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Stability of oil-in-water macro-emulsion with anionic surfactant: Effect of electrolytes and temperature

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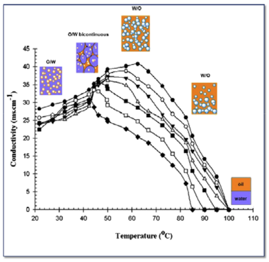
HIGHLIGHTS

- Effect of electrolytes on the stability of o/w emulsion with SDBS was investigated.
- PIT of o/w emulsion with SDBS was studied by electrical conductivity.
- As the valency of cations increases, PIT increases; the reverse is true for anions.
- Turbidity measurements show a decrease in the rate of de-emulsification with time.
- The destabilization of emulsion was governed by coalescence and Ostwald ripening.

GRAPHICAL ABSTRACT

Schematic representation of phase inversion temperature (PIT) of oil–anionic surfactant–water emulsion with different surfactant to oil (s/o) ratio (w/w): 0.1 (–●–); 0.2 (–○–); 0.3 (–▾–); 0.4 (–Δ–); 0.5 (–■–); 0.6 (–□–); and 0.7 (–◆–).



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ABSTRACT

This paper reports on the destabilization of oil-in-water macro-emulsions prepared with diesel oil dispersed in a continuous water phase and stabilized by an anionic surfactant—sodium dodecyl benzene sulphonate (SDBS). Phase inversion temperature (PIT) of anionic surfactant–oil–water emulsion system was determined by measuring the conductivity as a function of temperature at different surfactant to oil ratios. The influence of different kinds of inorganic salts on the PIT, electrophoretic properties and long-term stability of the o/w emulsion were studied by making measurements of conductivity, zeta potential and turbidity of the emulsion. PIT was found to be a linear function of logarithmic molar concentration of the electrolytes. Droplet size distribution of stable emulsion is found to have broader range for mono-valent electrolytes than that of higher valence cations. Larger the valence of cations, lower is the stability of the emulsion. By analyzing the evolution of emulsion droplet size, and turbidity of the resulting emulsion with time, the main destabilizing mechanisms of the o/w macro-emulsion were explained. It is found that coalescence, and Ostwald ripening could be the main destabilizing mechanisms of o/w macro-emulsion.

1. Introduction

An emulsion is a colloidal dispersion of two immiscible liquid phases, with one liquid phase present as small spherical droplets (a dispersed phase) in the other (a continuous phase). The emulsions are thermodynamically unstable and are provided with kinetic stability by an adsorbed layer of surface-active material, e.g. surfactant molecules (Dickinson, 1992). Since the total surface energy of the system is lowered by the coalescence of emulsion droplets, the stability of an emulsion system, therefore, depends on the rate of coalescence. The rate of coalescence depends on the height of the potential energy barrier preventing the tendency of approach of two emulsion droplets towards each other. If the barrier is much higher than thermal energy, the rate of coalescence is

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practically zero and the emulsion becomes stable. The potential energy barrier for charged oil droplets in water arises from the electrostatic interactions between the droplets. The stability of charged colloidal and emulsion particles in water can be explained by DLVO theory. According to this theory, the barrier height is determined by the van der Waals force and the electrostatic force. The electrostatic force is the sum of Maxwell's electric fields stress and the osmotic pressure. The van der Waals force and Maxwell's stress are always attractive, whereas the osmotic pressure is usually repulsive (Verway and Overbeek, 1948). This theory is based on the assumptions that the surface potentials of emulsion droplets are uniform and the same for all the droplets, as long as the separation distances between the droplets are much larger than the thickness of the diffuse electrical double layers around the droplets. When two droplets approach and come closer to each other and the distance between them is less than the thickness of the electrical double layer, electrostatic interaction occurs between the two surfaces, resulting in a change of the surface potentials. The surface ions adsorbed on the droplets then migrate to compensate for the induced potential change. If the surface charges move freely like conduction electrons on metallic spheres, the migration of the surface charges completely compensates the potential gradient on the surfaces. If the migration of surface charges is completely prohibited, the surface potentials continuously increase with a decrease in separation distance, and become infinite at zero separation distance. The actual situation for oil-in-water (o/w) or water-in-oil (w/o) emulsion droplets may lie somewhere between these two extreme cases (Ichikawa et al., 2006).

Macro-emulsion composed of drops in the micrometer-size range is not thermodynamically stable. Because of various sources of instability present in the system, phase separation occurs eventually. Emulsion type and stability are known to be associated with the equilibrium phase behaviour in surfactant-oil-water systems and also with the hydrophile–lipophile balance (HLB) of the system (as opposed to the empirical HLB number of the surfactant), which is related to the locus of aggregate formation in equilibrated mixtures (Binks, 1999; Binks et al., 2000). Macro-emulsions do not form spontaneously but rather require an input of energy. The common mechanisms leading to physical instability of o/w macro-emulsions include creaming or sedimentation, flocculation, and coalescence (Palanuwech and Coupland, 2003). Creaming or sedimentation of drops can occur depending on the density difference between the dispersed and continuous phases and can be enhanced or restricted by flocculation (Binks, 1999). Here, the original droplet size distribution of the emulsion is not altered during separation. A seemingly straightforward extension of creaming or sedimentation is flocculation where the droplets associate with each other forming weakly bound flocks of larger average size, thereby allowing gravitational influence to dominate the system.

For coalescence phenomenon to take place, the thinning of film between approaching drops must reach a critical thickness. It has been proposed that when two large drops of millimetre size approach each other, they deform and a planar film forms between them (Ivanov, 1980). The rate of thinning and the stability against rupture of this film determines the overall stability to coalescence of the emulsion. Another destabilization mechanism is the Ostwald ripening, but this phenomenon basically occurs for emulsions with very fine droplets, in the nanometre size range i.e. nano-emulsions. Ostwald ripening is the growth of large drops at the expense of smaller ones and relies on the transport and solubility of the dispersed phase in the continuous phase. Oil-in-water emulsions are stabilized mainly by electrostatic interactions and the adsorption of macromolecules or solid particles at the oil–water interface. The ionic strength of the continuous phase has a strong influence on the zeta potential of the oil droplets, and this parameter controls the electrostatic interactions, thereby influencing the emulsion stability (Ríos et al., 1998).

A majority of publications discussed about the formation and stability of w/o nano-emulsions with non-ionic surfactants. Shinoda and Saito (1969, 1970) investigated the effect of salt addition and temperature on the phase diagram and hydrophile–lipophile balance (HLB) of water–cyclohexane system stabilized with non-ionic surfactant (polyoxy-ethylene-nonylphenylether). Uson et al. (2004) studied the phase behaviour of water–non-ionic surfactant–oil system. Porrasa et al. (2004) studied the formation of w/o nano emulsion with mixed non-ionic surfactants along with emulsion breakdown mechanisms. Liu et al. (2006) studied the formation and stability of paraffinic o/w nano-emulsion stabilized with non-ionic surfactant (Tween 80/Span 80). Recently, a few studies reported on the effect of inorganic salts on the stability of o/w nano-emulsion with non-ionic surfactants. They used NaCl, KCl, $CaCl_2$, $AlCl_3$ and Na_2SO_4. They showed that the addition of salting out salts in water can reduce the phase inversion temperature (PIT) of the systems to an optimum temperature, exhibiting ease in the formation of nano-emulsions. Mei et al. (2011) studied the influence of different types of inorganic salts on the PIT and long-term stability of paraffin oil–water nano-emulsions with non-ionic surfactants (Tween 80/Span 80). Sharif et al. (2012) investigated the effect of NaCl and Na_2SO_4 concentration on the PIT of n-hexadecane–non-ionic surfactant ($C_{12}E_{14}$)–water system. Jiang et al. (2013) studied the effect of inorganic salts such as NaCl, $CaCl_2$ and Na_2SO_4 on the formation of water-in-oil (w/o) emulsion (not o/w emulsion) and its stability. They used a paraffinic oil and polyoxyethylene 4 lauryl ether (Brij 30) as a non-ionic hydrophilic surfactant in water to form w/o emulsion. They reported an increase in the stability with an increase in the salt concentration and found that the formation of nano w/o emulsion by the PIT method is difficult if it is stabilized at room temperature. Information about the stability of o/w macroemulsion stabilized with anionic surfactant is very limited. In this context, we have investigated the effect of various electrolytes and temperature on the stability of oil–anionic surfactant–water system. Moreover, the oil droplet distribution was observed systematically to evaluate the growth rate of the droplets and to figure out the possible emulsion instability mechanism.

In the present work, oil-in-water emulsions were prepared with diesel oil, and an anionic surfactant sodium dodecyl benzene sulphonate (SDBS)—was used along with water. The effect of various electrolytes, such as NaCl, Na_2SO_4, KCl, $CaCl_2$ and $AlCl_3$ on PIT, electrophoretic properties and long-term stability was studied. Droplet size distribution was measured for different surfactant to oil (s/o) ratios and electrolyte concentrations by a particle size analyser (CIS 100). The effects of electrolyte concentration and ionic charge on zeta potential of o/w emulsion have also been reported. The turbidity of o/w emulsions with different electrolyte concentrations was measured to monitor the performance of the demulsification process. The mechanism of instability of oil–anionic surfactant–water emulsion system was also studied.

2. Experimental

2.1. Materials

Diesel oil (density, $\rho=830\ \text{kg/m}^3$, viscosity, $\mu=2.0$–4.5 cSt) (Indian Oil Corporation Ltd., India), sodium dodecyl benzene sulphonate (SDBS) (Himedia, Mumbai), NaOH (RFCL, New Delhi), anhydrate Na_2SO_4 (Rankem, New Delhi), NaCl (SRL, Mumbai), KCl (SRL, Mumbai), anhydrate $AlCl_3$ (Rankem, New Delhi), $CaCl_2$ (Rankem, New Delhi), Na_2CO_3 (NICE, Cochin) were used in the