CLEARLY DIFFERENT

Lauren Kaminski and Siv Howard, Cabot Specialty Fluids, UK and John Downs, Formate Brine Ltd, UK, explain how cesium salts dissolved in non-aqueous solvents create a totally new class of clear heavy fluids.

Clear solids-free fluids are often required to provide well control during well construction, workover, stimulation and suspension operations in reservoir intervals. Traditionally these fluids are aqueous salt solutions ('brines'), or invert emulsions of the salt solutions in oil. The density of the clear fluids is controlled by the nature and concentration of the salts dissolved in the water phase. The absence of weighting solids in these fluids eliminates the risk of solids sag and ensures that they exert a constant/steady hydrostatic pressure over time for stable well control. The clean well environment created by the fluids eases the running, setting and activation of downhole equipment and seals. The use of clear fluids also reduces the risk of formation damage from solids invasion in the reservoir, helping to optimise oil and gas production. In order to qualify for use in those well operations where contact with hydrocarbon-bearing reservoirs is possible the clear fluid should meet the following performance criteria:

- The fluid density must be capable of controlling the highest sub-surface pressure regime.
- The fluid freezing and crystallisation temperatures should be lower than the lowest surface and subsurface temperature, corrected for pressure effects.
- The fluid must be chemically inert, or exhibit benign chemistry, under the most extreme sub-surface conditions.

- The fluid must be capable of formulation with soluble polymers, to modify rheology and/or provide fluid loss control across permeable formations.
- The fluid must be fully compatible with all of the reservoir components at reservoir temperature/pressure. It must not have any adverse effects on the permeability and strength of the reservoir rock surrounding the wellbore.
- The fluid must be fully compatible with all metallic and elastomeric well components, under the most extreme sub-surface conditions, for the duration of the operation.
- The fluid must have no potential for adverse interactions with other fluids/chemicals injected into the reservoir before or after its deployment in the well.
- The fluid must have no potential for creating hydrates in sub-surface or surface equipment, and ideally it should inhibit hydrate formation.
- The fluid must have a good HSE profile, meeting or exceeding local and international regulatory requirements – i.e. non-hazardous (toxicity, flash point, etc.) and non-polluting.
- The fluid must allow or enhance logging interpretation for accurate reservoir definition.

Figure 1. *Clear solution of cesium formate in MEG – density 2.22 g/cm^3.*

Cesium formate brine

The most compliant and adaptable clear fluid currently available on the market today is cesium formate brine.[1] Over the past 12 years, water and oil-based clear fluids weighted with cesium formate have been deployed in over 300 well operations in some of the world's most demanding and challenging gas field developments. The advent of cesium formate brine in 1999 enabled the oil industry to begin enjoying the full economic benefits of creating low-skin openhole completions in deep high angle HPHT gas wells. Reviews published in 2010[2] and 2011[3] found that drilling and completing deep HPHT gas reservoirs with heavy cesium formate brines enhanced project economics by:

- Virtually eliminating well control and differential pipe sticking incidents.
- Enabling the drilling of long high angle wells within narrow drilling windows.
- Typically reducing offshore HPHT well completion times by 30 days or more.
- Promoting sustained high rate gas production, in several cases delivering 90% of the recoverable gas reserves within seven years from start-up.
- Improving the definition and visualisation of the gas reservoirs.
- Eliminating the need for clean-ups, stimulation treatments or any other form of intervention to remove formation damage caused by the drilling fluid.

Clear invert emulsions

Clear invert oil emulsion (CIOE) fluids weighted with cesium formate brine have been used in the field since 2001 as completion fluids in oil reservoirs.[4] The use of solids-free cesium-weighted CIOE fluids in completion operations reduces the risk of formation damage from solids invasion and adverse interactions with oil-based mud filtrates. The only drawback with CIOE fluids is that the brine: oil ratio restrictions for stable invert emulsions means that their density ceiling is 1.52 g/cm^3 with cesium formate brine as the internal phase. This density limitation on invert oil emulsions led to the investigation of whether there were other ways of creating heavy non-aqueous fluids weighted with cesium salts.

Non-aqueous solvents

The first task was to make a shortlist of benign and environmentally acceptable non-aqueous fluids already in use by

Table 1. Some non-aqueous solvents and their properties

Solvent	Density (g/cm3) at 20 °C	Boiling point (°C)	Freezing point (°C)	Flash point* (°C)	Viscosity at 20 °C (cP)	Thermal conductivity (W/m/°C)
Monoethylene Glycol (MEG)	1.115	197	-13	126	16.9	0.26
Diethylene Glycol (DEG)	1.118	245	-9	154	35.7	0.19
Triethylene Glycol (TEG)	1.125	288	-4	177	49.0	0.19
Butyl Glycol (EGMBE)	0.90	171	-77	65	2.9	0.17
Glycerol	1.26	290	17.8	177	1499	0.28
Mineral oil	0.805	225	-29**	102	2.4	0.16

*Closed cup measurement. **Pour Point.

the oil industry (and approved by regulatory authorities) that might potentially serve as solvents for cesium salts. The short list of five solvents selected for testing comprised three common ethylene glycols, a glycol ether and glycerol. The properties of these fluids are compared in Table 1 with those of a mineral oil commonly used as the continuous fluid phase of oil-based muds.

All of the solvents selected are fully miscible with water in all proportions, but only the butyl glycol is miscible with oil. The butyl glycol (otherwise known as ethylene glycol monobutyl ether or EGMBE) is closest in its physical properties to those of mineral oil used in drilling fluids, particularly in terms of viscosity and thermal conductivity. The solvents all score highly in environmental rankings, rating Gold or Category E in the PARCOM Offshore Chemical Notification System. In fact MEG and glycerol are rated PLONOR – i.e. they feature in the OSPAR list of substances used and discharged offshore, which are considered to pose little or no risk to the environment.

The ethylene glycols are mainly used in gas dehydration and gas hydrate inhibition, exploiting their low water activity (0.034 A_w @25 ˚C). The EGMBE also has a low water activity (0.045 A_w @25 ˚C) but is primarily used as a mutual solvent in well stimulation operations. Glycerol (0.122 A_w @25 ˚C) is listed as being used a gas hydrate inhibitor.

Cesium salt solvency tests

The individual solubilities of high purity dry cesium formate, cesium acetate and cesium phosphate powders were determined for each of the solvents. Increasing amounts of the salts were added to each solvent over a number of days until the solutions were fully saturated at room temperature (around 20 ˚C). Tables 2 to 4 summarise the outcome of the tests, showing the percentage w/w salt solubility achieved for each salt-solvent combination compared with salt in water. The tables also show the density and water activity of the saturated solutions. Solution densities were measured using a Mettler Toledo DM-40 Densitometer. Water activity was measured with a Rotronic water activity meter.

The results show that MEG is a very good solvent for all three cesium salts. Cesium formate was found to be soluble to 82.9% w/w in MEG, yielding a clear solution with a density of 2.22 g/cm^3 (Figure 1). Cesium phosphate was the next most soluble salt at 68.4% w/w, giving a solution density of 2.01 g/cm^3. Cesium acetate was the least soluble of the three cesium salts in MEG, but a solution concentration of 61.1% w/w and density of 1.67 g/cm^3 was still achieved.

The general trend in the higher ethylene glycols (DEG and TEG) was for the solvency, and the resulting solution density, to decrease with increasing molecular weight of the glycol. So the cesium salts solubilised in DEG to yield to solution densities in the medium 1.51-1.67 g/cm^3 range, but only gave densities of around 1.39 g/cm^3 in TEG. Dissolving dry cesium formate in a polyethylene glycol of molecular weight 200 at 20 ˚C gave a solution density of 1.37 g/cm^3 with a water activity of 0.055. The only exception to this general trend was the relatively high solubility of cesium acetate in TEG, giving a solution density of 1.75 g/cm^3. In fact cesium acetate powder exhibited good solubility in all of the non-aqueous solvents, always giving solution densities of > 1.5 g/cm^3.

The glycol ether (EGMBE) was not a good solvent for cesium formate or cesium phosphate but, surprisingly; it did dissolve cesium acetate to a final solution concentration of 65.4% w/w. The density of the saturated cesium acetate solution in EGMBE was a respectable 1.52 g/cm^3. The original density of the base solvent was just 0.90 g/cm^3.

Glycerol was found to be a moderately good solvent for all of the cesium salts. The best performer was a 63.8% w/w cesium formate in glycerol solution with a density of 1.96 g/cm^3.

Some preliminary solubility test results were also obtained with methanol as a solvent. This lower alcohol does not fit the profile of a benign non-aqueous solvent, being quite hazardous and toxic, but it is used in the field in gas dehydration and hydrate inhibition operations. Cesium formate and cesium acetate were found to be highly soluble in methanol, yielding saturated solution of density 1.52 g/cm^3 and 1.57 g/cm^3 respectively. These solution densities represent a significant increase on the base solvent density of 0.796 g/cm^3.

Curiously, the solubility of cesium formate in MEG decreased with increasing temperature over the range 10 – 40 ˚C. At the time of writing, no further work had been done to see if a) the decrease continued at higher temperatures and b) the same phenomenon occurred with other salt/solvent combinations.

In general, the water activity of the non-aqueous solvents increased when saturated with the cesium salts. The increase in water activity was greatest with cesium phosphate in solution, and the least with cesium formate. The exceptions to this rule were:

- The water activity of glycerol dropped slightly when saturated with cesium formate or cesium acetate.
- The water activity of EGMBE dropped slightly when saturated with cesium formate.

Conclusions

It has been found that three cesium salts are moderately to highly soluble (i.e. 16 - 83% w/w) in a range of benign non-aqueous solvents currently used by the oil and gas industry in gas dehydration, hydrate inhibition and hydraulic control applications. In the best case, the solubilisation of cesium formate powder in MEG produced a clear non-aqueous fluid with a density of 2.22 g/cm^3 at 20 ˚C. This is a significant improvement on the fluid densities achievable with clear invert oil emulsions weighted with cesium formate brine.

These novel solids-free high-density water-free fluids could potentially be used in drilling, completion, workover and packer or suspension operations to provide well control. At the very least they could be used as weighted pills for placement in wells to (e.g.) melt hydrate plugs or prevent hydrates from forming. However, further characterisation and qualification work will need to be done on the fluids before they can be applied in the field. This further work might include investigations into:

- Formulation of mixed potassium/cesium salts in the solvents. Potassium formate and potassium acetate are known to be soluble to 40% w/w in MEG, and they improve the gas dehydration efficiency of MEG, DEG and TEG[5].
- Solubility of sodium and rubidium salts in non-aqueous solvents. It is already known that sodium formate is moderately soluble in MEG.[6]
- Measurement of the thermal conductivity of the solutions. It is possible that some of these novel heavy fluids will have very low thermal conductivities and good thermal insulation properties.

Table 2. Cesium formate solubility in non-aqueous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	83	2.30	0.25
MEG	1.11	83	2.22	0.05
DEG	1.12	57	1.66	0.20
TEG	1.13	33	1.38	0.11
EGMBE	0.90	16	1.01	0.03
Glycerol	1.26	64	1.96	0.08

Table 3. Cesium acetate solubility in non-aqeous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	90	2.34	0.07
MEG	1.11	61	1.67	0.06
DEG	1.12	48	1.51	0.10
TEG	1.13	69	1.75	0.06
EGMBE	0.90	57	1.52	0.08
Glycerol	1.26	64	1.74	0.08

- Effect of water contamination on the solubility of the salts in the non-aqueous solvents, and the solution properties.
- Effect of temperature and pressure on the salt solubility and fluid density.
- Effect of acid gas contamination on the fluid properties and chemistry.
- Corrosion of carbon steel and chrome/nickel alloy steels.

Table 4. Cesium phosphate solubility in non-aqueous solvents and water

Solvent	Solvent density at 20 °C (g/cm³)	Salt solubilised at 20 °C (% w/w)	Solution density at 20 °C (g/cm³)	Solution A_w at 25 °C (%)
Water	1.00	88	2.71	0.29
MEG	1.11	68	2.01	0.19
DEG	1.12	50	1.65	0.20
TEG	1.13	31	1.39	0.15
EGMBE	0.90	29	0.92	0.27
Glycerol	1.26	41	1.66	0.24

- Compatibility with elastomers.
- Compatibility with reservoir components.

It would also be interesting to extend this study to look at cesium salt solubility in two other well known non-aqueous solvents, namely monopropylene glycol (MPG) and N-methyl pyrrolidone (NMP). OT

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