EVALUATION THE POTASSIUM BROMIDE AND ZINC BROMIDE BRINES FOR WORKOVER OPERATIONS

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Clear brines are used extensively as workover fluids because of their low damage characteristics. This work was conducted to study the physical properties of potassium and zinc bromide brines and the compatibility of these brines with different API gravity Saudi crude oils and formation water. Also, the effect of temperature on brine viscosity was studied. It was found that true crystallization temperature for potassium and zinc bromide brines were (-14 °C) and (-25 °C), respectively. These brines were found incompatible with the tested Saudi crude oils where stable emulsions were formed but light crude oil (42 °API) was compatible with potassium bromide. Also, potassium bromide brine showed compatibility with formation water while zinc bromide was incompatible with formation water because of NaCl scale precipitation. The tested brines have shown non-Newtonian (dilatants) behavior and the viscosity of brines decrease with increase in temperature. Viscosity – temperature correlations were found for the tested brines with high accuracy.

Keywords: Workover Fluids, Brine Crystallization, Demulsifiers, Rheology, Brine Viscosities

INTRODUCTION

Clear brines are used extensively as workover fluids because of their low damage characteristics. These brines are sodium chloride (NaCl), sodium bromide (NaBr), sodium formates, potassium chloride (KCl), potassium formates, calcium chloride (CaCl₂), calcium bromide (CaBr₂), zinc bromide (ZnBr₂)/calcium bromide (CaBr₂), and ammonium chloride (NH₄Cl). There are three basic selection criteria for completion brines; density, crystallization temperature and compatibility between completion brines and formation rocks and fluids [1,2,3]. The required brine density at surface temperature should be increased for bottom hole conditions to control the formation pressure. The crystallization temperature is the temperature at which the first crystal starts to appear when cooling the brines, where the least soluble salts precipitate causing operation problems [4]. The crystallization temperature is measured in the lab using pour points apparatus. If brines are in contact with incompatible formation water scales are formed causing blocking and corrosion in pipes, tanks and surface equipments [5]. Compatibility of well completion brines with crude oil is shown by
forming oil-water emulsion and/or sludges which may block the pores and causing formatting damage [3,6,7]. Demulsifiers are added to prevent stable emulsions [8]. Incompatible brines may damage the formation by clay swelling and blocking the pores. Studying the rheological properties of the completion brines is very important for calculating the frictional pressure loss in workstring during pumping process [9].

EXPERIMENTAL WORK

The experimental work conducted in this study involves the measurements of the physical and the rheological properties, crystallization temperature of potassium bromide (KBr) and zinc bromide (ZnBr₂) completion fluids, and checking the compatibility between these brines and formation water and some Saudi crude oils. Also, the effect of temperature on brine viscosity was studied. The rheological characteristics of the tested brines were measured by Brookfield Viscometer and their crystallization temperature was measured by Seta-lec Cloud and Pour Point Refrigerator.

RESULTS AND DISCUSSIONS

Based on the experimental work conducted in this study, the physical properties, rheological characteristics, crystallization temperature of potassium bromide and zinc bromide brines and their interaction with formation fluids were experimentally determined. The properties of potassium bromide and zinc bromide are tabulated in Table 1. Fig. 1 shows the effect of salt concentration and density of brines at 21 °C. It is clear that density of brine increases with increasing salt concentration.

<table>
<thead>
<tr>
<th>Brine</th>
<th>Density, gm/cc</th>
<th>pH</th>
<th>FCTA, °C</th>
<th>TCT, °C</th>
<th>LCTD, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>1.16</td>
<td>5.3</td>
<td>5.3</td>
<td>-15</td>
<td>-4</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>1.46</td>
<td>4</td>
<td>4</td>
<td>-27</td>
<td>-15</td>
</tr>
</tbody>
</table>

Table 1

Properties of potassium bromide and zinc bromide brines.
RHEOLOGICAL BEHAVIORS OF THE TESTED BRINES

The rheological behaviors of the completion brines are needed for calculating the frictional loss in workstring during pumping process. The rheological behaviors of KBr and ZnBr$_2$ brines were determined by measuring the viscosity of brines using Brookfield Viscometer (LV model) at different temperatures and shear rates. Viscosity measurements are plotted versus shear rates in Figs 2 and 3. These figures show that the viscosity of brine increases with increasing shear rate. This means that the viscosity of brines exhibit non-Newtonian dilatants behavior. In this study power law equation was applied to study the rheological behavior of the tested brines as presented by the following equation:

$$\tau = k\gamma^n.$$

DETERMINATION OF RHEOLOGICAL BEHAVIOR PARAMETERS

On logarithmic coordinates, shear stress is plotted as a linear function of shear rate at various temperatures for (1.16 gm/cm$^3$) KBr and (1.46 gm/cm$^3$) ZnBr$_2$ brines as it is shown in Figs 4 and 5. The slope of the straight-line (n) and the intercept value of the line on the shear stress axis where shear rate equals unity, (K) determine the rheological behavior of the brines. The values of the rheological parameters n and K were found and tabulated in Tables 2 and 3 with high accuracy. These results show that the tested brines were non-Newtonian (dilatant) where n was larger than unity.

Figure 1. The effect of salt concentration on density of brine at 21 ºC
Figure 2. Brine viscosity vs. shear rate for 1.16 gm/cc potassium bromide at different temperatures

Figure 3. Brine viscosity vs. shear rate for 1.46 gm/cc zinc bromide at different temperatures
Figure 4. Shear Rate Vs. Shear Stress for 1.16 gm/cc Potassium Bromide Brine at different temperatures

Figure 5. Shear Rate Vs. Shear Stress for 1.46 gm/cc zinc bromide brine at different temperatures
Table 2

Rheological properties of 1.16 gm/cc potassium bromide brine

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>K, mPa. sec^n</th>
<th>n</th>
<th>Fluid type</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>1.422</td>
<td>1.154</td>
<td>Dilatant</td>
<td>0.997</td>
</tr>
<tr>
<td>24</td>
<td>0.435</td>
<td>1.247</td>
<td>Dilatant</td>
<td>0.989</td>
</tr>
<tr>
<td>35</td>
<td>0.542</td>
<td>1.236</td>
<td>Dilatant</td>
<td>0.990</td>
</tr>
<tr>
<td>50</td>
<td>0.342</td>
<td>1.254</td>
<td>Dilatant</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Table 3

Rheological properties of 1.46 gm/cc zinc bromide brine

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>K, mPa. sec^n</th>
<th>n</th>
<th>Fluid type</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>3.493</td>
<td>1.159</td>
<td>Dilatant</td>
<td>0.991</td>
</tr>
<tr>
<td>24</td>
<td>0.942</td>
<td>1.186</td>
<td>Dilatant</td>
<td>0.990</td>
</tr>
<tr>
<td>35</td>
<td>0.615</td>
<td>1.228</td>
<td>Dilatant</td>
<td>0.992</td>
</tr>
<tr>
<td>50</td>
<td>0.292</td>
<td>1.330</td>
<td>Dilatant</td>
<td>0.996</td>
</tr>
</tbody>
</table>

**EFFECT OF TEMPERATURE ON THE VISCOSITY OF THE TESTED BRINES**

Fig. 6 shows the variation in viscosity with temperature for 1.16 gm/cm^3 potassium bromide at shallow depth and 1.46 gm/cm^3 zinc bromide at medium depth has been carried out at temperatures -10, 25, 35 and 50 °C and shear rate of 36.71 sec^{-1}. It shows that viscosity of potassium bromide can be reduced by an average of 64% by heating from -10 °C to 50 °C. The variation in viscosity of 1.16 gm/cm^3 potassium bromide brines with temperature was found by the following correlation:

\[ \mu_{KBr} = -3E-06T^3 + 0.000T^2 - 0.04T + 2.028 \]  \( (1) \)

Also the viscosity of 1.46 gm/cm^3 zinc bromide brine can be reduced by an average of 82% by heating from -10 °C to 50 °C. The variation in viscosity of 1.46 gm/cm^3 zinc bromide brine with temperature was found by the following correlation:

\[ \mu_{ZnBr2} = -2E-05T^3 + 0.002T^2 - 0.147T + 4.025 \]  \( (2) \)

Viscosity-temperature correlations for the tested Brines were found with high accuracy \( (R^2 = 1) \). Other Brines can be useful for deep wells such as calcium chloride brines.
The crystallization temperature of brine is defined by the terms FCTA, TCT and LCTD. Crystallization temperatures of 1.16 gm/cm³ potassium bromide and 1.46 gm/cm³ zinc bromide brines are shown in Figs 7 and 8. Fig 7 shows that when KBr (1.16 gm/cm³) was cooled approximately at a rate 1 °C/min the first crystal appeared at -15 °C (FCTA). The heat of crystallization heated the brine up to -14 °C (TCT). Further cooling in the bath decreasing the brine temperature further, causing more crystals to fall out of solution. When the brine warmed to 1 °C/min the last crystal redissolved at -4 °C (LCTD). Fig 8 shows the crystallization curve of ZnBr₂ (1.46 gm/cm³). FCTA appeared at -27 °C, TCT was equal to -25 °C and LCTD was equal to -15 °C.

Figure 6. Viscosity of potassium bromide and zinc bromide vs. temperature at shear rate (36.71 sec⁻¹)

CRYSTALLIZATION TEMPERATURE
Figure 7. Crystallization curve for 1.16 gm/cc potassium bromide brine

Figure 8. Crystallization curve for 1.46 gm/cc inc Bromide Brine
COMPATIBILITY OF KBR AND ZNBR2 BRINES WITH SOME SAUDI CRUDE OILS

Heavy (10 °API), medium (22 °API) and light (42 °API) Saudi crude oils were added to 1.16 gm/cm³ potassium bromide and 1.46 gm/cm³ zinc bromide (80 % by volume crude oil and 20 % brine) to prevent stable emulsions with well shaking. It was found that brines were incompatible with the tested crude oil except light crude oil where unstable emulsion was formed with KBr/brine (water separated after 10 minutes). Therefore there in a need to add demulsifiers to prevent forming stable emulsions.

COMPATIBILITY OF KBR AND ZNBR2 BRINES WITH WATER

Incompatibility of brines with formation water will cause the formation of scales which cause formation damage. 50 ml of KBr (1.16 gm/cm³) and ZnBr2 (1.46 gm/cm³), were added to 50 ml of NaCl solution having various densities. Table 4 shows the compatibility data for KBr (1.16 gm/cm³) and ZnBr2 (1.46 gm/cm³) mixed with NaCl formation water having various densities at 21 °C and 71 °C. Brine densities are reported at a reference temperature of 21 °C. The data indicate that no precipitation was shown by mixing 1.44 gm/cm³ of NaCl with ZnBr2 (1.46 gm/cm³) at 21 °C. The solubility of NaCl increases as the temperature of the brine mixture increases.

CONCLUSION

Based on the results of the experimental work the following conclusions are obtained:

- The tested brines are incompatible with the tested crude oils but light crude oil (42°API) formed unstable emulsion with (1.16 gm/cm³) potassium bromide and there is a need to add demulsifiers to heavy crudes to prevent forming stable emulsions.
- Traces of NaCl scale precipitation formed with (1.46 gm/cm³) zinc bromide when density of NaCl increases to 1.44 gm/cm³.
- Potassium bromide and zinc bromide brines behave non-Newtonian (dilatant) where brine viscosity increases with increase in shear rate.
- Viscosity-temperature correlations were formed for the tested brines samples with high accuracy.
NOMENCLATURE

K = consistency index in power-law, mPa.s
n = flow behavior index in power-law
T = temperature, ºC
FCTA = first crystal to appear, ºC
TCT = true crystallization temperature, ºC
LCTD = last crystal to dissolve, ºC

Greek letters

µ = viscosity of brine, cp
τ = shear stress, mPa
γ = shear rate, s⁻¹

REFERENCES


