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Research Article

All Aqueous Nano-Emulsion for Acid Stimulation of Oil and Gas Reservoirs

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ABSTRACT

Fluids consisting of two immiscible aqueous phases are called Aqueous Biphasic Systems (ABSs). ABSs can form Water in Water (W/W) emulsions when an "emulsifier" is added to the mixture; they are gradually becoming more prominent due to lower prices and better alignment with environmental policies compared to Oil in Water (O/W) or Water in Oil (W/O) emulsions. Still, the understanding of suitable "emulsifiers" for W/W emulsions is still in the early stages and it is usually a challenge related to very low interfacial tensions and thick water-water interfaces. This paper presents a new case of successfully stabilized W/W emulsion originated from an ABS system using a completely new chemical package concept as the “emulsifier”. This innovative W/W emulsion, that also happened to be a nano emulsion, was created with the objective of being a greener type of emulsified acid system, containing no hydrocarbons in its formulation, capable of deeply stimulating oil and gas reservoirs. Ultimately this is a new acid system, belonging to a peculiar class of fluids, being introduced to oil and gas exploration industry for the first time with the potential to be diversified and used in many interesting new applications.

Keywords: Water in water emulsion; Aqueous biphasic system; Acid stimulation; Nanoemulsion; Gas reservoirs

INTRODUCTION

Water in Oil (W/O) emulsions have been used extensively in the oil and gas exploration industry as oil based drilling mud and emulsified acids for the stimulation of oil and gas reservoirs [1]. However, the fact that hydrocarbons take part in the formulation of W/O emulsions has also been a source of debates related to environmental restrictions [2]. On the other hand, Water in Water (W/W) emulsions, a relatively unknown type of fluid, do not require hydrocarbons and their components are generally low cost and biocompatible [3]. W/W emulsions were firstly stabilized by using particles adsorbed at the water-water interface as stabilizers. Currently this type of emulsion is mostly used as delivery systems and in microgels formation [4]. They are originated from Aqueous Biphasic Systems (ABSs) which are formed by two water soluble compounds that generates two immiscible aqueous phases above critical concentrations [5]. When an ABS contains an acid, it is called acidic ABS or AcABS. This article presents a novel W/W emulsion originated from an AcABS made of hydrochloric acid and a phosphonium based ionic liquid. Ultimately, it is a greener new class emulsified acid systems for the stimulation of oil and gas reservoirs [6].

This novel W/W emulsion was stabilized with a well known cationic surfactant, Cetyl Trimethyl Ammonium Chloride (CTAC). But CTAC was not used in its molecular form, instead it was used as colloidal droplets functioning as Pickering stabilizers able to adsorb in the large W/W interface [7].

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This novel W/W emulsion was stabilized with a well known cationic surfactant, Cetyl Trimethyl Ammonium Chloride (CTAC). But CTAC was not used in its molecular form, instead it was used as colloidal droplets functioning as Pickering stabilizers able to adsorb in the large W/W interface [10].

It is the first time that a W/W emulsion of hydrochloric acid in phosphonium based ionic liquid has been stabilized, and it is also the first time colloidal CTAC is used as a pickering stabilizer [11].

Aqueous Biphasic System (ABS)

ABSs, also known as aqueous two phase systems or all aqueous systems, are ternary systems formed by water and two water soluble compounds. They are produced when combinations of hydro soluble solutes display incompatibility in aqueous solution above critical concentrations. Examples of ABS forming compounds are two polymers, a polymer and a salt, two salts, an Ionic Liquid (IL) and a salt, or an IL and a polymer. Surfactants and alcohols are also other possible phase forming components of ABSs. In 1896, Martinus Beijerinck observed for the first time the formation of an ABS after dissolving concentrated starch and gelatin into water that separated into two immiscible phases. Further, in 1958 ABSs were revising covered by Per-Ake Albertsson who utilizes them to concentrate and isolate different types of materials [12].

ABSs are unique in the sense that each of the phases typically contains over 80% water on a molal basis, and yet the phases are immiscible, with distinct properties beyond those of traditional water organic solvent systems just as water and oil, two immiscible aqueous phases from the phase separated ABS also have an inherent interfacial tension. However, in contrast to the water and oil systems, the interfacial tension of the water aqueous biphasic systems is extremely low ranging from less than 0.01 mn/m to 1 mn/m, which is several orders of magnitude less than conventional water organic solvent systems [13].

ABS binodal curve

The binodal curve divides a region of component concentrations that will form two immiscible aqueous phases, *i.e.*, above the curve, from those that will form one phase, *i.e.*, at and below the curve (Figure 1). The coordinates for all feasible systems will lie on a Tie Line (TLL) that connects two nodes on the binodal. The nodes represent the final composition of the Top (T) and Bottom (B) phases that are in equilibrium [14].

The ABS systems have identical top and bottom phase compositions along the same TLL, but the Volume Ratio (VR) changes according to the global composition of the systems. Moving along the tie line coordinates denote systems with differing total compositions and volume ratios, but with the same final concentration of phase components in the top and bottom phases [15].

The Tie Line Length (TLL) is calculated by equation 1.

$$TLL = \sqrt{\Delta C_1^2 + \Delta C_2^2}$$

Where ΔC_1^2 and ΔC_2^2 are the absolute difference in the concentration of the phase forming constituents, in the bottom and top phases, respectively.

The tie lines are commonly parallel and as the TLL decreases, it approaches a Critical point (C_p) where TLL=0. At C_p, the composition and volume of both phases are virtually equal.

The Volume ratio (V_R) equation 2 is defined as the relation between the Volume of the top phase (V_T) and the Volume of the bottom phase (V_B).

$$V_R = \frac{V_T}{V_B}$$

There are three methods used for the determination of the binodal curve: (1) Cloud point method, (2) Turbidmetric titration, and (3) Determination of nodes. Traditionally, binodal curves are constructed following the cloud point. In this method concentrated stock solutions are added drop wise to each other until the visual detection of a cloudy solution when immiscibility occurs. After that, the mixture composition can be calculated by weight quantification of all components added.

Ionic liquid based ABS

Ionic Liquids (ILs) are organic low temperature melting salts which are composed of organic cations and either organic or inorganic anions (Figure 1).

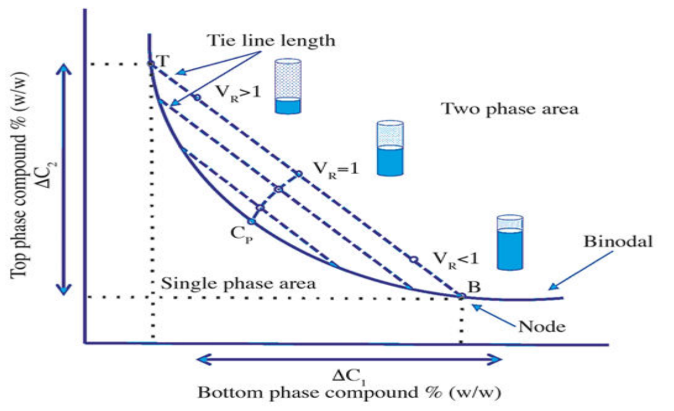

Figure 1: ABS phase diagram. By convention, the top phase component is plotted on the ordinate and the bottom phase component is plotted on the abscissa.

Ionic Liquids (ILs) have emerged as a viable alternative to volatile organic solvents due to their negligible vapor presssure and extended solvation ability. Other attractive properties include high thermal stability, wide electrochemical window, inflammability, and recyclability.

Ionic liquid based ABSs were firstly proposed by Huddleston, et al. Among ILs, Louros, et al., found that phosphonium based ILs is more promising than any other class of ILs in ABS formation. Additionally they are less toxic and more biodegradable than hydrophobic ILs.

Remarkably phosphonium based ILs, e.g., tributyl-tetradecyl phosphonium chloride ((P44414)Cl), are also promising surfactants to reduce capillary forces that trap the oil in rock pores and are commonly used as biocides in hydraulic fracturing gels.

Acidic Aqueous Biphasic System (AcABS)

Acidic Aqueous Biphasic Systems (AcABSs) were first reported by who presented an AcABS containing high amounts of HCl, (P44414) Cl and water [16-18].

An AcABS composed of (P44414) Cl, water and HCl display a pronounced thermo responsive behavior. The biphasic region of HCl (P44414) Cl/H_2O system is favored by the increase of temperature, *i.e.*, less amount of HCl is required to induce the ABS at higher temperatures. At HCl concentrations of 20 wt% or higher, the monophasic region contracts rapidly, becoming fully biphasic at room temperature.

Water in Water (W/W) emulsions

Water in water (W/W) emulsions can be prepared by applying mechanical agitation to aqueous biphasic systems and they are sometimes called ABS emulsions. W/W emulsion is a preferred term though because it is self defining, and already well accepted [19].

The stability of W/W emulsions is generally a challenge and the difficulties of stabilizing W/W emulsion droplets comes from the properties related to the W/W interface: A large thickness, and an ultralow interfacial tension. The thickness of the W/W interface is theoretically calculated to be from tens of nanometers to a few hundred of nanometers. Therefore, a surfactant molecule with a typical length of several nanometers, which is large enough to settle at the W/O interface, may not settle at a thick W/W interface. This incapability of settlement may explain why small molecules fail to stabilize W/W emulsion droplets [20].

However, the stability of W/W systems can be achieved with particles that adsorb in the W/W interface, acting as pickering stabilizers. Successfully stabilized W/W emulsions using latex nanoparticles and sub micron oil droplets at the W/W interface reported that the addition of a low fraction of small oil droplets can significantly inhibit the phase separation of the W/W mixtures [21].

MATERIALS AND METHODS

W/W (HCl in (P44414) Cl) emulsion mixing

In the present work, the stabilization of the (W/W) emulsion, HCl in (P44414) Cl, was achieved by Cetyl Trimethyl Ammonium Chloride (CTAC) droplets acting as Pickering stabilizers. In preparation for the tests, HCl 37% PA was purchased locally; (P44414) Cl 98% was provided by Pixeon Chemie, while CTAC 99% and Polyethylene Glycol Dioleate (PEG 400 DO) were provided by Praid industries [22].

To prepare the CTAC colloidal solution, initially 5% (V/V) of Poliethylene Glycol Dioleate (PEG 400 DO), a non-ionic stabilizer/dispersant with intermediate HLB index was mixed with 35% (V/V) of (tap) water. This mixture, 40% the (V/V) of the total final volume, was then mixed with 60% (V/V) of CTAC to finally produce the colloidal solution of CTAC droplets dispersed in water [23].

Then, to prepare the AcABS emulsion, 2% (V/V) of the previous CTAC colloidal solution was mixed with 33% (V/V) of (P44414) Cl diluted in tap water (1:3), producing the external phase of the W/W emulsion which represented 35% (V/V) of the final volume. The pre mixed external phase was mixed then with 65% (V/V) of 28% HCl, prepared as the internal phase of the W/W emulsion.

Each mixing step above was performed with a waring blender at 3000 rpm, for 5 min, at ambient temperature [24].

Figure 2 shows the CTAC colloidal solution (left) and the W/W emulsion (right). Both fluids did not show any phase separation for an indetermined very long time.

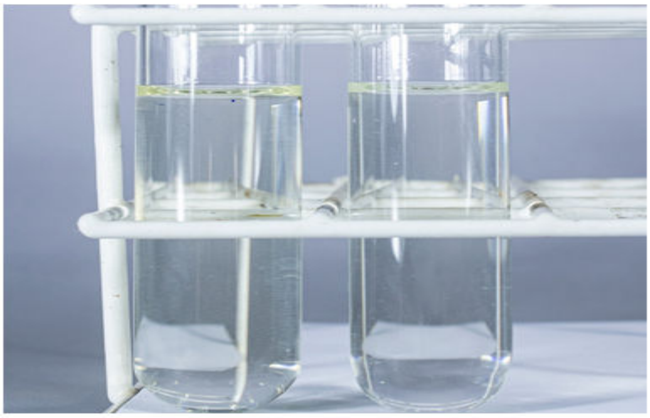

Figure 2: CTAC colloidal solution (left) and W/W emulsion (right) consisting of HCl emulsified in (P44414) Cl.

Immiscibility tests were performed to verify the composition of the internal and external phases of the two previously mixed systems: The CTAC colloidal solution and the W/W emulsion.

The arrows in Figure 3 shows the position of the liquid-liquid interfaces when immiscibility occurs between different liquid phases [25].

Test tube 1: (Tap) water was added to the CTAC colloidal solution there was no incompatibility and the original solution was simply diluted by the water added, showing that the external phase of the CTAC colloidal solution is just water.

Test tube 2: Pure CTAC was added to the colloidal solution of CTAC droplets the added CTAC sank to the bottom of the tube and did not mix with the colloidal solution indicating again that the external phase of the colloidal solution is made of water and that CTAC is the internal phase of the colloidal solution.

Test tube 3: 28% HCl was added to the W/W emulsion the drops of 28% HCl sank to the bottom of the test tube and did not dispersed or mixed with the W/W emulsion indicating that the external phase of the W/W emulsion is made of (P44414) Cl (immiscible with 28% HCl).

Test tube 4: (P44414) Cl diluted in (tap) water (1:3) was added to 28% HCl the two phases did not mix with each other forming an ABS.

Test tube 5: (P44414) Cl diluted in (tap) water (1:3) was added to the W/W emulsion total dispersion occurred indicating that the external phase of the W/W emulsion is a (P44414) Cl solution [26].

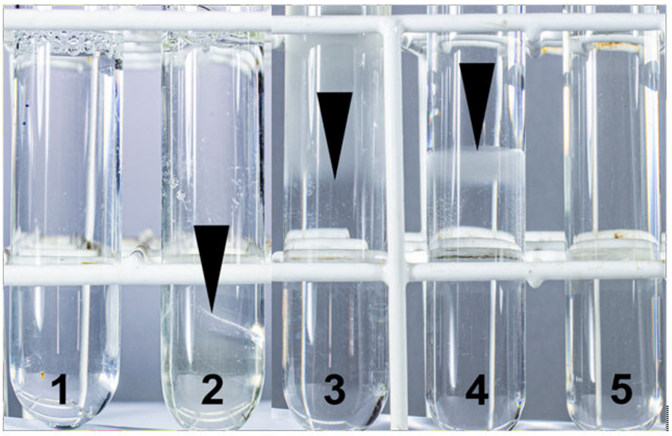

Figure 3: Immiscibility tests the arrows indicate the position of the liquid-liquid interfaces. Tube 1: CTAC colloidal solution and water; Tube 2: Pure CTAC and CTAC colloidal solution; Tube 3: 28% HCl and W/W emulsion; Tube 4: Diluted (P44414) Cl and 28% HCl; Tube 5: (P44414) Cl and W/W emulsion.

To show the relevance of CTAC droplets in the stabilization of the HCl in (P44414) Cl (W/W) emulsion, two additional tests were performed. The first one, on the left of Figure 4, is an attempt to mix the W/W emulsion without any stabilizer the (P44414) Cl quickly segregated on the top of the mixture and there was no emulsion forming. The second one, on the right side was an attempt to use only PEG 400 DO at 5% (V/V) as the stabilizer of the W/W emulsion [27].

PEG 400 DO alone failed to stabilize the W/W emulsion, even though it is an emulsifier commonly used for both W/O and O/W emulsions. This second test may serve as evidence that surfactant molecules are not large enough to settle in the large interface of W/W emulsions. As complementary information, the very first attempt to stabilize the HCl in (P44414) Cl emulsion was performed with oil droplets as sugested and it also failed [28].

RESULTS AND DISCUSSION

The CTAC colloidal solution was capable of stabilizing the W/W emulsion consisting of 28% HCl (internal phase) and (P44414) Cl (external phase) (Figure 4). The dark globules in Figure 5, about 20 nm in size, are the HCl droplets dispersed in the (P44414) Cl external phase. These acid droplets are much smaller than acid droplets usually observed in O/W emulsions which are normally a few µm in size [29].

The CTAC colloidal solution was prepared with tap water using a high speed waring blender and stabilized with Poliethylene Glycol Dioleate (PEG 400 DO).

The TEM used to capture the HCl nanodroplets image was a Tecnai model G2-12 FEI spirit biotwin 120 kv. The 3 µL sample of the W/W emulsion was "plunge frozen" over a 300 mesh Lacey carbon film using liquid ethane. Then it was metalized through glow discharge in the presence of argon [30].

Figure 4: Failed attempts to mix HCl in (P44414) Cl (W/W) emulsion. Left: No emulsifier was used; Right: Only PEG 400 DO tested as emulsifier for the W/W emulsion. The layer on top of both experiments is the (P44414) Cl.

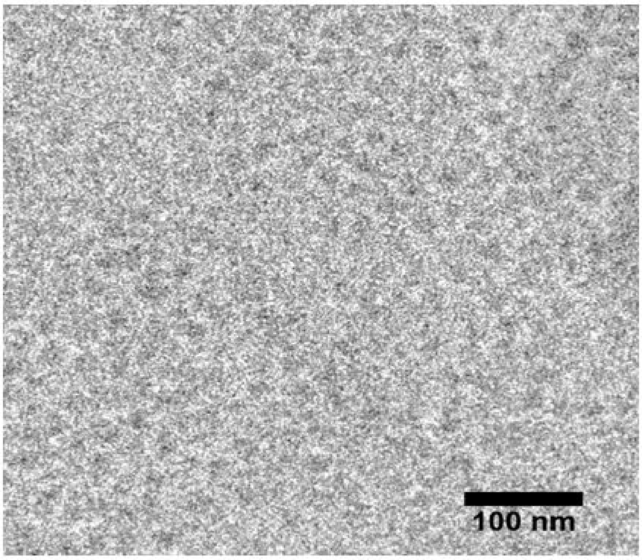

Figure 5: TEM image of the W/W emulsion. The acid (dark) droplets are about 20 nm in diameter.

The new system showed very long stability at room temperature. Aditionally, preliminary tests showed that increasing % (V/V) of the CTAC colloidal solution in the W/W emulsion, improves notably the stability of the system above 100°C. At these higher temperature conditions, even if the W/W emulsion starts to separate in two phases, it goes easily back no monophasic, with small agitation, and stays stable for very long periods again once the temperature drops down below 100°C. This behavior is not observed with W/O or O/W emulsions that hardly ever go to monophasic state again once "broken".

The fact that the external phase of the W/W emulsion is an ionic liquid, (P44414) Cl, makes it a good candidate to acid stimulate water sensitive formations (e.g., shale) as ionic liquids are well known for its clay swelling inhibition properties.

CONCLUSION

W/W emulsions are all aqueous systems with ultra low interfacial tensions and large W/W interfaces. These characteristics make the stabilization process of W/W emulsions a real challenge. Here we report the use of CTAC in the form of colloidal droplets, functioning as Pickering stabilizers at the W/W interface, able to produce a highly stable HCl in (P44414) Cl (W/W) emulsion.

This innovative acid system is a greener type of emulsified acid as it does not contain any hydrocarbons. The phosphonium based ionic liquid, (P44414) Cl, that replaces the "oil" in the W/O emulsion, is considered to be one of the most environmentally friendly ionic liquids.

On the other hand, because the acid is the internal phase of this W/W emulsion, the new system has a low reaction rate that was observed in preliminary tests with calcium carbonate samples. And just like the W/O acid emulsions it is expected to have deeper penetration and better stimulation capabilities in carbonate reservoirs compared to no emulsified acid systems. This is the first time that a W/W emulsion is introduced to the oil and gas industry and it could be the starting point of many new interesting applications.

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