



# Acid/base and metal complex solution chemistry of sulfonated polyacrylate copolymer versus temperature and ionic strength<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 24 June 2016

Received in revised form

7 November 2016

Accepted 9 November 2016

Available online 10 November 2016

### Keywords:

Mineral scale

Sulfonated polyacrylate copolymer (VS-Co)

Acid/base chemistry

Metal complex solution chemistry

Electrostatic model

## ABSTRACT

Sulfonated polyacrylate copolymer (also known as vinyl sulfonated co-polymer; VS-Co) have been widely used in mineral scale control. However, the speciation chemistry of such polymers in solution is not fully understood. In this paper, the acid-base and calcium complex solution chemistry of a VS-Co has been determined from 0.01 to 2 m ionic strength and from 25 to 90 °C by combining electrostatic theory with potentiometric titrations. To process the titration data, VS-Co is treated as a hypothetical, averaged monoacid, HA, with the same concentration of the active carboxylic functional groups of VS-Co. The acid and calcium dissociation reactions of this acid are simply considered as 1:1 type hypothetical reactions, namely  $HA \leftrightarrow H^+ + A^-$  and  $Ca(A \cdots A) \leftrightarrow Ca^{2+} + (A \cdots A)^{2-}$ , with  $(A \cdots A)^{2-}$  as an arbitrary combinations of two dissociated  $A^-$  units. The microconstants of the acid dissociation reaction are fitted with a linear electrostatic model with  $pK_a = pK_{a,intr} + b_{elec}\theta_{A^-}$ , where  $pK_{a,intr}$  is an intrinsic constant referring to the condition of zero dissociation,  $\theta_{A^-}$  is the deprotonated fraction of carboxylic functional groups and  $b_{elec}$  is an electrostatic factor based on polyelectrolyte theory. Similarly, the microconstants of the  $Ca^{2+}$  dissociation reaction are fitted with  $pK_{CaA_2} = pK_{CaA_2,intr} + 2b_{elec}\theta_{A^-}$  with doubled electrostatic effect since the complexation of  $Ca^{2+}$  with the polymer is considered to neutralize two negative charges. To quantitatively describe the speciation of VS-Co at various conditions, the  $pK_{a,intr}$ ,  $pK_{CaA_2,intr}$ , and  $b_{elec}$  values are fitted empirically as a function of temperature ( $T$ , K), and ionic strength ( $I$ , m):  $pK_{a,intr} = 5.068 - \frac{128.398}{T} - 0.924 \times I^{1/2} + 0.311 \times I$ ;  $pK_{CaA_2,intr} = 5.754 - \frac{888.644}{T} - 5.749 \times I^{1/2} + 2.221 \times I$

$b_{elec} = 3.234 - 1.321 \times I^{1/2} + 0.399 \times I$ . Fitted results suggests no significant effect of temperature on the electrostatic factor  $b_{elec}$ , which is consistent with electrostatic theory. Results from this study can be used to predict the equilibria of VS-Co in a solution, at various temperature, ionic strength, pH, and metal concentrations.

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## 1. Introduction

Mineral scale formation has long been a concern in industry. For the oil and gas industry alone, it costed \$2.0 billion dollars in 2014 (Kelland, 2014). Scale occurs in many industrial processes including oil/gas and thermal wells, power generators, boilers, and cooling towers. Scale forms when mineral precipitates deposit on the pipe wall or the surface of equipments. Chemical scale inhibitors have been widely used to prevent or control mineral scale formation (Cowan and Weintritt, 1976; Kan and Tomson, 2010; Kelland, 2014). Common classes of scale inhibitors includes nonpolymeric

phosphonates and aminophosphonates, and polymers such as polycarboxylates, phosphino polymers, polysulfonates, etc. Various copolymers and terpolymers with carboxylic, phosphonic acid, and/or sulfonic acid groups are also good scale inhibitors (Kan and Tomson, 2010; Kelland, 2014).

Among these of scale inhibitors, sulfonated polyacrylate copolymer (also known as vinyl sulfonated co-polymer; VS-Co) have been widely used because of their good scale inhibiting capability, high thermal stability, and calcium tolerance (Fink, 2015; Kelland, 2014; Wang et al., 2014; Yan et al., 2014). A typical structure of VS-Co molecules is shown in Fig. 1. However, the application of such inhibitors can be limited by the insufficient understanding on their physiochemical properties, e.g., acid/base and metal complex solution chemistry. Such information is critical because as it has been demonstrated previously, only the deprotonated and metal

<sup>☆</sup> This paper has been recommended for acceptance by Prof. M. Kersten.

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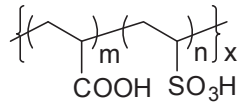


Fig. 1. Structure of sulfonated polycarboxylic acid. The ratio of  $-\text{SO}_3\text{H}$ :  $\text{COOH}$  functional groups of the polymer used in this study is  $\sim 0.73$ .

complexed fraction of inhibitor molecules are active in inhibiting the crystallization of mineral scales (Kan et al., 2005; Tomson et al., 2008, 1994; Xiao et al., 2001). In addition, the solubility of scale inhibitors in solution is important to understand certain processes such as the inhibitor squeeze treatment during oil and gas production (Tomson et al., 1994, 2006). In order to quantitatively predict the adsorption and precipitation of scale inhibitors at various physicochemical conditions, a better understanding of their speciation chemistry is a prerequisite.

The aim of this paper is therefore to characterize the acid/base and metal complex solution chemistry of commonly used VS-Co inhibitors combining potentiometric titrations and electrostatic models. The speciation chemistry of a typical VS-Co inhibitor was systematically studied under various temperature (25–90 °C) and ionic strength conditions (0.1–2 m). A relatively high ionic strength solution is used here to better mimic the produced brine during oil and gas production (Tomson et al., 1994; Xiao et al., 2001). Generally, the proton and metal association/dissociation reaction of polyelectrolytes can be expressed in several ways, such as the aqueous/polymer phase equilibria-Donnan model, Manning theory, and 1:1 type site binding reaction (Ephraim et al., 1986; Hermans and Overbeek, 1948; Katchalsky et al., 1954; Kotin and Nagasawa, 1962; Manning, 1981; Marinsky and Ephraim, 1986; Miyajima et al., 1997; Morel and Hering, 1993; Tanford, 1961; Tipping et al., 1990). In this paper, a simple empirical model was used to represent the experimental data over wide ranges of temperature and ionic strength. This model developed by Xiao et al. (2001) was justified in explaining the speciation chemistry of phosphino-polycarboxylic acid (PPCA), one commonly used inhibitor in scale control. A brief description of this model is provided below.

## 2. Equilibrium reactions and electrostatic model

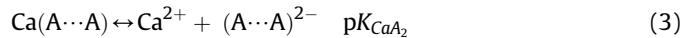
To solve the speciation chemistry of VS-Co, the functional groups on the polymer are simplified as a hypothetical, averaged monoacid, HA. The protonated and dissociated species are denoted as HA and  $\text{A}^-$ , respectively. The sulfonate groups are not specifically treated since (1) the sulfonate groups on each VS-Co molecule is always dissociated during the titration, and (2) the electrostatic effect due to the sulfonate group is constant for all the titrations. Since all carboxylic groups are physically seated on the same flexible backbone, both proton and metal association/dissociation reactions are treated as 1:1 type charge neutralization reactions. That is, the association of one monovalent cation or divalent cation with VS-Co neutralizes one or two charges, equivalent to one  $\text{A}^-$  or one  $(\text{A}\cdots\text{A})^{2-}$  unit, respectively. The two reactions are expressed by Eqs (1)–(4), respectively:



with

$$pK_a = -\log \frac{\{\text{H}^+\}[\text{A}^-]}{[\text{HA}]} \quad (2)$$

and



with

$$pK_{\text{CaA}_2} = -\log \frac{[\text{Ca}^{2+}][\text{A}\cdots\text{A}]^{2-}}{[\text{Ca}(\text{A}\cdots\text{A})]} \quad (4)$$

where  $pK_a$  is the conditional acid dissociation constant of A units on the polymer,  $pK_{\text{CaA}_2}$  the conditional constant of the  $\text{Ca}^{2+}$  dissociation reaction,  $\{\text{H}^+\}$  the activity given by  $\{\text{H}^+\} = 10^{-\text{pH}}$ , and  $[\ ]$  the concentration in molality. Note that the concentration of  $(\text{A}\cdots\text{A})^{2-}$  units will be half of  $\text{A}^-$ . Also, the  $(\text{A}\cdots\text{A})^{2-}$  unit here does not necessarily mean that the monomer units A are adjacent to each other on the polymer backbone. In fact, it is not possible to determine the position of a single A unit on a polymer based on titration data.

Since it is impossible to determine the microconstants of individual A groups, a polymer/electrostatic model can be used to describe such reactions considering that all the A groups on the polymer are the same. For example, Eq 2, and 4 can be rewritten as:

$$pK_a = \text{pH} - \log \frac{[\theta_{\text{A}^-}]}{[\theta_{\text{HA}}]} \quad (5)$$

$$pK_{\text{CaA}_2} = \text{pCa} - \log \frac{[\theta_{\text{A}^-}]}{[\theta_{\text{CaA}_2}]} \quad (6)$$

with

$$\theta_{\text{A}^-} = \frac{[\text{A}^-]}{C_A} = \frac{2[(\text{A}\cdots\text{A})^{2-}]}{C_A} \quad (7)$$

$$\theta_{\text{CaA}_2} = \frac{2[\text{Ca}(\text{A}\cdots\text{A})]}{C_A} \quad (8)$$

$$\theta_{\text{HA}} = \frac{[\text{HA}]}{C_A} = 1 - \theta_{\text{A}^-} - \theta_{\text{CaA}_2} \quad (9)$$

where  $\theta_{\text{A}^-}$  stands for the dissociated fraction of the averaged monoacid of VS-Co,  $\theta_{\text{CaA}_2}$  stands for the calcium-complexed fraction of the averaged monoacid of VS-Co,  $C_A$  the total concentration of VS-Co as an averaged monoacid, and  $\text{pCa}$  the negative logarithm of free  $\text{Ca}^{2+}$  concentration.

To quantify the change of  $pK_a$  and  $pK_{\text{CaA}_2}$  with  $\theta_{\text{A}^-}$ , an electrostatic model will be applied. The free energy of the reaction can be broken down into a chemical and a Coulombic part:

$$\Delta G_{\text{tot}} = -RT \ln K = \Delta G_{\text{chem}} + \Delta G_{\text{Coul}} \quad (10)$$

where  $\Delta G_{\text{chem}}$  is the intrinsic free energy term and  $\Delta G_{\text{Coul}}$  the electrostatic term which indicates that it presumably costs more free energy to remove a proton from a basic group embedded in an anionic polyelectrolyte field than from the isolated group (Manning, 1981). In other words, Eq (5) can be rewritten as:

$$pK_a = \text{pH} - \log \frac{[\theta_{\text{A}^-}]}{[\theta_{\text{HA}}]} = pK_{a,\text{intr}} + 0.434 \frac{e\psi}{kT} \quad (11)$$

where  $pK_{a,\text{intr}}$  stands for the intrinsic dissociation constant,  $e$  the electrostatic charge on the polymer,  $\psi$  the electrostatic potential at a proton site,  $k$  the Boltzmann constant (Katchalsky et al., 1954). Therefore, the relationship between  $pK_a$  and  $\theta_{\text{A}^-}$  can be determined as long as electrostatic free energy or  $\psi$  is calculated. Many groups

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