CHEMICAL AND PHYSICAL PROPERTIES

SECTION A3
WATER ACTIVITY AND COLLIGATIVE PROPERTIES

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VERSION 6 – 09/13

A3.1 Introduction

The physical properties of a solution are different from those of the pure solvent. Sodium, potassium, and cesium formate brines are aqueous solutions containing large amounts of dissolved salt. Although these brines are water based, they have properties that can deviate considerably from the properties of pure water. The extent to which the solution properties can deviate from pure water is related to the 'water activity' of the solution. Colligative fluid properties, such as boiling point, freezing point, vapor pressure, and osmotic pressure are directly related to the water activity of the fluid.

Low water activity in well construction fluids is generally beneficial because of its impact on some important colligative properties that determine the utility of the fluids. For example, a low water activity and high osmotic pressure are thought to be beneficial in slowing the destabilization of shales by water-based fluids. Low water activity is beneficial for other fluid properties that are dependent on hydration interactions, such as polymer stability.

A3.2 Water activity

An 'ideal solution' is defined as a solution in which the chemical potential of each species can be expressed by the chemical behavior of the pure species and their mole fractions. Typically, only very dilute solutions can be considered ideal. In more concentrated solutions, different (normally stronger) interactions will rather exist between the different species than between species of the same type. This causes a deviation from ideal behavior. In aqueous solutions of formate salts, this is explained by the fact that when water molecules interact with formate ions they are unavailable for other hydration interactions.

The term 'water activity' (a_w) describes the (equilibrium) amount of water available for hydration of materials. A value of unity indicates pure water whereas zero indicates the total absence of water molecules; addition of solutes always lowers the water activity. Water activity is the effective mole fraction of water, defined as:

$$a_w = \lambda_w X_w \quad (1)$$

where λ_w is the activity coefficient of water and X_w is the mole fraction of water in the aqueous solution.

Water activity can also be related to the relative humidity of the air surrounding the fluid:

$$a_w = \lambda_w X_w = p/p_0 \quad (2)$$

where p is the partial pressure of water above the fluid and p_0 is the partial pressure of pure water at the same temperature.

A3.2.1 Determination of water activity

Water activity can be experimentally determined by measuring the relative humidity of the air above the fluid when the air and the fluid are at equilibrium (Equation 2). At equilibrium, the water activity of the fluid and the relative humidity of the air are equal. The measurement is called an equilibrium relative humidity or ERH. The water activity may be expressed as:

$$a_w = p/p_0 \quad (3)$$

Note that the water activity of any aqueous solution in equilibrium with ice (a^i_w) is equal to the ratio between the water vapor pressure over ice to the water pressure over pure water. Therefore, this does not depend on the solute's nature or concentration. Solutions with the same ice melting point have the same water activity.

A3.2.2 Water activity in single-salt formate brines

By using the ERH method described above, Cabot Operations and Technical Support Laboratory in Aberdeen, UK, has measured water activity as a function of concentration for sodium, potassium, and cesium formate brines [1][2]. The measured water activity at 25°C / 77°F is shown in Table 1 and plotted as a function of fluid density in Figure 1. As can be seen, sodium and potassium formate brines have very similar water activity at a given density, whilst the water activity of cesium formate is higher.

The plot also shows water activity of two commercially available potassium formate brines. There is very little difference in water activity between the different potassium formate brines tested. The same applies to a 96% pure potassium formate powder, sourced from China. It is therefore reasonable to assume that water activity measured for analytical grade material is representative for most potassium formate brines used in the oilfield today.

For cesium formate, measurements were made on both analytical grade material and Cabot's cesium formate brine produced at the Tanco plant in Canada. The lower water activity of the Tanco material can be explained by small levels of lighter lithium, sodium, and rubidium formate present in the brine. Lithium and sodium do not contribute as much to the weight as cesium, and the presence of these components in the brine means that less water is needed to reach the same brine density, which again contributes to a reduction in water activity.

Table 1 shows water activities thought to be representative for the three formate brines commonly used for drilling and completion at 25°C / 77°F.

Table 1 Water activity in single-salt formate brines measured at 25°C / 77°F as a function of brine density. The water activity has been measured at Cabot Operations and Technical Support Laboratory in Aberdeen, UK, using the equilibrium relative humidity (ERH) method. Water activity is shown for analytical-grade sodium formate, analytical-grade potassium formate, analytical-grade cesium formate, and typical field-grade cesium formate.

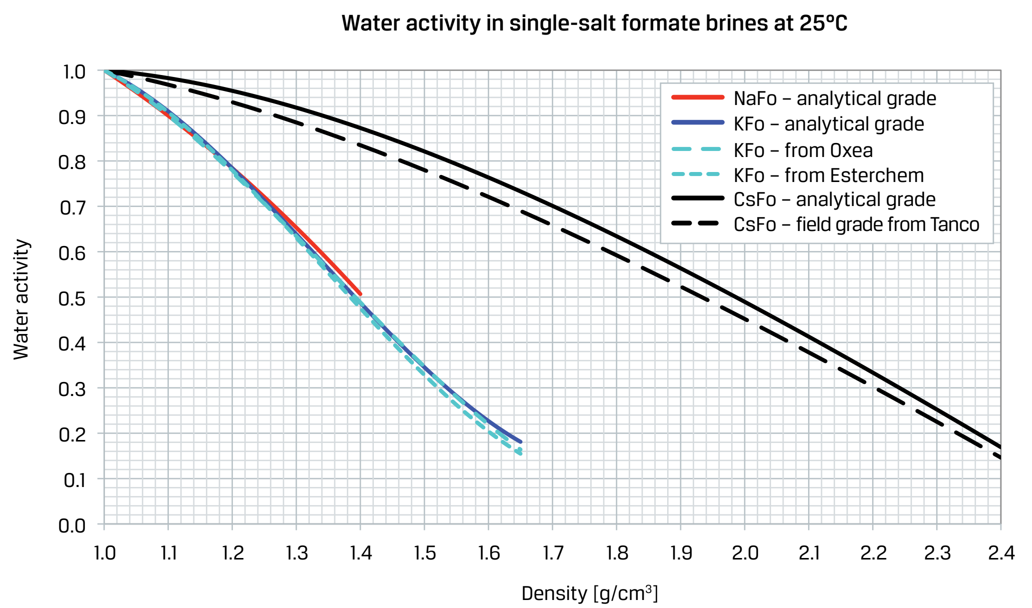
METRIC

Density [g/cm^3]	Water activity			
	NaFo	KFo	CsFo	CsFo field grade
1.00	1.000	1.000	1.000	1.00
1.02	0.981	0.985	0.997	0.99
1.04	0.962	0.969	0.994	0.99
1.06	0.942	0.951	0.991	0.98
1.08	0.921	0.931	0.987	0.98
1.10	0.900	0.909	0.983	0.97
1.12	0.878	0.887	0.978	0.96
1.14	0.855	0.863	0.972	0.95
1.16	0.832	0.837	0.967	0.95
1.18	0.809	0.811	0.961	0.94
1.20	0.784	0.784	0.955	0.93
1.22	0.759	0.756	0.948	0.92
1.24	0.734	0.727	0.941	0.91
1.26	0.707	0.698	0.933	0.90
1.28	0.681	0.669	0.926	0.89
1.30	0.653	0.639	0.917	0.88
1.32	0.625	0.608	0.909	0.88
1.34	0.596	0.578	0.900	0.87
1.36	0.567	0.548	0.891	0.86
1.38	0.537	0.517	0.882	0.85
1.40		0.487	0.873	0.83
1.42		0.458	0.863	0.82
1.44		0.429	0.853	0.81
1.46		0.400	0.842	0.80
1.48		0.372	0.832	0.79
1.50		0.345	0.821	0.78
1.52		0.319	0.810	0.77
1.54		0.294	0.799	0.76
1.56		0.270	0.787	0.74
1.58		0.248	0.775	0.73
1.60		0.227	0.764	0.72
1.62			0.751	0.71
1.64			0.739	0.70
1.66			0.727	0.68
1.68			0.714	0.67
1.70			0.701	0.66
1.72			0.688	0.65
1.74			0.675	0.63
1.76			0.661	0.62
1.78			0.648	0.61
1.80			0.634	0.59
1.82			0.620	0.58
1.84			0.606	0.56
1.86			0.592	0.55
1.88			0.578	0.54
1.90			0.563	0.52
1.92			0.549	0.51
1.94			0.534	0.49
1.96			0.519	0.48
1.98			0.505	0.47
2.00			0.490	0.45
2.02			0.474	0.44
2.04			0.459	0.42
2.06			0.444	0.41
2.08			0.428	0.39
2.10			0.413	0.38
2.12			0.397	0.36
2.14			0.381	0.35
2.16			0.366	0.33
2.18			0.350	0.32
2.20			0.334	0.30
2.22			0.317	0.29
2.24			0.301	0.27
2.26			0.285	0.26
2.28			0.269	0.24
2.30			0.252	0.23
2.32			0.236	0.21
2.34			0.219	0.19
2.36			0.203	0.18
2.38			0.186	0.16
2.40			0.169	0.15

FIELD

Density [lb/gal]	Water activity			
	NaFo	KFo	CsFo	CsFo field grade
8.34	1.000	1.000	1.000	1.00
8.40	0.994	0.995	0.999	1.00
8.60	0.971	0.977	0.996	0.99
8.80	0.947	0.956	0.992	0.98
9.00	0.923	0.932	0.987	0.98
9.20	0.897	0.907	0.982	0.97
9.40	0.871	0.879	0.976	0.96
9.60	0.844	0.850	0.970	0.95
9.80	0.815	0.819	0.963	0.94
10.00	0.786	0.786	0.955	0.93
10.20	0.756	0.753	0.947	0.92
10.40	0.726	0.719	0.938	0.91
10.60	0.694	0.683	0.929	0.90
10.80	0.661	0.647	0.920	0.89
11.00	0.628	0.611	0.910	0.88
11.20	0.593	0.575	0.899	0.86
11.40	0.558	0.539	0.889	0.85
11.60	0.522	0.502	0.877	0.84
11.80		0.467	0.866	0.83
12.00		0.432	0.854	0.81
12.20		0.398	0.841	0.80
12.40		0.364	0.829	0.79
12.60		0.332	0.816	0.77
12.80		0.302	0.802	0.76
13.00		0.273	0.788	0.75
13.20		0.246	0.774	0.73
13.40		0.221	0.760	0.72
13.60			0.746	0.70
13.80			0.731	0.69
14.00			0.715	0.67
14.20			0.700	0.66
14.40			0.684	0.64
14.60			0.668	0.63
14.80			0.652	0.61
14.90			0.636	0.59
15.00			0.619	0.58
15.20			0.603	0.56
15.40			0.586	0.54
15.60			0.568	0.53
15.80			0.551	0.51
16.00			0.533	0.49
16.20			0.516	0.48
16.40			0.498	0.46
16.60			0.480	0.44
16.80			0.461	0.42
17.00			0.443	0.41
17.20			0.424	0.39
17.40			0.406	0.37
17.60			0.387	0.35
17.80			0.368	0.34
18.00			0.349	0.32
18.20			0.330	0.30
18.40			0.310	0.28
18.60			0.291	0.26
18.80			0.271	0.24
19.00			0.252	0.22
19.20			0.232	0.21
19.40			0.206	0.19
19.60			0.187	0.17
19.80			0.168	

METRIC



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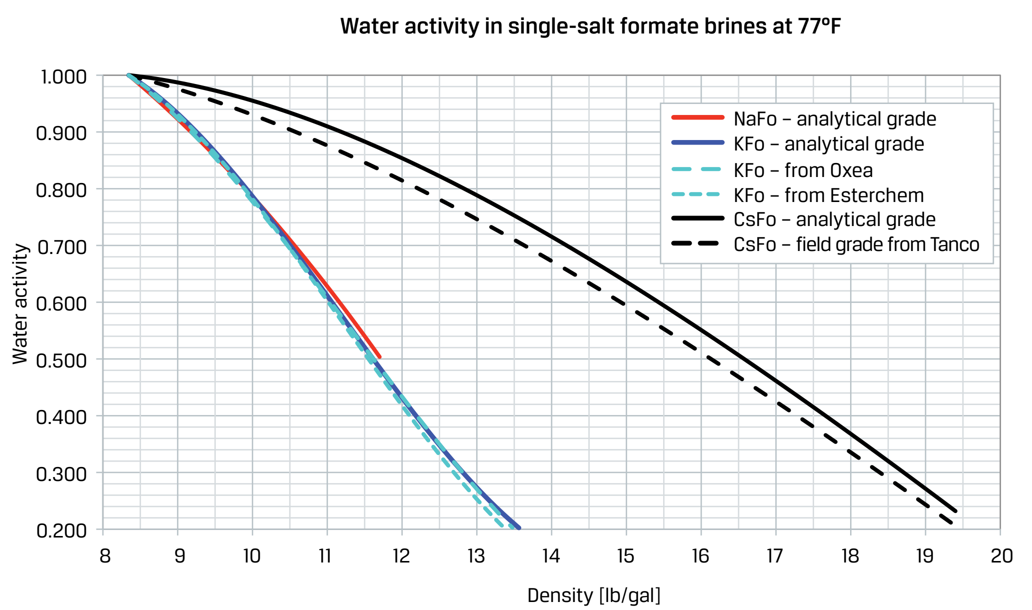

Figure 1 Water activity in single-salt formate brines measured at 25°C / 77°F as a function of brine density. The water activity has been measured at Cabot Operations and Technical Support Laboratory in Aberdeen, UK, using the equilibrium relative humidity (ERH) method.

A3.2.3 Water activity in potassium and cesium formate brine blends

Cabot Operations and Technical Support Laboratory in Aberdeen, UK, has also measured water activity for various blends of 2.20 g/cm^3 / 18.3 lb/gal cesium formate brine and 1.57 g/cm^3 / 13.1 lb/gal potassium formate brine [1]. A linear relationship was found between the water activity of the blend and the density of the blended brine, as shown in Figure 2. As the water activity of these two concentrated brines is very similar (approximately 0.3), any blends of these two brines will also have water activity in this range. As a rule of thumb, one can assume:

Any blend of 2.20 g/cm^3 / 18.3 lb/gal cesium formate brine and potassium formate brine in the density range 1.54 g/cm^3 / 12.8 lb/gal to 1.57 g/cm^3 / 13.1 lb/gal will have a water activity of approximately 0.3 or slightly less.

In special blends where additional water is added to the brines to lower TCT, slightly higher water activity can be expected.

A3.2.4 Water activity in sodium and potassium formate brine blends

Cabot has not measured water activity for blended sodium and potassium formate brines. However, from the measurements completed on the two individual single-salt brines (see Figure 1), there appears to be no significant difference in water activity between the two brines for any given density. Any blends of these two brines therefore result in brine that follows the same water activity vs. density relationship as the two individual brines shown in Figure 1.

A3.2.5 Water activity – temperature and pressure dependence

Water activity generally rises with increasing pressure. However, in solutions with high salt content, water activity is shown to decrease with increased pressure [3]. One would therefore expect the water activity for formate brines to decrease with increased pressure. Normally, water activity also increases with a rise in temperature, but there are also exceptions to this rule.

Cabot does not have any measured data on the temperature and pressure dependence of water activity in formate brines.

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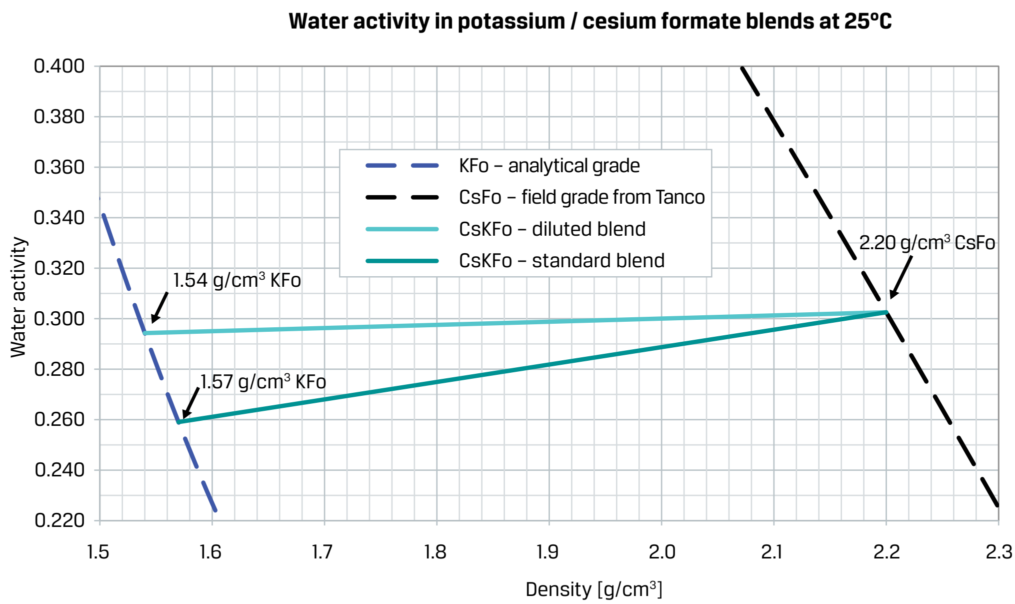

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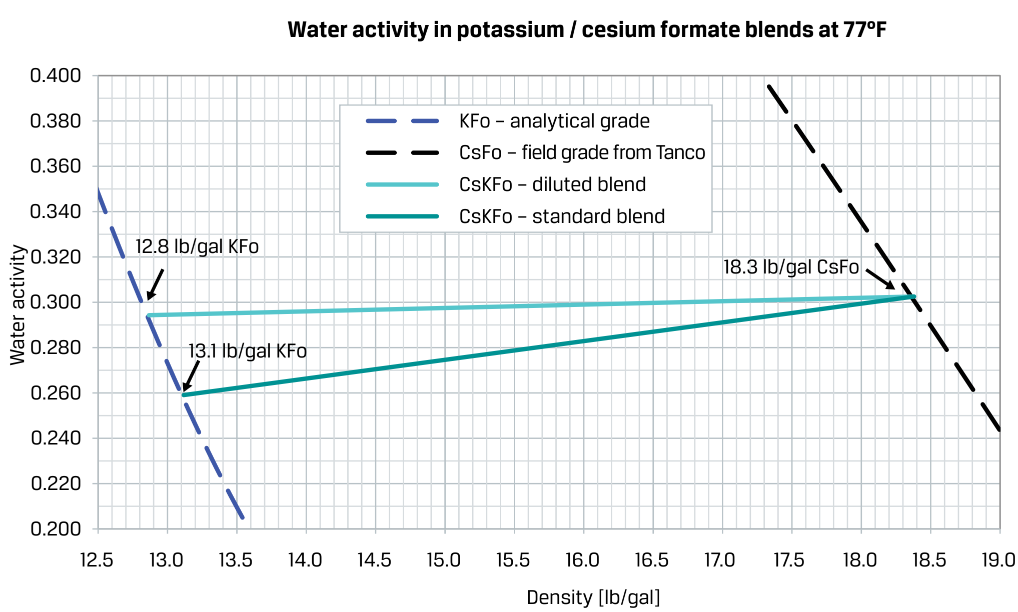


Figure 2 Water activity as a function of brine density for two different potassium and cesium formate blends at 25°C / 77°F. One is a standard blend based on 1.57 g/cm³ / 13.1 lb/gal potassium formate brine and 2.20 g/cm³ / 18.3 lb/gal cesium formate brine. The other is a diluted blend (1.54 g/cm³ / 12.8 lb/gal potassium formate and 2.20 g/cm³ / 18.3 lb/gal cesium formate) often used in the winter.

A3.3 Colligative properties

Colligative properties are properties that, in ideal solutions, only depend on the amount of solute particles in the solution (concentration) and are independent of the nature of the solute. These properties are:

1. Freezing point depression
2. Boiling point elevation
3. Vapor pressure lowering
4. Osmotic pressure

In non-ideal solutions, these properties are related to the water activity of the fluid rather than the concentration.

As discussed above, formate salts are extremely water soluble and form aqueous solutions with very low water activity. The colligative properties are therefore highly significant in concentrated formate brines, and give rise to a whole range of important fluid properties that are beneficial for many aspects of well construction fluids. The most important ones are freezing point depression (TCT, hydrate inhibition), and osmotic pressure (borehole stability by osmotic backflow), which are all discussed elsewhere in this manual.

There are also industrial applications for formate brines, where these properties are exploited to good effect. Examples are dehumidifying of natural gas and de-icing of airport runways.

A3.3.1 Boiling point

The boiling point of sodium, potassium, and cesium formate single-salt brines has been measured as a function of brine density by Cabot Operations and Technical Support Laboratory in Aberdeen, UK [4]. The boiling points are listed in Table 3 and plotted in Figure 3.

Boiling points have also been measured for several potassium and cesium formate blends, and are shown to vary linearly with the ratio of cesium formate to potassium formate. In Figure 3, boiling points are shown for a standard blend (1.57 g/cm^3 / 13.1 lb/gal *KFo* and 2.2 g/cm^3 / 18.3 lb/gal *CsFo*) and a more diluted blend (1.54 g/cm^3 / 12.8 lb/gal *KFo* and 2.2 g/cm^3 / 18.3 lb/gal *CsFo*).

A3.3.2 Vapor pressure

Concentrated formate brines, particularly concentrated potassium and cesium formate and their blends, exert very low vapor pressures at high concentrations.

The vapor pressure of three cesium formate brines of different concentrations have been measured over the temperature range 15°C / 60°F to 50°C / 122°F [5] [6]. The vapor pressures of these brines are listed in Table 3 and plotted in Figure 4 together with some reference data for water [7] and potassium formate brines at various concentrations [8]. Figure 5 shows the same plot at a different temperature scale.

There is no vapor pressure data available for cesium formate above 50°C / 122°F. Due to the similar water activity of concentrated cesium formate brine and concentrated potassium formate brine, one can assume that the vapor pressures of these two brines are also very similar. The vapor pressure of any blend of concentrated potassium formate brine and concentrated cesium formate brine can also be expected to fall in the same range.

References

[1] "Water Activity in Formate Brines", Report # LR-538, Cabot Operations and Technical Support Laboratory, Aberdeen, UK, June 2011.

[2] "Measurement of Water Activity in Formate Brines", Report # LR-594, Cabot Operations and Technical Support Laboratory, Aberdeen, UK, November 2011.

[3] London South Bank University, website (www.lsbu.ac.uk).

[4] "Boiling points of formate fluids", Laboratory report # LR-211, Cabot Operations and Technical Support Laboratory, Aberdeen, UK, March 2007.

[5] "Vapour Pressure Measurements in 2.00 and 2.20 g/cm^3 cesium formate brines." Report # LR-686 Version 2, Cabot Operations and Technical Support Laboratory, Aberdeen, UK, January 2013.

[6] Pelletier, M.T.: "Vapor Pressure of Cesium Formate Solution, Lot 30", Report # PF 98-072, Westport Technology Center International, October 1998.

[7] Handbook of Chemistry and Physics, CRC Press, 60th edition, 1979 – 1980.

[8] EcoForm information sheet.

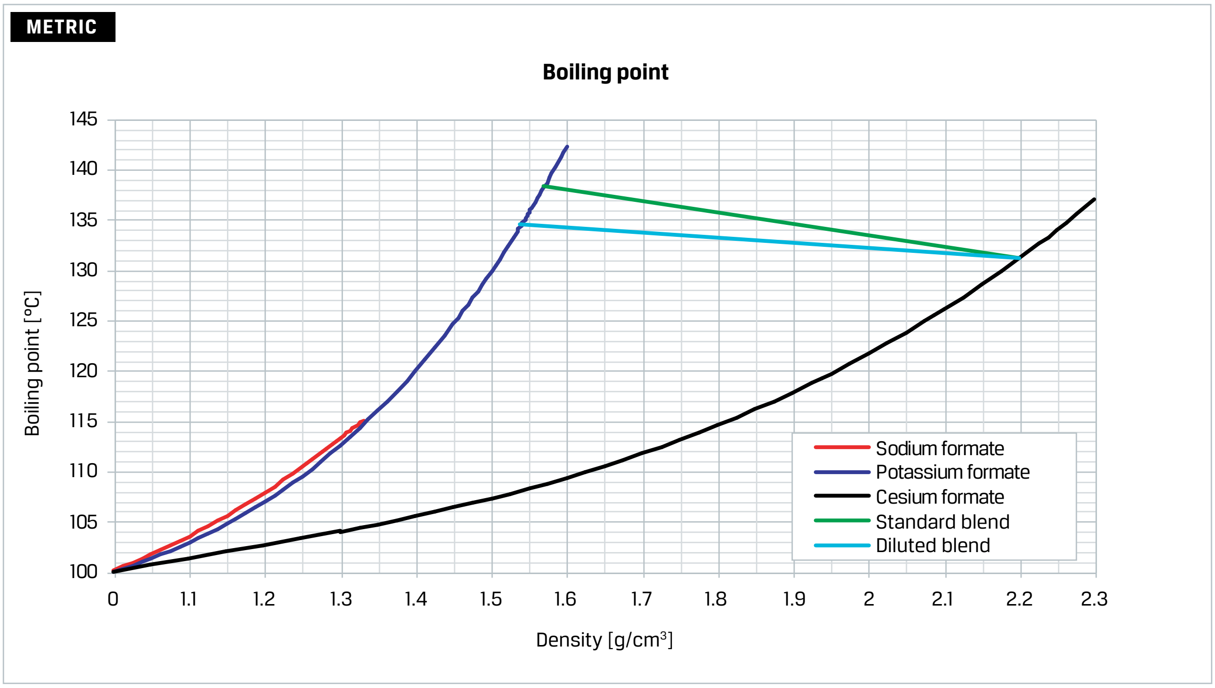
Table 2 Boiling point for sodium, potassium, and cesium formate single-salt brines as a function of brine density.

METRIC

Density [g/cm³]	Boiling point [°C]		
	NaFo	KFo	CsFo
1.00	100	100	100
1.05	102	101	101
1.10	104	103	101
1.15	106	105	102
1.20	108	107	103
1.25	110	110	103
1.30	113	113	104
1.35	116	116	105
1.40		120	106
1.45		125	106
1.50		130	107
1.55		136	108
1.60		142	109
1.65			111
1.70			112
1.75			113
1.80			115
1.85			116
1.90			118
1.95			120
2.00			122
2.05			124
2.10			126
2.15			129
2.20			131
2.25			134
2.30			137

FIELD

Density [lb/gal]	Boiling point [°F]		
	NaFo	KFo	CsFo
8.34	212	212	212
8.50	213	212	212
9.00	217	216	214
9.50	221	220	215
10.00	226	224	217
10.50	232	230	218
11.00	238	237	220
11.50		245	221
12.00		254	223
12.50		266	225
13.00		278	227
13.50		293	230
14.00			232
14.50			235
15.00			238
15.50			242
16.00			245
16.50			249
17.00			254
17.50			259
18.00			264
18.50			270
19.00			276



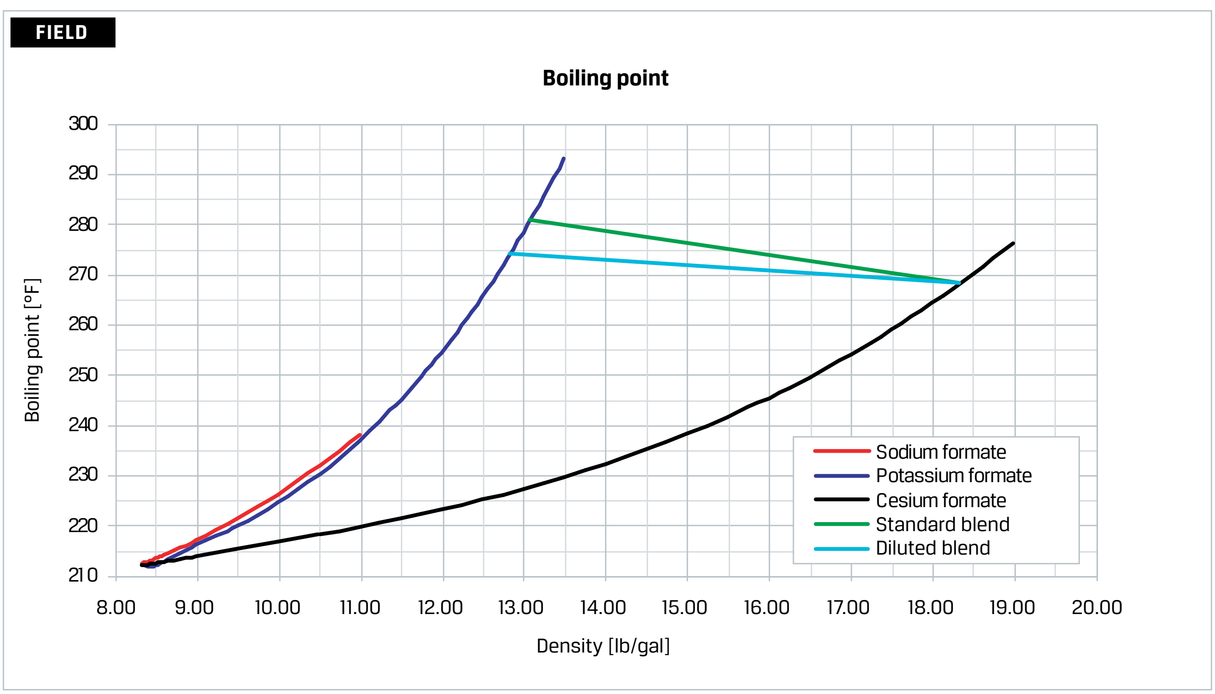


Figure 3 Boiling point as a function of density for sodium formate, potassium formate, cesium formate, a typical cesium / potassium formate standard blend (1.57 g/cm³ / 13.1 lb/gal KFo = 2.20 g/cm³ / 18.3 lb/gal CsFo), and a diluted blend (1.54 g/cm³ / 12.8 lb/gal KFo + 2.20 g/cm³).

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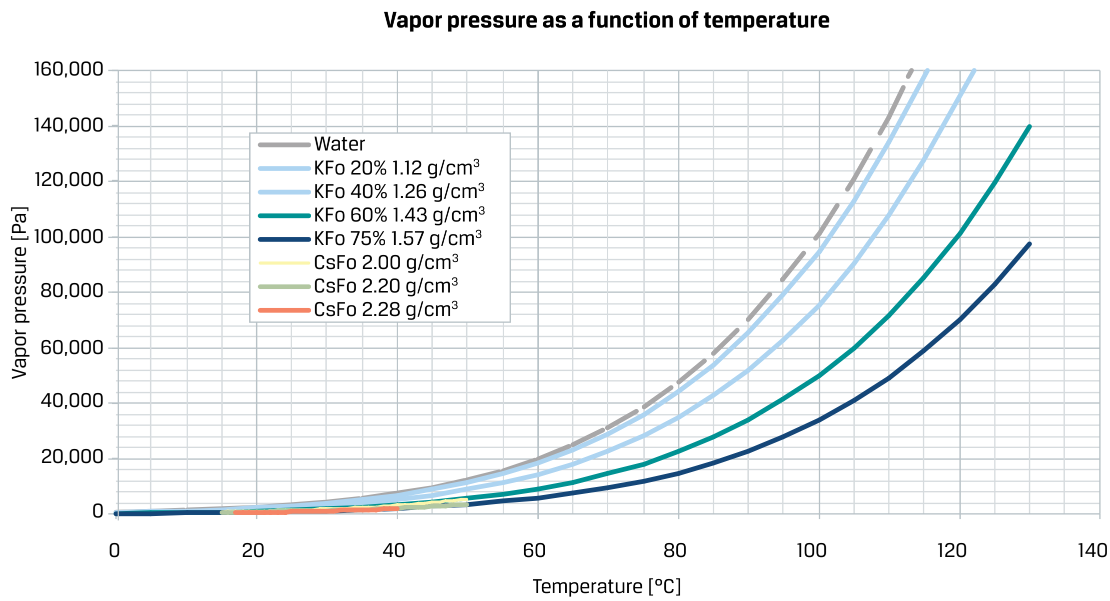

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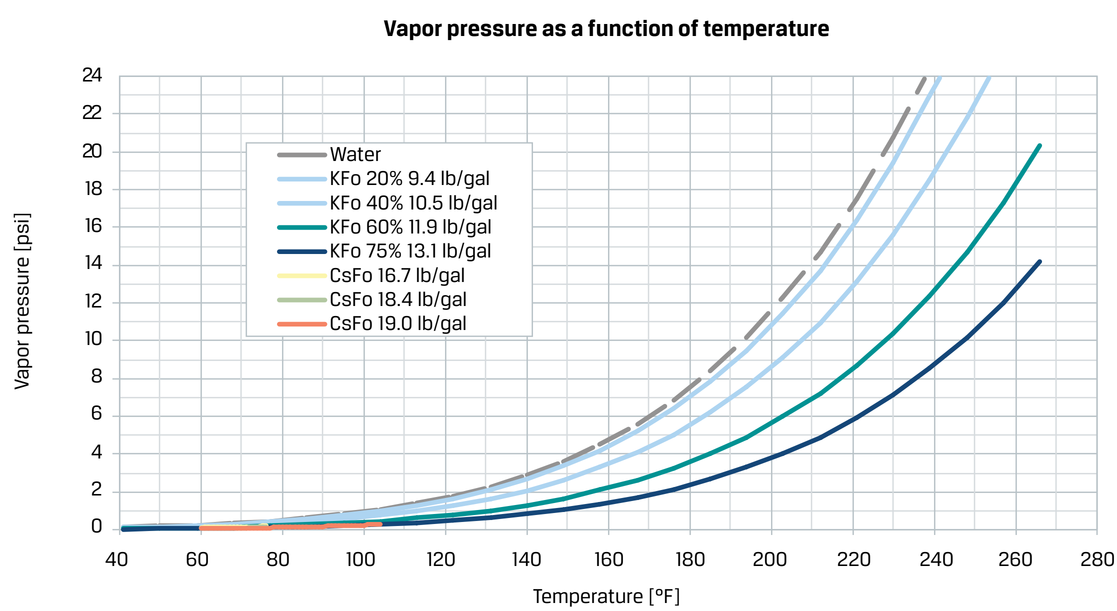
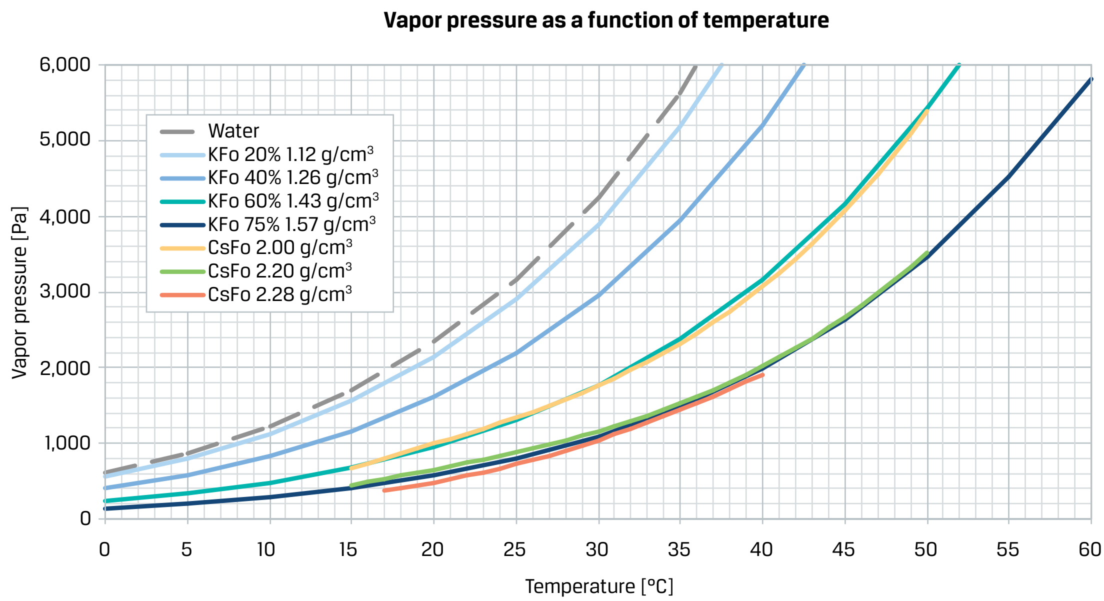


Figure 4 Vapor pressure of three cesium formate samples with different concentrations plotted together with vapor pressure for water and potassium formate brine of various concentrations taken from the literature [7][8]. Due to the very similar water activity of concentrated cesium formate brine and concentrated potassium formate brine, one can expect the vapor pressure of cesium formate and any blends of the two brines to be very similar to the vapor pressure of 75% (1.57 g/cm^3 / 13.1 lb/gal) potassium formate (blue line).

METRIC



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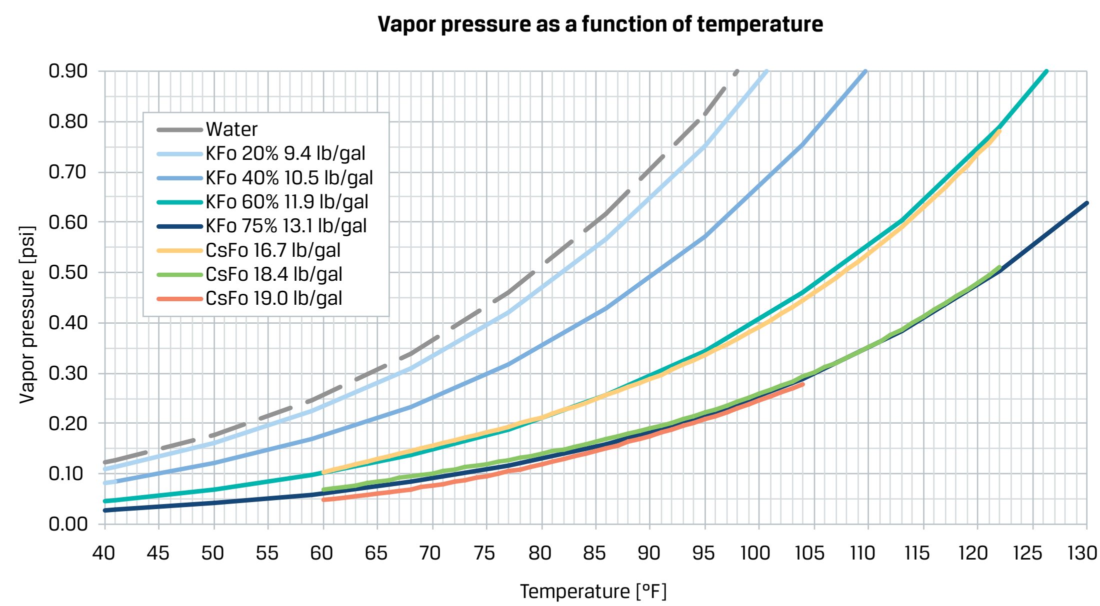

Figure 5 Vapor pressure of three cesium formate samples with different concentrations plotted together with vapor pressure for water and potassium formate brine taken from the literature [7][8].

Table 3 Vapor pressure for three different concentrations of cesium formate brines as a function of temperature.

METRIC

T [°C]	Vapor pressure [Pa]		
	2.00 g/cm³	2.20 g/cm³	2.28 g/cm³
15	671	443	
16	737	486	
17	802	528	376
18	867	570	409
19	931	612	444
20	996	654	483
21	1,061	697	525
22	1,128	741	570
23	1,196	786	618
24	1,267	833	669
25	1,340	881	723
26	1,416	932	781
27	1,496	984	841
28	1,580	1,040	905
29	1,669	1,098	972
30	1,762	1,160	1,042
31	1,861	1,225	1,115
32	1,965	1,294	1,191
33	2,077	1,367	1,270
34	2,194	1,444	1,352
35	2,320	1,527	1,438
36	2,453	1,614	1,526
37	2,594	1,706	1,618
38	2,744	1,804	1,712
39	2,903	1,908	1,810
40	3,071	2,018	1,911
41	3,250	2,134	
42	3,439	2,257	
43	3,639	2,387	
44	3,851	2,525	
45	4,075	2,670	
46	4,311	2,823	
47	4,560	2,984	
48	4,822	3,153	
49	5,099	3,332	
50	5,389	3,519	

FIELD

T [°F]	Vapor pressure [psi]		
	16.7 lb/gal	18.20 lb/gal	19.0 lb/gal
60	0.10	0.07	0.07
61	0.11	0.07	0.07
62	0.11	0.07	0.07
63	0.12	0.08	0.08
64	0.12	0.08	0.08
65	0.13	0.08	0.08
66	0.13	0.09	0.09
67	0.14	0.09	0.09
68	0.14	0.09	0.09
69	0.15	0.10	0.10
70	0.15	0.10	0.10
71	0.16	0.11	0.11
72	0.17	0.11	0.11
73	0.17	0.11	0.11
74	0.18	0.12	0.12
75	0.18	0.12	0.12
76	0.19	0.12	0.12
77	0.19	0.13	0.13
78	0.20	0.13	0.13
79	0.21	0.14	0.14
80	0.21	0.14	0.14
81	0.22	0.14	0.14
82	0.23	0.15	0.15
83	0.23	0.15	0.15
84	0.24	0.16	0.16
85	0.25	0.16	0.16
86	0.26	0.17	0.17
87	0.26	0.17	0.17
88	0.27	0.18	0.18
89	0.28	0.18	0.18
90	0.29	0.19	0.19
91	0.30	0.20	0.20
92	0.31	0.20	0.20
93	0.32	0.21	0.21
94	0.33	0.21	0.21
95	0.34	0.22	0.22
96	0.35	0.23	0.23
97	0.36	0.24	0.24
98	0.37	0.24	0.24
99	0.38	0.25	0.25
100	0.39	0.26	0.26
101	0.41	0.27	0.27
102	0.42	0.28	0.28
103	0.43	0.28	0.28
104	0.45	0.29	0.29
105	0.46	0.30	
106	0.47	0.31	
107	0.49	0.32	
108	0.51	0.33	
109	0.52	0.34	
110	0.54	0.35	
111	0.56	0.36	
112	0.57	0.38	
113	0.59	0.39	
114	0.61	0.40	
115	0.63	0.41	
116	0.65	0.42	
117	0.67	0.44	
118	0.69	0.45	
119	0.71	0.47	
120	0.73	0.48	
121	0.76	0.50	
122	0.78	0.51	