

## Proppant Suspension in Acid Emulsions for Well Stimulation

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### Abstract

Field applications of combined acid and proppant fracturing (CAPF) have increasingly been used since being originally proposed more than 30 years ago. Combining the deep wormholing ability of acidizing with proppant transportation, CAPF is a natural progression used to create highly effective stimulation of carbonate reservoirs. One obstacle related to effective usage of acid proppant treatment methods has been the production of effective proppant transport and reduction of proppant screenout. An effective solution is to use an invert emulsion acid (IEA), where a high volumetric ratio of acid is used as the internal phase and base oil as the continuous, or external, phase in the emulsion. This can provide both a sufficiently structured system for proppant transport and retardation of the acid action in the fracture. However, as is common, a balance must be maintained between sufficient proppant transport and over-treatment of the system, which can cause wellbore damage.

Recent work performed by Oliveira et al.<sup>1</sup> demonstrated improved retardation of the acid and effective stimulation during core flow testing using an IEA with added polymers for emulsion stability and rheological control. For this study, a similar formulation was used to investigate the potential for proppant transport. The sedimentation velocities of particles in water-in-oil emulsions were measured using a CCD camera and automatic particle-tracking software. The effect of different flow parameters on the sedimentation rate, including strain magnitude of oscillatory shear and the strain rate of continuous shear, was of particular interest. The interplay between the sedimentation rate, flow conditions, and emulsion properties is discussed.

### Introduction

During reservoir stimulation, proppant fracturing traditionally uses non-reactive fracturing fluids to place the proppant inside the fracture to retain fracture conductivity after the fracture closes. As an alternative, acid fracturing (also known as fracture acidizing) is proppant-free and depends on non-uniform acid-etching on the fracture surface. This creates increased fracture conductivity only if the differential etching can help prevent the fracture closure. In reality, the effective conductivity of the acid-etched fractures is often shortened by crushing of tight fracture channels attributed to high bottomhole pressures (BHPs). For clean and homogeneous carbonates, acid fracturing creates primarily uniform etched

fractures, which can close completely and have very low retained conductivity. To extend and sustain acid fracture conductivity, as well as use the features of both proppant fracturing and acid fracturing, the two combined methods were studied by Bale et al.<sup>2</sup> for carbonate stimulation. This work verified that retarded acids were the ideal choice for the combined stimulation method. Nevertheless, neither proppant transport capability nor wormhole characteristics of retarded acids were verified using laboratory experiments.

As noted, retarded acid systems provide several advantages when attempting combined acid fracturing using proppant. Hydrochloric (HCl), formic, and acetic acids are the key acids used during carbonate stimulation. Formic and acetic acids are naturally retarded, while HCl acid becomes retarded once it is gelled or emulsified because of decreased acid diffusion rates. The diffusion rate of gelled HCl is approximately one order of magnitude lower than ungelled HCl, and the diffusion rate of emulsified acid is approximately two orders of magnitude lower than plain acid.<sup>3</sup>

Emulsion acids have been largely used in the Middle East and West Africa because of their unique characteristics, some of which are listed as follows:

- Improved zonal coverage and less corrosion problems at high temperatures than neat acids.<sup>4</sup>
- Minimum formation softening effects, which help extend fracture conductivity and provide the best stimulation results for acid fracturing.<sup>5</sup>
- Wormholing occurs under a large range of flow rate conditions. Thus, opposed to other acid systems, there are no optimum injection rates to achieve the lowest pore volume to breakthrough (PVBT).<sup>6</sup>

This work presents sedimentation studies under shear for a new retarded emulsion acid containing oil soluble polymers (invert emulsion acid or IEA) with enhanced proppant transport characteristics and efficient wormholing for simultaneous acid and proppant fracturing.

To improve the proppant transport capability of emulsion acids for simultaneous acid and proppant fracturing, oil-soluble polymers were introduced into the formulation, resulting in excellent rheological properties. A new formulation based on the investigation of emulsion properties, such as stability, viscosity, and retardation, under different compositions, is presented. Static settling results are shown,

comparing proppant settling between the newly formulated invert emulsion and borate crosslinked fluid system. To understand the performance under dynamic conditions, the viscosity of the invert emulsion fluid is measured within a range of shear rates, and results at different polymer concentrations are compared. Furthermore, important physical parameters, such as viscous moduli and elastic moduli, to characterize the viscoelastic property of the emulsion fluid are also compared at different polymer concentrations.

### Formulation and Sample Preparation

It has been widely understood that the properties of emulsified acids are governed by internal acid volume fraction and emulsifier concentrations. The effects of internal acid volume fraction and emulsifier concentrations on system properties are briefly summarized in **Table 1**. It should be noted that the degree of retardation is dependent on the acid droplets diffusion rate and not on molecular diffusion.<sup>3</sup> Additionally, emulsifier concentration determines the size distribution of the acid droplets, which directly affects the emulsified acid properties.<sup>7</sup>

**Table 1—Properties Of Emulsified Acids**

Property	Increasing Internal (Acid) Volume Fraction	Increasing Emulsifier Concentration
Stability	Most stable at 0.7 <sup>7</sup>	Increased <sup>8</sup>
Viscosity	Increased <sup>3</sup>	Increased <sup>7</sup>
Retardation	Decreased <sup>3</sup>	Increased <sup>9</sup>

For sedimentation testing, two baseline formulations were evaluated (**Table 2**). The oil external phase chosen was a low-viscosity (2 cp) synthetic paraffin oil that consisted of a pure normal alkane mixture. This mixture was very lubricious, low in toxicity, and highly biodegradable. IEA samples were prepared using a Multi-Mixer<sup>®</sup> Model 9B. For these studies, a 15% KCl brine was used as a surrogate for the internal acid phase for the simplicity of handling. The aqueous phase was slowly poured into the hydrocarbon phase and left in the mixer for 30 minutes under high shear. Finally, an oil-soluble polymer was added to boost rheological behavior and increase emulsion stability. It was then allowed to mix for another 5 minutes. Two polymers were studied. Polymer 1, was a dimer/trimer fatty acid and was considered to viscosify the base oil. Polymer 2, was a polyamide, and was considered to bridge the emulsion droplets, resulting in an increase of structure in the network. The final IEA had a density approximately similar to water.

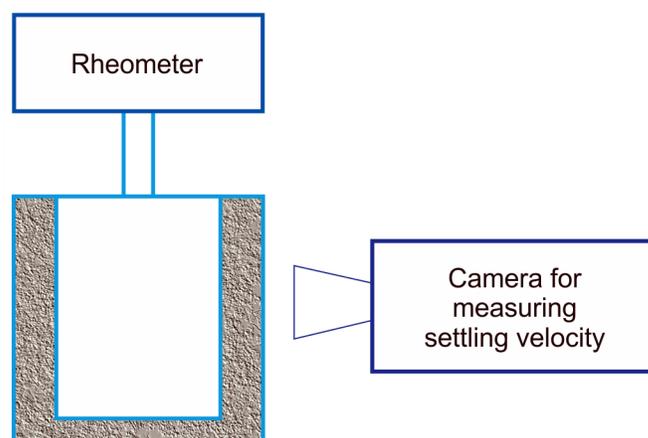
A proppant was added into the IEA formulations for testing of the sedimentation under shear. The proppant chosen was a 20/40-mesh bauxite with a specific gravity (SG) of 3.56. The dark color of the bauxite provided a good contrast for visualization inside the milky IEA.

**Table 2—Invert Emulsion Acid Formulation**

Components of Emulsion Formulation	Volume Concentration (%)
Synthetic paraffin (oil external phase)	Remainder (~27.5%)
Emulsifier (HLB index: 7 to 11)	2.5
Polymer 1 / Polymer 2	0.8 / 0.2
Aqueous phase (15% KCl brine)	70

### Experimental Methods

**Figure 1** illustrates the schematic of the sedimentation setup, which consisted of a transparent coquette flow cell and optical imaging system. The transparent flow cell was installed on a MCR702 rheometer so that simultaneous rheological measurements could be made using the sedimentation test. The diameters of the cup and bob were 35 and 31 mm, respectively. The particle imaging optics consisted of a zoom lens (Zoom 70XL) and CCD camera (XC-ST50, Sony). A proprietary particle tracking software was used to track the motion of a single particle among other particles. Because of technical limitations, the single particle tracking work was performed only in the oscillatory shear mode. During this study, a large amplitude oscillatory shear was used to simulate the effect of steady shear on particle sedimentation. The effective shear rate in the oscillatory mode is  $\omega\gamma$ , where  $\omega$  is the angular frequency, and  $\gamma$  is the strain amplitude. During the sedimentation tests,  $\omega$  was fixed at 1 rad/s, and  $\gamma$  was varied from 10 to 700%.

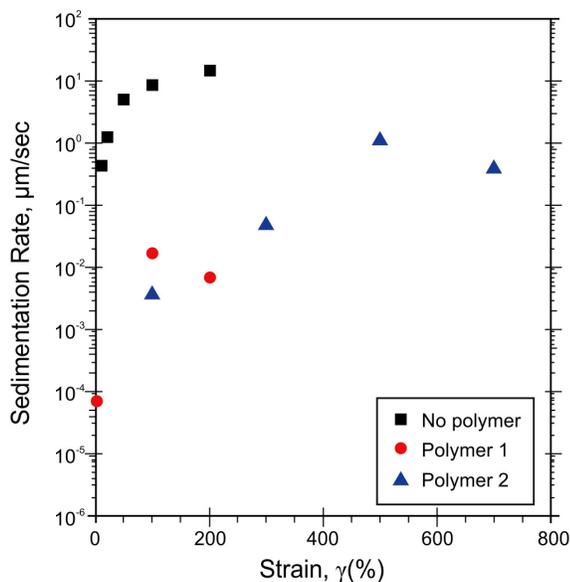


**Figure 1—Schematic of sedimentation setup.**

### Results

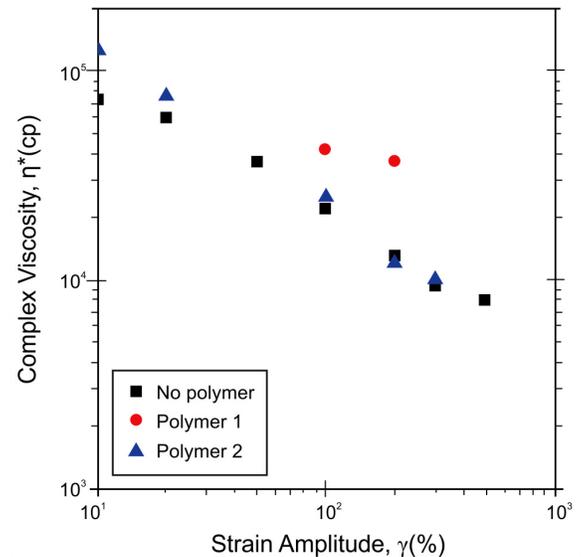
**Figure 2** illustrates that the sedimentation velocity increased with increased strain amplitude of the oscillatory shear for all of the samples. This general behavior is expected from emulsions and can be explained by the caging effect. In a concentrated emulsion, a given particle or emulsion droplet is confined by the neighboring droplets, which forms an effective cage that restricts the motion of the confined particle. Under static conditions, the cage remains in place for a long period of time because thermal energy is the only driving

force that can loosen the cage. However, under shear flow, the cage is continuously broken up and re-forms, shortening its effective lifetime. The balance of reformation and breakup is determined by the shear rate. The higher the shear rate or strain amplitude, the shorter the effective lifetime of the cage, and the particle can move with less restriction, causing increased settling velocity. Figure 2 also illustrates that the sedimentation rate reached a plateau as the strain amplitude increased. This is presumably caused by the cage effect becoming negligible at large strain amplitudes. Additionally, sedimentation was dictated by the viscosity of the base. It is interesting to note that the plateau was reached at a much larger strain amplitude for the emulsion created using Polymer 2 than the other two emulsions. This could be related to the fact that Polymer 2 is a bridging polymer, whereas Polymer 1 merely acted to increase the base oil viscosity.



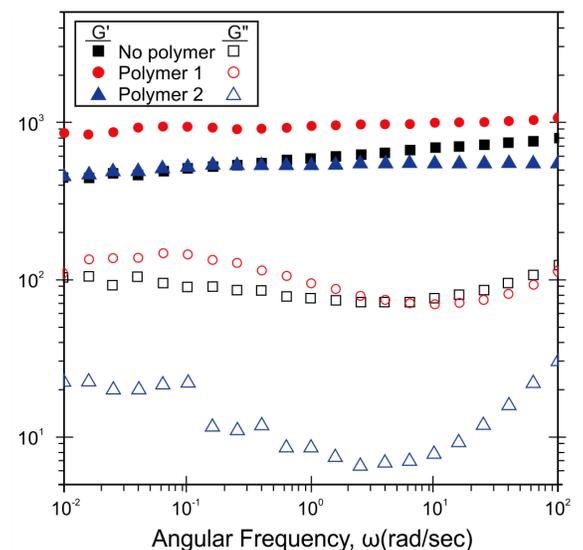
**Figure 2—Sedimentation velocity as a function of strain amplitude for three emulsions with and without added polymers. T = 75°F.**

Figure 2 also illustrates that the addition of polymers to the bare emulsion slowed the sedimentation by approximately three orders of magnitude at comparable strain magnitudes. An intuitive explanation for the retarded settling might be that the polymers increase the viscosity of the emulsion. However, this does not seem to be the case, particularly for the emulsion created using Polymer 2. **Figure 3** presents the viscosity curve as a function of the strain amplitude. The emulsion created using Polymer 2 was similar to the bare emulsion. The viscosity of the emulsion using Polymer 1 was only slightly larger than the bare emulsion. Therefore, the three orders of magnitude in the settling velocity cannot be explained based simply on the viscosity. It was speculated that the elastic stresses generated by the polymers could be responsible for the retarded particle settling.



**Figure 3—Viscosity as a function of strain amplitude as measured simultaneously during the sedimentation test by oscillatory shear at 1 rad/s for three emulsions with and without polymers. T = 75°F.**

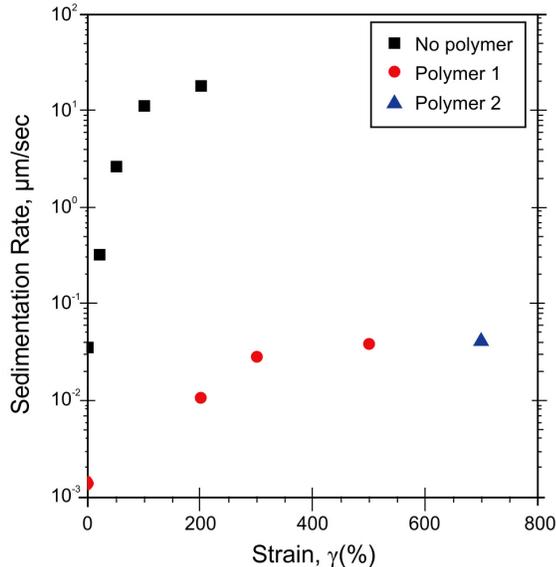
The linear viscoelastic behavior of the samples illustrated in **Figure 4** helps support this argument. It shows that the ratio of the loss modulus  $G''$  to the elastic modulus  $G'$  was larger for the emulsions created using added polymers across the whole frequency range, suggesting that the former two were more elastic, presumably because of the added polymers.



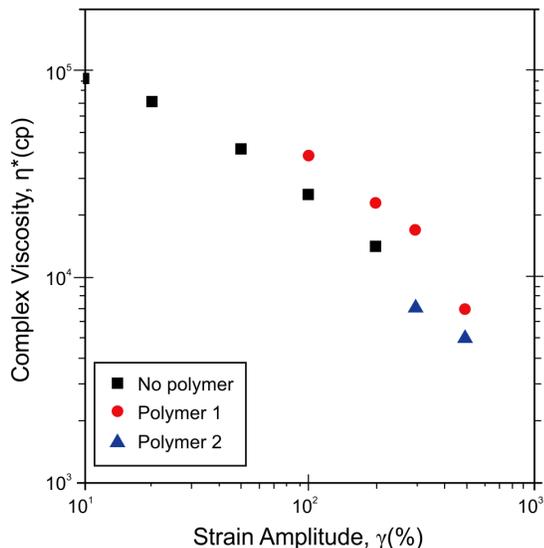
**Figure 4—Storage and loss moduli ( $G'$  and  $G''$ ) as a function of angular frequency measured at a small strain amplitude of 0.1% for three emulsions with and without polymers. T = 75°F.**

At elevated temperature (150°F), the sedimentation results were qualitatively similar to those at 75°F (**Figure 5**). Namely, the settling velocity was approximately three orders

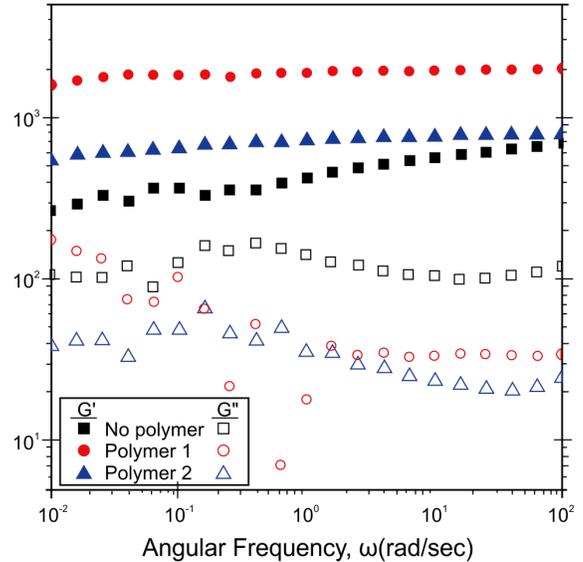
of magnitude smaller for the two emulsions using polymers. As **Figure 6** illustrates, the viscosities of the bare emulsion and those of Polymer 2 were again very similar, suggesting that the difference in the settling velocity was not caused by the viscosity. The linear moduli data in **Figure 7** indicate that the emulsions created using polymers were more elastic than the bare emulsion, which could be responsible for the retarded settling at 150°F.



**Figure 5—Sedimentation velocity as a function of strain amplitude for three emulsions with and without polymers. T = 150°F.**



**Figure 6—Viscosity as a function of strain amplitude as measured by oscillatory shear testing at 10 rad/s. for three emulsions with and without polymers. T = 150°F.**



**Figure 7—Storage and loss moduli ( $G'$  and  $G''$ ) as a function of angular frequency measured at a small strain amplitude of 0.1% for three emulsions with and without polymers. T = 150°F.**

## Conclusions

- Sedimentation in the emulsion was a function of shear/strain. The balance between the breakup and reformation of stress cages in the emulsion shifted to breakup under increased shear or strain, with a multiple order of magnitude increase to sedimentation rates for minimal changes in strain.
- The additions of select polymers affected sedimentation rates. Both polymers tested resulted in decreased sedimentation rates between two and four orders of magnitude.
- The impact on rheological behavior from the addition of the polymers was very different. Polymer 1 resulted in modestly increased viscosity, while Polymer 2 did not appreciably affect viscosity. The mechanism for improved suspension was likely elastic, which was observed from dynamic testing.
- The improved proppant transport demonstrated during this work presents an opportunity for improved proppant placement and effective combined acid proppant fracturing. However, additional work to optimize the polymer addition in light of treating pressures should be undertaken.

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