

Development of High-Performance Drilling Fluids using High-Throughput Methods

C.E. Mohler, R. L. Kuhlman, C. A. Witham, M. K. Poindexter, The Dow Chemical Company

Copyright 2011, AADE

This paper was prepared for presentation at the 2011 AADE National Technical Conference and Exhibition held at the Hilton Houston North Hotel, Houston, Texas, April 12-14, 2011. This conference was sponsored by the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individual(s) listed as author(s) of this work.

Abstract

The growing need to drill deeper and in deviated and/or horizontal wells creates an increasing demand for drilling fluids with enhanced performance. This paper focuses on the characterization and development of rheology modifiers for water-based muds (WBM), which are often preferred to oil-based fluids due to their ecological and cost benefits. The two most critical characteristics of a drilling fluid are density and viscosity, which are often controlled by dissolved salts and thickening agents. Since the chemical composition of a brine often has a significant influence on the rheology of dissolved polymers, it is advantageous to consider the effects of dissolved salts on rheological properties when developing new polymeric thickeners. Due to the large number of variables to be optimized in such an undertaking (e.g., polymer composition and architecture, concentration, brine identity and brine concentration), a combinatorial or high-throughput approach is highly desirable to accelerate the development of optimal drilling fluid polymers and their behavior in various brines.

High-throughput methods are presented here which enable the preparation and testing of a variety of drilling fluid formulations and rapid examination of the influences of brine chemistry on polymer performance. Specifically, brine tolerance and phase behavior can be quantitatively evaluated by digital image analysis of test solutions, which is a screen for polymer-salt compatibility. Using an automated rheometer, the viscosities and storage and loss moduli of numerous polymer-brine formulations can also be obtained rapidly. The tools and techniques for obtaining such data are discussed in the context of a newly developed rheology modifier.

Introduction

Polymers are increasingly important components of many formulations targeted for applications in the oil and gas industry.¹ Such applications include drilling and well completion, cementing, defoaming, demulsification, water clarification, asphaltene control and drag reduction. Reservoir drilling fluids, in particular WBMs often rely heavily on polymer-based systems to achieve the rheological properties necessary to suspend and remove cuttings, to display the shear thinning characteristics required to minimize pump backpressure, and to retain viscosity at high temperatures.

Furthermore, as the worldwide demand for energy increases, there is growing pressure to drill at even greater depths and in more difficult and challenging well geometries. This need places even higher performance demands on polymers used in drilling fluids, at the same time that governmental regulations require increasingly more environmentally favorable components. With these goals in mind, existing biopolymers such as cellulose, starch, xanthan, scleroglucan and welan gum are being optimized or modified to improve their rheological performance and extend their temperature range of use. Preferably, the improved rheological properties of these new biopolymers should be evident in a wide range of brines, since this improves their range of applicability and provides latitude in formulation design. A new biopolymer has recently been introduced which meets many of these requirements for freshwater and heavy brine compositions.² Nevertheless, more work is needed to develop new rheology modifiers for WBMs targeted for even more extreme conditions and in additional brines.

To accelerate the development of new polymers for drilling applications, a high-throughput approach is highly desirable. High-throughput or combinatorial approaches are especially useful when a large number of variables must be investigated to discover or develop a new material, improve a process, or optimize a formulation. For drilling fluid applications, these variables may include several details of polymer structure and composition (e.g., molecular weight, polydispersity, molecular architecture and degree of branching), polymer concentration, brine composition and brine concentration, and conditions of pressure and temperature. Due to ability of high-throughput methods to generate rapidly a large amount of useful data, this approach has been highly successful in a wide variety of research areas, including new catalyst development, new formulations for personal care and cleaning applications, food additives, architectural coatings, and biocidal formulations.³⁻⁹ For this reason high-throughput methodology has now been applied to accelerating the development of new polymers for drilling fluid formulations.

New high-throughput workflows have been developed to determine the brine tolerance and rheological characteristics of new polymers, since these are critical properties for polymers designed for drilling fluid applications. The workflows

described here include formulation preparation using robotic liquids and solids handlers, as well as formulation characterization such as a digital imaging-based process to determine the brine tolerance (brine solubility) of polymers, at both ambient and elevated temperatures. Additionally, a high-throughput automated rheology workflow has been developed to rapidly determine the rheological properties of polymer formulations in steady and oscillatory shear flows. The application and utility of the workflows will be discussed using examples of an existing biopolymer (xanthan), two experimental polymers as well as a newly introduced biopolymer known as EMBARK™ Rheology Modifier 160.²

Experimental

High-Throughput Solubility Workflow

The software application Library Studio (FreeSlate Inc., Sunnyvale, CA) was used to design the high-throughput solubility and rheology experiments and convert the design into a template that can be used by robotic liquid handlers. Solubility experiments were typically done using small scale samples (~1 mL) arranged in an 8 x 12 microtiter plate array. A typical experimental design is shown in Figure 1. Each row in the design corresponds to a given polymer, while the columns correspond to either water or brine solutions. In this design, four different polymers were evaluated (each at two different concentrations), each in water and in five different brines (NaCl, KCl, NaBr, CaCl₂, CaBr₂) at two different brine concentrations. In this manner, 96 different samples can be prepared in one experimental array.

A diagram of the solubility workflow is shown in Figure 2. Polymer powders are dispensed into the individual vials using a solids handling robot. Water and brine solutions are heated on the deck of a liquid handling robot (FreeSlate Inc, Sunnyvale, CA), and the liquids are delivered to each vial with a robotically controlled syringe while stirring. After completing the dispense, the samples are cooled and capped. All information about sample creation (weights, stirring and heating conditions, dates/time of creation) is automatically stored in a fully searchable database, archived for future retrieval and for further data analysis.

To determine the solubility properties of the formulations, the completed 8 x 12 plate of vials is placed in a custom-built phase identification and characterization apparatus (PICAI). Up to six sample plates can be placed on the deck of this robot, and their temperature controlled using a recirculating bath. For the solubility studies described here, the samples were heated from 20°C to 80°C in 5°C increments. At each temperature, each vial is removed from the plate by the robot arm and a digital image is collected. The length of time required for sample transfer and image collection was short (~30 seconds), and only a minimal change in sample temperature occurs during this time. The digital images are automatically stored in the database and are indexed to the library identification number associated with the sample generation information. Each digital image is processed automatically with an algorithm that extracts the number of phases present, the opacity of each phase, the homogeneity in

opacity within each phase and the fraction of each phase present. All results are stored in the database where trends and comparisons can be explored using various algorithms and statistical analyses. With these capabilities, the high-throughput solubility workflow enables the brine tolerance of many diverse polymers to be screened in a very short period of time. After sample preparation, as many as 96 samples can be screened for solubility at a given temperature in less than an hour.

High-Throughput Rheology Screen

Samples are prepared for the rheology measurements in a similar manner as that used for the solubility screen, except the larger quantities required for rheological measurements necessitate preparation in a 2 x 3 array using 20 g vials (Figure 3). Sample stirring is accomplished using high throughput overhead mixers also based on the 2 x 3 format, with specially designed impellers driven with variable speed control, and the added ability to heat the samples.

The rheology of the solutions is measured using an automated Anton-Paar MCR 301 rheometer with cone and plate sample fixtures (50 mm diameter, 0.5° cone angle). Samples are transferred to individual 10 mL vials for the experiment, which are arranged in a 4 x 6 microtiter plate format on the deck of the automated Anton-Paar. Up to four 4 x 6 plates can be placed on the deck, so 96 samples can be measured in any one session. Any bubbles observed in the samples are first removed by centrifugation before loading on the robot. Two six-axis robotic arms control the sample aspiration and dispensing functions, as well as automatic cleaning of the cone and plate between samples. For the measurement, a user-defined amount (typically less than 1 mL) of each formulation is automatically dispensed by syringe onto the bottom plate of the rheometer. The measurement temperature may also be varied, but was typically 25.0°C for the experiments described here. Steady shear flow viscosities are measured over a shear strain rate range from 0.1 to 1,000 1/sec with a 0.05 mm gap, using a 30 second initial pre-shear at 5 Hz and a 30 second/point measurement time. Oscillatory measurements are performed at a frequency of 0.5 Hz over a shear stress range of 0.1 to 100 Pa, with similar pre-shear conditions. All the rheological results are stored in the database, and are easily retrievable for further data analysis. Under the conditions described here, a full rheological characterization (including both steady and oscillatory flow) of almost 40 samples can be accomplished in a 24 hour period.

Results and Discussion

Polymer-Brine Solubility and Phase Transitions

Determining the brine tolerance of polymeric rheology modifiers is a critical part of assessing their performance in a drilling fluid. The high-throughput solubility workflow provides an extremely rapid way to compare relative polymer performance in this regard, as well as providing unique insight into brine-dependent polymer phase transitions. An example of typical solubility information obtained on several polymer formulations in different brines is shown in Figure 4. A 1

wt% aqueous solution of “Polymer 1” is clear at ambient temperature (20°C), and remains clear up to the highest temperature tested (80°C), indicating no apparent phase behavior changes. Similar behavior is observed for this polymer in a divalent calcium bromide brine. However in saturated monovalent brine (KCl), “Polymer 1” exhibits clear evidence of gelation at elevated temperatures (70°C), including even syneresis (separation of a polymer-poor fluid phase from the gel phase) as the temperature is increased further. Precipitation of polymers is also detectable with this methodology. For example, the biopolymer xanthan is shown to precipitate in half-saturated calcium bromide solutions (Figure 4). In contrast, a 1 wt % solution of the biopolymer Rheology Modifier 160 shows no evidence of phase transitions or precipitation in aqueous calcium bromide formulations over the temperature range tested. The presence of entrapped bubbles in this particular sample should also be noted. This phenomenon occurs due to the very high viscosity of this polymer in calcium bromide brine,² which is discussed in more detail below.

In addition to visual inspection, a quantitative metric of the opacity of any of the polymer formulations can be extracted using the automated image analysis algorithm. With this information, regions of polymer-brine solubility can be mapped out and shown graphically as in Figure 5. Regions of high solubility (i.e., compatibility) are indicated by blue spheres, where regions of increasingly poorer solubility are indicated by green, yellow or orange spheres. In this example, several polymers including Rheology Modifier 160 are soluble in half-saturated brines at 0.5 wt% polymer, but become only slightly less soluble as the brine concentration is increased. Many xanthan-brine solutions are found to be turbid (with the exception of calcium bromide, in which polymer precipitation caused a falsely low opacity in the largest phase), with a similar increase in turbidity with brine concentration.

The ability to screen comparative polymer performance and phase transitions in various brines gives valuable information that can guide the selection of polymers that will not precipitate or form phase-separated gels in the conditions of use. Furthermore, it may be possible to relate polymer solubility in various brines back to variations in polymer composition and/or architecture, potentially enabling the design of polymers with improved performance.

Automated Rheology of Polymer-Brine Formulations

Solution rheology is one of the most critical factors in assessing WBM performance, since flow characteristics and ability to suspend solids are key performance criteria. The high-throughput automated rheometer system enables rapid determination of both the steady and oscillatory shear flow rheology of polymer-brine blends over a wide range of strain, strain rates and temperatures. This enables the effect of brine on the rheological performance of individual polymers to be determined, as well as a comparison of the properties of different polymers in the same brine. For example, a family of flow curves (steady shear viscosity versus shear strain rate) for 1 wt % solutions of four different polymers in water and three

brines is shown in Figure 6. All four polymers show significant shear thinning in water and in the brines studied. In water, the viscosity of either a xanthan or Rheology Modifier 160 solution shows a power law dependence on shear rate in the experimental shear rate window, while the relationship of the other two polymer solutions are fit better by a Cross model.¹⁰ These characteristics indicate that xanthan and Rheology Modifier 160 have longer relaxation times than the other two polymers, suggesting either a larger or stiffer molecular structure. The same trends are also observed in the other brine formulations of these polymers; the larger structure or molecular stiffness may be slightly degraded for Rheology Modifier 160 in sodium chloride compared to the other brines, but not as much as the other two polymers (Polymer 1 and 2). However, Rheology Modifier 160 provides higher viscosities in all these formulations compared to xanthan and the other two polymers, over a wide range of shear rates. This increased viscosity is particularly evident in calcium bromide brines, and is consistent with the visual observations of entrapped bubbles in the solubility samples noted earlier.

In addition to the shear rate dependence of the viscosity, the automated rheometer system can also collect data in an oscillatory shear mode, in order to measure the shear storage (G') and shear loss (G'') moduli of polymer solutions. These oscillatory flow measurements were made for the polymer-brine combinations described above, and may provide additional insight into the rheology of the solutions beyond what is evident from the steady shear flow (viscosity) measurements. The brine dependence of the oscillatory rheology for all four polymers is depicted in Figure 7. For simplicity, results in only two formulations (water and calcium bromide) are shown. In aqueous and calcium bromide formulations, both xanthan and Rheology Modifier 160 show solid-like behavior ($G' > G''$) at 0.5 Hz over a wide range of shear stress, and also exhibit a yield stress. The limiting value of G' at low shear stress, $G'(\sigma \rightarrow 0)$, and the yield stress, σ_Y ($G' = G''$), are listed in Table 1. The aqueous formulation of xanthan appears to be slightly stiffer than that of Rheology Modifier 160 at the same polymer concentration, while the yield stress (defined as the point where G' and G'' cross) of the aqueous Rheology Modifier 160 solution is substantially higher than the corresponding xanthan solution (e.g., 48 vs 10 Pa). Furthermore, a 1 wt % formulation of Rheology Modifier 160 in half-saturated calcium bromide is significantly stiffer than that of xanthan over a wide range of shear stress. The yield stress of xanthan is higher in half-saturated calcium bromide than in water (38 vs 10 Pa), but the yield stress of Rheology Modifier 160 in calcium bromide solution appears to be even higher, beyond the upper shear stress (100 Pa) used in the study.

The other two polymers in Figure 7 display different oscillatory rheological properties. Both these polymers exhibit liquid-like behavior ($\eta' > \eta''$) in aqueous solutions, but solid-like behavior in half-saturated calcium bromide solutions. In water, their rheology is more appropriately represented as the in-phase (dynamic) viscosity (η') and the

out-of phase component (η'') of the complex viscosity (η^*). These quantities may be inter-converted for any given angular oscillation frequency, ω , by the relationship

$$G^* = G' + iG'' = -i\omega\eta^*$$

where $i \equiv [-1]^{1/2}$, and $\eta^* = \eta' - i\eta''$. Though the low-shear viscosities of these two polymers are competitive at least in calcium bromide with xanthan and Rheology Modifier 160, their rheological properties under oscillatory shear flows suggest that neither of these materials is expected to perform as well at suspending particles or cuttings in the brine compositions studied. The combination of steady and oscillatory shear flow rheological properties of polymer formulations is necessary to fully discern differences which may predict relative efficacy in drilling applications.

Conclusions

New high-throughput workflows have been developed that are capable of determining the brine tolerance and rheological properties of a large number of polymer formulations in a short period of time. Various forms of polymer insolubility and phase transitions (precipitation, gelation) in brines can be detected as a function of temperature with the solubility workflow. This information is important because such phase instabilities may adversely impact polymer performance.

In addition, a high-throughput workflow is reported that enables rapid determination of the steady and oscillatory shear flow rheological properties of polymer-brine blends, which can give insight on structure-property relationships as well as the effect of other mud components (such as brines) on polymer rheological performance. Using these workflows, the performance of the new biopolymer-based Rheology Modifier 160 is shown to have higher low shear viscosity, yield stress and low-shear stress elastic modulus than xanthan, in select monovalent and divalent brines. This suggests Rheology Modifier 160 is likely to have improved particle suspending abilities in these brines. The wealth of solubility and rheological information on polymer formulations that can be collected rapidly is expected to continue to accelerate the development of new high-performance drilling fluids in the future.

Acknowledgments

We would like to thank Emmett Partain, Dow Chemical Company, for providing some of the polymers for this study and providing many helpful insights; Tom Sanders and Jamie Lovelace for assistance with sample preparation and for rheological data collection.

References

- Lucas, E. F., Mansur, C. R. E., Spinelli, L., Queiros, Y. G. C., "Polymer Science Applied to Petroleum Production", Pure Appl. Chem., 81, 473-494, 2009.
- Ezell, R. G., Ezzat, A. M., Horton, D., Partain, E., "State of the Art Polymers Fulfill the Need for High Temperature Clay-free

Drill-in and Completion Fluids", American Association of Drilling Engineers Technical Conference, AADE-10-DF-HO-01, April 6-7, 2010.

- Peil, K. P., Neithamer, D. R., Patrick, D. W., Wilson, B. E., Tucker, C. J., "Applications of High Throughput Research at The Dow Chemical Company", Macromol. Rapid Comm., 24, 119-126, 2004.
- Tucker, C. J., Mohler, C. E., Harris, K., Som, A., Chen, H., "High Throughput Surfactant Synthesis, Characterization and Formulation", Proceedings 7th World Surfactants Conference CESIO, July 21-25, 2008.
- Tucker, C., Mohler, C., Harris, K., Nicoll, H., "High throughput surfactant synthesis, characterization and formulation", SOFW Journal 134(9), 80-90, 2008.
- Johnson, M., Roper, J., Keefe, M., Oh, J., Ortiz, R., Singh, A., Mecca, J., Smits, G., "High throughput methods for developing waterborne coating formulations", Proceedings of the 36th International Waterborne, High-Solids, and Powder Coatings Symposium, 81-90, 2009.
- Devore, D., Tuinstra, H., Schroden, R., McAdon, M., Shibata, H., "High throughput development at The Dow Chemical Company and a case study involving propane oxidative dehydrogenation catalysis", Preprints - American Chemical Society, Division of Petroleum Chemistry, 239th ACS National Meeting, San Francisco, CA, March 21-25, 2010.
- Mohler, C., Sammler, R., Boomgaard, T., Stoneburner, L., Gaynor, S., Tucker, C., "Accelerating cellulosic ether development with high throughput approaches", presented at 237th ACS National Meeting, Salt Lake City, March 22-26, 2009.
- Kalantar, T., Tucker, C., Zalusky, A., Boomgaard, T., Wilson, B., Ladika, M., Jordan, S., Li, W., Zhang, X., "High throughput workflow for coacervate formation and characterization in shampoo systems", Journal of Cosmetic Science 58(4), 375-383, 2007.
- Cross, M. M., J. Colloid Science, 20, 417, 1965.

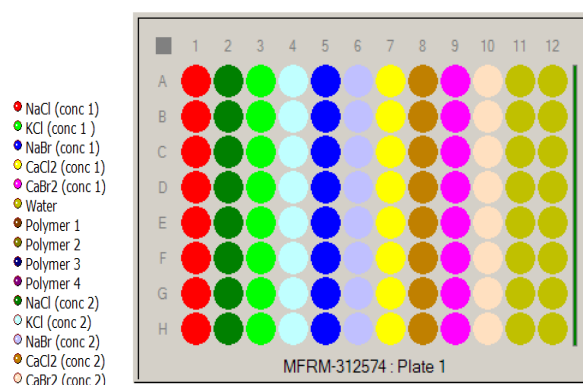


Figure 1. Typical experimental design for high-throughput solubility screens. Each row is reserved for a different polymer or polymer concentration, while brine and/or brine concentration is varied in each column.

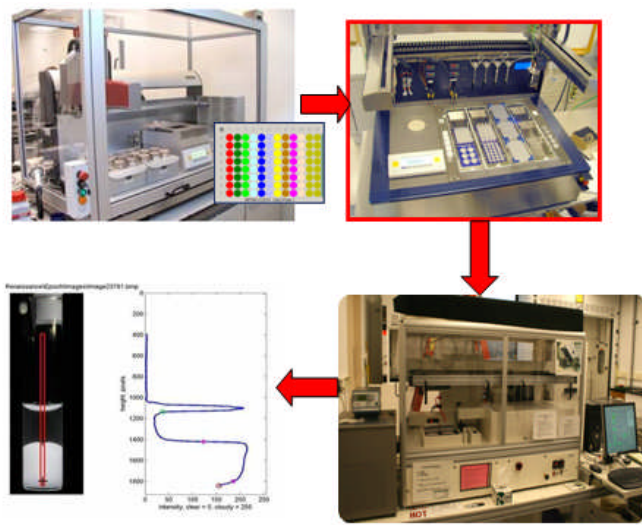


Figure 2. Diagram of a high-throughput workflow for preparing aqueous brine solutions of polymers and assessing their solubility and phase transition/stability behavior. Polymers are automatically dispensed into individual vials using a solids handling robot (upper left), to which brine solutions are added using a liquids handling robot (upper right). Digital images of the samples are collected using a custom-built imaging tool (bottom right). A typical vial image and output of the image analysis algorithm is shown (bottom left).

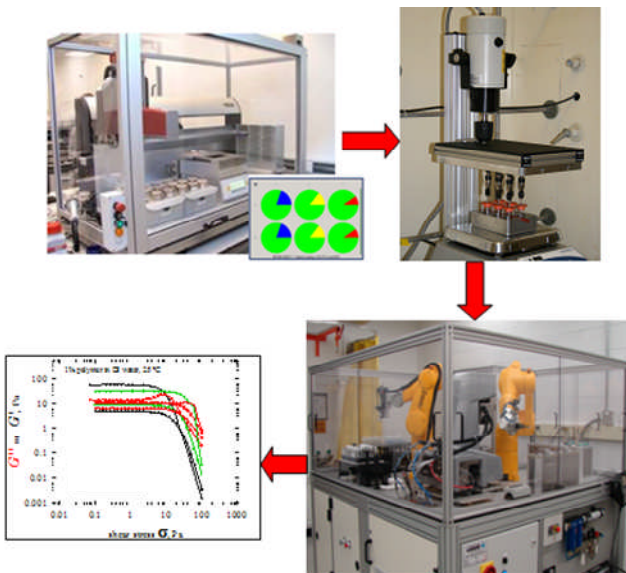


Figure 3. High-throughput workflow for rheology measurements of polymers in brines. Samples are prepared similarly as in the solubility workflow (Figure 2), except the vials are stirred using arrays of high-throughput overhead mixers (upper right). Samples are analyzed using an automated Anton-Paar rheometer (lower right).

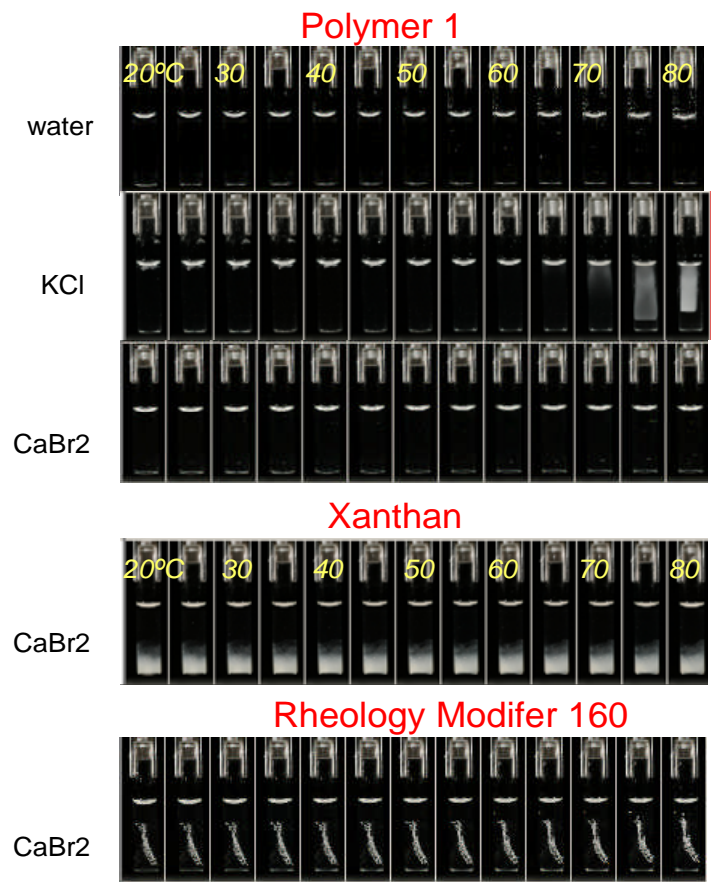


Figure 4. Solubility of 1 wt % formulations of various polymers in different brines as a function of temperature. The performance in saturated KCl and half-saturated CaBr₂ brines is shown. The white “streaks” observed in the Rheology Modifier 160 sample are caused by residual bubbles entrapped in the formulation when the stir bar is removed, reflecting the high viscosity of this sample.

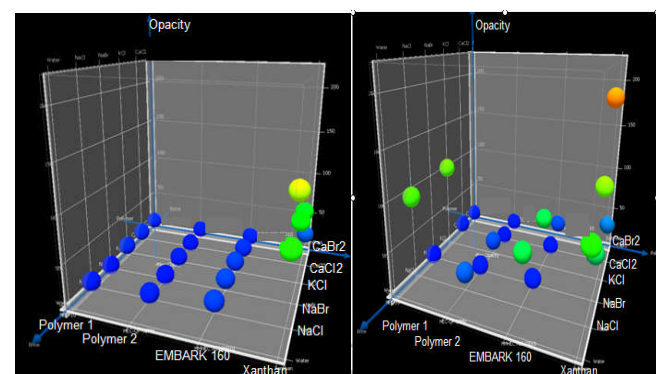


Figure 5. Three-dimensional representations of the opacity of various polymer-brine solutions. The plot on the left shows the clarity for four different polymers at 0.5 wt % in half-saturated brines, while the plot on the right is for saturated brines. Regions of high polymer solubility are indicated by blue spheres, while higher opacities (green, yellow or orange spheres) usually indicate lower polymer solubility.

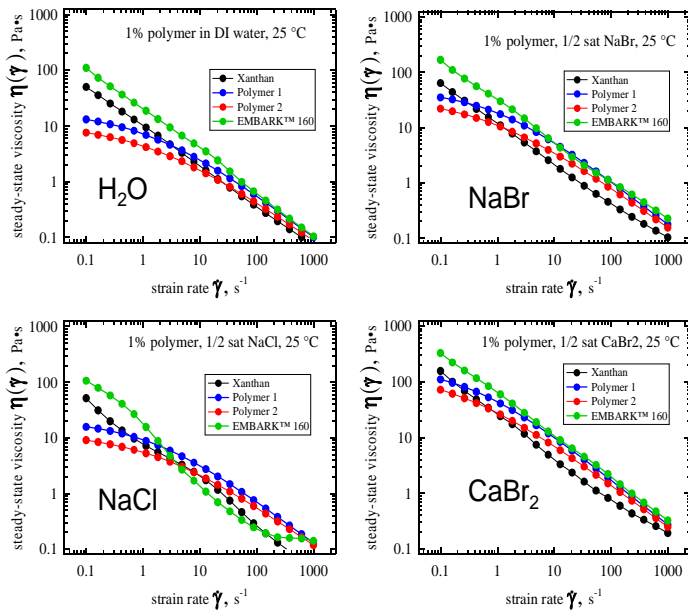


Figure 6. Flow curves for 1 wt % formulations of four different polymers in water and three brines (half-saturated NaCl, NaBr and CaBr₂).

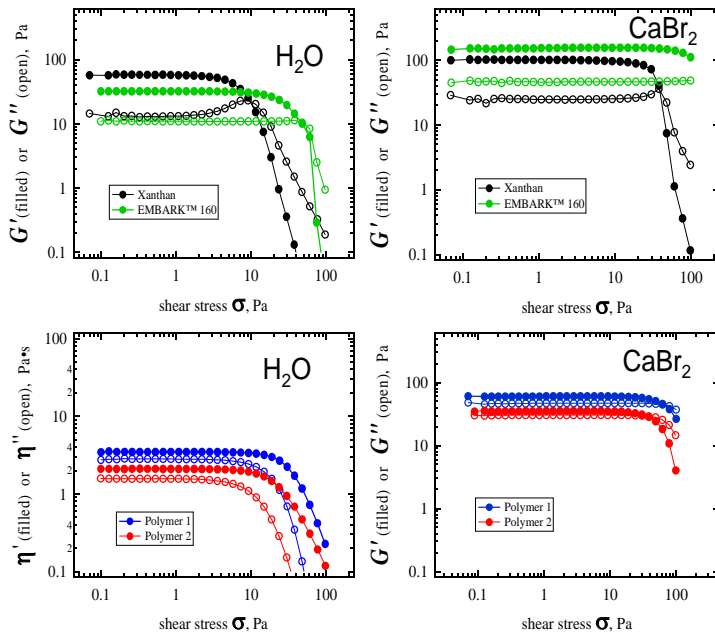


Figure 7. Oscillatory shear flow rheology of 1 wt % formulations of selected polymers (xanthan, Rheology Modifier 160, Polymer 1 and Polymer 2) in water and half-saturated CaBr₂ solutions. For solid-like solutions, the storage (G') and loss (G'') moduli are depicted with filled and open symbols, respectively. For liquid-like materials, the in-phase and out-of-phase components of the complex viscosity (η^*) are also represented by filled and open symbols.

Table 1. Low-shear stress modulus and yield stress of 1 wt % xanthan and Rheology Modifier 160 formulations (half-saturated brine concentrations)

	$G' (\sigma \rightarrow 0)$, Pa		$\sigma_Y (G' = G'')$, Pa	
	Xanthan	EMBARK™ Rheology Modifier	Xanthan	EMBARK™ Rheology Modifier
Water	57	32	10	48
NaBr	65	88	12	43
CaCl ₂	97	110	16	65
CaBr ₂	99	145	38	>100