GENERAL RESEARCH

Estimating the Hydrate Safety Margin Using Surface Tension Data of Salt Aqueous Solution

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Petroleum reservoir fluids are normally produced with saline water. One serious problem in production and transportation of these fluids is pipeline blockage due to hydrate formation giving rise to operational problems and other safety concerns. No means of controlling and monitoring are generally available along the pipelines and/or downstream to assess hydrate formation. High safety margins are used in many cases to account for the uncertainties in the operating conditions and to reduce the gas hydrate formation risks. In this work, the possibility of predicting the hydrate safety margin from surface tension data of salt aqueous solutions is investigated using a new equation. The developed method considers only the changes in surface tension of saline water with respect to surface tension of distilled water, and therefore there is no need to have the analytical analysis of the aqueous solution. Independent data are used to examine the reliability of this tool. The predictions of this method are in acceptable agreement with the independent data, demonstrating its reliability for estimating the hydrate safety margin in the presence of salt aqueous solutions.

1. Introduction

Gas hydrates are icelike structures in which water molecules, under pressure, form structures composed of polyhedral cages surrounding gas molecule "guests" such as methane and ethane. They can occur in staggering abundance in cold subsea, sea floor, and permafrost environments where temperature and pressure conditions ensure their stability. The natural gas trapped in these deposits represents a potential source of energy many times that of all known natural gas reserves. Gas hydrates can form as well in undersea piping and above-ground pipelines, where they pose a major and expensive problem for the petroleum industry.[1] For pipelines carrying a cocktail of multiphase fluids including hydrocarbons and formation water with various concentrations of salts, saline water may provide the required protection. However, no means of controlling and monitoring are generally available along the pipelines and/or downstream to assess hydrate formation risk, and therefore high safety margins are used to account for the uncertainties in the operating conditions and for reducing the risk of gas hydrate formation.

This work is a continuation of a previously reported study for estimating the hydrate safety margin from aqueous phase properties.[2,3] The possibility of predicting hydrate inhibition effects of saline solutions from surface tension data of the aqueous phase can have a practical use, as measuring the surface tension of the aqueous phase is easier than hydrate suppression temperature measurement. In the present work, a brief review is first made on the surface tension definition, thermodynamics, and measurement methods to provide a better understanding of surface tension phenomena. The predictions of a general predictive method[4] for hydrate suppression temperatures and surface tension data[5] of aqueous phase due to the presence of salt are used for developing a simple equation. Independent data are then used to examine the reliability of this method. The predictions of this equation are in acceptable agreement with the independent data, demonstrating the reliability of the predictive technique developed in this study.

2. Surface Tension

Surface tension is an effect within the surface layer of a liquid that causes the layer to behave as an elastic sheet. It is caused by the attraction between the molecules of the liquid, due to various intermolecular forces. In the bulk of the liquid each molecule is pulled equally in all directions by neighboring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inward by other molecules deeper inside the liquid, but there are no liquid molecules on the outside to balance these forces. All of the molecules at the surface are therefore subject to an inward force of molecular attraction which can be balanced only by the resistance of the liquid to compression. Thus the liquid squeezes itself together until it has the lowest surface area possible.[6]

Surface tension can therefore be considered as the force along a line of unit length perpendicular to the surface, or work done per unit area. This means that surface tension can also be considered as surface energy.[6] From a thermodynamic point of view surface tension (σ) is defined as[6]

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P,x} \tag{1}$$

where G is the Gibbs free energy and A is the area. Subscripts T, P, and x stand for temperature, pressure, and composition, respectively.

There are only empirical equations for calculating the influence of temperature (T) on surface tension. For example:[6]

Eötvös equation: $$\sigma V^{2/3} = k(T_C - T) \tag{2}$$

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where V is the molar volume of that substance, T_C is the critical temperature, and k is a constant for each substance reported in the original work.

Guggenheim−Katayama equation:

$$\sigma = \sigma^0\left(1 - \frac{T}{T_C}\right)^n \tag{3}$$

σ^0 is a constant for each liquid reported in the original work and n is an empirical factor, which is determined from experimental data.

Solutes can have different effects on surface tension depending on their structure:[6] (a) no effect, for example, sugars; (b) increase of surface tension, such as inorganic salts; (c) decrease of surface tension, for example, alcohols; (d) decrease of surface tension and, once a minimum is reached, no more effect, for example, surfactants.

The measurement methods of surface tension can be summarized as below:[6]

Du Noüy Ring Method. This is the traditional method used to measure surface or interfacial tension. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured.

Wilhelmy Plate Method. This is a universal method especially suited to check surface tension over long time intervals. A vertical plate of known perimeter is attached to a balance, and the force due to wetting is measured.

Spinning Drop Method. This technique is ideal for measuring low interfacial tensions. The diameter of a drop within a heavy phase is measured while both are rotated.

Pendant Drop Method. Surface and interfacial tension can be measured by this technique, even at elevated temperatures and pressures. The geometry of a drop is analyzed optically.

Bubble Pressure Method (Jaeger's Method). This is a measurement technique for determining surface tension at short surface ages. The maximum pressure of each bubble is measured.

Drop Volume Method. This is a method for determining interfacial tension as a function of interface age. A liquid of one density is pumped into a second liquid of a different density, and the time between drops produced is measured.

Limited information is available in the literature for surface tensions of aqueous solutions containing salt(s). In the present work, surface tension data at 293.15 K reported in *CRC Handbook of Chemistry and Physics*[5] are used.

3. Development of a New Equation

To develop a correlation between hydrate inhibition effects of salts and surface tension data of aqueous solutions, we have used the results coming from a general predictive method[4] for hydrate inhibition effects of salts and the data reported in *CRC Handbook of Chemistry and Physics*[5] for surface tensions of salt aqueous solutions. The reasons for using the results of the predictive method for hydrate inhibition effects of salts rather than real experimental data are as follows:

1. The amount of experimental hydrate suppression temperature is limited.

2. Because of the limited experimental data, any error could easily result in unreliable correlation.

3. Experimental data can be used for validation of correlation. For the salts listed in Table 1, the difference in surface tension of aqueous solutions due to the presence of salt and surface tension of distilled water (72.75 dyne/cm) at 293.15 K and hydrate suppression temperature data for various aqueous solutions of salts were used in developing the correlation. These typical salts are normally present in the formation water. All these aqueous systems were assumed to be in contact with methane, and the hydrate suppression temperatures for these systems were calculated at 20 MPa from the predictive method.[4] The effect of gas composition (and therefore hydrate structure) and the pressure of the system were ignored for engineering purposes.[1] The degree of hydrate inhibition was then plotted versus the difference in surface tension of aqueous solution for various salt systems, as shown in Figure 1. As can be seen, all the data collapse nearly onto one curve, suggesting a unique second-order polynomial behavior between hydrate suppression temperature and the difference of surface tension of aqueous phase (with respect to distilled water). The resulting correlation, which relates the hydrate dissociation temperature of the gas system to the difference in surface tension of aqueous phase, is then given by the following expression:

Table 1. Maximum Concentration of Salts in the Aqueous Phase Used in Developing This Method

salt	max concn, wt %
NaCl	22.6
KCl	13.9
$CaCl_2$	32
NaBr	13.4
KBr	13.4
K_2CO_3	13.7
$MgCl_2$	4.55
Na_2SO_4	6

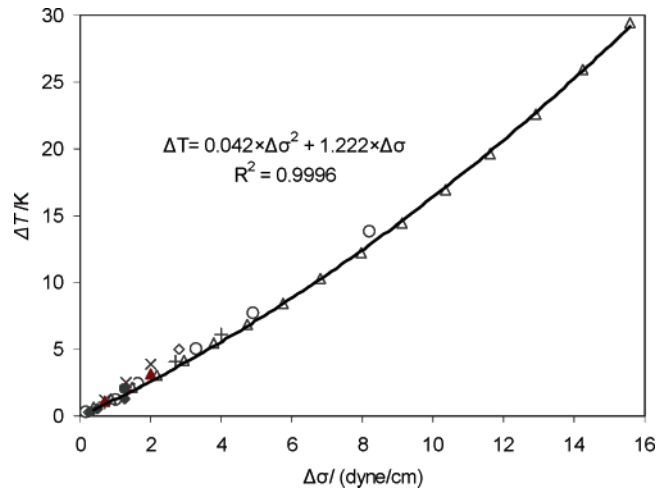

Figure 1. Collapse of the data for the salts shown in Table 1 onto one curve, suggesting approximately a second-order polynomial relationship between hydrate suppression temperature (ΔT) and difference in surface tension of aqueous solution with respect to distilled water ($\Delta\sigma$) at 293.15 K: (○), NaCl; (◇), KCl; (△), $CaCl_2$; (×), NaBr; (▲), KBr; (+), K_2CO_3; (●), $MgCl_2$; (◆), Na_2SO_4.

$$T = T_0 - 0.042\Delta\sigma^2 - 1.222\Delta\sigma \tag{4}$$

where T is the hydrate dissociation temperature of a fluid (K) in the presence of saline water, $\Delta\sigma$ stands for the difference in surface tension of aqueous phase with respect to distilled water (dyne/cm), and T_0 represents the hydrate dissociation temperature of the same fluid system in the presence of distilled water (K). As can be seen, the developed correlation is simple and enables fast calculation of the hydrate free zone of various systems in the presence of salt. The only prerequisite to use the correlation is the hydrate dissociation temperature of the same fluid system in the presence of distilled water (T_0), which

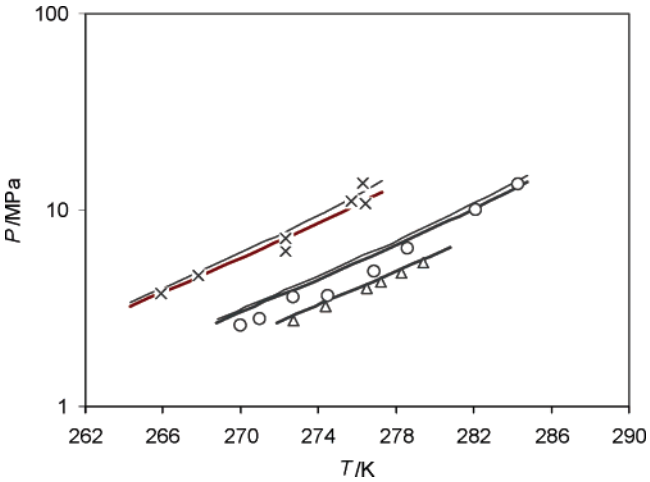

Figure 2. Hydrate phase boundary of methane in the presence of NaCl aqueous solutions. Experimental data: (△), 3 wt % NaCl;[8] (○), 10 wt % NaCl;[9] (×), 20 wt % NaCl.[9] Bold solid curves, predictions of this predictive method; solid curves, predictions of HWHYD model.[4] Deviations at high concentrations can be attributed to unreliability of experimental data.

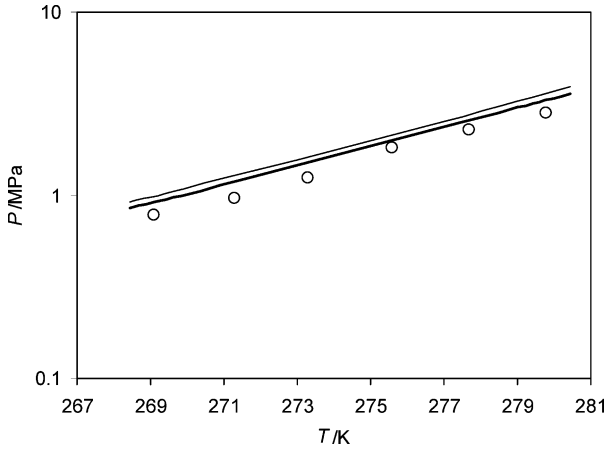

Figure 3. Hydrate phase boundary of a synthetic gas mixture containing 97.25% methane + 1.42% ethane + 1.08% propane + 0.25% 2-methylpropane in the presence of aqueous solution composed of 10 wt % KCl. Experimental data: ○, 10 wt % KCl.[10] Bold solid curve, predictions of this predictive method; solid curve, predictions of HWHYD model.[4]

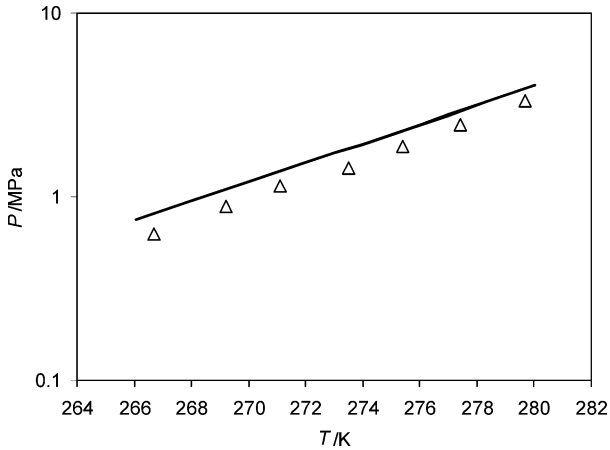

Figure 4. Hydrate phase boundary of a synthetic gas mixture containing 97.25% methane + 1.42% ethane + 1.08% propane + 0.25% 2-methylpropane in the presence of aqueous solution composed of 10 wt % $CaCl_2$. Experimental data: (△), 10 wt % $CaCl_2$.[10] Bold solid curve, predictions of this predictive method; solid curve: predictions of HWHYD model.[4]

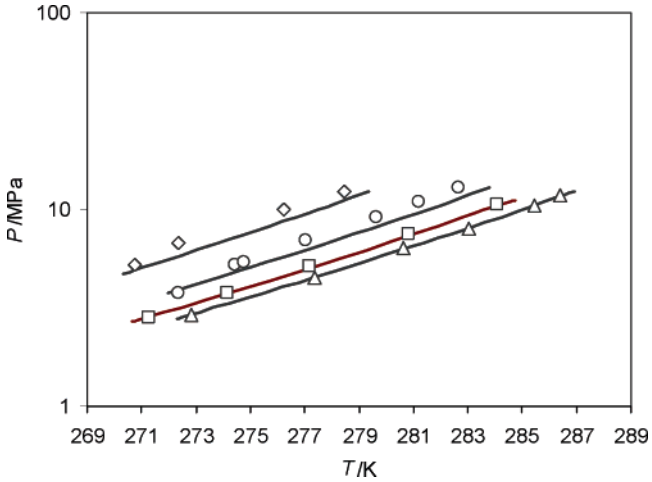

Figure 5. Hydrate phase boundary of methane in the presence of $MgCl_2$ aqueous solutions. Experimental data: (△), 3 wt % $MgCl_2$;[11] (□), 6 wt % $MgCl_2$;[11] (○), 10 wt % $MgCl_2$;[11] (◇), 15 wt % $MgCl_2$.[11] Bold solid curves, predictions of this predictive method. The HWHYD model[4] has not been developed for concentrations higher than 5 wt % $MgCl_2$.

can be calculated using an appropriate correlation such as the general correlation developed by Østergaard et al.[7]

4. Results and Discussion

The results predicted by the newly developed equation are compared with some independent experimental data reported in the literature. In all of these comparisons, the values of $\Delta\sigma$ are calculated from *Handbook of Chemistry and Physics*[5] and the values of T_0 are calculated using the general correlation developed by Østergaard et al.[7]

Figure 2 shows a comparison between the predictions from this method, the HWHYD model,[4] and experimental data[8,9] for hydrate dissociation conditions of methane in the presence of various concentrations of NaCl aqueous solutions. As shown in the figure, the predictions of the newly developed correlation are in acceptable agreement with the independent data. However, the results of this predictive method and the HWHYD model[4] show some deviations at high concentrations of NaCl. These deviations can be attributed to the unreliability of experimental data.

Limited information is available on hydrate dissociation conditions of fluids in the presence of calcium chloride and potassium chloride aqueous solutions. Figures 3 and 4 compare predictions of the method developed in this work and the HWHYD model[4] with experimental data[10] for hydrate dissociation conditions of a synthetic gas mixture containing 97.25% methane + 1.42% ethane + 1.08% propane + 0.25% 2-methylpropane in the presence of aqueous solutions composed of 10 wt % KCl and $CaCl_2$, respectively. As shown in the figures, the predictions of both methods are in relatively acceptable agreement with the independent data. The deviations can be attributed to the unreliability of experimental data.

A comparison is also made between the predictions of this correlation and experimental data[11] for the hydrate phase boundary of methane in the presence of $MgCl_2$ aqueous solutions (see Figure 5). As can be seen, the new equation shows acceptable predictions even at higher concentrations of $MgCl_2$ used for developing this predictive method (Table 1). It should be noted that the HWHYD model[4] has not been developed for concentrations higher than 5 wt % $MgCl_2$, and therefore the results of this model are not shown in Figure 5.

The use of this predictive method is not recommended at very high concentrations of salts, as data up to intermediate concentrations of salts (Table 1) have been used for developing this

correlation. The capability of the method can be further investigated by generating surface tension/hydrate data for more mixed salt aqueous solutions.

5. Conclusions

The possibility of estimating the hydrate safety margin for petroleum fluids in the presence of salt aqueous solutions using surface tension data of aqueous solution was investigated in this work by developing a new and simple equation. The method achieved acceptable accuracy when compared with independent experimental data for various systems.

Nomenclature

A = area
G = Gibbs free energy
k = constant
n = empirical factor
T = temperature/hydrate dissociation temperature in the presence of saline water
T_C = critical temperature
T_0 = hydrate dissociation temperature in the presence of distilled water
ΔT = hydrate suppression temperature
V = molar volume of substance

Greek Symbols

σ = surface tension
σ^0 = constant for liquid
$\Delta\sigma$ = difference in surface tension of aqueous phase (with respect to distilled water)

Subscripts

P = pressure
T = temperature
x = composition

Literature Cited

(1) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(2) Mohammadi, A. H.; Richon, D. On Estimating the Hydrate Safety Margin in the Presence of Salt or Organic Inhibitor Using Refractive Index Data of Aqueous Solutions. Accepted for publication in *Ind. Eng. Chem. Res.* **2006**.

(3) Mohammadi, A. H.; Richon, D. Use of boiling point elevation data of aqueous solutions for estimating hydrate stability zone. Accepted for publication in *Ind. Eng. Chem. Res.* **2006**.

(4) Heriot-Watt University Hydrate model: http://www.pet.hw.ac.uk/research/hydrate/. (Also: Østergaard, K. K.; Masoudi, R.; Tohidi, B.; Danesh, A.; Todd, A. C. A general correlation for predicting the suppression of hydrate dissociation temperature in the presence of thermodynamic inhibitors. *J. Pet. Sci. Eng.* **2005**, *48* (1−2), 70−80.)

(5) Weast, R. C.; Astle, M. J.; Beyer, W. H. *CRC Handbook of Chemistry and Physics*, 65th ed.; CRC Press Inc.: Boca Raton, FL, 1984−1985. (Also: Mohammadi, A. H. Personal Communication, 2006.)

(6) Wikipedia encyclopedia: http://en.wikipedia.org/wiki/Surface_tension.

(7) Østergaard, K. K.; Tohidi, B.; Danesh, A.; Todd, A. C.; Burgass, R. W. A General Correlation for Predicting the Hydrate-Free Zone of Reservoir Fluids. *SPE Prod. Facil.* **2000**, *15* (4), 228−233. (Also: Heriot-Watt University Hydrate model: http://www.pet.hw.ac.uk/research/hydrate/.)

(8) Dholabhai, P. D.; Englezos, P.; Kalogerakis, N.; Bishnoi, P. R. Equilibrium Conditions for Methane Hydrate Formation in Aqueous Mixed Electrolyte Solutions. *Can. J. Chem. Eng.* **1991**, *69*, 800−805.

(9) Kobayashi, R.; Withrow, H. J.; Williams, G. B.; Katz, D. L. Gas Hydrate Formation with Brine and Ethanol Solutions. *Proc., Annu. Conv., Nat. Gasoline Assoc. Am., Tech. Pap.* **1951**, *30*, 27−31.

(10) Mei, D. H.; Liao, J.; Yang, J. T.; Guo, T. M. Hydrate Formation of a Synthetic Natural Gas Mixture in Aqueous Solutions Containing Electrolyte, Methanol, and (Electrolyte + Methanol). *J. Chem. Eng. Data* **1998**, *43*, 178−182.

(11) Kang, S.-P.; Chun, M.-K.; Lee, H. Phase equilibria of methane and carbon dioxide hydrates in the aqueous $MgCl_2$ solutions. *Fluid Phase Equilib.* **1998**, *147*, 229−238.

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