



# A general correlation for predicting the suppression of hydrate dissociation temperature in the presence of thermodynamic inhibitors

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## Abstract

Thermodynamic inhibitors can be used in avoiding gas hydrate problems in natural gas and oil production and transportation. A new correlation for predicting the suppression of the hydrate dissociation temperature of various petroleum fluids in the presence of different thermodynamic inhibitors (e.g., electrolytes and organic inhibitors) is presented. The correlation, which can be applied to drilling and reservoir fluids, requires inhibitor concentration, pressure of the system and, if known, the dissociation pressure of the fluid in the presence of distilled water at 273.15 K.

The correlation has been developed using hydrate phase boundaries for methane and seven natural gases in the presence of various single inhibitors generated by a well-proven comprehensive thermodynamic model. It covers nine electrolyte solutions and six organic inhibitors, which may be available and/or added to the reservoir and drilling fluids. The developed correlation is generic and could be easily extended to other salts and organic inhibitors.

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## 1. Introduction

Gas hydrates are a serious concern in oil and gas exploration and production due to potential blockage of wells, flowlines and other process facilities. To control the risk of gas hydrate formation in drilling and production operations, it is common to add thermodynamic inhibitors (e.g., electrolytes and organic inhibitors) to the fluid systems. Accurate knowledge of the thermodynamic stability of hydrates as a function of concentrations of inhibitors is crucial to the

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success of any flow assurance strategy. Considerable efforts are therefore put into the development of methods and tools, capable of predicting hydrate phase boundaries for different fluids at various temperature and pressure conditions.

Since 1945, the gas gravity method given by Katz (1945) has been an indispensable and simple tool for predicting the gas hydrate stability zone. Despite the development of more sophisticated predictive tools, such as the vapour–solid equilibrium ratio ( $K_i$  value) method (Carson and Katz, 1942; Wilcox et al., 1941) or the solid solution theory of Van der Waals and Platteeuw (1959), the gas gravity method has kept its popularity among engineers in the petroleum industry. The main advantage of this technique is the availability of input data (it only requires the specific gravity of the mixture, i.e., the molecular mass of the gas mixture divided by that of air) and the simplicity of the calculation, which can be performed by using charts or hand-held calculators. The original gas gravity method is only applicable to dry gas systems. However, the development of offshore/arctic oil and gas-condensate fields necessitated a robust and simple method for predicting the hydrate stability zone for these systems.

Østergaard et al. (2000) developed a method similar to the gas gravity method, applicable to all reservoir fluids, in the presence of distilled water, from natural gas to black oil, which only requires information on the specific gravity and the concentration of the hydrate forming components in the system. The method can take into account the effect of non-hydrocarbon gases (i.e., CO<sub>2</sub> and N<sub>2</sub>) in the petroleum fluid.<sup>3</sup>

There also exist simple tools for estimating the hydrate inhibition effect of salts and organic inhibitors. The most famous one is the Hammerschmidt (1934) equation, but also equations by Nielsen and Bucklin (1983) and Yousif and Young (1993) are available. These equations calculate the suppression of the hydrate dissociation temperature,  $\Delta T$ , compared to that of distilled water (i.e., the hydrate phase boundary in the presence of distilled water should be determined separately). Inherently, they

have the following simplifying assumptions, reducing their accuracy:

- $\Delta T$  is independent of the system pressure.
- $\Delta T$  is independent of gas/oil composition and hydrate structure.
- $\Delta T$  is independent of the inhibitor.

In addition to the above shortcomings, to our knowledge, there is no reported general correlation in the open literature that is capable of estimating the hydrate inhibition effects of various salts and organic inhibitors, which might be available and/or added to the reservoir and drilling fluids.

In this communication, first, the effective parameters, which are important to be taken into account in developing any reliable hydrate inhibition correlation, are discussed. A general equation, then, is presented which is capable of predicting hydrate inhibition effect of various salts and organic inhibitors. The correlation relates the suppression of hydrate dissociation temperature of hydrocarbon fluids to the concentration of inhibitor, hydrate dissociation pressure of the fluid in the presence of distilled water and pressure of the system.

The predictions of the developed correlation have been compared with experimental data, predictions of a comprehensive thermodynamic model and some other correlations reported in the literature. The results demonstrate the reliability of the developed correlation, despite its relative simplicity.

## 2. Effect of important parameters on the hydrate inhibition characteristics of aqueous solutions of salts and/or organic inhibitor

In order to develop a reliable, yet simple, correlation for predicting the gas hydrate inhibition there are some difficulties (such as inaccurate experimental data and thermodynamic models, pressure effect, hydrocarbon fluid composition, inhibitor effect and ionisation effect), which should be considered in a comprehensive correlation. In the followings, the importance of the above parameters on the hydrate prevention and the shortcomings of the existing correlations are discussed, on the basis of which the new correlation is developed.

<sup>3</sup> A free copy of the spreadsheet is available at the Hydrate Group's website: [www.pet.hw.ac.uk/research/hydrate](http://www.pet.hw.ac.uk/research/hydrate).

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