

A Practical Model for the Effect of Salinity on Gas Hydrate Formation

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Abstract

This paper is based on a previously developed thermodynamic model for gas hydrates and hydrate inhibition. The model uses a cubic equation of state for the fluid phases and parameters have already been determined for the following inhibitors: methanol, MEG, DEG and TEG.

The paper describes the extension of the model to include the effect of salinity in produced water or sea water on hydrate formation. To ensure the model would be of practical value, it was designed with the following characteristics: it should be simple to use requiring as input no more than a typical ion analysis table from a laboratory report. It should be based on a cubic equation of state suitable for engineering calculations and the model should operate reliably at temperatures and pressures normally encountered in oil and gas production.

The model represents the ionic components in water by a single salt pseudocomponent of the equation of state. The physical properties of the pseudocomponent were set by regressing them to experimental data for sodium chloride solutions. Results will be presented to show that the model can simultaneously represent the lowering of the hydrate dissociation temperatures, the depression of the freezing point of water and the reduction in the water vapour pressure (osmotic coefficient).

As sodium chloride is usually the dominant component in produced water or sea water, other salts are handled on a sodium chloride equivalent basis, so that only one salt pseudocomponent is needed for practical calculations. Data for the effect of natural waters supports the use of this approximation.

In practice, a hydrate inhibitor may be added to the water phase so it is important that the inhibition model can give accurate predictions in the presence of saline solutions. This

has been confirmed by investigating the salting-out effect for methanol and results are shown for salt-water-methanol mixtures.

Practical ways of accessing and applying the model are summarised. These include using the model as a stand-alone computer program, accessing the model via a spreadsheet or using the model as an object code library or as a dynamic link library.

Introduction

Gas hydrates are a well appreciated hazard in oil and gas pipelines and processing equipment. They may also occur in certain conditions during drilling operations giving rise to gas kick. If operating conditions are such that hydrates may form, hydrate inhibitors such as methanol or glycols have to be injected into the hydrocarbon fluids. If produced water or sea water is in contact with the hydrocarbon fluid, the salinity of the water will itself inhibit hydrate formation. The object of this work is to devise a practical engineering method to predict the effect of salinity on hydrate formation in combination with added chemical inhibitors.

Existing Hydrate Model. The authors have previously developed an original computer algorithm for solving multiphase equilibrium problems involving any number and combination of solid, liquid or gas phases¹. The phases may have quite different properties calculated from different thermodynamic models. The algorithm can perform all the normal engineering flash calculations; it automatically determines which phases will be present under given conditions and returns the relative amounts, compositions and properties of the phases.

To model the fluid phases, a commonly used equation of state was required. The choice was between the SRK² or Peng-Robinson³ equations. The SRK equation was selected as it appears to give more accurate fugacities for natural gases⁴. The tendency of the SRK equation to give poor liquid densities was addressed by correcting the SRK densities using the Peneloux volume shift method⁵.

In order to apply the SRK equation to hydrate calculations, two extensions were necessary. The first was that the equation of state *a* parameter for water was regressed as a polynomial function of temperature to match the vapour pressure of water. This proved to be essential in order to obtain reliable hydrate predictions.

Ice was modelled by calculating its properties relative to pure liquid water and using experimental data for the changes in enthalpy, heat capacity and volume on fusion at the normal melting point. The vapour pressure curve of water has to be extrapolated below the triple point to use the ice model. The extrapolated vapour pressures of water were set so as to reproduce the known sublimation pressure of ice down to about 230K. This covers the range of practical interest for most oil and gas operations.

The second extension of the SRK equation was the introduction of a modified mixing rule. In order to model the properties of water and hydrate inhibitors, an excess Gibbs energy mixing rule was used based on the Huron-Vidal mixing rule⁶. The form of the mixing rule is:

$$a = b \sum_i n_i \frac{\sum_j n_j b_j \xi_{ji} G_{ji}}{\sum_j n_j b_j G_{ji}} \dots\dots\dots(1)$$

where:

$$\xi_{ji} = \frac{2\sqrt{a_i a_j} (1 - k_{ji})}{b_i + b_j} \dots\dots\dots(2)$$

and:

$$G_{ji} = \exp\left(\frac{\alpha_{ji} (\xi_{ji} - \xi_{ii})}{RT}\right) \dots\dots\dots(3)$$

In general, $k_{ji} \neq k_{ij}$ whereas α_{ij} is taken to be symmetric, i.e. $\alpha_{ji} = \alpha_{ij}$. The advantage of this formulation is that if α_{ij} is set to zero, the mixing rule reduces to the conventional Van der Waals mixing rule that is normally used with the SRK equation:

$$a = \sum_{ij} \sqrt{a_i a_j} (1 - k_{ij}) n_i n_j \dots\dots\dots(4)$$

where the interaction parameters are now symmetric, i.e. $k_{ji} = k_{ij}$.

For mixtures of hydrocarbons and light gases, therefore, normal characterisation procedures are used with conventional interaction parameters, k_{ij} . For interactions with water and hydrate inhibitors, the extended mixing rule, Eqn. 1 is used. Currently, parameters have been established for the following inhibitors: methanol, monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG)⁷. The advantage of this approach is that the properties of the inhibitors are handled in a thermodynamically consistent way allowing all the effects of adding inhibitors to be modelled including the depression of hydrate points, the depression of the ice point and the reduction in the vapour pressure of water. The model also predicts the partitioning of inhibitor between oil, gas and water phases and the change in the hydrate point resulting from different phase ratios.

The hydrate phases were modelled with the Van der Waals-Platteeuw hydrate model with all parameters

redetermined by the authors^{7,8} by regressing all available data for hydrate formation from the data collection of Sloan⁹.

Requirements for Modelling Salinity. The action of inhibitors is indirect in that they do not enter the hydrate phase, and do not alter its properties. Inhibitors act by modifying the thermodynamic properties of the fluid phases, in particular the aqueous liquid phase. Adding inhibitor lowers the fugacity of water thereby reducing its tendency to form hydrate. To predict the effect of inhibitors, it is necessary to devise a model for the fugacities of mixtures of hydrocarbons, water and inhibitor. In this respect, mineral salts are no different from other hydrate inhibitors except that they remain in the aqueous liquid phase or else crystallise out; effectively, they do not enter the gas phase or the hydrocarbon liquid phase.

As salts remain in the aqueous liquid phase, the only property that must be modelled for hydrate predictions is their lowering of the fugacities of water. The electrochemistry of aqueous salt solutions is complex, but for hydrate inhibitions calculations it is desirable to hide this complexity and reduce the model to its essential features. In this study, it was decided to devise a model to satisfy the following objectives:

1. The model should be as compatible as possible with the authors' existing hydrate model based on the SRK equation.
2. The model should work reliably under all conditions encountered in oil and gas processing, i.e. it can be used to calculate high pressure phase equilibria.
3. The model should work for produced water and sea water where sodium chloride is the dominant saline component.
4. It should be possible to set the model up with no more than typical laboratory ion analysis data for the aqueous phase. Detailed information on the electrochemistry of the aqueous liquid should not be required.

Summary of Approach. The approach adopted was to introduce a pseudocomponent into the equation of state, the salt component, that would represent the properties of aqueous sodium chloride solutions without further modifications of the equation of state model. The data for the salt-water binary were matched by optimising the parameters of the salt component and the interaction parameters for the salt-water binary.

For natural brines, rules have been devised to convert them to a sodium chloride equivalent basis, so that the salinity can be represented as simply as possible by a single component. This approach is possible because the only effect considered is the reduction of the fugacity of water. It is assumed that the salts remain in the aqueous liquid phase and therefore that the relative amounts of the salts does not change. This assumption will be valid provided none of the salts crystallises out of solution, which will normally be the case for hydrate inhibition studies. It is therefore possible to calculate the concentration of sodium chloride that will have the same effect as other salts. This ignores the interactions between different salts in aqueous solutions and treats the salts as though their effect is purely additive. This proves to be a reasonable approximation provided that sodium chloride is the dominant component.

Model for Aqueous Sodium Chloride Solutions

Osmotic Coefficients and Depression of the Ice Point. A salt component was set up in the equation of state model to represent sodium chloride in aqueous solution. Osmotic coefficient data in the temperature range 298K-373K and data for the depression of the ice point as a function of sodium chloride concentration from 273K to 248K were selected as these properties directly depend on the fugacity of water as a function of sodium chloride concentration in the solution. The osmotic coefficient data were converted into the more familiar form of a bubble point pressure versus mole fraction diagram, Fig. 1. The critical parameters T_c , p_c and ω of the salt component and the three salt-water binary interaction parameters k_{ij} , k_{ji} and α_{ij} were fitted to the data using a non-linear regression routine that is coupled to the phase equilibrium algorithm.

Figs. 1 and 2 show the results of the regression. The data are represented to near experimental accuracy over a temperature range of 125K. The values of the parameters of the salt component are model specific and do not have physical meaning as the model is invalid for pure sodium chloride. However, the results show that the model is able to represent the thermodynamic properties of aqueous solutions of sodium chloride accurately.

Sodium Chloride Partitioning. If sodium chloride is to be represented in phase equilibrium calculations as an equation of state component, the model must ensure that it stays in the aqueous liquid phase. The critical parameters obtained for the salt component by regressing the above-mentioned data are $T_c = 991.7\text{K}$ and $p_c = 1.86\text{MPa}$. The high critical temperature and low critical pressure are typical of a very heavy component, and when used in phase equilibrium calculations, they predict that sodium chloride is non-volatile giving effectively zero concentration in the gas phase under normal conditions. Setting the interaction parameters between the salt component and hydrocarbons and light gases to a suitably large value ensures that the salt component will not enter the liquid hydrocarbon phase.

Crystallisation of Sodium Chloride. It is possible to obtain an unrealistic result from the model if an aqueous solution of sodium chloride is flashed at very low pressure. This will cause the water to vaporise leaving a liquid that is effectively pure sodium chloride. In reality, the sodium chloride will crystallise out as soon as its concentration reaches the solubility limit which is in the region of a mole fraction of about 0.1.

The problem is avoided by allowing for the formation of solid sodium chloride in the phase equilibrium calculations. Using the same non-linear regression routine, the parameters that control the solidification of the salt component were fitted to the data for sodium chloride giving the result shown in Fig. 3. These parameters consist of the normal melting point, the enthalpy of fusion and the change in specific heat on fusion. The parameter values obtained are again model specific and not physically significant, but they do allow the model to reproduce the experimental data.

When the model is extended to handle natural water containing a mixture of salts, the prediction of the point of crystallisation is no longer valid as it only applies to sodium chloride. However, it is still useful as it still avoids the possibility of forming a liquid phase at low pressures that is almost all salt. This aspect of the problem does not have any direct bearing on the calculation of hydrate formation.

Hydrate Inhibition. The model was now extended to include the depression of the hydrate point by sodium chloride. The data were taken from the collection of Sloan⁹. More data exist for methane hydrate than for any other pure hydrate. However, the experimental data are not mutually consistent. Fig. 4 shows the depression of the hydrate point for each experimentally determined hydrate curve interpolated to a pressure of 5MPa plotted against the sodium chloride concentration. The line shows the calculated result using the parameters obtained by fitting the osmotic coefficients and depression of the ice point.

The model was not able to reproduce the hydrate lines for the highest sodium chloride concentrations. The hydrate data could be better fitted but only if the model was allowed not to fit the ice point curve in Fig. 2. The difficulty arises because the osmotic coefficient data and the ice point data show a more linear dependence on the concentration of sodium chloride in aqueous solution than the data for methane hydrate. Either the model is deficient or the data are inconsistent. If the problem is the former, it can be ignored for calculations with formation water or sea water as the salt concentrations tend to be lower than those that give difficulties. If the problem is the latter, the ice point data should be taken in preference to hydrate data, as the ice point is far easier to determine.

When the methane hydrate data are included in the regression, it makes no effective difference to the result, so the parameters obtained using only osmotic coefficient and ice point data were adopted for hydrate calculations. Fig. 5 shows the results for the methane hydrate lines on a pressure versus temperature plot.

The model was then tested on other hydrate data reported in Ref. 9. Figs. 6-10 show the results for the hydrates of propane, propane and butane, isobutane, carbon dioxide and hydrogen sulphide. As for methane, many of the data sets show a certain degree of mutual inconsistency. Generally, the calculated results lie within 1K of the experimental points with no obvious overall bias to higher or lower temperatures. The largest absolute deviation occurred for hydrogen sulphide hydrate, Fig. 10. This could be because the data are less reliable or the model is deficient, possibly owing to the relatively high solubility of hydrogen sulphide in water; soluble gases lower the fugacity of water in the aqueous liquid phase thereby inhibiting formation of their own hydrate. However, carbon dioxide is also relatively soluble in water and the model reproduces the data for carbon dioxide well, but at lower concentrations of sodium chloride in the aqueous liquid.

Salting-out of Methanol. The model for hydrate inhibition by sodium chloride needs in practice to be applied together with models for common chemical inhibitors such as methanol or glycols. In the case of methanol, experimental data exist for its salting out by sodium chloride which are

presented in Fig. 11. Using the authors' existing model for methanol⁷, the three salt-methanol binary interaction parameters, k_{ij} , k_{ji} and α_{ij} , were fitted to the data using the non-linear regression routine. The result is shown in Fig. 11. Most of the bubble point temperatures are reproduced to within 1K over the entire concentration range of the water-methanol binary.

Unfortunately, no experimental data exist for the salting out of MEG, DEG or TEG by sodium chloride. The interaction parameters between the glycols and sodium chloride have been assumed to be the same as for methanol and sodium chloride in the absence of any information. It would be very desirable if some experimental measurements were made of water-glycol-sodium chloride mixtures.

Extension of the Model to Produced Water or Sea Water.

Method. The method used to represent the properties mixed salt solutions is very simple. For the mass fraction of each component present, the mass fraction of sodium chloride is calculated that would reduce the fugacity of water by the same amount. The mass fractions of sodium chloride are then added to give the total mass fraction of sodium chloride that is equivalent to the salt solution in question.

The conversion factors are calculated from the cryoscopic constants, i.e. the mass fraction of a component in liquid water that depresses the ice point by 1K. Values of the cryoscopic constant were calculated from data reported in Ref. 10 and are presented in Table 1 together with the resulting conversion factors.

Results. Dholabhai et al.¹¹ have presented experimental data for the effect of a synthetic sea water on the formation of methane hydrate. Table 2 shows the reported composition of the sea water and the calculation of the equivalent sodium chloride mass fraction. Using this mass fraction, the methane hydrate curve was calculated, the results being shown in Fig. 12.

Tohidi et al.¹² have presented experimental data for the effect of Forties formation water and a synthetic formation water on a number of petroleum fluids including a gas and a black oil. Tables 3 and 4 show the reported compositions of Forties formation water and the synthetic formation water together with the calculation of the equivalent sodium chloride mass fractions. Using these mass fractions, calculations were performed for the effect of the formation waters on the hydrate curves. For the gas and the black oil, the compositions were taken from the paper of Tohidi et al. However, it was necessary to tune the critical properties of the plus fraction of the black oil in order to match the reported bubble point of 9.411MPa at 373.15K with the SRK equation of state. Experience shows that it is important to match the known PVT properties of black oils, especially the bubble points, in order to obtain good predictions of the hydrate point.

The results for the hydrate calculations are presented in Figs. 13 and 14. Good agreement was obtained with the data apart from the case of the black oil and the synthetic formation water where the calculated result is slightly high in temperature. This may be because the assumption of the

model that sodium chloride is the dominant salt component is less valid for the synthetic formation water; in this case, calcium chloride amounts to about 36% of the total mass of sodium chloride present. The calculated results for the inhibition of black oil hydrate by a mixture of methanol and Forties formation water is in good agreement with experiment confirming that the model can be used for cases where methanol has been added to formation water.

Accessing the Model

The model exists as a stand-alone computer program which was used to produce the results presented in this paper. However, for many engineering applications, phase equilibrium calculations need to be combined with other calculations inside much larger simulation programs. To facilitate this, the code for the model can be used in the form of an object code library that can be linked into a larger program. It can also be converted to a dynamic link library (DLL) under Microsoft WindowsTM. This allows any other Windows program that supports DLL to access the model. One particular example of this is the Microsoft ExcelTM spreadsheet that can access the model as a DLL via an Excel Add-In. Using the Excel Add-In it is possible to produce figures like those presented in this paper; however, if any of the assumed conditions on the spreadsheet are changed, the model is automatically recalled and the figures replotted to show the effect of the change.

Conclusions

The model for the effect of salinity on hydrate formation is a practical tool for engineering calculations. The petroleum fluid is represented by the SRK equation with conventional mixing rules and conventional values for the binary interaction parameters, k_{ij} . For water, methanol, the glycols and the 'salt component', an extension of the mixing rules is required that is compatible with the normal mixing rules used for the petroleum components. The additional parameters needed for water, methanol, the glycols and the 'salt component' have been determined. It is therefore possible to perform robust phase equilibrium calculations with no more difficulty than if inhibitors were not present. The results for the effect of salinity are generally in good agreement with available experimental data.

No data exist for the salting out of glycols, and this is an area of uncertainty in the model that will only be resolved if and when experimental data are published.

Nomenclature

a	=	mixture average of equation of state parameter a
b	=	mixture average of equation of state parameter b
a_i	=	equation of state parameter a for component i
b_i	=	equation of state parameter b for component i
n_i	=	number of moles of component i
k_{ij}	=	binary interaction parameter
α_{ij}	=	binary interaction parameter
T_c	=	critical temperature (K)
p_c	=	critical pressure (Pa)

ω = acentric factor

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SI Metric Conversion Factors

$$\begin{aligned} ^\circ\text{R} \div 1.8 &= \text{K} \\ \text{psi} \times 6.894 &= \text{E}-03 = \text{Pa} \end{aligned}$$

TABLE-1 CRYOSCOPIC CONSTANTS FOR WATER		
Salt	Mass fraction to depress ice point by 1K	Mass fraction relative to NaCl
NaCl	0.0169	1
CaCl ₂	0.0227	1.34
MgCl ₂	0.0188	1.11
KCl	0.0217	1.28
SrCl ₂	0.0320	1.89

BaCl ₂	0.0429	2.54
Na ₂ SO ₄	0.0350	2.07
NaHCO ₃	0.0257	1.52
KBr	0.0341	2.02

TABLE-2 SYNTHETIC SEA WATER		
Salt	Mass fraction of salt	NaCl equivalent mass fraction
NaCl	0.02394	0.02394
CaCl ₂	0.00115	0.00086
MgCl ₂	0.00508	0.00457
KCl	0.00069	0.00054
SrCl ₂	0.00002	0.00001
Na ₂ SO ₄	0.00401	0.00194
KBr	0.00011	0.00005
NaF	0.00009	0.00009
Total		0.03195

TABLE-3 FORTIES FORMATION WATER		
Salt	Mass fraction of salt	NaCl equivalent mass fraction
NaCl	0.06993	0.06993
CaCl ₂	0.00735	0.00547
MgCl ₂	0.00186	0.00167
KCl	0.00066	0.00051
SrCl ₂	0.00099	0.00052
BaCl ₂	0.00036	0.00014
Total		0.07824

TABLE-4 SYNTHETIC FORMATION WATER		
Salt	Mass fraction of salt	NaCl equivalent mass fraction
NaCl	0.08460	0.08460
CaCl ₂	0.03043	0.02266
MgCl ₂	0.00865	0.00778
Total		0.11504

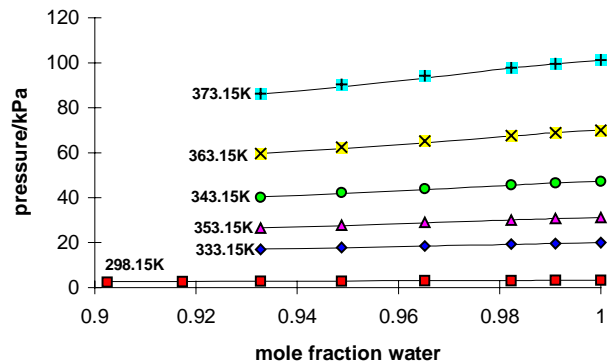


Fig. 1. Water-Sodium Chloride. Experimental and calculated vapour pressure curves. Experimental data from Ref. 13.

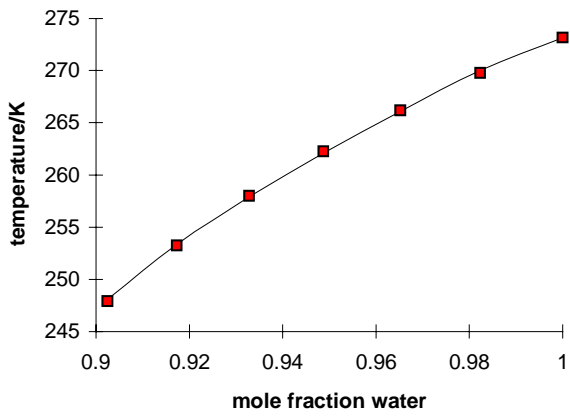


Fig. 2. Water-Sodium Chloride. Experimental and calculated ice point curves. Correlated experimental data from Ref. 14.

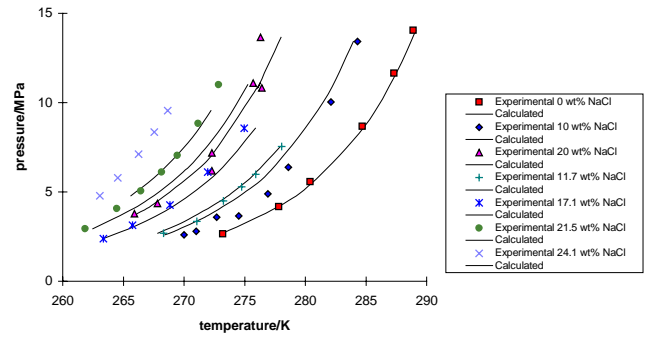


Fig. 5. Methane hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

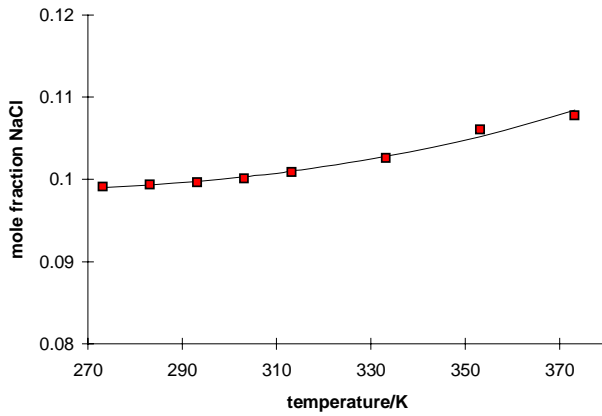


Fig. 3. Water-Sodium Chloride. Experimental and calculated NaCl solubilities. Experimental data from Ref. 15.

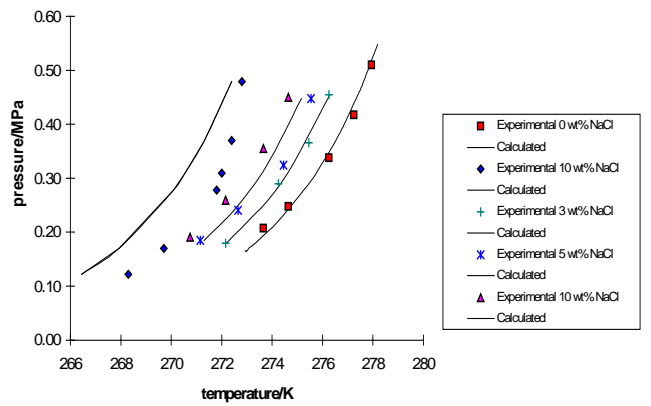


Fig. 6. Propane hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

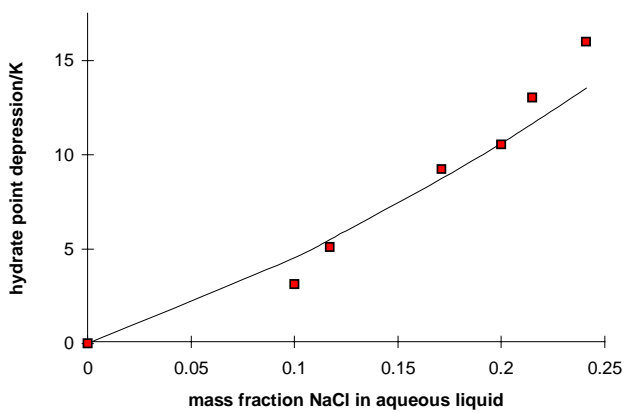


Fig. 4. Methane hydrate with aqueous NaCl. Experimental and calculated depression of hydrate point at 5MPa. Experimental data from Ref. 9.

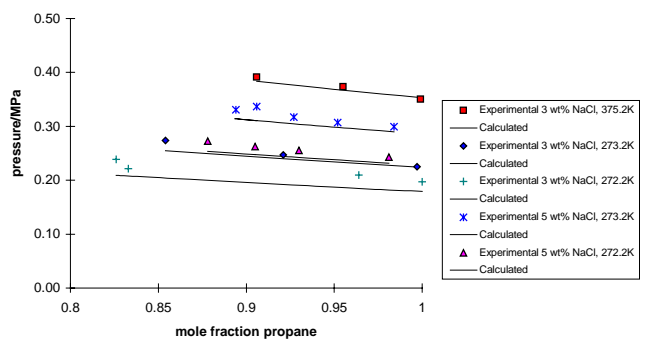


Fig. 7. Propane-butane mixed hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

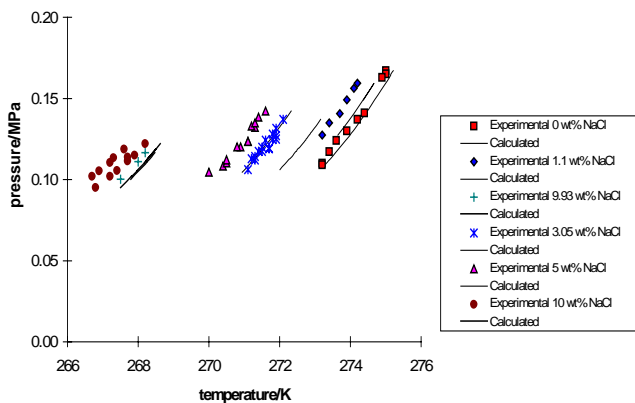


Fig. 8. Isobutane hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

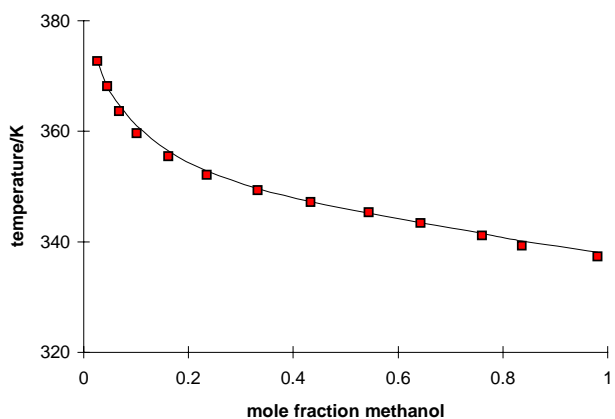


Fig. 11. Water-methanol saturated with NaCl. Experimental and calculated bubble point temperatures. Experimental data from Ref. 16.

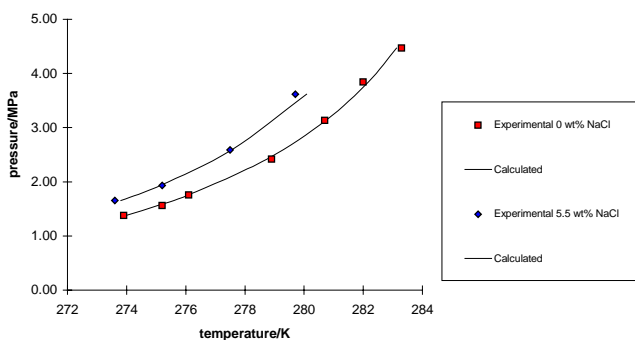


Fig. 9. Carbon dioxide hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

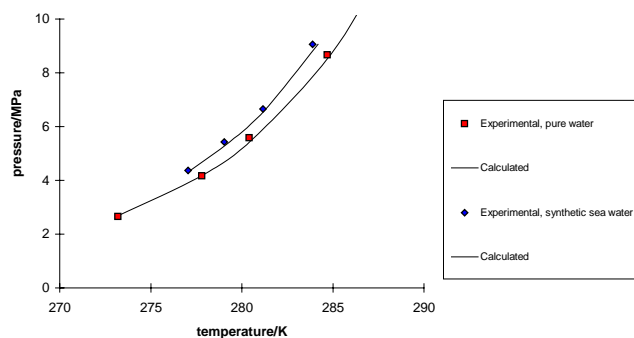


Fig. 12. Methane hydrate with synthetic sea water. Experimental and calculated hydrate curves. Experimental data from Ref. 12.

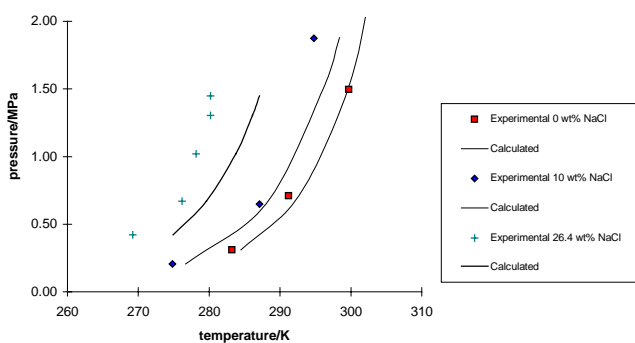


Fig. 10. Hydrogen sulphide hydrate with aqueous NaCl. Experimental and calculated hydrate curves. Experimental data from Ref. 9.

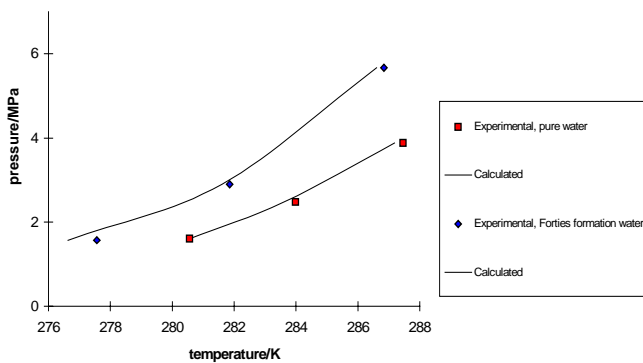


Fig. 13. Natural gas with Forties formation water. Experimental and calculated hydrate curves. Experimental data from Ref. 12.

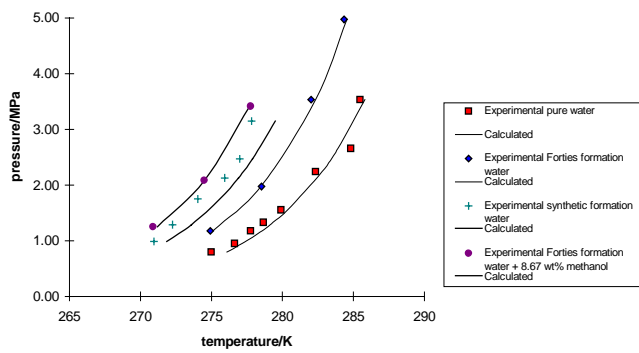


Fig. 14. Black oil with Forties formation water, synthetic formation water and methanol. Experimental and calculated hydrate curves. Experimental data from Ref. 12.