COMPATIBILITIES AND INTERACTIONS

SECTION B14
SOLUBILITY IN NON-AQUEOUS SOLVENTS

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CABOT

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B14.1 Introduction

When dissolved in water, alkali metal formate salts form highly concentrated brines with very high density. However, it is not only water that dissolves high concentrations of these salts. Several non-aqueous solvents are also good solvents for formate salts. Cesium formate can dissolve in non-aqueous solvents to form high-density fluids up to 2.22 g/cm^3 / 18.53 lb/gal. Potassium and sodium formate salts can form non-aqueous fluids with moderately high density.

B14.2 Non-aqueous solvents

Tests carried out by Cabot Corporation show that alkali metal formate salts are soluble in a number of non-aqueous solvents used every day in the oil industry. The solvents tested were from the following chemical groups:

B14.2.1 Alcohols

Alcohols are derivatives of hydrocarbons where one or more hydrogen atom is replaced by a hydroxyl (–OH) functional group. Most alcohols are colorless liquids or solids at room temperature. Alcohols of low molecular weight are highly soluble in water. The higher molecular weight alcohols are less soluble in water, and their boiling points, vapor pressures, densities, and viscosities are higher. The alcohol can be monohydric (single –OH group) or polyhydric (multiple –OH groups).

Monohydric alcohols

The best-known simple monohydric alcohols are ethanol and methanol. Methanol is used in the oilfield as a thermodynamic hydrate inhibitor and desiccant for dewatering pipelines or pipeline conditioning.

Dihydric alcohols (diols)

Ethylene glycols and polyethylene glycols
The ethylene glycols (EG) and polyethylene glycols (PEG) are aliphatic organic compounds composed of two hydroxyl groups. The four commercial EG (mono, di-, tri- and tetra-) are clear, colorless and virtually odorless liquids with high boiling points. At room temperature, PEGs are liquid at molecular weights up to 600, and waxy solids at higher molecular weights. All PEGs are water-miscible, but their solubility in water decreases with increasing molecular weight. Liquid EG and PEG are excellent solvents for many organic compounds. Aqueous solutions of PEG can display phase separation when heated or when mixed with other water-soluble polymers or certain salts [1]. This aqueous biphasic separation (ABS) behavior is exploited to purify and concentrate other solutes present in solution. EG and PEG are widely used as industrial coolants, heat transfer fluids and anti-freeze agents.

The oil industry uses large volumes of these glycols for gas dehydration and hydrate inhibition, exploiting their low water activity (a_w = 0.034 at 25°C / 77°F). Potassium formate may be dissolved in gas dehydration glycols to improve their performance and reduce contamination with aromatic hydrocarbons such as benzene, toluene and xylene [2]. Several patents claim use of glycols weighted with inorganic salts as drilling, completion and general well fluids [3–5]. The highest density claimed is 2.16 g/cm^3 / 17.96 lb/gal for a clear solution of zinc bromide dissolved in ethylene glycol [3]. A patent first filed in 2008 claims a formulation based on a high-density solution of cesium formate in ethylene glycol can be used as non-aqueous breaker fluid for solubilizing filter cakes from oil-based muds [6].

EG and PEG all score highly in environmental rankings, including gold or category E in the PARCOM Offshore Chemical Notification System. Monoethylene glycol (MEG) is rated PLONOR, i.e. it is included in the OSPAR list of substances used and discharged offshore that pose little or no risk to the environment. EG are moderately toxic, although some higher molecular-weight PEGs are practically non-toxic and are approved for food use. PEGs are also used as 'green' solvents and phase-transfer agents for organic synthesis reactions [1].

Propylene glycols and polypropylene glycols
Propylene glycols (PG) and polypropylene glycols (PPG) form another grouping of aliphatic organic compounds with two hydroxyl groups (diols). They are clear, colorless, odorless liquids with high boiling points and low freezing points. PG and PPG are excellent solvents for many organic compounds and are completely water-miscible at 20°C / 68°F up to a molecular weight of around 2,000. They are practically non-toxic and are approved as additives for food, pharmaceuticals and cosmetics. Their main oil industry application is in gas dehydration and oil dispersant operations. Propylene glycol is one of the ingredients in Corexit oil dispersant, which was used to break up oil slicks from the Deepwater Horizon accident.

Trihydric alcohols

The best-known example of a trihydric alcohol (triol) is glycerol. This is a non-toxic colorless, odorless, sweet-tasting viscous liquid widely used in foods and pharmaceutical formulations. As it depresses the freezing point of water, it is an effective anti-freeze agent. Glycerol has low water activity (a_w = 0.122 at 25°C / 77°F) and is used in oilfield operations as a gas hydrate inhibitor. Glycerol is rated PLONOR, i.e. it is included in the OSPAR list of substances used and discharged offshore that pose little or no risk to the environment.

B14.2.2 Glycol ethers

Glycol ethers are products of alcohols reacted with ethylene oxide or propylene oxide. They are clear liquids with high boiling points and low freezing points, and are characterized by their excellent solvency, chemical stability, and miscibility with both water and organic solvents. Glycol ethers are widely used as solvents in paint, coatings, inks and hard-surface cleaning fluids.

One of the best-known glycol ethers is butyl glycol, also known as 2-butoxyethanol or ethylene glycol monobutyl ether (EGMBE). Oilfield applications of EGMBE include i) stuck pipe release pills, ii) mutual solvents in well-stimulation operations, and iii) use in oil-spill dispersants. EGBME has the closest physical properties to mineral oils used in well drilling fluids, particularly in terms of viscosity and thermal conductivity.

B14.2.3 2-Pyrrolidone

N-methyl-2-pyrrolidone (NMP) is a member of a family of chemically-stable dipolar aprotic solvents with a five-membered lactam structure. It is a colorless to slightly yellow liquid that is miscible with water and most common solvents. NMP is used in a variety of chemical synthesis processes as an inert solvent and reaction medium. As hydrocarbons are very soluble in NMP, it is used on a large-scale to recover pure hydrocarbons while processing petrochemicals and in desulfurization of natural gases to remove hydrogen sulfide, carbon dioxide and organic sulfur compounds. It is also employed as an industrial solvent for plastic, waxes, resins and paints.

Several patents claim that NMP can be used for ion separation and purification in aqueous solutions. For instance, US patent 4,976,946 states NMP can separate potassium fluoride from organic salts of potassium in aqueous solution [7] and US patent 8,344,179 claims NMP can separate halide-based contaminants from formate brines [8].

In an invention far ahead of its time, US patent 4,498,994 claimed in 1985 that high-density clear solutions of calcium bromide dissolved in NMP could be used as HPHT well drilling and completion fluids [9]. The Mobil inventor found that these heavy NMP fluids could be viscosified with polyvinyl pyrrolidone polymer to yield clear non-aqueous drilling and completion fluids that retain their viscosity at 220°C / 428°F. The high-density NMP fluid had many beneficial features for drilling, including absorption of acid gases, shale stabilization, and reduced corrosion of metals.

B14.3 Formate solubility in non-aqueous solvents

The properties of the 12 non-aqueous solvents used for formate solubility tests are shown in Table 1, together with those of typical mineral oil used as the continuous phase of oil-based invert emulsion drilling fluids for comparison purposes. The listed non-aqueous solvents

Table 1 Non-aqueous solvents and their properties.

Solvent	Density at 20°C / 68°F		Boiling point		Freezing point		Flash point[1]		Viscosity at 20°C / 68°F	Thermal conductivity
	[g/cm^3]	[lb/gal]	[°C]	[°F]	[°C]	[°F]	[°C]	[°F]	[cP]	[W/m/K]
Monoethylene glycol (MEG)	1.11	9.31	197	386	-13	9	126	259	17	0.26
Diethylene glycol (DEG)	1.12	9.33	245	473	-9	16	154	309	36	0.19
Triethylene glycol (TEG)	1.13	9.39	288	550	-4	25	177	351	49	0.19
Polyethylene glycol (PEG 200)	1.13	9.39	>200	>392	-65	-85	185	365	60	0.23
Monopropylene glycol (MPG)	1.04	8.61	187	369	<-60	<-76	104	219	49	0.20
Dipropylene glycol (DPG)	1.03	8.59	232	450	<-60	<-76	124	255	75	0.17
Tripropylene glycol (TPG)	1.02	8.50	265	509	<-60	<-76	143	289	57	0.16
Polypropylene glycol (PPG 425)	1.01	8.42	>200	>392	-47	-53	>200	>392	84	0.16
Butyl glycol (EGMBE)	0.90	7.5	171	340	-77	-107	65	149	3	0.17
***N*-methyl-2-pyrrolidone (NMP)**	1.03	8.59	202	396	-24	-11	91	196	2	1.63
Methanol	0.79	6.59	65	149	-97	-144	12	54	1	0.20
Glycerol	1.26	10.5	290	554	18	64	177	351	1.5	0.28
Mineral oil	0.81	6.8	225	437	-29[2]	-20[2]	102	216	2	0.16

1) Closed-cup measurement. 2) Pour point.

Table 2 Solubility of sodium formate in non-aqueous solvents and water.

Solvent	Solvent density at 15.6°C / 60°F		Salt solubilized at 20°C / 68°F[1)]	Solution density at 15.6°C / 60°F		Solution a_w at 25°C / 77°F	
	[g/cm³]	[lb/gal]	[%wt]	[g/cm³]	[lb/gal]	Pure solvent	Saturated solution
Water	1.00	8.34	47	1.33	11.10	1.00	0.61
MEG	1.11	9.26	23	1.20	10.01	0.03	0.20
DEG	1.12	9.35	16	1.17	9.76	0.03	0.29
TEG	1.13	9.43	15	1.17	9.76	0.04	0.30
EGMBE	0.90	7.51	9	0.92	7.68	0.05	ND
Glycerol	1.26	10.52	24	1.33	11.10	0.12	0.26

1) Reported solubility might be slightly too high as salt was added in excess amounts.

are all relatively non-toxic, environmentally acceptable and already approved by regulatory oil industry authorities. The majority of these solvents score highly in environmental rankings, including 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 that pose little or no risk to the environment.

Solubility of high-purity dry cesium formate was determined for each of the 12 solvents in Table 1 [10]. Sodium formate and potassium formate solubilities were calculated in only five or six of the listed solvents.

An increasing amount of formate salt was added to each solvent over several days until the solutions were fully saturated at room temperature (around 20°C / 68°F). Tables 2, 3, and 4 summarize the outcome of the tests by showing percentage by weight of formate salt solubility achieved for each salt-solvent combination compared with salt solubility in water. As salts were added to excess in each case, leaving undissolved crystals present in equilibrium with the saturated solutions, reported solubility figures are slightly higher than real solubilities. Tables 2, 3 and 4 also show fluid density and water activity of the saturated formate solutions. Water activities of the formate solutions were generally higher than those of the solvent. This increased water activity could have been caused by absorption of water from the air during preparation, as the non-aqueous solvents are hygroscopic.

B14.3.1 Sodium formate

Sodium formate was moderately soluble in ethylene glycols, yielding solutions in the density range 1.17 – 1.20 g/cm³ / 9.8 – 10.0 lb/gal (Table 2). It was less soluble in EGMBE and solution density was lower than water. Sodium formate exhibited its highest solubility in glycerol. The saturated solution had density of 1.33 g/cm³ / 10.1 lb/gal, which matches saturated aqueous solutions of sodium formate. In all cases, water activities of non-aqueous solutions were much higher than solvents, but they were still at least 50% lower than saturated aqueous sodium formate solutions. No tests were carried out on polyethylene glycol, propylene glycols, polypropylene glycol, NMP or methanol.

B14.3.2 Potassium formate

Potassium formate showed good solubility in ethylene glycols (Table 3). The saturated MEG solution had density of 1.39 g/cm³ / 11.6 lb/gal. The saturated DEG and TEG solutions had densities of 1.30 g/cm³ / 10.8 lb/gal and 1.26 g/cm³ / 10.5 lb/gal respectively. Potassium formate also proved soluble in MPG with saturated solution density of 1.32 g/cm³ / 11.0 lb/gal. Potassium formate exhibited its highest solubility in glycerol. The saturated solution had density of 1.48 g/cm³ / 12.4 lb/gal, which is only 20% lower than saturated aqueous solutions of potassium formate. In all cases, water activities of non-aqueous solutions were much higher than solvents, but still up to 50% lower than saturated aqueous potassium formate solutions.

Potassium formate dissolved readily in EGMBE, but the solution then separated into two clear fluid phases. The same phenomenon was observed when potassium formate dissolved in NMP. Further investigation is required to i) find out what causes the phase separation, ii) how potassium formate is distributed between the two phases, and iii) what densities can be achieved in the two phases.

No tests were carried out on the polyethylene glycol, DPG and TPG propylene glycols, polypropylene glycol or methanol.

Table 3 Solubility of potassium formate in non-aqueous solvents and water.

Solvent	Solvent density at 15.6°C / 60°F		Salt solubilized at 20°C / 68°F 1)	Solution density at 15.6°C / 60°F		Solution a_w at 25°C / 77°F	
	[g/cm³]	[lb/gal]	[%wt]	[g/cm³]	[lb/gal]	Pure solvent	Saturated solution
Water	1.00	8.34	77	1.59	13.27	1.00	0.24
MEG	1.11	9.26	53	1.39	11.52	0.03	0.09
DEG	1.12	9.35	38	1.30	10.85	0.03	0.14
TEG	1.13	9.43	28	1.26	10.52	0.04	0.16
MPG	1.04	8.65	53	1.32	34.38	ND	0.17
EGMBE	0.90	7.51	Phase separated				
Glycerol	1.26	10.52	52	1.48	12.35	0.12	0.10

1) Reported solubility might be slightly too high as salt was added in excess amounts.

B14.3.3 Cesium formate

Cesium formate was generally more soluble than other formate salts in non-aqueous solvents. It showed good solubility in ethylene glycols (Table 4) and the saturated MEG solution containing 83% w/w cesium formate had remarkably high density of 2.22 g/cm³ / 18.53 lb/gal. The saturated DEG and TEG solutions had densities of 1.66 g/cm³ / 13.9 lb/gal and 1.38 g/cm³ / 11.5 lb/gal respectively. Cesium formate also proved to be soluble in propylene glycols. Density of saturated MPG was 1.76 g/cm³ / 14.7 lb/gal, reducing to 1.30 g/cm³ / 10.8 lb/gal in DPG and 1.20 g/cm³ / 10.0 lb/gal in TPG. Cesium formate exhibited high solubility in glycerol with the saturated solution achieving density of 1.96 g/cm³ / 16.4 lb/gal. It was also moderately soluble in methanol, providing fluid with density of 1.52 g/cm³ / 12.7 lb/gal. In most cases, water activities of non-aqueous solutions were higher than those of base solvents.

Cesium formate dissolved readily in PPG 425 and NMP, but in both cases the solutions then separated into two fluid phases. The lower phase of the PPG solution reached an astonishing density of 2.57 g/cm³ / 21.4 lb/gal before crystallizing (see Figure 1). The upper phase of the PPG 425 solution had density of 1.04 g/cm³ / 8.7 lb/gal. The lower phase of the saturated NMP solution was 2.53 g/cm³ / 21.1 lb/gal. The cesium formate solubility experiment with EGMBE needs to be repeated because the investigator may have terminated the test before salt saturation had been fully established.

Table 4 Solubility of cesium formate in non-aqueous solvents and water.

Solvent	Solvent density at 15.6°C / 60°F		Salt solubilized at 20°C / 68°F 1)	Solution density at 15.6°C / 60°F		Solution a_w at 25°C / 77°F	
	[g/cm³]	[lb/gal]	[%wt]	[g/cm³]	[lb/gal]	Pure solvent	Saturated solution
Water	1.00	8.34	83	2.30	19.19	1.00	0.25
MEG	1.11	9.26	83	2.22	18.53	0.03	0.05
DEG	1.12	9.35	57	1.66	13.85	0.03	0.20
TEG	1.13	9.43	33	1.38	11.52	0.04	0.11
PEG 200	1.13	9.43	30	1.37	11.42	ND	0.05
MPG	1.04	8.65	66	1.76	14.69	ND	0.12
DPG	1.03	8.59	33	1.30	10.84	ND	0.23
TPG	1.02	8.50	25	1.20	10.00	ND	0.29
PPG 425	1.01	8.42	ND	2.57 2)	21.43 2)	ND	ND
NMP	1.03	8.59	79	2.53 2)	20.35 2)	ND	ND
Methanol	0.80	6.67	36	1.52	12.67	ND	ND
EGMBE	0.90	7.51	16	1.01	8.43	0.05	0.03
Glycerol	1.26	10.52	64	1.96	16.36	0.12	0.08

1) Reported solubility might be slightly too high as salt was added in excess amounts.
2) The fluid formed two phases after addition of cesium formate. Density of the lower phase is shown here.

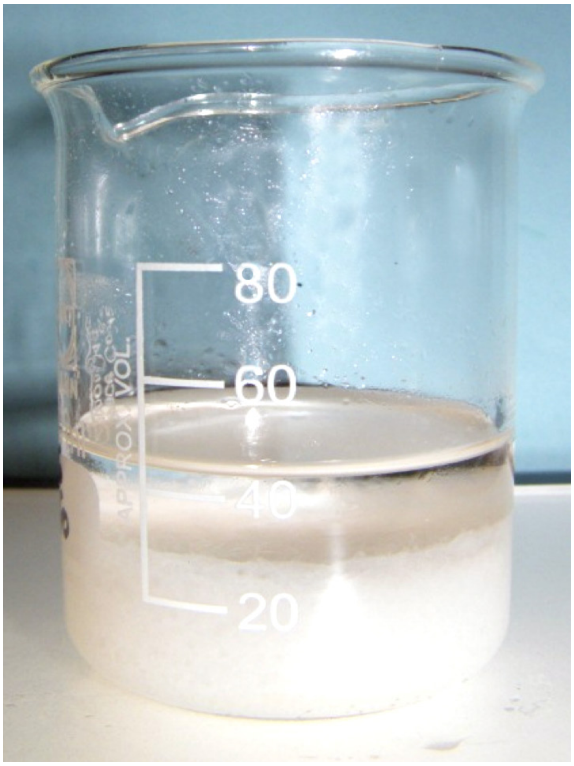

Figure 1 Phase separation in a solution of cesium formate dissolved in PPG 425. The lower phase turned back to a liquid on heating to 70°C / 158°F.

Testing was carried out with cesium formate dissolved in MEG to see how salt saturation levels varied with temperature. Results shown in Table 5 seem to indicate that solubility of cesium formate in MEG may decrease with increasing temperature. Further testing is required at temperatures above 40°C / 104°F.

Table 5 Solubility of cesium formate in MEG as a function of temperature.

Sample temperature		Density of saturated solution		Salt solubilized at 20°C / 68°F
[°C]	[°F]	[g/cm^3]	[lb/gal]	[%wt]
10	**50**	2.265	18.90	82.1
20	**68**	2.225	18.57	82.9
40	**104**	2.161	18.03	80.2

B14.3.4 Conclusions

All of the non-aqueous solvents assessed by Cabot in this study of formate solubility are approved and used in various upstream and downstream operations by the oil and petrochemical industries. The majority showed good solvency for formates and behaved in a conventional manner, forming clear and stable single-phase fluids. A small number of solvents (PPG, EGMBE and NMP) behaved in an unconventional manner, forming two distinct phases comprising a dense formate-rich solution at the bottom and a solvent-rich phase at the top. The volume of the solvent-rich upper phase reduced as more formate salt was added.

Cesium formate was the most soluble of the formate salts in non-aqueous solvents, yielding the highest density solutions. The solvents forming the highest density single-phase solutions with formate salts were MEG and glycerol, followed by MPG. Both MEG and glycerol are rated PLONOR (posing little or no risk to the environment) by the Paris Commission. It was interesting to find that methanol, with density of 0.80 g/cm^3 / 6.7 lb/gal, could be weighted up with cesium formate to form clear fluid with maximum density of 1.52 g/cm^3 / 12.7 lb/gal.

The highest single-phase solution density achieved was 2.22 g/cm^3 / 18.5 lb/gal with cesium formate dissolved in MEG. The non-aqueous solvents forming the highest density two-phase solutions with formate salts were NMP and PPG 425. Both solvents formed lower-phase solutions with densities greater than 2.5 g/cm^3 / 20.9 lb/gal in cesium formate, although these must have been super-saturated because they crystallized at room temperature over time. Formate salt solvation times in these solvents were occasionally very long, taking days or weeks of mixing to achieve full saturation levels.

Only half of the non-aqueous solvents listed in Table 1 were tested with sodium formate and potassium formate. Further tests are required to check solubility of these formates in the remaining solvents. The behavior of formate solutions in NMP, PPG and EGMBE also needs further investigation to explain the creation of two distinct fluid phases.

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