The Study of Donor-Acceptor Equilibria in Oil-Displacing Compositions Based on Acid Coordinating Solvents

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Abstract. The acidity of donor-acceptor complexes of boric acid with glycerol and sorbitol has been studied in aqueous solutions using pH-metry and electrical conductivity methods. A theoretical model of donor-acceptor acid-base equilibria in boric acid – polyol – water systems has been created. The constants of polyol boric acids formation and ionization were determined. The constants of glycerol and sorbitol boric acids formation were 0.05 and 0.06 \( l^2 \cdot mol^{-2} \), and those of glycerol and sorbitol boric acids ionization were 7.1 \( \cdot 10^{-6} \) mol \( \cdot l^{-1} \) and 3.2 \( \cdot 10^{-3} \) mol \( \cdot l^{-1} \), respectively. The systems studied were used to create new oil-displacing compositions for enhanced oil recovery.

1. Introduction

Currently, the actual scientific and technical problem is the development of physicochemical methods to increase the oil recovery of heavy high-viscosity oil deposits [1, 2]. These deposits are predominantly located in carbonate reservoirs. Among physical-chemical methods of influencing carbonate oil-saturated reservoirs with the aim of increasing oil recovery, the most widely used is injection of solutions of acid oil-displacing compositions. To improve constantly the compositions, make them more complex and extend a range of their useful functions is a general trend. Along with individual acids, complex acids, which are formed as a result of donor-acceptor interaction of the components of the composition are used. The composition and properties of complex acids are regulated by the concentrations and ratios of the donor and acceptor. Complex acids have surface-active properties and can increase the oil recovery of a low-permeability matrix of the reservoir at the same time due to dissolution and capillary counter-current impregnation of fractured-porous rock.

In this work, the acidic properties of complex acids based on boric acid and coordination solvents – polyatomic alcohols (polyols), such as glycerol and sorbitol, are investigated. Inorganic polyacid-polyol systems form complex acids, which are much stronger than the initial acid, due to donor-acceptor interaction [3, 4]. Donor-acceptor interaction enhances the acidic properties of oil-displacing compositions and increases the duration of their action in the reservoir by increasing the buffer capacity and expanding the range of the buffer action in the acidic pH range. Donor-acceptor interaction proceeds in the medium of an aqueous solution of a polyol (polyhydric alcohol) – glycerol and sorbitol. Such a solution is a coordinating solvent the polyol in it is a Lewis base, an electron pair donor. Dissolved in a coordinating solvent, Lewis acid – boric acid – as well as aqua ions of some metals: calcium, magnesium, iron, and aluminum – are acceptors of the donor electron pair. A donor-acceptor chemical bond has the properties of a polarized covalent bond and is called a coordination or...
dative bond. The interaction of the donor and the acceptor leads to the formation of a donor-acceptor molecular complex called the coordination compound or adduct. The complex is a much stronger acid than the original Lewis acid. This fact aroused interest in Russia and abroad in the use of complex acids in physical-chemical technologies for enhancing oil recovery.

2. Donor-acceptor equilibria in solutions

Molecules of the complex acid are able to interact with metal aqua ions due to their hydroxyl alcohol groups. Figure 1 shows the reaction scheme, which reflects the stereochemical feature of the glycerol boric acid molecule – its ability to form soluble outer-sphere cyclic complexes with metal ions due to terminal hydroxyl groups. When the concentration of metal aqua ions in solution increases, along with cyclic structures, the formation of polymer-like associates is possible, in which metal aqua ions play the role of bridges connecting the complex acid molecules to linear and branched spatial associative structures. As a rule, such a structure rotation leads to a significant increase in viscosity. The method of regulating the viscosity and density by adding salts of these metals can be useful for regulating the physicochemical and rheological properties of the compositions. In addition, this interaction contributes to the compatibility of complex acids based on polyols with formation waters, especially with highly mineralized, with a high content of calcium and magnesium salts.

![Diagram of the interaction of glycerol boric acid with a metal cation in solution with the formation of a soluble outer-sphere cyclic complex.](image)

Figure 1. Diagram of the interaction of glycerol boric acid with a metal cation in solution with the formation of a soluble outer-sphere cyclic complex.

The quantitative characteristic of donor-acceptor interactions in solutions of polybasic acids and polyols are the complexation and ionization (dissociation) constants. Knowing of the constants allows one to calculate the acidity of oil-displacing compositions, their buffer capacity, to predict and model their behavior under reservoir conditions, in particular, their interaction with reservoir water and reservoir rock. The theoretical aspects of the calculation of the constants for the formation and ionization of donor-acceptor complexes of polybasic acids with polyols are summarized below using experimental data obtained by methods of pH-metry and electrical conductivity. The presentation is conducted on the example of glycerol boric acid. Calculations are given for all investigated acids and aqua metals.

Boric acid, when dissolved in an aqueous glycerol solution, almost instantaneously forms glycerol boric acid, dissociating into monobasic acid ions. The solution is established dynamic equilibrium of two consecutive stoichiometric reactions:

- formation of glycerol boric acid:
  \[ \text{H}_3\text{BO}_3 + 2 \text{C}_3\text{H}_6\text{O}_3 = \text{C}_6\text{H}_{12}\text{O}_6\text{BH} + 3 \text{H}_2\text{O}; \]
- ionization, acid dissociation of glycerol boric acid:
  \[ \text{C}_6\text{H}_{12}\text{O}_6\text{BH} = \text{C}_6\text{H}_{12}\text{O}_6\text{B}^- + \text{H}^+. \]

In symbolic form, these reactions can be represented as:

- formation of glycerol boric acid:
  \[ \text{HB} + 2 \text{G} = \text{HBG}_2; \]
  \[ \text{HBG}_2 = \text{BG}_2^- + \text{H}^+. \]

where HB is boric acid, G is glycerol, HBG₂ is glycerol boric acid.
The formula for the formation constant $K_c$ of glycerol boric acid is:

$$K_c = \frac{c_{hbg2}}{c_{hb} \cdot c_g^2}, \quad (1)$$

where $c_{hbg2}$ is the concentration of glycerol boric acid, $c_{hb}$ is the concentration of boric acid, and $c_g$ is the concentration of glycerol.

Since the concentrations of the anion of glycerol boric acid and the hydrogen cation are equal, the formula for the ionization constant $K_d$ of glycerol boric acid is:

$$K_d = \frac{c_{bg2}}{c_{hbg2}} \quad \text{or} \quad K_d = \frac{c_h^2}{c_{hbg2}}, \quad (2)$$

where $c_{bg2}$ is the concentration of the glycerol boric acid anion, $c_h$ is the concentration of the hydrogen cation.

The material balance equation, which takes into account the formation and ionization of glycerol boric acid, has the form:

$$c_{hbg0} = c_{hb} + c_{hbg2} + c_{bg2}, \quad (3)$$

where $c_{hbg0}$ is the stoichiometric concentration of glycerol boric acid.

The concentration of anions of glycerol boric acid $c_{bg2}$, which is an organic acid, is much less than the concentration of molecular forms. Therefore, the material balance equation can be written in the form:

$$c_{hbg0} = c_{hb} + c_{hbg2}, \quad (4)$$

The joint solution of equations (1, 2, and 4) makes it possible to obtain a formula expressing the dependence of the concentration of hydrogen cations or anions of glycerol boric acid on the concentrations of boric acid and glycerol. The formula makes it possible to calculate the constants of formation and ionization of glycerol boric acid on the basis of experimental data of methods of pHmetry and electrical conductivity:

$$h(c_{hbg0}, c_g^0) = \frac{K_d K_c c_{hbg0}^2 c_g^2}{1 + K_c c_{hbg0}^2 c_g^2}, \quad (5)$$

The pH value is the negative decimal logarithm of the concentration of hydrogen ions:

$$pH(c_{hb0}, c_g^0) = -\log\left(h(c_{hb0}, c_g^0)\right).$$

Logarithmic equation (5) for the concentration of hydrogen ions, we get:

$$pH(c_{hb0}, c_g^0) = -\frac{1}{2} \log\left(\frac{K_d K_c c_{hbg0}^2 c_g^2}{1 + K_c c_{hbg0}^2 c_g^2}\right). \quad (6)$$

In studies using the method of electrical conductivity, various concentration dependences of the specific electrical conductivity (SEC or $\kappa$ – greek kappa) solutions were measured. The theoretical formula linking the SEC with the constants of formation and ionization of glycerol boric acid can be obtained on the basis of the theory of electrolytes. According to the theory, the SEC is related to the equivalent electrical conductivity $\lambda_{hbg2}$ of glycerol boric acid by the formula:

$$\kappa = \lambda_{hbg2} \cdot c_{hbg2} = \lambda_{hbg2} \cdot c_{hbg2}^2, \quad (7)$$

where $\nu = 2$ is the stoichiometric coefficient of the reaction of ionization of glycerol boric acid.

The equivalent electrical conductivity of glycerol boric acid is equal to the sum of the equivalent electrical conductivities of the hydrogen cation $\lambda_h$ and the glycerol boric acid anion $\lambda_{bg2}$:

$$\lambda_{hbg2} = \lambda_h + \lambda_{bg2}, \quad (8)$$

The equivalent electrical conductivity of the ion $\lambda_i$ according to the Walden – Pisarzhevsky rule is related to the viscosity of the solvent $\eta$ and the radius of the hydrated ion $r_i$ by the formula:

$$\lambda_i = \frac{c_e N_f}{\eta r_i}, \quad (9)$$

where $c_e$ is the electron charge, $N_f$ is the Faraday number.

The combination of formulas (5, 7-9) allows to obtain the equation linking the experimental values of SEC and viscosity with the constants of the formation and ionization of glycerol boric acid:
The radius of the hydrated hydrogen cation \( r_h = 0.25 \text{ nm} \) is calculated by formula (9) using the reference value of the limit equivalent electrical conductivity of the hydrated hydrogen ion \( \lambda_{i} = 330 \text{ S} \cdot \text{cm}^{-2} \cdot \text{mol}^{-1} \) and viscosity \( \eta = 1 \text{ MPa} \cdot \text{s} \) at 22 °C [5]. The radius of the anion of glycerol boric acid is calculated by the formula

\[
\kappa(c_{\text{chho}}, c_{\text{g}}) = \sqrt{\frac{K_d c_{\text{chho}}}{1 + K_d c_{\text{chho}}} \cdot \frac{z_0 N_F}{6 \pi \eta \eta v} \left( \frac{1}{r_{\text{chho}}} + \frac{1}{r_h} \right)},
\]

where \( m_{w_g} = 92.1 \text{ g/mol} \) is the molecular weight of glycerin, \( \rho_g = 1.26 \text{ g/cm}^3 \) is the density of glycerol, \( N_A \) is the Avogadro number.

3. Materials and methods

For laboratory studies of acid-base equilibria in systems with donor-acceptor interactions: polybasic inorganic boric acid and polyhydric alcohol (glycerol and sorbitol) were prepared solutions of boric acid with concentrations of 1, 5 and 10% wt. in water-alcohol solvents with concentrations of polyhydric alcohols from 10 to 70% wt. Chemically pure reagents and distilled water were used. The dependence of pH, specific conductivity, viscosity and density of solutions on the concentration of components was determined. The pH values of the solutions were determined by a potentiometric method using a microprocessor laboratory pH meter manufactured by HANNA Instruments, the specific electrical conductivity using an ANION 4120 conductometer, and the density by a pycnometric method. The viscosity of solutions of polyatomic alcohols was determined using the vibration “Reokinetic” viscometer with a tuning fork sensor. The measurements were carried out at a temperature of 20–23 °C. The research results are presented in Figures 2-6 and in Table 1.

4. Results and discussion

Figures 2 - 5 show the experimental graphs of pH and SEC solutions of the polyol concentration at a constant concentration of boric acid and calculated by equations (6) and (10). The graphs in Figures 3 and 5 demonstrate the strong influence of the viscosity of the solvent on the electrical conductivity. In the framework of the theory of nonequilibrium phenomena in electrolyte solutions, this is due to the dual effect of the polyol. On the one hand, an increase in the concentration of the polyol leads to an increase in the concentration of the electric current carriers – anions of polyol boric acid and hydrogen cations in accordance with the reactions of formation and ionization of the acid. On the other hand, an increase in the concentration of the polyol leads to an increase in viscosity, which causes inhibition of the movement of current carriers and, thus, to a decrease in SEC. Initially, the formation of current carriers dominates, then, after the point of extremum, viscous drag becomes the main factor. Extremum SEC is in the range of concentration 25-35% wt. glycerol and sorbitol.

From figures 2, it can be seen that the decrease in pH with increasing concentration of the polyol is monotonic. This is due to the continuous shift of ionization equilibrium reaction, conjugate with a shift reaction to form a complex of boric acid with a polyol.

The extreme nature of the concentration dependences for SEC and monotonic for pH indicates changes in the structure of the coordinating solvent, starting from 30% wt. polyol.

The coordinated processing of experimental concentration dependences of pH and specific conductivity of glycerol boric and sorbitol boric acids solutions by equations (6) and (10) allowed us to obtain the values of the formation constants and ionization of glycerol boric and sorbitol boric acids in the polyol coordinating solvent (Table 1). As can be seen from the table, sorbitol boric acid is much stronger than glycerol boric acid. Therefore, of interest is the combined use of glycerol and sorbitol in oil-displacing compositions.
Table 1. Concentration constants of formation and ionization of glycerol boric and sorbitol boric acids in a polyol coordinating solvent.

| Acid type     | $K_c$, L$^2$·mol$^{-2}$ | $K_d$, mol·L$^{-1}$ |
|---------------|--------------------------|---------------------|
| Glycerol boric| 0.05                     | 7.1·10$^{-6}$       |
| Sorbitol boric| 0.06                     | 3.2·10$^{-3}$       |

Figure 2. Solutions pH of glycerol boric acid, depending on the concentration of glycerol at a constant concentration of boric acid.

Figure 3. Specific conductivity of solutions of glycerol boric acid, depending on the concentration of glycerol at a constant concentration of boric acid.

Figure 4. Solutions pH of sorbitol boric acid, depending on the concentration of sorbitol at a constant concentration of boric acid.

Figure 5. Specific conductivity of solutions of sorbitol boric acid, depending on the concentration of sorbitol at a constant concentration of boric acid.

The obtained values of the constants were used to calculate the buffer capacity of the compositions. Buffer capacity is the amount of acid or alkali, by adding which the pH of the buffer solution is changed by one. The higher the buffer capacity, the more the solution resists changing its pH with the addition of acids, alkalis or dilution. For a buffer system consisting of polyol boric acid and its salt, the analytical expression for the buffer capacity $\beta$ is:

$$\beta(pH, c_a) = 2.303 \cdot \left( \frac{K_a \cdot 10^{-pH}}{(K_a + 10^{-pH})^{0.5}} + 10^{-pH} + \frac{10^{-pK_w}}{10^{-pH}} \right),$$  \hspace{1cm} (12)

where pH is a pH value; $c_a$ is the acid concentration; $K_a$ is the acid dissociation constant, $pK_w$ is the ionic product of water.

Figure 6 shows the graphs of the buffer capacity of systems of glycerol and sorbitol acids separately and mixed with each other, depending on pH. The graphs are calculated by equation (12).
Figure 6. Buffer capacity of solutions for glycerol boric (βgb), sorbitol boric (βsb) acids and solution of their mixture in a ratio of 7:3 (βgb + βsb).

As can be seen from the figure, range buffering acid mixture is a sum of individual acid ranges systems. This circumstance makes it possible to adjust the range of the buffer action by using in the compositions a mixture of polyol boric acids in different ratios.

5. Conclusions
A theoretical model of donor-acceptor acid-base equilibria in coordinating polyol solvents was created, which made it possible to determine the constants of the formation and ionization of polyol boric acids using pH-measurement and electrical conductivity methods. The obtained values of the constants were used to calculate the buffer capacity of the compositions. The possibility of regulating the range of the buffer action is shown by using a mixture of polyol boric acids in compositions in different ratios. The congruence of experimental data with the results of calculations using a theoretical model indicates the perspectives of developing oil-displacing acidic compositions based on surfactants, coordinating solvents and complex compounds in order to intensify the development and increase oil recovery of heavy high-viscosity oil.

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