. As shown in (Fig. 2, top), the amine terminated dendrimers possessed very high surface free energy, between 69 and 70 mN/m, which is very close to that of water. This result indicates that all amine terminated dendrimers in Fig. 1, no matter what generation it is, cannot reduce the surface tension of air-water interface. Consequently, they do not behave like surfactants, at least for air-water interface.

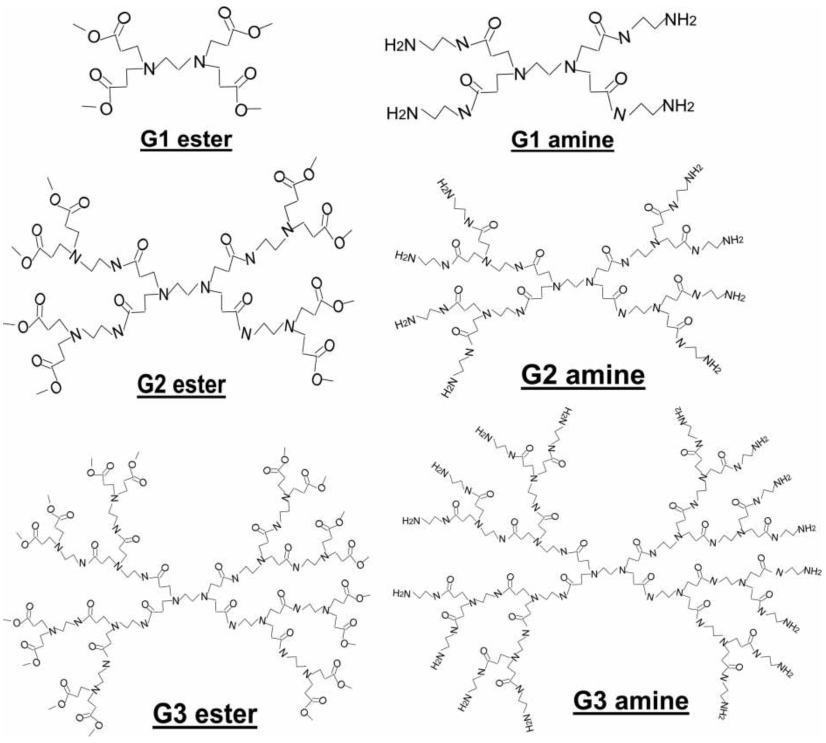


Figure 1. Structures of the dendrimers to be studied.

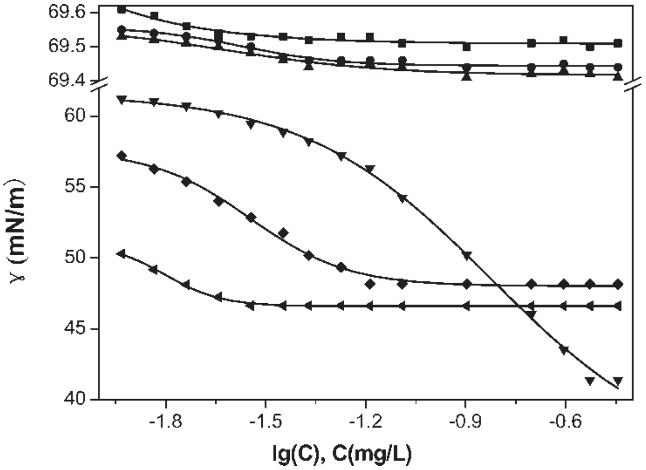


Figure 2. Surface free energy of different dendrimers. Top: amine terminated dendrimers. (■) G1; (●) G2; (▲) G3. Bottom:ester terminated dendrimers. (▼) G1; (◆) G2; (◀) G3.

A different situation was observed for ester terminated dendrimers (Fig. 2, bottom). All these three dendrimers possessed significantly lower surface free energy in comparison to pure water (about 72.5 mN/m at 20°C). This means that these ester based dendrimers can behave like surfactants for the air-water interface although they are not ideal ones in comparison to common surfactants.

All ester based dendrimers did not show any sign of demulsification. Under the same conditions, amine based dendrimers with different generation numbers demonstrate excellent performance for demulsification of crude oil emulsion in water (Fig. 3).

For the following experiments, both types of dendrimers were tested simultaneously. Since ester based ones did not show any demulsificaiton, only the data for amine based ones will be discussed in detail below.

Although the concentration of the amine based dendrimers was low (50 mg/L), all three dendrimers showed significant demulsification effects (Fig. 3). Each curve can be approximated to an exponential function. The demulsification ratio, increases substantially from G1, to G2, and G3.

The concentration of the amine based dendrimers affects the demulsification efficiency significantly (Fig. 4). When the concentration of the G3 amine dendrimers was 100 mg/L (equivalent to 0.01%), which is still very low, about 60% of the oil was separated in 10 minutes. In one hour, about 80% of the oil was separated. In addition, the oil-water interface was very neat and the water phase was clear, indicating that they are excellent demulsifiers for this emulsion.

Amine based dendrimers worked as excellent demulsifiers not only for the simulated crude oil emulsion but also for the crude oil extract from Daqing oil field. As shown in Table 2, when the concentration of the G3 amine dendrimers

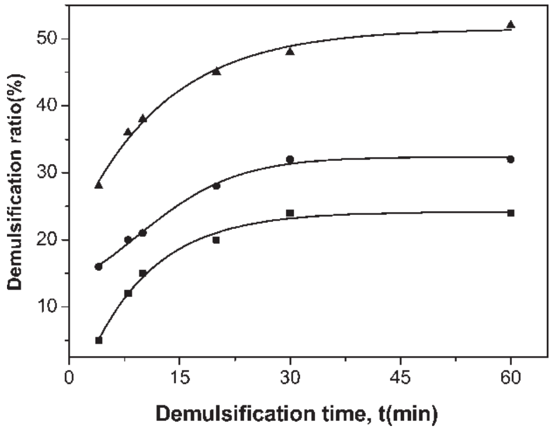


Figure 3. Demulsification ratio (see definition in the experimental section) of amine based dendrimers at 30°C. (■) G1; (●) G2; (▲) G3.

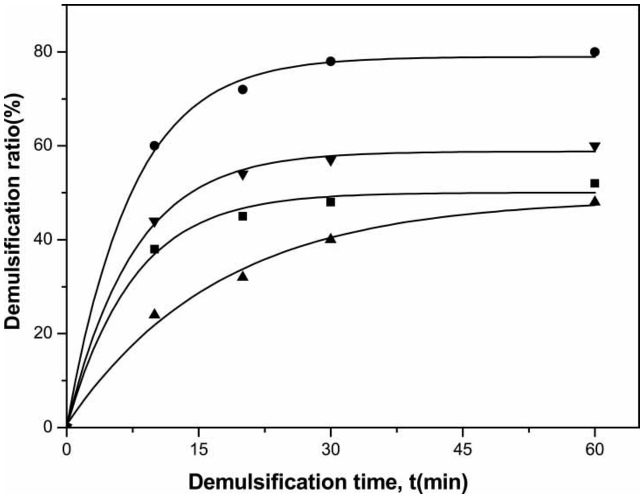


Figure 4. Concentration dependence of demulsification using G3 amine dendrimers at 30°C. (▼) 30 mg/L; (■) 50 mg/L; (▼) 70 mg/L; (●) 100 mg/L

was 30 mg/L, about 90% of the oil was separated in 60 minutes. In addition, the oil-water interface was very distinct or clear. Comparing with the commercial polyether demulsifier, the concentration of G3 amine dendrimers had significantly better performance although the concentration of the G3 dendrimers was about 1/3 of that for commercial ones. In fact, the demulsification of amine-based G3 dendrimers compared favorably with that of the commercial demulsifiers when its concentration was 1/5 of that for the commercial ones.

The results shown above are encouraging for using dendirmers as demulsifiers. At this point, it is unlikely to completely clarify the mechanisms. However, the results may shine some light on the demulsificaiton mechanisms using dendrimers, which should at least provide some hints for the future design of dendrimer based demulsifiers.

The dendrimers may act as "nano-containers" which dissolves the existing surfactants in the emulsion inside their interior as they often do in

Table 2. The demulsiflcation of dendrimer for produced fluid

Demulsifier	Concentration/ mg/L	Demulsification temperature/°C	Demulsification ratio/%	Interfacial state
G3 amine	10	45	78.1	Distinct
G3 amine	20	45	84.6	Distinct
G3 amine	30	45	90.6	Clear
SP-169	100	45	81.5	Distinct
BP-169	100	45	78.8	Distinct

other cases, such as for drug delivery (12, 13). On the other hand, the amine terminal groups will be positively charged in water unless the pH of the bulk aqueous solution is significantly basic, namely above $\text{pH} = 10$. In our simulated oil-water emulsions, the solution was more or less neutral. Therefore, the surface charge for amine based dendrimers should interact with the surfactant strongly (14). It should be pointed out that the amine groups in the interior of both types of dendrimers should also be positively charged. However, for electrostatic interactions, the strong steric hinders should make these interior positive charge centers less reachable.

The emulsion should become unstable if either of the above two processes occurred, encapsulation or adsorption. In our measurement, the single droplet method, a droplet of emulsion stabilized with a monolayer of surfactants came into a bulk solution of water with or without demulsification reagents. If the surfactants could be quickly captured by the demulsificaiton reagents in the bulk water solution, the emulsion droplet shall break down and merge into the bulk oil phase on the top of the water phase.

The first process, encapsulation of surfactants into dendrimers, would be relatively slow but efficient as the amine based dendrimers do not behave like surfactants, indicated by the results in Fig. 2. The second process, surface adsorption, should occur very fast. However, the resulting dendrimer-surfactant complex might still behave like a surfactant, as the dendrimer part is hydrophilic and the surfactants are hydrophobic. As a result, the demulsificaiton by the surface adsorption process occurred through drastically decreasing the total surface area of stabilization offered by the original surfactants.

The difference in saturation of the demulsification ratio (the plateau values in Fig. 3) with differently sized dendrimers could be explained using either of the processes. A larger dendrimer should have a higher solubilization power for the existing surfactants in the emulsion because of its larger interior nano-cage. On the other hand, a large dendrimer would adsorb more surfactants onto its surface, which should provide a better reduction of the total stabilization area as discussed above. For the same reasons, the concentration effects of dendrimers (Fig. 4) could also be explained through both the processes.

One evidence, however, seems to support the surface adsorption hypothesis. As shown in Fig. 3, a significant demulsificaiton effect was observed even for G1 amine based dendirmers. This dendrimer is not large in size in comparison to the surfactants and does not show much cage effects in literature. The difference between ester based dendrimersis and amine based ones, on the other hand, does not conflict with either hypothesis.

CONCLUSIONS

Amine based dendrimers were found to be efficient for demulsification of oil-water emulsion by acting as nano-containers for the surfactants presented in the emulsion, through either surface adsorption or internal encapsulation of the surfactants. The dendrimers terminated with amine exhibited excellent demulsification performance for O/W crude oil emulsion. As demulisifer, they were superior to the commercial polyether ones (SP-169 and BP-169). The high demulsification efficiency illustrated here implies that dendrimers with proper structures have a great potential for oil extraction from today's dominating raw oil products, oil-water emulsions.

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