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(54) Title: SECONDARY POLYETHERAMINES AS LOW DOSAGE NATURAL GAS HYDRATE INHIBITORS

(57) Abstract: Embodiments described herein provide ways of controlling and reducing gas hydrates in natural gas containing mix-
tures. In one aspect, a method of controlling gas hydrate formation in a mixture includes blending with the mixture a secondary poly-
ether diamine, which may be an N,N'-dialkyl polyalkylene glycol diamine.



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SECONDARY POLYETHERAMINES AS LOW DOSAGE NATURAL GAS HYDRATE INHIBITORS

FIELD

[0001] Embodiments described herein are generally related to natural gas production. More specifically, a novel method of inhibiting formation of natural gas hydrates is described.

BACKGROUND

[0002] Natural gas is an attractive energy source. It is relatively clean, abundant, easy to handle, easy to transport, and easy to use as a fuel. Natural gas is produced when a well is drilled into a geologic formation containing hydrocarbons, and the natural gas flows to the surface at high pressures. Often, water is entrained in the flowing gas as ground water seeps into the well. The water may be steam, water vapor, or water mist that mixes with the flowing gas. At high enough pressures and low enough temperatures, the water and gas may combine to form natural gas hydrates. Gas hydrates form when water molecules crystallize around guests molecules. The water/guest crystallization process has been recognized since its discovery by Sir Humphrey Davy in 1810, is well characterized and occurs with sufficient combination of pressure and temperature. Light hydrocarbons, methane-to-heptanes, nitrogen, carbon dioxide and hydrogen sulfide are the guest molecules of interest to the natural gas industry.

[0003] Depending on pressure and gas composition, gas hydrates may build up at any place where water coexists with natural gas at temperatures as high as 30°C. Formation of undesired gas hydrates can be eliminated or hindered by several conventional methods. Thermodynamic hydrate prevention (THP) methods control or eliminate elements necessary for hydrate formation: the presence of hydrate forming gas, the presence of water, high pressure and low temperature. The elimination of any one of these four elements from the system

would preclude the formation of hydrates. Heating and insulating transmission lines is a common mechanical solution to the hydrate problem often encountered in long subsea pipelines. Gas dehydration is another method of removing a hydrate component. However, in a practical oil and gas operation, water can be economically removed only to a certain vapor pressure and residual water vapor is always present in a dry gas. Hydrate plugs in "dry" gas lines have been reported in the past.

[0004] The addition of chemicals to the gas/water streams is the most common method of preventing hydrate formation today. Large amounts of alcohols, glycols and salts are being utilized. Such inhibitors are called Thermodynamic Hydrate Inhibitors (THI); they thermodynamically destabilize hydrates and effectively lower the temperature of hydrate formation. They function by bonding to water molecules through hydrogen bonds or solvation. Hydrate prevention with methanol and glycols can be quite expensive due to the required high effective dosages, 20% to 50% of the water phase. Ethylene glycol is usually recovered downstream and recycled. Methanol is not usually recovered and poses an environmental problem. Methanol partitions to the oil or condensate phase and is carried to refining facilities where it has to be washed out. It greatly increases oxygen demand of any water effluent resulting in a possibility of discharge permit violations and/or additional expenses of wastewater treatment. Due to acidic impurities and dissolved oxygen, methanol accelerates equipment and tubular corrosion and aggravates potential scale problems by lowering scaling salts solubility in water and precipitating most known scale inhibitors.

[0005] Shutting down natural gas extraction to remove gas hydrate fouling is costly due to lost production and due to manpower and supplies needed to cycle a well off and back on. Conventional methods of controlling gas hydrates include heating, dehydration, and addition of large amounts of alcohols, glycols, or salts to affect the thermodynamics of hydrate formation. Such methods are typically only minimally effective, however, because the gas must be cooled to a manageable

temperature at some point, water can be removed by dehydration only to a certain vapor pressure, and because large amounts of hydrate formation suppressing additives must be used to achieve effective suppression. Replacing thermodynamic inhibitors with hydrate growth inhibitors that are ten to hundreds times more efficient offers a significant cost reduction to gas producers and pipeline operators. Thus, there is a need in the industry for improved ways of managing and minimizing the effect of gas hydrates on natural gas production and processing.

SUMMARY

[0006] The inventions described herein provide ways of controlling and reducing gas hydrates in natural gas containing mixtures. In one aspect, a method of controlling gas hydrate formation in a mixture include blending with the mixture a secondary polyether diamine having a molecular weight of at least about 270 Daltons. The secondary polyether diamine may be an N, N'-dialkyl polyalkylene glycol diamine, and may have a molecular weight of 190 Daltons to 1,000 Daltons.

[0007] In another aspect, a solution is described that is useful in controlling or reducing gas hydrate formation. The solution contains a compound that has a backbone.

DETAILED DESCRIPTION

[0008] The inventors have discovered that N,N' alkylated polypropylene glycol diamines can effectively inhibit formation of gas hydrates through kinetic means. The compounds of interest may be primary diamines molecules with a polyether backbone. The compounds resemble Gemini surfactants with one or more amine hydrogens remaining on each nitrogen atom. Each of the nitrogen atoms of the diamine ends of the molecules may be bonded to an alkyl group, leaving one amine hydrogen bonded to each amine nitrogen atom. Thus, the compounds described herein may be secondary amino compounds. Although the exact mechanism of inhibition is not currently proven, it is thought that the amine

hydrogens may participate in a hydrogen bonding complex with oxygen in a gas hydrate molecule to inhibit further growth of the gas hydrate crystal.

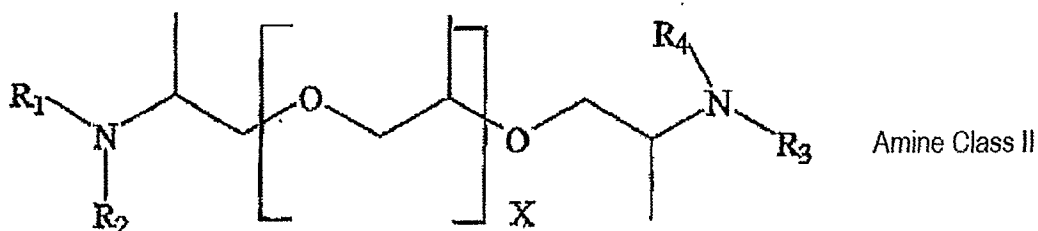
[0009] Compounds with improved gas hydrate inhibition performance have the general structure $R^1R^2N-(PO)_a-(EO)_b-(PO)_a-(CH_2)_c-CH(R)-NR^1R^2$ (amine class I), where PO and EO are inserted propylene oxide and ethylene oxide moieties, $a+b = 0$ to 100 or more, R is hydrogen or methyl, R^1 and R^2 are each hydrogen or an alkyl group such as C_nH_{n+1} , where n is 1 to 10, examples of which include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, and tert-butyl, and $c=1-6$, where one of R^1 and R^2 is hydrogen.

[0010] The polyether backbone may be substituted, if desired, to achieve a convenient molecular weight. As noted above, alkylated polypropylene glycol diamines, with a methyl group attached to each carbon of the polyether backbone, are effective, but polyethylene glycols, and mixed alkylated polyalkylene glycol diamines, such as a random or block PP/PE glycol diamine, or a random or block polypropylene/polyethylene/polybutylene glycol diamine may be used.

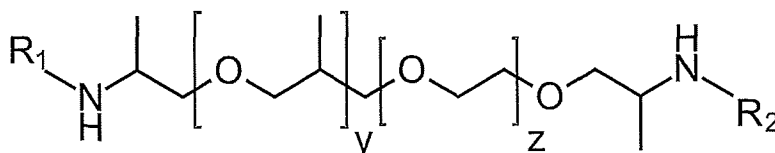
[0011] Alkyl groups that may be bonded to the nitrogen atoms of the diamine typically have 1 to 10 carbon atoms, so that the general structure of the alkyl groups is C_nH_{n+1} , where n is 1 to 10. Exemplary alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, and tert-butyl, in any mixture. Any substituent that does not appreciably interfere with the function of the amine portions of the molecule in complexing with gas hydrate molecules may be used.

[0012] Polyalkylene glycol diamines that are useful in controlling gas hydrates may have molecular weight from about 190 Daltons up to about 1,000 Daltons, for example from about 274 Daltons to about 818 Daltons, such as about 512 Daltons. In one example, the polyalkylene glycol backbone of the molecule has a molecular weight of at least about 270 Daltons. A moderate molecular weight reduces volatility of the molecules so they remain in the water phase readily.

[0013] One class of compounds that may be used have the general formula



where R_1 and R_3 are H, R_2 and R_4 may each be an alkyl group having 1 to 10 carbon atoms, for example having the structure C_nH_{n+1} , where n is 1 to 10, examples of which include methyl, ethyl, isopropyl, n-propyl, n-butyl, sec-butyl, and tert-butyl in any combination, and X is 2 to 8, such as about 2.5 on average (amine class II). In one example, another class of compounds that may be used has the general formula



wherein $y+z$ is between 1 and 4, and R_1 and R_2 are each, independently, an alkyl group having 1 to 10 carbon atoms, with a structure of C_nH_{n+1} , where n is 1 to 10, examples of which include methyl, ethyl, isopropyl, n-propyl, n-butyl, sec-butyl, and tert-butyl. It should be noted that, in either of the structures above, short hydrocarbon chains may be between the amino groups and the ether groups, and/or between the ether groups, if desired, to adjust molecular weight and water solubility. Adding hydrocarbon chains in place of ether groups will reduce water solubility somewhat.

[0014] Other types of compounds that may be used to inhibit gas hydrate formation include polyether glycol alkanolamines, which are similar to the

structures described above with one nitrogen atom replaced by an oxygen atom. Compounds wherein one or both of the amino hydrogens are substituted by amino groups that have amino or hydroxyl hydrogens may also be used, since the amino or hydroxyl hydrogens of the substituent groups would be expected to hydrogen bond with the gas hydrates. Instead of a diamine, one or more of the amino groups in the compounds described above may be an amide group, with an acyl group alpha to the nitrogen atom.

[0015] Generally, the compounds useful as gas hydrate inhibitors include a backbone with a polyether component and a secondary functional group at each end of the backbone, each secondary functional group having a reactive hydrogen atom. The polyether component may include polyoxypropylene, polyoxyethylene, and polyoxybutylene units in any desired proportion, along with hydrocarbon sections if desired. The backbone may thus be designed to afford a desired solubility in water.

[0016] The secondary functional groups may be amino groups, as described above. Alternately, any of the secondary functional groups may be hydroxyl groups, amide groups, carboxylic acid groups, aldehyde groups, and the like.

[0017] Other compounds that have improved gas hydrate inhibition performance are bis-ethylamine triethylene glycol (amine III) and bis-isopropylamine triethylene glycol (amine IV). These molecules have short polyether backbones with secondary amine ends.

[0018] The compounds described above may be delivered in a solution with an aqueous solvent, such as water or an alcohol. Methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and the like may be used as solvents for the compounds described above. Non-polar solvents such as kerosene and aromatic distillate may also be used. Combinations of any of the above solvents may also be used. The compounds may also be used neat at temperatures above their melting points (to facilitate delivery into a flowing gas

stream). Generally, delivery is by a liquid spray into an area desirous of suppressing gas hydrate formation.

[0019] The amount of a compound needed to effectively suppress gas hydrate formation is between about 0.1% and about 5% of the amount of methanol that would be required. So, if the amount of methanol needed to inhibit gas hydrate formation is known for a particular instance, the amount of polyalkylene glycol diamine, as described herein, needed for the same job may be calculated. To facilitate delivery, the polyalkylene glycol diamine may be dissolved in a solvent or mixture of solvents, as described above. An exemplary gas hydrate inhibitor solution may contain 0.1% to 15% by weight of a secondary polyether diamine in water. Some methanol, for example 1-10% by weight, may also be included in the solution.

[0020] The resulting gas hydrate suppression solution is sprayed into equipment prone to developing gas hydrates. Such equipment may include well bores, surface valving and piping, and gas plant locations in which methane and water coexist at high pressures and low temperatures. The solution components typically prefer water, and will typically selective enter the water rather than remain with the gas, so gas purification is not complicated.

[0021] Tests were done to determine performance of various gas hydrate inhibitors. Experiments were performed in a custom-built 500 ml volume, 10.5 MPa pressure rated testing cell. Gas pressure, temperature, stirrer speed and torque are controlled and continuously recorded. The fluid was stirred at 250 rpm. The high pressure testing was a two-step process. First, the cell was loaded with the fluid and gas, and fast cooled to the desired p/T conditions. Sometimes, a minor pressure adjustment was necessary at the end of this step. Second, the fluid was kept at constant temperature to the point of 10% gas to hydrate conversion. The fluid was continuously stirred during both steps or the stirrer could be stopped for a period of time to simulate gas flow stop and restart.

[0022] After the completion of each test the cell was warmed up to 45°C for 6 hours, the old solution was drained and the cell was rinsed with a hot ~50°C solution of the next system to be tested, which was also drained. Finally, the fresh test solution was added to the cell, which was pressurized with a test gas and the cooling was activated. This cell loading procedure sufficiently protects the experiments integrity by removing any hydrate residues from the previous test; thus, eliminating a water "memory" effect that causes accelerated hydrate formation in water/gas systems going through hydrates/warm up cycles.

[0023] Each test was performed using 200 ml of hydrate inhibitor water solution. An established laboratory benchmark, "Green Canyon" gas mixture was used for testing. Such gas composition is typical for natural gas encountered in gas wells worldwide and produces a mixture of small and large hydrate cages (SII hydrate). Gas composition is provided in Table 1.

Table 1
Green Canyon Gas Composition

Component	Mol %	Component	Mol %
Nitrogen	0.4	i-Butane	0.5
Methane	87.2	n-Butane	0.8
Ethane	7.6	i-Pentane	0.2
Propane	3.1	n-Pentane	0.2

[0024] Tests were performed using 1% solutions of KHI in deionized water (DIW) at 2°C @ 550 psi. Such conditions correspond to subcooling temperature, $\Delta T = 12^\circ\text{C}$. All tests were duplicated or triplicated. Results are reported in Table 2 and depicted in graphs below. Different gas mixtures would produce slightly different results; however, the overall trend of hydrates suppression efficiency remains the same.

[0025] Water exposed to natural gas under high pressure and low temperature starts producing hydrates almost instantly and hydrate production is fast. Experimental results tabulated below in Table 2 show this in Experiment A with no inhibitor. Designations in the column labeled "Compound amine class" refer to designations of structures and compounds above.

Table 2
Hydrate Formation Testing Results of 1% Various Amine Solutions in DIW at ΔT 12°C

Experiment code and amine order	Compound amine class	Detailed structure	Time to first hydrate observation	5% gas to hydrate conversion	Number of experiments
A	water	Deionized water	0 h	1 h	2
B primary	II	$R^1, R^2, R^3, R^4 = H$; $x = 2.5$	2 h	4.5 h	2
C primary	II	$R^1, R^2, R^3, R^4 = H$; $x = 3$	0 h	2.5 h	2
D primary	II	$R^1, R^2, R^3, R^4 = H$; $x = 5$	3.75 h	5.5 h	3
E primary	II	$R^1, R^2, R^3, R^4 = H$; $x = 6$	0 h	4.5 h	2
F primary	I	$R, R^1, R^2 = H$; $a = 0$; $b, c = 1$	0.5 h	9 h	4
G primary	I	$R = CH_3$; $R^1, R^2 = H$ $a, c = 1$; $b = 2$	0.25 h	3 h	2
H primary	I	$R, R^1, R^2 = H$; $a, c = 0$; $b = 2$	3.75 h	5.1 h	2
I secondary	I (amine III)	$R, R^1, R^3 = H$; $R^2, R^4 = Et$; $a = 0$; $b = 2$; $c = 1$	11.6 h	13.6 h	2
J secondary	I (amine IV)	$R, R^1, R^3 = H$; $R^2, R^4 = i-Pr$; $a = 0$; $b = 2$; $c = 1$	7.0 h	9.2 h	2
K secondary	II	$R^1, R^3 = H$; $R^2, R^4 = i-Pr$; $x = 2.5$	20 h	31 h	13
L secondary	II	$R^1, R^3 = H$; $R^2, R^4 = i-Pr$ $x = 4$;	20 h	28 h	4
M secondary	II	$R^1, R^3 = H$; $R^2, R^4 = i-Pr$; $x = 5$;	12 h	20 h	4

[0026] In pure water, hydrates start forming instantly at experimental conditions (Experiment A). Experiments B through H represent test results of hydrates formation in the presence of 1% primary amines in water solutions while tests I through M represent data obtained after testing the same concentrations of secondary amines having identical or similar backbones to previously tested primary amines. Table 2 shows the time elapsed until hydrates are first observed, and the time until 5% of the gas is converted to hydrates. The data clearly prove that polyether amines inhibit hydrates formation. Moreover, secondary polyetheramines

are significantly more effective Kinetic Hydrate Inhibitors than primary polyetheramines. The inhibitor used in experiments K and L are JEFFAMINE® SD-231, commercially available from Huntsman Chemical Corp. of The Woodlands, Texas.

[0027] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

Claims:

1. A method of controlling gas hydrate formation in a mixture, comprising:
blending a secondary polyether diamine having a molecular weight of at least about 270 Daltons into a mixture containing methane and water.
2. The method of claim 1, wherein the secondary polyether diamine is an N, N'-dialkyl polyalkylene glycol diamine.
3. The method of claim 2, wherein the secondary polyether diamine is an N, N'-di-isopropyl polypropylene glycol diamine.
4. The method of claim 3, wherein the secondary polyether diamine has a molecular weight not more than about 1,000 Daltons.
5. The method of claim 4, wherein blending the secondary polyether diamine with the mixture comprises dissolving the secondary polyether diamine in an aqueous solvent and spraying the resulting solution into the mixture.
6. The method of claim 4, wherein the mixture is a natural gas containing stream flowing in a wellbore.
7. The method of claim 4, wherein the mixture is a natural gas containing stream flowing through surface gas processing equipment.
8. The method of claim 5, wherein spraying the resulting solution into the mixture comprises positioning a dispenser upstream from a treatment location and atomizing the solution into the flowing mixture.
9. The method of claim 5, wherein the aqueous solvent is methanol.
10. The method of claim 1, wherein the secondary polyether diamine has the general structure $R^1R^2N-(PO)_a-(EO)_b-(PO)_a-(CH_2)_c-CH(R)-NR^1R^2$, wherein PO and EO are inserted propylene oxide and ethylene oxide moieties, $a+b = 0$ to 100, R is

hydrogen or methyl, R^1 and R^2 are each hydrogen or an alkyl group having 1 to 10 carbon atoms, where one of R^1 and R^2 is hydrogen.

11. The method of claim 10, wherein R^1 or R^2 is i-propyl.
12. The method of claim 11, wherein the secondary polyether diamine is dissolved in an aqueous solvent to form a gas hydrate inhibitor mixture.
13. The method of claim 12, wherein the solvent is methanol, ethylene glycol, diethylene glycol, triethylene glycol, water, kerosene, aromatic distillate, or a combination thereof.
14. The method of claim 13, wherein the gas hydrate inhibitor mixture is a solution of the secondary polyether diamine and methanol in water.
15. The method of claim 14, wherein the gas hydrate inhibitor mixture has from 0.1% to 15% by weight of the secondary polyether diamine.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/14638

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C04B 33/04 (2015.01)

CPC - C09K 8/524; C09K 8/52; C09K 2208/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C04B 33/04 (2015.01)

CPC: C09K 8/524; C09K 8/52; C09K 2208/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 507/90 (key word limited; see Search Terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar

Search Terms used: controlling gas hydrate formation, blend polyether diamine, molecular weight, methane, water

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0223713 A1 (Pakulski et al.) 05 October 2006 (05.10.2006); para [0006], [0018]-[0019], [0021]-[0023], [0027]-[0036], [0039], [0041], [0046]-[0050]	1-15
Y	US 2013/0237681 A1 (Burckhardt) 12 September 2013 (12.09.2013); para [0237], [0358]	1-15
A	US 2009/0325823 A1 (Pakulski et al.) 31 December 2009 (31.12.2009) entire document	1-15
A	US 6,025,302 A (Pakulski) 15 February 2000 (15.02.2000) entire document	1-15
A	WO 1997/013824 A1 (Pakulski) 17 April 1997 (17.04.1997) entire document	1-15

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