



Phase inversion pathways of emulsions stabilized by ethoxylated alkylamine surfactants



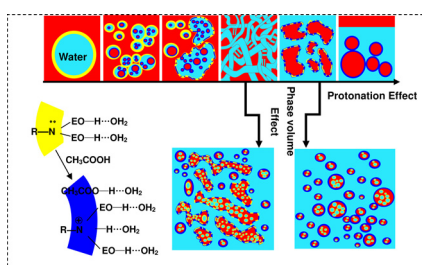
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HIGHLIGHTS

- Two phase inversion pathways in ethoxylated alkylamine emulsion are proposed.
- Two pathways have the same threshold and different destinations.
- Phase inversion is induced by the addition of acetic acid, but not exclusively.
- Phase inversion mechanisms rely on changes in the spontaneous curvature.
- Structural transition images help in understanding phase inversion mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Composition changes are performed on an invert emulsion stabilized by ethoxylated alkylamine surfactants by adding acetic acid solutions. The addition of acetic acid induces a phase inversion that evolves through the following stages: W/O emulsion, O/W/O dual emulsion, bicontinuous state (studded with lamellar phase), random-shaped O/W emulsion, and normal O/W emulsion. The addition of excess acetic acid will always lead to the separation of pure oil. The speed and direction of the phase inversion can be influenced by the water/oil volume ratio; increasing this ratio facilitates the phase transition or causes it to switch to another direction with the W/O/W emulsion state as the destination. Three critical observations help to elucidate the mechanisms that control the phase inversion: increases in both the hydration radius and pliability of the surfactant layer, which result from the protonation and disorganization of rigid water structures at the interface; an increase in the effective volume fraction of the dispersed phase, which results from the formation of multiple emulsions; and a kinetic phase volume effect, which results in a kinetic phase separation and the nucleation of both oil and water domains.

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1. Introduction

Emulsion phase inversion is a typical feature of instability [1], for which mechanisms have been reported as early as 1940 [2].

Because the inversion process has been used as an effective method to prepare nano-emulsions [3,4] and reversible emulsion drilling fluids [5], the importance of understanding the mechanisms for these processes and controlling for specific properties has motivated continued research interests.

Emulsion phase inversion can be induced by the methods of phase inversion composition (PIC) and phase inversion temperature (PIT). PIC consists of either continuous addition of the

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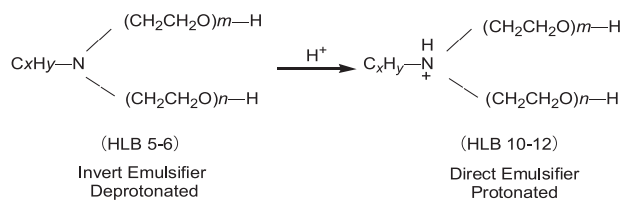


Chart 1. Chemical structure and protonation formula of ethoxylated alkylamine surfactants ($8 \leq x \leq 22$, $1 \leq m+n \leq 3$).

dispersed phase [6,7] or continuous agitation at a fixed dispersed-to-continuous phase ratio. In the latter case, agitation leads to the formation of multiple emulsions. Both methods give rise to increases in the effective volume of the dispersed phase [8,9], resulting in a catastrophic inversion in an abrupt manner [10]. Recently, some researchers have found that the PIC process causes a gradual change in the spontaneous curvature that proceeds through some transient structures, indicating the real cause of the catastrophic inversion [11–13]. PIT utilizes a jump in temperature to cause changes in the affinity of the surfactant toward the water and oil phases. This transitional inversion is identified as a more gradual one that involves intermediate stages of different emulsion structures [14–16]. The differences in pathways for these two types of inversion are not always clear when concomitant changes in both the composition parameter (e.g., hydration) and intensive parameter (e.g., temperature) occur along the path of inversion. In some instances, the combined paths fall into one of the previous cases, while in other instances, both catastrophic and transitional inversions overlap and some synergistic effects can be attained [1,17,18]. For either inversion type, the real cause of phase inversion should be interpreted in terms of the spontaneous curvature of the surfactant layer [19].

Historically, the phase inversion is related to the use of the CmEn amphiphiles because the spontaneous curvature can then be tuned according to temperature and aqueous phase fraction [12]. We now turn to a new class of amphiphiles, ethoxylated alkylamine surfactants. These molecules are composed of a C8 to C22 hydrocarbon chain that serves as the lipophilic portion and an ethoxylated amine as the hydrophilic part. The Hydrophile–Lipophile Balance (HLB) for this class of amphiphiles can be increased by protonation of the amine unit (Chart 1) [20]. Because the emulsion type is influenced strongly by the HLB of the surfactant phase, i.e., a low HLB facilitates W/O emulsion, whereas a high HLB facilitates O/W emulsion [21], it is expected that the ethoxylated alkylamine emulsion transforms from W/O type to O/W type through interactions with acids (Fig. 1). We propose the name Phase Inversion Protonation (PIP) to describe this inversion method, by analogy to PIT. Its inversion pathway may be different than those induced by PIC or PIT. Supposing that the inductive effects described above occur concomitantly, a novel inversion pathway is expected to be observed.

In fact, this new class of surfactants, which includes diethoxylated tallow amine and diethoxylated soya amine, has recently been used to prepare a novel Reversible Emulsion Drilling Fluid that apparently inverts from W/O type to O/W type under acidic

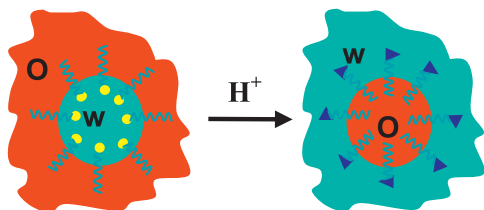


Fig. 1. Schematic illustrating the inversion effects for emulsions stabilized by ethoxylated alkylamine surfactants.

conditions. The inverted drilling fluid exhibits increased water solubility, which facilitates the removal of oil from cuttings and the cleanup of oil-based mud cake [5,20,22,23]. Unfortunately, there is little understanding of the mechanisms of this phase inversion and the conditions involved. The transition states through which phase inversion evolves are not well understood, and many questions arise: What are their structures? How are these states formed, and what causes them to transform? What is the correlation between the acid content and phase inversion stage? Therefore, there is a lack of efficient methods for controlling the phase inversion process for the fast and stable inversion of Reversible Emulsion Drilling Fluids.

In the present work, we propose new approaches to explore the phase inversion process in an emulsion that consists of diethoxylated tallow amine (TAM-2) as the surfactant, calcium chloride brine as the water phase, #5 white oil as the oil phase, and a glacial acetic acid (HOAc) solution as the inducer. The goal is to describe the structural transformations that occur in the inversion process from oil-continuous to water-continuous emulsions as a HOAc solution is added into a W/O coarse emulsion. The impact of the phase volume effect on the protonation effect is also investigated at the main inversion stages, which is critical to understanding the conditions that are associated with the phase behaviors. Based on the available data, two phase inversion pathways are proposed for emulsions stabilized by the ethoxylated alkylamine surfactant.

2. Experimental

2.1. Materials

The surfactant TAM-2 is a diethoxylated tallow amine, with a purity > 99.5% and a density of 0.916 g/cm^3 , which was obtained from Ethox Chemicals, LLC (Greenville, South Carolina). Its chemical structure is shown in Chart 1, where $x=18$, $y=35$, $m=1$, and $n=1$. #5 white oil, with a chain length of 11–31 carbons, a purity of level 7, a density of 0.87 g/cm^3 and a kinematic viscosity of $4.8\text{--}5.3 \text{ mm}^2/\text{s}$, was provided by Beijing Jin Baoli Trading Firm (Beijing, China). Calcium chloride (CaCl_2) and glacial acetic acid (HOAc) were of analytical grade and were purchased from the Sinopharm Chemical Reagent Co. (Beijing, China). These materials were used without further purification. Double-distilled water was used for all experiments.

2.2. Emulsion inversion process

The initial state of the emulsion prior to inversion is characterized as a W/O coarse emulsion. Surfactant TAM-2, #5 white oil and 25% CaCl_2 brine were weighed and emulsified for 10 min at 6000 rpm using an Ultra Turrax homogenizer. In one experiment, 25% HOAc solutions were added into several initial coarse emulsions with various surfactant/water/oil ratios. In a second experiment, several solutions differing in the concentration of HOAc (with %-by-volume ratios less than or equal to 35%) were added to an initial coarse emulsion. During the inversion process, the temperature was maintained at 30°C and the stirring speed at 3000 rpm. The salinity was maintained constant at 25% by mass using calcium chloride.

2.3. Determination of phase transition stage

By utilizing a combination of macroscopic and microscopic methods, the characteristics of the phase transition stages were identified. An aqueous solution of methylene blue and a Sudan I oleic solution were used to dye the inverted state in each transitional stage to identify the continuous phase. Cryo-TEM and phase contrast microscopy were used to observe the microstructures of

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