A1.1 General chemistry

Formate brines are aqueous solutions of the alkali metal formate salts. 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:

- **Sodium formate**: \( H - C \equiv O^- Na^+ \)
- **Potassium formate**: \( H - C \equiv O^- K^+ \)
- **Cesium formate**: \( H - C \equiv O^- Cs^+ \)

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 (\( Na^+ \), \( K^+ \), and \( Cs^+ \)) 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.

<table>
<thead>
<tr>
<th>Brine</th>
<th>Formula</th>
<th>Molecular weight [g/mol]</th>
<th>Solubility at 20°C / 68°F [mol/L]</th>
<th>Solution density [g/cm³]</th>
<th>[lb/gal]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium formate</td>
<td>NaCHOO</td>
<td>68.01</td>
<td>9.1</td>
<td>1.33</td>
<td>11.1</td>
</tr>
<tr>
<td>Potassium formate</td>
<td>KCHOO</td>
<td>84.12</td>
<td>14.5</td>
<td>1.59</td>
<td>13.3</td>
</tr>
<tr>
<td>Cesium formate</td>
<td>CsCHOO</td>
<td>177.92</td>
<td>–</td>
<td>2.30</td>
<td>19.2</td>
</tr>
<tr>
<td>Cesium formate monohydrate</td>
<td>CsCHOO • H₂O</td>
<td>195.94</td>
<td>10.7</td>
<td>2.30</td>
<td>19.2</td>
</tr>
<tr>
<td>Formate ion</td>
<td>CHOO⁻</td>
<td>45.02</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The formate anion is also an anti-oxidant, 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 (Clarke-Sturman, 1986).

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 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 an oxygen scavenger and a polyethylene glycol, stability can be raised further to around 204°C / 400°F (Messler et al., 2004, Howard et al., 2015).

Compared with other alkali metal cations, the cesium cation is heavier and more electropositive. Cesium is the heaviest of the stable group 1 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 formate salt.
A1.2 Molecular structure

A crystal structure study has been conducted by the Department of Chemistry, Warwick University, UK for Cabot (Rodger et al., 2002). Reliable single-crystal structures were available in the literature for sodium and potassium formate. Substantial errors were found in 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 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 formate ions and those within the flat planes.

Potassium formate

The potassium ion is too large to fit into gaps between formate ions and therefore packs in between the formate layers. It still allows hydrogen bond-like chains to form between 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 (at 10,000 – 20,000 ppm in pollucite ore from which 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.

Packing of ions in sodium cesium diformate is illustrated in Figure 2.

Potassium cesium formate blends

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

References


<table>
<thead>
<tr>
<th>View</th>
<th>Crystalline A axis</th>
<th>Crystalline B axis</th>
<th>Crystalline C axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium formate</td>
<td><img src="image1.png" alt="Sodium formate" /></td>
<td><img src="image2.png" alt="Sodium formate" /></td>
<td><img src="image3.png" alt="Sodium formate" /></td>
</tr>
<tr>
<td>Potassium formate</td>
<td><img src="image4.png" alt="Potassium formate" /></td>
<td><img src="image5.png" alt="Potassium formate" /></td>
<td><img src="image6.png" alt="Potassium formate" /></td>
</tr>
<tr>
<td>Cesium formate</td>
<td><img src="image7.png" alt="Cesium formate" /></td>
<td><img src="image8.png" alt="Cesium formate" /></td>
<td><img src="image9.png" alt="Cesium formate" /></td>
</tr>
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</table>

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

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</thead>
<tbody>
<tr>
<td>Sodium cesium diformate</td>
<td><img src="image10.png" alt="Sodium cesium diformate" /></td>
<td><img src="image11.png" alt="Sodium cesium diformate" /></td>
<td><img src="image12.png" alt="Sodium cesium diformate" /></td>
</tr>
</tbody>
</table>

**Figure 2** Three views of the crystal structure of 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.