Thermodynamic (non)co-operation between Phase Equilibria and Ionic Dissociation of Organic acids in Water/Condensate/Gas systems

Amrit Kalra, Ray French, Sheila Dubey, Ashok Dewan

Shell Global Solutions (US) Inc.
3333 Highway 6 South, Houston TX 77082

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Volatile Fatty Acids (VFAs)

Source: 1) Can be naturally found in oil field waters  2) Acid stimulation of wells

Volatile Fatty acids: Low molecular weight carboxylic acids

\[
\begin{align*}
\text{HCOOH} & \quad \text{CH}_3\text{COOH} & \quad \text{CH}_3\text{CH}_2\text{COOH} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\
\text{Formic acid} & \quad \text{Acetic acid} & \quad \text{Propionic Acid} & \quad \text{Butyric acid}
\end{align*}
\]

Highlight:

Dissociation: \[
K_{\text{diss}} \Rightarrow \left[ \text{HAc} \right]_{\text{aq}} \rightarrow \left[ \text{H}^+ \right] + \left[ \text{Ac}^- \right]
\]

VLE partitioning: \[
K_{\text{Henry}} \Rightarrow \left[ \text{HAc} \right]_{\text{v}} \leftrightarrow \left[ \text{HAc} \right]_{\text{aq}}
\]

Use:

- Thermodynamics / Chemistry framework
- Experimental Physical Properties Data
- OLI Stream Analyzer
VFAs can increase CO₂ corrosion rates

Questions?

• Thermodynamics/Phase Behavior of organic acids?
• Electrochemical properties of organic acids?
• Mechanism of CO₂ corrosion in presence of VFAs?
• Effect of VFAs on formation andprotectiveness of Iron Carbonate scale?
VFA’s influence on TOL and BOL Corrosion

Top-of-Line (TOL) & Bottom-of-Line (BOL) Corrosion
Phase distribution of Acetic acid in Water/Gas/Condensate

Main Issue: Phase distribution is more complicated than simple Henry’s Law when the species can ionize and dimerize.

Underlying principle: Chemical potential of species is equal in all phases.
Effect of pH and temperature on Ionic Chemistry of H$_2$S, CO$_2$ and NH$_3$
Dissociation of Organic acids (C1-C4) in water

- $pK_d$ of Formic acid is one pH unit less than (C2-C4) acids.
- Not recommended to lump them all together for Corrosion and Phase Equilibria calculations.

- Temperature effect on $K_d$: factor of 5 [0 to 200°C]
- Pressure effects are relatively small: factor of 1.04 [1 to 100 atm]

Dissociation of Organic acids (C1-C4) in water, Stream and Experimental data.
Henry’s Law constants of Organic acids (C1-C4)

- Lack of good literature data on temperature dependent $K_H$
- Assuming Infinite Dilution Activity Coefficient (IDAC) independent of temperature, vapor pressures of pure components are instead used to provide T dependence (Refer: Sep 2007 Chemical Engineering Progress, Avoid Common Pitfalls When Using Henry's Law, F.L. Smith and A.H. Harvey)

$K_{Henry} = \frac{M_i}{P_i}$

$M_i$ is molality and $P_i$ is partial pressure

**Experiment Data**

- $K_h$ (C1), Johnson
- $K_h$ (C2), Johnson
- Vap. Press. (C1)
- Vap. Press. (C2)
- Vap. Press. (C3)
- Vap. Press. (C4)
- $K_h$ for C1, Khan
- $K_h$ for C2, Khan
- $K_h$ for C3, Khan
- $K_h$ for C4, Khan
- $K_h$ for C2, Renon
Thermodynamic (non) co-operation

\[
\begin{align*}
K_H \text{ True} & \quad (\text{HAc})_v \\
K_H \quad \downarrow & \\
(\text{HAc})_\text{aq} & \\
K_{diss} & \\
(\text{H}^-) + (\text{Ac}^-) & \\
K_H \text{ Apparent} & \quad (\text{HAc})_v \\
K_H & \\
(\text{HAc})_\text{aq} & \\
K_{diss} & \\
(\text{HAc}) & \xrightarrow{\text{aq}} (\text{Ac}^-) + (\text{H}^+) \\
\end{align*}
\]

From Stream Analyzer:

Acetic acid at pH = 5, 1 atm, 25 °C, HAc + Ac^- = 1mM

\[
\begin{align*}
[\text{HAc}]_\text{aq} & = 0.054 \text{ mM} \\
[\text{Ac}^-] & = 0.946 \text{ mM} \\
[P_{\text{HAc}}]_\text{vap} & = 9.79 \times 10^{-9} \text{ atm} \\
K_H \text{ True} & = 5500 \text{ M/atm} \quad K_H \text{ Apparent} = 100000 \text{ M/atm}
\end{align*}
\]

- Usually, total concentration (dissociated + undissociated) is measured in water analysis
- \(K_{\text{Henry}}\) should be coupled with degree of dissociation
Partitioning of Organic acids between Oil and Water

- Linear plot for $K_{o/w}$ as a function of carbon number, for organic acids.
- All four acids (C1-C4) should not be lumped together.
- Simulations done in Stream Analyzer for model HC’s.
- $K_{o/w}$ is a weak function of temperature.

Phase distribution of Acetic acid in Water/Gas/Condensate

Engineering data and Thermodynamic Framework for four organic acids (C1-C4) is obtained for different operating conditions

Dimerization can be ignored for
OA in Water phase < 10%
OA in gas phase < 1 %
Acetic Acid: Comparison of MSE and H⁺ models

- Dissociation of Acetic acid
- Not significant difference in the value of pKd

Henry’s Law Constant

- MSE : 63.21 M atm⁻¹
- H⁺ : 92.57 M atm⁻¹
Conclusions

• Determination of “Free” organic acids is the key in Corrosion studies; correct thermodynamic model is essential

• Organic acids show competing behavior for dissociation and partitioning into the vapor phase

• $K_H$ is very temperature sensitive

• Good confirmation of experimental data with Stream Analyzer for the H+ model

• Need additional data modeling efforts on organic acids for MSE model to represent influence of methanol & glycols
Questions??