



# CHEMICAL AND PHYSICAL PROPERTIES

## Section A1

# Chemistry

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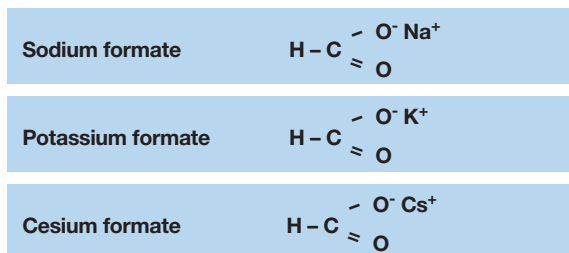
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## A1.1 General chemistry

Formate brines are the aqueous solutions of the alkali metal salts of formic acid. These salts are readily soluble in water, yielding high-density brines with low crystallization temperatures.

The chemical structures of the three formate salts used in the oilfield are as follows:



The formate anion is the most hydrophilic of the family of carboxylic acid anions, yet it retains significant organic characteristics when compared with halides. This organic character is seen in the solubility of formate salts in organic solvents, such as methanol or ethylene glycol.

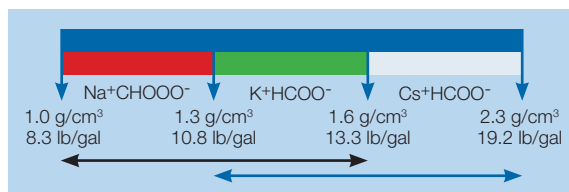
The alkali metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ ) are all monovalent, giving them their unique compatibility with biopolymers while at the same time contributing to their non-damaging behavior in reservoirs. Their molar and weight percentage solubilities in water at 20°C / 68°F are shown in Table 1.

**Table 1** Basic properties of sodium, potassium, and cesium formate salts.

Brine	Formula	Molecular weight [g/mol]	Solubility at 20°C / 68°F		Solution density	
			[mol/L]	[% wt]	g/cm <sup>3</sup>	lb/gal
Sodium formate	NaCHOO	68.01	9.1	46.8	1.33	11.1
Potassium formate	KCHOO	84.12	14.5	76.8	1.59	13.2
Cesium formate	CsCHOO	177.92	-	-	2.30	19.2
Cesium formate monohydrate	CsCHOO • H <sub>2</sub> O	195.94	10.7	83	2.30	19.2
Formate ion	CHOO <sup>-</sup>	45.02	-	-	-	-

The formate anion is also an anti-oxidant (reductant), readily scavenging hydroxyl free radicals. This means formate brines in general can provide thermally-sensitive solutes, such as water-soluble polymers, with considerable protection against oxidative degradation at high temperatures [1].

Formate brines cover the entire fluid density range normally required in drilling and completion.



The alkali metal formates in solution also exert a structuring effect on surrounding water molecules, making water more ice-like in nature. This water-structuring behavior has a beneficial effect on the conformation of dissolved macromolecules, making them more ordered, rigid and stable at high temperatures. The combination of anti-oxidant and water-structuring properties imparts formate brines with the potential to extend the thermal stability ceiling of many common drilling fluid polymers. An example of this is the commonly used viscosifier xanthan gum, which in a concentrated formate brine can be stabilized up to around 180°C / 356°F for 16 hours. This is significantly higher than in any other brines. By adding some other anti-oxidant chemicals and oxygen scavengers, stability can be raised further to around 204°C / 400°F [2].

Compared with other alkali metal cations, the cesium cation is heavier and more electropositive. Cesium is the heaviest of the stable group I elements, with an atomic weight of 132.9. Cesium is also the most electropositive of all the stable elements making cesium formate the most ionic of the formate salts.

## A1.2 Molecular structure

A crystal structure study has been conducted by The Department of Chemistry, Warwick University, UK for Cabot Specialty Fluids [3]. Reliable single crystal structures were available in the literature for sodium and potassium formate. Substantial errors were found in the previously published structures of cesium formate. New, single crystal structures were therefore determined as part of the study. The new structure made it possible to identify trends in the family of alkali formate structures, and thereby understand the effect of blending formate brines.

### A1.2.1 Molecular structure single salts

Images of the sodium, potassium, and cesium formate structures are shown in Figure 1. These structures show a clear trend with increasing cation size. In all three cases, formate ions are stacked in flat parallel planes.

#### Sodium formate

Sodium ions are small enough to fit into gaps between the formate ions and those within the flat planes.

#### Potassium formate

The potassium ion is too large to fit into gaps between the formate ions and therefore packs in between the formate layers. It still allows hydrogen-bond-like chains to form between the formate ions within each plane.

#### Cesium formate

Cesium gives a similar structure to potassium, but the larger size of cesium distorts the packing of formate ions so that hydrogen bonded chains of formate ions are no longer found in the cesium structure.

### A1.2.2 Molecular structure blended salts

#### Sodium cesium formate blends

The crystal structure study at Warwick University shows that this formate blend forms preferentially as a dual sodium cesium diformate. As sodium is present in commercial cesium formate brine (present at 10,000 – 20,000 ppm in the pollucite ore from which the cesium formate is produced) and is also a common impurity in oilfield applications, this dual formate is the first salt to precipitate from saturated solutions.

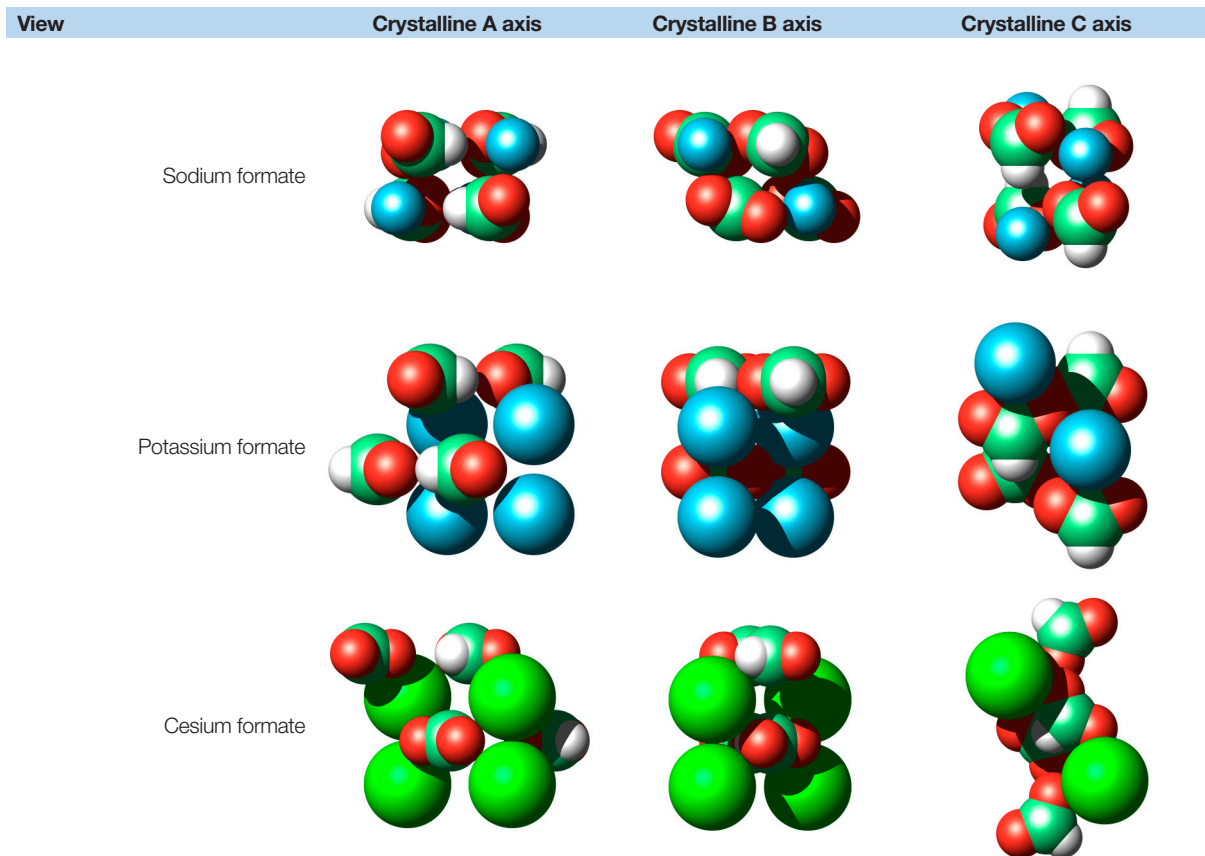
An illustration of the packing of ions in cesium sodium diformate is shown in Figure 2.

#### Potassium cesium formate blends

Conversely, the addition of potassium ions to a cesium solution enables a less compact crystal structure.

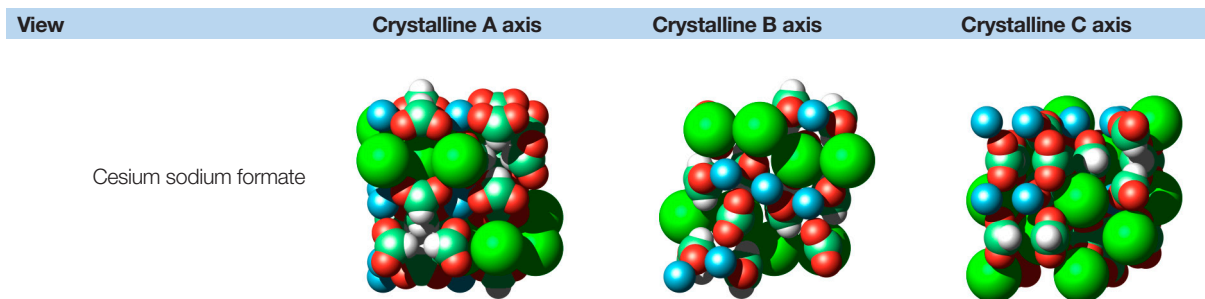
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- [1] Clarke-Sturman, A.J., Pedley, J.B., and Sturla, P.L.: "Influence of anions on the properties of microbial polysaccharides in solution," *Int. J. Biol. Macromol.*, (December 1986) 8, 355.
- [2] Messler, D., Kippie, D., Broach, M.: "A Potassium formate Milling Fluid Breaks the 400° Fahrenheit Barrier in Deep Tuscaloosa Coiled Tubing Clean-out", SPE 86503, Lafayette 2004.
- [3] Rodger, P.M. and Wilson, M.P.: "Crystallization Suppression of Cesium Formate", Department of Chemistry, University of Warwick, report, June 2002.



**Figure 1:** Three views of the sodium, potassium, and cesium formate crystal structures. Note the effect of cation size: sodium is small enough to fit between the formate ions, but potassium and cesium are too big and force the formate layers apart.

Key: Formate ions are fused dull green (C), red (O), and white (H) spheres;  $\text{Na}^+$  and  $\text{K}^+$  ions are blue spheres;  $\text{Cs}^+$  ions are large green spheres.



**Figure 2:** Three views of the crystal structure of the sodium cesium diformate. The first view clearly shows the similarity to both sodium formate and cesium formate, with sodium fitting within the formate 'layers' and cesium fitting between them.

Key: Formate ions are fused dull green (C), red (O), and white (H) spheres;  $\text{Na}^+$  ions are blue spheres;  $\text{Cs}^+$  ions are large green spheres.